Chemical Properties of Electronically Excited Halogen Atoms $X(^2P_{1/2})$ (X=F,Cl,Br,I)

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The experimental data on elementary processes (collisional deactivation, chemical reactions, photodissociation) involving spin-orbitally excited $X(^2P_{1/2})$ atoms (X =F,Cl,Br,I) published up to the middle of 2005 are summarized in the present compilation. Critical evaluation of the data and limited comparison to theoretical calculations are also presented. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2137724]

Key words: excited atom; halogens; spin-orbital excitation.

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1. Introduction

The absence of any review on the properties of spin-orbitally excited X*($^2P_{1/2}$) halogen atoms (X = F,Cl,Br,I) in the literature is noteworthy, this fact gave large impetus to the present work. In the present compilation the data on the elementary processes involving X*($^2P_{1/2}$) atoms published up to the middle of 2005 are presented. For convenience, hereafter the spin-orbitally excited X*($^2P_{1/2}$) will be denoted as X*, and the ground state X($^2P_{3/2}$) will be denoted as X. The processes fall into the categories:

(1) collisional deactivation of X*, reactive and nonreactive, at T = 300 K,
(2) formation of X* atoms in the photodissociation,

(3) formation of X* atoms in chemical reactions,
(4) high-energy studies on X* scattering, and
(5) exotics, such as collisionally induced transitions between hyperfine levels, or heterogeneous processes.

The main aim of the paper consists in collecting all available experimental data on these processes. Where it is possible, critical evaluation of the data is presented, where special attention is paid to the accuracy of the experimental measurements. In many cases the originally published data may be recalculated and corrected. For example, the X*/X branching ratio for the products of photodissociation is often determined by REMPI; it may be recalculated by using the best value of the calibration factor. Or, the rate constant obtained by relative measurements may be corrected using the best rate constant of the reference reaction. These corrections have not been done in this paper, almost all the data are presented here like they were originally published by the authors. Usually, the data on the yields of X* atoms in the broadband photolysis are omitted, since they are usually very uncertain; however, in some cases they are presented. The theoretical results are presented very briefly, mainly by references, although some theoretical models are discussed in relation to experimental data where appropriate. To the best of the author's knowledge, in the literature there are no reviews on the chemical properties of X* atoms except very early papers.[1–5]

In this paper, the collisional deactivation of X* atoms is characterized by the rate constants at $T=300$ K. These constants usually do not differentiate between chemical reaction and physical quenching of X* atoms. Only in some cases are the branching ratio between the probabilities of reactive and nonreactive pathways or the temperature dependencies of the rate constants available; this rare information is presented usually in footnotes or in comments.

The relative yield of X* atoms in photodissociation processes is characterized by the branching fraction

$$\Gamma=\frac{[\mathrm{X}^*]}{[\mathrm{X}^*]+[\mathrm{X}]}=\frac{[\sigma^*]}{[\sigma^*]+[\sigma]}, \tag{1}$$

where $\sigma^*=\sigma(\mathrm{X}^*)$ and $\sigma=\sigma(\mathrm{X})$ are the cross sections for the production of excited and ground state atoms, respectively; [X] and [X*] denote concentrations of these atoms. Note that excited $^2\mathrm{P}_{1/2}$ and ground $^2\mathrm{P}_{3/2}$ levels contain two and four M_J electronic sublevels, respectively; hence in the case of $\Gamma=1/3$ the populations of X* and X are equal.

For a one-photon electric dipole transition the c.m. angular distribution of X* atoms produced in photodissociation is given by[6–8]

$$f(\theta)=1+\beta P_2(\cos\theta), \tag{2}$$

where θ is the angle between the electric field vector ($\mathbf{e}$) of the dissociating light and the recoil direction ($\mathbf{v}$) of the photofragment, and $P_2(x)=(3x^2-1)/2$ is the second Legendre polynomial. The anisotropy parameter β describes the spatial distribution of X* atoms and has a value between -1 [$\mathbf{e}\perp\mathbf{v}$, perpendicular transition, $f(\theta)=(3/2)\sin^2\theta$] and 2 [$\mathbf{e}\|\mathbf{v}$, parallel transition, $f(\theta)=3\cos^2\theta$]. The β parameter can be related to the angle (χ) between the direction of the transition dipole in the molecule and the recoil direction by

$$\beta=2\kappa P_2(\cos\chi), \tag{3}$$

where $0\leqslant\kappa\leqslant1$ is a parameter that takes into account any decrease in the observed β due to rotational, vibrational, and translational motion of the parent molecule. Usually the largest contribution to κ comes from rotational motion.[9] It may be estimated as[8]

$$\kappa=\frac{1+\eta^2}{1+4\eta^2}, \tag{4}$$

where η is the angle between the recoil velocity vector that would result if the molecule was not rotating and the vector that actually results. If the dissociation process is fast relative to rotation of the parent molecule, then the factor κ is equal to unity ($\eta=0$). In this case, the β parameter may be reduced due to the thermal motion of the parent molecule by the factor[10]

$$\kappa=1-3kT/\sqrt{2}E_t, \tag{5}$$

where E_t is the thermal energy of parent molecule, $kT\ll E_t$ is assumed.

In this paper, the yield of X* atoms in photodissociation is characterized by Γ and β parameters. Only in several outstanding cases (like HI, ICN, or CH_3I) does there exist experimental information in addition to these parameters; this information is presented briefly in footnotes or in comments. The production of X* atoms in chemical reactions is usually characterized by the branching fraction Γ. The results of high-energy studies on the X* scattering are characterized by collisional cross sections.

In large tables of this paper, molecules—precursors of X* atoms or collisional partners of X* atoms—are listed in the order of increasing number of atoms in the molecule. The molecules with equal number of atoms are listed in the order of increasing mass. The results on each molecule are presented in chronological order.

1.1. Spin-Orbit Splittings and Radiative Lifetimes

The mean radiative lifetime τ_e for the spin-orbitally excited state $^2\mathrm{P}_{1/2}$ is given by

$$1/\tau_e=A(^2\mathrm{P}_{1/2}\rightarrow{}^2\mathrm{P}_{3/2})=\frac{2(\Delta E)^3\mu^2}{3\hbar^4c^3}, \tag{6}$$

where μ is the reduced matrix element of the magnetic dipole operator

$$\mu^2=3\sum_{M_J',M_J''}|\langle{}^2\mathrm{P}_{1/2,M_J'}|\mu_z|{}^2\mathrm{P}_{3/2,M_J''}\rangle|^2. \tag{7}$$

Here, a magnetic dipole transition between $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$ states is assumed, μ_z is the z component of the magnetic dipole operator, and $\Delta E=E(^2\mathrm{P}_{1/2})-E(^2\mathrm{P}_{3/2})$ is the spin-

TABLE 1. Spin-orbit splittings and radiative lifetimes in X* atoms

X* atom	$\Delta E(\mathrm{cm}^{-1})$	Lifetime τ_e, s	
		Experiment	Calculated
$F(2p^5\ ^2P_{1/2})$	404[11]	772[12]	838[a]
	404.082[13]	660±165[13]	
	404.141[14]		
$Cl(3p^5\ ^2P_{1/2})$	882.35304[15b]	87.9±19[16]	80.6[a]
		86±20[c17]	
$Br(4p^5\ ^2P_{1/2})$	3685.24	0.96±0.09[18d]	0.903[a]
			0.897[e]
$I(5p^5\ ^2P_{1/2})$	7603.15	0.1372[19f]	0.126[a]
		0.127[20f]	0.165[g]
		0.130[21f]	
		0.0257[22f]	
		0.125±0.025[23f]	
		0.1116[24f]	
		0.0484[25f]	
		0.145±40[26f]	

[a]Calculated with Eq. (6).
[b]ΔE is equal to 882.35283(23) cm^{-1} and 882.35367(23) cm^{-1} for ^{35}Cl and ^{37}Cl, respectively.[15] See previous values in three studies.[27–29]
[c]The ratio $\tau_e(\mathrm{Cl})/\tau_e(\mathrm{I})$ was measured, $\tau_e(\mathrm{I})=0.125$ s reported by Engelman *et al.*[23] was assumed.
[d]Several previous values are presented.[2,25,30]
[e]Relativistic calculation using Dirac–Fock–Breit calculation.
[f]Extensive review on all previous values are presented by Ha *et al.*,[26] in this table only values obtained after 1980 are presented in chronological order.
[g]Multiconfiguration Hartree–Fock calculation.[26]

orbital splitting. In Russell–Sanders L-S coupling approximation $\mu_z=\mu_B(L_z+g_eS_z)$ and the reduced matrix element may easily be calculated as

$$\mu^2=\tfrac{4}{3}(g_e-1)^2\mu_B^2, \tag{8}$$

where g_e is the electron spin gyromagnetic ratio ($g_e=2.00232$), $\mu_B=e\hbar/2m_ec$ is the Bohr magneton, and L_z and S_z are the z components of the operators $\mathbf{L}$ and $\mathbf{S}$, the electron angular and spin momenta, respectively. The spin-orbit splittings, the latest experimental values of τ_e, and the values of τ_e calculated with Eqs. (6)–(8) are summarized in Table 1.

The contribution of the electric quadrupole moment to the overall transition probability in the iodine atom has been determined from the experimental ratio $S(J=1/2,F=2\rightarrow J=3/2,F=4)/S(J=1/2,F=3\rightarrow J=3/2,F=4)=0.0035$, where S denotes the strength of the absorption line. From these data the contribution of the electric quadrupole moment may be calculated to be 0.52%.[26]

The validity of the L-S approximation has recently been confirmed by He *et al.*,[18] in which a theoretical calculation for the magnetic dipole transition moment in Br atoms was carried out using a relativistic Dirac–Fock–Breit *ab initio* atomic structure formulation. The theoretical value was in excellent agreement with the value predicted assuming L-S coupling (see Table 1). *Ab initio* calculations of expression (7) using a multiconfiguration Hartree–Fock level program were done by Ha *et al.* for transitions in the iodine atom.[26] The calculations gave the result $\tau_e=0.165$ s, which is in moderate agreement with experiment and the result of the simplest analytical L-S coupling model, $\tau_e=0.126$ s.

Note that for a given element in the single electron approximation the ΔE splitting is proportional to the reduced mass of the electron-nucleus pair.[29] Hence the difference in ΔE for different isotopes of Cl and Br may easily be calculated.

1.2. Hyperfine Structure

The hyperfine structure Hamiltonian for a halogen atom can be written as[31–35]

$$H_{hfs}=a_JH^D+b_JH^Q+c_JH^O, \tag{9}$$

$$H^D=\mathbf{I}\cdot\mathbf{J}, \tag{10}$$

$$H^Q=\frac{3(\mathbf{I}\cdot\mathbf{J})^2+(3/2)(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \tag{11}$$

where H^D, H^Q, and H^O are the operators for magnetic dipole, electric quadrupole, and magnetic octupole interactions, respectively; a_J, b_J, and c_J are the constants of these interactions, respectively. $\mathbf{J}$ is the total electron angular momentum ($\mathbf{J}=\mathbf{L}+\mathbf{S}$, $L=1$, $S=1/2$, $J=1/2,3/2$), $\mathbf{I}$ is the nuclear spin, and $\mathbf{F}$ is the total angular momentum ($\mathbf{F}=\mathbf{J}+\mathbf{I}$). Note that for the upper state of the fine structure ($J=1/2$) the second and the third terms in Eq. (9) are equal to zero. The energy levels of the atom may conveniently be obtained from Eq. (9) as[31,32,35–37]

$$E_{JF}=a_JC/2+b_J\frac{(3/4)C(C+1)-D}{2I(2I-1)J(2J-1)}+c_J\{C^3+4C^2+4C[J(J+1)+I(I+1)+3-3D]/5+4D\}, \tag{12}$$

where $C=F(F+1)-I(I+1)-J(J+1)$ and $D=I(I+1)J(J+1)$.

Because of large spin-orbital splitting, the $J=1/2$ and $J=3/2$ levels only perturb each other to a very small extent. For given F, matrix elements of the H^D operator are nondiagonal with respect to J. The off-diagonal terms are proportional to the additional $a_{1/2,3/2}$ coupling constant

$$\langle I,M_I,J,M_J|H^D|I,M_I,J-1,M_J\rangle=a_{J-1,J}M_I(J^2-M_I^2)^{1/2}. \tag{13}$$

Note that $a_{3/2}$, $a_{1/2}$, and $a_{1/2,3/2}$ are often denoted as a', a'', and a''', respectively. These constants may be estimated using simple theory as[33,38] $a_{3/2}=-15g_I\mu_B^2\langle r^{-3}\rangle/15$, $a_{1/2,3/2}=-a_{3/2}(5-16\beta')/[16(1+\beta')]$, and $a_{1/2}=5a_{3/2}$, where g_I is the nuclear g factor, β' is a small fractional contribution by s electrons to the measured $a_{3/2}$ constant,[39,40] and $\langle r^{-3}\rangle$ is taken over the $2p$ wave function. The $a_{1/2,3/2}$ constants have been determined experimentally for fluorine[14,40] and chlorine.[41]

The parameters for expressions (9), (12) for the halogen atoms are listed in Table 2. The constants a_J, b_J, and c_J may be determined from experimental data with or without the second-order correction Eq. (13). In Table 2 the contri-

TABLE 2. Spin-orbit and hyperfine parameters for stable isotopes of halogen atoms, uncertainties are shown in parentheses; for example, 1.23(45) = 1.23 ± 0.45

X	[a]	I[b]	$a_{3/2}$, (MHz)	$a_{1/2}$, (MHz)	$b_{3/2}$, (MHz)	$c_{3/2}$, (kHz)	$a_{1/2,3/2}$ (MHz)	$(F',F'')\Delta E_{F',F''}$[d] ($cm^{-1}$)
^{19}F	1.000	1/2	2009.99(1)[40,42]	10244.21(3)[42]	0	0	−446(10)[14,40]	(1,2) 404.176(1)[14,43]
^{35}Cl	0.758	3/2	205.04687(3)[33,36,44]	1037.209(14)[44,45]	54.87290(6)[33,36,44]	−0.0072(12)[36,44]	44.0(1.0)[41]	(2,3) 882.3626[16c]
^{37}Cl	0.242	3/2	170.68637(3)[33,36,44]	863.39(6)[44,45]	43.24524(6)[33,36,44]	−0.0055(12)[36,44]	37.9(1.0)[41]	(2,3) 882.3626[16c]
^{79}Br	0.5052	3/2	884.809774(62)[35,37]	5332.55(4)[38,46]	−384.882835(200)[35,37]	0.388(8)[35,37]		(2,3) 3685.23(10)[47]
^{81}Br	0.4948	3/2	953.768180(62)[35,37]	5748.15(3)[38,46]	−321.524277(200)[35,37]	0.430(8)[35,37]		(2,3) 3685.23(10)[47]
^{127}I	1.000	5/2	827.265(3)[34]	6625(90)[48]	1146.356(10)[34]	2.45(37)[34]		(3,4) 7603.1382(3)[49,50]

[a]Natural abundance of isotopes.[51]
[b]Nuclear spin.[51]
[c]The values calculated from data of Braun *et al.*[15] are 882.362931 and 882.362099 cm^{-1} for ^{35}Cl and ^{37}Cl, respectively.
[d]$\Delta E_{F',F''} = E_{1/2,F'} - E_{3/2,F''}$, quantum numbers F' and F'' are shown in brackets.

bution from these off-diagonal terms is taken into account. The uncorrected constants for I and Br may be taken from papers of King and Jaccarino[37] and Brown and King,[35] respectively. In X*−X absorption spectra the strongest component is the $(J=3/2, F=I+3/2) \rightarrow (J=1/2, F=I+1/2)$ line. In the last column of Table 2 the energies of these strongest transitions are presented.

1.3. Detection Methods

1.3.1. Detection Methods: Summary, Abbreviations, and Sensitivities

A number of methods have been applied to detect the X* atoms, they are summarized in Table 3. The second column of the table gives the abbreviations for detection methods which are used through all this paper. These abbreviations may consist of three parts: the first one denotes the detection method, the second denotes spectral region ("IR," "VIS," "UV," and "VUV" mean infrared, visible, ultraviolet, and vacuum ultraviolet, respectively), and the third shows which particle is detected ("CP," "PF," "PP," "RP," and "CP PF" mean collisional partner, photofragment, photolysis products, reaction product, and collisional partner of photofragment, respectively). If the particle is not mentioned, it usually means direct detection of X* atoms. In the table all indirect detection methods are shown by italic letters, but it does not mean that they are less reliable than direct methods. For example, direct detection of A atoms in the photodissociation of a diatomic AX molecule is often even more informative than direct detection of X* or X atoms. The third column of the table gives the wavelength for the detection methods, the wavelength for the strongest line is presented. The column is normally empty for nonoptical and for indirect methods.

Modifications of the detection methods may be shown; we denote all REMPI-based ion imaging methods,[52,53] including the velocity mapping variant of the technique as REMPI/I, LMR/S means the fast-magnetic-field-jump version of time-resolved laser magnetic resonance,[54,55] SE IR/SS means steady-state infrared spontaneous emission,[56] and notation REMPI is used instead of REMPI (2+1).

Typical sensitivities of several detection methods are summarized in Table 4. The sensitivities of several recent methods continue to increase. For example, in the early experiments, Arepalli *et al.* reported the detection limit for REMPI (2+1) as $[Br^*]_{min} = 10^{10}$ cm^{-3}.[98] According to Ashikhmin *et al.*, this sensitivity is limited mainly by the dimension of the probed volume.[100] For example, if the probe volume is 0.04 mm^3, the probability of ionization of X* atom in the volume is 0.25, and the detection limit is 25 ions per pulse, then the sensitivity of REMPI detection becomes $[Br^*]_{min} = 2.5\times10^6$ cm^{-3}.[100]

However, for the modern REMPI ion imaging methods the probability of ionization may be increased up to unity, and the detection limit is one ion per pulse; hence the sensitivity may be two orders of magnitude higher.

1.3.2. Calibration Factors for REMPI Detection

REMPI (2+1) is the most popular method for studying photodissociation dynamics. However, there has been some uncertainty in the intensity factors relating the strengths of the REMPI signals to the $^2P_{1/2}$ and $^2P_{3/2}$ spin-orbit states. The transitions in halogen atoms, which are usually used for REMPI detection, are collected in Table 5.

Generally, the calibration factor is the ratio of the transition probabilities for REMPI transitions in atoms A and B, these probabilities are denoted here as $P_A(\lambda_A)$ and $P_B(\lambda_B)$, where λ denotes the corresponding wavelength of radiation. The calibration factor is usually used as

$$\frac{[A]}{[B]} = \frac{P_B(\lambda_B)}{P_A(\lambda_A)} \frac{S_A}{S_B}, \tag{14}$$

where [] represents the corresponding number density, and S_A and S_B are line strengths of the REMPI signals of A and B atoms, respectively. The calibration factors for halogen atoms are presented in Table 6 in chronological order for each atom.

In several early studies of Kawasaki and co-workers[189–191] the ratio $P_{Cl}(235.336)/P_{Cl^*}(237.808)$ was assumed to be unity based on the theoretical approach of Pindzola[192] in which only $\Delta S = 0$ transitions were taken into account. In reality $\Delta S > 0$ transitions contribute strongly to the REMPI

TABLE 3. Detection methods for X* halogen atoms

X*	Detection method[a]	Wavelength/Frequency	Reference
F*	EPR		42, 57
	ARF VUV	97.77 nm	58
	ARA VUV	95–98 nm	59, 60
	AS-DL	404 cm^{-1}	13, 61
	HR-TOF	121.6 nm	62
	REMPI (3+2)	285.9 nm	63
	AS VUV	95.85 nm	64
	REMPI (3+1)	234.08 nm	65
Cl*	EPR		41, 57, 66
	Fl VUV	136.34, 135.17 nm	67
	ARA VUV	135–136 nm	68, 69
	LMR	882.2875 cm^{-1}	15, 29, 70
	AS-DL	882.35 cm^{-1}	16, 71, 72
	LIF	210 nm	73
	REMPI	235.205 nm	74
	ARA IR	882.35 cm^{-1}	75
	REMPI (3+2)	405.3 nm	76
	CARS	653.2/691.3 nm	77
	Fl IR CP		78
	ARF VUV	134–139 nm	79
	LIF VUV	135.166 nm	80–82
	ARA IR RP		83
	HR-TOF	121.6 nm	84
	REMPI (1+1′)	120.13 nm	85
Br*	AKS VUV	153.2 nm	86
	EPR		38
	Fl IR RP		87
	ARA VUV	153.2 nm	88, 89
	ARA VUV PF		90
	Br-laser	3685 cm^{-1}	91
	TOF-MS		92
	LA IR CP		93
	SE IR	3685 cm^{-1}	94
	Fl IR CP PF		95
	LIF VUV	153.2 nm	96
	ARA IR	3685 cm^{-1}	97
	REMPI	232–277 nm	98–102
	AS-FCL	3685 cm^{-1}	18, 103
	AS-DL CP		104
	DI		105
	Fl IR CP		106
	HR-TOF	121.6 nm	107
	REMPI PF		108
	TOF-MS PF		109
	REMPI (3+2)	472.32 nm	110
I*	*TR-SM IR*		111
	GC PP		112
	ARA UV	206.2 nm	113
	TR-SM VIS		114
	TR-MS PP		115
	ARF VUV	206.2, 179.9 nm	116–119
	MCD		120
	Fl IR CP		121
	CT PP		122
	SE IR	7603 cm^{-1}	94, 123
	Lum RP	580 nm	123
	ARA VUV PF		124
	LIF-DS PF		125
	Fl IR PF		126
	EPR		20
	ARA IR	3685 cm^{-1}	22
	REMPI	268–313 nm	127
	REMPI PP		127–129
	REMPI (3+2)	492.6, 485.2, 464.8 nm	130
	TP-LIF	306.7 nm	131–133

TABLE 3. Detection methods for X* halogen atoms—Continued

X*	Detection method[a]	Wavelength/Frequency	Reference
	TOF-MS		134
	MS PP		135
	SE VIS RP		136
	AS-DL	7603 cm^{-1}	26, 137, 138
	LOAT		139
	TOF-MS PF		140
	I-laser	7603 cm^{-1}	141, 142
	REMPI (1+1′)	145.9 nm	143–145
	REMPI PF		52, 146
	LIF VUV	206.2/178.2 nm[b]	147, 148
	LIF VUV PF		149
	FMDS PF	790–840 nm	150, 151
	LIF PF		152–154

[a]In the table, the detection methods are listed in chronological order for each atom. The abbreviations (listed in alphabetical order) are:
AKS VUV=absorption kinetic spectroscopy of Br* atoms in the vacuum ultraviolet.
ARA=atomic resonance absorption.
ARF=atomic resonance fluorescence.
AS=absorption spectroscopy.
AS-DL=diode laser absorption spectroscopy (I*–I is usually detected by an InGaAsP diode laser.)
AS-FCL=F-color-center laser is used for Br*–Br absorption spectroscopy.
Br-laser=study of photodissociative Br*–Br laser threshold gain, the relaxator is added in the active medium of the laser.
CARS=time-resolved polarized coherent anti-Stokes Raman spectroscopy of Cl* atoms.
CT PP=chemical trapping of I* atoms. Analysis of photolysis products.
DI=a combination of one-dimensional Doppler technique with a two-dimensional imaging technique was used to detect H atoms from the photodissociation of HBr.
EPR=electronic paramagnetic resonance.
Fl VUV=resonance fluorescence of excited Cl* atoms.
Fl IR=infrared fluorescence of vibrationally excited molecules.
Fl IR CP PF=infrared fluorescence of vibrationally excited collisional partners of photofragments. (For example, $HBr+h\nu_{UV}\rightarrow Br^*/Br+H^*$, $H^*+AB\rightarrow H+AB^*$, $AB^*\rightarrow AB+h\nu_{IR}$, where H* denotes translationally "hot" atoms.)
FMDS=transient frequency-modulated Doppler spectroscopy.
GC PP=gas chromatography of photolysis products.
HR-TOF=detection of H atoms by high-*n* Rydberg time-of-flight technique.
ICS=intracavity spectroscopy based on a pulsed photodissociative I*–I laser.
I-laser=study of photodissociative I*–I laser threshold gain, the relaxator is added in the active medium of the laser.
LIF=laser induced fluorescence.
LIF-DS=LIF Doppler spectroscopy (of H atoms).
LMR=laser magnetic resonance of Cl* atoms ($^{13}CO_2$-laser).
LOAT=laser optoacoustic technique.
Lum RP=detection of the luminescence of excited I_2^* arising in the recombination $I^*+I\rightarrow I_2+h\nu$.
MCD=magnetic circular dichroism.
MS PP=mass spectrometry of photolysis products.
REMPI (n+m)=resonance-enhanced multiphoton ionization, number of photons is shown in brackets.
SE IR=spontaneous $^2P_{1/2}\rightarrow{}^2P_{3/2}$ emission in the infrared.
SE VIS RP=spontaneous emission in visible wavelength range of excited reaction products ($I^*+I\rightarrow I_2^*$, $I_2^*\rightarrow I_2+h\nu$).
TOF-MS=time-of-flight mass spectrometry.
TP-LIF=two-photon laser induced fluorescence.
TR-MS PP=time-resolved mass spectrometry of photolysis products.
TR-SM=time-resolved spectrometry.
[b]206.2 nm and 178.2 nm are the excitation and fluorescence wavelengths, respectively.[131,148]

TABLE 4. Sensitivities of the detection methods for X* atoms

X* atom	Method	$[X^*]_{min}$ (cm^{-3})	Reference
X*	EPR	$10^{11}-10^{12}$	155, 156
F*	ARA VUV	10^{11}	60
Cl*	ARA VUV	5×10^{9}	157
	TP-LIF[a]	1×10^{13}	73
	ARA IR	2×10^{13}	75
	discharge-flow LMR	2×10^{9}[b]	158
	time-resolved LMR	4×10^{10}[b]	159
Br*	REMPI	10^{10}	98
	REMPI	2.5×10^{6}	100
I*	ARA IR	10^{12}	83
	ARA IR	10^{13}	160
	ARF VUV	10^{11}	58
	REMPI (3+2)	3×10^{13}	130
	TP-LIF	10^{11}	131

[a]Obtained for ground state Cl atoms.
[b]Obtained with a Ge–Au photoresistor. With the Ge–Hg photoresistor the sensitivity must be an order of magnitude higher.[158]

signals. Later Kawasaki and co-workers have measured the ratio and obtained the value of 2.5.[175,193] The value for the ratio $P_{Cl}(235.336)/P_{Cl*}(235.205)$ was determined several times to be 1.25,[176] 0.85,[177] 1.11,[178] 1.17,[179] and 1.06.[180] The value of Liyanage *et al.*[177] is mentioned briefly as a footnotes and probably is less reliable, all other values are in rather good agreement. Note also, that the theoretical calculations of the calibration factors are rather accurate, they may be used to choose the most reliable factors.[176,179]

It is useful to mention that two-photon laser induced fluorescence (TP-LIF) uses the same two-photon transitions as REMPI does. For example, the I* and I atoms may be probed by TP-LIF at 306.73 nm $[6p\ ^2D_{3/2}\leftarrow 5p\ ^2P_{1/2}]$ and 304.67 nm $[6p\ ^2D_{5/2}\leftarrow 5p\ ^2P_{3/2}]$, respectively. The TP-LIF calibration factor $P_{I*}(306.73)/P_I(304.67)$ was obtained by Das *et al.*[194–196] to be 1, and by Brewer *et al.*[131] to be 1.12. However, the same calibration factor for REMPI detection of iodine atoms is another, it is equal to 1.63.[185] Hence the calibration factors for REMPI and for TP-LIF may be different.

1.4. Lasing System

The development of infrared lasers employing the $^2P_{1/2}$-$^2P_{3/2}$ transition of halogen atoms strongly stimulated the study of the chemical properties of these atoms.[197,198] A review of these lasers is not a purpose of the present paper, and hence only a brief summary, mainly of chemical interest, will be given here.

1.4.1. Chlorine Laser

A photodissociative-chemical repetitively pulsed laser operating on the Cl*–Cl transition was created in 1986.[199] The major steps in the kinetic scheme of the laser are as follows:

$$ICl+h\nu\rightarrow I^*/I+Cl^*/Cl, \quad (15a)$$

$$I^*+ICl\rightarrow Cl^*+I_2, \quad (15b)$$

TABLE 5. Selected REMPI (2+1) detection of halogen atoms

Atom	Upper state	λ (nm)
Cl	[a]	235.25[161]
	$4p(^2D_{3/2})$	235.336[74]
	$4p(^2D_{5/2})$	236.284[74]
	$4p(^4D_{5/2})$	236.73[74,162]
	$4p(^4P_{3/2})$	240.592[74,163]
Cl*	[a]	235.13[161]
	$4p(^2P_{1/2})$[b]	235.205[74]
	$4p(^2D_{3/2})$	237.808[74]
	$4p(^4D_{5/2})$	240.248[163]
Br	$5p(^2P_{3/2})$	229.220[101]
	$6p(^4P_{3/2})$	233.6 (233.69,[164] 233.6,[165] 233.70,[166] 233.618,[167] 233.634[168])
	$5p(^2P_{1/2})$	250.41[169]
	$5p(^2S_{1/2})$[c]	250.434[98,102,167]
	$5p(^2D_{3/2})$	250.9 (250.978,[98,102] 250.88[167,170])
	$5p(^4D_{5/2})$	264.2 (264.236,[98,102] 264.14[167,170])
	$5p(^2S_{3/2})$[d]	264.85[98,102]
	$5p(^4P_{3/2})$	266.6 (266.650,[98,102] 266.551,[167] 266.580[168])
Br*	$4p(^1S)5p(^2P_{3/2})$	231.980[101]
	$6p(^2S_{1/2})$	233.96 (233.9,[165] 234.03,[164] 233.95[167] 233.957,[170] 233.974[168])
	$6p(^4P_{1/2})$	243.6 (243.583,[98,102] 243.38,[167] 243.534,[170])
	$6p(^4D_{5/2})$	243.4 (243.518,[98,102] 243.32[167] 243.475[170])
	$6p(^4P_{3/2})$	244.125 (244.216,[98,102] 244.125[167,170])
	$6p(^4P_{5/2})$	244.294 (244.394,[98,102] 244.294[167,170])
	$5p(^2P_{3/2})$[d]	264.85 (264.945,[98,102] 264.8,[166] 264.849,[170] 264.86[167])
	$5p(^4S_{3/2})$	266.64 (266.613,[167] 266.643,[168] 266.713[98,102])
	$5p(^4P_{1/2})$	277.3[98,99]
	$5p(^4D_{5/2})$	277.744[98,102]
I	$(^3P_0)6p([1]_{3/2})$	277.87[171–173]
	$(^3P_2)6p([1]_{3/2})$	298.23[172,173]
	$(^3P_2)6p([1]_{1/2})$	303.69[172,173]
	$6p(^2D_{5/2})$	304.67[171]
I*	$(^1D_2)6p([1]_{1/2})$[e]	277.40[172,173]
	$(^1D_2)6p([3]_{5/2})$	281.73[172,173]
	$(^3P_1)6p([1]_{1/2})$[e]	304.03[172,173]

[a]No assignment.
[b]The upper state is a mixture of a $^2P_{1/2}$ and a $^2S_{1/2}$ states.
[c]According to Rakitzis *et al.*, the upper state is $5p(^2P_{1/2})$.[169]
[d]Different assignments have been proposed: Br→→$^2S_{3/2}$,[98,102] Br→→$4p(^4(^3P),5p(^4D_{7/2})$,[165] and Br*→→$^2P_{3/2}$.[167,170]
[e]According to Kang *et al.*,[171] at 277.38 and 304.02 nm the intermediate states are $(^3P_0)6p([1]_{3/2})$ and $6p(^4D_{1/2})$, respectively.

$$Cl+ICl\rightarrow I+Cl_2, \quad (15c)$$

$$Cl^*\rightarrow Cl+h\nu. \quad (15d)$$

The first step Eq. (15a) is a broadband photolysis of ICl. It produces a population inversion on the Cl*–Cl transition at the wide range of wavelengths, 225–530 nm (see Table 10). Moreover, a high quantum yield of I* atoms also occurs at 248–404 nm (see Table 19). The second step Eq. (15b) is a chemical reaction which transfers the spin-orbital excitation from iodine to chlorine atoms. The yield of Cl* from the I*+ICl reaction has been determined by Nadkhin *et al.*[200] (≥70%) and by Sotnichenko[201] (60%±15%). Formation of Cl^*+I_2 is found to account for 63%±17% of the overall

TABLE 6. Calibration factors for REMPI detection of halogen atoms

$P_B(\lambda_B)/P_A(\lambda_A)$		Reference
$P_{Cl}(235.336)/P_{Cl*}(237.808)=$	2.7 ± 0.3[a]	174
	2.5 ± 0.1[b]	175
$P_{Cl}(237.73)/P_{Cl*}(237.808)=$	1.51 ± 0.01[c]	162
$P_{Cl*}(235.205)/P_{Cl*}(237.808)=$	2.0 ± 0.5[d]	176
$P_{Cl}(235.336)/P_{Cl*}(235.205)=$	1.25[e]	176
	0.85 ± 0.1[e]	177
	$1/(0.9\pm0.1)$[e]	178
	1.17 ± 0.14[f]	179
	1.06 ± 0.17[f]	180
$P_{Cl}(235.25)/P_{Cl*}(235.13)=$	?[g]	161
$P_{Br}(229.220)/P_{Br*}(231.980)=$	4[h]	101
$P_{Br}(233.6)/P_{Br*}(233.96)=$	0.42 ± 0.02[i]	165, 181
	0.26[j]	182
	0.349[i]	167
	0.32[i]	170
$P_{Br}(264.9)/P_{Br*}(264.8)=$	0.73 ± 0.02[i]	165
$P_{Br}(266.6)/P_{Br*}(266.64)=$	0.578[i]	167
	0.70[i]	170
	0.544[i]	168
$P_{Br*}(234.03)/P_{Cl}(235.336)=$	1.24 ± 0.30[k]	166
$P_{Br}(233.69)/P_{Cl}(235.336)=$	3.35 ± 0.84[k]	166
$P_{Br}(233.69)/P_{Cl*}(235.204)=$	1.46 ± 0.42[k]	166
$P_{Br*}(234.03)/P_{Cl*}(235.204)=$	3.94 ± 0.97[k]	166
$P_I(277.87)/P_{I*}(277.38)=$	0.094[l]	171
$P_I(304.03)/P_{I*}(304.67)=$	0.80 ± 0.05[l]	171, 183
	0.769[l]	146
	0.77 ± 0.11[l]	184
	0.90[m]	185
	1.00 ± 0.05[l]	186

[a]ARA IR detection of Cl* and Cl in photolysis of HCl.
[b]LIF VUV detection of Cl* and Cl in photolysis of HCl.
[c]REMPI detection of Cl* at 237.808 nm and Cl at 237.73 and 235.336 nm. The ratio $P_{Cl}(235.336)/P_{Cl*}(237.808)=2.5$[175] was used.
[d]Two methods: theoretical calculation and REMPI detection of Cl*.
[e]Calculated from R_1 and R_2, where $R_1=P_{Cl*}(235.205)/P_{Cl*}(237.808)$ and $R_2=P_{Cl}(235.336)/P_{Cl*}(237.808)=2.5$.[175] The ratio R_1 was determined by REMPI detection of Cl*.[178]
[f]HR-TOF detection of H atoms in photolysis of HCl.
[g]The value and the measurement of the calibration factor are not described.
[h]TOF-MS of NO in photolysis of BrNO.[187]
[i]TOF-MS of Br* and Br in photolysis of Br_2.
[j]The measurement of the calibration factor is not described.
[k]TOF-MS of Cl*, Cl, Br*, and Br in photolysis of BrCl.
[l]REMPI detection of I* and I in the photolysis of I_2 near 304 nm. Only $I_2 \rightarrow I^*+I$ channel is assumed.
[m]The yield of I* in the photolysis of CH_3I have been compared with that studied by TOF-MS[188] and SE IR.[137]

rate of the deactivation of I* by ICl;[200–202] the rate constant for the overall I*+ICl deactivation is $(2.4\pm0.9)\times10^{-11}$ cm^3/molecule·s.[56,203,204] The third step Eq. (15c) is a chemical removal of ground state chlorine atoms, the rate of this reaction is 8×10^{-12} cm^3/molecule·s.[75,77,83,205,206] It is 33 times larger than the rate of deactivation of Cl* by ICl.[77,83,206] The advantages of this laser are simplicity and quick restoring of working gas after the laser pulse.[207] Since ICl absorbs well in a spectral region of maximum solar radiation, this chlorine laser based on the photodissociation of ICl is interesting because it may be pumped by solar radiation. Later, this Cl*–Cl laser was applied by Sotnichenko *et al.* for study of collisional quenching of Cl*.[75,208]

Also, the inversion population on the Cl*–Cl transition was observed in microwave and radio-frequency discharges in ICl/Ar mixtures.[209] The density of the population inversion was about 2×10^{12} cm^{-3} for both kinds of discharge. This value is not enough to create a continuous wave laser.

1.4.2. Bromine Lasers

In spite of the large number of molecules which produce population inversion on the I*–I transition in photodissociation processes there are only several molecules (see Table 13), which give population inversion on this transition in the bromine atom. The lasing action on the Br*–Br transition was first observed by Guiliano and Hess in 1969,[210] who used flash photolysis of gaseous IBr. Later, the Br*–Br laser emission has been observed during flash photolysis (190–225 nm) of CF_3Br by Campbell and Casper.[47] Efficient, repetitively pulsed Br*–Br lasers driven by photodissociation of static IBr or Br_2 samples were proposed,[211–213] where broadband flash photolysis was used, and later by Pastel *et al.* who pumped the bromine laser by radiation of a Nd:YAG laser with $\lambda=532$ nm.[197] The kinetic scheme for IBr laser coincides in all details with that for ICl laser [Eqs. (15a)–(15d)]. As chlorine laser based on photodissociation of ICl, this bromine laser may also be pumped by solar radiation. Usually the energy efficiency of these Br*–Br lasers are much smaller than that of iodine I*–I lasers.

Note that continuous Br*–Br lasers have never been created.[198,213–215] According to Boriev and Gordon,[216,217] the problem is connected with vibrationally excited IBr:

$$\mathrm{IBr}+h\nu\rightarrow\mathrm{IBr}^*, \tag{16a}$$

$$\mathrm{IBr}^*+\mathrm{IBr}\rightarrow2\mathrm{IBr}^*(v<40), \tag{16b}$$

$$\mathrm{Br}^*+\mathrm{IBr}^*(v<7)\rightarrow\mathrm{I}^*+\mathrm{Br}_2, \tag{16c}$$

$$\mathrm{I}^*+\mathrm{IBr}\rightarrow\mathrm{Br}^*+\mathrm{I}_2, \tag{16d}$$

where the first step (16a) is photoexcitation of IBr, the second step (16b) is collisional production of vibrationally excited IBr*, and the last two steps are the chain decomposition of IBr.

The population inversion on the Br*–Br transition may be used to create different infrared lasers pumped by electronic-vibrational (E-V) energy transfer from Br* atoms,

$$\mathrm{Br}^*+\mathrm{M}\rightarrow\mathrm{Br}+\mathrm{M}^{**} \tag{17a}$$

$$\mathrm{M}^{**}\rightarrow\mathrm{M}^*+h\nu, \tag{17b}$$

where M* and M** denote vibrationally excited M molecules, the inversion population is created on the M**–M* transition which has the energy $h\nu$.[218] Infrared lasers pumped by the E-V energy transfer from Br* to CO_2, N_2O, HCN, H_2O, and C_2H_2 are reported by Leone *et al.*[219–221] In these studies, gas mixtures containing excited Br* atoms were prepared by flash photolysing Br_2 in the presence of a polyatomic molecule. The ensuing E-V process is selective

and pumps the polyatomic molecule into specific energy states. In addition to obtaining gain and/or stimulated emission at CO_2 and N_2O laser frequencies, stimulated emission from HCN at 3.85, 7.25, and 8.48 μm, and from C_2H_2 in the region 7–8 μm have been obtained.[219] Wittig and coworkers constructed a 5.3 μm laser which they attributed to the NO ($v=2\rightarrow v=1$) transition pumped by Br^*+NO collisions.[222] The inverted vibrational distribution of excited NO ($[NO(v=2)]/[NO]\approx 0.84$) was confirmed later by Wight.[223]

The dynamics of a Br^*-Br pulsed laser and a Br^*-NO ($v=2\rightarrow v=1$) transfer laser driven by photolysis of IBr was later studied by Johnson *et al.*[224] A CO_2 laser operating on the 10(0)1-10(0)0 transition at $\lambda=4.3$ μm and pumped by *E-V* energy transfer from Br* has been demonstrated recently by Johnson *et al.*[225] This laser was driven by photolysis of IBr or Br_2 by a frequency-doubled Nd:YAG laser or Ar^+ laser, respectively. The output energy and gain of this laser is adversely affected by rapid vibrational *V-V* relaxation of CO_2 molecules.

1.4.3. Iodine Lasers

The atomic iodine photodissociation laser was created in 1964 by Kasper and Pimentel, who have observed a spontaneous emission from the UV photolysis of CF_3I and CH_3I.[226] The emission was interpreted as the generation due to

$$CX_3I+h\nu\rightarrow CX_3+I^*,\quad X=H,F, \tag{18a}$$

$$I^*\rightarrow I+h\nu_0,\quad \lambda_0=1.316\ \mu m. \tag{18b}$$

Later the laser emission was obtained from the photolysis of the other alkyl iodides, and as most efficient compound i-C_3F_7I was found.[227,228] Since then, the iodine laser has been studied intensively.[229–231] For example, it was found that additional chemical generation of the population inversion on the I^*-I transition comes from the reaction $CF_3^*+CF_3I\rightarrow C_2F_6+I^*$, where CF_3^* denotes excited radicals, or indirectly in the reaction $CF_3+I\rightarrow CF_3I$, which removes the ground state iodine atoms.[232,233]

Later Derwent and Trash[234] suggested that a I^*-I laser could be constructed based upon the following energy-transfer equilibrium

$$O_2(a\,^1\Delta_g)+I\leftrightarrow O_2(X\,^3\Sigma_g^-)+I^*, \tag{19}$$

since $O_2(a\,^1\Delta_g)$ is extremely metastable with respect to both spontaneous radiation (half-time $\sim$45 min)[235,236] and collisions (typically 10^6 collisions are required); the rate constants of direct and reverse reactions [Eq. (19)] are fast, they are equal to $(7.6\pm2.5)\times10^{-11}$ and $(2.6\pm0.9)\times10^{-11}$ cm^3/molecule·s, respectively.[237] The chemical oxygen–iodine laser (COIL) was discovered, when the chemical generation of a population inversion between the spin-orbit states of atomic iodine was observed by Pritt *et al.*[238] The first continuous wave COIL was developed by McDermott *et al.* in 1978,[239] since then the COIL technology has undergone numerous improvements[240–242] and chemical efficiencies as high as 27%–30% using helium diluent have been demonstrated;[243] now multikilowatt lasers are routinely constructed.[244–247]

Much of the development of the iodine laser technology to date has focused on a new generator of $O_2(^1\Delta)$. One approach is to provide the necessary atomic iodine and $O_2(^1\Delta)$ purely by electrical discharge.[248–252] It has been found by Ivanov *et al.* that excitation of molecular oxygen in a glow discharge at around 1 Torr provides significant concentrations of $O_2(^1\Delta)$, up to 2×10^{15} cm^{-3}.[249] Researchers in Japan have demonstrated very large yields of the $O_2(^1\Delta)$ precursor molecules, up to 32%, using a microwave and rf discharges in the mixtures of O_2, N_2, NO, and NO_2; it was demonstrated that added gases increased the yield of singlet oxygen.[250,251]

Another, and very promising, approach is replacement of singlet oxygen with chemically generated nitrene metastables such as $NCl(a\,^1\Delta)$ or $NF(a\,^1\Delta)$. This approach led to an all gas-phase iodine laser, it eliminates the heavy, water-based COIL chemistry based on very corrosive hydrogen peroxide. In 1995, Ray and Coombe created a pulsed I^*-I laser pumped by energy transfer from $NCl(a\,^1\Delta)$; the iodine atoms and NCl were produced by photodissociation of CH_2I_2 and ClN_3 at 193 nm.[253,254] Excited $NCl(a\,^1\Delta)$ molecules exchange energy with atomic iodine in a manner analogous with oxygen in COIL

$$NCl(a\,^1\Delta)+I\rightarrow NCl(X\,^3\Sigma^-)+I^*, \tag{20}$$

with the rate constant of 2×10^{-11} cm^3/molecule·s.[255] Using an optical double-resonance technique, Yang *et al.*[253] have observed a population inversion between the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic iodine, produced in this reaction. Recently, Henshaw *et al.*[256,257] developed the all gas-phase iodine laser based on the energy transfer process (20), where reactions of Cl with HN_3 were used for the generation of excited nitrogen chloride:

$$Cl+HN_3\rightarrow HCl+N_3, \tag{21a}$$

$$Cl+N_3\rightarrow NCl(a\,^1\Delta)+N_2. \tag{21b}$$

The rate constants for reactions (21a) and (21b) are 1.1×10^{-12} and 1.5×10^{-11} cm^3/molecule·s, respectively.[258–260] This is the first major breakthrough in energy donor generator technology in the last 10 years.

