

Time-resolved laser magnetic resonance study of deactivation of $\text{Cl}(^2P_{1/2})$

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Rate constants for the collisional deactivation of spin-orbitally excited Cl^* ($\equiv \text{Cl}(^2P_{1/2})$) atoms by some selected gases have been determined using time-resolved laser magnetic resonance (LMR) techniques. Cl^* atoms were produced by photodissociation of ICl at 248 nm, and the relative quantum yield of Cl^* atoms is determined to be 0.47 ± 0.06 . The rate constants for the relaxation of Cl^* ($\times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$, $\pm 2\sigma$) by $\text{H}_2(5.5 \pm 1.6)$, $\text{HF}(1.4 \pm 0.4)$, $\text{DF}(0.7 \pm 0.2)$, $\text{DCI}(0.7 \pm 0.2)$, $\text{HBr}(1.2 \pm 0.36)$, $\text{DBr}(1.4 \pm 0.4)$, $\text{NO}(0.66 \pm 0.2)$, $\text{SO}_2(1.9 \pm 0.5)$, $\text{N}_2\text{O}(0.63 \pm 0.2)$, $\text{NF}_3(22 \pm 6)$, $\text{CH}_4(1.9 \pm 0.6)$, $\text{CD}_4(13 \pm 4)$, $\text{CF}_4(2.4 \pm 0.7)$, $\text{SiF}_4(14 \pm 4)$, and $\text{SF}_6(18 \pm 5)$ at 298 K are reported. The rate constants of the reactions of ground state $\text{Cl}(^2P_{3/2})$ atoms with HBr and DBr were found to be, in units of $\times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$, 0.75 ± 0.15 and 0.50 ± 0.10 , respectively. The study of the deactivation process $\text{I}(^2P_{1/2}) + \text{ICl} \rightarrow \text{Cl}^* + \text{I}_2$ (a), $\text{Cl} + \text{I}_2$ (b), $\text{I} + \text{ICl}$ (c) yielded the ratios $k_a/(k_a + k_b) = 0.63 \pm 0.17$, $k_a/(k_a + k_b + k_c) \geq 0.70$. © 2000 American Institute of Physics. [S0021-9606(00)01406-9]

I. INTRODUCTION

There has been considerable work in the past two decades on the collisional deactivation of spin-orbitally excited $\text{Cl}[3p^5(^2P_{1/2})]$ atoms. For convenience, hereafter the spin-orbitally excited $\text{Cl}(^2P_{1/2})$ and $\text{I}(^2P_{1/2})$ states will be denoted Cl^* and I^* , while the ground $^2P_{3/2}$ states are denoted Cl and I ; spin-orbit splittings in chlorine and iodine atoms are 882 cm^{-1} and 7603 cm^{-1} , respectively. The first studies were reported by Husain *et al.*,¹⁻⁵ who detected Cl^* atoms by time-resolved atomic resonance absorption in the vacuum ultraviolet. Later, the deactivation of Cl^* atoms was studied by the time-resolved laser magnetic resonance (LMR) technique in the work of our group.⁶⁻¹¹ For several quenchers, our data appear to disagree substantially (by two orders of magnitude) with those obtained by Husain *et al.* Note that the time-resolved LMR was used in two modifications; fast magnetic field jump method^{6,9,10} and laser photolysis method;^{7-9,11} in both cases the same results were obtained.

The rate of deactivation of Cl^* by ICl was found to be 33 times lower than the rate of the $\text{Cl} + \text{ICl}$ reaction,⁷ and this fact has stimulated the creation of a photodissociative-chemical laser, operating on the spin-orbital transition of the chlorine atom.¹² This laser was applied by Sotnichenko *et al.* to study collisional quenching of Cl^* ,^{13,14} 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.^{15,16} 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.¹⁷

This paper reports measurements of rate constants for the quenching of Cl^* by 15 simple gases, including 4 for which the rate constants have been measured previously by other methods. Of particular interest are those deactivation

processes which should occur via $E-R, T$ energy transfer. The rates of these processes are unexpectedly large, in strong contradiction with theoretical estimates.^{18,19}

Another impetus of this research is the study of the deactivation of I^* by ICl . While the overall deactivation rate constant for this process is reported in the literature,²⁰⁻²² to date there exists only one quantitative study reported by Nadkhin and Gordon²³ concerning the relative importance of the three available pathways.

Also, the yield of Cl^* from the photodissociation of ICl at 248 nm is remeasured because our previous determination²⁴ was based on the assumption that the yield of I^* is negligible.^{25,26} Direct observation of I^* atoms from the photodissociation of ICl reported by Tonokura *et al.* invalidated this assumption.²⁷

II. EXPERIMENT

A. LMR spectrometer

The intracavity LMR apparatus used here is similar to that described elsewhere,^{7,8,11} and it is shown schematically in Fig. 1. Excited Cl^* or ground state Cl atoms were produced by pulsed laser photolysis of ICl or COCl_2 , respectively. The photolysis source was a KrF-laser (ELI-94, 248 nm, 50 mJ/pulse, at 3 Hz). Gas mixtures were pumped through a photolysis cell (2.9 cm i.d.) at a rate of $\sim 3 \text{ m/s}$. The cell was inserted into the cavity of a CO_2 -laser and was subjected to oscillating (150 kHz, 200 W, double modulation amplitude is 65 G) and constant magnetic fields. The cell incorporated two NaCl windows for CO_2 -laser radiation and one quartz window for UV radiation. The spaces between the windows and reaction zone of the cell ($\sim 30 \text{ cm}$) were continuously flushed with Ar. The reaction zone (limited by the modulation field length) was 12 cm long. The unfocused excimer laser beam was directed into the cell at a small angle (about 3°) to the CO_2 -laser radiation beam. This geometry ensured a large overlap area of the beams. The diameter of

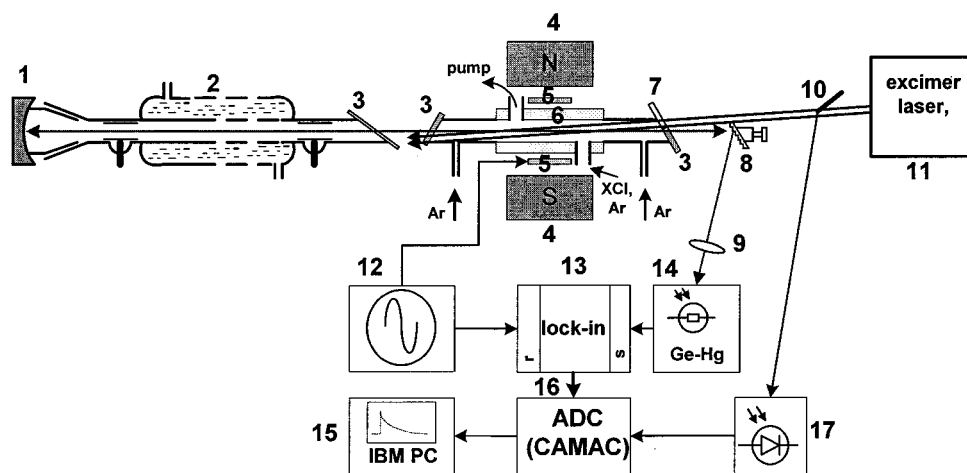


FIG. 1. Schematic representation of the LMR spectrometer. (1) spherical mirror, (2) thermostated discharge tube of CO_2 laser (14 mm i.d., 2 m long), (3) NaCl or AsGa Brewster window, (4) pole pieces of electromagnet (20 cm), (5) rectangular modulation coils cooled by forced air, (6) Teflon photolysis cell, (7) quartz window, (8) reflection grating (100 grooves/mm) set on piezoelectric translator, (9) NaCl lens, (10) mirror, (11) UV excimer laser, (12) modulation generator, (13) lock-in amplifier, (14) Ge-Hg photoresistor, (15) computer, (16) ADC (10-bit, 4096 channels), (17) photodiode with amplifier.

the excimer laser beam was larger than the diameter of the CO_2 -laser beam. The exiting CO_2 -laser radiation (≈ 0.5 W) went to a Ge-Hg photoresistor, cooled by solid N_2 (53 K). The signal of the photoresistor was detected by a lock-in amplifier, digitized, and transferred to a computer.

Cl atoms were detected by fine structure absorption using the 11 P(36) line of a $^{13}\text{CO}_2$ -laser (882.287 cm^{-1}) in $E \perp B$ polarization.^{28,29} The intense line of the LMR spectrum at ≈ 3.1 kG and the weak line at ≈ 1.1 kG were employed. Results were the same in both cases.

B. Gas handling

To reduce the $\text{H} \leftrightarrow \text{D}$ exchange problem, one flow line was used for deuterium-containing gases only, it was purged by DCl for a period of several weeks before the experiments; the second line was used for H-containing gases only. The ICl/Ar gas mixture was prepared by slow passage of Ar over crystalline ICl at room temperature. Downstream these mixtures were passed through a cooled trap at $5-18^\circ\text{C}$ before entering the low pressure reactor. The ICl pressure in the reactor was determined by the magnitude of the gas flow and the temperature of the trap. The pressure of HF (or DF) in the gas flow lines and the intermediate storage vessel was no more than 0.1 atm. At this pressure the deviation of the association factor from unity is < 0.012 .³⁰ Hence, the association was negligibly small.

ICl, DF, DCl, HBr, DBr, SO_2 , SiF_4 , and COCl_2 were prepared by standard techniques³¹ and contained $< 2\%$ of impurities. The deuterated gases DF, DCl, DBr were prepared in reactions $\text{CaF}_2 + \text{D}_2\text{SO}_4$, $\text{PCl}_3 + \text{D}_2\text{O}$, $\text{P} + \text{Br}_2 + \text{D}_2\text{O}$, respectively. Passivation of mass spectrometer lines by deuterated gases was not complete, hence the measured $[\text{H}]/[\text{D}]$ ratio was found to be < 0.1 ; presumably it is ≈ 0.01 . All other gases were commercial grades stated by the manufacturer to have the following purities: H_2 , 99%; HF, 99%; NO, 98%; N_2O , 99.5%; NF_3 , 97%; CH_4 , 99.9%; CD_4 , 99.7% ($[\text{H}]/[\text{D}] = 0.02$); CF_4 , 99.6%; SF_6 , 99.2%; Ar, 99.998%.

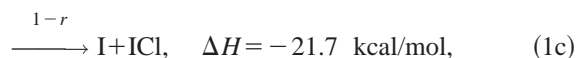
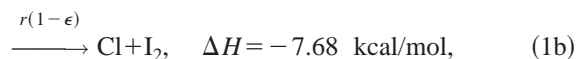
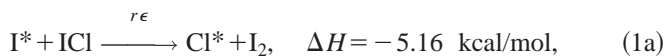
The purity of COCl_2 was checked by UV photometry; the purity of all other gases was controlled by mass spectrometry.

III. PHOTOLYTIC AND REACTIVE YIELDS OF Cl^* ATOMS

Yields of Cl^* atoms from the photodissociation of ICl at 248 nm and from the reaction of I^* with ICl were obtained by measuring the amplitudes of LMR signals of chlorine atoms following 248 nm photolysis of $\text{ICl}/(\text{O}_2)/(\text{SF}_6)/\text{Ar}$ mixtures.

The relative yields of Cl^* and I^* atoms in the photolysis of ICl are defined as $\beta \equiv [\text{Cl}^*]_0 / ([\text{Cl}^*]_0 + [\text{Cl}]_0)$ and $\gamma \equiv [\text{I}^*]_0 / ([\text{I}^*]_0 + [\text{I}]_0)$, respectively. Here $[\text{X}]_0$ and $[\text{X}^*]_0$ are the concentration of ground and excited atoms, respectively, immediately after a photodissociating pulse. Experimental data on these yields available from the literature are summarized in Table I.