1.5. Excited Halogen Atoms and Ozone Depletion

The role of Cl* atoms in stratospheric chemistry is discussed by Tyndall *et al.*[79] It is assumed that at 30 km altitude the main source of Cl* atoms is photodissociation of $ClONO_2$, and the main removal process is deactivation by O_2. It was concluded that the excited Cl* atoms are unimportant in the stratosphere, since the rate of the photolytic production of the Cl* atoms is small ($\leqslant$1%) in comparison with production of the Cl* atoms in $Cl+O_2\rightarrow Cl^*+O_2$ process.

Atomic bromine exhibits a 40 times more powerful atmospheric ozone depletion potential than a chlorine atom, in the

stratosphere it depletes ozone via several chain reactions.[261] The contribution of excited Br* atoms in the depletion of ozone may easily be estimated from the data of the present review. Briefly, the main quencher of Br* atoms in the atmosphere must be CO_2 with a rate constant of 1.5×10^{-11} cm^3/molecule·s; the key reactions of bromine atoms in atmosphere are Br+M (M=O_3, H_2CO, HO_2) with the rate constants of $\sim 10^{-11}$ cm^3/molecule·s; since the concentration of CO_2 is several orders of magnitude larger than the concentrations of M molecules, the role of excited Br* is negligible.

The role of F* and I* atoms in the depletion of ozone is expected to be negligible also.

2. Excited Fluorine Atoms F*($^2P_{1/2}$)

Kinetics measurements on processes involving F* atoms are beset at least with two difficulties. One is the lack of simple and sensitive methods to detect F* atoms. The first resonant electronic transition occurs in the far vacuum ultraviolet (VUV) region at 95.5 nm, well below the LiF window cutoff at 106 nm. Therefore, one-photon excitation requires VUV generation and windowless conditions. Two-photon excitation seems even less promising because it requires large technical effort since the simultaneous absorption of two photons below 200 nm is necessary. The IR absorption lies near 400 cm^{-1}, this wavelength is available only for diode laser absorption spectroscopy. Another difficulty, arising in the case of photolytic production of F* atoms, is that only a few precursor molecules yield fluorine atoms from photolysis in the visible or UV spectral ranges. Hence the data on the chemistry of excited F* atoms are very limited.

2.1. Collisional Deactivation of F* Atoms

2.1.1. Molecular Beam Studies and Theoretical Predictions

In 1979, the interaction potentials for F(^{2}P) +Ne,Ar,Kr,Xe systems were constructed from experimental differential cross sections for inelastic scattering obtained by Lee *et al.* in experiments with crossed molecular beams.[262–264] In these measurements, very low collisional energy was achieved (0.02 eV for F+Xe and 0.036 eV for F+Ar). The authors employed the potentials to calculate inter and intramultiplet changing cross sections for F–Ar and F–Xe.[264] These cross sections may be used to calculate the bimolecular deactivation rate constants at $T=300$ K, the "temperature of collision" T is estimated from the energy of collision E as $kT=\pi E/4$. The results are presented in Table 7.

Later, Aquilanti *et al.* continued the molecular beam studies of fluorine atoms.[265,266] A magnetic beam technique with magnetic analysis of substates of fluorine atoms was used to measure absolute integral cross sections for scattering of fluorine atoms by Ar, Kr, and Xe. Using own experimental absolute integral cross sections, differential cross sections of Lee *et al.*, relative integral cross sections of Müller,[267] and some spectroscopic data, Aquilanti *et al.* obtained new interaction potentials for F–Ar, F–Kr, and F–Xe. Unfortunately, it is rather difficult to calculate the room temperature deactivation rate constants from these data.

TABLE 7. F*+M cross sections (σ) and rate constants (k) for spin-orbital deactivation and for EPR-line broadening ($T=300$ K)

M	σ (Å^2)	k (cm^3/molecule·s)[a]	Method	Reference
He	0.19±0.05	2.6×10^{-12}	EPR-H[b]	272, 273
	0.36±0.06	4.9×10^{-12}	EPR-G[c]	272, 273
	0.127–0.305	$(1.77–4.23)\times10^{-12}$	Theory[d]	268, 269
	0.31±0.045	4.3×10^{-12}	EPR-G[c]	156
Ne	0.013–0.185	$(1.0–15)\times10^{-13}$	Theory[d]	268, 269
	≤0.064	$\leq 5.2\times10^{-13}$	EPR-G[c]	156
Ar	0.34±0.10	2.4×10^{-12}	EPR-H[b]	273
	0.00096	6.7×10^{-15}	Mol.beam[e]	264
	0.003–0.007	$(2.1–4.9)\times10^{-14}$	Theory[d]	268, 269
	0.065±0.011	4.56×10^{-13}	EPR-G[c]	156
Kr	0.002–0.004	$(1.3–2.6)\times10^{-14}$	Theory[d]	268, 269
	0.080±0.013	5.1×10^{-13}	EPR-G[c]	156
Xe	0.0128	7.9×10^{-14}	Mol.beam[e]	264
	0.001–0.011	$(1–11)\times10^{-15}$	Theory[d]	268, 269
N_2	0.506±0.077	3.8×10^{-12}	EPR-G[c]	156
O_2	5.72±2.03	4.2×10^{-11}	EPR-G[c]	156
F_2	0.40±0.09	0.28×10^{-11}	EPR-H[b]	272
	1.94±0.14	1.37×10^{-11}	EPR-G[c]	156
WF_6	~0.51	$\sim 3\times10^{-12}$	Br-laser[f]	97
UF_6	$\sim 1.7\times10^{-5}$	$\sim 1\times10^{-16}$	Br-laser[f]	97
F	25±1	2×10^{-10}	EPR-H[b]	272

[a] $k=v\sigma$, where v is the average speed of the F*+M collision.
[b] The H-line of the EPR spectrum (F,m_F:1,0↔1,−1) of F* atoms was used.
[c] The G-line of the EPR spectrum (F,m_F:0,0↔1,−1) of F* atoms was used.
[d] Theoretical predictions for F*+M→F+M deactivation rate constant. The range of the values obtained for different potentials is presented.
[e] Molecular beam study at very low collisional energy.[264]
[f] Only F*+Br_2→Br*+BrF, F+Br_2→Br+BrF reactions for removal of fluorine atoms were assumed, the bromine atoms were detected by a Br laser.

Using interatomic potentials from molecular beam studies of Lee *et al.* and Aquilanti *et al.*, Reznikov and Umanskii have theoretically calculated the cross sections and the rate constants both for F*+M deactivation[268] (see Table 7) and for EPR line broadening.[269] There are large disagreements, about 1–2 orders of magnitude, between the rate constants calculated by Reznikov and Umanskii and by Lee *et al.*[264] for collisional deactivation F*+Ar, Xe at low collisional energies. Reznikov and Umanskii concluded that this disagreement is due to uncertainty in the experimental data on the interatomic potentials.

In closing the discussion of the theory of F*+atom scattering we note, that close-coupled calculations for deactivation of F* by protons H^+ have been done by Mies in 1973.[270,271]

2.1.2. EPR Linewidth Studies

The cross sections of the broadening of the gas phase EPR linewidth of F* atoms by different gases have been measured by Miller *et al.*[272–274] and by Boltnev *et al.*[156] Using these cross sections, one may calculate the broadening rate con-

stants (see Table 7), which may be treated as the upper limits for the deactivation rate constants. Boltnev *et al.* concluded that in the case of $F^* + He$ the contribution of the collisional depolarization of F^* atoms is small ($\leqslant 20\%$), and hence the measured rate constant for EPR linewidth broadening is close to the deactivation rate constant.

2.2. Reactions of F* with H_2 and HBr

2.2.1. Reaction $F^* + H_2$

There is a discussion in literature on the relative reactivity of excited and unexcited fluorine atoms in the reaction with hydrogen

$$F + H_2 \rightarrow HF + H, \tag{22a}$$

$$F^* + H_2 \rightarrow HF + H. \tag{22b}$$

There are three potential energy surfaces for these reactions, two of them (denoted $1^2A'$ and $1^2A''$ for collinear reaction) correlate to $F + H_2$, and one ($2^2A'$) to $F^* + H_2$. The $2^2A'$ is strongly repulsive, and thus $F^* + H_2$ collisions must be completely nonreactive in the adiabatic limit. However, reaction (22b) may occur due to nonadiabatic crossing from the $2^2A'$ to the $1^2A'$ surface. In 1974, using classical-path calculations on diatomic-in-molecules surface, Tully demonstrated the importance of the nonadiabatic channel (22b) and predicted that $k_{22b} \approx 0.1 k_{22a}$.[275] Since that time, a lot of theoretical predictions on the spin-orbital effects in the $F + H_2$ system have been done.[276–310] Also, Baer and co-workers have published several theoretical papers on the reactions (22a), (22b) in a strong laser field.[311–314] A top-level theoretical study was done by Alexander *et al.*, who used a full *ab initio* calculation of the complete set of diabatic potential energy surfaces and spin-orbital terms for this system.[299] The fitted surfaces and couplings have been used to perform exact time-dependent quantum scattering calculations of reaction transition probabilities. The main conclusion of this calculation is close to that of Tully, $k_{22b} \sim 0.04 k_{22a}$. One of possible the mechanisms for reaction (22b), clearly speculative but very popular, involves nonadiabatic electronic-rotational (E-R) energy exchange followed by reaction on the adiabatic $F + H_2$ surface in a single collision event

$$F^* + H_2(j=0) \rightarrow [F - H_2(j=2)] \rightarrow H + HF. \tag{23}$$

Note that the efficiency of the first step, E-R exchange, was confirmed in many theoretical studies.

In large contrast with the large amount of theoretical studies, until quite recently there have been no experiments that have confirmed the presence of the nonadiabatic channel (22b). Moreover, in 1985 Lee and co-workers employed a high-resolution crossed molecular beam study, and no HF reaction product attributable to F^* was detected neither in $F^* + H_2$,[315] nor in $F^* + D_2$, HD[316] reactions. However, recently channel (22b) was finally observed in an experimental study of Nizkorodov *et al.*, who used infrared laser absorption to investigate the vibrational and rotational distribution of HF molecules in low-density crossed supersonic jets under single collision conditions.[317,318] In these experiments, product states in the HF ($v=3$) manifold were observed that are energetically accessible only to channel (22b). This experimental study stimulated new theoretical studies[299–304,306–310,319–322] in which it has been found that, except for very cold reactants, the F^* state plays a minor role in determining the reactivity.

Recently Rusin *et al.* have studied reactions (22a), (22b) by measuring the high-resolution time-of-flight spectra of HF at collision energies $E = 69–81$ meV.[323] The results were compared with exact coupled-channel quantum mechanical calculations based on the Stark–Werner *ab initio* energy surface.[324] Excellent agreement between the experimental and computed rotational distributions is found for the HF($v=1,2$), this fact confirms that the reaction dynamics for these product states is determined by pathway (22a) only. For HF ($v=3, j \geqslant 2$), however, the agreement is less satisfactory, hence considerable contribution of pathway (22b) is assumed.

Note, however, that a new *ab initio* energy surface has been developed for the $F + H_2$ reaction just recently by Hayesa *et al.*[325] Hayesa *et al.* carried out several preliminary scattering calculations using this new surface and predicted that the differential cross sections at low collision energy for the $F + H_2$ reaction may be drastically modified from the predictions based on the Stark–Werner surface.

2.2.2. Reactions of F* with HBr and DBr

Polanyi and co-workers carried out a crossed molecular beam study of the $F^*/F + HBr$ (DBr) reactions.[96] The ratio $[F^*]/[F]$ was varied by changing the temperature of the source. From the insensitivity of the product Br atom spin-orbit distribution to the incident $[F^*]/[F]$ ratio, they concluded that, first, there is a substantial barrier to the adiabatic process $F^* + HBr \rightarrow HF + Br^*$, and, second, excited Br^* atoms appeared due to the nonadiabatic process $F + HBr \rightarrow HF + Br^*$. The conclusions on the reaction of F^*/F with DBr are the same.

2.3. Production of F* Atoms by Photolysis

To the knowledge of the author there is only one measurement of F^* quantum yields from photodissociation. In 1996 Zhang *et al.* have studied photodissociation of HF ($v=3$) in the VUV, where HF was vibrationally excited by a Ti:sapphire laser through an overtone transition, and H atoms were detected by the high-n Rydberg time-of-flight technique.[62] From the time-of-flight profiles of H atoms the F^* relative quantum yield was found to be 0.42 ± 0.02 and 0.41 ± 0.08 at 193.3 and 121.6 nm, respectively. The β parameter was determined to be -1.0 ± 0.05 at 193.3 nm photolysis for both $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic fluorine; hence both channels derive from the perpendicular transition $A\,^1\Pi \leftarrow X\,^1\Sigma^+$.

In the adiabatic limit, when the atoms separate slowly, the relative yield of F^* atoms should be 0; in the diabatic limit when the atoms separate quickly, this yield should be 1/3; the experimental value is higher than both. The last theoretical

calculations of Brown and Balint–Kurti on the photodissociation of HF ($v=0$),[326] HF ($v=1,2,3$) and DF ($v=1,2,3$)[327] agree well with the experimental results of Zhang *et al.* and predict a rather complicated dependence of the relative yield of F* atoms on the photon energy.

Also, the yields of F* atoms in the photolysis of WF_6 and UF_6 have been determined to be $\geqslant 0.4$ and ~ 0.07, respectively, in an indirect study of Gordon *et al.*[97] In this study, F*/F atoms were converted to Br*/Br atoms by the reactions $F^*/F + Br_2 \rightarrow Br^*/Br + BrF$, and the bromine atoms were detected by a Br laser. Note that this conversion mechanism has never been confirmed experimentally.

3. Excited Chlorine Atoms Cl*($^2P_{1/2}$)

3.1. Collisional Deactivation of Cl* Atoms at $T=300$ K

The first studies on collisional deactivation of Cl* were reported by Husain *et al.*,[69,328–331] who detected Cl* atoms by time-resolved atomic resonance absorption in the vacuum ultraviolet (ARA VUV). Later, the deactivation of Cl* atoms was studied by the time-resolved laser magnetic resonance (LMR) technique by Krasnoperov and Chichinin.[54,55,159,206,332,333]

The rate of deactivation of Cl* by ICl was found to be 33 times lower than the rate of the $Cl + ICl \rightarrow I + Cl_2$ reaction,[206] and this fact has stimulated the creation of a photodissociative-chemical laser, operating on the spin-orbital transition of the chlorine atom.[199] This laser was applied by Sotnichenko *et al.* to study collisional quenching of Cl*,[75,208] and the results were in agreement with those obtained in LMR studies. At the same time, tunable diode laser absorption spectroscopy was originally applied to study Cl* quenching processes.[72,334] Also, the rate constant for deactivation of Cl* by SO_2 has been measured by Dolson and West by monitoring the infrared fluorescence from the fundamental SO_2 stretching levels.[78] Recently, Hitsuda *et al.* have used laser-induced fluorescence in the vacuum ultraviolet (LIF VUV) to detect Cl* and Cl atoms near 135 nm. LIF VUV and LMR methods are probably the best for studying Cl* deactivation processes, they have nearly equal sensitivity, about $[Cl^*] \sim 10^{10}$ cm^{-3}, but the time resolution of LIF VUV is better.

The rate constants for the collisional deactivation of Cl* at room temperature are listed in Table 8 in chronological order for each quencher.

3.1.1. First ARA VUV Measurements

The substantial disagreement (by orders of magnitude) between all ARA VUV data obtained in 1977–1984 by Husain *et al.*,[69,328–331] and the data obtained by other methods is almost total. An agreement occurs only in four cases (Ne, CF_2Cl_2, CF_4, CCl_4); in three of them the rate constants are close to the gas-kinetic collision limit. The reasons for this disagreement have been discussed in several papers. The conclusion of the consideration is that these ARA VUV data cannot be recommended even as rough estimate. The probable sources of error in ARA VUV experiments have been outlined in Chichinin.[158] Some of these sources are:

(1) The VUV radiation used in these experiments photolyses many quenchers (for example, Cl_2, O_2) and yields atoms other than Cl*. The concentration of these atoms A is proportional to the concentration of the quencher Q, $[A] \sim [Q]$. From theoretical considerations it is known that the atoms A must deactivate Cl* rather quickly. Hence the measured rate constant for deactivation of Cl* may be overestimated due to contribution of the $Cl^* + A \rightarrow Cl + A$ quenching process.

(2) The rate constants $k(M)$, where M=He,Ne,Ar,Kr,Xe, have been obtained from the $\tau^{-1} = \tau_0^{-1} + k(M)\,[M]$ dependencies, where τ is the first-order rate constant for the decay of the Cl* signal.[335] The increase of τ^{-1} was very small, about 10%, and may be explained by other reasons except deactivation of Cl* by M. The only system in which the τ^{-1} increased strongly (~ 2 times) is the Cl*+Ne system, but in this particular case there is an agreement with the LMR data.

(3) In order to detect Cl* atoms, Husain *et al.* used the absorption line $3p^4\,4s(^2P_{3/2}) \leftarrow 3p^5\,(^2P_{1/2})$ near 136.34 nm. In the work of Clyne and Nip it was found that this line is not suitable to detect Cl* atoms since at this wavelength there is also a strong absorption of ground state Cl($^2P_{3/2}$) atoms.[68]

3.1.2. Cl*+ICl, I_2

The rate constant for deactivation of Cl* reported by Park *et al.*[334] is 1 order of magnitude higher than the constants obtained by Chichinin and Krasnoperov,[206] Wang and Jones,[77] and by Boriev.[83] This discrepancy is in fact surprising since the rate constant for the similar process Cl* +NOCl reported by Park *et al.* is consistent with the value obtained by LMR method. The reason for the discrepancy is not clear, but it seems noteworthy that Park *et al.* overestimated several times the rather well established[75,77,83,205,206] rate constant for the reaction $Cl + ICl \rightarrow I + Cl_2$. As it was proposed in Park *et al.*,[333] the $7\% \pm 3\%$ admixture of I_2 in ICl in the work of Park *et al.* would explain both (Cl* +ICl and Cl+ICl) discrepancies between Park *et al.*[334] and the other authors, although it is not clear where such a large I_2 admixture in ICl should have come from. If this explanation is correct, one can estimate the rate constant for the $Cl^* + I_2$ deactivation process to be $(5.3 \pm 2.6) \times 10^{-11}$ cm^3/molecule·s.

3.1.3. Deactivation of Cl* Atoms by Hydrides

In contrast to the situation with excited I* and Br* atoms, from Table 8 it is apparent that deactivation of Cl* by H_2, D_2, HF, DF, HCl, DCl, and H_2O (and presumably CH_4) at $T=300$ K is predominantly due to E-R, T energy transfer since all E-V channels are endothermic; here E, V, R, and T denote electronic, vibrational, rotational, and translational energies. Note that the deactivation of Cl* via chemical reaction is unlikely, the deactivation proceeds mainly by physical quenching; this was proven in several cases (H_2, D_2, DCl, CH_4) in experiments in which the kinetics of ARA IR,

TABLE 8. Summary of Cl* deactivation rate constant (k) determinations at 300 K (powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times 10^{-c}$)

M	k (cm^3/molecule·s)	Detection	Reference
H	~7(−11)	ARA VUV	328
He	3.8±0.6 (−15)	ARA VUV	69, 335
	7.3±2.0 (−14)	LMR	332, 333
	6.0±1.0 (−14)	ARF VUV	79
	5.7±0.3 (−14)	LIF VUV	336
Ne	4.0±0.5 (−14)	ARA VUV	331, 335
	≤4.2(−14)	LMR	332
	≤8(−16)	LIF VUV	336
Cl	3.0±1.5 (−10)	ARA IR	208
	4.7±1.5 (−12)	EPR	155
Ar	1.1±0.3 (−12)	ARA VUV	331, 335
	≤1.0(−14)	LMR/S	54
	≤1.0(−14)	ARA IR	75
	≤2.7(−15)	LMR	159, 332
	≤1(−15)	EPR	155
	3.0±1.0 (−16)	ARF VUV	79
	≤5(−16)	LIF VUV	336
Kr	1.4±0.2 (−12)	ARA VUV	331, 335
	~5.4(−15)	LMR	332, 333
I	5±2 (−12)	ARA IR	201, 208
Xe	1.8±0.2 (−11)	ARA VUV	331, 335
	≤4.5(−14)	LMR	332
H_2	7(−12)	ARA VUV	328
	$\leq 6\times 10^{-13}$	ARA VUV	331
	5.0±1.2 (−11)	ARA IR	75
	2.6±0.7 (−11)	EPR	155
	8.0±2.0 (−11)	LMR	333
	5.5±1.6 (−11)	LMR	202
D_2	1.1±0.3 (−11)	ARA IR	75
	1.7±0.4 (−11)	LMR	333
HF	1.4±0.4 (−11)	LMR	202
DF	0.7±0.2 (−11)	LMR	202
CO	~6(−12)	ARA VUV	331
	8.0±2.0 (−14)	ARA IR	75
N_2	6.3±1.0 (−13)	ARA VUV	331
	4.0±1.0 (−13)	ARA IR	75
	5.0±1.5 (−15)	ARF VUV	79
	3.9±1.5 (−14)	LMR	333
	7.6±0.8 (−15)	LIF VUV	336
NO	0.66±0.2 (−11)	LMR	202
O_2	2.1±0.5 (−11)	ARA VUV	69
	2.3±0.3 (−11)	ARA VUV	331
	1.7±0.4 (−13)	LMR/S, LMR	54, 206
	1.3±0.3 (−13)	ARA IR	75
	1.9±0.2 (−13)	CARS	77
	3.5±0.5 (−13)	ARF VUV	79
HCl	6(−12)	ARA VUV	328
	1.1±0.1 (−12)	ARA VUV	331
	1.2±0.2 (−11)	AS-DL	72
	1.2±0.3 (−11)	LMR	333
	7.8±0.8 (−12)	LIF VUV	82
DCl	0.7±0.2 (−11)	LMR	202
Cl_2	4.5±0.4 (−11)	ARA VUV	69
	7.4±2.6 (−13)	LMR/S	54
	7.2±2.0 (−13)	LMR	206
HBr	1.2±0.36 (−11)	LMR	202
DBr	1.4±0.4 (−11)	LMR	202
ICl	3.3±0.5 (−13)	LMR	206
	4.0±1.0 (−12)	AS-DL	334
	3.2±0.2 (−13)	CARS	77
	4.4±0.8 (−13)	ARA IR RP	83
H_2O	2.6±0.5 (−12)	ARA VUV	331
	7.8±2.3 (−11)	LMR/S	55
CO_2	<5(−13)	ARA VUV	331

TABLE 8. Summary of Cl* deactivation rate constant (k) determinations at 300 K (powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times 10^{-c}$)—Continued

M	k (cm^3/molecule·s)	Detection	Reference
	1.5±0.4 (−11)	ARA IR	75
	9.0±3.0 (−12)	LMR	333
	1.2±0.1 (−11)	LIF VUV	81
N_2O	3.7±0.6 (−13)	ARA VUV	331
	6.3±2.0 (−12)	LMR	202
O_3	~1(−11)	ARA VUV	68
	~7(−12)	LMR	332
NOCl	1.8±0.4 (−11)	LMR	159
	1.1±0.5 (−11)	AS-DL	334
SO_2	1.8±0.2 (−11)[a]	Fl IR CP	78
	1.9±0.5 (−11)	LMR	202
NF_3	2.2±0.6 (−10)	LMR	202
$COCl_2$	3.0±1.0 (−10)	LMR	333
PCl_3	1.3±0.2 (−11)	AS-DL	72
CH_4	3.9±0.8 (−12)	ARA VUV	331
	2.2±0.3 (−11)	ARF VUV	79
	3.0±0.3 (−11)[b]	LIF VUV	81
	1.9±0.6 (−11)	LMR	202
CH_2D_2	1.1±0.1 (−10)[b]	LIF VUV	81
CD_4	[b]	LIF VUV	81
	1.3±0.4 (−10)	LMR	202
CH_3F	>9(−12)[c]	MS	337, 338
	6.4±0.5 (−11)	LIF VUV	82
CH_3Cl	5±2 (−10)	AS-DL	72
CH_2Cl_2	2.0±1.0 (−10)	AS-DL	72
CF_4	1.5±0.4 (−10)	ARA VUV	330
	2.7±0.8 (−11)	LMR/S	55
	2.3±0.3 (−11)	ARF VUV	79
	2.4±0.7 (−11)	LMR	202
	2.3±0.4 (−11)	LIF VUV	82
$ClONO_2$	1.7±0.3 (−10)	ARF VUV	79
CF_2Cl_2	2.1±0.4 (−10)	ARA VUV	330
	1.8±0.4 (−10)	LMR/S	54
	1.8±0.4 (−10)	LMR	332
	3.3±0.5 (−10)	ARF VUV	79
CCl_4	5(−11)	ARA VUV	328
	2.0±0.2 (−10)	ARA VUV	69
	2.1±0.4 (−10)	ARA VUV	330
	1.8±0.6 (−10)	LMR/S	55, 332
CF_3I	1.0±0.3 (−10)	ARA IR	208
SF_6	1.5±0.05 (−10)	ARA IR	75
C_2H_6	1.22±0.09 (−10)	LIF VUV	82
	0.0±1.0 (−11)[d]	LIF VUV	339
C_2D_6	2.4±0.2 (−10)	LIF VUV	82
C_2H_5F	1.9±0.2 (−10)	LIF VUV	82
CH_3CF_3	2.0±0.2 (−10)	LIF VUV	82
C_3H_8	1.74±0.11 (−10)	LIF VUV	339
	4.5±1.2 (−11)[d]	LIF VUV	339
C_3D_8	3.08±0.21 (−10)	LIF VUV	339
	0.0±1.5 (−11)[d]	LIF VUV	339
C_6H_5Cl	5±1 (−10)	AS-DL	72
n-C_4H_{10}	2.05±0.10 (−10)	LIF VUV	339
	6.4±1.6 (−11)	LIF VUV	339
i-C_4H_{10}	2.13±0.12 (−10)	LIF VUV	339
	4.7±1.4 (−11)	LIF VUV	339

[a]$Cl^*+SO_2\rightarrow Cl+SO_2(\nu_1=1)/SO_2(\nu_3=1)$. The ν_3/ν_1 population ratio was found to be 1.6±0.5, even through excitation of ν_3 mode is 210 cm^{-1} more endoergic than ν_1.[78]

[b]The reaction rate constant is $<10^{-11}$ cm^3/molecule·s.[81]

[c]The value is recalculated from experimental data,[338] using the new rates of Cl^*+Cl_2, CH_3F processes.[54,82]

[d]Chemical reaction only.

LMR, and ARF VUV signals of Cl* atoms have been compared for Cl* + hydrides and unreactive Cl* + $CF_2Cl_2(CCl_4)$ systems.[75,79,202] For Cl* + H_2 system this conclusion was obtained from direct detection of H atoms.[155]

Very small deactivation rates should be expected for Cl* + hydride systems, since the *E-R* energy exchange requires multiquantum rotational transitions in the hydrides. In reality, see Table 8, the rates of these processes are unexpectedly large, indicating a large probability for nonadiabatic *E-R* transitions, in strong contradiction with theoretical estimates.[277,340] For example, Resnikov and Umanskii have carried out calculations for the Cl* + H_2, D_2 quenching processes.[340] The Landau–Zener formula with quadrupole-quadrupole interaction as a perturbation was used. It was found that the main contribution comes from Cl* + $H_2(J=4) \rightarrow$ Cl + $H_2(J=6)$ and Cl* + $D_2(J=5) \rightarrow$ Cl + $D_2(J=7)$ transitions; the total rate constants for deactivation of Cl* by H_2 and D_2 are 5×10^{-13} and 7×10^{-15} cm^3/molecule·s, respectively, in strong disagreement with what is found experimentally.

3.1.4. The Reactions of Cl* Atoms with Organic Compounds

Almost all existing kinetic data for quenching of Cl*($^2P_{1/2}$) atoms do not distinguish between chemical reaction and physical quenching of the excited atoms. The only exception are the LIF VUV studies of Matsumi *et al.*, in which the ratios $k_R/(k_Q+k_R)$ have been determined for the reactions of Cl* with CH_4, CH_2D_2, CD_4, C_2H_6, C_3H_8, C_3D_8, n-C_4H_{10}, and i-C_4H_{10}, respectively.[81,82,339] Here, k_R and k_Q are the rate constants for chemical reaction and physical quenching. The ratios have been determined to be <0.1, <0.3, <0.3, <0.08, 0.26±0.07, <0.05, 0.31±0.08, and 0.22±0.07, respectively. The rate constants for reactions of Cl* with C_3H_8, n-C_4H_{10}, and i-C_4H_{10} are ~30% of those for ground state Cl atoms. This observation suggests that the reactions of Cl* and Cl with alkanes RH proceed via different mechanisms. The reactant state Cl + RH adiabatically correlates to the product ground state HCl($^1\Sigma^+$) + R, while Cl* + RH correlates to a highly excited product state. Hence the reaction Cl* + RH should occur via non-adiabatic coupling between the two surfaces.[339]

3.1.5. Theoretical Predictions for the Deactivation Processes

To date there exist theoretical studies for the deactivation processes of Cl* atoms by rare gases,[268,341–343] by H_2, D_2, and HD,[277,340,344,345] and by HCl.[346–351] For illustrative purpose, in Table 9 we present a brief summary of theoretical predictions for deactivation at $T=300$ K. As for the Cl* + He,Ne,Ar,Kr,Xe series, the predictions are in excellent agreement with experiment for Cl* + He, in all other cases both experimental and theoretical data have too large uncertainties, see Table 8. The theoretical estimates for Cl* + H_2,D_2 are far from experimental results; however, the estimates illustrate, the *E-R* near-resonant energy exchange is much more efficient for Cl* + H_2 that for Cl* + D_2, in contradiction with experiment.

TABLE 9. Theoretical predictions for the Cl* + M deactivation rate constants at $T=300$ K

	k (cm^3/molecule·s)	Method	Reference
He	4.2×10^{-14}	NT, QMT[a]	268
	2.4×10^{-14}	EP[b]	341
	5.3×10^{-14}	AIP[c]	341
Ne	1.1×10^{-17}	NT, QMT[a]	268
	2.4×10^{-17}	EP[b]	341
	9.9×10^{-17}	AIP[c]	341
Ar	7.7×10^{-19}	NT, QMT[a]	268
	2.2×10^{-18}	EP[b]	341
	2.0×10^{-17}	AIP[c]	341
Kr	5.8×10^{-20}	NT, QMT[a]	268
Xe	1.4×10^{-20}	NT, QMT[a]	268
H_2	5×10^{-13}	NT, ERT[d]	352
D_2	7×10^{-15}	NT, ERT[d]	352

[a]NT, QMT = nonadiabatic transitions between quasimolecular terms. The terms are made by asymptotic method within approximate semiclassical model of Preston *et al.*[353]
[b]EP = Empirical potential is taken from the molecular beam study of Aquilanti *et al.*[354]
[c]AIP = *ab initio* potential is used.
[d]NT, ERT = a simple Landau–Zener curve crossing description, nonadiabatic transitions between electrorotational terms are assumed.

3.2. High-Energy Reactions and Deactivation of Cl* Atoms

3.2.1. Early Studies on Cl* Atom Scattering

In 1979, Lee and co-workers used a molecular beam technique to obtain the interaction potential for Cl–Xe.[264,355] In these works the parameters of the potential were clarified and a cross section $\sigma(1/2\rightarrow3/2)=7.8\times10^{-5}$ Å^2 at collisional energy of 0.00282 eV was calculated. Note that this collisional energy corresponds to the temperature $T=26$ K. Later, Aquilanti *et al.* continued molecular beam studies of Cl* atoms, and the parameters for the three lowest potential energy surfaces and the nonadiabatic coupling matrix for Cl*/Cl + He, Ne, Ar, Kr, Xe, H_2, D_2, and CH_4 systems were obtained.[354]

3.2.2. The Reaction of Cl* Atoms with CH_4

In reactions of halogen atoms, the ground spin-orbit state $^2P_{3/2}$ is generally considered to be more reactive than the excited $^2P_{1/2}$ state due to the adiabatic nature of the corresponding potential surfaces.[5] A laser flash photolysis-resonance fluorescence kinetics study of the reaction Cl(^{2}P) + $CH_4 \rightarrow CH_3$ + HCl was studied by Ravishankara and Wine at $T=221-375$ K.[356] The low temperature result obtained in this investigation, the non-Arrhenius behavior of the rate constant, and all previous investigations can be rationalized in terms of a model which assumes that the Cl*($^2P_{1/2}$) state reacts with CH_4 much faster than the Cl($^2P_{3/2}$) state.[356]

The indirect comparison of Cl* and Cl reactivity with CH_4 near the reaction threshold (collision energy of 0.13–0.16 eV) have been done recently by Kim *et al.*[182] In this study Cl* atoms were produced by photodissociation of BrCl at 420 nm and CH_3 product spatial anisotropy was studied by

REMPI (2+1); that is, PHOTOLOC (photoinitiated bimolecular reaction by low-of-cosines) technique was used. Kim *et al.* cannot claim that the $Cl^* + CH_4$ channel is less reactive than $Cl + CH_4$, but they can rule out the possibility of the role of Cl* reactivity in the explanation of the non-Arrhenius behavior at low temperatures.

3.2.3. The Reaction of Cl* Atoms with H_2

Until 1999, the reaction of Cl atoms with H_2 was assumed to proceed via adiabatic the ground state surface only, $Cl(^2P_{3/2}) + H_2 \rightarrow H + HCl$, and the upper $Cl^*(^2P_{1/2})$ state was assumed to be nonreactive.[357] However, "a rule is done to be broken;" recently, Lee *et al.* have studied the reactions

$$Cl^*/Cl + H_2 \rightarrow HCl + H, \tag{24a}$$

$$Cl^*/Cl + D_2 \rightarrow DCl + D, \tag{24b}$$

$$Cl^*/Cl + HD \rightarrow DCl + H, \tag{24c}$$

$$Cl + HD \rightarrow HCl + D, \tag{24d}$$

with a rotating-source, crossed-beam technique. Two different sources for generating the $Cl(^2P)$ beam were used, the concentrations of the two reactants (Cl* and Cl) and the H and D atom product were monitored by REMPI (1+1′).[85,344,358] Lee *et al.* reported that in reaction (24a) the excited Cl* atom is two times more reactive to H_2 than the ground state Cl reactant in the range of collisional energies from threshold near 3.8 kcal/mol till 9 kcal/mol: $\sigma^*/\sigma \approx 2$, here σ^* and σ denote reaction cross sections for Cl* and Cl atoms, respectively. For reactions (24b) and (24c) the relative reactivity of Cl* is lower than that of Cl atoms at small collisional energies and higher at large collisional energies; for reaction (24d) the ground state Cl atom is always more reactive than the excited Cl* atom.[85] Lee *et al.* have also pointed out that in the ion-molecular reaction $Ar^+(^2P_{1/2,3/2}) + H_2 \rightarrow ArH^+ + H$ studied by Tanaka *et al.*[359,360] the spin-orbitally excited $Ar^+(^2P_{1/2})$ ion is more reactive than the ground state $Ar^+(^2P_{3/2})$ ion by a factor of ~ 1.4.

However, the recent molecular beam study of Balucani *et al.*[361] put the results of Lee *et al.* in some doubt. In this study a combined experimental and theoretical determination of the differential cross sections of the $Cl^*/Cl + H_2$ reaction was done q1 at 3.85, 4.25, and 5.85 kcal/mol collisional energies. Balucani *et al.* have found that the Cl* atom is much less reactive than it was reported by Lee *et al.*; the product rotational distributions were also different. However, the direct comparison between the results of Balucani *et al.* and Lee *et al.* is not possible, because of the differences in the initial H_2 rotational distributions and in the collisional energies.

In addition, one should note the last calculations[362–364] on $Cl^* + H_2$ system based on the potential surface of Alexander *et al.*[362] The results of these calculations disagree with the measurements of Lee *et al.*[344,358] and Dong *et al.*,[85] the relative reactivity of Cl* was found to be lower than that of Cl atoms.

Recently, the scattering in $Cl^* + D_2$, He systems was studied by Parsons and Chandler by means of crossed-molecular-beam techniques with velocity-mapped ion imaging.[365] These experiments were done at collision energies E above and below the energy of the reaction barrier (4.9 kcal/mol). The upper limit for the cross section for electronically nonadiabatic quenching

$$Cl^* + D_2(j=0) \rightarrow Cl + D_2 \tag{25}$$

was determined to be $\sigma \leqslant 15^{+44}_{-15}$ Å^2 at $E = 7.6$ kcal/mol, the probability of process [Eq. (25)] was found to be indistinguishable to that for the kinematically identical system of $Cl^* + He$.

3.3. Production of Cl* Atoms by Photolysis

The data for Cl* relative quantum yields and β parameters are presented in Table 10 in chronological order for each parent molecule M.

3.3.1. Photodissociation of HCl and DCl

In recent years, the yield of Cl* atoms in the photodissociation of HCl was studied in a number of experimental (see Table 10) and theoretical works.[369,426–430] Its first UV absorption bands correspond to the singlet electronically excited state $A\,^1\Pi$ and to several triplet states. The $A\,^1\Pi$ and three other triplet excited electronic surfaces ($a\,^3\Pi_2$, $a\,^3\Pi_1$, and $a\,^3\Pi_{0^-}$) correlate adiabatically with H+Cl while the $a\,^3\Pi_{0^+}$ and $t^3\Sigma_1^+$ surfaces correlate with $H + Cl^*$.[175,189,190,193] The spin-orbit interaction in the chlorine atom is rather small (in comparison with iodine and bromine atoms) and therefore the photoexcitation is restricted primarily to spin-conserving transitions, i.e., the perpendicular transition $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ is much more important than those to triplet states. Hence the yield of Cl* atoms in photodissociation through photoexcitation of $a\,^3\Pi_{0^+}$ and $t^3\Sigma_1^+$ states must be very small, and the β parameter is close to -1.

In reality, the yields of Cl* atoms in photodissociation of HCl (and DCl) at 143–235 nm are close to the statistical limit of 1/3 (see Table 10), indicating strong nonadiabatic coupling between the $t^3\Sigma_1^+$ and $A\,^1\Pi$ excited surfaces at large H–Cl distances. Quantitative agreement has been reported between experimental studies of Lambert *et al.*[179] and a high-level, time-independent quantum dynamics computation involving *ab initio* electronic states and coupling terms of Alexander *et al.*[427] Recently, Regan *et al.* have studied the photodissociation of HCl in selected rovibrational states ($v = 1-3$) at 235 nm.[369] The branching Cl*/Cl ratio measured with the REMPI technique have been compared with theoretical predictions. The experimental results and the predictions share a common qualitative trend, although quantitative agreement occurs only for $HCl(v=2)$. New refined *ab initio* calculations of HCl potentials have recently been published[431] and might improve this agreement. It is interesting, that Gilvertz and Balint-Kurti have predicted that Cl*/Cl

TABLE 10. Summary of Cl* relative quantum yield and β parameter determinations from photodissociation

M	λ[a] (nm)	[Cl*]/([Cl]+[Cl*]) (%)[a]	β	Detection	Reference
HCl	193	33±3		AS-DL	72
	157	47±4	~−1	REMPI	189, 193[b]
	193	33±2	~−1	REMPI	189, 193[b]
	193	33±3		AS-DL	334, 366
	193	33.7±2.2		REMPI	174
	157	44.8±4		LIF VUV	175
	193	33.3±3.7		LIF VUV	175
	119–193	31–41		REMPI	177
	193	41±0.7	−0.94±0.07	HR-TOF	84
	193	33.6±3		REMPI	367
	235	33.3±2		REMPI	367
	193–235	33.4–47.5[c]		REMPI	179
	201–210	42–48[d]	≠−1	HR-TOF	180
	193	40.0±3.2		LIF VUV[e]	368
(v=1–3)	235	41–53[f]		REMPI	369
	135	35.9±1.2		LIF VUV[g]	370
	193		−0.87±0.06	REMPI/I	169
DCl	157	9.9±2.4		REMPI	190, 193[b]
	193	7.4±2.6		REMPI	190, 193[b]
	193	18.7±2.0		REMPI	174
	193	13.5±5.2		LIF VUV[e]	175
	193	18.7±3.3		LIF VUV[g]	175
	200–220	22–30[h]		REMPI	371
ClO	235	<3		REMPI	372
Cl_2	354	<33		LMR	159
	323.6–331.0	~0		REMPI(3+1)	373
	308	≤2.4		REMPI	374
	308	≤1		AS-DL	334
	340–355	≤1		AS-DL	334
	308–485	4–32[i]	−0.7–2.0[i]	REMPI	375
	351	<5		LMR	376
	238	23±1/30±3		REMPI	162
	308		−0.95±0.05	REMPI/I	377
	364.6,360.4	7.4±0.9	1.78±0.05	REMPI/I (2+1),(3+1)	378
	350–370	0.3–43[j]	−0.64–2[j]	REMPI/I	163
	404.17		1.4±0.2	REMPI (3+1)/I	379
BrCl	390–500	11–62[k]		REMPI	176
	235–540	[l]	[l]	REMPI/I	380
	235	16±2	−1.04±0.05	REMPI/I	166
	330–570	30–82[m]	≈2	REMPI/I	381
ICl	530	>33		LMR	382
	480–530	25–52[n]		TOF-MS	92
	530	55±5		LMR	206
	437–532	41–79[o]		LMR	383
	266	65±6		LMR	383
	248	67±5		LMR	376
	237.8	40.5±3.5		REMPI	384
	236.284	[p]	2	REMPI	385
	235	[q]	−1±0.1	REMPI/I	386
	304		[r]	REMPI/I	387
	248	47±6		LMR	202
HOCl	235	23±4		REMPI	388
	235,266	~0		REMPI/I	389
NOCl	266,354	~50		LMR	159
	236	31±2		REMPI/I	390
	248,351	88±12[s]		LMR	376
	355–600	0–45[t]		REMPI	391
	235	30	1.2–2.0[u]	REMPI/I	392
	212	48±3	~0[u]	LIF VUV	80
	235	30	1.6±0.4[u]	LIF VUV	80
	248	52±3	[u]	LIF VUV	80
OClO	362	~0.17	0.15±0.10[v]	REMPI	393
Cl_2O	248	18±2		LMR	376
	235	7.1±0.9	1.2±0.2	REMPI/I	389
	207		0.2±0.2	REMPI	394

TABLE 10. Summary of Cl* relative quantum yield and β parameter determinations from photodissociation—Continued

M	λ[a] (nm)	[Cl*]/([Cl]+[Cl*]) (%)[a]	β	Detection	Reference
	235		0.7±0.2	REMPI	394
SCl_2	235	38±4	[u]	REMPI/I	395
COFCl	235	50±30[w]		REMPI	396
$COCl_2$	248	<10		LMR	376
	235	15±3		REMPI	397–399
	235	22±3	0.52±0.08[u]	REMPI/I	400
$SCCl_2$	248	33±3		AS-DL	334
	235	47±3	0.06±0.06[u]	REMPI/I	401
$SOCl_2$	235	24	0.7±0.2	REMPI/I	392
	235	35±5	0.73±0.2	REMPI	402
	235	35±3	0.42±0.05[x]	REMPI/I	403
PCl_3	193	36.6±2		AS-DL	72
	248	44.1±2		AS-DL	72
	193	33±3		AS-DL	334
	248	44.1±3		AS-DL	334
	248	44.7±2.1		LIF VUV	175
	193	35.8±2.1		LIF VUV	175
	248	44±3		LMR	376
	238	33±2/35±1		REMPI	162
	235	46±2	0±0.2[u]	REMPI/I	395
S_2Cl_2	266	<33		LMR	159
	193	20±3		AS-DL	334
	248	21±3		AS-DL	334
	308	48±6		AS-DL	334
	235	35±3	0.13±0.07[u]	REMPI/I	404
CH_3Cl	193	33±3		AS-DL	72
	157	39±5		REMPI	189, 193[b]
	193	36.6±2	~2	REMPI	189, 193[b]
	193	40.7±2.8		LIF VUV	175
	193	38.2±2		REMPI	367
	235	21.3±0.6		REMPI	367
[y]	238	51.9±2		REMPI	367
	193	45±1		REMPI	405
	212	39±1	1.0±0.2	REMPI	405
	235	26.6±1		REMPI	405
$v=5$[z]	235	59±1		REMPI	405
$v=3$[z]	235	57.2±1		REMPI	406
$v=4$[z]	235	51.9±3		REMPI	406
CD_3Cl	193	39±5		REMPI	191, 193[b]
	157	33±2		REMPI	191, 193[b]
CH_2Cl_2	193	33±3		AS-DL	72
	193	22.6±6.0		REMPI	191, 193[b]
	157	31±6		REMPI	191, 193[b]
	193	25.7±4.4		LIF VUV	175
$v=3$[z]	235	55±12	0.37±0.05	REMPI	407
CD_2Cl_2	193	19±3		REMPI	191, 193[b]
	157	31±5		REMPI	191, 193[b]
CHF_2Cl	193	26.4±1.6		REMPI	408
$ClONO_2$[A]	308	30±5		ARF VUV	79
	308	33		ARF VUV	409
	235	34	1.2±0.15	REMPI	161
$CHFCl_2$[B]	235	33[B]		REMPI	410
	235		0.34–0.43[C]	REMPI	411
$CHCl_3$	193	20±3		REMPI	191, 193[b]
	157	37±2		REMPI	191, 193[b]
	238	43±4/(~0)		REMPI	162
$CDCl_3$	193	23±3		REMPI	191, 193[b]
	157	35±8		REMPI	191, 193[b]
CF_3Cl	354	86±7		ARA VUV	331
	157	<12		REMPI	191, 193[b]
	118,125		[u]	REMPI	10
	117–120	10±5		REMPI	412
CF_2Cl_2	354	75±10		REMPI	331
	157	<12		REMPI	191, 193[b]
	193	19±2		REMPI	191, 193[b]

TABLE 10. Summary of Cl* relative quantum yield and β parameter determinations from photodissociation—Continued

M	λ[a] (nm)	[Cl*]/([Cl]+[Cl*]) (%)[a]	β	Detection	Reference
	187	—	[u]	REMPI	10
$CFCl_3$	354	79±8		ARA VUV	331
	157	<12		REMPI	191, 193[b]
	193	23±5		REMPI	191, 193[b]
	187	—	[u]	REMPI	10
CCl_4	354	78±8		AS-DL	331
	157	<12		REMPI	191, 193[b]
	193	23±6		REMPI	191, 193[b]
	193	15±3		AS-DL	334
	193	19.2±3.3		LIF VUV[e]	175
	193	22.5±1.2		LIF VUV[g]	175
	238	20±2/44±3		REMPI	162
	235	20	0.0±0.1	REMPI/I	392
	135	21.1±1.1[D]		LIF VUV[g]	370
	193	26.7±1.3[D]		LIF VUV[g]	370
	235	21.9±3		REMPI	413
CF_2ClBr[E]	235	[w]		REMPI/I	164
CH_2CHCl	193	23.0±3		REMPI	414
$CH_2CH-^{35}Cl$	193	23.4±0.9		REMPI	414, 415
$CH_2CH-^{37}Cl$	193	22.5±1.5		REMPI	414, 415
	193	21.2±2	0.94±0.02[u, F]	REMPI/I	178
	210	24.2±2	0.85±0.2[u, F]	REMPI/I	178
trans-CHClCHCl	193	13.0±2	0.61±0.06	REMPI	414
	214	20.6±2		REMPI	416
	220	27.1±12		REMPI	416
cis-CHClCHCl	214	18.4±5		REMPI	416
	220	22.1±13		REMPI	416
CH_2CCl_2	193	21.8±3	−0.09±0.01	REMPI	414
	214	39.0±1.5		REMPI	416
	220	44.1±8		REMPI	416
C_2H_5Cl	193	39±5		REMPI	191, 193[b]
	157	33±6		REMPI	191, 193[b]
CH_3CF_2Cl	193	15.3±2.7		REMPI	417
	193	28.1±5.7[D]		LIF VUV[e]	368
CH_3CFCl_2	193	13.8±3		REMPI	417
$v=0$[z]	235	28.6±3.6		REMPI	418
$v=1$[z]	235	37.5±3.5		REMPI	418
	193	26.5±4		LIF VUV	419
C_3H_5Cl	234	33	0.01±0.05[u]	REMPI/I	420
	235	33.2±2	0.06	REMPI/I	421
n-C_3H_7Cl	193	41±3		REMPI	191, 193[b]
	157	30±2		REMPI	191, 193[b]
C_6H_5Cl	193	12.2±2.3		LIF VUV	175
	193	16±2[G]		AS-DL	72
n-C_4H_9Cl	193	33±4		REMPI	191, 193[b]
	157	37±5		REMPI	191, 193[b]
$(CH_3)_3COCl$	248		1.9±0.1	TOF-MS	422
	235	42	1.8±0.2	REMPI/I	392
o-$C_6H_4I(CH_2Cl)$	222–304	~0		REMPI	423

[a]The photolysis wavelength λ (or the range for λ) and yield of Cl* (or the range for the yields) are presented. The relative yields for ^{35}Cl* and ^{37}Cl* isotopes are presented as Γ_{35}/Γ_{37}. Γ~0 means "below the detection limit."

[b]The wrong values for Cl*/Cl ratios measured by Matsumi *et al.*[189–191] have been corrected later.[193]

[c]The yields of Cl* are 40.8±3.3, 40.4±2.4, 47.5±1.9, 40.8±2.8, 44.4±2.1, 41.3±2.3, 34.5±2.9, and 33.4±4.8% for 193.3, 205.5, 209, 214, 220, 225, 230.4, and 235.3 nm, respectively.

[d]The yields of Cl* are 42.3, 44.3, 45.2, 48.4, and 44.1% (±7%) for 201, 203, 205.5, 208.2, 210 nm, respectively.

[e]LIF VUV: tripling technique, CO is used for tripling of 405 nm photons.

[f]The yields of Cl* are 51±5, 53±6, 44±7, 43±6, 40±6 and 41±7% for $(v,J)=(1,0)$, (1,5), (2,0), (2,11), (3,0), and (3,7) rovibrational states of HCl.

[g]LIF VUV: four-wave mixing ($2\omega_1-\omega_2$, $\omega_1=212.56$ nm, $\omega_2\sim500$ nm) technique: compared to the tripling technique, it is much more intensive and stable.

[h]The yields of Cl* are 28±5, 29±12, 22±8, 30±6, and 28±8% for 200, 205.5, 210, 215, and 220 nm, respectively.

[i]The yields of Cl* are 0.94±0.2, 1.57±0.1, 4.1±0.3, 5.0±0.3, 8.3±0.5, 12.5±0.5, 14.9±1.3, 20±2, 21.9±2.5, 22.5±1.2, 27.0±1.1, 23.7±2.4, 30.1±1, 31.0±1, 32.0±2.4, 28.6±1, 20.6±1.3% for 308, 355, 375, 380, 385, 390, 395, 400, 405, 450, 455, 460, 465, 470, 475, 480, and 485 nm, respectively. The β parameters are −0.7±0.2, 1.8±0.2, 2.0±0.2, and 2.0±0.2 for 308, 355, 370, and 400 nm, respectively.

[j]The yields of Cl* are 0.30, 0.60, 1.00, 1.96, 4.58, 5.30, 8.34, 10.31, 17.56, 21.94, 30.02, 40.62, 42.03, 42.99, 41.38, 40.30, 40.83, and 40.65% for 350, 355, 360, 365, 370, 375, 380, 385, 390, 395, 400, 420, 430, 440, 450, 460, 465, and 470 nm, respectively. The β parameters are 2±0.08, 1.73, 1.68, 1.58, 1.54,

1.15, 0.84, 0.24, −0.06, −0.33, −0.47, and −0.64 for >370, 360, 355, 350, 345, 340, 335, 330, 325, 320, 315, and 310 nm, respectively. There is a contradiction: in the text it is mentioned that $\beta=-0.9$ at 310 nm.

[k]The yields of Cl* are 51.0, 60.0, 62.0, 50.0, 25.9, and 11% for 500, 480, 450, 420, 400, and 390 nm, respectively.

[l]$\beta\sim-1$ and $\beta=1.0-1.6$ for the 235–262 nm and 400–540 nm wavelength ranges, respectively. In the 320–410 nm range the yield of Cl* is close to zero.

[m]The yields of Cl* are 30.4, 38.5, 40.7, 50.6, 51.6, 53.6, 58.6, 62.0, 63.3, 66.9, 66.4, 67.1, 68.6, 66.8, 64.9, 60.6, 50.7, and 38.7% for 526, 518, 510, 502, 497, 495, 488, 481, 474, 467, 461, 455, 448, 442, 437, 431, 425, and 420 nm, respectively, in the photodissociation of BrCl($v=0$); 43.5, 54.2, 61.8, 68.4, 71.7, 74.6, 74.9, 75.5, 81.7, 82.0, 74.4, 42.4, 15.6, 8.9, 7.6, 10.2, 15.1, 1.1, and 8.5% for 534, 526, 518, 510, 502, 497, 495, 488, 481, 474, 467, 461, 455, 448, 442, 437, 431, 425, and 420 nm, respectively, in the photodissociation of BrCl($v=1$); 68.6, 63.1, 84.9, 71.5, 70.4, 60.0, and 37.8% for 551, 542, 534, 526, 518, 510, and 502 nm, respectively, in the photodissociation of BrCl($v=2$).

[n]The yields of Cl* are 51.5, 40.8, 37.0, 33.3, 26.6, and 25.0% for 530, 520, 510, 500, 490, and 480 nm, respectively. These Γ values presents the yield of Cl* from the photodissociation of ICl($B^3\Pi_{0+}$) state only due to parallel transition.

[o]The yields of Cl* are 41, 58, 66, 73, 75, 76, 78, 79, 77, 76, 77, 76, 75, 73, 71, and 58% for 437, 450, 455, 460, 465, 470, 475, 480, 485, 490, 495, 500, 505, 510, 520, 532 nm, respectively.

[p]$s^*/s=0.20\pm0.04$ is the ratio of REMPI signals of Cl* and Cl atoms at 237.808 and 236.286 nm, respectively.

[q]Rogers *et al.* have concluded from analysis of angular and velocity distributions of chlorine atoms that I*+Cl and Cl*+I channels dominate over I+Cl and I*+Cl*.

[r]The β parameter is measured for each of the two channels: ICl→I*+Cl*/Cl, 30%, $\beta=1.7$ and ICl→I+Cl*/Cl, 70%, $\beta=-0.5$.

[s]This previous value is incorrect.

[t]The yields of Cl* are <2, <2, 14±2, and 45±4% for 600, 562, 478, and 355 nm, respectively.

[u]The speed distribution of Cl* atoms and the speed dependence of the β parameter are obtained.

[v]The quantum yield of chlorine atoms (both Cl and Cl*) is determined.

[w]The signals of Cl* and Cl atoms were of the same order of magnitude.

[x]The speed distributions of Cl* atoms contains 3 peaks, at 2540, 1810, and 1075 m/s; $\beta=0.68$, 0.10, and 0.00–0.10, respectively.

[y]Vibrational energy of CH_3Cl^* is ≈13800 cm^{-1}.

[z]Vibrationally mediated photodissociation: the C–H stretch overtone level in the vibrationally excited molecule is shown.

[A]The overall [i.e., Cl*+Cl] quantum yield for chlorine atoms is 0.72,[79] 0.8±0.20,[409] and 0.42±0.1.[161] See also references in the paper of Tyndall *et al.*[409]

[B]The yields of Cl* in the photodissociation of excited $CHFCl_2$ in 3_1, $7/2_2$, and 4_1 vibrational states (vibrational energies are 8708, 9905, and 11387 cm^{-1}) are 34.2, 32.4, and 32.9%, respectively.

[C]$\beta=0.36\pm0.06$, 0.43±0.05, and 0.34±0.04 for the photodissociation of excited $CHFCl_2$ in 3_1, 4_1, and 5_1 vibrational states.

[D]Relative values, reference comparison process is photodissociation of HCl.

[E]The probabilities of CF_2Cl+Br and CF_2Br+Cl channels are 0.96 and 0.04, respectively.

[F]Photolysis of C_2H_3Cl at 193 and 210 nm: $\beta_{193}=0.30\pm0.02$ and $\beta_{210}=0.32\pm0.2$ for low-speed Cl* atoms, $\beta_{193}=1.09\pm0.2$ and $\beta_{210}=0.96\pm0.2$ for high-speed Cl* atoms.

[G]Different velocity distributions for Cl* and Cl are assumed. The assumption is based on photofragment spectroscopy results.[424,425]

branching ratio depends quasiperiodically on vibrational energy of excited HCl molecule.[426] Another theoretical prediction on the effect of parent vibration on the Cl*/Cl branching ratio is presented by Gersonde *et al.*[428]

3.3.2. Isotope Effect in the Photodissociation of Chlorides

In 1994, Deshmukh and Hess used REMPI techniques and observed very large and ununderstandable isotope effects in the photodissociation of CCl_4, $CHCl_3$, and Cl_2.[162] Recently, the result was checked by Maul *et al.*[413] for CCl_4, and the isotope effect was not observed at all, $[^{35}Cl^*]/([^{37}Cl^*]=[^{35}Cl]/([^{37}Cl]=3$. This fact put in doubt the existence of the large isotope effects and hence all these data of Deshmukh and Hess.

3.3.3. Velocity Distributions of Cl* in Three-Body Decay

The photoion imaging technique[432] yields a great deal of information on the photodissociation dynamics; recently, the technique was used to study the photodissociation of several chlorides ($COCl_2$,[400] S_2Cl_2,[404] $SOCl_2$[403]) where three-body decay is possible. The analysis of the velocity (speed and angle) distributions of Cl* and Cl photofragments gave a deeper insight into the dynamics of the photodissociation: it includes not only information on the excited states which participate in the process, but also on the mechanism of three-body decay, which may be, in principle, sequential, synchronously concerted and asynchronously concerted.[398,399] Note that the velocity distributions for Cl* and Cl photofragments may be very different, as it was observed for $COCl_2$ and $CSCl_2$.

3.3.4. Vibrationally Mediated Photodissociation of Chlorides

The effect of vibrational excitation of polyatomic chlorides on the Cl*/Cl branching ratio in the photolysis of these chlorides was studied by groups of Dagdigian *et al.* and Rosenwaks *et al.* Lambert and Dagdigian have shown that the vibrational excitation in the fourth C–H stretch overtone in CH_3Cl greatly increases the Cl*/Cl branching ratio in the photolysis near 238 nm, from 0.27 for unexcited to 1.08 for an excited molecule.[367] The reason for this effect is unclear. There was no detectable dependence of the Cl*/Cl ratio upon rotational excitation of CH_3Cl.[367] The degree of enhancement of the signals of H atoms was much less than that for Cl atoms.[433]

Later, the Cl*/Cl branching ratio was determined in the photodissociation of vibrationally excited CH_3Cl,[367,406,433] CHD_2Cl,[405] CH_3CFCl_2,[418] $CHFCl_2$,[410,411] and CH_2Cl_2[407] (see Table 10). All these determinations may be summarized as follows: the Cl*/Cl ratio increases with vibrational excitation, going to the statistical ratio $[Cl^*]/[Cl]=1/2$ for all these chlorides, except CH_3Cl, where this ratio is higher.

Note that the Cl*/Cl branching ratio measured in photo-

dissociation of hydrogen-containing chlorides is often less informative on the nature of the upper electronic state of the transition, in comparison with photodissociation of iodides, since almost normally the ratio is dictated by nonadiabatic dynamics as the photofragments separate and not in the initial excitation.[179,367]

3.3.5. Kinetic Energy Distribution Determination by Infrared Absorption Methods

The average kinetic energy of halogen atoms may be determined from the Doppler width of the absorption lines of the $^2P_{1/2}$-$^2P_{3/2}$ transition by IR absorption methods. It is useful to notice that this method may produce a very large error, if the velocity distributions of X and X* atoms are different.

For example, the average kinetic energy of chlorine atoms produced by the photolysis of S_2Cl_2 was determined by Park *et al.* from the IR spectral widths to be 7 ± 1 and 10 ± 3 kcal/mol at 248 and 193 nm, respectively.[334] Using a three-dimensional variant of the ion imaging method, Einfeld *et al.* have determined that the average kinetic energy of the chlorine atoms produced by the photolysis of S_2Cl_2 at 235 nm is much larger, 24 and 13 kcal/mol, for Cl* and Cl, respectively.[404] This disagreement may be explained by the speed distributions of the atoms: excited Cl* atoms are much faster than the ground state Cl atoms.[404] As a result, the IR absorption on Cl*–Cl transition is saturated for fast atoms and hence only slow atoms contribute to the width of the IR spectral lines.

3.3.6. MOCl→MO($^2\Pi_\Omega$)+Cl*/Cl (M=N,H): Correlation of Spin-Orbit States of Products

Cao *et al.*[391] have demonstrated that the absorption band of NOCl consists of five bands; A and B bands correlate to Cl*+NO and Cl+NO*, C and D bands correlate to Cl+NO, and the band E correlates to Cl+NO*; here NO and NO* denote ground state $^2\Pi_{1/2}$ and excited $^2\Pi_{3/2}$ spin-orbital states of NO. These correlations have been observed experimentally and explained with the correlation diagram analysis.

Offer and Balint-Kurti have predicted theoretically that in the photodissociation of HOCl at the peak of absorption maximum (244 nm), first, the Cl*/Cl branching ratio is 0.45 for OH($^2\Pi_{3/2}$) channel and 0.59 for OH($^2\Pi_{1/2}$) channel; second, there is a strong variation of the Cl*/Cl ratio with the rotational number j of OH.[434]

3.3.7. Aligned Molecules: Effect on the Yield of Cl* Atoms

A strong nonresonant laser field may be used to align the molecules due to the interaction of the induced dipole moment of the molecule with the electric field of the laser radiation. The alignment may be studied by measurement of the velocity anisotropy of the photofragments obtained in the photodissociation of the aligned molecules.

In experiments of Sugita *et al.*[379] nonresonant Nd:YAG radiation (1.06 μm) was used to align Cl_2 molecules and the degree of alignment was determined from the velocity anisotropy of the Cl($^2P_{3/2}$) atoms obtained from the photodissociation of Cl_2 molecules at 404.17 nm,

$$Cl_2(X\,^1\Sigma_g,\Omega=0)+h\nu\rightarrow Cl_2(B^3\Pi_u^+,\Omega=0)\rightarrow Cl+Cl^* \tag{26a}$$

$$\rightarrow Cl_2(^1\Pi_u,\Omega=1)\rightarrow Cl+Cl. \tag{26b}$$

The branching ratio without alignment is $\Phi_\parallel/\Phi_\perp=2.0\pm0.1$, where $\Phi_\parallel$ and $\Phi_\perp$ are quantum yields of channels (26a) and (26b), respectively. The β parameter for channel (26a) was found to be 1.4. It was demonstrated that the ratio $\Phi_\parallel/\Phi_\perp$ increases by a factor of 1.5 with the power of the Nd:YAG laser.

Note that the yield of Cl* atoms in the UV photodissociation of Cl_2 was recently studied theoretically by Buenker *et al.*[435] In this *ab initio* configuration interaction study, potential energy curves for the $X\,^1\Sigma_g^+$ ground state and $\Omega=0_u^+$, 1_u valence states and dipole moments for transitions between these states were determined. The calculated yield of Cl* atoms as a function of excitation wavelength was shown to be in good agreement with experimental results of Samartzis *et al.*[163]

3.4. Production of Cl* Atoms in Chemical Reactions

3.4.1. Reactions of I* Atoms with Cl_2 and ICl

Since the production of X* atoms in chemical reactions has been reviewed by Dagdigian,[5] here we discuss only some processes. The data for Cl* relative quantum yields from chemical reactions are presented in Table 11, in all cases the Cl* atoms were detected by direct methods. As one can see from Table 11, the reaction of I* with ICl is a new good example of Y*+XZ→X*+YZ (X, Y, and Z are halogen atoms) electronic-excitation-transfer reaction.

There is some doubt concerning the deactivation of I* by Cl_2,

$$I^*+Cl_2\rightarrow Cl^*+ICl, \tag{27a}$$

$$\rightarrow Cl+ICl, \tag{27b}$$

$$\rightarrow I+Cl_2. \tag{27c}$$

According to Lilenfeld *et al.*, the fraction of channel (27b) is about 1/3, and the main channel is (27c); that is, $k_{27b}=(5.5\pm0.8)\times10^{-15}$, $k_{27a}+k_{27b}+k_{27c}=(1.7\pm0.7)\times10^{-14}$ cm^3/molecule·s, and $k_{27b}>k_{27a}$.[56] However, Lilenfeld *et al.* wrote: "...the rate constant k_{27b} is the largest of the reactive rate constants [although Cl*($^2P_{1/2}$) could be formed and deactivated to Cl($^2P_{3/2}$) before detection under these flow conditions]." Hence, no strict conclusions may be drawn in this situation on the yield of Cl* atoms in the I*+Cl_2 process.

TABLE 11. Yields of Cl* atoms from chemical reactions

Reaction	[Cl*]/([Cl]+[Cl*]) (%)	Conditions	Detection	Reference
$H+HCl \rightarrow H_2+Cl^*/Cl$	6 ± 3	$E_{col}=1$ eV	LIF VUV	436
	7 ± 1	$E_{col}=1.4$ eV	LIF VUV	437
	19 ± 2	$E_{col}=1.7$ eV	LIF VUV	437
$H+DCl \rightarrow HD+Cl^*/Cl$	6 ± 2	$E_{col}=1.0$ eV	LIF VUV	438
	7 ± 1	$E_{col}=1.4$ eV	LIF VUV	438
	16 ± 1	$E_{col}=1.7$ eV	LIF VUV	438
$O(^1D)+HCl \rightarrow OH+Cl^*/Cl$	16.6 ± 4	$E_{col}=0.330$ eV	REMPI	439
	19 ± 4	$T=300$ K	LMR	440
$O(^1D)+DCl \rightarrow OD+Cl^*/Cl$	15.3 ± 3	$E_{col}=0.334$ eV	REMPI	439
	20 ± 4	$T=300$ K	LMR	441
$O(^1D)+Cl_2 \rightarrow ClO+Cl^*/Cl$	$\leqslant3$[a]	$E_{col}=0.382$ eV	REMPI	439
	$\leqslant5$[a]	$T=300$ K	LMR	440
$O(^1D)+COCl_2 \rightarrow Cl^*/Cl+\ldots$	$\leqslant10$[a]	$T=300$ K	LMR	440
$I^*+ICl \rightarrow I_2+Cl^*/Cl$	60 ± 15	$T=300$ K	ARA IR	200
$I^*+Cl_2 \rightarrow ICl+Cl^*/Cl$	<50[b]	$T=300$ K	SE IR/SS	56

[a]Upper limit. No Cl* observed.
[b]See text.

3.4.2. *R-E* Energy Exchange: Nonadiabatic Transitions in the Exit Channel

Let us discuss the reactions $A+HCl \rightarrow Cl^*/Cl+AH$, where A is an atom. The correlation diagrams for $A=O(^1D)$ and F are presented in studies[439,442] and studies,[5,87,443] respectively; for A=H the diagram is given in many papers devoted to $F+H_2$ and $Cl+H_2$ reactions. In all these cases the reaction proceeds via the ground potential energy surface which correlates with ground state Cl atoms as products of the reactions. The exception is the reaction $O(^1D)+HCl$, but the available excited state $^1A''$ of HOCl molecule also correlates with $OH+Cl(^2P_{3/2})$. Thus, in the adiabatic limit the [Cl*]/[Cl] branching ratio must be zero; hence, the production of the X* atoms is due to nonadiabatic transitions. These transitions must take place in the exit channel region at large distances between the products of the reaction, where the energy difference between the surfaces correlating to Cl and Cl* is minimal.[439] It is interesting to note that this large-distance interaction is rather efficient in the case of interaction of chlorine atoms with several hydrides.

As discussed above, it is established that many Cl^*+HA deactivation processes (HA=HF, DF, HCl, DCl, H_2O,…) occur via rather quick electronic-rotational *E-R* energy transfer. It is tempting to propose that an efficient *E-R* energy exchange for Cl* atoms plays the same key role as *E-V* energy exchange for Br* and I* atoms; that is, not only these deactivation processes but also the production of Cl* atoms in several chemical reactions [$O(^1D)+HCl$,$F+HCl$,…] and from several photodissociation processes ($HOCl+h\nu$,…) occur via nonadiabatic *E-R* energy exchange.

Thus, the yields of Cl* atoms in the $O(^1D)+HCl(DCl)$ reactions via *E-R* energy exchange $OH(j)+Cl \rightarrow OH(j')+Cl^*$ due to long-range dipole–quadrupole interaction between OH(OD) and Cl were estimated.[442] These yields were found to be in agreement with experimental results for the $O(^1D)+HCl$ reaction, but a significant disagreement was found for the $O(^1D)+DCl$ reaction.

4. Excited Bromine Atoms $Br^*(^2P_{1/2})$

4.1. Collisional Deactivation of Br* Atoms at $T=300$ K

The data for the collisional deactivation of Br* at room temperature are presented in Table 12. From the table it can be seen that the studies of collisional deactivation of Br* may be divided into three groups. The first is a broad study from 1970 by Donovan and Husain by means of flash photolysis-atomic resonance absorption in the vacuum ultraviolet (ARA VUV).[1–3,86,444,445] The second group is made before 1980 and consists of numerous studies of different authors who mainly used detection of spontaneous infrared emission from Br* atoms (SE IR); the third group is the study of Johnson, Perram, and Roh in 1996.[446] The results of the first group usually are unreliable and in strong disagreement with all later measurements.

4.1.1. The Study of Johnson, Perram, and Roh

Most of the recent data on collisional deactivation of Br* was obtained in the study of Johnson, Perram, and Roh.[446] In the study, pulsed lifetime measurements yielded absolute rate constants for the Br^*+Br_2 and Br^*+CO_2 deactivation processes, and the rates for many other gases relative to that for Br_2 ($k_{Br_2}=1.24\times10^{-12}$ cm^3/molecule·s), were determined in steady-state photolysis experiments.

Note also that, according to Johnson *et al.*, the lowest quenching rate constants (Br^*+He, Ne, Ar, Kr, Xe, O_2) should be regarded as upper bounds to the true value. One can estimate that the measured lowest values may be explained either by impurities in the buffer gases, by trimolecular relaxation $Br^*+Br+M \rightarrow Br_2+M$, or by bimolecular relaxation $Br^*+Br \rightarrow 2\ Br$; these estimates are based on the rather short experimentally observed lifetime of Br* and on the rather large degree of decomposition of Br_2. Note that such a situation is not rare; for example, the rate

constant for $I^* + Cl_2$ deactivation was overestimated by several authors because of neglecting the contribution from the $I^* + Cl \rightarrow I + Cl$ quenching process.[203]

4.1.2. $Br^* + H_2$ Studies

Nesbitt and Leone have carefully studied the quenching of Br^* atoms by H_2.[447] It was found that this process must be studied in the absence of complicating effects which can arise from the previously unreported equilibrium process

$$Br^* + H_2(v=0) \rightleftarrows Br + H_2(v=1). \tag{28}$$

Nesbitt and Leone inspected the experimental conditions in the previously reported studies[88,445,448] of this process and concluded that this equilibrium is probably responsible for the large discrepancies in these early measurements.

Truhlar *et al.* have confirmed by converged quantum reactive scattering calculations that the deactivation of Br^* by H_2 proceeds mainly via the near-resonant *E-V* energy transfer (28).[449–451] The same conclusion was obtained by Miller *et al.*[452,453] Later, using a (2×2) diabatic model originally developed by Truhlar and co-workers, Takayanagi and Kurosaki have found that the contribution of the chemical reaction $Br^* + H_2 \rightarrow HBr + H$ is small.[454]

Nesbitt and Leone also concluded, that $Br^* + H_2(v=1)$ is efficiently quenched to $Br + H_2(v=2)$ in the entrance channel, followed by a subsequent H atom abstraction from vibrationally excited H_2:

$$Br^*(^2P_{1/2}) + H_2(v=1) \rightarrow [Br(^2P_{3/2}) \cdots H_2(v=2)] \rightarrow HBr + H. \tag{29}$$

Ab initio calculations for the $Br \cdots H_2$ prereactive complex have been published recently by Klos *et al.*[455]

4.1.3. Selective Spin-Orbit Effect: Reactions of Br^* with IBr

The relative reactivity of Br^* and Br atoms in collisions with IBr,

$$Br + IBr \rightarrow I + Br_2, \tag{30}$$

$$Br^* + IBr \rightarrow I + Br_2, Br + IBr, \tag{31}$$

was first correctly established by Clyne and Cruse[456] and by Haugen *et al.*[457] The ground state reaction (30) ($k_{30} = 4.6\times10^{-11}$,[457] 3.5×10^{-11} cm^3/molecule·s[205]) proceeds at a rate $\geqslant 18$ times faster than the rate of the total Br^* deactivation, $k_{31} = 1.9\times10^{-12}$ cm^3/molecule·s. This fact is important for the development of a Br^*-Br laser based on the photolysis of IBr, since the selective ground state depletion significantly enhances the laser gain.

4.1.4. *E-V* Energy Transfer

It is well established that deactivation of Br^* and I^* atoms by polyatomic molecules usually occurs via electronic to vibrational *E-V* energy transfer. Originally such processes were discussed in terms of two possible mechanisms: near-resonance long-range multipolar interactions and nonadiabatic curve crossings (see discussion in Sec. 6.2). The temperature dependence of the deactivation rate constants must be negative in the first case and may be different in the second. In experiments of Reisler and Wittig[458,459] a negative temperature dependence for the $Br^* + CO_2$ deactivation was measured; thus, a dominance of the near-resonance long-range multipolar interaction mechanism is possible. In the case of $Br^* + HCl$ the rate constant is nearly independent of temperature, and the energy defect for *E-V* energy transfer is large (789 cm^{-1}).[458,459] Hence the curve-crossing mechanism is likely to be responsible for the deactivation of Br^* by HCl.

4.2. Production of Br^* Atoms by Photolysis

The data for Br^* relative quantum yields and β parameters are presented in Table 13 in chronological order for each parent molecule M. In addition to the table, we should mention the work of Dzvonik *et al.* in which several rare molecules (1-naphthyl bromide, 4-biphenyl bromide, 9-anthracyl bromide) have been studied by TOF-MS at broadband (240–340 nm) photolysis and the β parameters have been obtained for all of them.[9] As one can see from the table, the most studied parent molecules are HBr, IBr, and Br_2 molecules, and REMPI remains the most informative and popular detection method. To the knowledge of the author bromine atoms have not yet been detected by two-photon laser-induced fluorescence (TP-LIF).

4.2.1. Photodissociation of IBr

The photodissociation of IBr is well studied[86,92,146,217,483,484,487–489,508] and now it is one of benchmark photodissociation processes. Note that the correlation diagram for the photodissociation of low-lying states of IBr have two crossings, the first (lowest) one changes the Br^*/Br branching ratio, and the second one is responsible for the transition between the $Br^* + I$ and $Br + I^*$ energy surfaces.[488,489]

In the wavelength range 440–685 nm, the most complete photodissociation study (the dependences of the Br^*/Br branching ratio and of the anisotropy parameter β on the excitation wavelength) using the velocity map imaging technique was reported recently by Wrede *et al.*[489] The β parameter dependence allowed the mapping of the partial cross sections for parallel $(\Delta\Omega=0)$ and perpendicular $(\Delta\Omega=\pm1)$ absorptions and thus the deconvolution of the IBr absorption spectrum into contributions associated with excitation from the $X^1\Sigma^+(0^+)$ ground state to the $A^3\Pi(1)$, $B^3\Pi(0^+)$ and $^1\Pi(1)$ excited states. Such analyses of the absorption spectrum of IBr, taken together with previous spectroscopic data for the bound levels supported by the *A* and *B* state potentials, has allowed the determination of the potential energy curves and transition moments to each of these excited states.

The IBr molecules initially excited to the *B* state dissociate diabatically to $I + Br^*$ and adiabatically to $I + Br$ products.

TABLE 12. Summary of Br* deactivation rate constant (k) determinations at 300 K [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times 10^{-c}$]

M	k (cm^3/molecule·s)	Detection	Reference
H	≤1(−12)	EPR	155
He	(1.6±0.3)(−14)[a]	SE IR	446
Ne	(1.1±0.3)(−14)[a]	SE IR	446
Ar	<2(−16)	AKS VUV	1
	(6.0±0.4)(−15)[a]	SE IR	446
Br	1.6(−11)	AKS VUV	86
	≤3(−12)	EPR	155, 460
Kr	(5.9±0.2)(−15)[a]	SE IR	446
I	1.5(−11)	ARA IR	201
Xe	(7.5±0.5)(−15)[a]	SE IR	446
H_2	4.7(−12)	AKS VUV	445
	(1.8±0.2)(−11)	ARA VUV	88
	(2.7±0.3)(−12)[b]	SE IR	448
	(6.3±1)(−12)	SE IR	447
	(2.35±0.22)(−12)	SE IR	446
$H_2(v=1)$	(6.0±3)(−12)[c]	SE IR	447
D_2	5.7(−12)	AKS VUV	445
	(1.8±0.2)(−12)	ARA VUV	88
	(6.7±0.4)(−13)[b]	SE IR	448
	(7.0±0.6)(−13)	SE IR	447
	(9.7±0.6)(−13)	SE IR	446
HD	(3.6±0.5)(−11)	ARA VUV	88
	(6.4±0.3)(−12)[b]	SE IR	448
HF	(3.4±0.6)(−11)	Fl IR CP	461
HCl	(8.6±0.7)(−12)	SE IR	462
	(8.3+1−4.2)(−12)[d]	SE IR, Fl IR CP	462
	[e]	LA IR CP	93
	(8.6±0.4)(−12)[f]	SE IR	458
	(1.71±0.2)(−11)	SE IR	446
HBr	(1.1±0.1)(−12)	AKS VUV	86
	(1.38±0.2)(−12)	SE IR	462
	(7.1±3.5)(−13)[d]	SE IR, Fl IR CP	462
	(3.48±0.19)(−12)	SE IR	446
HI	2.5(−12)	Fl IR RP	87
	(9.0±0.5)(−12)	SE IR	446
CO	1.2(−15)	AKS VUV	463
	7.3(−15)	AKS VUV	445
	(1.08±0.05)(−14)	SE IR	448
	(1.2±0.1)(−14)	SE IR	446
N_2	2.5(−15)	AKS VUV	445
	(1.4±0.07)(−14)	SE IR	446
NO	4.7(−11)	AKS VUV	445
	(1.9±0.6)(−12)	Br-laser	91
	(5.3±0.9)(−12)[g]	Fl IR CP	223
	(1.9±0.2)(−12)	SE IR, IR Fl	464
	(2.39±0.10)(−12)	SE IR	446
O_2	3.4(−11)	AKS VUV	1
	(6.4±1.8)(−14)	Br-laser	91
	$1.5^{+0.4}_{-1.5}$(−15)	AS-FCL	465
	(3.3±1.4)(−15)[a]	SE IR	446
Cl_2	(2.2±1.4)(−14)	SE IR	466
BrCl	(2.9±1.4)(−14)	SE IR	466
Br_2	1.9(−11)	AKS VUV	1
	(7.9±0.8)(−13)	SE IR	462
	(1.0±0.2)(−12)	Fl IR CP	461
	(1.2±0.3)(−12)	Fl IR CP	467
	(7.8±0.9)(−13)	SE IR, Fl IR CP	468
	(8.0±0.8)(−13)	ARA VUV	469
	(9.3±1.9)(−13)	Fl IR CP[h]	470
	(4.7±0.4)(−13)	SE IR	466
	(1.0±0.1)(−12)	SE IR	471
	(1.24±0.08)(−12)	SE IR	446
ICl	(9±4)(−13)	SE IR	466
IBr	3(−12)[i]	ARA VUV	472
	(1.00±0.14)(−12)	SE IR	466
	(2±1)(−12)	ARA IR	97
	(1.9±0.4)(−12)	AS-FCL	457

TABLE 12. Summary of Br* deactivation rate constant (k) determinations at 300 K [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]—Continued

M	k (cm^3/molecule·s)	Detection	Reference
	3.7(−12)[j]	ARA IR	473
I_2	(1.86±0.37)(−12)	SE IR	466
H_2O	3.2(−11)	AKS VUV	445
	(6.2±1.2)(−11)	Fl IR CP[h]	470
	(5.1±0.3)(−11)	AS-FCL	465
HDO	(1.9±0.4)(−11)	AS-FCL	465
D_2O	9.6(−12)	AKS VUV	445
	(2.2±0.4)(−12)	AS-FCL	465
H_2S	(6.2±1.6)(−13)	ARA IR	474
	(8.0±1.1)(−12)	SE IR	446
HCN	(2.0±0.2)(−11)[k]	Fl IR CP	467
	(1.8±0.4)(−11)[l]	Fl IR CP	467
N_2O	(2.6±0.8)(−12)	SE IR, Fl IR CP	219–221
	(3.1±0.9)(−12)	SE IR	471
	(2.79±0.21)(−12)	SE IR	446
NO_2	(0.53±0.27)(−12)	SE IR	446
CO_2	(1.5±0.1)(−11)[m]	SE IR, Fl IR CP	219–221
	(1.5±0.1)(−11)	SE IR, Fl IR CP	468
	(1.5±0.6)(−11)[f]	Fl IR CP	458, 459
	(1.5±0.2)(−11)[n]	AS-DL CP	104
	(1.32±0.03)(−11)	SE IR	446
$^{13}CO_2$	(7.1±0.3)(−12)[f]	Fl IR CP	459
COS	(1.4±0.1)(−12)	SE IR, Fl IR CP	468
	(1.59±0.05)(−12)	SE IR	446
SO_2	(1.1±0.2)(−13)	Fl IR CP[o]	106
	(3.6±0.4)(−13)	SE IR	446
CS_2	(1.1±0.1)(−12)	SE IR, Fl IR CP	468
BrCN	(4.1±3.0)(−12)	AS-FCL	18
NOBr	(1.5±0.2)(−11)	IR Fl	475
CH_4	4.2(−12)	AKS VUV	445
	(2.39±0.05)(−12)	SE IR	446
CH_3F	[p]	LA IR CP	476, 477
CH_3Br	(7.7±0.7)(−12)	ARA VUV	89
CH_3I	(1.9±0.1)(−11)	ARA VUV	469
CD_3I	(1.4±0.1)(−12)	ARA VUV	469
CF_4	2.1(−13)	AKS VUV	445
	(0.62±0.006)(−12)	SE IR	446
CF_3Br	(4.95±0.15)(−14)	AKS VUV	86
	(1.2±0.2)(−13)	ARA VUV	89
	(1.2±0.3)(−13)	ARA IR	474
SF_6	(9.0±4.8)(−14)	SE IR	446
C_2H_5Br	(1.21±0.08)(−11)	ARA VUV	89
C_2F_5Br	(2.7±0.4)(−13)	ARA VUV	89
C_3H_8	(1.99±0.052)(−11)	AS-FCL	18
$C_3H_6Br_2$	~10(−10)	[q]	478
n-C_3F_7Br	(3.8±0.3)(−13)	ARA VUV	89
C_3F_7I	(4.6)(−13)	SE IR	204

[a]Upper bound to the true value.

[b]The lower limit to the number of vibrational quanta excited per Br* deactivation is 0.60±0.11, 0.78±0.22, and 0.094±0.033 for H_2, D_2, and HD, respectively.[448]

[c]The rate for the $Br^*+H_2(v=1)\rightarrow HBr(v=0)+H$ reaction.

[d]The rate constant for the $Br^*+HX\rightarrow Br+HX(v=1)$ energy exchange.

[e]$Br^*+HCl\rightarrow Br+HCl$ energy transfer: $E-V(78\%)$, $E-R(16\%)$, $E-T(6\%)$.

[f]Quenching rate constants at 300–600 K are obtained.

[g]≈84% of the E-V transfer collisions excite $NO(v=2)$.

[h]$Br^*+H_2O\rightarrow Br+H_2O(\nu_1,\nu_3)$.

[i]Reaction only.

[j]The deactivation rate constants are 1.1, 2.7, 3.7, 7.8, and 35×10^{-12} cm^3/molecule·s for $T=6$, 21, 24, 36, and 48 °C, respectively.

[k]$Br^*+HCN\rightarrow Br+HCN(001)$: $(1.8\pm0.4)\times10^{-11}$ cm^3/molecule·s.

[l]The rate for the $Br^*+HCN\rightarrow Br+HCN(001)$ channel.

[m]$Br^*+CO_2\rightarrow Br+CO_2(\nu_3)$: $(5.6\pm2.8)\times10^{-12}$ cm^3/molecule·s, 40% of the total quenching rate.

[n]$Br^*+CO_2\rightarrow Br+CO_2(10^01)$: 66% of the total quenching rate.

[o]$Br^*+SO_2\rightarrow Br+SO_2(\nu_1=1)/SO_2(\nu_3=1)$. ν_3 ($\Delta E=480$ cm^{-1}) is excited preferentially despite the existence of the more resonant ν_1 mode ($\Delta E=270$ cm^{-1}).

[p]The reactive rate constant for $Br^*+CH_3F\rightarrow HBr+CH_2F$ is $10^{-2.6\pm0.5}\exp[-(10100/RT)]$ cm^3/molecule·s at 60–200 °C. Vibrational excitation of CH_3F accelerates the reaction $Br+CH_3F$ and does not influence the reaction Br^*+CH_3F.

[q]Obtained by absorption of the reaction product at 460–530 nm.

TABLE 13. Summary of Br* relative quantum yield and β parameter determinations from photodissociation

M	λ[a] (nm)	[Br*]/([Br]+[Br*]) (%)[a]	β	Detection	Reference
HBr	193	≈15		Fl IR CP PF	95, 479
	193	14	−1.0	TOF-MS PF[b]	480, 481
	193	15.25±2.1	0.00±0.10	REMPI PF(H)	108
	205	15.25±1.4	0.68±0.16	HR-TOF	482
	205	17.36±1.4	1.50±0.17	HR-TOF	482
	205	15.97±2.1	0.60±0.50	HR-TOF	107
	205	15.25±4.3	0.38±0.30	REMPI PF	108
	201–253	13.8–23.1	0.1–2.0	HR-TOF	107
	210–242	15.8–18.6	0.68–1.51		[c]
	243	10.7	2.00	DI	105
	243	16.67±2.1	2.00±0.70	HR-TOF	107
	243	16.67±2.1	1.96±0.05	REMPI PF	108
	193		−0.21±0.10	REMPI/I	169
$(HBr)_n$, $n\sim9$	243	15.25±2.1	2.00±0.10	REMPI PF	108
	193	14.53±2.2	−0.20±0.15	REMPI PF	108
BrO	235	25	1.5±0.1	REMPI	372
BrCl	235–262	~100[d]	2.0±0.1	REMPI/I	380
	320–410	~0[d]		REMPI/I	380
	>400	~0[d]		REMPI/I	380
	235		0.58±0.05	REMPI/I	166
	235		1.98±0.05	REMPI/I	166
Br_2	444–530	[e]		Fl IR CP	483
	434–511	7–37[f]		ARA VUV PF	90
	445–530	44–87[g]		AS-FCL	484
	510–550	86–12		AS-FCL	103
	360–430	~0		REMPI/I	485
	430–500	≈50	≈1.5[h]	REMPI/I	485
	265	50±5[i]	−0.8±0.1	REMPI/I	486
	234	50	−1.0±0.05	REMPI/I	181
	265	47	−0.8±0.05	REMPI/I	181
IBr	480–530	28–61[j]		TOF-MS	92, 487
	450–530	28–73[k]		AS-FCL	484
	444–570	[e]		Fl IR CP	483
	304	22[l]	−0.7	REMPI	146
	248	83±6[l]	−0.97	REMPI	488
	267	60±3[l]	−0.85±0.1	REMPI	488
	304	26±3[l]	−0.64	REMPI	488
	262.5	[l]	−0.74±0.1	REMPI	488
	440–685	75–12	~2[m]	REMPI/I	489
BrCN	193	30.6±0.41		AS-FCL	18
	193–248	[n]	[n]	LIF PF	490
	206–260	0–100[o]	1.0±0.2	LIF PF	491
NOBr	231.98	90[p]	0.92	REMPI, REMPI PF	101
	266	90[p]	1.14	REMPI, REMPI PF	101
	355	90[p]	1.57	REMPI, REMPI PF	101
	355	[q]	1.95±0.2	REMPI PF	187
CH_3Br	[r]	15±12		ARA VUV	89
	205	~1–2		REMPI/I	492
	215–229		1.86–1.94[s]	REMPI/I	493
	218–245	40–61[t]		REMPI/I PF	493
	243–277		1.2–1.4[u]	REMPI PF	102
	234		[m]	REMPI/I	494
	267	30.3	[m]	REMPI/I	494
CH_2BrCl	193		1.2±0.4[v]	TOF-MS	495
	248		1.6±0.4[v]	TOF-MS	495
	248–269	9–16[w]	1.3–1.5[w]	REMPI	496
	234	35±3	1.5±0.1	REMPI/I	497
CF_3Br	[r]	66±7		ARA VUV	89
	193	56±5		SE IR	94
	[r]	⩾33		AKS VUV	86
	234	80±5	1.83±0.05	REMPI/I	498
CF_2ClBr^A	234	29.1±2.5	1.6±0.1	REMPI/I	164
	267		[m]	REMPI/I	499
CH_2Br_2	234	24		REMPI	167
	267	29		REMPI	167

TABLE 13. Summary of Br* relative quantum yield and β parameter determinations from photodissociation—Continued

M	λ[a] (nm)	[Br*]/([Br]+[Br*]) (%)[a]	β	Detection	Reference
$CBrCl_3$	234	31±1	−0.34	REMPI/I	165
	265	68±2	1.43	REMPI/I	165
	248	~0	−0.4	TOF-MS PF	500
	193		1.3		501
CF_2Br_2	234	28±2.5	0.65±0.03	REMPI/I	502
	265	47±2	0.73±0.03	REMPI/I	502
CH_2BrI	248		0.6±0.1	TOF-MS PF	503
	210		0.6±0.3	TOF-MS PF	503
	193		~0	TOF-MS PF	503
$CHBr_3$	193	~0		TOF-MS	504
	234	17		REMPI	167
	267	30		REMPI	167
$C_2H_2Br_2$	193	5.66±2.7		REMPI/I	505
C_2H_5Br	[r]	<10		ARA VUV	89
	234	17		REMPI	167
	267	31		REMPI	167
	234	28.6		REMPI	170
	267	33.8		REMPI	170
CH_2BrCH_2Cl	266	25±15	0.8±0.2	TOF-MS PF	109
1,2-$C_2H_4Br_2$	234	14		REMPI	167
	267	18		REMPI	167
C_2F_5Br	193	16±8		SE IR	94
	[r]	48±2		ARA VUV	89
1,2-C_2F_4IBr	193	7±5[B]		SE IR	94
	193	38±12[C]		SE IR	506
	193		1.85[D]	TOF-MS	134
C_3H_5Br	234	66±5	0.37	REMPI/I	420
n-C_3H_7Br	234	35.6		REMPI	170
	267	29.4		REMPI	170
n-C_3F_7Br	[r]	<10		ARA VUV	89
n-C_4H_9Br	234	42.8		REMPI	170
	267	34.1		REMPI	170
1,4-$C_4H_8Br_2$	234	31		REMPI	168
	267	20		REMPI	168
n-$C_5H_{11}Br$	234	44.7		REMPI	170
	267	25.7		REMPI	170

[a]The photolysis wavelength λ (or the range for λ) and yield of Br* (or the range for the yields) are presented. Γ~0 means "below the detection limit."
[b]Velocity-aligned Doppler spectroscopy (VADS) of H atoms.
[c]Private communication from Lacombe *et al.*, the data from this work are shown by Poilly and Monnerville:[507] the yields of Br* are 18.6, 15.8, 15.8, 15.8, and 17.4%, the β parameters are 0.676, 0.866, 1.310, 1.204, and 1.507 for 209, 214, 220, 224.6, and 242 nm, respectively.
[d]At 235–262 and at 320–410 nm, the main products are Cl+Br* and Cl+Br, respectively.[380]
[e]Only the relative yield of Br* is obtained.
[f]ARA VUV was used to detect Br($^2P_{3/2}$) at 148.9 nm. The yields of Br* are 7.15, 6.01, 12.9, 11.6, 20.3, 14.9, 19.0, 26.2, 36.0, 27.2, 30.0, 30.7, 29.8, 38.9, 37.4, 35.0, and 36.3% for 434, 438, 444, 448, 451, 453, 458, 463, 468, 468, 472, 472, 477, 482, 492, 502, and 511 nm.
[g]The yields of Br* are 44, 49, 62, 67, 74, 78, 83, 84, 87, 83, 67, 61, and 40% for 445, 450, 460, 466, 470, 475, 480, 490, 500, 510, 518, 520, and 530 nm, respectively.
[h]$\beta\approx1.5$ and 450 nm, declining to $\beta\approx0.6$ at the longest excitation wavelength (500 nm).
[i]The upper limits for $Br_2\rightarrow Br+Br$ and $Br_2\rightarrow Br^*+Br^*$ channels were below 5% and 10%, respectively.
[j]The yields of Br* are 61.3, 49.3, 38.9, 35.1, 29.9, and 28.2% for 530, 520, 510, 500, 490, and 480 nm, respectively. These Γ values present the yields of Br* from the photodissociation of IBr($B^3\Pi_{0+}$) state only due to a parallel transition.
[k]The yields of Br* are 28, 30, 33, 36, 44, 46, 54, 62, 68, 73, 72, 71, and 68% for 450, 455, 457, 460, 465, 470, 475, 480, 490, 500, 510, 520, and 530 nm, respectively.
[l]The I*+Br* channel was below the detection limit, <1%.
[m]The speed dependence of the β parameter was obtained.
[n]Vibrational and rotational state distributions for CN radicals were obtained for 193, 202, 220, 242, and 248 nm.
[o]The β parameter is 1.0±0.2 for 209.4 and 248 nm. The yield of Br* is determined for different rotational states of CN at 206.1, 209.4, 222, 248, and 260 nm. Unequal populations in the F_1 and F_2 spin-rotation components of CN have been observed.
[p]Relative yields for Br*/Br were obtained by comparing the REMPI line intensities with those from the work of Cao *et al.*[187]
[q]As the rotation qantum number for NO fragments increases from 55.5 to 61.5, the yield of Br* falls from ≈1 to ≈0.5.[187]
[r]Broad band photolysis.
[s]β=1.86±0.15, 1.91±0.05, and 1.94±0.05 for 215.00, 220.14, and 229.22 nm, respectively.
[t]The yields of Br* atoms are 61, 54, 46, 50, 48, 47, 40, 41, 48, 54, 50, 54, 50, 46, and 46 (±5)% for 218, 220, 222.25, 220.50, 220.75, 221, 222, 223, 224, 225, 226, 230, 235, 240, and 245 nm, respectively.
[u]The β parameters for Br* atoms are 1.4±0.2, 1.3±0.08, 1.2±0.2, 1.3±0.1, and 1.2±0.2 for 243.52, 251.00, 264.95, 266.71, and 277.74 nm, respectively. However, the β parameters are 1.88±0.04 and 1.9±0.1 at 251.00 nm for Br*+$CH_3(\nu_2=0)$ and Br*+$CH_3(\nu_2=1)$ channels, respectively.