Deactivation of I^* by ICl can proceed via three competing pathways,



here the relative yield of Cl^* atoms and the fraction of the total deactivation rate attributed to reactive channels are denoted as ϵ and r , respectively.

The method of data analysis for determination of β value has been described previously.^{7,33} We take advantage of the fact that I^* , in contrast to Cl^* , is deactivated relatively rapidly by O_2 with a rate constant of $(2.35 \pm 0.17) \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$;^{20,36-38} rapid nonreactive quenching of Cl^* may be attained by adding SF_6 (or NF_3 , or SiF_4).

TABLE I. Summary of Cl* and I* relative quantum yield determinations from ICl photodissociation.

λ nm ^a	Quantum yield	Detection	Ref.
530	$\beta=0.55\pm 0.05$	Cl LMR	7
480–530	$\beta(^3\Pi)=0.66-0.80$ ^b	Cl PFS ^c	32
447–532	$\beta=0.41-0.79$	Cl LMR	33
304.67/304.02	$\gamma=0.231$	I REMPI	34
266	$\beta=0.65\pm 0.06$	Cl LMR	33
248.5	$\beta=0.67\pm 0.05$ ^d	Cl LMR	24
248.5	$\beta=0.47\pm 0.06$	Cl LMR	this study
248.5	$\gamma=0.413\pm 0.09$	I LIF	27
235.336/237.808	$\beta=0.405\pm 0.035$	Cl REMPI	27
235.336/237.808	$\beta+\gamma\leq 1$ ^e	Cl REMPI	27
236.286/237.808	$s^*/s=0.20\pm 0.04$ ^f	Cl REMPI	25
236.286/237.808	$\gamma\approx 0$ ^g	Cl REMPI	25
235.336/235.205	$\beta+\gamma=1$ ^h	Cl REMPI	35

^aWavelengths for X/X* (X=Cl,I) are shown for REMPI detection.

^b $\beta(^3\Pi)$ is Cl* relative yield from the photodissociation of ICl($B^3\Pi_{0+}$) state.

^cPFS = photofragment spectroscopy.

^dThis previous value is incorrect.

^eConcluded from analysis of Doppler profiles of chlorine atoms.

^f s^*/s is the ratio of REMPI signals.

^gConcluded from the unimodal velocity distribution of chlorine atoms.

^hConcluded from analysis of angular and velocity distributions of chlorine atoms.

The quantitative information was obtained in this study from comparison of three LMR signal amplitudes measured (i) without O₂ and SF₆, (ii) in excess O₂ but without SF₆, and (iii) in excess of O₂ and SF₆. These amplitudes were obtained by extrapolation of experimental kinetics to the moment of photolysis (Fig. 2), they are denoted as S_m^{**} , S_m^* , and S_m , respectively.

Generally, the LMR signal amplitude may be expressed as^{7,8}

$$S(t) = \Theta[\text{Cl}(t)] - (f^*/f) [\text{Cl}^*(t)], \quad (2)$$

here f and f^* are the statistical populations of the sublevels probed relative to the total populations of the $^2P_{3/2}$ and $^2P_{1/2}$ states, respectively ($f=1/16$, $f^*=1/8$); the Θ factor converts the chlorine atom concentration into LMR signal amplitude. With Eq. (2) the three amplitudes measured after complete deactivation of I* but before appreciable decay of Cl may be expressed as

$$S_m^{**}/\Theta = [\text{Cl}]_0 - 2[\text{Cl}^*]_0 + (1-3\epsilon)r[\text{I}^*]_0, \quad (3)$$

$$S_m^*/\Theta = [\text{Cl}]_0 - 2[\text{Cl}^*]_0 + \delta r(1-3\epsilon)[\text{I}^*]_0, \quad (4)$$

$$S_m/\Theta = [\text{Cl}]_0 + [\text{Cl}^*]_0 + \delta r[\text{I}^*]_0, \quad (5)$$

where $\delta \equiv \bar{k}_1[\text{ICl}]/(\bar{k}_{O_2}[\text{O}_2] + \bar{k}_1[\text{ICl}])$, \bar{k}_1 and \bar{k}_{O_2} denote overall rate constant for deactivation of I* by ICl and O₂, respectively; $\bar{k}_1 = k_{1a} + k_{1b} + k_{1c} = (2.4 \pm 0.9) \times 10^{-11}$ cm³/molecule·s.^{20–22}

Equation (5) implies the complete deactivation of Cl* by SF₆, Eqs. (3) and (4) imply that no appreciable decay of Cl* had occurred. Rearrangement of these equations gives the final relations,

$$S_m^*/S_m = (1-3\beta) + \frac{3\delta r\gamma(\beta-\epsilon)}{1+\delta r\gamma}, \quad (6)$$

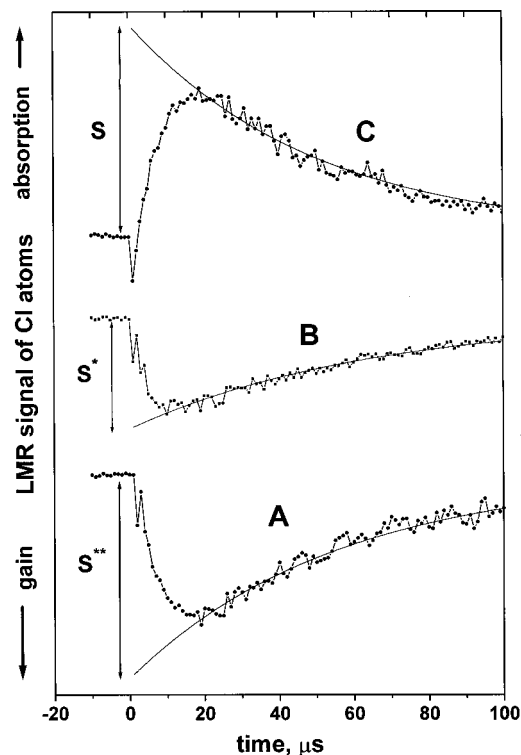


FIG. 2. Typical transient absorption LMR signal obtained on Cl($^2P_{1/2}-^2P_{3/2}$) transition when 0.07 Torr of ICl in 10 Torr of Ar is photolysed. (A) No added deactivating gases; (B) excess O₂ is added; (C) O₂ and SF₆ are present in excess. Typical experimental conditions were $[\text{ICl}] = 3 \times 10^{15}$, $[\text{O}_2] = 2 \times 10^{16}$, $[\text{SF}_6] = 7 \times 10^{15}$, $[\text{Ar}] = 3 \times 10^{17}$, all in units of cm⁻³.

$$(S_m^{**} - S_m^*)/S_m = r\gamma(1-3\epsilon) \frac{1-\delta}{1+\delta r\gamma}. \quad (7)$$

Ideally, the excess of O₂ means $\delta=0$ and the expressions in square brackets may be omitted. In reality, the δ parameter was varied from 0.1 to 0.3; extrapolation to the $\delta=0$ limit made it possible to obtain the $(3\beta-1)$ and $r\gamma(3\epsilon-1)$ values.

In a more rigorous approach, the temporal behavior of transient species (Cl, Cl*, I*) was obtained as a solution of three kinetic equations; these two values were obtained from comparison of the experimental kinetics curves with those obtained from the solution of kinetic equations. It was found that the final result is rather insensitive to reasonable variations of the parameters of equations.

Finally, the analysis yields the values $\beta=0.47\pm 0.06$ and $r\gamma(3\epsilon-1)=0.45\pm 0.08$. After substitution of the γ value from the literature²⁷ the latter may be presented as $r(3\epsilon-1)=1.10\pm 0.32$. Errors quoted here are 2σ and represent mainly reproducibility of the data.

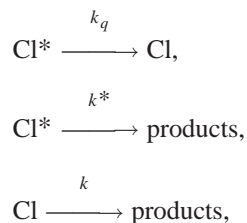
IV. DEACTIVATION OF Cl*

Total rate constants for Cl* deactivation by various M molecules were obtained by monitoring the kinetics of LMR signal following 248 nm photolysis of ICl/O₂/M/Ar mixtures.

The method of data analysis has been described previously^{7,8,11} and only a brief outline will be given here.

Photolysis of ICl at 248 nm produces excited Cl^* and I^* atoms. In all experiments molecular oxygen was present in excess to quench I^* on a time scale of a 1–3 μs , shorter than the time resolution of our LMR spectrometer (4 μs),⁶ therefore, under our experimental conditions excited I^* atoms were of no importance.

A simple kinetic scheme describing the time evolution of the chlorine atom concentration after photodissociation is provided below,



here k_q and k^* are the pseudo-first-order rate constants for nonreactive and reactive deactivation of Cl^* , respectively; k is the pseudo-first-order rate constant for decay of the ground state Cl atoms. They are related with bimolecular rate constants by expressions,

$$k_q = k_{qM}[\text{M}] + k_{q\text{O}_2}[\text{O}_2] + k_{q\text{Ar}}[\text{Ar}] + k_{q\text{ICl}}[\text{ICl}],$$

$$k^* = k_M^*[\text{M}] + k_D^*,$$

$$k = k_{\text{ICl}}[\text{ICl}] + k_M[\text{M}] + k_D,$$

where k_D^* and k_D correspond to diffusion of chlorine atoms, $k_{\text{ICl}} = (8 \pm 1) \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$.³⁹

From the kinetic scheme, two differential equations are obtained governing the temporal behavior of Cl^* and Cl. The solution of these equations is

$$S(t) = \Theta[\text{Cl}^*]_0 (C_k \exp(-kt) + C_\lambda \exp(-\lambda t)), \quad (8)$$

where $S(t)$ is defined by Eq. (2), $\lambda \equiv k_q + k^*$, and

$$C_k = 1/\beta - 1 - k_q/(k - \lambda), \quad (9)$$

$$C_\lambda = k_q/(k - \lambda) - f^*/f. \quad (10)$$

Figure 3 shows examples of the LMR signal kinetics at various pressures of a quencher M under conditions where both $[\text{ICl}]$ and $[\text{O}_2]$ are constant. As follows from Eq. (8), the procedure to obtain the rate constant for deactivation of Cl^* by the M quencher is as follows. The temporal profiles are decomposed into the sum of two exponentials; the inverse lifetimes of these exponentials are plotted vs $[\text{M}]$. These plots must be linear; their slopes are reaction rate constant k_M and deactivation rate constant $k_{qM} + k_M^*$. If there is no $\text{Cl}^* + \text{M}$ reaction, one of the plots (k) must be $[\text{M}]$ independent. Figure 4 shows examples of the variations of λ with $[\text{M}]$.

This procedure for data analysis has several drawbacks: First, it does not use all experimental information since C_k and C_λ remain unused; second, it is impossible *a priori* to assign exponents to either the Cl reaction or the Cl^* deactivation when $k_q/(k - k^*) > 2/3$;⁷ third, the least squares fit becomes insensitive to the difference between λ and k when $\lambda \approx k$. Hence, a more elaborate procedure was employed; all the kinetics obtained at various $[\text{M}]$ were fitted simulta-

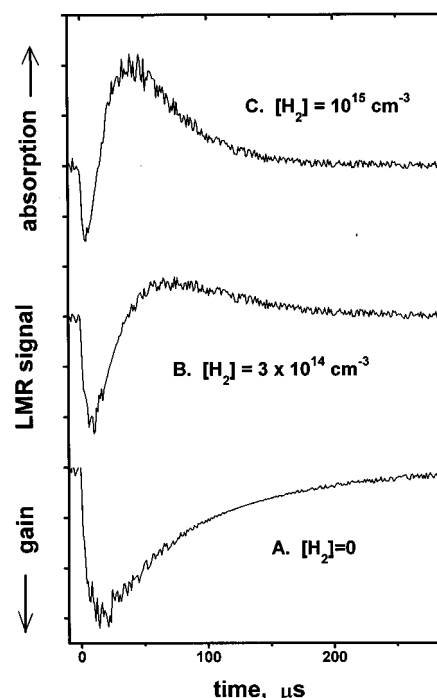


FIG. 3. Typical LMR signal kinetics of Cl atoms obtained in the photolysis of ICl at various concentrations of the quencher H_2 . The kinetics were decomposed into the sum of two exponents, see Eq. (8). One of these exponents correspond to the removal of excited Cl^* atoms due to deactivation by H_2 , O_2 , and ICl and another exponent correspond mainly to reaction of unexcited Cl atoms with ICl. The reciprocal time for the later case was constant ($\approx 30 \text{ ms}^{-1}$). Typical experimental conditions were $[\text{ICl}] = 2 \times 10^{15}$, $[\text{O}_2] = 2.5 \times 10^{16}$, and $[\text{Ar}] = 3 \times 10^{17}$, all in units cm^{-3} .