[v]The β parameters were measured for $Br(^2P_{1/2}, ^2P_{3/2})$ atoms. Most of the atoms are assumed to be in $^2P_{1/2}$ state.
[w]The yields of Br* atoms are 9, 16, and 14 (±10)% for 267, 261.5, and 248.5 nm, respectively; the β parameters for Br* atoms are 1.5, 1.4, 1.4, 1.4, and 1.3 (±0.2) for 248.5, 262.5, 264.9, 266.7, 268.8 nm, respectively.
[A]The probabilities of CF_2Cl+Br^*/Br and CF_2Br+Cl^*/Cl channels are 0.96 and 0.04±0.1, respectively.
[B]The absolute yield of Br* is shown.
[C]According to Wight and Leone,[506] the yield of Br* is 0.14±0.04. According to Krajnovitch *et al.*,[134] the yield of Br* and Br atoms is 0.37; hence the relative yield of Br* is 0.38±0.12.
[D]Br* and Br atoms were not distinguished.

The experimentally obtained nonzero Br*/Br branching ratios are due to nonadiabatic transitions $B^3\Pi(0^+) \rightarrow Y^3\Sigma^-(0^+)$, at the first (lower) curve crossing. These transitions have been well described by a one-dimensional Landau–Zener model.[92,487,489,509]

Also, REMPI studies were reported by Jung *et al.*[146] and by McGivern *et al.*[488] for photodissociation of IBr in the ultraviolet at 248, 266, and 304 nm. β parameters and relative probabilities have been obtained for all three product channels, Br+I, Br*+I, and Br+I*; the Br*+I* channel was not observed, because it was below the detection limit. The ultraviolet absorption spectrum of IBr has been decomposed into three components, corresponding to the $^3\Pi_{0+}$, $^1\Pi_1$, and $^3\Pi_1$ excited states. Also, nonadiabatic curve crossing probabilities for the second (upper) curve crossing have been determined for several wavelengths between 250 and 270 nm.[488]

4.2.2. Photodissociation of HBr

The spectrum of HBr peaking around 185 nm is assigned to a superposition of three transitions: two perpendicular ($X^1\Sigma^+ \rightarrow A^1\Pi_1, a^3\Pi_1$; $\beta^* = -1$) and one parallel ($X^1\Sigma^+ \rightarrow a^3\Pi_{0+}$, $\beta = 2$). Here β^* and β correspond to Br* and Br, respectively. The perpendicular transitions correlate to Br, while the parallel one correlates to Br*.[510,511] Another source of Br* atoms is the nonadiabatic transition $^1\Pi_1 \rightarrow {}^3\Sigma_1^+$ occurring at large internuclear distances. This nonadiabatic transition is unimportant at 248 nm, hence $\beta^*(248) \approx 2$; at 193 nm the probability of the nonadiabatic transition increases, hence the Br* atoms are produced directly via $a^3\Pi_{0+}$ state and also via the nonadiabatic transition; as a result, $\beta^*_{193} \approx 0$.[108]

Note that Xu *et al.* have reported the value $\beta^*_{193} \approx -1$,[481] which contradicts the value $\beta^*_{193} \approx 0 \pm 0.1$ reported later by Baumfalk *et al.*[108] Although the result of Xu *et al.* was confirmed by calculations of Pouilly and Monnerville,[512] we recommend the result of Baumfalk *et al.*: one can easily see from Fig. 3 of paper of Xu *et al.*, that in reality the value β^*_{193} was measured with very large uncertainty, $\approx -1 \pm 1$; hence, there is no large contradiction.

Only a few theoretical studies exist concerning the photodissociation of HBr. Predictions on the wavelength dependencies of the β parameter and the ratio Br*/Br for vibrationally excited HBr($v = 0,1,2$) are presented by Poilly *et al.*[512,513]

4.2.3. Photodissociation of Br_2

The absorption spectrum of Br_2 has continuous bands with two peak maxima at 225 and 420 nm; the correlation diagram is given, for example, by Jung *et al.*[486]

Photolysis of Br_2 near $\lambda = 500$ nm produces nearly equal proportions of Br and Br* via the repulsive limb of the $B^3\Pi_u(0_u^+)$ electronic state. The quantum yield of Br* peaks at 87% for $\lambda = 500$ nm and decreases to 30% at $\lambda = 440$ nm due to the absorption to the repulsive $^1\Pi_u(1_u)$ state.[484] The experimental yields of Br* are in excellent agreement with the calculations of Le Roy *et al.*,[514] except for the long-wavelength region.

Jung *et al.* have found that the spectrum around 225 nm is mainly due to the perpendicular transition $X\,^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+(1_u)$, which produces Br*+Br products.[486] The small relative contribution of the parallel component was found to be $X_\parallel = 0.07$ from the standard relationships $\beta = \beta_\parallel X_\parallel + \beta_\perp X_\perp$, $X_\parallel + X_\perp = 1$, where $\beta_\parallel = 2$ and $\beta_\perp = -1$.

4.3. Production of Br* Atoms in Chemical Reactions and *V-E* Energy Exchange Processes

4.3.1. Reactions of I* and F* Atoms with Br_2

Since the production of X* atoms in chemical reactions has been reviewed by Dagdigian,[5] here we discuss only some doubtful processes. No Br* atoms have been observed by Argawalla *et al.* in the reaction of F*/F atoms with Br_2,[515] which puts in doubt the results of experiments with photodissociation of WF_6 and UF_6 of Gordon *et al.*,[97] in which quick reaction $F^* + Br_2 \rightarrow BrF + Br^*$ was assumed.

Also, there is some doubt concerning the deactivation of I* by Br_2,

$$I^* + Br_2 \rightarrow Br^* + IBr, \quad (32a)$$

$$\rightarrow Br + IBr, \quad (32b)$$

$$\rightarrow I + Br_2. \quad (32c)$$

According to Hofmann and Leone, the probability of channel (32a) is 15±5% only.[204] Since a large yield of Br* atoms was confirmed in several studies (see Table 14) that is, $k_{32a} \gg k_{32b}$, the main process must be the physical quenching channel (32c). But, according to Wiesenfeld and Wolk,[469] the probabilities of channels (32a), (32b), and (32c) differ from that, they are 72±18%, 18±18%, and 10±10%, respectively. Hence, the deactivation of I* with Br_2 occurs mainly via an adiabatic reaction leading to Br*+BrI. These last data have been confirmed by Gordon *et al.*, who measured the

TABLE 14. Yields of Br* atoms from chemical reactions

Reaction	[Br*]/([Br*]+[Br]) (%)	Detection	Reference
H+BrCl→HCl+Br*/Br	<0.4[a]	SE IR	519
H+Br_2→HBr+Br*/Br	<1[a]	SE IR	520
	1.5±0.4	SE IR	521
H+HBr→H_2+Br*/Br	≤1.3	SE IR	521
H+IBr→HI+Br*/Br	<8	ARA IR	474
F+HBr→HF+Br*/Br	6.5±3	SE IR	522
	9.1±4[b]	SE IR	523
	5.3±0.4	LIF VUV	96
F+DBr→DF+Br*/Br	1±0.16	LIF VUV	96
F+Br_2→BrF+Br*/Br	<1[a]	SE IR	515
	>33	ARA IR	97
O+Br_2→BrO+Br*/Br	[c]	ARA VUV	524
	≤4	EPR	460
O+BrO→O_2+Br*/Br	≤4	EPR	460
I*+Br_2→IBr+Br*/Br	80±15	ARA VUV	469
	[d]	IS SE[a]	204
	>85	ARA IR	212
	86±10	ARA IR	97
I*+IBr→I_2+Br*/Br	[d]	IS SE[a]	204
	50±10	ARA IR	201
Br_2^*+M→Br*/Br+…	[e]	SE IR	525

[a]Upper limit. No Br* observed.
[b]However, the contribution from HF($v=1$)+Br→Br*+HF cannot be ruled out.[523]
[c]Br* atoms detected, but the yield is not measured.
[d]Analysis of the infrared emission from I* atoms. The fractions of the total deactivation rate constants attributed to the reactive channel I*+M→Br*+M′ are 15±5 and 13±5%, for M=Br_2 and IBr, respectively.
[e]Br_2^* denotes $Br_2(B\,^3\Pi_{0_u^+})$. The rate constants for Br_2^*+M→Br*+Br+M are 2.9, 1.2, and 0.54, all in 10^{-10} cm^3/molecule·s units, for M=Br_2, Xe, and Ar, respectively.

probabilities for these channels to be 79±10, 13±10, and 8±3%, respectively.[97] These last two sets of data are preferable.

4.3.2. *V-E* Energy Exchange

The rate constant for the production of Br* atoms in energy exchange process

$$\mathrm{Br+HF}(v=1)\rightarrow \mathrm{Br^*+HF}(v=0) \qquad (33)$$

was determined by Quigley and Wolga,[516] from the analysis of the kinetics of HF($v=1$) fluorescence, and a value of $k_{33}=(3.1\pm1.5)\times10^{-12}$ cm^3/molecule·s has been reported. The same method was used and almost the same value, $k_{-33}=(3.4\pm0.6)\times10^{-12}$ cm^3/molecule·s, was obtained later by Wodarczyk and Sakett for the reverse process.[461] The rate constant for the direct process (33) is related to the rate constant for the reverse process through the detailed balance relation,

$$k_{-33}/k_{33}=(g_{3/2}/g_{1/2})\exp(\Delta E/kT), \qquad (34)$$

where g_J is the degeneracy of the ^2P_J state, and $\Delta E=-277$ cm^{-1} is the defect of resonance. Substituting the appropriate values, one finds $k_{-33}/k_{33}=0.53$, hence the detailed balance is obeyed within a factor of 2.[461]

The energy exchange process

$$\mathrm{Br+HBr}(v=1)\rightarrow \mathrm{Br^*+HBr}(v=0) \qquad (35)$$

was studied by Karny and Katz[517] who observed IR emission from Br*, and by Donovan *et al.*,[518] who used ARA VUV. The rate constants have been found as $(2.2\pm0.2)\times10^{-14}$ and $(1.6\pm0.7)\times10^{-12}$ cm^3/molecule·s, respectively. Since the work of Donovan *et al.* is indirect, and the authors of this work claim that the data for process (35) are less accurate than their other data, the data of Karny and Katz are preferable. Note also, that the rate constant for process (35) may be calculated from the detailed balance relation by using the rate constant for the reverse process obtained by Leone and Wodarczyk,[462] $k_{-35}=(7.1\pm3.5)\times10^{-13}$ cm^3/molecule·s. Surprisingly, this calculated rate constant is 200 times smaller than the rate constant of Karny and Katz.[517]

5. Excited Iodine Atoms I*($^2P_{1/2}$)

5.1. Collisional Deactivation of I* Atoms at *T*=300 K

The rate constants for the collisional deactivation of I* at room temperature are listed in Tables 15 and 16 in chronological order for each quencher M.

5.1.1. Deactivation of I* by Halogen and Interhalogen Molecules

The rate constants for I* deactivation by Br_2, Cl_2, IBr, and ICl reported by Donovan, Hathorn, and Husain[472] by the ARA UV method differ significantly from the rate constants determined by several other groups who used several different methods. This disagreement may probably be explained by an excess of I* atoms in the study of Husain *et al.*[204]

Hofmann and Leone have proposed that the deactivation of I* by I_2, Br_2, Cl_2, IBr, ICl, and BrCl occurs mainly via reaction through the formation of a collisional intermediate complex. Basic properties of these trihalogen complexes are:

(A) complexes containing iodine are more stable than those containing only bromine and chlorine,

(B) the presence of chlorine atoms decreases the stability of the complex,

(C) the most stable configuration has the most electropositive atom (I>Br>Cl) in the central position.[204]

5.1.2. *E-V* Energy Transfer: I*+HF

Coombe and Pritt have determined the fraction of the total quenching of I* by HF that occurs due to *E-V* energy exchange processes[121]

$$\mathrm{I^*+HF}(v=0)\rightarrow \mathrm{I+HF}(v=2)+146\ \mathrm{cm^{-1}}, \qquad (36)$$

$$\mathrm{I^*+HF}(v=0)\rightarrow \mathrm{I+HF}(v=1)-3641\ \mathrm{cm^{-1}}. \qquad (37)$$

TABLE 15. Rate constants for quenching of I* atoms at 300 K by atoms and diatomic molecules [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]

M	k (cm^3/molecule·s)	Detection	Reference
He	<5(−18)	ARA UV	526
Cl	1.5(−11)	SE IR	203
	~2(−10)	SE IR	527
Ar	<2(−18)	SE IR, ARA UV	528–530
	<8(−15)	GC PP[a]	112, 531
I($^2P_{3/2}$)	<1.6(−14)	ARA UV	2, 530, 532
	[b]	SE VIS RP	136
I*($^2P_{1/2}$)	[c]	SE VIS RP	136
Xe	<1.6(−18)	ARA UV	463
H_2	8.8(−14)	ARA UV	526
	(8.8±2)(−14)	GC PP[a]	112, 531
	~4(−13)	SE IR	528
	2.15(−13)	SE IR	533
	(1.23±0.34)(−13)[d]	ARA UV	534
	(1.3±0.1)(−13)	ARA UV	535
	(1.2±0.1)(−13)	ARA UV	536
	(1.15±0.07)(−13)	SE IR	537
	9.3(−14)	AS-DL	137
D_2	1.1(−13)	ARA UV	526
	2.2(−15)	SE IR	528
	(2.1±0.0)(−15)[d]	ARA UV	534
	(3.6±0.3)(−15)	ARA UV	469
	1.4(−15)	SE IR	537
HD	3.0(−13)	SE IR	537
HF	2.7(−12)	[e]	538
	(3±1)(−12)[f]	SE IR, ARA UV	539
	(8.9±0.1)(−13)	SE IR	540
DF	$<(1.05^{+0.15}_{-0.5})(-14)$	SE IR	540
CO[g]	1.2(−15)	ARA UV	463
	1.2(−15)	SE IR	528
N_2	2.1(−16)	ARA UV	530
	1.5(−16)	SE IR	528
	(4.2±4.2)(−16)	GC PP[a]	112, 531
	(5.0±2)(−17)[d]	ARA UV	534
NO	1.1(−11)	ARA UV	463
	(1.57±0.3)(−12)	ARA UV	535
	(1.2±0.1)(−13)	SE IR	541
HCl	(1.5±0.5)(−14)	ARA UV	535
	(6.5±0.9)(−15)	SE IR, ARA UV	539
	(1.52±0.12)(−14)	ARA UV	542
	(1.4±0.24)(−14)	SE IR	541
	1.5(−14)	ARF VUV	543
	(3.2±0.1)(−15)	SE IR	540
DCl	(4.3+0.4−1.9)(−15)	ARA UV	542
	4.3(−15)	ARF VUV	543
HBr	(1.3±0.1)(−13)	ARA UV	542
	(1.58±0.07)(−13)	SE IR, ARA UV	539
	(1.5±0.1)(−13)[h]	ARA UV	119
	(1.1±0.4)(−13)	SE IR	541
	(1.23±0.12)(−13)[i]	LIF VUV	544
	1.3(−13)	ARF VUV	543
DBr	≤(4.9±0.3)(−14)	ARA UV	542
	(3.1±0.2)(−14)[h]	ARA UV	119
	4.5(−14)	ARF VUV	543
HI	(1.3±0.2)(−13)	ARA UV	526
	(1.5±0.4)(−13)	SE IR	545
	(5±1)(−14)	SE IR, ARA UV	539
	(5.2±0.4)(−14)	ARA UV	542
	(1.5±0.2)(−13)	ARA UV	546
	5.2(−14)	ARF VUV	543
	(5.7±1)(−14)	SE IR	547
DI	(1.2±0.2)(−13)	ARA UV	526
	(5.0±0.2)(−14)	ARA UV	542

TABLE 15. Rate constants for quenching of I* atoms at 300 K by atoms and diatomic molecules [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]—Continued

M	k (cm^3/molecule·s)	Detection	Reference
	5.0(−14)	ARF VUV	543
O_2	9.3(−12)[j]	ARA UV	463
	2.7(−11)	SE IR	234
	(2.6±0.3)(−11)	ARA UV	548
	(2.5±0.8)(−11)[d]	ARA UV	534
	(2.5±0.3)(−11)	ARA UV	549
	(2.7±0.6)(−11)	ARA IR	22
	(2.67±0.1)(−11)[k]	SE IR	550
	(2.1±0.1)(−11)	SE IR	203
	3.0(−11)	AS-DL	137
	(2.7±0.3)(−11)	ARA UV	551
	(4.2±1.4)(−11)[l]	SE IR	552
	(4.6±1.0)(−12)[T=150 K][m]	SE IR	553
	(7.0±0.7)(−12)[T=150 K]	SE IR, LIF VUV	147
$O_2(^1\Delta)$	2.7(−14)	SE IR RP	234
	2(−13)	SE IR[n]	547
	(1.1±0.3)(−13)[o]	SE IR[n]	554
$NF(a^1\Delta)$	(5±2)(−11)[T=448 K]	Fl IR CP	555
F_2	(5±3)(−14)	SE IR	556
	<8.7(−14)	SE IR	557
ClF	(1.3±0.3)(−13)	SE IR	557
Cl_2	2.1(−13)[d]	ARA UV	472
	1.3(−13)	ARA UV	113
	(1.7±0.2)(−12)	SE IR	204
	(1.7±0.7)(−14)	SE IR/SS	56
	(5.5±0.8)(−15)[d]	SE IR/SS	56
	8(−15)		[p]
	(2.0±0.1)(−14)	SE IR	203
	≤8(−15)	SE IR	527
BrCl	(2.7±0.2)(−11)	SE IR	204
IF	(1.3±0.6)(−11)[T=400 K]	SE IR, ARA UV	557
Br_2	(1.5±0.2)(−12)[d]	ARA UV	472
	(6.0±0.4)(−11)	SE IR	558
	(5.2±0.3)(−11)	SE IR	204
	(5.6±0.2)(−11)[q]	ARA UV	536
ICl	3.4(−12)[d]	ARA UV	472
	2.4(−11)	ARA UV	113
	(2.3±0.2)(−11)	SE IR	204
	(3.3±0.4)(−11)	SE IR	203
	(1.5±0.5)(−11)	SE IR/SS	56
	(1.8±0.4)(−11)	ARA IR	201
IBr	4.3(−12)[d]	ARA UV	472
	(6.6±0.3)(−11)	SE IR	204
I_2[r]	5.0(−12)	ARA UV	559
	(6.9±0.17)(−11)	GC PP[a]	112, 531
	(1.1±0.8)(−11)[d]	ARA UV	534
	(3.1±0.1)(−11)	ARF VUV	116
	(3.6±0.3)(−11)	ARA UV	549
	(2.4±0.3)(−11)	SE IR	560
	(0.07−2.2)(−11)[s]	SE IR	561
	(3.8±0.25)(−11)	SE IR	541
	(3.1±0.5)(−11)	SE IR	204
	(3.0±0.1)(−11)	SE IR	203
	(5±1)(−11)	ARA IR	160
	(2.89±0.06)(−11)	AS-DL	562
	(3.5±0.45)(−11)[l]	SE IR	552

[a]The rate constants from two studies[112,531] were multiplied by 16/5.7 (see text).
[b]The main channel is $I^*+I+M\rightarrow I_2^*(B^3\Pi_0^+)+M$, followed by chemiluminescence.
[c]The main channel is $I^*+I+M\rightarrow I_2^*(^3\Delta_{1u})+M$, followed by chemiluminescence at around 655–685 nm.
[d]The temperature dependence of the deactivation rate constant at 295–410 K is obtained (see Table 17).
[e]The rate constant was extrapolated from shock tube experiments at 1200–3500 K.
[f]The rate constant is wrong because of an error in the HF concentration determination, it has been remeasured in Pritt and Patel.[540]

[g]The vibrational distribution of CO is 1.00:0.094:0.043 ($v=1$, $v=2$, $v=3$).[563]
[h]The fractions of the reactive channel are 0.96 ± 0.12 and 0.94 ± 0.13 for HBr and DBr, respectively.
[i]A weak negative temperature dependence of the deactivation rate constants at $T=253-427$ K was obtained.
[j]According to Deakin *et al.*,[548] this rate constant is incorrect due to the contribution of the $I+O_2(^1\Delta)\rightarrow I^*+O_2$ process.
[k]The physical quenching rate constant was determined to be $(0.9\pm4)\times10^{-12}$ cm^3/molecule·s.
[l]Quenching rate constants at 295–600 K are obtained.
[m]This value is incorrect because of the nonstatistical population of the $F=2,3$ hyperfine sublevels of I* atoms obtained by photolysis of I_2 at 498 nm.[147]
[n]Infrared emission from $O_2(^1\Sigma)$ was detected.
[o]Only the channel leading to $O_2(^1\Sigma)+I$. The rate constants are 0.9, 1.1, 1.2, and 1.3 in 10^{-13} cm^3/molecule·s units for $T=268$, 298, 320, and 353 K.
[p]Private communication of Houston, published in Lilenfield *et al.*[56]
[q]$90\pm10\%$ of the I^*+Br_2 collisions result in chemical reaction, the yield of Br* is 80%.
[r]The deactivation of I* by I_2 results in vibrationally excited $I_2^*(X,25\leqslant v\leqslant43)$.[564] It is interesting that this excited I_2^* molecule may be dissociated by further energy transfer from $O_2(^1\Delta)$ on subsequent collisions.[565]
[s]The quenching rate constant is given by the expression $8\cdot10^{-11}\exp(-4.4\cdot T/1000)$ cm^3/molecule·s ($T=293-1000$ K).

TABLE 16. Rate constants at 300 K for quenching of I* atoms by polyatomic molecules [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]

M	k (cm^3/molecule·s)	Detection	Reference
H_2O	9.4(−13)	ARA UV	463
	(7.2±1.6)(−13)	ARA UV	535
	(8.4±1.1)(−13)	ARA UV	542
	(2.5±0.5)(−12)	ARA UV	549
	(2.1±0.3)(−12)	SE IR	566
	(2.4±0.3)(−12)	ARA UV	567
D_2O	(6.2±0.8)(−14)	ARA UV	463
	(1.8±0.4)(−14)	ARA UV	542
	(4.3±0.6)(−14)	ARA UV	549
	(3.7±0.7)(−14)	SE IR	566
HDO	(1.9±0.3)(−12)	SE IR	566
HCN	(6.8±0.7)(−14)	ARF VUV	543
	(3.3±0.2)(−14)	ARA UV	141
	(8.3±0.1)(−14)	I-laser	141
CO_2	1.3(−16)	ARA UV	463
	1.7(−16)	SE IR	528
	<4.8(−15)	GC PP[a]	112, 531
	(1.3±0.2)(−16)	ARA UV	549
N_2O	1.3(−15)	ARA UV	568
O_3	(1.1±0.1)(−11)	ARA UV	551
SCO	1.6(−15)	ARF VUV	543
ClCN	(1.2±0.1)(−15)	ARA UV	569
NOCl	6.2(−12)	ARA UV	568
	(1.24±0.3)(−10)[b]	CT PP	570
BrCN	(5.2±0.7)(−15)	ARA UV	569
NOBr	9.6(−12)	ARA UV	568
ICN	6.0(−14)	ARA UV	568
	(2.6±0.4)(−14)	ARA UV	569
HgI_2	(4.5±0.2)(−10)[c]	SE IR	571
CH=CH	(4.2±1.0)(−14)[d]	ARA UV	534
H_2O_2	(1.3±0.2)(−16)	ARA UV IR	549
$(CN)_2$	(2.2±0.2)(−15)	ARA UV	141
CF_3	(3.7±0.3)(−12)[e]	TR-SM IR	111
CH_4	5.9(−14)	ARA UV	463
	(1.0±0.2)(−13)	SE IR	528
	(6.8)(−14)[f]	GC PP[a]	572
	(9.3±3.0)(−14)[d]	ARA UV	534
	(1.1±0.5)(−13)	ARA UV	535
	(9.7±0.3)(−14)[g]	ARA UV	119
	(9.4±0.4)(−14)	ARF VUV	573
	(7.52±0.12)(−14)	SE IR	574
CH_3Cl	(3.1±0.3)(−13)	ARA UV	575
CF_3H	4.6(−14)	ARA UV	463
CH_2Cl_2	(1.28±0.08)(−13)	ARA UV	575
CF_4	4.5(−15)	ARA UV	463
	4.6(−16)	SE IR	528

TABLE 16. Rate constants at 300 K for quenching of I* atoms by polyatomic molecules [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]—Continued

M	k (cm^3/molecule·s)	Detection	Reference
$CHCl_3$	(5.7±0.3)(−14)	ARA UV	575
CH_3I	1.23(−14)[h]	TOF-MS	576
	1.7(−12)	ARA UV	577, 578
	<1.7(−15)[f]	ARA UV	578
	<4(−14)[i]	TR-MS PP	115
	(2.6±0.6)(−13)	ARA UV	579, 580
	(6.2±1.4)(−13)	ARA UV	581
	(5.7±0.6)(−13)	ARA UV	546
	(2.0±1.0)(−13)	I-laser	582
	(2.6±0.2)(−13)	ARA UV	536
	[j]	ARA UV	583
	(2.5±0.4)(−13)	SE IR, Fl IR PF	126
	(2.76±0.22)(−13)	SE IR	574
	(2.9±0.4)(−13)	SE IR	584
CD_3I	(4.6±0.8)(−15)	ARA UV	579, 580
	(1.8±0.2)(−14)	ARA UV	546
	(1.0±0.2)(−14)	ARA UV	585
CCl_3F	(3.9±0.4)(−15)	ARA UV	575
CCl_4	(2.3±0.3)(−15)	ARA UV	575
CF_3I	~3.7(−15)	ARA UV	526
	(3.5±0.6)(−16)	SE IR	528, 529
	5.4(−17)	SE IR	586
	(4.3−7)(−17)	TR-SM VIS	114
	(2.55)(−16)	ARA IR	587
	6(−17)	TR-SM VIS	588
	(3.3±0.5)(−17)	ARA UV	585
	(3.5±0.5)(−17)	SE IR	574
CH_2I_2	(3.6±0.3)(−13)	SE IR, Fl IR PF	126
	(3.4±0.4)(−13)	LOAT	589
$CH_2{=}CH_2$	(7.0±1.2)(−14)	ARA UV	328
	(2.3±0.5)(−13)[d]	ARA UV	534
CH_3OH	(5.5±0.8)(−12)	ARA UV	567
CH_3CN	(1.2±0.1)(−13)	ARA UV	141
	(1.6±0.1)(−13)	I-laser	141
CD_3CN	(7.3±0.2)(−14)	I-laser	141
	(5.3±0.5)(−14)	ARA UV	141
$CF_2{=}CHF$	(5.3±1.7)(−14)	ARA UV	328
$CF_2{=}CF_2$	(3.7±0.1)(−15)	ARA UV	328
$N{\equiv}C\text{-}CF_2I$	(9±2)(−16)	ARA UV	585
SF_6	3.1(−15)	ARA UV	463
	2.4(−17)	SE IR	528
C_2H_6	(1.19±0.14)(−13) (T=60 °C)	GC PP[a]	112, 531
	(5.9)(−14)[f]	GC PP[a]	572
	(8.7±2.0)(−14)[d]	ARA UV	534
C_2H_5I	(1.9±0.2)(−13)	ARA UV	578, 590
	~3.2(−13)	ARA UV	86, 590
	(3.7±0.7)(−13)	ARA UV	530
	(6.2±1.4)(−13)	ARA UV	581
	(6.1±0.3)(−13)	ARA UV	546
	(2.85±0.40)(−13)	SE IR	574
	(3.6±0.4)(−13)	SE IR	584
C_2F_6	(0.8±0.1)(−17)	ARA UV	591
CF_3CFHI	(3.4±0.4)(−14)	ARA UV	585
C_2F_5I	(1.8±0.1)(−17)	ARA UV	592
	(2.1±0.2)(−17)	ARA UV	585
C_3H_6	1.6(−13)	ARA UV	328
	(3.8±0.8)(−13)[d]	ARA UV	534
	$(0.25^{+1.0}_{-0.12})(-13)$[b]	CT PP	593
C_2H_5OH	(8±1)(−12)	ARA UV	567
C_2H_5CN	(1.3±0.1)(−13)	ARA UV	141
$CH_2{=}CHCH_2Cl$	1.3(−13)	ARA UV	568
$CH_2{=}CHCH_2Br$	2.4(−13)	ARA UV	568
$CH_2{=}CHCH_2I$	4.2(−13)	ARA UV	568
$i\text{-}C_3H_7$	5(−13)	ARA UV	546
C_3H_8	5.7(−14)	ARA UV	526, 530
	(1.7±0.1)(−13)	SE IR	528

TABLE 16. Rate constants at 300 K for quenching of I* atoms by polyatomic molecules [powers of 10 in parentheses, $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$]—Continued

M	k (cm^3/molecule·s)	Detection	Reference
	(8.16)(−14)[f]	GC PP[a]	572
	(1.9±0.5)(−13)[d]	ARA UV	534, 535
	(1.6±0.1)(−13)[g]	ARA UV	119
	$(0.25^{+0.4}_{-0.1})(-13)$[b]	CT PP	593
C_3F_8	(1.1±0.2)(−17)	ARA UV	591
n-C_3H_7I	(2.0±0.2)(−13)	ARA UV	578
	(8.0±0.7)(−13)	ARA UV	546
	(5.1±0.3)(−13)	SE IR	584
i-C_3H_7I	(2.0±0.2)(−13)	ARA UV	578
	(6.3±1.9)(−13)	ARA UV	546
	(4.6±0.8)(−13)	SE IR	584
n-C_3F_7I	(2.3)(−16)	TR-SM VIS	588
	(4.6±0.3)(−17)	ARA UV	594
	(1.7±0.2)(−16)	ARA UV	585
	(4.6±0.3)(−17)[k]	LIF VUV	148
i-C_3F_7I	(2.8)(−16)	TR-SM VIS	588
	(2.0±0.2)(−17)	ARA UV	585
n-C_4H_8	(1.6±0.3)(−13)	ARA UV	328
t-C_4H_8	(2.1±0.4)(−13)	ARA UV	328
	(6.2±3)(−13)[b]	CT PP	570
c-C_4H_8	2.2(−13)	ARA UV	328
i-C_4H_8	3.0(−13)	ARA UV	328
n-C_3H_7OH	(10±1)(−12)	ARA UV	567
C_6H_6	(4.6±0.7)(−13)	ARF VUV	595
C_6D_6	(9.9±1.0)(−15)	ARF VUV	595
C_6H_5I	(5.2±0.4)(−13)	ARA UV	596
	(3.4±0.3)	SE IR	94
C_6F_5I	(2.1±0.2)(−13)	ARA UV	596
$CF_3OC_2F_4I$	(4.2±0.1)(−15)	ARA UV	585
s-C_4H_9	7(−13)	ARA UV	546
t-C_4H_9	5(−13)	ARA UV	546
n-C_4H_{10}	(3.1±0.7)(−13)[d]	ARA UV	534
	(1.16±0.17)(−13)[f]	GC PP[a]	572
n-C_4H_9I	(2.9±0.2)(−13)	ARA UV	578
	(9.3±0.3)(−13)	ARA UV	546
i-C_4H_9I	(2.9±0.2)(−13)	ARA UV	578
	(1.11±0.07)(−12)	ARA UV	546
t-C_4H_9I	(3.8±1.3)(−13)	ARA UV	578
	⩾5.2(−13)	ARA UV	546
s-C_4H_9I	(1.2±0.24)(−12)	ARA UV	546
n-C_4F_9I	(1.0±0.1)(−15)	ARA UV	585
$(CF_3)_3CI$	2.1(−13)	SE IR, Lum RP	123
n-C_4H_9OH	(11.1±0.9)(−12)	ARA UV	567
i-C_4H_9OH	(9.8±0.9)(−12)	ARA UV	567
s-C_4H_9OH	(7.1±0.7)(−12)	ARA UV	567
t-C_4H_9OH	(4.1±0.4)(−12)	ARA UV	567
$(CF_3)_2$-CF-$(CF_2)_2I$	(1.9±0.3)(−15)	ARA UV	591
C_6H_{12}	(6.3±1.2)(−13)	ARA UV	328
$C_3F_7OC_2F_4I$	(8.3±0.9)(−15)	ARA UV	585
$(CF_3)_2$-CF-$(CF_2)_4I$	(2.6±0.4)(−15)	ARA UV	591

[a]The rate constants from two studies[112,531] were multiplied by 16/5.7 (see text).
[b]Relative measurement (see text).
[c]$T=453$ K.
[d]The temperature dependence of the deactivation rate constant at 295–410 K is obtained, see Table 17.
[e]This value is obtained in 100 Torr of Ar, at $T=25$ °C. The values in Ar, N_2, and CO_2 at different pressures and temperatures are also presented.
[f]Relative measurement, the reference process is the deactivation of I* by I_2 for which we assumed the rate constant of 3.4×10^{-11} cm^3/molecule·s. The H atom abstraction reaction rate constant is also measured.
[g]The fractions of the reactive channel are 0.03±0.11 and 0.03±0.16 for CH_4 and C_3H_8, respectively.
[h]The result is controversial.[576]
[i]The reaction rate constant is estimated as $(1\pm0.6)\times10^{-14}$ cm^3/molecule·s at $T=316$–447 K.
[j]The reaction channel is <0.01 of the total quenching.
[k]The $I^*+C_3F_7I\rightarrow I_2+C_3F_7$ reaction rate constant is found to be $\leqslant(3\pm1.5)\times10^{-19}$ cm^3/molecule·s.

For example, the rate constant for channel (36) has been found to be $(9.63\pm4.0)\times10^{-13}$ cm^3/molecule·s. Since the total deactivation rate constant for I* by HF was assumed to be about 3×10^{-12} cm^3/molecule·s,[538,539] it was concluded that the fractions are 0.35 ± 0.04 for channel (36) and 0.05 ± 0.04 for channel (37); hence ~60% of the deactivation of I* by HF occurs via *E-R*, *T* energy transfer.

However, later the total deactivation rate constant has been remeasured and a new, more correct value $[(8.9\pm0.1)\times10^{-13}$ cm^3/molecule·s$]$ has been obtained.[540] Thus, the conclusion has been changed: deactivation of I* by HF occurs mainly via *E-V* energy exchange through channels (36) and (37) and the role of *E-R*, *T* channels is very small.

5.1.3. Recombination Reactions of Excited I* Atoms

From spectroscopic and kinetic arguments Stephan-Rossbach and Comes have concluded that the trimolecular recombination of excited I* atoms proceeds mainly via two pathways,

$$\mathrm{I}(^2\mathrm{P}_{3/2})+\mathrm{I}(^2\mathrm{P}_{1/2})\xrightarrow{+M}\mathrm{I}_2^*(B^3\Pi_0^+)\rightarrow\mathrm{I}_2(\mathrm{X})+h\nu_1, \quad (38)$$

$$\mathrm{I}(^2\mathrm{P}_{1/2})+\mathrm{I}(^2\mathrm{P}_{1/2})\xrightarrow{+M}\mathrm{I}_2^*(^3\Delta_{1\mathrm{u}})\rightarrow\mathrm{I}_2(\mathrm{X})+h\nu_2. \quad (39)$$

While the chemiluminescence spectrum for reaction (38) is broad, it lies at $\nu_1>500$ nm and has a maximum at ~560 nm,[136,148] the chemiluminescence spectrum for reaction (39) is narrow: 655 nm$<\nu_2<$685 nm.[136] The trimolecular rate constant for reaction (38) is determined by the LIF VUV method to be $(1.0\pm0.5)\times10^{-32}$ cm^6/molecule^2·s for M$=C_3F_7I$ and in the limit of low pressure.[148,597] An upper limit of the rate constant for a possible bimolecular reaction of I* with n-C_3F_7I yielding $\mathrm{I}_2(X\,^1\Sigma_{og}^+)$ was found to be $(3\pm1.5)\times10^{-19}$ cm^3/molecule·s.[597]

Andreeva *et al.* have estimated the rate constant to be $\leqslant2\times10^{-33}$ cm^6/molecule^2·s from a rather complicated modeling of experiments in which I_2 was detected by time-resolved visible spectrometry after the photolysis of CF_3I.[114] The same method was used by Kuznetsova and Maslov[588] to determine the recombination rate constants I*+R→RI, for which the values of (1.2–4), (0.42–3.5), and (0.18–1.4), all in 10^{-12} cm^3/molecule·s, have been obtained for R $=CF_3I$, n-C_3F_7I, and i-C_3F_7I, respectively. Note that these rate constants are 1 order of magnitude lower than the rate constants for the I+R→RI recombination processes. This seems to be a general rule: the excited I* atoms recombinate slower than ground state I atoms. The method of quantitative laser induced chemiluminescent kinetic spectroscopy was developed by Egorov *et al.* for the study of chemiluminescence reactions.[598] This method was used to obtain spectral distributions of chemiluminescence rate constants and total chemiluminescence rate constants for processes (38) and (39).

Also, the bimolecular photorecombination reaction followed by chemiluminescence

$$\mathrm{I}(^2\mathrm{P}_{1/2})+\mathrm{R}\rightarrow\mathrm{RI}(^3\mathrm{Q}_0^{+\mathrm{A}})\rightarrow\mathrm{RI}(\mathrm{X})+h\nu, \quad (40)$$

where R$=C_3H_7$ and R$=CF_3CFCF_3$ has been observed by Pravilov *et al.*[599]

5.1.4. Chemical Trapping: I*+NOCl→NO+ICl

One of the first methods to study the processes of I* atoms was the chemical trapping method, which was developed by Pravilov *et al.*[122,570,584,593,600–604] The method is based on the competition of the reaction

$$\mathrm{I}^*+\mathrm{NOCl}\rightarrow\mathrm{NO}+\mathrm{ICl}, \quad (41)$$

and the physical quenching of I* atoms by some other molecules, for example, by C_3H_8 (a), C_3H_6 (b), C_4H_8I (c), and CH_3I (d); the quenching rate constants are denoted here k_a, k_b, k_c, and k_d, respectively. Note that the physical quenching I*+NOCl→I+NOCl and the reaction I+NOCl→NO +ICl are slow, so that they can be neglected.[122,593] Relative measurements gave the ratios $k_{41}/k_a=(5\pm3)\times10^3$, $k_{41}/k_b=(5\pm4)\times10^3$, $k_c/k_{41}=(0.5\pm0.2)\times10^{-3}$, and $k_d/k_{41}=(2.1\pm0.5)\times10^{-3}$.[570,593] The rate constant k_d is well established now to be $(2.6\times10^{-13}$ cm^3/molecule·s$)$, so from the ratio k_d/k_{41} we can calculate the rate constant $k_{41}=(1.24\pm0.3)\times10^{-10}$ cm^3/molecule·s. Using this value, we can calculate the rate constants $k_a=(0.25^{+0.4}_{-0.10})\times10^{-13}$, $k_b=(0.25^{+1.0}_{-0.12})\times10^{-13}$, and $k_c=(6.2\pm3)\times10^{-11}$ cm^3/molecule·s; these values are presented in Table 16. These values contradict the data obtained in 1969 by Donovan *et al.*,[328] and by Hathorn *et al.*,[568] but the reason for the disagreement is unclear.

5.1.5. Temperature Dependence of Deactivation Rate Constants

The temperature dependence of deactivation rate constants for I* atoms by various molecules were determined by Callear and Wilson (H_2, I_2, N_2, C_2H_6, and C_3H_8, 30–90 °C),[112,531] by Broadbent and Callear (CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}, 303–373 K),[572] by Deakin and Husain (H_2, D_2, N_2, O_2, I_2, CH═CH, CH_4, CH_2═CH_2, C_2H_6, C_3H_8, CH_3CH═CH_2, n-C_4H_{10}, 180–410 K),[534] by Kartazaev *et al.* (I_2, 295–1000 K),[561] by Fotakis and Donovan (HBr, 253–427 K),[544] by Cline and Leone (I_2, 300–800 K),[562] by Burde *et al.* (O_2 and I_2, 295–600 K),[552] and by Van Marter and Heaven (O_2, 150 K).[147] Arrhenius parameters for the deactivation of I* atoms by various molecules are presented in Table 17, some of them have been calculated in the present review.