neously by expression (8). Normally, the variables of the fit were k_{qM} and Θ parameters; otherwise the Θ parameter was individual for every kinetics curve; the k value was determined beforehand from single-exponent kinetics obtained at

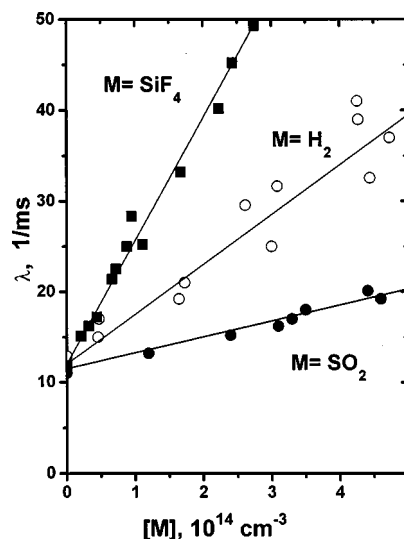


FIG. 4. Typical plots of reciprocal time for removal of Cl^* atoms vs concentration of deactivating gases, $\text{M} = \text{SiF}_4$, H_2 , SO_2 . Lines are obtained from least squares analyses and give the deactivation rate constants. The intercept of the plots corresponds mainly to deactivation of Cl^* by O_2 , ICl, Ar, and impurities.

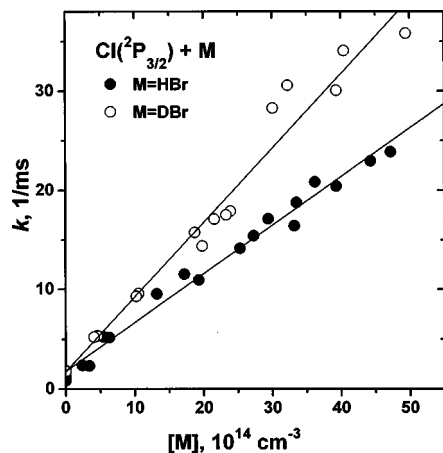


FIG. 5. Typical plots of reciprocal time for removal of ground state Cl atoms vs concentration of reagents, HBr and DBr. Cl atoms are obtained in the photolysis of COCl_2 at various pressures of HBr and DBr in 10 Torr of Ar. Lines are obtained from least squares analyses and give the reaction rate constants. The intercept of the plots corresponds mainly to diffusion of Cl atoms from the detection zone. Experimental conditions were $[\text{COCl}_2]=4 \times 10^{15}$, $[\text{Ar}]=3 \times 10^{17}$, all in units of cm^{-3} .

excess of quencher ($\lambda \gg k$). Also, the quantum yield of excited Cl^* atoms β was optimized. Within experimental error, the optimal value of this parameter agrees with the value obtained in LMR measurements described above. The $k_{\text{ICl}}^*/k_{q\text{ICl}}$ ratio was varied also. However, the mean squares residual was found to be insensitive to this ratio.

In some cases (H_2 , DCl , CH_4 , CD_4) a nearly termoneutral reaction between quencher and Cl^* is possible. Hence the dependence of k^* on $[\text{M}]$ was included in the fit. It was found for all these cases that the contribution of chemical reaction is negligible. In two other cases, $\text{Cl}^* + \text{HBr}(\text{DBr})$, the simplest data analysis was used: since the ground state Cl atoms react rapidly with HBr and DBr, $k_{\text{HBr}}^* + k_{q\text{HBr}}$ and $k_{\text{DBr}}^* + k_{q\text{DBr}}$ were easily extracted from the observed single exponential decays of Cl^* atoms.

V. Cl+HBr, DBr REACTIONS

If any H \leftrightarrow D exchange occurs in the flow lines or in the photolysis cell, the measured values for deactivation of Cl^* by deuterated reagents (DF, DCl, DBr, CD_4) are in doubt. This possibility was tested by measuring the rate constants known in the literature for the reactions of ground state Cl atoms with HBr and DBr.

The experimental approach is quite straightforward. It involves time-resolved LMR detection of Cl atoms following 248 nm pulsed laser photolysis of $\text{COCl}_2/\text{HBr}(\text{DBr})/\text{Ar}$ mixtures. Photolysis of COCl_2 at 248 nm produces CO and chlorine atoms of which $>95\%$ are formed in the ground spin-orbit state;²⁴ hence spin-orbit excitation of Cl atoms can be neglected. The LMR signal of Cl atoms displays a fast rise limited by time resolution of the LMR spectrometer followed by a slow exponential decay. The decay component is due mainly to the reaction of Cl with HBr or DBr. Figure 5 shows plots of the inverse decay time as a function of $[\text{HBr}]$ and $[\text{DBr}]$. The reaction rate constants obtained from the

TABLE II. Summary of Cl+HBr, DBr rate constant determinations.

$k(\text{Cl}+\text{HBr})^a$	Ref.	$k(\text{Cl}+\text{DBr})^a$	Ref.
7.5 ± 1.5	this work	5.0 ± 1.0	this work
7.4 ± 0.67	40	4.96 ± 0.5	40
3.4	41		
10.2 ± 1.5	42		
9.0	43		
7.9 ± 1.0	44		
8.4	45		
7.61 ± 1.8	46		

^aRate constants are in $10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$ units.

slopes of these plots are consistent with previous measurements, as summarized in Table II.

VI. DISCUSSION

A. Photolytic yields of Cl^* atoms

The present yield of Cl^* atoms from the photodissociation of ICl at 248 nm lies between the yields obtained by Tonokura *et al.* at 235–238 nm (Ref. 27) and by Mashnin *et al.* obtained at 266 nm.³³ Hence a smooth wavelength dependence of the yield seems reasonable.

Probably the most detailed experimental study on the mechanism of the photodissociation of ICl at 235–238 nm was carried out recently by Rogers *et al.*³⁵ The analysis of angular and speed distributions of Cl^* and Cl atoms led to the conclusion that there exist only $\text{I} + \text{Cl}^*$ and $\text{I}^* + \text{Cl}$ channels, hence $\beta + \gamma = 1$. To within experimental error, this conclusion is consistent with the present determination of β , although it is not clear if this conclusion is valid for the photodissociation of ICl at 248 nm.

B. Deactivation of I^* by ICl

Two parameters, ϵ and r , govern the deactivation of I^* by ICl. Only the $r(3\epsilon - 1)$ product is determined in the present study; from this product the estimates for the ϵr , ϵ , and r values have been obtained. In summary, the $\text{Cl}^* + \text{I}_2$ channel accounts for $r\epsilon = (63 \pm 17)\%$ of the overall deactivation rate of process (1), the yield of Cl^* in the reaction of I^* with ICl is $\epsilon \geq (70 \pm 10)\%$.

To date there exists only one other experimental study of Nadkhin and Gordon concerning the relative importance of the three pathways in $\text{I}^* + \text{ICl}$ deactivation process.²³ In this study, the $r\epsilon$ product was determined to be 0.54 ± 0.12 , in good agreement with the value obtained in the present study. Note that the measurements of Nadkhin and Gordon can not be attributed to the room temperature conditions, as a ‘‘hot atom’’ effect cannot be ruled out.

C. Deactivation of Cl^*

1. Consistency

The present results are summarized in Table III. Also shown are all the data on the deactivation of Cl^* available in the literature. In four cases there are data in the literature with which to compare our results. The present $\text{Cl}^* + \text{SO}_2$ deactivation rate constant is in excellent agreement with the

TABLE III. Summary of Cl^* deactivation rate constant determinations.

M	Rate constant ^a	Detection ^b	Ref.	M	Rate constant ^a	Detection ^b	Ref.
He	$3.8 \pm 0.6(-15)$	ARA VUV	2,3	NO	$0.66 \pm 0.2(-11)$	LMR	^c
	$7.3 \pm 2.0(-14)$	LMR(s), LMR	11	Cl_2	$4.5 \pm 0.4(-11)$	ARA VUV	2
Ne	$4.0 \pm 0.5(-14)$	ARA VUV	3,5		$7.4 \pm 2.6(-13)$	LMR(s)	6
	$\leq 4.2(-14)$	LMR(s)	9		$7.2 \pm 2.0(-13)$	LMR	7
Ar	$1.1 \pm 0.3(-12)$	ARA VUV	3,5	ICI	$3.3 \pm 0.5(-13)$	LMR	7
	$\leq 1.0(-14)$	LMR(s)	6		$4.0 \pm 1.0(-12)$	DLA	16
	$\leq 1.0(-14)$	ARA IR	13	CO	$\sim 6(-12)$	ARA VUV	5
	$\leq 2.7(-15)$	LMR	8,9		$8.0 \pm 2.0(-14)$	ARA IR	13
Kr	$1.4 \pm 0.2(-12)$	ARA VUV	3,5	CO_2	$< 5(-13)$	ARA VUV	5
	$\leq 5.4(-15)$	LMR(s), LMR	9		$1.5 \pm 0.4(-11)$	ARA IR	13
Xe	$1.8 \pm 0.2(-11)$	ARA VUV	3,5		$9.0 \pm 3.0(-12)$	LMR	11
	$\leq 4.5(-14)$	LMR(s), LMR	9	NOCl	$1.8 \pm 0.4(-11)$	LMR	8
H	$\sim 7(-11)$	ARA VUV	1		$1.1 \pm 0.5(-11)$	DLA	16
Cl	$3.0 \pm 1.5(-10)$	ARA IR	14	H_2O	$2.6 \pm 0.5(-12)$	ARA VUV	5
I	$5 \pm 2(-12)$	ARA IR	14		$7.8 \pm 2.3(-11)$	LMR(s)	10
H_2	$\leq 6 \times 10^{-13}$	ARA VUV	5	SO_2	$1.8 \pm 0.2(-11)$	Fluor. IR	17
	$7(-12)$	ARA VUV	1		$1.9 \pm 0.5(-11)$	LMR	^c
	$5.0 \pm 1.2(-11)$	ARA IR	13	N_2O	$3.7 \pm 0.6(-13)$	ARA VUV	5
	$8.0 \pm 2.0(-11)$	LMR	11		$6.3 \pm 2.0(-12)$	LMR	^c
D_2	$5.5 \pm 1.6(-11)$	LMR	^c	O_3	$\sim 7(-12)$ ^d	LMR	9
	$1.1 \pm 0.3(-11)$	ARA IR	13	NF_3	$2.2 \pm 0.6(-10)$	LMR	^c
	$1.7 \pm 0.4(-11)$	LMR	11	PCl_3	$1.3 \pm 0.2(-11)$	DLA	15
HF	$1.4 \pm 0.4(-11)$	LMR	^c	COCl_2	$3.0 \pm 1.0(-10)$	LMR	11
DF	$0.7 \pm 0.2(-11)$	LMR	^c	CF_3I	$1.0 \pm 0.3(-10)$	ARA IR	14
HCl	$1.1 \pm 0.1(-12)$	ARA VUV	5	CH_4	$3.9 \pm 0.8(-12)$	ARA VUV	5
	$6(-12)$	ARA VUV	1		$1.9 \pm 0.6(-11)$	LMR	^c
	$1.2 \pm 0.2(-11)$	DLA	15	CD_4	$1.3 \pm 0.4(-10)$	LMR	^c
	$1.2 \pm 0.3(-11)$	LMR	11	CCl_4	$2.1 \pm 0.4(-10)$	ARA VUV	4
DCl	$0.7 \pm 0.2(-11)$	LMR	^c		$2.0 \pm 0.2(-10)$	ARA VUV	2
HBr	$1.2 \pm 0.36(-11)$	LMR	^c		$5(-11)$	ARA VUV	1
DBr	$1.4 \pm 0.4(-11)$	LMR	^c		$1.8 \pm 0.6(-10)$	LMR(s)	9,10
	$2.3 \pm 0.3(-11)$	ARA VUV	5	CF_4	$1.5 \pm 0.4(-10)$	ARA VUV	4
O_2	$2.1 \pm 0.5(-11)$	ARA VUV	2		$2.7 \pm 0.8(-11)$	LMR(s)	10
	$1.7 \pm 0.4(-13)$	LMR(s)	6,7		$2.4 \pm 0.7(-11)$	LMR	^c
	$1.3 \pm 0.3(-13)$	ARA IR	13	CH_2Cl_2	$2.0 \pm 1.0(-10)$	DLA	15
	$1.3 \pm 0.3(-13)$	ARA IR	13	CF_2Cl_2	$2.1 \pm 0.4(-10)$	ARA VUV	4
N_2	$6.3 \pm 1.0(-13)$	ARA VUV	5		$1.8 \pm 0.4(-10)$	LMR(s)	6
	$4.0 \pm 1.0(-13)$	ARA IR	13		$1.8 \pm 0.4(-10)$	LMR	9
	$3.9 \pm 1.5(-14)$	LMR	11				