Several deactivation rate constants were determined by Callear and Wilson at 30, 60, and 90 °C.[112,531] This was an indirect study, in which the products of the $C_3H_8+I_2$ photolysis by visible light were analyzed by gas chromatography. The rate data from Callear and Wilson were determined relative to the I*+C_3H_8 rate constant of Donovan and Husain ($k'=5.7\times10^{-14}$ cm^3/molecule·s).[526,530] In Tables 15, 16, and 18 we present the rate constants of Callear and

TABLE 17. Arrhenius parameters $[k=A\exp(-E/RT)]$ for the deactivation of I* atoms by various molecules

M	$\log_{10}A$ (cm^3/molecule·s)	E (kcal/mol)	T (K)	Reference
H_2	−11.65±0.14	1.7±0.2	180–410	534
D_2	−15.56±0.01	−1.2±0.6	180–410	534
N_2	−15.19±0.29	1.5±0.1	180–410	534
O_2	−10.45±0.18	0.2±0.2	180–410	534
O_2	−9.258	0.5±0.2	295–600	552
HBr[a]	−12.45	−0.645±0.05	253–427	544
I_2	−13.41±0.67	−3.3±1.1	180–410	534
I_2	−10.54±0.06	≈0	300–800	562
I_2	−8.453	0.8±0.3	295–700	552
CH=CH	−13.45±0.12	−0.1±0.1	180–410	534
CH_4	−13.40±0.17	−0.5±0.2	180–410	534
CH_4[b]		⩾13.2	303–373	572
$CH_2=CH_2$	−13.09±0.1	−0.6±0.1	180–410	534
C_2H_6	−13.43±0.11	−0.5±0.1	180–410	534
C_2H_6[b]	−12.86	7.70±0.3	303–373	572
C_2H_6	−13.36	7.0±0.3	180–410	531
C_3H_8	−13.24±0.14	−0.7±0.1	180–410	534
C_3H_8[b]	−12.70	5.69±0.3	303–373	572
C_3H_8[b]	−13.53	5.0±0.3	180–410	531
$CH_3CH=CH_2$	−12.42±0.1	0.0±0.1	180–410	534
n-C_4H_{10}	−12.73±0.11	−0.3±0.1	180–410	534
n-C_4H_{10}[b,c]	−12.56	5.54±0.3	303–373	572
n-C_4H_{10}[b,d]	−13.12	6.93±0.3	303–373	572

[a]Non-Arrhenius behavior starts from 410 K.
[b]Reaction rate constants.
[c]Secondary H atom abstraction reaction rate constant.
[d]Primary H atom abstraction reaction rate constant.

Wilson multiplied by $k''/k'=16/5.7$, since the last and more correct rate reported by Wiesenfeld and Wolk is $k''=1.6\times10^{-13}$ cm^3/molecule·s.[119]

5.1.6. Deactivation of I* by O_2

The deactivation of excited I* atoms by ground state ($^3\Sigma$) oxygen occurs mainly via the near-resonant energy exchange process

$$I^*+O_2(X^3\Sigma)\rightarrow I+O_2(^1\Delta). \quad (42)$$

The physical quenching $I^*+O_2(X)\rightarrow I+O_2(X)$ is found to be insignificant.[234,605] The reverse process

$$I+O_2(^1\Delta)\rightarrow I^*+O_2(X^3\Sigma), \quad (43)$$

TABLE 18. Temperature dependence of deactivation rate constants for I* atoms obtained by Callear and Wilson,[112,531] $(a\pm b)(-c)\equiv(a\pm b)\times10^{-c}$

M	$T=30$ °C	$T=60$ °C	$T=90$ °C
H_2	(8.8±2)(−14)		(3.7±0.2)(−13)
N_2		(4.2±4.2)(−16)	(1.24±0.4)(−15)
I_2	(6.9±0.17)(−11)	(6.9)(−11)	(6.9)(−11)
C_2H_6		(1.19±0.14)(−13)	(1.8±0.14)(−13)
C_2H_6[a]		(6.5)(−19)	(1.52)(−18)
C_3H_8	1.6(−13)	(2.2±0.08)(−13)	(3.0±0.1)(−13)
C_3H_8[a]	8.9(−18)	(1.95)(−17)	(3.55)(−17)

[a]Reaction rate constants.

is also quick, $k_{43}/k_{42}=2.94$ at room temperature.[234] These forward and reverse rate constants have been measured at room temperature[234,534,550,552] and at $T=150$ K.[147,553]

The temperature dependence for the rate constant k_{43} was determined at 180–410 K by Deakin and Husain.[534] The activation energy of the deactivation process (43) was found to be 0.2±0.2 kcal/mol, less than the exothermicity of the process. To explain this finding, Deakin and Husain suggested that the rate constant may be inversely dependent on temperature. Since then, it is a common practice to model the temperature dependence for the rate constant using expressions

$$k_{42}=A_{42}\exp(-T_{42}/T), \quad (44)$$

$$k_{43}=A_{43}(T_{43}/T), \quad (45)$$

where $A_{43}=7.8\times10^{-11}$ cm^3/molecule·s, $T_{43}=295$ K, $A_{42}=10.4\times10^{-11}$ cm^3/molecule·s, and $T_{42}=401.4$ K. However, the last measurements of van Marter and Heaven ($k_{42}=7.0\times10^{-12}$ cm^3/molecule·s at $T=150$ K)[147] disagree both with the predictions of the Arrhenius expression reported by Deakin and Husain ($k_{42}=1.8\times10^{-11}$ cm^3/molecule·s at $T=150$ K) and expression (44) ($k_{42}=1.4\times10^{-11}$ cm^3/molecule·s at $T=150$ K). Hence, the temperature dependencies of the rate constants for these processes remain unclear.

Long-range multipolar interactions or nonadiabatic surface crossings are usually suggested to be responsible for the energy transfer between small molecules. Kaledin *et al.* have calculated potential energy surfaces for all states correlating with the $I+O_2(^1\Delta)$ and $I^*+O_2(X)$ dissociation limits using high-level *ab initio* methods.[606,607] Long-range attractive forces were found to be relatively weak, with no state bound by more than 250 cm^{-1}. Hence the energy exchange process (43) is likely due to the surface crossings, and thus the rate constant for this process must have a positive temperature dependence. This prediction is in agreement with the experimental data.[147,534]

The deactivation of I* atoms by excited ($^1\Delta$) oxygen also occurs mainly via the near-resonant energy exchange process,

$$I^*+O_2(^1\Delta)\rightarrow I+O_2(^1\Sigma), \quad (46)$$

suggested by Ogryzlo *et al.*[608] and studied by Heidner *et al.*[554]

5.1.7. Theoretical Considerations

The first quantum-mechanical study of the collinear reaction I^*+H_2 were done by Zimmerman and George.[277,609,610] Later, using the analogy with the related $Xe+H_2$ system, Resnikov and Umanskii estimated the long-range interaction potential for $I^*/I+H_2$ and carried out a calculation for the I^*+H_2 quenching processes.[268] The Landau–Zener formula with quadrupole-quadrupole interaction as a perturbation was used. It was found that the main contribution comes from E-V energy exchange $I^*+H_2(v)\rightarrow I+H_2(v')$ where $v=0,1,2$ and $v'=v+2$. The temperature dependence of the

rate constants for the deactivation of I* by H_2 was found to be in excellent agreement with experiment, while the absolute value was four times smaller. Since no fitting parameters were used in the model, this agreement may be called satisfactory.

5.2. Production of I* Atoms by Photolysis

A great deal of work has been done on the photodissociation of iodine-containing compounds, see reviews of Okabe,[611] Pravilov,[612] Jackson and Okabe,[613] and Hirota.[614] The data for β parameters and relative quantum yields of I* atoms for the photodissociation of small (up to seven atoms) and large (more than seven atoms) parent molecules M are presented in Tables 19 and 20, respectively, in chronological order for each molecule M. Several broad-band studies are not mentioned here; however, the work of Dzvonik *et al.* should be mentioned, since several rare molecules (phenyl iodide, 1-naphthyl iodide, 2-naphthyl iodide, 4-biphenyl iodide, 3-biphenyl iodide) have been studied by TOF-MS at broadband (240–340 nm) photolysis and the β parameters have been obtained for all of them.[9]

5.2.1. Correction of the I* Yield in the Photolysis of n-C_3F_7I

One of the most efficient photolytical sources of I* atoms is n-C_3F_7I, which has a very large yield of I* atoms at 205–315 nm. Until recently, the yield of I* atoms at 266 nm was expected to be unity, based on the infrared luminescence measurements of Ershov *et al.* $(97.8\pm1.2\%)$[123] and the diode laser absorption study of Hess *et al.* $(102\pm4\%)$.[137] However, Alekseev *et al.* have found that in reality this yield is lower, it is $\approx92\%$.[584] This conclusion was confirmed recently in two works. The ground state I atoms have been observed in the photodissociation of n-C_3F_7I by Kavita and Das $(\Gamma=83\pm2\%)$[196,665] and by Baklanov *et al.* $(\Gamma=92\pm1\%)$,[145] who used two-photon LIF and REMPI $(1+1')$, respectively. Baklanov *et al.* have pointed out that the yield of I* atoms in the study of Ershov *et al.* has probably been overestimated due to the formation of exciplexes $I^*-C_3F_7I$, since the formation of these exciplexes should result in an increase of the radiative transition rate of I* atoms.[669] Also, Baklanov *et al.* have noticed that the yield of I* atoms in the study of Hess *et al.* was probably overestimated due to the uncertainty in the results of the decomposition of the experimental kinetics into a sum of two exponents in the case where the rise and fall times of the kinetics are very comparable.

Note that the photodissociation of n-C_3F_7I has been used as a reference source with unity yield of I* atoms in a series of measurements.[94,126,547,555,571,655,656,668,669] Now, all the results of these measurements should be recalculated, and the reported yield of I* atoms should be decreased.

5.2.2. Photodissociation of HI and DI

According to Mulliken's prediction,[510] the first absorption continuum (A-X band: 190–300 nm, peaks at 220 nm) of HI consists of the following transitions to the three upper states of the Q-group:

$$HI(^1\Sigma_0^+)+h\nu\rightarrow HI(^3\Pi_1,{}^1\Pi_1)\rightarrow H+I(^2P_{3/2}),$$
$$\Delta\Omega=\pm1\quad(\beta=-1), \tag{47a}$$
$$HI(^3\Pi_0)\rightarrow H+I^*(^2P_{1/2}),\quad \Delta\Omega=0\quad(\beta=2), \tag{47b}$$

and the strongest transition must be $^1\Pi_1\leftarrow{}^1\Sigma^+$. Mulliken also predicted that, at the equilibrium bond length of the ground state of HI, the highest in energy in the $^1\Pi_1$ state, and the lowest is the $^3\Pi_1$ state, with $^3\Pi_0$ in the middle. Hence one would expect that the I* production due to the parallel transition would peak in the middle of the A band, or at the red end of the A band. Later De Vries and co-workers suggested that I* is produced not only by the parallel transition (47b), but by the perpendicular $HI(^1\Sigma_0^+)\rightarrow HI(^3\Sigma_1^+)$ transition also.[616] This suggestion is discussed in detail, for example, by Langford *et al.*[620]

The studies on the yield of I* atoms from the photolysis of HI has been reviewed recently by Regan *et al.*[621] In this analysis the early data[526,545,581,682,683] were omitted. Also, the results of Langford *et al.* have been recalculated, since in the measurements of Langford *et al.* the H atoms were detected by the H-Rydberg atom time-of-flight technique (HR-TOF) and the bandwidth of the probe laser was too narrow. The Monte Carlo modeling of these HR-TOF experiments gave new values for the yields of I* atoms, presented in footnotes to Table 19. Finally, there exists good agreement between all available data on the yield of I* atoms from photodissociation of HI.[621] However, later Manzhos *et al.*[622] have determined by photofragment imaging technique that the yields of I* atoms are consistently lower than the ones obtained by Regan *et al.*[621] The experimental data were used for the reconstruction of potential energy curves of HI molecule using three-potential[149,615,622] and four-potential[92,622,684] fits.

There are several theoretical predictions on the photodissociation of HI in the literature.[615,685,686] In the most recent treatment of Balakrishnan *et al.*,[686] the wavelength dependence of the I*/I branching ratio is in good agreement with the experimental data.

Also, in the recent study of Jodoin and Brown the angular distribution of iodine atoms have been calculated, and the orientation and alignment parameters $a_Q^{(K)}(p)$ were predicted.[687]

5.2.3. Photodissociation of ICN

In the linear geometry, three excited states, $^3\Pi_{0^+}$, $^3\Pi_1$, and $^1\Pi_1$, are involved in the photodissociation of ICN in the A-X band continuum (210–340 nm). A conical intersection between the $^3\Pi_{0^+}$ and $^1\Pi_1$ surfaces causes nonadiabatic coupling, and as a result, both of these surfaces may lead to the I* product. In bent geometries, the doubly degenerate

TABLE 19. Summary of I* relative quantum yield and β parameter determinations from photodissociation of small molecules

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
HI	253.7	55±25		SE IR	545
	266	36±5	2.0	TOF-MS	615
	266	40±5	2	LIF-DS PF	125
	248	47±3		TP-LIF	131
	193	9±5		TOF-MS PF	616
	222	43±4	0.39±0.02	TOF-MS PF	616
	248	57±4	0.54±0.02	TOF-MS PF	616
	193	10±3[b]		SE IR	617
	248	33±3[b]		SE IR	617
	248	65±4		SE IR	547
	193	≤10		TOF-MS[c]	481
	248	46±5	1.7±0.2	TOF-MS[c]	481
	248		~2.0	TOF-MS[c]	481
	193	5±2		SE IR	555
	248	51±5		SE IR	555
	266	49[d]	~2.0	REMPI/I PF	618
	205	13		REMPI	619
	208–303	3–35[e]	1.9±0.2[f]	HR-TOF	620
	212–266	24–50[g]	1.85–2.00	LIF VUV PF	149
	222–280	20–33[h]		REMPI	621
	273–288	11–37[i]		REMPI/I PF	622
DI	214	33±10		[j]	623
	240	60±7		[j]	623
	253.7	46±5		[j]	623
	280	−8±27		[j]	623
	266.2	26±3		TOF-MS	615
	205.2	20	≈2	REMPI/I PF	52
	243.2	56	≈2	REMPI/I PF	52
	307.8	~0		REMPI/I (3+1) PF	52
ICl	248	41.3±9		TP-LIF	384
	237.8	~0		REMPI PF	385
	304	30	1.7	REMPI	387
	235	[k]	1.8±0.2[k]	REMPI/I	386
IBr	248	16±6[l]	2.00	REMPI	488
	267	27±3[l]	1.90±0.2	REMPI	488
	304	7±3[l]	2.00	REMPI	488
	250.3	95±4	1.9±0.1	REMPI	488
	250.9	83±4	2.0±0.1	REMPI	488
	260.6	81±4	1.9±0.1	REMPI	488
	304	10[l]	1.8	REMPI PF	146
I_2	480–450	31–46[m]		TOF-MS	624
	502–533	8–44[n]		GC PP	625
	266	50		TOF-MS	626
	470–525	5–50[o]		ARA UV	627
	460–498	16–34[p]		ARA UV PF	124
	458–514	27–68[q]		LOAT	139
	304		−0.92±0.01	REMPI	628
	480	30.4±0.1		AS-DL	562
ICN	266	60		TOF-MS	629
	280–240	11–68[r]		SE IR	630
	235	2.3±0.6[s]		LIF PF	152
	248	35±6[s]		LIF PF	152
	266	52±11[s]		LIF PF	152
	280	38±14[s]		LIF PF	152
	290	16±7[s]		LIF PF	152
	266	65±5[t]	1.6±0.2	SE IR, SE IR PF	631
	248–284	44–66[u]		AS-DL	632
	248	43±3[v]	[v]	LIF PF	633
	222,248,266,308	[w]	[x]	FMDS PF[x]	150
	266	[y]	2.0	REMPI	634
	250	[y]	≤2	REMPI	634
	262	0–100[z]		FMDS PF	151
HgI_2	265–320	0–50[A]		SE IR[A]	571
CH_3I	266	78±11		TOF-MS	188
	304	~75		MCD	120

TABLE 19. Summary of I* relative quantum yield and β parameter determinations from photodissociation of small molecules—Continued

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
	245–308	21–75[B]		LOAT	635
	248	81±3		SE IR, Fl IR PF	126
	248	0.81±0.03		SE IR	94
	308	~0.05[C]		SE IR	94
	248	76±2		TP-LIF	131
	244–310	19–78[D]		CT PP	570
	247.5–312.5	19–76[E]		LOAT	636
	248	71±3		PRTS	637
	248	70		TOF-MS	638
	155–210	[F]		MS PP	135
	193	100	[G]	TOF-MS	639
	266	73±4		AS-DL	137
	248	73	1.95	TOF-MS	140
	193	70±4		AS-DL	640
	248	76±4		AS-DL	640
	266	95	~2	REMPI/I	641
	248	72±8		MCD	642
	229.4		1.6±0.1	TOF-MS	643
	266.2		1.9±0.05	TOF-MS	643
	266–275	[H]	1.8±0.1	REMPI	644
	326–334	47–92[I]		REMPI PF	645
	248	73		TOF-MS	646
	333.45	<10[J]	~2	REMPI PF	647
	266		[K]	REMPI/I	648
	304	≈43	[K]	REMPI/I	648
	304	40–48		REMPI	649, 650
	222	63±2		TP-LIF	651
	222	63±2		TP-LIF	194
	266	79±2		TP-LIF	194
	305	43±2		TP-LIF	194
	266		1.9±0.1	REMPI	652
	304	47.6±3	1.9±0.1	REMPI	652
	304	20[L]		REMPI	183
	240–333	[M]	≈1.9	REMPI/I	185
	266	71±3		REMPI (1+1′)	145
$(CH_3I)_{2--3}$	266	57		REMPI	649, 650
$(CH_3I)_{2--3}$	304	>33		REMPI	649, 650
CD_3I	248	75±2		TP-LIF	131
	274	73		LOAT	653
	247.5–312.5	8–73[N]		LOAT	636
	248	81		PRTS	637
	266	[H]		REMPI	644
	313–339	57–95		REMPI PF	645
	248	83			654
	248	82		TOF-MS	646
CH_2ICl	222–304	38–55[O]		REMPI	186
CF_3I	266	91±0.5		Se IR, Lum RP	123
	200–350	98^{+2}_{-9}[P]		Se IR	602
	248	75±5		Se IR	655
	308	83±5		SE IR	655
	248	89±1		TP-LIF	131
	248	88±6		SE IR	547
	247.5–312.5	21–78[Q]		LOAT	636
	234–316	47–107[R]		SE IR	656
	248	92	0.64	TOF-MS	657
t	248	86.5±5		MCD	642
	248	93		TOF-MS	503
	266	92±7		SE IR	584
	248	92		TOF-MS	658
	248	87	0.05±0.1 (T=100 °C)	TOF-MS	659
	248	83	0.2±0.1 (T=400 °C)	TOF-MS	659
	248	88	−0.2	TOF-MS	660
	304		1.66±0.02	REMPI	661
	308	21	1.78±0.05	TOF-MS	662
	304	69±2		REMPI	183

TABLE 19. Summary of I* relative quantum yield and β parameter determinations from photodissociation of small molecules—Continued

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
	277	87	1.83	REMPI/I	663
	275–308	38–92[S]	1.43–1.91[T]	TOF-MS PF	664
	222–305	63–89[U]		TP-LIF	196,665
	277–304		1.4–1.93[V]	REMPI/I	666
CH_2BrI	248	43	1.0±0.1	TOF-MS PF	503
	193		~0	TOF-MS PF	503
CH_2I_2	266	~0		TOF-MS	667
	248	46±4		SE IR, F1 IR PF	126
	308	25±2		SE IR, F1 IR PF	126
	193	~0.05		SE IR	94
	248	46±4		SE IR	94
	308	25±2[B]		SE IR	94
	365	36.4		LOAT	589
	248	47.6		LOAT	589
	265–333	2–44[W]		SE IR	668,669
	266	40±3		REMPI (1+1′)	145
	277–304		1.27–1.33[X]	REMPI/I	173
CF_2I_2	248	86	1.1±0.05	TFTS	670
	351	2		TFTS	671
	337	17		TFTS	671
	308	67	1.0±0.1	TFTS	671

[a]The photolysis wavelength λ (or the range for λ) and the yield of I* (or the range for the yields) are present. Γ~0 means "below the detection limit."
[b]Relative values, reference process is the photodissociation of n-C_3H_7I.
[c]Velocity-aligned Doppler spectroscopy (VADS) of H atoms.
[d]This is a value corrected later by Langford *et al.*[620]
[e]The recalculated yields of I* are 14.9, 24.8, 30.7, 31.8, 38.9, 41.8, 48.1, 51.1, 52.2, 53.1, 54.1, 50.2, 47.1, 43.9, 42.0, 34.0, 23.9, 17.0, 13.0, 5.9, and 3.0% for 208, 213, 218, 222, 228, 233, 235, 238, 243, 248, 253, 258, 260, 263, 266, 278, 283, 287, 293, 298, and 303 nm, respectively (see text). These data are taken from Fig. 3 of paper of Regan *et al.*[621]
[f]The β parameters are 2.0, 1.8, 1.8, 1.9, and 1.9 (all ±0.3) for 208, 222, 233, 243.6, and 266 n, respectively.
[g]The yields of I* are 38.2±1.1, 44.9±1.8, 49.7±2.0, 45.6±0.6, 40.5±0.9, 36.0±0.6, 28.4±0.9, 24.7±5.0, and 23.9±1.1% for 266, 257, 248, 240, 232.5, 225, 216.7, 215, 212.5 nm, respectively.
[h]The yields of I* are 35.0, 50.2, 49.5, 44.1, and 24.2% for 222, 248, 258, 266, and 280 nm, respectively. These data are taken from Fig. 2 of paper of Regan *et al.*[621]
[i]The yields of I* are 11±1, 14±1.3, 16, 14.6±1.5, 18.8±0.4, 19.5±0.2, 22.5±3, 23.2±1.3, 23, 23±0.1, 27.5±0.2, 28.4, 26.3±0.2, 29.1±1, 31.8 0.5, 20.8±0.1, and 34.5±2% for 288, 287, 286, 285, 284, 283, 282, 281, 280.2, 280, 279, 278, 277.92, 271, 275, 274, and 273 nm, respectively.
[j]Paper of Betts[623] is unavailable for the author. The data are taken from paper of Clear *et al.*[615]
[k]From the analysis of angular and velocity distributions of Cl* and Cl it was concluded that there are only two channels: ICl→I* +Cl, Cl* +I. Hence β for I* is assumed to be equal to β of Cl.
[l]The I* +Br* channel was below the detection limit, <1%.
[m]The yields of I* are 46, 44, and 31% for 479.6, 464.9, and 449.8 nm, respectively.
[n]The yield of I* at 483.5 nm was assumed to be 0.5. The relative measurements gave the yields of I* of 44±2, 33±1, and 8±3% for 502.0±1.5, 515.5±1.5, and 533.0±4 nm, respectively; all at T=373 K.
[o]The yields of I* are 49.7, 50.5, 48.2, 49.7, 51.2, 50.5, 49.2, 44.4, 29.1, 15.3, 9.9, and 4.8 for 470, 475, 480, 485, 490, 495, 500, 505, 510, 515, 520, and 525 nm, respectively.
[p]The yields of I* are 16.3, 21.3, 24.2, 27.3, 28.6, 30.7, 31.3, 33.3, and 34.1% for 460, 470, 475, 480, 485, 490, 492, 495, and 498 nm, respectively.
[q]The yields of I* are 29±6, 41±3, 62±2, 64±3, 68±2, and 27±3% for 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm, respectively.
[r]The yields of I* are 32±4, 35±9, 51±3, 68±2, 60±2.2, 45±2, 19±1, and 11±1% for 280, 277.5, 270, 266, 262, 258, 246.9, and 239.5 nm, respectively.
[s]The yields of I* are obtained from molecular beam experiments with cold ICN (T=3.2 K). The yields of I* from room temperature ICN are 65±10, 61±17, and 44±12% for 266, 280, and 290 nm, respectively.
[t]From summation of the Doppler resolved CN rotational state distribution.
[u]The yields of I* are 53.4±2, 57.7±2, 62.9±2, 64.5±4, 66±2, 62.5±3, and 44.0±4% for 284, 280, 276, 272, 266, 260, and 248 nm, respectively.
[v]The β parameters and I*/I branching ratios are obtained as a function of the CN(v=0) rotational state.
[w]For 266 nm, the I*/I branching ratio is in good agreement with the value of Wittig *et al.*[631]
[x]Velocity and β parameters of the CN photofragment are determined for both I* and I channels; a Ti:sapphire ring laser was used.
[y]The polarization ratio is obtained as a function of the electric field strength.
[z]The I* quantum yield is obtained as a function of CN rotational state.
[A]The yield of I* decreases smoothly from 50% at 270 nm to 1% at 320 nm.[571] A femtosecond study of the photodissociation of IHgI is presented by Dantus *et al.*[672]
[B]The yields of I* are 59, 63, 75, 47, and 21% for 245.5, 250.6, 275, 292, and 308 nm, respectively.
[C]The data of Pence *et al.*[94] have been corrected by Smedley and Leone:[669] Γ=4 and 21% for 308 nm photodissociation of CH_3I of CH_2I_2, respectively.
[D]The yields of I* are 19.2, 49.1, 76.5, 78.4, 63.7, and 59.2% for 310, 295, 276, 267, 251, and 244 nm, respectively.
[E]The yields of I* are 59±4, 60±4, 76±9, 48±5, and 19±4% for 247.5, 251.5, 275.5, 296.0, and 312.5 nm, respectively.
[F]The yields of I* are 91±30, 24±30, 48±15 24±15% for 210–187, 180–162, 162–158, 158–155 nm, respectively.
[G]The vibrational population in the CH_3 mode ν_2 is determined.
[H]The I/I* ratios are <0.05, 0.09, 0.19, and 0.68 for the ν_2=0–3 vibrational modes of CD_3 from photodissociation of CD_3I, and 0.08, 0.37, and 1.1 for the ν_2=0–2 modes of CH_3 from photodissociation of CH_3I.

[I]The yields of I* are 92, 77, and 47% for 333.5, 329.4, 325.8 nm, respectively. They are determined for the 0_0^0, 2_1^1, and 2_2^2 vibrational bands of CH_3, respectively.
[J]The yield of I* is ~10% for the parallel transition, an it is below the detection limit for the perpendicular transition.
[K]Estimates by the pinhole-field deflection method gave a ratio $\sigma_\perp/\sigma_\parallel$ of 0.00–0.10 at 266 nm and 0.20–0.30 at 304 nm.
[L]Kang *et al.* reported the yield of I* to be 30%, but the value has been recalculated by Eppink and Parker.[185] $(CH_3I)_n$ clusters have also been observed by Kang *et al.*
[M]The yields of I* are 94, 83, and 51% for the $\nu_2=0$, 1, and 2 vibrational states of CH_3; however, the authors estimate these data to be too uncertain.
[N]The yields of I* are 62±4, 70±5, 73±9, 67±8, 48±5, and 8±7% for 247.5, 251.5, 274.0, 280.5, 296.0, and 312.5 nm, respectively.
[O]The yields of I* are 47±2, 51±1, 51±2, 55±3, and 38±1% for 222, 236, 266, 280, and 304 nm, respectively.
[P]Here the average yield of I* atoms over the A-band (200–350 nm) is given. The dependence of the yield on the wavelength is presented in Fig. 4 of paper of Ivanov *et al.*[602]
[Q]The yields of I* are 65±4, 78±5, 63±6, 44±7, 36±3, and 21±3% for 247.5, 274.0, 287.5, 296.0, 301.5, and 312.5 nm, respectively.
[R]The yields of I* are 47±25, 86±13, 91, 91±9, 107±14, and 75±25% for 234, 246, 266, 283, 299, and 316 (±5) nm, respectively.
[S]The yields of I* are 91.7±0.8, 90.1±0.8, 88.5±0.8, 84.0±1.4, 80.6±1.3, 69.0±1.4, 68.0±1.5, 62.9±1.7, 60.6±1.8, 47.4±1.3, 41.2±1.3, and 37.5 ±1.1%, for 275, 279, 283, 290, 293, 295, 296, 297, 298, 300, 302, and 303 nm, respectively.
[T]β=1.91±0.02, 1.82±0.03, 1.70±0.03, 1.6±0.05, 1.44±0.04, 1.43±0.03, 1.43±0.04, 1.65±0.05, 1.64±0.07, 1.64±0.07, and 1.68±0.05 for 275, 279, 283, 290, 293, 295, 296, 297, 298, 300, and 308 nm, respectively.
[U]The yields of I* are 71±7, 72±3, 89±5, 79±3, and 63±2%, for 222, 236, 266, 280, and 305 nm, respectively.
[V]In the photodissociation of $CF_3I(\nu_2)$, the wavelength-dependent $\beta(\lambda)$ parameters are determined. The $\beta(\lambda)$ dependencies vary in the ranges 1.8–1.9, 1.8–1.94, 1.7–1.9, and 1.4–1.7 for $\nu_2=0$, 1, 2, and 3, respectively.
[W]The data of Koffend and Leone[668] have been corrected by Smedley and Leone:[669] Γ=1.9, 5.8, 5.5, 6.8, 8.2, 8.8, 21, 23, 29, 34, 38, 36, 38, 36, 39, 43, and 44% for 332.7, 329.2, 328.0, 324.1, 321.8, 319.9, 308.7, 305.7, 299.8, 296.0, 291.6, 290.9, 287.9, 286.2, 284.4, 268.1, and 265.4 nm, respectively.
[X]β=1.27±0.06, 1.32±0.05, and 1.33±0.06 for 277.40, 281.73, and 304.03 nm, respectively.

TABLE 20. Summary of I* relative quantum yield and β parameter determinations from photodissociation of large molecules

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
C_2H_5I	254	79±8		CT PP	600
	248	67.5±2		TP-LIF	131
	155–210	[b]		MS PP	135
	248	78±7		MCD	642
	248	67		TOF-MS	673
	248	62±3		TP-LIF	133
	248	64	1.7	TOF-MS	140
	266	67±5		SE IR	584
	240–290	62–74[c]		CT PP	604
	222	57±2		TP-LIF	194, 651
	266	72±2		TP-LIF	194
	305	39±2		TP-LIF	194
	304	22±1		REMPI	183
	222–305	39–72[d]		TP-LIF	195
CH_2Cl-CH_2I	248	60		TOF-MS	674, 675
	266	75		TOF-MS	674, 675
	248	70±3		TP-LIF	133
CF_3-CH_2I	248	82		TOF-MS	673
	248	80±3		TP-LIF	133
	248	82	1.85	TOF-MS	140
	222–305	52–81[e]		TP-LIF	195
CH_2Br-CH_2I	248	95–100	1.6	TOF-MS	676
	266	90	1.6±0.2	TOF-MS	676
	308	<20	1.2	TOF-MS	676
CF_2Br-CH_2I	248	77	1.6	TOF-MS	677
	266	89	1.6±0.2	TOF-MS	677
	308	33	1.2	TOF-MS	677
	248	75	1.25	TOF-MS	676
	266	90	1.6	TOF-MS	676
	308	33	1.2	TOF-MS	676
C_2F_5I	200–350	96_{-9}^{+4}[f]		SE IR	602
	268	100±4		SE IR	94
	248	101±5		SE IR	655
	308	104±5		SE IR	655
	248		1.87	TOF-MS	678
	266	102±8		SE IR	584
	304		1.63±0.06	REMPI	679
	222–305	74–97[g]		TP-LIF	195, 196, 665
	355	17.8±2.5		REMPI(1+1′)	145

TABLE 20. Summary of I* relative quantum yield and β parameter determinations from photodissociation of large molecules—Continued

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
	266	92.1±1		REMPI(1+1′)	145
CF_2Br-CF_2I	248	100	1.8	TOF-MS	678
	266	100	1.8	TOF-MS	678
	308	77	1.2–1.8	TOF-MS	676
1,2-C_2F_4IBr	193	~0[h]		SE IR	94
	268	96±4		SE IR	94
	193	50±14		SE IR	506
	193		1.85[i]	TOF-MS	134
	248		1.84	TOF-MS	134
	266		~1.8	TOF-MS	134
CF_2ICF_2I	308	>70	1.8	TOF-MS	676
1,2-$C_2F_4I_2$	248	60±10		SE IR	655
	308	90±10		SE IR	655
n-C_3H_7I	254	78±8		CT PP	593
	248	56	1.75	TOF-MS	140
	248	60±2		TP-LIF	131
	155–210	27–72[j]		MS PP	135
	266	76±6		SE IR	584
	240–290	46–77[k]		CT PP	604
	222	54±2		TP-LIF	651
i-C_3H_7I	254	40±20		CT PP	593
	248	26±2		TP-LIF	131
	155–210	45–74[l]		MS PP	135
	266	18±1		SE IR	584
	248	23	1.9	TOF-MS	140
	222	40±2		TP-LIF	194
	266	44±3		TP-LIF	194
	305	19±2		TP-LIF	194
C_5H_4NI	266	2.2	1.6	TOF-MS	680
	304	0.6	1.5	TOF-MS	680
n-C_3F_7I	266	97.8±1.2		SE IR, Lum RP	123
	235–315	78–100		CT PP	601
	200–350	88±9[f]		SE IR	602
	265–336	57–103[m]		SE IR	669
	247.5–312.5	21–71[n]		LOAT	636
	234–316	79–109[o]		SE IR	656
	266	102±4		AS-DL	137
	266	92±6		SE IR	584
	248	>95±5		TP-LIF	133
	266		1.5±0.1	AS-DL	138
	304	20±1		REMPI	183
	222–305	76–90[p]		TP-LIF	196, 665
	266	91.9±1.1		REMPI(1+1′)	145
	355	29.6±2.9		REMPI(1+1′)	145
i-C_3F_7I	200–350	52±9[f]		SE IR	602
	265–336	57–103[q]		SE IR	669
	248	93±5		SE IR	655
	308	101±5		SE IR	655
	266	102±7		AS-DL	137
	266	87±6		SE IR	584
	222–305	64–89[r]		TP-LIF	196, 665
	266	90±1.5		REMPI(1+1′)	145
	355	39.6±3.4		REMPI(1+1′)	145
$(CF_3)_2CI$	234–333	65–99[s]		SE IR	656
C_6H_5I	193	8±2		SE IR	94
	248	25±1		SE IR	94
	308	<0.4[t]		SE IR	94
	304	0.5		REMPI	184
C_6F_5I	304	7	0.4–1.2	REMPI	184
$CF_3OCF_2CF_2I$	200–350	99^{+1}_{-7}[f]		SE IR	602
n-C_4H_9I	254	67±7		CT PP	600
	248	53±3		TP-LIF	131
	155–210	13–82[u]		MS PP	135
	266	98±7		SE IR	584
	248	49		TOF-MS	140
	304	14±2		REMPI	171, 183
	277	61	0.9±0.1	REMPI	171
	222	51±2		TP-LIF	651
t-C_4H_9I	254	80±8		CT PP	600
	248	3.8±2		TP-LIF	131
	248	<10±8		TP-LIF	133
	248	41±11		MCD	642

TABLE 20. Summary of I* relative quantum yield and β parameter determinations from photodissociation of large molecules—Continued

M	λ[a] (nm)	[I*]/([I]+[I*]) (%)[a]	β	Detection	Reference
	222	33±3		TP-LIF	194
	266	20±3		TP-LIF	194
	305	12±3		TP-LIF	194
s-C_4H_9I	248	20±2		TP-LIF	131
$(CH_3)_2CHCH_2I$	254	75±7		CT PP	600
	155–210	17–72[v]		MS PP	135
$C_3F_7CH_2I$	248	77±3		TP-LIF	133
n-C_4F_9I	222–305	68–87[w]		TP-LIF	196, 665
$(CF_3)_3CI$	266	87.7±1.3		SE IR, Lum RP	123
	266	83±6		SE IR	584
	234–343	64–109[x]		SE IR	656
cyclo-C_5H_9I	248	35±4		TP-LIF	133
$C_6H_5CH_2I$	193	10±1		SE IR	94
	248	82±5		SE IR	94
	308	70±2		SE IR	94
ortho-C_7H_7I	266	8	1.5	TOF-MS	681
	304	1	1.6	TOF-MS	681
meta-C_7H_7I	266	12	1.7	TOF-MS	681
	304	1	1.5	TOF-MS	681
para-C_7H_7I	266	13	1.5	TOF-MS	681
	304	1	1.2	TOF-MS	681
o-$C_6H_4I(CH_2Cl)$	222–304	[y]		REMPI	423
n-$C_5H_{11}I$	222	50±3		TP-LIF	651
cyclo-$C_6H_{11}I$	248	27±4		TP-LIF	133
n-$C_6F_{13}I$ *n*-$C_6F_{13}I$	248	103±5		SE IR	655
	308	96±5		SE IR	655
	222–305	69–82[z]		TP-LIF	196, 665
$C_6F_{13}CH_2CH_2I$	222–305	65–74[A]		TP-LIF	195
n-$C_8F_{17}I$	222–305	67–83[B]		TP-LIF	195, 665
$C_8F_{17}CH_2CH_2I$	222–305	42–61[C]		TP-LIF	195
$C_{18}F_{17}I$	222–305	67–83[w]		TP-LIF	195

[a]The photolysis wavelength λ (or the range for λ) and the yield of I* (or the range for the yields) are presented. Γ∼0 means "below the detection limit."

[b]The yields of I* are 46±15, 79±25, 66±13, 48±16, and 46±12% for 210–187, 187–180, 180–162, 162–158, 158–155 nm, respectively.

[c]The yields of I* are 68±7, 72±8, 74±9, 71±7, 71±6, 66±7, and 62±6% at 240, 250, 260, 270, 280, 286, and 290 nm, respectively.

[d]The yields of I* are 57±2, 72±2, 60±2, 39±2%, for 222, 266, 280, 305 nm, respectively.

[e]The yields of I* are 80±7, 78±3, 81±3, 73±2, and 52±5%, for 222, 236, 266, 280, and 305 nm, respectively.

[f]Here the average yield of I* atoms over the A-band (200–350 nm) is given. The dependence of the yield on the wavelength is presented in Fig. 4 of paper of Ivanov *et al.*[602]

[g]The yields of I* are 74±7, 78±3, 97±3, 75±3, and 83±5%, for 222, 236, 266, 280, and 305 nm, respectively.

[h]This result is wrong, it was corrected by Wight and Leone.[506]

[i]I* and I atoms were not distinguished.

[j]The yields of I* are 72±10, 27±15, 40±10, 49±8, and 42±12% for 210–187, 187–180, 180–162, 162–158, 158–155 nm, respectively.

[k]The yields of I* are 67±5, 77±5, 67±5, 60±3, 58±4, and 46±3% at 240, 250, 260, 270, 280, and 290 nm, respectively.

[l]The yields of I* are 68±15, 74±25, 52±10, 45±9, 49±13% for 210–187, 187–180, 180–162, 162–158, 158–155 nm, respectively.

[m]The yields of I* are 100±3, 96, 95, 92, 90, 82, 84, 75, 68, 68, 59, 44, and 40% for 265–292, 295, 298, 301, 304, 308, 312, 316, 320, 324, 328, 332, and 336 nm, respectively.

[n]The yields of I* are 52±7, 60±4, 71±4, 71±4, 57±4, 49±4, 36±6, and 21±3% for 247.5, 251.5, 274, 275.5, 280.5, 287.5, 296.0, 301.5, and 312.5 nm, respectively.

[o]The yields of I* are 79±15, 98±5, 100, 99±2, 109±7, 109±9, and 79±30% for 234, 246, 266, 283, 299, 316, and 333 (±5) nm, respectively.

[p]The yields of I* are 87±8, 76±3, 83±2, 89±3, and 90±5%, for 222, 236, 266, 280, and 305 nm, respectively.

[q]The yields of I* are 100±3, 96, 92, 91, 85, 82, 80, 72, 61, and 75% for 265–301, 304, 308, 312, 316, 320, 324, 328, 332, and 336 nm, respectively.

[r]The yields of I* are 68±6, 64±2, 83±1, 80±3, and 89±2%, for 222, 236, 266, 280, and 305 nm, respectively.

[s]The yields of I* are 65±13, 84±5, 84, 84±3, 99±4, 98±4, and 87±25% for 234, 246, 266, 283, 299, 316, and 333, (±5) nm, respectively.

[t]The data of Pence *et al.*[94] have been corrected by Smedley and Leone:[669] the yield of I* is <0.3 and 57% for 308 nm photodissociation of C_6H_5I and $C_6H_5CH_2I$, respectively.

[u]The yields of I* are 18±10, 82±20, 13±8, 45±8, and 25±14% for 210–187, 187–180, 180–162, 162–158, 158–155 nm, respectively.

[v]The yields of I* are 24±15, 72±20, 17±10, 53±8, and 43±8% for 210–187, 187–180, 180–162, 162–158, 158–155 nm, respectively.

[w]The yields of I* are 68±6, 83±3, 75±3, 80±3, 87±2%, for 222, 236, 266, 280, and 305 nm, respectively.

[x]The yields of I* are 91±22, 99±12, 88, 93±9, 93±9, 93±12, 64±15, and 109±20% for 234, 246, 266, 283, 299, 316, 333, 343, (±5) nm, respectively.

[y]The yields of I* are 52±2, 57±1, 52±2, 45±1, and 42±1%, for 222, 236, 266, 280, and 304 nm, respectively.

[z]The yields of I* are 78±7, 69±2, 82±2, 74±3, 82±1%, for 222, 236, 266, 280, and 305 nm, respectively.

[A]The yields of I* are 69±6, 65±3, 70±2, 74±2, and 71±3% for 222, 236, 266, 280, and 305 nm, respectively.

[B]The yields of I* are 67±6, 83±3, 76±2, 75±2, 73±3%, for 222, 236, 266, 280, and 305 nm, respectively.

[C]The yields of I* are 61±5, 44±2, 59±1, 48±4, and 42±2%, for 222, 236, 266, 280, and 305 nm, respectively.

$^3\Pi_1$ state splits into the $2A''$ and $3A'$ components, and the $^1\Pi_1$ state splits into the $4A''$ and $5A'$ components; $^3\Pi_{0+}$ becomes the $4A'$ state.

Brief reviews of the photodissociation of ICN have been published by Black *et al.* in 1990,[633,688] by Amatatsu *et al.* in 1994,[689] and by Costen *et al.* in 1999.[150]

a. Experiment. The following is a brief summary of experimental information on the photodissociation of ICN.

(i) The I^*/I branching ratio peaks at 266 nm and remains significant in the 239–290 nm wavelength.[630,632,633,688,690] Note that the energetic threshold for forming I^*+CN is 295 nm. The wavelength dependence of the ratio was measured by Hess and Leone[632] and by Pitts and Baronavski.[630] The results agree near 266 nm and do not agree near 280 nm.

The I^*/I branching ratio changes significantly with increased temperature of ICN, consistent with the increased width of the state-dependent CN rotational distribution, but the β parameter remains almost unchanged ($\beta=0.49$ at $T=100\,°C$ and $\beta=0.58$ at $T=400\,°C$).[151,152,691]

(ii) Rotational distributions of CN are different for I^* and I channels and they change substantially with photolysis wavelength.[152,632,633,688,690,692–698] The I^* channel leads to cold CN(N) rotational distributions ($N<30$) which are peaked at low N, and the I channel produces a hot CN(N) rotational distribution peaked at high N ($20<N<60$).[152,631,699]

(iii) Vibrational excitation of CN is small.[631,692,694,695,700,701] For example, the relative population $[v=0]:[v=1]:[v=2]$ was found to be 0.88:0.10:0.02,[700] and 0.91:0.06:0.03[693] for photodissociation at 308 and 299.4 nm, respectively.

(iv) The anisotropy parameter β for the I^* channel is higher than for the I channel.[150,631,698,699] For example, at 266 nm, $\beta_I=1.3\pm0.2$ and $\beta_{I^*}=1.6\pm0.2$,[150,631] and at shorter wavelengths the difference $\beta_{I^*}-\beta_I$ is even larger.[150]

(v) Measurements of rotational alignment of CN photofragments are also reported.[150,153,154,696,699] Low rotational states of CN display negative alignment, with the rotation axis preferentially perpendicular to the photolysis polarization, and higher rotational states have very small alignment.

In the experiments with photodissociation of ICN by circularly polarized photolysis light at 248 nm, a large net orientation of the CN angular momentum relative to the direction of laser beam has been observed.[698,702]

(vi) The relative populations of F_1 and F_2 spin-rotation components of CN radicals show nonstatistical behavior over a wide range of rotational numbers N for both I^* and I atom state exit channels.[633] The populations oscillate as the CN rotational quantum numbers increase.[695,703]

(vii) The femtosecond technique has been applied to ICN photodissociation, as a test case for femtosecond transition spectroscopy.[704–711] From the clocking measurements it was obtained that the transition state lives for only ~50 fs, and the "dissociation" time is 205 ± 30 fs.[707]

b. Theory. A lot of theoretical studies on the photodissociation of ICN have been reported. Classical or semiclassical trajectory calculations,[152,689,693,712–715] the Franck–Condon overlap model,[716,717] infinite order sudden approximations,[718] time-dependent,[719,720] and time-independent[721–724] quantum mechanical simulations have been applied. Almost all of them assumed that two excited states contribute to the process and fail to explain the I^* yield peak near 260 nm. Several authors have pointed out that at least three excited states should be taken into account.[714,719] The contribution of the third excited state was confirmed experimentally by Black in 1993.[688]

Probably the most important contribution to theory is the *ab initio* potential energy surface calculated by Amatatsu, Yabushita, and Morokuma.[689,725] Almost all calculations after 1994[720,726–730] are based on this energy surface.