^a $a(-b) \equiv a \times 10^{-b}$, rate constants are in $\text{cm}^3/\text{molecule} \cdot \text{s}$ units.

^bARA VUV = atomic resonance absorption in the vacuum ultraviolet, LMR(s) = monitoring of saturation kinetics of LMR signal, LMR = laser photolysis followed by LMR signal detection, ARA IR = atomic resonance absorption in the infrared, DLA = diode laser absorption spectroscopy, Fluor. IR = fluorescence in the infrared.

^cThis work. The quoted error are 2 standard deviation in 3–4 determinations of the specified rate coefficient.

^dPreliminary data only.

result of Dolson and West determined by infrared fluorescence observations of $E-V$ energy transfer from Cl^* to SO_2 .¹⁷ Also the rate constants measured here for Cl^* deactivation by H_2 and SF_6 compare well to Sotnichenko's values obtained with a laser gain pulse method.¹³ Finally, the present result on deactivation of Cl^* by CF_4 is consistent with our previous LMR measurement with the fast magnetic field jump method.¹⁰

In general, the present results as summarized in Table III agree favorably with all recent Cl^* kinetic studies. The most serious differences exist with the early flash photolysis studies where Cl^* was monitored by resonant absorption in VUV. This disagreement was discussed earlier.⁶

2. $E-V$ energy exchange

By analogy with the nonreactive collisional deactivation of spin-orbitally excited I^* and Br^* , $E-V$ energy exchange

is apparently the dominate route for Cl^* quenching in most cases presented in Table III. Two energy transfer mechanisms are used at present time; long-range near-resonant transfer proposed by Ewing⁴⁷ and nonadiabatic curve-crossing proposed by Nikitin.^{48,49}

Both the mechanisms predict that the rate constant for deactivation of Cl^* by quencher M may be expressed as

$$k_{qM} = \sum_i A(I_i/\nu_i) \exp(-|\Delta E_i|/B), \quad (11)$$

here summation is over vibrational modes of the quencher, I_i and ν_i are the intensity and frequency of the i th absorption band of the quencher, $\Delta E_i \equiv h\nu_i - E_{\text{Cl}^*}$ is the energy defect of the $E-V$ transfer process, A and B are parameters. Here

TABLE IV. Data illustrating $E-V$ energy transfer from Cl^* to M .

M^a	mode	ν_i^b	I_i^c	ΔE_i	k_{exp}^d	k_{calc}^e	$k_{\text{exp}}/k_{\text{calc}}$
ICI		381	3.24	501	0.0033	0.0018	1.80
O_3^f	ν_3	1042	44.6 ^g	-160	0.07	0.83	0.08
	ν_1	1103	1.23 ^g	-221			
	ν_2	701	2.13 ^g	181			
CO_2	$\nu_2(2)$	667	27.0	215	0.090	0.29	0.31
NOCl	ν_3	596	92 ^h	287	0.18	0.54	0.33
N_2O	ν_2	1285	28.6	-403	0.063	0.040	1.56
	$\nu_3(2)$	589	4.25	293			
NF_3	$\nu_3(2)$	906	199	-24	2.2	1.8 ⁱ	1.22
SO_2	ν_1	1151	10.4	-269	0.18	0.10	1.82
	ν_3	1361	94	-479			
	ν_2	518	13	364			
COCl_2	ν_4	850	117.5	32	3.0	1.8 ⁱ	1.67
PCl_3	ν_1	515	18 ^h	367	0.13	0.21	0.63
	ν_3	504	78 ^h	378			
CH_4^f	$\nu_4(3)$	1306	17.5	-424	0.19	0.0077	25
CD_4	$\nu_4(3)$	996	10.8	-114	1.3	0.45	2.91
CCl_4	$\nu_3(3)$	776	194	106	1.8	1.8 ⁱ	1.00
CF_4	$\nu_3(3)$	1283	509	-401	0.27	0.36	0.75
	$\nu_4(3)$	632	4.67	250			
CCl_3F	$\nu_4(2)$	847	186.5	35	2.2	1.8 ⁱ	1.22
	ν_1	1085	87.3	-203			
CF_3I	ν_1	1080	230 ^j	-198	1.0	1.8 ⁱ	0.56
	$\nu_4(2)$	1187	230 ^j	-305			
	ν_2	742	14 ^j	140			
CH_3Cl	ν_3	732	11.0	150	0.50	0.37	1.36
	$\nu_6(2)$	1017	2.33	-135			
CH_2Cl_2	ν_9	758	60.1	124	2.0	1.8 ⁱ	1.11
	ν_3	717	3.8	165			
	ν_7	898	0.59	-16			
CF_2Cl_2	ν_9	902	154	-20	1.8	1.8 ⁱ	1.00
	ν_1	1101	149	-219			
	ν_2	667	6.18	215			
SiF_4	$\nu_3(3)$	1031	295	-149	1.4	1.8 ⁱ	0.78
SF_6	$\nu_6(3)$	947	537	-65	1.8	1.8 ⁱ	1.00
	$\nu_5(3)$	613	31.4	269			

^aSelected quenchers from Table III.

^b ν_i and ΔE_i are in cm^{-1} units, I_i is in $10^{-8} \text{ cm}^2/\text{molecule}\cdot\text{s}$ units, k_{exp} and k_{calc} are in $10^{-10} \text{ cm}^3/\text{molecule}\cdot\text{s}$ units.

^cMost of the absorption band intensities are taken from Refs. 50,51.

^dExperimental rate constants; data from Refs. 1-5 are not used.

^eThe rate constants are calculated with Eq. (11).

^fNot included in the fit.

^gReference 52.

^hOur *ab initio* SCF HF estimate with 6-311G(3d) and TZV+(3df) basis sets for PCl_3 and NOCl , respectively; PC GAMESS program (Refs. 53,54) was used.

ⁱGas-kinetic value, k_{calc} is too large.

^jTaken equal to those in CF_3Br and CF_3Cl molecules.

only vibrational excitation of fundamental levels of molecule M are included, and rotational and multiquantum vibrational transitions are neglected.

Table IV lists the cases for which $E-V$ energy exchange seems to be the dominant pathway. Although in several cases (ICI , NOCl , O_3) a reactive quenching can compete favorably with the energy exchange, these cases are also included. Equation (11) was used in the present study to fit experimental rate constants listed in this table; the optimal A and B values are found to be 145 and 77 cm^{-1} , respectively. Note that expression (11) may predict an abnormally large rate constant, greater than the gas-kinetic one. In this case the rate constant was truncated to the gas-kinetic value. It can be

seen from Table IV that Eq. (11) estimates the Cl^* deactivation rates rather well, one standard deviation in $\ln(k_{\text{exp}}/k_{\text{calc}})$ is about 0.6. This generally good agreement between the fit and experiment is not reproduced for two quenchers, O_3 and CH_4 . The disagreement in this case of O_3 probably indicates that our preliminary rate constant $k_{q\text{O}_3}$ is wrong; in the case of CH_4 the disagreement may result from the large contribution of $E-R, T$ deactivation processes.

Interestingly, Eq. (11) predicts the internal state distribution from deactivation of Cl^* by SO_2 to be $[\text{SO}_2(\nu_3=1)]/[\text{SO}_2(\nu_1=1)]=2.0$, in fair agreement with the experimental value, 1.6 ± 0.5 .¹⁷

3. $E-R, T$ energy exchange

The present results, taken in conjunction with those reported earlier,^{10,11,13,15} indicate that quenching of Cl^* by H_2 , D_2 , HF , DF , HCl , DCl , and H_2O (and presumably CH_4) is predominantly due to $E-R, T$ energy transfer since all $E-V$ channels are endothermic. Note that chemical reaction between Cl^* and these molecules is unlikely; in several cases (H_2 , DCl , CH_4) it is proved experimentally in the present study and in the case of H_2 and D_2 it was proved by Sotnichenko *et al.*¹³ Furthermore, the rate constants for reactions of Cl with H_2 , HCl , H_2O , and CH_4 are $3.7 \times 10^{-11} \exp(-2310/T)$,⁵⁵ $2.5 \times 10^{-12} \exp(-2365/T)$,⁵⁶ $2.8 \times 10^{-11} \exp(-8670/T)$,⁵⁷ and $1.1 \times 10^{-11} \exp(-1409/T)$ (Ref. 58) $\text{cm}^3/\text{molecule}\cdot\text{s}$, respectively. Even if the spin-orbit excitation energy of Cl^* is effective in overcoming the reaction's activation barrier and thus the activation energies are decreased by the energy of Cl^* , nevertheless the rates of reactions of Cl^* with these species remain significantly smaller than those observed experimentally.

Using analogy with related $\text{Ar}+\text{H}_2$ system, Resnikov and Umanskii have estimated the long-range interaction potential for $\text{Cl}(^2P_{1/2}, ^2P_{3/2})+\text{H}_2$ and then carried out a calculation for the Cl^*+H_2 , D_2 quenching processes.¹⁹ The Landau-Zener formula with quadrupole-quadrupole interaction as a perturbation was used. It was found that the main contribution comes from $\text{Cl}^*+\text{H}_2(\nu=4)\rightarrow\text{Cl}+\text{H}_2(\nu=6)$ and $\text{Cl}^*+\text{D}_2(\nu=5)\rightarrow\text{Cl}+\text{D}_2(\nu=7)$ transitions; the total rate constants for deactivation of Cl^* by H_2 and D_2 are 5×10^{-13} and $7 \times 10^{-15} \text{ cm}^3/\text{molecule}\cdot\text{s}$, respectively, in strong disagreement with what is found experimentally.

Recently, the long-range potential energy surface correlating with $\text{Cl}(^2P_{1/2})+\text{HCl}$ was estimated by Dubernet and Hutson.⁵⁹ Using the surface, one can calculate the rate for quenching of Cl^* by HCl . A very small quenching rate should be expected for this system also, since the occurrence of curve-crossing requires a multiquantum transition ($\Delta N > 6$) in HCl . Obviously, theoretical studies are necessary to refine the $E-R, T$ mechanism for the Cl^* deactivation processes.

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