5.2.4. Photodissociation of CH_3I

Brief reviews of the photodissociation of CH_3I have been published by Johnson *et al.*[731] and by Amatatsu, Yabushita, and Morokuma.[732,733,126,734]

There are at least five potential energy surfaces energetically accessible in the A-X band (210–350 nm). In Mulliken's notation, they are $^3Q_2$, $^3Q_1$, $^3Q_{0+}$, $^3Q_{0-}$, and $^1Q_1$.[510] Three of them are dipole allowed, the $^3Q_{0+}$ state correlates asymptotically to I^* via a parallel transition, while the $^3Q_1$ and $^1Q_1$ states correlate to the I atom via a perpendicular transition

$$CH_3I(X,A_1)+h\nu\rightarrow CH_3I(^3Q_1 2E,\ ^1Q_1 3E)\rightarrow CH_3+I,$$
$$\Delta\Omega=\pm1,\ \ \beta=-1, \tag{48a}$$
$$\rightarrow CH_3I(^3Q_0^+ 2A_1)\rightarrow CH_3+I^*,\quad \Delta\Omega=0,\ \ \beta=2. \tag{48b}$$

Here, A_1 and E are appropriate C_{3v} notation. The photodissociation of CH_3I is direct, single photon excitation results in a $n\rightarrow\sigma^*$ transition breaking the C–I bond in <1 ps.[735]

a. Experiment. The following is a brief summary of experimental information on the photodissociation of CH_3I.

(i) The peak component absorption wavelengths (and percentage total absorption strengths) have been determined by Gedanken and Rowe in 1975 to be 300 nm (1%), 261 nm (78%), and 240 nm (21%), for $^3Q_1$, $^3Q_{0+}$, and $^1Q_1$, respectively.[120] This decomposition analysis, based on a magnetic dichroism measurement, has served as the main guideline for many superb theoretical efforts for more than 2 decades. Contrary to this result, the contribution of the $^1Q_1$ and $^3Q_1$ states to the total A-band absorption spectrum were determined recently by Eppink and Parker by means of the velocity map imaging technique to be only 1.1% and 0.2%, respectively.[185]

(ii) The I^*/I ratios are very different for different vibrational states of CH_3.[644]

(iii) The vibrational distribution of the CH_3 photoproduct has been studied in many papers; of special interest is the distribution over the umbrella mode ν_2. The long-standing consensus was that the available energy is preferentially channeled into the ν_2 mode, resulting in an inverted distribution peaked at $v=2$ in the dominant I^*+CH_3

channel.[128,637–639,736–740] However, more recent experimental[185,644–646,741–746] and theoretical[732,747–750] studies have provided contradictory evidence. The story of the revision has also been reported in several reviews.[614,751,752]

The distribution of the CH_3 radical over vibrational modes has been probed by time-of-flight mass-spectrometry,[646] REMPI,[644,645] CH_3 velocity map imaging,[185,753] detection of infrared emission,[744] photoionization techniques, including zero kinetic energy (ZEKE),[754–756] conventional photoelectron spectroscopy,[757] and by photoelectron spectroscopy obtained from velocity map imaging.[746] The yield of I* atoms depends on the vibrational state of CH_3: for example, at 266 nm photodissociation of CH_3I it is found to be 95, 89, 72, and $\leqslant$33% for the ground vibrational state and for the $v_2=0$, $v_2=1$, $v_1=1$ vibrational states of CH_3.[641,753]

(iv) The rotational distribution and alignment of CH_3 and CD_3 photoproducts have been determined.[128,645,734,753,758–760]

(v) Note that REMPI of CH_3I may occur via different pathways. The study of Garrett *et al.* has shown that absorption in the 330–335 nm wavelength region leads to competition between nonresonant multiphoton ionization of CH_3I and single photon ionization through the *A* band.[761]

b. Theory. A lot of theoretical studies on the photodissociation of CH_3I have been reported.[750] The most often used model treats the system as a pseudotriatomic; that is, C–H bond lengths are fixed and the C_{3v} symmetry is assumed.[737] More recent work has included two coupled dissociative potentials[739,749,762] and more than two degrees of freedom.[749] The last *ab initio* surface, which does not assume the C_{3v} symmetry is presented by Amatatsu *et al.*[732] Based on this new *ab initio* surface, 3D wave packet calculations were performed.[748,749] Time-independent wave packet quantum mechanical simulation,[763] close coupled calculations,[737,739] classical trajectory calculations,[732] self-consistent eikonal approximation,[764,765] spin-orbit *ab initio* study,[766] and full quantum calculations[762] of different aspects of CH_3I photodissociation have been reported.

5.2.5. Photodissociation of CF_3I

a. Absorption band analysis. The first absorption *A* band (230–330 nm) of CF_3I is due to a $n\rightarrow\sigma^*$ transition and it consists of three overlapping transitions from ground $^1A_1$ state to $^3Q_1$, $^3Q_0$, and $^1Q_1$ states, similarly to the situation with photolysis of CH_3I, see processes (48a) and (48b). According to the decomposition analysis from 1987, based on a magnetic dichroism measurement, the peak component absorption wavelengths (and percentage of total absorption strengths) are 302 nm (7%), 264 nm (84%), and 238 nm (9%), for $^3Q_1$, $^3Q_{0+}$, and $^1Q_1$, respectively.[642] Furlan *et al.* have determined the wavelength-dependent β and β^* parameters and the I*/I ratios in the 275–303 nm wavelength range under cold molecular beam conditions ($T=2.7$ K).[664] The analysis of these data includes the $^3Q_1\leftarrow X$ and $^3Q_0\leftarrow X$ optical transitions and the $^3Q_0\rightarrow{}^1Q_1$ nonadiabatic transition. The probability of this nonadiabatic transition was found to be 0.09 at 275 nm and 0.24 at 300 nm. However, this interpretation remains qualitative mainly due to the lack of an accurate optical absorption cross section of CF_3I at $T=2.7$ K.[664] Similar results were obtained by Kim *et al.*;[663] for example, the $^3Q_0\rightarrow{}^1Q_1$ crossing probabilities have been found to be 0.038, 0.089, and 0.40 for the photodissociation of CFI* at 248, 277, and 208 nm, respectively.

Kavita and Das[196] have obtained lower values of the I*/I ratio, than the values obtained by Furlan *et al.*[664] and by Kim *et al.*[663] This was explained by the fact that the experiments of Kavita and Das were done at a much higher temperature. A strong temperature dependence of the absorption cross section was found by Felder.[662] A theory of curve crossing in photodissociation of CF_3I was presented by Clary,[767] see also the recent spin-orbit *ab initio* study of Ajitha *et al.*[766]

b. Vibrational state distributions and energy relaxation of CF_3. The photolysis of CF_3I at 248 nm yields mainly I* $+CF_3$. The distribution of CF_3 over the ν_2 vibrational mode in this process has been determined recently by Wang *et al.* by TOF-MS.[768]

The photodissociation of CF_3I at 304 nm has been studied by Hwang and El-Sayed.[661] For the I* channel, a strong photon energy dependence of the CF_3 internal excitation was observed; this fact suggests strong final state interaction in the dynamics of the $^3Q_0$ potential as suggested by a number of model calculations. The best agreement obtained with the model calculation of van Veen *et al.*[637,639] supports the assumption of the dominant involvement of the ν_2 umbrella vibration.

Quack *et al.* have studied infrared multiphoton dissociation of CF_3I. Absolute rate parameters have been obtained from quantum dynamics, statistical mechanics, and the direct measurements.[769]

Also, Suh *et al.* have studied the energy relaxation dynamics of CF_3 fragments produced from the photodissociation of CF_3I in argon at 266 nm by means of the time-resolved probe beam deflection technique.[770] The vibrational reflection principle in model calculations for photodissociation of CF_3I was presented by Schinke *et al.*[771]

c. Formation of exciplexes. In 1982 Gerck has found that the optical I*–I transition at 1.3152 μm may be enhanced by collisions of I* atoms with parent RI molecules (CF_3I, C_2F_5I, i-C_3F_7I, and n-C_3F_7I).[772] The enhancing mechanism is exciplex emission of the RI-I* molecule at 1.3 μm, with different rates for each iodide. The influence of this effect on the measurement of the quantum yields of I* and of the respective reaction rates by infrared fluorescence was discussed.

5.3. Production of I* Atoms in Chemical Reactions and in *V,E-E* Energy Exchange Processes

The data for I* yields from chemical reactions and energy exchange processes are presented in Table 21. Since the production of X* atoms in chemical reactions has been reviewed by Dagdigian,[5] here we just add several new references.

Trickl and Wanner have observed the bimodal IF vibrational distribution from the $F+I_2$, IBr, and ICl reactions and

TABLE 21. Yields of I* atoms from chemical reactions and V, E-E energy transfer processes

Reaction	I*/(I*+I) (%)	Detection	Reference
$H+HI\rightarrow H_2+I^*/I$	<2[a,b,c]	SE IR	533
$H+ICl\rightarrow HCl+I^*/I$[c]	~0.1	SE IR	519
	~0	SE IR	778
$H+IBr\rightarrow HBr+I^*/I$	<15	ARA IR	474
$F+HI\rightarrow HF+I^*/I$	<0.5[a]	SE IR	523
	50	ARA UV	118
	<2[a]	SE IR	779
	<1	TP-LIF	773
$Cl+HI\rightarrow HCl+I^*/I$	<0.5	SE IR	97
$F+I_2\rightarrow IF+I^*/I$	<0.04[a]	SE IR	515
	89[d]	TOF-MS	780
	<1	TP-LIF	773
	3	SE IR	774
$F+CH_3I\rightarrow CH_3F+I^*/I$	42±14	TP-LIF	781
$F+C_2H_5I\rightarrow C_2H_5F+I^*/I$	32±13	TP-LIF	781
$F+i\text{-}C_3H_7I\rightarrow i\text{-}C_3H_7F+I^*/I$	~0	TP-LIF	781
$I+O_2(^1\Delta)\rightarrow I^*+O_2$	[e]	SE IR, SE IR RP	234, 237, 565
$I+NCl(a\ ^1\Delta)\rightarrow I^*+NCl$	[f]	SE IR	782
$I+NF(b\ ^1\Sigma^+)\rightarrow I^*/I+\ldots$	[g]	Fl IR CP	555
$I+HF(v=2)\rightarrow I^*+..$	[h]	ICS	783
$D+NCl_3+HI\rightarrow I^*/I$	[h]	SE IR	784

[a]See also experimental work of Nazar *et al.*[785] and theoretical study of Dinur and Levine.[786]
[b]Upper limit. No I* observed.
[c]According to Callear and Wilson, the yield of I* must be very small.[531]
[d]Suggestion based on the bimodal distribution of IF.
[e]The rate constant is $(7.8\pm0.6)\times10^{-11}$ cm^3/molecule·s.[234,565]
[f]I* was detected, but the yield was not determined.
[g]The rate constant for quenching of $NCl(a\ ^1\Delta)$ by $I(^2P_{3/2})$ was found to be $\geqslant1\times10^{-10}$ cm^3/molecule·s. It is interpreted as evidence of an efficient near-resonant energy transfer process $NCl(a\ ^1\Delta,v=0)+I\rightarrow NCl(X\ ^3\Sigma^-,v=2)+I^*$.
[h]The rate constants for $I+NF(b\ ^1\Sigma^+)\rightarrow I^*+NF(a\ ^1\Delta)$ and $I+NF(b\ ^1\Sigma^+)\rightarrow products$ processes are $(3.1\pm1)\times10^{-11}$ and $(8.8\pm4.4)\times10^{-11}$ cm^3/molecule·s, respectively.

proposed an explanation based on a high yield of excited I* atoms in these reactions. This explanation contradicts the direct measurements of other authors.[515,773,774] An alternative explanation comes from quasiclassical trajectory calculations made by Urrecha *et al.*[775]

Also, production of I* atoms in the O+HI reaction was observed by Cadman[776] and Smith.[777]

6. Different Subjects Concerning X* Atoms

6.1. X+YZ→XY+Z Reactions

Different correlation diagrams for collinear reactions of the types

$$X^*/X+YZ\rightarrow XZ+Y^*/Y, \tag{49}$$

$$X^*/X+HY\rightarrow HX+Y^*/Y, \tag{50}$$

where X, Y, and Z are halogen atoms are presented in several papers.[5,87,443,557,558,775] These diagrams predict: (1) that X*+YZ(HY) reactants and the Y*+XZ(HX) products are adiabatically correlated via the $2^2A'$ second excited surface and suggest a barrier to this X*→Y* reaction and (2) that the X+YZ(HY) reactants and the Y+XZ(HX) products are also correlated via both $^2A'$ ground-state and excited $^2A''$ surfaces, the first one not having any barrier. Hence X→Y and X*→Y* reactions are normal adiabatic channels; the last one has a barrier and thus it normally must be much less probable than the first one. Note also, that there are not any adiabatic correlations for X*→Y and X→Y* pathways; moreover, even curve crossings for the appropriate nonadiabatic transitions are absent.

However, Wiesenfeld and Wolk have extended these correlation diagram to noncollinear collisions.[469] It was pointed out that no activation barrier is predicted if the attack of the X* atom on the YZ molecule occurs via the side-on approach. Hence, the X*→Y* reactions may be fast. There are two good examples for such reactions: $I^*+Br_2\rightarrow Br^*+IBr$[97,212,469,558] and $I^*+ICl\rightarrow Cl^*+I_2$.[200,201]

6.2. *E-V* Energy Exchange

Donovan, Husain, and Stephenson[518] and Leone and Wodarzcyk[462] were the first to provide direct evidence for an electronic-to-vibrational E-V energy transfer mechanism, which often dominates the deactivation process. The quenching rates are particularly rapid for near resonant E-V energy transfer.[467,468] Additionally, the E-V transfer can be mode specific.[223,467] Vibrational distributions can be easily inverted; for example, several Br* transfer lasers have been

demonstrated.[197,219–222] A detailed discussion of such processes is presented, for example, in the review of Houston.[4]

Two mechanisms, long-range multipolar interactions[787,788] and nonadiabatic curve crossings[789,790] have been suggested as being responsible for the E-V energy transfer. Both predict a strong correlation of the deactivation probabilities with the energy defect for the case of E-V energy exchange. Correlation plots are presented in a large number of papers.[4,470,539,791] Sometimes these two mechanisms may be distinguished by the temperature dependence of the deactivation rate constants: while the long-range multipolar interactions lead to negative dependence ($P_{EV} \sim 1/T$), nonadiabatic curve crossings may give negative ($\ln P_{EV} \sim 1/T^{1/2}$) or positive ($\ln P_{EV} \sim -1/T$) dependencies, depending on the activation energy to the crossing region. Calculations based on the long-range multipolar interactions mechanism have been done for $Br^* + H_2O$, D_2O,[542] $I^* + HF,HCl,HBr,HI$,[539] $I^* + H_2, D_2$, and HD,[792] $Br^* + CO_2$,[459] $I^* + HBr$,[544] and $O(^1D) + HCl(DCl)$.[442] The nonadiabatic curve crossings approach has been used to study the $Br^* + HF,HCl$ and $I^* + HF,HCl$ systems[793] and $Cl^* + H_2$, D_2 quenching processes.[340] Note that a large number of more accurate quantum-mechanical studies are not mentioned here.

Several empirical relations to predict the rate constant of E-V exchange have been proposed.[202,539,791] The relation proposed by Dobychin *et al.* for the $A^* + M \rightarrow A + M^*$ deactivation process seems to be one of the best:[791]

$$k = 0.083 k_0 n^{1.15} \exp\left(-0.68 \frac{\nu_A}{\nu_B} \frac{I_M}{EA_A}\right). \qquad (51)$$

Here k is the deactivation rate constant, $k_0 = \langle \sigma_0 v \rangle$ is the gas-kinetic rate constant, n is the number of near-resonant vibrations in the M molecule or the degeneracy of vibration, I_M is the ionization potential of the M molecule, EA_A is the electron affinity of the A atom, ν_A and ν_B are the frequencies of the spin-orbit transition in the halogen atom, and the vibrational transition in the M molecule, respectively. This relation was used to fit a large amount of experimental rate constants, and all numerical values were obtained by the least-squares method. However, it works mainly with iodine and bromine atoms (A=Br or A=I), while the predictions for chlorine atoms very often are poor.

6.3. Pressure Induced Broadening and Frequency Shift

The pressure induced line broadening of halogen atoms X* and X is determined first of all by the depolarization processes

$$X^*(M_J = 1/2) + A \rightarrow X^*(M'_J = -1/2) + A, \qquad (52)$$

$$X(M_J) + A \rightarrow X(M'_J \neq M_J) + A, \qquad (53)$$

where A denotes the collision partner. While processes (52) are very slow, processes (53) are very quick. Normally they have gas-kinetic kinetic rate constants. This fact may be explained either by the theorem of Kramers, which says that the electric field is unable to remove the twofold degeneracy in a system with odd summary spin[794] or, less generally but more concretely, it was explained by Gallagher.[795] Sometimes it is called the $m_j \nleftrightarrow -m_j$ selection rule for a j multiplet of an atom with an odd number of electrons.[796,797]

In other words, while process (53) occurs due to van der Waals interactions, process (52) is possible only due to Coriolis mixing of adiabatic electronic molecular states; hence it usually has low probability.[798] For example, one can see rather low cross sections for EPR line broadening of F* atoms (see Table 7), Cl* atoms (<0.020 Å^2 for Cl* + He and <0.031 Å^2 for Cl* + Ar),[155,156] and Br* atoms (<0.02 Å^2 for Br* + Ar).[460] Note also that the depolarization cross section for $Tl(^2P_{1/2})$ and $Cs(^2P_{1/2})$ atoms in collisions with He and Ne atoms are 4 orders of magnitude lower than the cross section for $^2P_{3/2}$ states of these atoms.[797,799,800] However, when particle A has electronic momentum, depolarization processes (52) may be rather quick also.[801] For example, cross sections for EPR line broadening for $F^* + O_2$ and $Br^* + O_2$ are 5.7 Å^2,[156] and 42 Å^2,[460] respectively.

As one can see from these considerations, the pressure broadening of the halogen $^2P_{1/2}$-$^2P_{3/2}$ transition is determined mainly by the ground $^2P_{3/2}$ state. Pressure broadening coefficients for several gases are reported for the F*–F transition,[13,802] for the Cl*–Cl transition,[54,75] and for the I*–I transition,[23,803–805] The temperature dependence of the I*–I broadening is reported by Zagidullin *et al.*[805] A quasiclassical theory of the pressure broadening is developed by Reznikov and Umanskii[806] and applied to the broadening of the F*–F transition by He and Ar.

Note also that the pressure induced frequency shift in the atomic iodine laser is reported by Muchtar *et al.*[807]

6.4. Transitions between Hyperfine States

The transitions between hyperfine sublevels in excited X* halogen atoms are determined by processes (52) and may also be by the depolarization of nuclear spin. To the knowledge of the author there has been only a few direct experimental determinations for the rates of the collisional relaxation in X* atoms between the hyperfine sublevels. In these studies the quick relaxation by O_2 and slow relaxation by nonparamagnetic particles was observed, in agreement with the theoretical prediction of Yukov.[801]

Chichinin and Krasnoperov have determined the rate constant for the relaxation inside the hyperfine structure of Cl* due to collisions with O_2

$$Cl^*(F=2, M_F=2) + O_2 \rightarrow Cl^* + O_2, \qquad (54)$$

$k = (4.0 \pm 0.8) \times 10^{-12}$ cm^3/molecule·s.[54] In this study the Cl* atoms were excited in the Cl* ($F=2, M_F=2$) state from the ground $^2P_{3/2}$ state by the fast magnetic field jump version of the time-resolved laser magnetic resonance (LMR) technique.[54] These experiments were done in the presence of a constant magnetic field (967 G), in which the $^2P_{1/2}$ state of the Cl* atom is split into eight components.

In experiments of van Marter and Heaven I* atoms were generated by 498 nm photolysis of I_2, and laser induced fluorescence (LIF VUV) was used to detect I* atoms in the $F=2$ and $F=3$ hyperfine sublevels.[147] The nascent population distribution of the hyperfine levels was found to be nonstatistical, with $N(F=2)/N(F=3)=1.3\pm0.1$. Collisions with O_2 caused a fast $F=2\leftrightarrow F=3$ transfer

$$I^*(F=3)+O_2 \rightleftharpoons I^*(F=2)+O_2. \tag{55}$$

The analysis of $F=2$ and $F=3$ decay kinetics yielded hyperfine transfer rate constants of $k(2\rightarrow3)=(2.6\pm0.3)\times10^{-11}$ and $k(3\rightarrow2)=(1.9\pm0.2)\times10^{-11}$ cm^3/molecule·s, both at $T=150$ K. Churassy *et al.* obtained an estimate of the $k(3\rightarrow2)$ rate constant from a computational model of the iodine laser, where the value of 1×10^{-10} cm^3/molecule·s has been obtained.[808] A similar approach was used $[k(3\rightarrow2)+k(2\rightarrow3)=\sqrt{T/300}\times10^{-10}$ cm^3/molecule·s$]$ and a similar result was obtained by Zagidullin *et al.*[244–247] A detailed discussion on hyperfine relaxation of I* atoms in collisions with O_2 is presented by van Marter and Heaven.[147]

Thieme and Fill analyzed the kinetics of pumping of the $F=3$ sublevel of I* atoms by the $F=2$ sublevel until equilibrium is reached; the initial nonequilibrium between these sublevels was created by a strong pulse of an iodine laser on the I* $(F=3)$–I$(F=4)$ transition. Atomic iodine in the ground state was assumed to be the main relaxator. The hyperfine transfer rate constants for the process

$$I^*(F=2)+I\rightarrow I^*(F=3)+I, \tag{56}$$

was determined to be $k_{23}=(1.01\pm0.25)\times10^{-9}$ cm^3/molecule·s.[809]

Also, Cerny *et al.* proposed a new way to determine the rates for hyperfine relaxation from pressure-broadening coefficients.[804] For the I^*+O_2 system the result was $k(3\rightarrow2)+k(3\rightarrow3)=1.57\times10^{-10}$ cm^3/molecule·s, where $k(F\rightarrow F')$ is the inelastic scattering rate constant for the process $I^*(F)+O_2(J)\rightarrow I^*(F')+O_2(J')$. Note that all such rate constants $k(3\rightarrow2)+k(3\rightarrow3)$ were found to be gas kinetic and almost equal for many systems (I^*+Ne,Ar,Kr,Xe,O_2). Since these values are orders of magnitude higher than the typical EPR pressure broadening coefficients for X* atoms, the interpretation of Cherny's experiment is unclear.

6.5. Picosecond Studies of Geometrically Restricted Reactions

6.5.1. Br^*+I_2

A picosecond time-resolved study of the interaction of Br* with I_2 has been presented by Wright, Tuchler, and McDonald.[810,811] The electronically excited complex BrI_2 was prepared by photodissociation of the van der Waals dimer $HBr\cdot I_2$ (or $DBr\cdot I_2$) at 220 nm. Results show that the interaction begins on the excited potential surface Br^*+I_2. The originally formed excited BrI_2 complex does not have enough internal energy to dissociate directly, but must undergo an internal conversion to a lower electronic state in order to continue to reactants or products. The evolution of the complex was probed by picosecond REMPI of I atoms and I_2 molecules. Two reaction pathways have been observed: the first leads mainly to $Br(^2P_{3/2})+I_2(v>0)$, the second pathway leads to IBr+I.

6.5.2. I^*+CO_2, OCS

The photodissociation of I_2^- at 395 nm embedded in clusters of CO_2 or OCS molecules has been studied experimentally by Sanov *et al.*[812] and theoretically by Delaney *et al.*[813] and by Sanov *et al.*[814] The photoexcitation promotes I_2^- to a dissociative state correlating with $I^-+I^*(^2P_{1/2})$, the only near-ultraviolet channel for unsolvated I_2^-. In $I_2^-\cdot(CO_2)_n$ and $I_2^-\cdot(OCS)_n$ clusters, interactions with the solvent are observed and result in extremely fast spin-orbit relaxation, which occurs by electron transfer from I^- to $I^*(^2P_{1/2})$, giving $I(^2P_{3/2})+I^-$. The energy produced by this transition is bridged by differential solvation due to solvent asymmetry. Mechanisms of direct quenching of I* atoms by the solvent are ruled out.

6.6. Coherent Control Theories

Quantum control theories (see study of Lu *et al.*[815] and references therein) propose a new and interesting way to study photodissociation processes. One of such theories was used by Lu *et al.* to stimulate the control of the relative product yield of the photodissociation of CH_3I and IBr.[815] The calculation shows that it is possible to vary the yields of I* atoms over the range of 26%–98% in dissociation of CH_3I and the yield of Br* atoms over 9%–94% in the dissociation of IBr. Also, coherent effects[816] in the photodissociation of ICN have been predicted recently by Batista and Brumer.[817] The I*/I branching ratio can be controlled over a broad range of values, simply by changing the relative phases of two lasers that photoexcite an initial superposition state to the same final energy state in the *A* continuum.

6.7. Heterogeneous Interactions

Muller-Markgraf and Rossi have studied the kinetics of the interaction of Cl and Cl* atoms with polycrystalline nickel surfaces,[76] and the interaction of Br and Br* atoms with teflon and polycrystalline nickel surfaces.[818] Although the sticking coefficients were found to be almost the same for $^2P_{1/2}$ and $^2P_{3/2}$ states of the halogen atoms, the reaction mechanisms were found to be different for these two atomic states.

Also, the rate of deactivation of I* atoms by the wall was determined by Haaland and Meyer to be $4\times10^{-2}(T/P)$ s^{-1}, where P is the pressure in Torr, and T is the temperature in K.[115]

6.8. Three-Body Ionic Recombination Reactions

Excited RgX* excimers play the central role in the gas excimer lasers (here Rg denotes a rare gas and X denotes a halogen atom). One of the two processes producing these

excited excimers is the three-body ionic recombination reaction. The formation of RgX*, Rg*, and X*, by the reactions

$$Rg(^2P_{1/2}, ^2P_{3/2})^+ + X^- + He \rightarrow RgX^* + He, \quad (57a)$$

$$\rightarrow Rg^* + X + He, \quad (57b)$$

$$\rightarrow Rg + X^* + He, \quad (57c)$$

has been studied by Tsuji *et al.* by the flowing-afterglow method for the Rg=Xe/X=Br[819] and for the Rg=Ar,Kr,Xe/X=Cl systems.[820,821] It is interesting that in the Rg=Xe/X=Br system the yield of Br* atoms is 19% for the $Xe^+(^2P_{1/2})$ state and only 0.67% for the $Xe^+(^2P_{3/2})$ state.[819]

6.9. Photodissociation in Liquid or Solid Environment

6.9.1. Photodissociation of HI and HBr in Solid Rare Gases

Pettersson and Niemien have recently observed I*–I and Br*–Br transitions from the UV photolysis of HI or HBr in solid rare gases (Ar, Kr, Xe).[822] These absorptions consist of zero-phonon lines and of phonon side bands. Some of the zero-phonon lines are split and the phonon side bands show structures at lowest temperatures (7 K). The splitting is attributed to the atoms being in slightly different, but well defined environments.

It is interesting, that the radiative lifetimes of X* atoms in solid gas matrices are shorter than in the gas phase; for example, the I*→I transition has a lifetime of 0.13 s in the gas phase, and 1–5 ms in rare gas matrices.[823–825]

6.9.2. Photodissociation of ICN in Solid Ar

The photodissociation of ICN in solid Ar has been studied experimentally (see study of Helbing and Chergui[826] and references therein) and theoretically.[827,828] According to the calculations of Amatatsu and Morokuma on the photolysis of ICN at 260 nm in liquid Ar at $T=100$ K, out of 100 trajectories 38 are dissociative, 38 are trapped in the INC region, and 24 are trapped in the ICN region. Most dissociative trajectories (36 out of 38 above) go to the I* channel.[828]

6.9.3. Photodissociation of CH_3I Thin Films

The first study of the photolysis of CH_3I absorbed on various substrates was reported by Barker, Purnell, and Young, who observed C_2 and C_3 hydrocarbons produced in the photolysis of CH_3I films at 77 K.[829] Dissociative desorption, photoproduct characterization, and dynamics of the photolysis of CH_3I have been studied in thin films on Ag(111) at 248 nm by Coon *et al.*,[830] in condensed CH_3I at 266 nm,[831] and on LiF(001) and NaCl(001) at 248 nm[832] by Polanyi *et al.* and by Kutzner *et al.*,[833] and on MgO(100) by Fairbrother *et al.*[834,835] In all cases the yield of I* atoms was found to be smaller than it is in the gas phase (73%). For example, in thin films on Ag(111) it was 0.52 ± 0.05 and the yield was dependent on the film thickness.[830] However, in thick layers the behavior of the yield is more complicated.[833–835]

The 257 nm photochemistry of CD_3I adsorbed on MgO(100) has been investigated by Trentelman *et al.*[836] It was found that the laser-induced desorption of methyl iodide competes with dissociation at the surface. The total cross section for removal of adsorbed CD_3I from the surface was comparable to the gas phase cross section. A significant portion of the atomic iodine fragments remain trapped at the surface with preferential trapping of I*.

6.9.4. I*–I* Contact Pair Emission in Condensed Media and in Matrices

Fluorescence spectra of molecular iodine in room temperature solutions (solvents: CS_2, $C_2F_3Cl_3$, $CHCl_3$,...) and in cryogenic rare gas matrices (Ar, Kr, Xe, Kr/Xe; $T=12-30$ K) were obtained by two-photon excitation in the 500–600 nm range by Apkarian and Apkarian.[837] The emission spectra were assigned to the dipole allowed $I^*I^*(^2P_{1/2}+^2P_{1/2},0_g^+)\rightarrow I^*I[^2P_{1/2}+^2P_{3/2},B(0_u^+)]$ transitions, that is, to pairs of spin-excited I* atoms which are strictly bound in the solvent (matrix) cage. The interaction between two excited I* atoms leads to three potentials, 0_g^+, 0_g^-, and 1_u, which are repulsive; however, the pair of I* atoms is stabilized by the cage effect. The decay kinetics of I*I* is remarkably different in solid matrices and in liquid solutions.

In condensed media, emission of I*I* provides a simple and sensitive means for determining the size of the cavity in which the molecule resides. Although the spectral width of these transitions is broad, a rather accurate determination of cavity sizes, to within ±0.1 Å, is possible in the range 8–12 Å. Also, the analysis yields a refined I*I* potential.[837] In cryogenic matrices, the emission spectra are analyzed to characterize cage potentials and contact distances.[838]

7. Conclusions

It is believed that practically all studies on the X* atoms are mentioned in the present compilation, which is planed to be a basis for the electronic database on excited atoms. The analysis of this literature is far from being complete; attention is focused mainly on several items: the detection methods, the deactivation rate constants, the rate constants for the reactions producing X* atoms, the β parameters, and the yields of the X* atoms in the photodissociation. The author hopes that all available data of these kinds are presented here; in almost all cases the evaluation of these data may be done on the basis of this paper without reading the original literature. The author will be grateful to readers who bring to his attention publications that have been inadvertently omitted.

The weakness of this study is the shortcoming of another kind of data, the absence of recommendations and recommended values, and the absence of discussion on theoretical results. As one can see even from this paper, at the present time the contributions from molecular dynamics studies and

from the theoretical studies to the understanding of processes involving X* atoms are growing. However, these data are outside the frame of this work.

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9. References

[1] D. Husain and R. J. Donovan, Chem. Rev. **70**, 489 (1970).
[2] D. Husain and R. J. Donovan, Adv. Photochem. **8**, 1 (1971).
[3] D. Husain, Ber. Bunsen Ges. Phys. Chem. **81**, 168 (1977).
[4] P. L. Houston, Adv. Chem. Phys. **47**, 381 (1981).
[5] P. J. Dagdigian and M. P. Campbell, Chem. Rev. **87**, 1 (1987).
[6] R. N. Zare, Mol. Photochem. **4**, 1 (1972).
[7] G. E. Busch and K. R. Wilson, J. Chem. Phys. **56**, 3638 (1972).
[8] S. Yang and R. Bersohn, J. Chem. Phys. **61**, 4400 (1974).
[9] M. Dzvonik, S. Yang, and R. Bersohn, J. Chem. Phys. **61**, 4408 (1974).
[10] M. Yen, P. M. Johnson, and M. G. White, J. Chem. Phys. **99**, 126 (1993).
[11] J. C. Cummings and D. P. Aeschliman, Opt. Commun. **31**, 165 (1979).
[12] H. Schlossberg, J. Appl. Phys. **47**, 2044 (1976).
[13] A. C. Stanton and C. E. Kolb, J. Chem. Phys. **72**, 6637 (1980).
[14] G. A. Laguna and W. H. Beattie, Chem. Phys. Lett. **88**, 439 (1982).
[15] V. R. Braun, L. N. Krasnoperov, and V. N. Panfilov, Opt. Spektroskopiya **52**, 428 (1982).
[16] A. C. Stanton, Chem. Phys. Lett. **122**, 385 (1985).
[17] S. A. Sotnichenko, V. C. Bokun, and A. I. Nadkhin, Opt. Spektroskopiya **67**, 1013 (1989).
[18] G. He, M. Seth, I. Tokue, and R. G. Macdonald, J. Chem. Phys. **110**, 7821 (1999).
[19] J. J. Bannister, H. J. Baker, T. A. King, and W. G. McNaught, Phys. Rev. Lett. **44**, 1062 (1980).
[20] H. V. Lilenfeld, R. J. Richardson, and F. E. Hovis, J. Chem. Phys. **74**, 2129 (1981).
[21] M. Galanti, W. Thieme, and K. J. Witte, IEEE J. Quantum Electron. **17**, 1817 (1981).
[22] A. A. Bibyshev, I. A. Boriev, A. I. Nadkhin, S. A. Sotnichenko, and E. B. Gordon, Opt. Spektroskopiya **51**, 488 (1981).
[23] R. Engelman, B. A. Palmer, and S. J. Davis, J. Opt. Soc. Amer. **73**, 1585 (1983).
[24] G. Xu and T. A. King, Phys. Rev. **30**, 354 (1984).
[25] A. A. Efimenko, I. A. Boriev, and E. B. Gordon, Sov. J. Quantum Electron. **15**, 1127 (1985).
[26] T. K. Ha, Y. He, J. Pochert, M. Quack, R. Ranz, G. Seyfang, and I. Thanopoulos, Ber. Bunsen Ges. Phys. Chem. **99**, 384 (1).
[27] B. Edlen, Z. Phys. **98**, 445 (1936).
[28] C. E. Moore, *Atomic Energy Level*, Vol. 1 (National Bureau of Standards, Washington, D.C., 1971).
[29] M. Dagenais, J. W. C. Johns, and A. R. W. McKellar, Can. J. Phys. **54**, 1438 (1976).
[30] I. A. Boriev, E. B. Gordon, A. I. Nadkhin, and S. A. Sotnichenko, Opt. Spektroskopiya **54**, 233 (1983).
[31] H. A. Kramers, Proc. Roy. Acad. Amsterdam **34**, 965 (1931).
[32] H. B. G. Casimir and G. Karreman, Physica **9**, 494 (1942).
[33] L. Davis, Jr., B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **76**, 1076 (1949).
[34] V. Jaccarino, J. G. King, R. A. Satten, and H. H. Stroke, Phys. Rev. **94**, 1798 (1954).
[35] H. H. Brown and J. G. King, Phys. Rev. **142**, 53 (1966).
[36] V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).
[37] J. G. King and V. Jaccarino, Phys. Rev. **94**, 1610 (1954).
[38] P. B. Davies, B. A. Thrush, A. J. Stone, and F. D. Wayne, Chem. Phys. Lett. **17**, 19 (1972).
[39] G. F. Koster, Phys. Rev. **86**, 148 (1952).
[40] H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, Phys. Rev. **123**, 153 (1961).
[41] K. A. Uslu, R. F. Kode, and J. S. M. Harvey, Can. J. Phys. **52**, 2135 (1974).
[42] J. S. M. Harvey, Proc. R. Soc. (London) Ser. A **285**, 581 (1965).
[43] A. C. Stanton and R. G. Brown, Proceedings of Symposium on Lasers in Chemistry, Vancouver, 1981.
[44] J. H. Holloway, B. B. Aubrey, and J. G. King, Proc. Phys. Soc. (London) **76**, 984 (1960).
[45] J. G. King and V. Jaccarino, Phys. Rev. **84**, 852 (1951).
[46] N. Bessis, J. Picart, and J. P. Desclaux, Phys. Rev. **187**, 88 (1969).
[47] J. D. Campbell and J. V. V. Kasper, Chem. Phys. Lett. **10**, 436 (1971).
[48] V. S. Zuev, V. A. Katulin, and V. Yu. Nosach, JETP **62**, 1673 (1972).
[49] E. Luc-Koenig, C. Morillon, and J. Verges, Physica **70**, 175 (1973).
[50] R. Engelman, R. A. Keller, and B. A. Palmer, Appl. Optics **19**, 2767 (1980).
[51] A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Iones*, Vol. 31 of *Chemical Physics* (Springer-Verlag, Berlin, Heidelberg, 1985).
[52] A. J. R. Heck and D. W. Chandler, Ann. Rev. Phys. Chem. **46**, 335 (1995).
[53] A. Eppink and D. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).
[54] A. I. Chichinin and L. N. Krasnoperov, Chem. Phys. Lett. **124**, 8 (1986).
[55] A. I. Chichinin and L. N. Krasnoperov, Chem. Phys. Lett. **160**, 448 (1989).
[56] H. V. Lilenfeld, P. D. Whitefield, and G. R. Bradburn, J. Phys. Chem. **88**, 6158 (1984).
[57] A. Carrington, D. H. Levy, and T. A. Miller, J. Chem. Phys. **45**, 4093 (1966).
[58] P. P. Bemand and M. A. A. Clyne, J. Chem. Soc. Faraday Trans. 2 **72**, 191 (1975).
[59] P. P. Bemard and M. A. A. Clyne, Chem. Phys. Lett. **21**, 555 (1973).
[60] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 2 **73**, 1308 (1977).
[61] G. W. Loge, N. Nereson, and H. A. Fry, Appl. Optics **33**, 3161 (1994).
[62] J. Zhang, C. W. Riehn, M. Dulligan, and C. Wittig, J. Chem. Phys. **104**, 7027 (1996).
[63] W. K. Bischel and L. E. Jusinski, Chem. Phys. Lett. **120**, 337 (1985).
[64] K. Sasaki, Y. Kawai, and K. Kadota, Appl. Phys. Lett. **70**, 1375 (1997).
[65] M. Roth, C. Maul, K.-H. Gericke, T. Senga, and M. Kawasaki, Chem. Phys. Lett. **305**, 319 (1999).
[66] V. Beltran-Lopez and H. G. Robinson, Phys. Rev. **123**, 161 (1961).
[67] P. P. Bemand and M. A. A. Clyne, J. Chem. Soc. Faraday Trans. 2 **71**, 1132 (1975).
[68] M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 2 **72**, 838 (1976).
[69] I. S. Fletcher and D. Husain, Chem. Phys. Lett. **49**, 516 (1977).
[70] A. I. Chichinin, Chem. Phys. Reports **19**, 1599 (2000).
[71] P. B. Davies and D. K. Russel, Chem. Phys. Lett. **67**, 440 (1979).
[72] E. Tiemann, H. Kanamori, and E. Hirota, J. Chem. Phys. **88**, 2457 (1988).
[73] M. Heaven, T. A. Miller, P. R. Freeman, J. C. White, and J. Bokor, Chem. Phys. Lett. **86**, 458 (1982).
[74] S. Arepalli, N. Presser, D. Robie, and R. J. Gordon, Chem. Phys. Lett. **118**, 88 (1985).
[75] S. A. Sotnichenko, V. Ch. Bokun, and A. I. Nadkhin, Chem. Phys. Lett. **153**, 560 (1988).
[76] W. Muller-Markgraf and M. J. Rossi, J. Phys. Chem. **95**, 825 (1991).
[77] L. X. Wang and W. E. Jones, Appl. Phys. B **54**, 52 (1992).
[78] D. A. Dolson and D. S. West, Chem. Phys. Lett. **216**, 258 (1993).
[79] G. S. Tyndall, J. J. Orlando, and C. S. Kegley-Owen, J. Chem. Soc. Faraday Trans. **91**, 3055 (1995).
[80] V. Skorokhodov, Y. Sato, K. Suto, Y. Matsumi, and M. Kawasaki, J. Phys. Chem. **100**, 12321 (2000).
[81] Y. Matsumi, K. Izumi, V. Skorokhodov, M. Kawasaki, and N. Tanaka, J. Phys. Chem. A **101**, 1216 (1997).
[82] K. Hitsuda, K. Takahashi, Y. Matsumi, and T. J. Wallington, J. Phys. Chem. **105**, 5131 (2001).
[83] I. A. Boriev, Chem. Phys. Reports **16**, 1807 (1997).
[84] J. Zhang, M. Dulligan, and C. Wittig, J. Chem. Phys. **107**, 1403 (1997).
[85] F. Dong, S.-H. Lee, and K. Liu, J. Chem. Phys. **115**, 1197 (2001).
[86] R. J. Donovan and D. Husain, Trans. Faraday Soc. **62**, 2643 (1966).
[87] K. Bergmann, S. R. Leone, and C. B. Moore, J. Chem. Phys. **63**, 4161 (1975).
[88] J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys. **65**, 1506 (1976).

[89] W. L. Ebenstein, J. R. Wiesenfeld, and G. L. Wolk, Chem. Phys. Lett. **53**, 185 (1978).
[90] T. G. Lindeman and J. R. Wiesenfeld, J. Chem. Phys. **70**, 2882 (1979).
[91] E. B. Gordon, A. I. Nadkhin, and S. A. Sotnichenko, Chem. Phys. Lett. **68**, 97 (1979).
[92] M. Vries, N. Veen, M. Hutchinson, and A. Vries, Chem. Phys. **51**, 159 (1980).
[93] O. D. Krogh, Chem. Phys. Lett. **69**, 452 (1980).
[94] W. H. Pence, S. L. Baughcum, and S. R. Leone, J. Phys. Chem. **85**, 3844 (1981).
[95] F. Magnotta, D. J. Nesbitt, and S. R. Leone, Chem. Phys. Lett. **83**, 21 (1981).
[96] J. W. Hepburn, K. Liu, R. G. Macdonald, F. J. Northrup, and J. C. Polanyi, J. Chem. Phys. **75**, 3353 (1981).
[97] E. B. Gordon, A. I. Nadkhin, S. A. Sotnichenko, and I. A. Boriev, Chem. Phys. Lett. **86**, 209 (1982).
[98] S. Arepalli, N. Presser, D. Robie, and R. J. Gordon, Chem. Phys. Lett. **117**, 64 (1985).
[99] Q. X. Xu, J. Chem. Phys. **91**, 3477 (1989).
[100] M. V. Ashikhmin, Yu. E. Belyaev, A. V. Dem'yanenko, E. A. Ryabov, and V. S. Letokhov, Chem. Phys. Lett. **227**, 343 (1994).
[101] H. P. Loock and C. X. W. Qian, J. Chem. Phys. **108**, 3178 (1998).
[102] J. G. Underwood and I. Powis, Phys. Chem. Chem. Phys. **2**, 747 (2000).
[103] J. E. Smedley, H. K. Haugen, and S. R. Leone, J. Chem. Phys. **87**, 2700 (1987).
[104] A. J. Sedlacek, R. E. Weston, Jr., and G. W. Flynn, J. Chem. Phys. **93**, 2812 (1990).
[105] T. Kinugawa and T. Arikawa, J. Chem. Phys. **96**, 4801 (1992).
[106] D. A. Dolson, A. Liu, and K. M. Schreier, Chem. Phys. Lett. **212**, 118 (1993).
[107] P. M. Regan, S. R. Langford, A. J. Orr-Ewing, and M. N. R. Ashfold, J. Chem. Phys. **110**, 281 (1999).
[108] R. Baumfalk, U. Buck, C. Frischkorn, N. H. Nahler, and L. Huwel, J. Chem. Phys. **111**, 2595 (1999).
[109] G. J. Wang, H. Zhang, R. S. Zhu, K. L. Han, G. Z. He, and N. Q. Lou, Chem. Phys. **241**, 213 (1999).
[110] P. C. Samartzis, T. N. Kitsopoulos, and M. N. R. Ashfold, Phys. Chem. Chem. Phys. **2**, 453 (2000).
[111] T. Ogawa, G. A. Carlson, and G. C. Pimentel, J. Phys. Chem. **74**, 2090 (1970).
[112] A. B. Callear and J. F. Wilson, Trans. Faraday Soc. **63**, 1358 (1967).
[113] J. J. Deakin and D. Husain, J. Photochem. **1**, 353 (1972).
[114] T. L. Andreeva, S. V. Kuznetsova, A. I. Maslov, I. I. Sobelman, and V. N. Sorokin, Khimiya Vysokih Energii **6**, 418 (1972).
[115] D. M. Haaland and R. T. Meyer, Int. J. Chem. Kinet. **6**, 297 (1974).
[116] I. Arnold, F. J. Comes, and S. Pionteck, Chem. Phys. **9**, 237 (1975).
[117] R. J. Donovan, H. M. Gillespie, and R. H. Strain, J. Chem. Soc. Faraday Trans. 2 **73**, 1553 (1977).
[118] I. Burak and M. Eyal, Chem. Phys. Lett. **52**, 534 (1977).
[119] J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys. **67**, 509 (1977).
[120] A. Gedanken and M. D. Rowe, Chem. Phys. Lett. **34**, 39 (1975).
[121] R. D. Coombe and A. T. Pritt, Jr., J. Chem. Phys. **66**, 5214 (1977).
[122] L. G. Karpov, A. M. Pravilov, and F. I. Vilesov, Khimiya Vysokih Energii **8**, 483 (1974).
[123] L. S. Ershov, Y. Yu. Zalesskii, and V. N. Sokolov, Sov. J. Quantum Electron. **8**, 494 (1978).
[124] J. R. Wiesenfeld and R. H. Young, Chem. Phys. **58**, 51 (1981).
[125] R. Schmiedl, H. Dugan, W. Meier, and K. H. Welge, Z. Physik A **304**, 137 (1982).
[126] S. L. Baughcum and S. R. Leone, J. Chem. Phys. **72**, 6531 (1980).
[127] A. Gedanken, M. B. Robin, and Y. Yafet, J. Chem. Phys. **76**, 4798 (1982).
[128] J. F. Black and I. Powis, J. Chem. Phys. **89**, 3986 (1988).
[129] J. F. Black and I. Powis, Chem. Phys. **125**, 375 (1988).
[130] P. A. Hackett, P. John, M. Mayhew, and D. M. Rayner, Chem. Phys. Lett. **96**, 139 (1983).
[131] P. Brewer, P. Das, G. Ondrey, and R. Bersohn, J. Chem. Phys. **79**, 720 (1983).
[132] J. J. Tiee, M. J. Ferris, G. W. Loge, and F. B. Wamper, Chem. Phys. Lett. **96**, 422 (1983).
[133] F. G. Godwin, P. A. Gorry, P. M. Hughes, D. Raybone, and T. J. C. Whitehead, Chem. Phys. Lett. **135**, 163 (1987).
[134] D. Krajnovitch, L. J. Butler, and Y. T. Lee, J. Chem. Phys. **81**, 3031 (1984).
[135] A. M. Pravilov and S. E. Ryabov, Khim. Phys. **3**, 939 (1984).
[136] A. Nebel, F. J. Comes, and K.-H. Stephan-Rossbach, Chem. Phys. **94**, 257 (1985).
[137] W. P. Hess, S. J. Kohler, H. K. Haugen, and S. R. Leone, J. Chem. Phys. **84**, 2143 (1986).
[138] J. I. Cline, C. A. Taatjes, and S. R. Leone, J. Chem. Phys. **93**, 6543 (1990).
[139] T. F. Hunter and C. M. Leong, Chem. Phys. **111**, 145 (1987).
[140] F. G. Godwin, F. Paterson, and P. A. Gorry, Mol. Phys. **61**, 827 (1987).
[141] R. G. Badini, L. E. Pasteris, and G. A. Arguello, J. Chem. Soc. Faraday Trans. 2 **85**, 1877 (1989).
[142] J. W. Nicholson, W. Rudolph, and G. Hager, J. Chem. Phys. **104**, 3537 (1996).
[143] A. V. Baklanov, V. P. Maltsev, L. Karlsson, B. Lindgren, and U. Sassenberg, Chem. Phys. **184**, 357 (1994).
[144] A. V. Baklanov, L. Karlsson, B. Lindgren, and U. Sassenberg, J. Phys. B **30**, L259 (1997).
[145] A. V. Baklanov, M. Aldener, B. Lindgren, and U. Sassenberg, Chem. Phys. Lett. **325**, 399 (2000).
[146] K. Jung, J. A. Griffiths, and M. A. El-Sayed, J. Chem. Phys. **103**, 6999 (1995).
[147] T. V. Marter and M. C. Heaven, J. Chem. Phys. **109**, 9266 (1998).
[148] K. H. Stephan and F. J. Comes, Chem. Phys. Lett. **65**, 251 (1979).
[149] D. J. Gendron and J. W. Hepburn, J. Chem. Phys. **109**, 7205 (1998).
[150] M. L. Costen, S. W. North, and G. E. Hall, J. Chem. Phys. **111**, 6735 (1999).
[151] R. Li, W. S. McGivern, and S. W. North, Chem. Phys. Lett. **334**, 47 (2001).
[152] W. J. Marinelli, N. Sivakumar, and P. L. Houston, J. Phys. Chem. **88**, 6685 (1984).
[153] K. J. Franks, H. Li, and W. Kong, J. Chem. Phys. **111**, 1884 (1999).
[154] K. J. Franks, H. Li, S. Kuy, and W. Komg, Chem. Phys. Lett. **302**, 151 (1999).
[155] I. B. Bykhalo, E. B. Gordon, A. P. Perminov, and V. V. Filatov, Khim. Phys. **11**, 1097 (1992).
[156] R. E. Boltnev, I. B. Bykhalo, E. B. Gordon, and V. V. Filatov, Khim. Phys. **13**, 3 (1994).
[157] J. C. Miller and R. J. Gordon, J. Chem. Phys. **78**, 3713 (1983).
[158] L. N. Krasnoperov, Master's thesis, Institute of Chemical Physics, Moscow (1991).
[159] S. A. Chasovnikov, A. I. Chichinin, and L. N. Krasnoperov, Chem. Phys. **116**, 91 (1987).
[160] I. A. Boriev, E. B. Gordon, A. A. Efimenko, and S. M. Chernin, Opt. Spektroskopiya **59**, 277 (1985).
[161] P. Zou, J. Park, B. A. Schmitz, T. Nguyen, and S. North, J. Phys. Chem. A **106**, 1004 (2002).
[162] S. Deshmukh and W. P. Hess, J. Photochem. Photobiol. A **80**, 17 (1994).
[163] P. C. Samartzis, B. L. G. Bakker, T. P. Rakitzis, D. H. Parker, and T. N. Kitsopoulos, J. Chem. Phys. **110**, 5201 (1999).
[164] S.-H. Lee and K.-H. Jung, Chem. Phys. Lett. **350**, 306 (2001).
[165] Y. J. Jung, M. S. Park, Y. S. Kim, K. H. Jung, and H. R. Volpp, J. Chem. Phys. **111**, 4005 (1999).
[166] M.-S. Park, Y.-J. Jung, S.-H. Lee, D.-C. Kim, and K.-H. Jung, Chem. Phys. Lett. **322**, 429 (2000).
[167] Y. Tang, L. Ji, B. Tang, R. Zhu, S. Zhang, and B. Zhang, Chem. Phys. Lett. **392**, 493 (2004).
[168] L. Ji, Y. Tang, R. Zhu, B. Tang, and B. Zhang, Chem. Phys. **314**, 173 (2005).
[169] T. P. Rakitzis, P. C. Samartzis, R. L. Toomes, and T. N. Kitsopoulos, J. Chem. Phys. **121**, 7222 (2004).
[170] R. Zhu, B. Tang, L. Ji, Y. Tang, S. Zhang, and B. Zhang, Optics Comm. **235**, 325 (2004).
[171] W. K. Kang, K. W. Jung, K.-H. Jung, and H. J. Hwang, J. Phys. Chem. **98**, 1525 (1994).
[172] Y. J. Jung, Y. S. Kim, W. K. Kang, and K. H. Jung, J. Chem. Phys. **107**, 7187 (1997).
[173] H. Xu, Y. Guo, S. Liu, X. Ma, D. Dai, and G. Sha, J. Chem. Phys. **117**, 5722 (2002).
[174] V. J. Barclay, B. A. Collings, J. C. Polanyi, and J. H. Wang, J. Phys. Chem. **95**, 2921 (1991).

[175] K. Tonokura, Y. Matsumi, M. Kawasaki, Sh. Tasaki, and R. Bersohn, J. Chem. Phys. **97**, 8210 (1992).
[176] J. Cao, H.-P. Loock, and C. X. W. Qian, Can. J. Chem. **72**, 758 (1994).
[177] R. Liyanage, Y. Yang, S. Hashimoto, R. J. Gordon, and R. W. Field, J. Chem. Phys. **103**, 6811 (1995).
[178] K. Tonokura, L. B. Daniels, T. Suzuki, and K. Yamashita, J. Phys. Chem. A **101**, 7754 (1997).
[179] H. M. Lambert, P. J. Dagdigian, and M. H. Alexander, J. Chem. Phys. **108**, 4460 (1998).
[180] P. M. Regan, S. R. Langford, D. Ascenzi, Ph. A. Cook, A. J. Orr-Ewing, and M. N. R. Ashfold, Phys. Chem. Chem. Phys. **1**, 3247 (1999).
[181] Y.-L. Jee, Y.-J. Jung, and K.-H. Jung, J. Chem. Phys. **115**, 9739 (2001).
[182] Z. H. Kim, A. J. Alexander, H. A. Bechtel, and R. N. Zare, J. Chem. Phys. **115**, 179 (2001).
[183] W. K. Kang, K. W. Jung, D. C. Kim, and K. H. Jung, J. Chem. Phys. **104**, 5815 (1996).
[184] J. A. Griffiths, K.-W. Jung, and M. A. El-Sayed, J. Phys. Chem. A **100**, 7989 (1996).
[185] A. T. J. B. Eppink and D. H. Parker, J. Chem. Phys. **109**, 4758 (1998).
[186] D. Senapati, K. Kavita, and P. K. Das, J. Phys. Chem. A **106**, 8479 (2002).
[187] J. Cao, H.-P. Loock, and C. X. W. Qian, J. Chem. Phys. **101**, 3395 (1994).
[188] S. J. Riley and K. R. Wilson, Faraday Discuss. Chem. Soc. **53**, 132 (1972).
[189] Y. Matsumi, P. K. Das, and M. Kawasaki, J. Chem. Phys. **92**, 1696 (1990).
[190] Y. Matsumi, K. Tonokura, M. Kawasaki, and T. Ibuki, J. Chem. Phys. **93**, 7981 (1990).
[191] Y. Matsumi, K. Tonokura, M. Kawasaki, G. Inoue, S. Satyapal, and R. Bersohn, J. Chem. Phys. **94**, 2669 (1991).
[192] M. S. Pindzola, Phys. Rev. A **17**, 1021 (1978).
[193] Y. Matsumi, P. K. Das, and M. Kawasaki, J. Chem. Phys. **97**, 5261 (1992).
[194] S. Uma and P. K. Das, J. Chem. Phys. **104**, 4470 (1996).
[195] K. Kavita and P. K. Das, J. Phys. Chem. A **105**, 315 (2001).
[196] K. Kavita and P. K. Das, J. Chem. Phys. **112**, 8426 (2000).
[197] R. L. Pastel, G. D. Hager, H. C. Miller, and S. R. Leone, Chem. Phys. Lett. **183**, 565 (1991).
[198] L. E. Zapata and R. J. DeYoung, J. Appl. Phys. **54**, 1686 (1983).
[199] V. Ch. Bokun, E. B. Gordon, L. N. Krasnoperov, S. A. Sotnichenko, and A. I. Chichinin, Kvantovaya Elektronika **13**, 1319 (1986).
[200] A. I. Nadkhin and E. B. Gordon, Khim. Phys. **13**, 3 (1994).
[201] S. A. Sotnichenko, Khim. Phys. **14**, 87 (1995).
[202] A. I. Chichinin, J. Chem. Phys. **112**, 3772 (2000).
[203] M. D. Burrows, J. Chem. Phys. **81**, 3546 (1984).
[204] H. Hofmann and S. R. Leone, J. Chem. Phys. **69**, 641 (1978).
[205] M. A. A. Clyne and H. W. Cruse, J. Chem. Soc. Faraday Trans. 2 **68**, 1377 (1972).
[206] A. I. Chichinin, S. A. Chasovnikov, and L. N. Krasnoperov, Chem. Phys. Lett. **138**, 371 (1987).
[207] A. I. Nadkhin and E. B. Gordon, Khim. Phys. **13**, 3 (1994).
[208] A. I. Nadkhin, Ph.D. thesis, Institute of Energetical Problems in Chemical Physics, Moscow, 1989.
[209] A. I. Chichinin and L. N. Krasnoperov, Khim. Phys. **6**, 418 (1987).
[210] C. R. Guiliano and L. D. Hess, J. Appl. Phys. **40**, 2428 (1969).
[211] V. A. Dudkin, I. N. Knyazev, and V. I. Malyshev, Kr. Soobsh. Fiz. FIAN **5**, 32 (1970).
[212] D. J. Spencer and C. Wittig, Opt. Lett. **4**, 1 (1979).
[213] H. Bony, M. Shapiro, and A. Yogev, Chem. Phys. Lett. **107**, 603 (1984).
[214] L. E. Zapata and R. J. DeYoung, J. Appl. Phys. **57**, 760 (1985).
[215] A. Yogev, I. Levy, and M. Shapiro, *Gas Flow and Chemical Lasers*, Vol. 15 (Springer, Berlin, 1986).
[216] I. A. Boriev and E. B. Gordon, Khim. Phys. **15**, 87 (1996).
[217] I. A. Boriev, Chem. Phys. Reports **18**, 451 (1999).
[218] S. Lemont and G. W. Flynn, Ann. Rev. Phys. Chem. **28**, 261 (1977).
[219] A. B. Petersen, C. Wittig, and S. R. Leone, Appl. Phys. Lett. **27**, 305 (1975).
[220] A. B. Petersen, C. Wittig, and S. R. Leone, Bull. Am. Phys. Soc **20**, 1510 (1975).
[221] A. B. Petersen, C. Wittig, and S. R. Leone, J. Appl. Phys. **47**, 1051 (1976).
[222] A. B. Petersen, L. W. Braverman, and C. Wittig, J. Appl. Phys. **48**, 230 (1977).
[223] C. A. Wight, J. Phys. Chem. **90**, 2683 (1986).
[224] R. O. Johnson, G. P. Perram, and W. B. Roh, Appl. Phys. B **65**, 5 (1997).
[225] R. O. Johnson, S. J. Karis, G. P. Perram, and W. B. Roh, Appl. Phys. B **66**, 411 (1998).
[226] J. V. V. Kasper and G. C. Pimentel, Appl. Phys. Lett. **5**, 231 (1964).
[227] J. V. V. Kasper, J. H. Parker, and G. C. Pimentel, J. Chem. Phys. **43**, 1827 (1965).
[228] J. V. V. Kasper, J. H. Parker, and G. C. Pimentel, Phys. Rev. Lett. **14**, 352 (1965).
[229] K. Hohla, *High Power Lasers and Applications* (Springer, Berlin, 1979).
[230] K. J. Witte, G. Brederlow, K. Eidmann, R. Volk, E. Fill, K. Hohla, and R. Bradmann, *High Power Lasers and Applications* (Springer, Berlin, 1979).
[231] N. G. Basov, V. N. Volkov, L. K. Gavrilina, Yu. S. Leonov, and V. A. Sautkin, Kvantovaya Elektronika **14**, 300 (1987).
[232] P. Gensel, K. Hohla, and K. L. Kompa, Appl. Phys. Lett. **18**, 48 (1971).
[233] T. L. Andreeva, V. I. Malyshev, A. I. Maslov, I. I. Sobelman, and V. N. Sorokin, Pisma JETF **10**, 423 (1969).
[234] R. G. Derwent and B. A. Thrush, Chem. Phys. Lett. **9**, 591 (1971).
[235] J. Habdas, S. Watengaonkar, and D. W. Setser, J. Phys. Chem. **91**, 451 (1987).
[236] D. R. Yarkony, J. Chem. Phys. **86**, 1642 (1987).
[237] R. G. Dervent and B. A. Trush, Faraday Discuss. Chem. Soc. **53**, 162 (1972).
[238] A. T. Pritt, Jr., R. D. Coombe, D. Pilipovich, R. I. Wagner, D. Benard, and C. Dymek, Appl. Phys. Lett. **31**, 745 (1977).
[239] W. E. McDermott, N. R. Pchelkin, D. J. Benard, and R. R. Bousek, Appl. Phys. Lett. **32**, 469 (1978).
[240] D. J. Benard, W. E. McDermott, N. R. Pchelkin, and R. R. Bousek, Appl. Phys. Lett. **34**, 40 (1978).
[241] G. Brederlow, E. Fill, and K. Witte, *The High-Power Iodine Laser*, Vol. 34 of *Springer Series in Optical Sciences* (Springer-Verlag, Berlin, New York, 1993).
[242] K. Truesdell, S. Lamberson, and G. Hager, AIAA Paper **92-3003** (1992).
[243] T. Rittenhouse, S. Phipps, and C. Helms, IEEE J. Quantum Electron. **35**, 857 (1999).
[244] M. V. Zagidullin, V. D. Nikolaev, M. I. Svistun, N. A. Khvatov, and N. I. Ufimtsev, Kvantovaya Elektronika **24**, 201 (1997).
[245] M. V. Zagidullin, V. D. Nikolaev, M. I. Svistun, and N. A. Khvatov, Kvantovaya Elektronika **26**, 114 (1999).
[246] M. V. Zagidullin, V. D. Nikolaev, M. I. Svistun, and N. A. Khvatov, Kvantovaya Elektronika **30**, 161 (2000).
[247] M. V. Zagidullin, V. D. Nikolaev, M. I. Svistun, N. G. D. Heiger, and T. J. Madden, Kvantovaya Elektronika **31**, 30 (2001).
[248] N. P. Vagin, V. S. Pazyuk, and N. N. Yuryshev, Kvantovaya Elektronika **22**, 776 (1995).
[249] V. V. Ivanov, K. S. Klopovsky, D. V. Lopaev, A. T. Rakhimov, and T. T. Rakhimova, IEEE Trans. Plasma Science **27**, 1279 (1999).
[250] S. Itami, Y. Nakamura, A. Nakamura, K. Shinagawa, M. Okamura, and H. Fujii, Proceedings of AHPLA'99, Osaka, 1999.
[251] H. Fujii, S. Itami, Y. Kihara, K. Fufisaki, M. Okamura, E. Yoshitani, K. Yano, T. Miyatake, and J. Schmiedberger, Proceedings of Laser Ablation Conference, Santa Fe, 2000.
[252] D. L. Carroll and W. C. Solomon, Proceedings of the 13th International Symposium on Gas Flow and Chemical Lasers and High Power Laser Conference, Florence, 2000, pp. 40–44.
[253] T. Yang, V. T. Gylys, R. D. Bower, and L. F. Rubin, Opt. Lett. **17**, 1803 (1992).
[254] A. J. Ray and R. D. Coombe, J. Phys. Chem. **99**, 7849 (1995).
[255] T. L. Henshaw, S. D. Herrera, and L. Schlie, J. Phys. Chem. A **102**, 6239 (1998).
[256] J. M. Herbelin, T. L. Henshaw, B. D. Rafferty, B. T. Anderson, R. F. Tate, T. J. Madden, G. C. Manke II, and G. D. Hager, Chem. Phys. Lett. **299**, 583 (1999).
[257] T. L. Henshaw, G. C. Manke II, T. J. Madden, M. R. Berman, and G. D. Hager, Chem. Phys. Lett. **325**, 537 (2000).
[258] G. C. Manke II and D. W. Setser, J. Phys. Chem. A **102**, 153 (1998).
[259] G. C. Manke II and D. W. Setser, J. Phys. Chem. A **102**, 7257 (1998).
[260] G. C. Manke II, T. L. Henshaw, T. J. Madden, and G. D. Hager, Chem. Phys. Lett. **310**, 111 (1999).

[261] R. P. Wayne, *The Chemistry of Atmospheres*, 2nd ed. (Oxford University Press, New York, 1991).
[262] C. H. Becker, P. Casavecchia, and Y. T. Lee, J. Chem. Phys. **69**, 2377 (1978).
[263] C. H. Becker, P. Casavecchia, and Y. T. Lee, J. Chem. Phys. **70**, 2986 (1979).
[264] C. H. Becker, P. Casavecchia, Y. T. Lee, R. E. Olson, and W. A. Lester, Jr., J. Chem. Phys. **70**, 5477 (1979).
[265] V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, Chem. Phys. Lett. **90**, 382 (1982).
[266] V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, J. Chem. Phys. **89**, 6165 (1988).
[267] K. Mueller, Ph.D. thesis, Max-Plank Institute Fur Stromungsforschung, 1984.
[268] A. I. Reznikov and S. Y. Umanskii, Khim. Phys. **9**, 1299 (1990).
[269] A. I. Reznikov and S. Y. Umanskii, Khim. Phys. **13**, 37 (1994).
[270] F. H. Mies, Phys. Rev. A **7**, 942 (1973).
[271] F. H. Mies, Phys. Rev. A **7**, 957 (1973).
[272] T. J. Cook and T. A. Miller, J. Chem. Phys. **59**, 1352 (1973).
[273] B. R. Zegarski, T. J. Cook, and T. A. Miller, J. Chem. Phys. **62**, 2952 (1975).
[274] G. L. Fisanick-Englot and T. A. Miller, J. Chem. Phys. **64**, 786 (1976).
[275] J. C. Tully, J. Chem. Phys. **60**, 3042 (1974).
[276] R. L. Jaffe, K. Morokuma, and T. F. George, J. Chem. Phys. **63**, 3417 (1975).
[277] I. H. Zimmerman and T. F. George, J. Chem. Soc. Faraday Trans. 2 **71**, 2030 (1975).
[278] F. Rebentrost and J. W. A. Lester, J. Chem. Phys. **63**, 3737 (19).
[279] A. Komornicki, T. F. George, and K. Morokuma, J. Chem. Phys. **65**, 4312 (1976).
[280] F. Rebentrost and J. W. A. Lester, J. Chem. Phys. **64**, 4223 (1976).
[281] F. Rebentrost and J. W. A. Lester, J. Chem. Phys. **64**, 3879 (1976).
[282] F. Rebentrost and J. W. A. Lester, J. Chem. Phys. **67**, 3367 (1977).
[283] A. Komornicki, A. MoroKuma, and T. F. George, J. Chem. Phys. **67**, 5012 (1977).
[284] L. D. Thomas, W. A. Lester, Jr., and F. Rebentrost, J. Chem. Phys. **69**, 5489 (1978).
[285] S. L. Latham, J. F. McNutt, R. E. Wyatt, and M. J. Redmon, J. Chem. Phys. **69**, 3746 (1978).
[286] F. Rebentrost, Chem. Phys. Lett. **58**, 18 (1978).
[287] I. H. Zimmerman, M. Baer, and T. F. George, J. Chem. Phys. **71**, 4132 (1979).
[288] R. E. Wyatt, Chem. Phys. Lett. **63**, 503 (1979).
[289] R. E. Wyatt and R. B. Walker, J. Chem. Phys. **70**, 1501 (1979).
[290] M. J. Redmon and R. E. Wyatt, Chem. Phys. Lett. **63**, 209 (1979).
[291] C. W. McCurdy, H. D. Meyer, and W. H. Miller, J. Chem. Phys. **70**, 3177 (1979).
[292] J. F. McNutt and R. E. Wyatt, Chem. Phys. **58**, 423 (1981).
[293] D. E. Fitz and D. J. Kouri, J. Chem. Phys. **74**, 3933 (1981).
[294] B. Lepetit, J. M. Launay, and M. L. Dourneuf, Chem. Phys. **106**, 111 (1986).
[295] M. Gilibert and M. Baer, J. Phys. Chem. **98**, 12822 (1994).
[296] M. Gilibert and M. Baer, J. Phys. Chem. **99**, 15748 (1994).
[297] G. D. Billing, L. Y. Rusin, and M. B. Sevryuk, J. Chem. Phys. **103**, 2482 (1995).
[298] D. E. Manolopoulos, J. Chem. Soc. Faraday Trans. **93**, 673 (1997).
[299] M. H. Alexander, H. J. Werner, and D. E. Manolopoulos, J. Chem. Phys. **109**, 5710 (1998).
[300] P. Honvault and J.-M. Launay, Chem. Phys. Lett. **287**, 270 (1998).
[301] V. Aquilanti, S. Cavalli, D. Fazio, A. Volpi, A. Aguilar, X. Gimenez, and J. M. Lucas, J. Chem. Phys. **109**, 3805 (1998).
[302] P. Honvault and J. M. Launay, Chem. Phys. Lett. **303**, 657 (1999).
[303] V. Aquilanti, S. Cavalli, D. Fazio, A. Volpi, A. Aguilar, X. Gimenez, and J. M. Lucas, Phys. Chem. Chem. Phys. **1**, 1091 (1999).
[304] F. J. Aoiz, L. Banares, and J. F. Castillo, J. Chem. Phys. **111**, 4013 (1999).
[305] P. Casavecchia and F. J. Cartechini, Faraday Discuss. **113**, 201 (1999).
[306] M. H. Alexander, D. E. Manolopoulos, and H. J. Werner, J. Chem. Phys. **113**, 11084 (2000).
[307] V. Aquilanti, S. Cavalli, F. Pirani, A. Volpi, and D. Cappelletti, J. Phys. Chem. A **105**, 2401 (2001).
[308] V. Aquilanti, S. Cavalli, D. Fazio, and A. Volpi, Int. J. Quantum. Chem. **85**, 368 (2001).
[309] V. Aquilanti, S. Cavalli, D. D. Fazio, A. Volpi, A. Aguilar, X. Gimenez, and J. Lucas, Phys. Chem. Chem. Phys. **4**, 401 (2002).
[310] V. Aquilanti, S. Cavalli, D. Fazio, A. Volpi, A. Aguilar, X. Gimenez, and J. M. Lucas, Chem. Phys. Lett. **371**, 504 (2003).
[311] I. Last, M. Baer, I. H. Zimmerman, and T. F. George, Chem. Phys. Lett. **101**, 163 (1983).
[312] I. Last, J. Chem. Phys. **80**, 1001 (1984).
[313] M. Baer, I. Last, and Y. Shima, Chem. Phys. Lett. **110**, 163 (1984).
[314] I. Last and M. Baer, J. Chem. Phys. **82**, 4954 (1985).
[315] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, J. Chem. Phys. **82**, 3045 (1985).
[316] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **82**, 3067 (1985).
[317] S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon, and D. J. Nesbitt, J. Chem. Phys. **111**, 8404 (1999).
[318] S. A. Nizkorodov, W. W. Harper, and D. J. Nesbitt, Faraday Discuss. Chem. Soc. **113**, 107 (1999).
[319] R. Krems and A. Dalgarno, J. Chem. Phys. **117**, 118 (2002).
[320] Y.-R. Tzeng and M. Alexander, J. Chem. Phys. **121**, 5812 (2004).
[321] Y.-R. Tzeng and M. Alexander, J. Chem. Phys. **121**, 5183 (2004).
[322] Y. Zhang, T.-X. Xie, K.-L. Han, and J. H. Zhang, J. Chem. Phys. **120**, 6000 (2004).
[323] L. Y. Rusin, M. B. Sevryuk, and J. P. Toennies, J. Chem. Phys. **122**, 134314 (2005).
[324] K. Stark and H.-J. Werner, J. Chem. Phys. **104**, 6515 (1996).
[325] M. Hayesa, M. Gustafssona, A. Mebelb, and R. T. Skodje, Chem. Phys. **308**, 259 (2005).
[326] A. Brown and G. G. Balint-Kurti, J. Chem. Phys. **113**, 1870 (2000).
[327] A. Brown and G. G. Balint-Kurti, J. Chem. Phys. **113**, 1879 (2000).
[328] R. J. Donovan, D. Husain, and C. D. Stevenson, Trans. Faraday Soc. **65**, 2941 (1969).
[329] I. S. Fletcher and D. Husain, J. Photochem. **8**, 355 (1978).
[330] R. H. Clark and D. Husain, J. Photochem. **24**, 103 (1984).
[331] R. H. Clark and D. Husain, J. Chem. Soc. Faraday Trans. 2 **80**, 97 (1984).
[332] S. A. Chasovnikov, A. I. Chichinin, and L. N. Krasnoperov, Proceedings of 10th Int. Symp. on Gas Kinetics, Swansea, Great Britain, 1988, p. 38.
[333] A. I. Chichinin, Khim. Phys. **15**, 49 (1996).
[334] J. Park, Y. Lee, and G. W. Flynn, Chem. Phys. Lett. **186**, 441 (1991).
[335] I. S. Fletcher and D. Husain, J. Chem. Soc. Faraday Trans. 2 **74**, 203 (1978).
[336] F. Taketani, A. Yamasaki, K. Takahashi, and Y. Matsumi, Chem. Phys. Lett. **406**, 259 (2005).
[337] L. N. Krasnoperov and V. N. Panfilov, Theor. Exper. Khim. **15**, 348 (1979).
[338] L. N. Krasnoperov and V. N. Panfilov, React. Kinet. Catal. Lett. **10**, 191 (1979).
[339] K. Hitsuda, K. Takahashi, Y. Matsumi, and T. J. Wallington, Chem. Phys. Lett. **346**, 16 (2001).
[340] A. I. Resnikov and S. Ya. Umanskii, Khim. Phys. **11**, 851 (1992).
[341] R. Burcl, R. V. Krems, A. A. Buchachenko, M. M. Szczesniak, G. Chalasinski, and S. M. Cybulski, J. Chem. Phys. **109**, 2144 (1998).
[342] R. V. Krems and A. A. Buchachenko, J. Phys. B **33**, 4551 (2000).
[343] A. A. Buchachenko, R. V. Krems, M. M. Szczesniak, Y.-D. Xiao, L. A. Viehland, and G. Chalasinski, J. Chem. Phys. **114**, 9919 (2001).
[344] S.-H. Lee and K. P. Liu, J. Chem. Phys. **111**, 6253 (1999).
[345] A. I. Reznikov and S. Y. Umanski, Russ. J. Phys. Chem. **76**, s. 1, S13 (2002).
[346] G. C. Schatz, J. Phys. Chem. **99**, 7522 (1995).
[347] C. S. Maierle, G. C. Schatz, M. S. Gordon, P. McCabe, and J. N. L. Connor, J. Chem. Soc. Faraday Trans. **93**, 709 (1997).
[348] G. C. Schatz, P. McCabe, and J. N. L. Connor, Faraday Discuss. **110**, 139 (1998).
[349] A. J. Dobbyn, J. N. L. Connor, N. A. Besley, P. J. Knowles, and G. C. Schatz, Phys. Chem. Chem. Phys. **1**, 957 (1999).
[350] T. W. J. Whiteley, A. J. Dobbyn, J. N. L. Connor, and G. C. Schatz, Phys. Chem. Chem. Phys. **2**, 549 (2000).
[351] G. C. Schatz, M. Hankel, T. W. J. Whiteley, and J. N. L. Connor, J. Phys. Chem. A **107**, 7278 (2003).
[352] A. I. Reznikov and S. Y. Umanskii, Khim. Phys. **11**, 851 (1990).

[353] R. K. Preston, C. Sloane, and W. H. Miller, J. Chem. Phys. **60**, 4961 (1974).
[354] V. Aquilanti, D. Cappelletti, and F. Pirani, J. Chem. Soc. Faraday Trans. **89**, 1467 (1993).
[355] C. H. Becker, J. J. Valentini, P. Casavecchia, S. J. Sibner, and Y. T. Lee, Chem. Phys. Lett. **61**, 1 (1979).
[356] A. R. Ravishankara and P. H. Wine, J. Chem. Phys. **72**, 25 (1980).
[357] M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, E. Kleef, G. G. Volpi, F. J. Aoiz, L. Banares, D. W. Schwenke, T. C. Allison, *et al.*, Science **273**, 1519 (1996).
[358] S. H. Lee, L. H. Lai, K. P. Liu, and H. Chang, J. Chem. Phys. **110**, 8229 (1999).
[359] K. Tanaka, J. Durup, T. Kato, and I. Koyono, J. Chem. Phys. **73**, 586 (1980).
[360] K. Tanaka, J. Durup, T. Kato, and I. Koyono, J. Chem. Phys. **74**, 5561 (1981).
[361] N. Balucani, D. Skouteris, L. Cartechini, G. Capozza, E. Segoloni, P. Casavecchia, M. H. Alexander, G. Capecchi, and H. J. Werner, Phys. Rev. Lett. **91**, 013201 (2003).
[362] M. H. Alexander, G. Capecchi, and H.-J. Werner, Science **296**, 5568 (2002).
[363] M. H. Alexander, G. Capecchi, and H.-J. Werner, Faraday Discuss. **127**, 59 (2004).
[364] S. Ghosal and S. Mahapatra, J. Chem. Phys. **121**, 5740 (2004).
[365] B. Parsons and D. Chandler, J. Chem. Phys. **122**, 174306 (2005).
[366] J. Park, Y. Lee, and G. W. Flynn, Chem. Phys. Lett. **192**, 138 (1992).
[367] H. M. Lambert and P. J. Dagdigian, Chem. Phys. Lett. **275**, 499 (1997).
[368] R. A. Brownsword, P. Schmiechen, H. R. Volpp, H. P. Upadhyaya, Y. J. Jung, and K. H. Jung, J. Chem. Phys. **110**, 11823 (1999).
[369] P. M. Regan, D. Ascenzi, A. Brown, G. G. Balint-Kurti, and A. J. Orr-Ewing, J. Chem. Phys. **112**, 10259 (2000).
[370] A. Hanf, A. Lauter, and H.-R. Volpp, Chem. Phys. Lett. **368**, 445 (2003).
[371] D. Ascenzi, P. M. Regan, and A. J. Orr-Ewing, Chem. Phys. Lett. **310**, 477 (1999).
[372] P. Zou, H. Kim, and S. North, J. Chem. Phys. **116**, 4176 (2002).
[373] L. Li, R. J. Lipert, J. Lobue, W. A. Chupka, and S. D. Colson, Chem. Phys. Lett. **151**, 335 (1988).
[374] Y. Matsumi, M. Kawasaki, T. Sato, T. Kinugawa, and T. Arikawa, Chem. Phys. Lett. **155**, 486 (1989).
[375] Y. Matsumi, K. Tonokura, and M. Kawasaki, J. Chem. Phys. **97**, 1065 (1992).
[376] A. I. Chichinin, Chem. Phys. Lett. **209**, 459 (1993).
[377] P. C. Samartzis, T. Gougousi, and T. N. Kitsopoulos, Laser Chem. **17**, 185 (1997).
[378] P. C. Samartzis, I. Sakellariou, T. Gougousi, and T. N. Kitsopoulos, J. Chem. Phys. **107**, 43 (1997).
[379] A. Sugita, K. Suto, M. Kawasaki, and Y. Matsumi, Chem. Phys. Lett. **340**, 83 (2001).
[380] M. J. Cooper, P. J. Jackson, L. J. Rogers, A. J. Orr-Ewing, and B. J. Whitaker, J. Chem. Phys. **109**, 4367 (1998).
[381] M. Beckert, E. Wouters, M. R. Ashfold, and E. Wrede, J. Chem. Phys. **119**, 9576 (2003).
[382] L. N. Krasnoperov and V. N. Panfilov, Kinetika i Kataliz **20**, 447 (1979).
[383] T. S. Mashnin, A. V. Chernychev, and L. N. Krasnoperov, Chem. Phys. Lett. **207**, 105 (1993).
[384] K. Tonokura, Y. Matsumi, M. Kawasaki, H. L. Kim, S. Yabushita, S. Fujimura, and K. Saito, J. Chem. Phys. **99**, 3461 (1993).
[385] C. K. Ni and G. W. Flynn, Chem. Phys. Lett. **210**, 333 (1993).
[386] L. J. Rogers, M. N. R. Ashfold, Y. Matsumi, M. Kawasaki, and B. J. Whitaker, Chem. Phys. Lett. **258**, 159 (1996).
[387] K.-W. Jung, T. S. Ahmadi, and M. A. El-Sayed, J. Phys. Chem. **101**, 6562 (1997).
[388] A. J. Bell, S. A. Boggis, J. M. Dyke, J. G. Frey, R. Richter, N. Shaw, and M. Tabrizchi, J. Chem. Soc. Faraday Trans. **91**, 17 (1994).
[389] Y. Tanaka, M. Kawasaki, Y. Matsumi, H. Fujiwara, T. Ishiwata, L. J. Rogers, R. N. Dixon, and M. N. R. Ashfold, J. Chem. Phys. **109**, 1315 (1998).
[390] H. L. Kim, Y. Mo, Y. Matsumi, and M. Kawasaki, Bull. Korean Chem. Soc. **13**, 162 (1992).
[391] J. Cao, Y. Wang, and X. W. Qian, J. Chem. Phys. **103**, 9653 (1995).
[392] M. Kawasaki, K. Suto, Y. Sato, Y. Matsumi, and R. Bersohn, J. Phys. Chem. **100**, 19853 (1996).
[393] E. Bishenden, J. Haddock, and D. J. Donaldson, J. Phys. Chem. **95**, 2113 (1991).
[394] M. Roth, T. Einfeld, K.-H. Gericke, and C. Maul, Phys. Chem. Earth (C) **26**, 513 (2001).
[395] A. I. Chichinin, T. Einfeld, O. Ott, C. Maul, K.-H. Gericke, R. Marom, S. Rosenwaks, and I. Bar (in press).
[396] C. Maul, C. Dietrich, T. Haas, and K.-H. Gericke, Phys. Chem. Chem. Phys. **1**, 1441 (1999).
[397] C. Maul, T. Haas, and K.-H. Gericke, J. Chem. Phys. **102**, 3238 (1995).
[398] C. Maul, T. Haas, and K.-H. Gericke, J. Phys. Chem. A **101**, 6619 (1997).
[399] C. Maul and K.-H. Gericke, Int. Rev. Phys. Chem. **16**, 1 (1997).
[400] T. Einfeld, A. Chichinin, C. Maul, and K.-H. Gericke, J. Chem. Phys. **116**, 2803 (2002).
[401] T. Einfeld, A. Chichinin, C. Maul, and K.-H. Gericke, J. Chem. Phys. **117**, 1123 (2002).
[402] M. Roth, C. Maul, and K.-H. Gericke, Phys. Chem. Chem. Phys. **4**, 2932 (2002).
[403] A. Chichinin, T. Einfeld, K.-H. Gericke, J. Grunenberg, C. Maul, and L. Schafer (in press).
[404] T. Einfeld, C. Maul, K.-H. Gericke, and A. Chichinin, J. Chem. Phys. **117**, 4214 (2002).
[405] H. M. Lambert and P. J. Dagdigian, J. Chem. Phys. **109**, 7810 (1998).
[406] C. Tao and P. J. Dagdigian, Chem. Phys. Lett. **350**, 63 (2001).
[407] R. Marom, A. Golan, S. Rosenwaks, and I. Bar, Chem. Phys. Lett. **378**, 305 (2003).
[408] A. Melchior, P. Knupfer, I. Bar, S. Rosenwaks, T. Laurent, H.-R. Volpp, and J. Wolfrum, J. Phys. Chem. **100**, 13375 (1996).
[409] G. S. Tyndall, C. S. K. Owen, J. J. Orlando, and J. G. Calvert, J. Chem. Soc. Faraday Trans. **93**, 2675 (1997).
[410] A. Melchior, X. Chen, I. Bar, and S. Rosenwaks, J. Phys. Chem. A **104**, 7927 (2000).
[411] X. L. Chen, R. Marom, S. Rosenwaks, I. Bar, T. Einfeld, C. Maul, and K.-H. Gericke, J. Chem. Phys. **114**, 9033 (2001).
[412] D. Ardelt and F. Stuhl, Chem. Phys. Lett. **304**, 323 (1999).
[413] C. Maul, A. I. Chichinin, and K.-H. Gericke (private communication, 2005).
[414] Y. Mo, K. Tonokura, Y. Matsumi, M. Kawasaki, T. Sato, T. Arikawa, P. T. A. Reilly, Y. Xie, Y. Yang, Y. Huang, *et al.*, J. Chem. Phys. **97**, 4815 (1992).
[415] P. T. A. Reilly, Y. Xie, and R. J. Gordon, Chem. Phys. Lett. **178**, 511 (1991).
[416] K. Sato, Y. Shishira, S. Tsunashima, H. Umemoto, T. Takayanagi, K. Furukawa, and S. Ohno, J. Chem. Phys. **99**, 1703 (1993).
[417] A. Melchior, I. Bar, and S. Rosenwaks, J. Chem. Phys. **107**, 8476 (1997).
[418] A. Melchior, X. Chen, I. Bar, and S. Rosenwaks, Chem. Phys. Lett. **315**, 421 (1999).
[419] A. Lauter, D. Suresh, and H.-R. Volpp, J. Chem. Phys. **118**, 5821 (03).
[420] M. Park, K. W. Lee, and K.-H. Jung, J. Chem. Phys. **114**, 10368 (2001).
[421] Y. Liu and L. Butler, J. Chem. Phys. **121**, 11016 (2004).
[422] M.-A. Thelen, P. Felder, J. G. Frey, and J. R. Huber, J. Phys. Chem. **97**, 6220 (1993).
[423] D. Senapati and P. Das, Chem. Phys. Lett. **402**, 450 (2005).
[424] T. Ichimura, Y. Mori, H. Shinohara, and N. Nishi, Chem. Phys. Lett. **122**, 51 (1985).
[425] T. Ichimura, Y. Mori, H. Shinohara, and N. Nishi, Chem. Phys. Lett. **125**, 263 (1986).
[426] S. C. Givertz and G. G. Balint-Kurti, J. Chem. Soc. Faraday Trans. **82**, 1231 (1986).
[427] M. H. Alexander, B. Pouilly, and T. Duhoo, J. Chem. Phys. **99**, 1752 (1993).
[428] I. H. Gersonde, S. Henning, and H. Gabriel, J. Chem. Phys. **101**, 9558 (1994).
[429] T. Duhoo and B. Pouilly, J. Chem. Phys. **103**, 182 (1995).
[430] S. Lee and K. H. Jung, J. Chem. Phys. **112**, 2810 (2000).
[431] Y. Li, O. Bludsky, G. Hirsch, and R. J. Buenker, J. Chem. Phys. **112**, 260 (2000).
[432] B. Whitaker, ed., *Imaging in Molecular Dynamics: Technology and Applications* (Cambridge University Press, Cambridge, 2003).
[433] A. Melchior, H. M. Lambert, P. J. Dagdigian, I. Bar, and S. Rosenwaks, Isr. J. Chem. **37**, 455 (1997).
[434] A. R. Offer and G. G. Balint-Kurti, J. Chem. Phys. **104**, 563 (1996).

[435] D. Kokh, A. Alekseyev, and R. Buenker, J. Chem. Phys. **120**, 11549 (2004).
[436] R. A. Brownsword, C. Kappel, P. Schmiechen, and H. H.-R. Volpp, Chem. Phys. Lett. **289**, 241 (1998).
[437] F. J. Aoiz, L. Banares, T. Bohm, A. Hanf, V. J. Herrero, K.-H. Jung, A. Laeuter, K. W. Lee, M. Menendez, V. S. Rabanos, *et al.*, J. Phys. Chem. A **104**, 10452 (2000).
[438] A. Hanf, A. Luter, D. Suresh, H.-R. Volpp, and J. Wolfrum, Chem. Phys. Lett. **340**, 71 (2001).
[439] Y. Matsumi, K. Tonokura, M. Kawasaki, K. Tsuji, and K. Obi, J. Chem. Phys. **98**, 8330 (1993).
[440] A. I. Chichinin, J. Chem. Phys. **106**, 1057 (1997).
[441] A. I. Chichinin, Chem. Phys. Lett. **316**, 425 (2000).
[442] A. I. Chichinin, Chem. Phys. Reports **16**, 635 (1997).
[443] P. J. Dagdigian, *Spin-Orbit Effects in Chemical Reactions* (Kluwer Academic, Dordrecht, 1988).
[444] R. J. Donovan and D. Husain, J. Chem. Soc. Faraday Trans. 2 **62**, 2023 (1962).
[445] R. J. Donovan and D. Husain, Trans. Faraday Soc. **62**, 2987 (1966).
[446] R. O. Johnson, G. P. Perram, and W. B. Roh, J. Chem. Phys. **104**, 7052 (1996).
[447] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **73**, 6182 (1980).
[448] A. J. Grimley and P. L. Houston, J. Chem. Phys. **70**, 5184 (1979).
[449] S. L. Mielke, G. J. Tawa, D. G. Truhlar, and D. W. Schwenke, Chem. Phys. Lett. **234**, 57 (1995).
[450] S. L. Mielke, D. Truhlar, and D. W. Schwenke, J. Phys. Chem. A **99**, 16210 (1995).
[451] Y. L. Volobuev, M. D. Hack, and D. G. Truhlar, J. Phys. Chem. A **103**, 6225 (1999).
[452] D. Ali and W. Miller, Chem. Phys. Lett. **103**, 470 (1984).
[453] A. E. Orel, D. P. Ali, and W. H. Miller, Chem. Phys. Lett. **79**, 137 (1981).
[454] T. Takayanagi and Y. Kurosaki, J. Chem. Phys. **113**, 7158 (2000).
[455] J. A. Klos, G. Chalasinski, and M. M. Szczsniak, J. Phys. Chem. A **106**, 7362 (2002).
[456] M. A. A. Clyne, J. A. Coxon, and A. R. W. Fat, J. Chem. Soc. Faraday Trans. 2 **53**, 82 (1972).
[457] H. K. Haugen, E. Weitz, and S. R. Leone, Chem. Phys. Lett. **119**, 75 (1985).
[458] H. Reisler and C. Wittig, J. Chem. Phys. **68**, 3308 (1978).
[459] H. Reisler and C. Wittig, J. Chem. Phys. **69**, 3729 (1978).
[460] I. B. Bykhalo, E. B. Gordon, A. P. Perminov, and V. V. Filatov, Khim. Phys. **4**, 770 (1985).
[461] F. J. Wodarczyk and P. B. Sackett, Chem. Phys. **12**, 65 (1976).
[462] S. R. Leone and F. J. Wodsrczyk, J. Chem. Phys. **60**, 314 (1974).
[463] R. J. Donovan and D. Husain, Trans. Faraday Soc. **62**, 2023 (1966).
[464] M. R. Hawks, R. O. Johnson, and G. P. Perram, Chem. Phys. **195**, 395 (1995).
[465] C. A. Taatjes, C. M. Lovejoy, B. J. Opansky, and S. R. Leone, Chem. Phys. Lett. **182**, 39 (1991).
[466] H. Hofmann and S. R. Leone, Chem. Phys. Lett. **54**, 314 (1978).
[467] A. Hariri, A. B. Petersen, and C. Wittig, J. Chem. Phys. **65**, 1872 (1976).
[468] A. Hariri and C. Wittig, J. Chem. Phys. **67**, 4454 (1977).
[469] J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys. **69**, 1805 (1978).
[470] A. Hariri and C. Wittig, J. Chem. Phys. **68**, 2109 (1978).
[471] V. S. Kushawaha, Phys. Scr. **20**, 75 (1979).
[472] R. J. Donovan, F. G. M. Hathorn, and D. Husain, Trans. Faraday Soc. **64**, 1228 (1968).
[473] I. A. Boriev, Khim. Phys. **15**, 126 (1996).
[474] I. A. Boriev, E. B. Gordon, and A. A. Efimenko, Chem. Phys. Lett. **120**, 486 (1985).
[475] A. J. Sedlacek and C. A. Wight, J. Chem. Phys. **86**, 2787 (1987).
[476] L. N. Krasnopyorov and V. N. Panfilov, Chem. Phys. **25**, 375 (1977).
[477] L. N. Krasnopyorov, N. K. Serdyuk, V. P. Strunin, and V. N. Panfilov, React. Kinet. Catal. Lett. **7**, 321 (1977).
[478] K. B. McAfee, Jr., R. M. Lum, and R. S. Hozack, J. Chem. Phys. **64**, 5073 (1976).
[479] S. R. Leone, Acc. Chem. Res. **16**, 88 (1983).
[480] Z. Xu, B. Koplitz, and C. Wittig, J. Chem. Phys. **87**, 1062 (1987).
[481] Z. Xu, B. Koplitz, and C. Wittig, J. Phys. Chem. **92**, 5518 (1988).
[482] D. L. Lacombe, Ph.D. thesis, Univ. Waterloo, Canada, 1997.
[483] A. B. Petersen and I. W. Smith, Chem. Phys. **30**, 407 (1978).
[484] H. K. Haugen, E. Weitz, and S. R. Leone, J. Chem. Phys. **83**, 3402 (1985).
[485] M. J. Cooper, E. Wrede, A. J. Orr-Ewing, and M. N. R. Ashfold, J. Chem. Soc. Faraday Trans. **94**, 2901 (1998).
[486] Y. Jee, M. S. Park, Y. S. Kim, Y.-J. Jung, and K.-H. Jung, Chem. Phys. Lett. **287**, 701 (1998).
[487] M. Vries, N. Veen, and A. Vries, Chem. Phys. Lett. **56**, 15 (1978).
[488] W. S. McGivern, R. Li, P. Zou, T. Nguyen, and S. W. North, Chem. Phys. **249**, 237 (1999).
[489] E. Wrede, S. Laubach, S. Schulenburg, A. Brown, E. R. Wouters, A. J. Orr-Ewing, and M. N. R. Ashfold, J. Chem. Phys. **114**, 2629 (2001).
[490] J. A. Russell, I. A. McLaren, W. M. Jackson, and J. B. Halpern, J. Phys. Chem. **91**, 3248 (1987).
[491] E. A. J. Wannenmacher, H. Lin, W. H. Fink, A. J. Paul, and W. M. Jackson, J. Chem. Phys. **95**, 3431 (1991).
[492] W. P. Hess, D. W. Chandler, and J. W. Thoman, Jr., Chem. Phys. **163**, 277 (1992).
[493] T. Gougousi, P. C. Samartzis, and T. N. Kitsopoulos, J. Chem. Phys. **108**, 5742 (1998).
[494] D. Xu, J. Francisco, J. Huang, and W. Jackson, J. Chem. Phys. **117**, 2578 (2002).
[495] W. B. Tzeng, Y. R. Lee, and S. M. Lin, Chem. Phys. Lett. **227**, 467 (1994).
[496] W. S. McGivern, R. Li, P. Zou, T. Nguyen, and S. W. North, J. Chem. Phys. **111**, 5771 (1999).
[497] S.-H. Lee, Y.-J. Jung, and K.-H. Jung, Chem. Phys. **260**, 143 (2000).
[498] T. Kim, M. S. Park, K. W. Lee, and K.-H. Jung, J. Chem. Phys. **115**, 10745 (2001).
[499] J. H. Huang, D. Xu, J. Francisco, and W. M. Jackson, J. Chem. Phys. **119**, 3661 (2003).
[500] Y. R. Lee, W. B. Tzeng, Y. J. Yang, Y. Y. Lin, and S. M. Lin, Chem. Phys. Lett. **222**, 141 (1994).
[501] Y. R. Lee, Y. J. Yang, Y. Y. Lin, and S. M. Lin, J. Chem. Phys. **103**, 6966 (1995).
[502] M. S. Park, T. K. Kim, S.-H. Lee, K.-H. Jung, H.-R. Volpp, and J. Wolfrum, J. Phys. Chem. A **105**, 5606 (2001).
[503] L. J. Butler, E. J. Hintsa, S. F. Shane, and Y. T. Lee, J. Chem. Phys. **86**, 2051 (1987).
[504] W. S. McGivern, O. Sorkhabi, A. Suits, A. Derecskei-Kovacs, S. North, S. McGivern, R. Li, P. Zou, T. Nguyen, and S. W. North, J. Phys. Chem. A **104**, 10085 (2000).
[505] H. Katayanagi, N. Yonekuira, and T. Suzuki, Chem. Phys. **231**, 345 (1998).
[506] C. A. Wight and S. R. Leone, J. Phys. Chem. **87**, 5299 (1983).
[507] B. Poilly and M. Monnerville, Chem. Phys. **238**, 437 (1998).
[508] R. J. Donovan and D. Husain, Trans. Faraday Soc. **64**, 2325 (1968).
[509] M. S. Child, Mol. Phys. **32**, 1495 (1976).
[510] R. S. Mulliken, Phys. Rev. **51**, 310 (1937).
[511] R. S. Mulliken, J. Chem. Phys. **8**, 382 (1940).
[512] B. Pouilly and M. Monnerville, Chem. Phys. **238**, 437 (1998).
[513] G. Peoux, M. Monnerville, T. Duhoo, and B. Pouilly, J. Chem. Phys. **107**, 70 (1997).
[514] R. Roy, R. G. MacDonald, and G. Burns, J. Chem. Phys. **65**, 1485 (1976).
[515] B. S. Agrawalla, J. P. Singh, and D. W. Setser, J. Chem. Phys. **79**, 6416 (1983).
[516] G. P. Quigley and G. J. Wolga, J. Chem. Phys. **62**, 4560 (1975).
[517] Z. Karny and B. Katz, Chem. Phys. Lett. **14**, 295 (1976).
[518] R. J. Donovan, D. Husain, and C. D. Stevenson, Trans. Faraday Soc. **66**, 2148 (1970).
[519] J. C. Poianyi and W. J. Skrlac, J. Chem. Phys. **23**, 167 (1977).
[520] K. G. Anlauf, D. S. Horne, R. G. MacDonald, J. C. Polanyi, and K. B. Woodall, J. Chem. Phys. **57**, 1561 (1972).
[521] S. H. P. Bly, D. Brandt, and J. C. Polanyi, Chem. Phys. Lett. **65**, 399 (1979).
[522] D. Brandt, L. W. Dickson, L. N. Y. Kwan, and J. C. Polanyi, Chem. Phys. **39**, 189 (1972).
[523] J. P. Sung and D. W. Setser, Chem. Phys. Lett. **48**, 413 (1977).
[524] M. A. A. Clyne and H. W. Cruse, Trans. Faraday Soc. **67**, 2855 (1971).
[525] J. E. Smedley, H. K. Haugen, and S. R. Leone, J. Chem. Phys. **86**, 6801 (1987).
[526] R. J. Donovan and D. Husain, Trans. Faraday Soc. **62**, 1050 (1966).

[527] G. E. Hall, S. Arepalli, P. L. Houston, and J. R. Wiesenfeld, J. Chem. Phys. **82**, 2590 (1985).
[528] D. Husain and J. R. Wiesenfeld, Trans. Faraday Soc. **63**, 1349 (1967).
[529] D. Husain and J. R. Wiesenfeld, Nature (London) **213**, 1227 (1967).
[530] R. J. Donovan and D. Husain, Trans. Faraday Soc. **62**, 11 (1966).
[531] A. B. Callear and J. F. Wilson, Trans. Faraday Soc. **63**, 1983 (1967).
[532] E. W. Abrahamson, D. Husain, and J. R. Wiesenfeld, Trans. Faraday Soc. **64**, 833 (1968).
[533] P. Cadman and J. C. Polanyi, J. Phys. Chem. **72**, 3715 (1968).
[534] J. J. Deakin and D. J. Husain, J. Chem. Soc. Faraday Trans. 2 **68**, 1603 (1972).
[535] J. J. Deakin and D. Husain, J. Chem. Soc. Faraday Trans. 2 **68**, 41 (1972).
[536] J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys. **69**, 1797 (1978).
[537] A. J. Grimley and P. L. Houston, J. Chem. Phys. **70**, 4724 (1979).
[538] J. A. Blauer and W. C. Solomon, Proc. Int. Symp. Combust. **14**, 18 (1972).
[539] A. T. Pritt, Jr. and R. D. Coombe, J. Chem. Phys. **65**, 2096 (1976).
[540] A. T. Pritt, Jr. and D. Patel, J. Chem. Phys. **81**, 1337 (1984).
[541] A. J. Grimley and P. L. Houston, J. Chem. Phys. **68**, 3366 (1978).
[542] R. J. Donovan, C. Fotakis, and M. F. Golde, J. Chem. Soc. Faraday Trans. 2 **72**, 2055 (1976).
[543] C. Fotakis, M. Trainer, and R. J. Donovan, J. Photochem. **10**, 231 (1979).
[544] C. Fotakis and R. J. Donovan, Chem. Phys. Lett. **54**, 91 (1978).
[545] P. Cadman, J. C. Polanyi, and I. W. M. Smith, J. Chem. Phys. **69**, 14 (1967).
[546] T. Donohue and J. R. Wiesenfeld, J. Phys. Chem. **80**, 437 (1976).
[547] J. B. Koffend, C. E. Gartner, and R. F. Heidner, J. Chem. Phys. **80**, 1861 (1984).
[548] J. J. Deakin, D. Husain, and J. R. Wiesenfeld, Chem. Phys. Lett. **10**, 146 (1971).
[549] D. H. Burde and R. A. McFarlane, J. Chem. Phys. **54**, 1850 (1976).
[550] A. T. Young and P. L. Houston, J. Chem. Phys. **78**, 2317 (1983).
[551] C. M. de Vohringer, R. G. Badini, G. A. Arguello, and E. H. Staricco, Ber. Bunsen Ges. Phys. **94**, 1387 (1990).
[552] D. H. Burde, T. T. Yang, and R. A. McFarlane, Chem. Phys. Lett. **205**, 69 (1993).
[553] T. Marter, M. C. Heaven, and D. Plummer, Chem. Phys. Lett. **260**, 201 (1996).
[554] R. F. Heidner III, C. E. Gardner, T. M. El-Sayed, G. I. Segal, and J. V. V. Kasper, J. Chem. Phys. **74**, 5618 (1981).
[555] J. B. Koffend, B. H. Weiller, and R. F. Heidner III, J. Phys. Chem. **96**, 9315 (1992).
[556] M. R. Berman and P. D. Whitefield, J. Chem. Phys. **84**, 4281 (1986).
[557] M. A. Chowdhury, A. T. Pritt, Jr., D. Patel, and D. J. Benard, J. Chem. Phys. **84**, 6687 (1986).
[558] P. L. Houston, Chem. Phys. Lett. **47**, 137 (1977).
[559] R. J. Donovan and D. Husain, Nature **206**, 171 (1965).
[560] Yu. A. Tolmachev and V. A. Kartazaev, Opt. Spektroskopiya **41**, 162 (1976).
[561] V. A. Kartazaev, N. P. Penkin, and Yu. A. Tolmachev, Sov. J. Quantum Electron. **7**, 608 (1977).
[562] J. I. Cline and S. R. Leone, J. Phys. Chem. **95**, 2917 (1991).
[563] M. C. Lin and R. G. Shortridge, Chem. Phys. Lett. **29**, 42 (1974).
[564] G. E. Hall, W. J. Marinelli, and P. L. Houston, J. Phys. Chem. **87**, 2153 (1983).
[565] R. F. Heidner III, C. E. Gardner, G. I. Segal, and T. M. El-Sayed, J. Phys. Chem. **87**, 2348 (1983).
[566] A. J. Grimley and P. L. Houston, J. Chem. Phys. **69**, 2339 (1978).
[567] M. S. Chiappero, R. G. Badini, and G. A. Arguello, Int. J. Chem. Kinet. **29**, 155 (1997).
[568] F. G. M. Hathorn and D. Husain, Trans. Faraday Soc. **65**, 2678 (1969).
[569] R. G. Badini, Int. J. Chem. Kinet. **21**, 634 (1989).
[570] A. B. Alekseev and A. M. Pravilov, Khimiya Vysokih Energii **18**, 99 (1984).
[571] H. Hofmann and S. R. Leone, J. Chem. Phys. **69**, 3819 (1978).
[572] T. W. Broadbent and A. B. Caller, Trans. Faraday Soc. **67**, 3030 (1971).
[573] R. J. Donovan, H. M. Gillespie, W. H. Breckenridge, and C. Fotakis, J. Chem. Soc. Faraday Trans. 1 **75**, 1557 (1979).
[574] Z.-N. Gu, A. T. Young, and P. L. Houston, Int. J. Chem. Kinet. **16**, 669 (1984).
[575] M. S. Chiappero and G. A. Arguello, Int. J. Chem. Kinet. **30**, 799 (1998).
[576] R. T. Meyer, J. Chem. Phys. **46**, 4146 (1967).
[577] R. J. Donovan, F. G. M. Hathorn, and D. Husain, J. Chem. Phys. **49**, 953 (1968).
[578] R. J. Donovan, F. G. M. Hathorn, and D. Husain, Trans. Faraday Soc. **64**, 3192 (1968).
[579] R. J. Donovan and C. Fotakis, J. Chem. Phys. **61**, 2159 (1974).
[580] R. J. Butcher, R. J. Donovan, C. Fotakis, D. Fernie, and A. G. A. Rae, Chem. Phys. Lett. **30**, 398 (1975).
[581] T. Donohue and J. R. Wiesenfeld, Chem. Phys. Lett. **33**, 176 (1975).
[582] R. E. Palmer and T. D. Padrick, J. Chem. Phys. **64**, 2051 (1976).
[583] C. Fotakis and R. J. Donovan, J. Chem. Soc. Faraday Trans. 2 **11**, 2099 (1978).
[584] A. B. Alekseev, A. M. Pravilov, I. I. Sidorov, and V. A. Skorokhodov, Kvantovaya Elektronika **14**, 2421 (1987).
[585] S. L. Dobychin, L. D. Mikheev, A. B. Pavlov, V. P. Fokanov, and M. A. Khodarkovskii, Sov. J. Quantum Electron. **8**, 1383 (1978).
[586] V. Yu. Zalesskii and T. I. Krupenikova, Opt. Spektroskopiya **30**, 439 (1971).
[587] K. Hohla and K. L. Kompa, Chem. Phys. Lett. **14**, 445 (1972).
[588] S. V. Kuznetsova and A. I. Maslov, Kvantovaya Elektronika **6**, 31 (1973).
[589] T. F. Hunter and K. S. Kristjansson, Chem. Phys. Lett. **90**, 35 (1982).
[590] R. J. Donovan and D. Husain, Nature **209**, 609 (1966).
[591] L. N. Kosareva, B. nd A. B. Pavlov, V. P. Fokanov, and M. A. Khodarkovskii, Khimiya Vysokih Energii **14**, 519 (1980).
[592] F. J. Comes and S. Pionteck, Chem. Phys. Lett. **42**, 558 (1976).
[593] L. G. Karpov, A. M. Pravilov, and F. I. Vilesov, Khimiya Vysokih Energii **8**, 489 (1974).
[594] F. J. Comes and S. Pionteck, Chem. Phys. Lett. **58**, 616 (1978).
[595] R. J. Donovan and H. M. Gillespie, Chem. Phys. Lett. **56**, 189 (1978).
[596] M. N. S. Rayo, C. Fotakis, and R. J. Donovan, J. Photochem. **9**, 433 (1978).
[597] K. H. Stephan and F. J. Comes, J. Mol. Struct. **61**, 259 (1980).
[598] S. M. Egorov, A. M. Pravilov, and V. A. Skorokhodov, Chem. Phys. **165**, 371 (1992).
[599] A. M. Pravilov, I. I. Sidorov, and V. A. Skorokhodov, Kinetika i Kataliz **27**, 1044 (1985).
[600] L. G. Karpov, A. M. Pravilov, and F. I. Vilesov, Sov. J. Quantum Electron. **7**, 497 (1977).
[601] A. M. Pravilov, F. I. Vilesov, V. A. Elokhin, V. S. Ivanov, and A. S. Kozlov, Sov. J. Quantum Electron. **8**, 666 (1978).
[602] V. S. Ivanov, A. S. Kozlov, A. M. Pravilov, and E. P. Smirnov, Sov. J. Quantum Electron. **10**, 566 (1980).
[603] A. B. Alekseev and A. M. Pravilov, Kvantovaya Elektronika **14**, 408 (1987).
[604] A. B. Alekseev, A. M. Pravilov, and S. E. Ryabov, Sov. J. Quantum Electron. **19**, 484 (1989).
[605] J. R. McDonald and J. K. Hancock, Naval Research Laboratory Memorandum Report, Washington, DC., 1976, Vol. 3395.
[606] A. L. Kaledin, M. C. Heaven, and K. Morokuma, Chem. Phys. Lett. **289**, 110 (1998).
[607] A. L. Kaledin, M. C. Heaven, and K. Morokuma, J. Chem. Phys. **114**, 215 (2001).
[608] S. J. Arnold, N. Finlayson, and E. A. Ogryzlo, J. Chem. Phys. **44**, 2529 (1966).
[609] I. H. Zimmerman and T. F. George, J. Chem. Phys. **61**, 2468 (1974).
[610] I. H. Zimmerman and T. F. George, Chem. Phys. **7**, 323 (1975).
[611] H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).
[612] A. M. Pravilov, Kvantovaya Elektronika **8**, 1397 (1981).
[613] W. M. Jackson and H. Okabe, Adv. Photochem. **13**, 1 (1986).
[614] E. Hirota, Ann. Rev. Phys. Chem. **42**, 1 (1991).
[615] R. D. Clear, S. J. Riley, and K. R. Wilson, J. Chem. Phys. **63**, 1340 (1975).
[616] G. Veen, K. A. Mohamed, T. Baller, and A. Vries, Chem. Phys. **80**, 113 (1983).
[617] C. A. Wight and S. R. Leone, J. Chem. Phys. **79**, 4823 (1983).
[618] T. N. Kitsopoulos, M. A. Buntine, D. Baldwin, R. N. Zare, and D. Chandler, Proc. SPIE **1858**, 2 (1993).
[619] D. W. Chandler, T. N. Kitsopoulos, M. A. Buntine, D. Baldwin, R. I. McKay, A. J. R. Heck, and R. N. Zare, *Spring. Ser. Chem. Phys.* (Springer, New York, 1996).
[620] S. R. Langford, P. M. Regan, A. J. Orr-Ewing, and M. N. R. Ashfold, Chem. Phys. **231**, 245 (1998).

[621] P. M. Regan, D. Ascenzi, C. Clementi, M. N. R. Ashfold, and A. J. Orr-Ewing, Chem. Phys. Lett. **315**, 187 (1999).
[622] S. Manzhos, H.-P. Loock, B. L. G. Bakker, and D. H. Parker, J. Chem. Phys. **117**, 9347 (2002).
[623] J. A. Betts, Ph.D. thesis, California Institute of Technology, Ann Arbor, MI, 1971.
[624] R. J. Oldman, R. K. Sandler, and K. R. Wilson, J. Chem. Phys. **54**, 4127 (1971).
[625] T. W. Broadbent and A. B. Caller, J. Chem. Soc. Faraday Trans. 2 **68**, 1367 (1972).
[626] R. D. Clear and K. R. Wilson, J. Mol. Spectr. **47**, 39 (1973).
[627] D. H. Burde, R. A. McFarlane, and J. R. Wiesenfeld, Phys. Rev. A **10**, 1917 (1974).
[628] H. J. Hwang and M. A. El-Sayed, J. Phys. Chem. **95**, 8044 (1991).
[629] J. H. Ling and K. R. Wilson, J. Chem. Phys. **63**, 101 (1975).
[630] W. M. Pitts and A. P. Baronavski, Chem. Phys. Lett. **71**, 395 (1980).
[631] I. Nadler, D. Mahgerefteh, H. Reisler, and C. Wittig, J. Chem. Phys. **82**, 3885 (1985).
[632] W. P. Hess, S. R. Leone, J. Chem. Phys. **86**, 3773 (1987).
[633] J. F. Black, J. R. Waldeck, and R. N. Zare, J. Chem. Phys. **92**, 3519 (1990).
[634] H. Li, K. J. Franks, and W. Kong, Chem. Phys. Lett. **300**, 247 (1999).
[635] T. F. Hunter and K. S. Kristjansson, Chem. Phys. Lett. **58**, 291 (1978).
[636] T. F. Hunter and C. M. Leong, Chem. Phys. Lett. **104**, 538 (1984).
[637] G. Veen, T. Baller, A. Vries, and N. Veen, Chem. Phys. **87**, 405 (1984).
[638] M. D. Barry and P. A. Gerry, Mol. Phys. **52**, 461 (1984).
[639] G. Veen, T. Baller, and A. Vries, Chem. Phys. **97**, 179 (1985).
[640] W. P. Hess, R. Naaman, and S. R. Leone, J. Phys. Chem. **91**, 6085 (1987).
[641] D. W. Chandler and P. L. Houston, J. Chem. Phys. **87**, 1445 (1987).
[642] A. Gedanken, Chem. Phys. Lett. **137**, 462 (1987).
[643] S. M. Penn, C. C. Hayden, K. J. C. Muyskens, and F. F. Crim, J. Chem. Phys. **89**, 2909 (1988).
[644] R. Loo, G. E. Hall, H. P. Haerri, and P. L. Houston, J. Phys. Chem. **92**, 5 (1988).
[645] R. Loo, H. P. Haerri, G. E. Hall, and P. L. Houston, J. Chem. Phys. **90**, 4222 (1989).
[646] Q. Zhu, R. E. Continetti, X. Zhao, B. Balko, E. Hintsa, and Y. T. Lee (private communication, 1992, see Guo[749]).
[647] D. H. Fairbrother, K. A. Briggman, E. Weitz, and P. C. Stair, J. Chem. Phys. **101**, 3787 (1994).
[648] R. A. Hertz and J. A. Syage, J. Chem. Phys. **100**, 9265 (1994).
[649] J. A. Syage, Chem. Phys. Lett. **245**, 605 (1995).
[650] J. Syage, Chem. Phys. **207**, 411 (1996).
[651] S. Uma and P. K. Das, Chem. Phys. Lett. **241**, 335 (1995).
[652] J. Syage, J. Chem. Phys. **105**, 1007 (1996).
[653] T. F. Hunter, S. Lunt, and K. S. Kristjansson, J. Chem. Soc. Faraday Trans. 2 **79**, 303 (1983).
[654] R. E. Continetti, B. Balko, and Y. T. Lee (private communication, 1991, Ref. 8 in Syage[659]).
[655] E. Gerck, J. Chem. Phys. **79**, 311 (1983).
[656] T. P. Zhurilo, V. Yu. Zalesskii, and A. M. Kokushin, Kvantovaya Elektronika **12**, 1017 (1985).
[657] G. Veen, T. Baller, A. Vries, and M. Shapiro, Chem. Phys. **93**, 277 (1985).
[658] P. Felder, Chem. Phys. **143**, 141 (1990).
[659] M. D. Person, P. W. Kash, and L. J. Butler, J. Chem. Phys. **94**, 2557 (1991).
[660] P. Felder, Chem. Phys. **155**, 435 (1991).
[661] H. J. Hwang and M. A. El-Sayed, J. Phys. Chem. **96**, 8728 (1992).
[662] P. Felder, Chem. Phys. Lett. **197**, 425 (1992).
[663] Y. S. Kim, W. K. Kang, and K.-H. Jung, J. Chem. Phys. **105**, 551 (1996).
[664] A. Furlan, T. Gejo, and J. R. Huber, J. Phys. Chem. **100**, 7956 (1996).
[665] K. Kavita and P. K. Das, Chem. Phys. Lett. **338**, 118 (2001).
[666] F. Aguirre and S. T. Pratt, J. Chem. Phys. **118**, 1175 (2003).
[667] P. M. Kroger, P. C. Demou, and S. J. Riley, J. Chem. Phys. **65**, 1823 (1976).
[668] J. B. Koffend and S. R. Leone, Chem. Phys. Lett. **81**, 136 (1981).
[669] J. E. Smedley and S. R. Leone, J. Chem. Phys. **79**, 2687 (1983).
[670] E. A. Wannenmacher, P. Felder, and J. R. Huber, J. Chem. Phys. **95**, 986 (1991).
[671] G. Baum, P. Felder, and J. R. Huber, J. Chem. Phys. **98**, 1999 (1993).
[672] M. Dantus, R. M. Bowman, M. Gruebele, and A. H. Zewail, J. Chem. Phys. **91**, 7437 (1989).
[673] C. Paterson, F. G. Godwin, and P. A. Gorry, Mol. Phys. **60**, 729 (1987).
[674] T. K. Minton, P. Fader, R. J. Brudzynski, and Y. T. Lee, J. Chem. Phys. **81**, 1759 (1984).
[675] T. K. Minton, G. M. Nathanson, and Y. T. Lee, Laser Chem. **7**, 297 (1987).
[676] G. M. Nathanson, T. K. Minton, S. F. Shane, and Y. T. Lee, J. Chem. Phys. **90**, 6157 (1989).
[677] T. K. Minton, G. M. Nathanson, and Y. T. Lee, J. Chem. Phys. **86**, 1991 (1987).
[678] D. Krajnovich, L. J. Butler, and Y. T. Lee, J. Chem. Phys. **81**, 3031 (1984).
[679] H. J. Hwang and M. A. El-Sayed, J. Chem. Phys. **94**, 4877 (1991).
[680] J. E. Freitas, M. A. El-Sayed, and H. J. Hwang, J. Phys. Chem. **99**, 7395 (1995).
[681] J. E. Freitas, H. J. Hwang, and M. A. El-Sayed, J. Phys. Chem. **98**, 3322 (1994).
[682] G. A. Oldershaw, D. A. Porret, and A. Smith, J. Chem. Soc. Faraday Trans. 1 **68**, 2218 (1972).
[683] T. Donohue and J. R. Wiesenfeld, J. Chem. Phys. **63**, 3130 (1975).
[684] R. Roy, G. T. Kraemer, and S. Manzhos, J. Chem. Phys. **117**, 9353 (2002).
[685] I. Levy and M. Shapiro, J. Chem. Phys. **89**, 2900 (1988).
[686] N. Balakrishnan, A. Alekseyev, and R. Buenker, Chem. Phys. Lett. **341**, 594 (2001).
[687] D. N. Jodoin and A. Brown, J. Chem. Phys. **123**, 054301 (2005).
[688] J. F. Black, J. Chem. Phys. **98**, 6853 (1993).
[689] Y. Amatatsu, S. Yabushita, and K. Morokuma, J. Chem. Phys. **100**, 4894 (1994).
[690] I. Nadler, H. Roister, and C. Wittig, Chem. Phys. Lett. **103**, 451 (1984).
[691] P. W. Kash and L. J. Butler, J. Chem. Phys. **96**, 8923 (1992).
[692] W. Krieger, J. Hager, and J. Pfab, Chem. Phys. Lett. **85**, 69 (1982).
[693] A. P. Baronavski, Chem. Phys. **66**, 217 (1982).
[694] W. H. Fisher, R. Eng, T. Carrington, C. H. Dugan, S. V. Filseth, and C. M. Sadowski, Chem. Phys. **89**, 457 (1984).
[695] F. Shokoohi, S. Hay, and C. Wittig, Chem. Phys. Lett. **110**, 1 (1984).
[696] M. A. O'Halloran, H. Joswig, and R. N. Zare, J. Chem. Phys. **87**, 303 (1987).
[697] E. Hasselbrink, J. R. Waldeck, and R. N. Zare, Chem. Phys. **126**, 191 (1988).
[698] J. F. Black, E. Hasselbrink, J. R. Waldeck, and R. N. Zare, Mol. Phys. **71**, 1143 (1990).
[699] G. E. Hall, N. Sivakumar, and P. L. Houston, J. Chem. Phys. **84**, 2120 (1986).
[700] W. H. Fisher, T. Carrington, S. V. Filseth, C. M. Sadowski, and C. H. Dugan, Chem. Phys. **82**, 443 (1983).
[701] K. Chen, C. Kuo, M. Tzeng, M. Shian, and S. E. Chung, Chem. Phys. Lett. **221**, 341 (1994).
[702] W. Hasselbrink, J. R. Waldeck, and R. N. Zare, Chem. Phys. **126**, 191 (1989).
[703] H. Joswig, M. A. O'Halloran, R. N. Zare, and M. S. Child, Faraday Discuss. Chem. Soc. **82**, 79 (1986).
[704] M. Dantus, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. **87**, 2395 (1987).
[705] M. J. Rosker, M. Dantus, and A. H. Zewail, J. Chem. Phys. **89**, 6113 (1988).
[706] M. J. Rosker, M. Dantus, and A. H. Zewail, Science **241**, 1200 (1988).
[707] M. Dantus, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. **89**, 6128 (1988).
[708] A. H. Zewail, Science **242**, 1645 (1988).
[709] R. Heather and H. Metiu, Chem. Phys. Lett. **157**, 505 (1989).
[710] M. H. M. Janssen, R. M. Bowman, and A. H. Zewail, Chem. Phys. Lett. **172**, 99 (1990).
[711] C. Wan, M. Gupta, and A. H. Zewail, Chem. Phys. Lett. **256**, 279 (1996).
[712] M. D. Pattengill, Chem. Phys. **87**, 419 (1984).
[713] B. A. Wait, H. Helvajian, B. I. Dunlap, and A. P. Baronavski, Chem. Phys. Lett. **111**, 544 (1984).
[714] E. M. Goldfield, P. L. Houston, and G. S. Ezra, J. Chem. Phys. **84**, 3120 (1986).
[715] Y. Wang and C. X. W. Qian, Chem. Phys. Lett. **219**, 389 (1994).
[716] M. D. Morse, K. F. Freed, and Y. B. Band, J. Chem. Phys. **70**, 3620 (1979).
[717] J. A. Beswick and W. M. Gelbart, J. Phys. Chem. **84**, 3148 (1980).

[718] R. Schinke and V. Engel, J. Chem. Phys. **83**, 5068 (1985).
[719] H. Guo and G. C. Schatz, J. Chem. Phys. **92**, 1634 (1990).
[720] J. Qian, D. J. Tannor, Y. Amatatsu, and K. Morokuma, J. Chem. Phys. **101**, 9597 (1994).
[721] R. D. Coalson and M. Karplus, J. Chem. Phys. **93**, 3919 (1990).
[722] C. J. Williams, J. W. Qian, and D. J. Tannor, J. Chem. Phys. **95**, 1721 (1991).
[723] S.-Y. Lee, J. Chem. Phys. **97**, 227 (1992).
[724] R. Baer and R. Kosloff, Chem. Phys. Lett. **200**, 183 (1992).
[725] S. Yabushita and K. Morokuma, Chem. Phys. Lett. **175**, 518 (1990).
[726] Y. Wang and Ch. X. W. Qian, J. Chem. Phys. **100**, 2707 (1994).
[727] Y. Wang and C. X. W. Qian, Chem. Phys. Lett. **219**, 389 (1994).
[728] J. M. Bowman, R. C. Mayrhofer, and Y. Amatatsu, J. Chem. Phys. **101**, 9469 (1994).
[729] H. Wei and T. Carrington, Jr., J. Chem. Phys. **105**, 141 (1996).
[730] F. N. Dzegilenko, J. M. Bowman, and Y. Amatatsu, Chem. Phys. Lett. **264**, 24 (1997).
[731] R. O. Johnson, C. Littrell, P. B. Kelly, and J. L. Kinsey, J. Chem. Phys. **100**, 7743 (1996).
[732] Y. Amatatsu, K. Morokuma, and S. Yabushita, J. Chem. Phys. **94**, 4858 (1991).
[733] Y. Amatatsu, S. Yabushita, and K. Morokuma, J. Chem. Phys. **104**, 9783 (1996).
[734] K. Q. Lao, M. D. Person, P. Xayariboun, and L. J. Butler, J. Chem. Phys. **92**, 823 (1990).
[735] J. L. Knee, L. R. Khundkar, and A. H. Zewaii, J. Chem. Phys. **83**, 1996 (1985).
[736] P. K. Sparks, K. Shobadake, L. R. Carlson, and Y. T. Lee, J. Chem. Phys. **75**, 3838 (1981).
[737] M. Shapiro and R. Berson, J. Chem. Phys. **73**, 3810 (1980).
[738] H. W. Hermann and S. R. Leone, J. Chem. Phys. **76**, 4766 (1982).
[739] M. Shapiro, J. Phys. Chem. **90**, 3644 (1986).
[740] W. K. Kang, K. W. Jung, D. C. Kim, K.-H. Jung, and H.-S. Im, Chem. Phys. **196**, 363 (1995).
[741] H. Kanamori, S. R. Leone, and E. Hirota, IMS Ann. Rev., Inst. Mol. Sci. **II-A-9** (1988).
[742] R. E. Continetti, B. A. Balko, and Y. Lee, J. Chem. Phys. **89**, 3383 (1988).
[743] G. E. Hall, T. J. Sears, and J. M. Frye, J. Chem. Phys. **90**, 6234 (1989).
[744] T. Suzuki, H. Kanamori, and E. Hirota, J. Chem. Phys. **94**, 6607 (1991).
[745] M. Zahedi, J. A. Harrison, and J. W. Nibler, J. Chem. Phys. **100**, 4043 (1993).
[746] P. C. Samartzis, B. L. G. Bakker, D. H. Parker, and T. Kitsopoulos, J. Phys. Chem. A **103**, 6106 (1999).
[747] H. Guo, K. Q. Lao, G. C. Schatz, and A. D. Hammerich, J. Chem. Phys. **94**, 6562 (1991).
[748] H. Guo, J. Chem. Phys. **96**, 2731 (1992).
[749] H. Guo, J. Chem. Phys. **96**, 6629 (1992).
[750] A. D. Hammerich, U. Manthe, R. Kosloff, H. D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **101**, 5623 (1994).
[751] R. Schinke, *Photodissociation Dynamics: Spectroscopy and Fragmentation of Small Polyatomic Molecules* (Cambridge Univ. Press, London, 1993).
[752] S. North, T. Sears, G. Hall, and T. Suzuki, Chem. Phys. **211**, 515 (1996).
[753] D. W. Chandler, J. W. Thoman, Jr., M. H. M. Janssen, and D. H. Parker, Chem. Phys. Lett. **156**, 151 (1989).
[754] Y. F. Zhu and E. R. Grant, J. Phys. Chem. **97**, 9582 (1993).
[755] A. Strobel, A. Lochschmidt, I. Fischer, G. Niedner-Schatteburg, and V. Bondybey, J. Chem. Phys. **99**, 733 (1993).
[756] A. Strobel, I. Fischer, A. Lochschmidt, K. Muller-Dethlefs, and V. Bondybey, J. Phys. Chem. **98**, 2024 (1994).
[757] T. Schultz and I. Fischer, J. Phys. Chem. A **101**, 5031 (1997).
[758] I. Powis and J. F. Black, J. Phys. Chem. **93**, 2461 (1989).
[759] J. A. Syage and J. Steadman, J. Phys. Chem. **94**, 7343 (1990).
[760] M. H. M. Janssen, J. W. G. Mastenbroek, and S. Stolte, J. Phys. Chem. A **101**, 7605 (1997).
[761] S. J. Garrett, D. H. Fairbrother, V. P. Holbert, E. Weitz, and P. C. Stair, Chem. Phys. Lett. **219**, 409 (1994).
[762] H. Guo and G. C. Schatz, J. Chem. Phys. **93**, 393 (1990).
[763] S. Y. Lee and E. J. Heller, J. Chem. Phys. **76**, 3035 (1982).
[764] P. K. Swaminathan, C. D. Stoden, and D. A. Icha, J. Chem. Phys. **90**, 5501 (1989).
[765] D. A. Micha and C. D. Stodden, J. Phys. Chem. **105**, 2890 (2001).
[766] D. Ajitha, M. Wierzbowska, R. Lindh, and P. A. Malmqvist, J. Chem. Phys. **121**, 5761 (2004).
[767] D. C. Clary, J. Chem. Phys. **84**, 4288 (1986).
[768] X. Wang, Z. Tian, T. Shi, X. Shi, D. Yang, and Q. Zhu, Chem. Phys. Lett. **380**, 600 (2003).
[769] M. Quack, E. Sutcliffe, P. A. Hackett, and D. M. Rayner, Faraday Discuss. Chem. Soc. **82**, 229 (1986).
[770] M. Suh, W. Sung, S. U. Heo, and H. J. Hwang, J. Phys. Chem. A **103**, 8365 (1999).
[771] S. Hennig, V. Engel, and R. Schinke, J. Chem. Phys. **84**, 5444 (1986).
[772] E. Gerck, Opt. Commun. **41**, 102 (1982).
[773] P. Das, T. Venkitachalam, and R. Bersohn, J. Chem. Phys. **80**, 4859 (1984).
[774] H. Brunet, Ph. Chauvet, M. Marbu, and L. Torchin, Chem. Phys. Lett. **117**, 371 (1985).
[775] M. I. Urrecha, F. Castano, and J. Iturbe, J. Chem. Soc. Faraday Trans. 2 **82**, 1077 (1986).
[776] P. Cadman, Faraday Discuss. Chem. Soc. **53**, 170 (1972).
[777] I. Smith, Faraday Discuss. Chem. Soc. **53**, 170 (1972).
[778] J. P. Sung, R. J. Malins, and D. W. Setser, J. Phys. Chem. **83**, 1007 (1979).
[779] P. Beadle, M. R. Dunn, N. B. H. Jonathan, J. P. Liddy, and J. C. Nayor, J. Chem. Soc. Faraday Trans. 2 **74**, 2170 (1978).
[780] T. Trickl and J. Wanner, J. Chem. Phys. **78**, 6091 (1983).
[781] T. V. Venkitachalam, P. Das, and R. Barson, J. Am. Chem. Soc. **105**, 7452 (1983).
[782] R. D. Bower and T. T. Yang, J. Opt. Soc. Amer. B **8**, 1583 (1991).
[783] J. Wanner, Ber. Bunsen Ges. Phys. Chem. **81**, 129 (1977).
[784] R. W. Schwenz, J. V. Gilbert, and R. D. Coombe, Chem. Phys. Lett. **207**, 526 (1993).
[785] M. A. Nazar, J. C. Polanyi, and W. J. Skrlac, Chem. Phys. Lett. **29**, 473 (1974).
[786] U. Dinur and R. D. Levine, Chem. Phys. Lett. **31**, 410 (1975).
[787] R. D. Sharma and C. A. Brau, J. Chem. Phys. **50**, 924 (1969).
[788] J. Ewing, Chem. Phys. Lett. **29**, 50 (1974).
[789] E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon, Oxford, New York, 1974).
[790] E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer, Berlin, 1974).
[791] S. L. Dobychin, A. B. Pavlov, V. P. Fokanov, and V. S. Shpak, DAN SSSR **253**, 383 (1980).
[792] N. P. D. French and K. P. Lawley, Chem. Phys. **22**, 105 (1977).
[793] M. Y. Ovchinnikova, Khim. Phys. **1**, 44 (1982).
[794] V. A. Alekseev, T. L. Andreeva, V. N. Volkov, and E. A. Yukov, Sov. Phys.-JETP **63**, 452 (1972).
[795] A. Gallagher, Phys. Rev. **163**, 206 (1967).
[796] F. A. Franz, G. Leutert, and R. T. Shuey, Hel. Phys. Acta. **40**, 778 (1967).
[797] A. Gallagher, Phys. Rev. **157**, 68 (1967).
[798] E. P. Gordeyev, E. E. Nikitin, and M. Ya. Ovchinnikova, Can. J. Phys. **47**, 1819 (1969).
[799] H. M. Gibbs, G. G. Churchill, T. R. Marshall, J. F. Papp, and F. A. Franz, Phys. Rev. Lett. **25**, 263 (1970).
[800] A. Gallagher, Phys. Rev. **172**, 88 (1968).
[801] E. A. Yukov, Sov. J. Quantum Electron. **3**, 117 (1973).
[802] A. C. Stanton, J. C. Wormhoudt, and J. W. Duff, *Spectral Line Shapes*, Vol. 2 (Walter de Gruyter, Berlin, 1993).
[803] T. D. Padrick and R. E. Palmer, J. Chem. Phys. **62**, 3350 (1975).
[804] D. Cerny, R. Bacis, B. Bussery, M. Nota, and J. Verges, J. Chem. Phys. **95**, 5790 (1991).
[805] M. V. Zagidullin, V. D. Nikolaev, M. I. Svistun, and N. A. Khvatov, Kvantovaya Elektronika **31**, 373 (2001).
[806] A. I. Reznikov and S. Y. Umanskii, Chem. Phys. Reports **16**, 171 (1997).
[807] E. S. Muchtar, H. J. Baker, and T. A. King, Chem. Phys. Lett. **24**, 167 (1978).
[808] S. Churassy, R. Bacis, A. J. Bouvier, C. dit Mery, B. Erba, J. Bachar, and S. Rosenwaks, Appl. Phys. Lett. **62**, 31 (1987).
[809] W. Thieme and E. Hill, Opt. Commun. **36**, 361 (1981).
[810] S. Wright, M. F. Tuchler, and J. D. McDonald, Chem. Phys. Lett. **226**, 570 (1994).
[811] M. F. Tuchler, S. Wright, and J. D. McDonald, J. Chem. Phys. **106**, 2634 (1997).

[812] A. Sanov, T. Sanford, S. Nandi, and W. C. Lineberger, J. Chem. Phys. **111**, 664 (1999).
[813] N. Delaney, J. Faeder, and R. Parson, J. Chem. Phys. **111**, 651 (1999).
[814] A. Sanov, J. Faeder, R. Parson, and W. C. Lineberger, Chem. Phys. Lett. **313**, 812 (1999).
[815] J. Lu, F. Shao, and K. Fan, Chem. Phys. Lett. **329**, 461 (2000).
[816] M. Shapiro and P. Brumer, *Advances in Atomic, Molecular and Optical Phisics* (Academic, San Diego, CA, 2000).
[817] V. S. Batista and P. Brumer, J. Phys. Chem. A **105**, 2591 (2001).
[818] W. Muller-Markgraf and M. J. Rossi, Int. J. Chem. Kinet. **27**, 403 (1995).
[819] M. Tsuji, M. Ide, E. Oda, and Y. Nishimura, J. Chem. Phys. **109**, 3374 (1998).
[820] M. Tsuji, M. Furusawa, H. Kouno, and Y. Nishimura, J. Chem. Phys. **94**, 4291 (1991).
[821] M. Tsuji, T. Muraoka, H. Kouno, and Y. Nishimura, J. Chem. Phys. **97**, 1079 (1992).
[822] M. Pettersson and J. Nieminen, Chem. Phys. Lett. **283**, 1 (1998).
[823] M. Macler, J.-P. Nicolai, and M. C. Heaven, J. Chem. Phys. **91**, 674 (1989).
[824] R. Bohling, J. Langen, and U. Schurath, Chem. Phys. **130**, 419 (1989).
[825] W. G. Lawrence and V. A. Apkarian, J. Chem. Phys. **101**, 1820 (1994).
[826] J. Helbing and M. Chergui, J. Phys. Chem. A **104**, 10293 (2000).
[827] A. I. Krylov and R. B. Greber, J. Chem. Phys. **100**, 4242 (1994).
[828] Y. Amatatsu and K. Morokuma, Chem. Phys. Lett. **245**, 469 (1995).
[829] P. G. Barker, J. H. Purnell, and B. C. Young, Trans. Faraday Soc. **66**, 2244 (1970).
[830] S. R. Coon, K. B. Myli, and V. H. Grassian, J. Phys. Chem. **99**, 16416 (1995).
[831] E. T. Jensen and J. C. Polanyi, J. Chem. Phys. **97**, 2257 (1993).
[832] J. C. Polanyi, N. Sze, and J. Wang, J. Phys. Chem. A **101**, 6679 (1997).
[833] J. Kutzner, G. Lindeke, K. H. Welge, and D. Feldmann, J. Chem. Phys. **90**, 548 (1989).
[834] D. H. Fairbrother, K. A. Briggman, P. C. Stair, and E. Weitz, J. Phys. Chem. **98**, 13042 (1994).
[835] D. Fairbrother, K. A. Briggman, P. C. Stair, and E. Weitz, J. Chem. Phys. **102**, 7267 (1995).
[836] K. A. Trentelman, D. H. Fairbrother, P. G. Strupp, P. C. Stair, and E. Weitz, J. Chem. Phys. **96**, 9221 (1992).
[837] M. Karavitis and V. A. Apkarian, J. Phys. Chem. B **106**, 8466 (2002).
[838] A. V. Benderskii, R. Zadoyan, and V. A. Apkarian, J. Chem. Phys. **107**, 8437 (1997).