Dependence of the average energy transferred per collision of highly vibrationally excited polyatomic molecules on the excitation energy

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Abstract

The analytical model interpreting and predicting the dependence of the average energy transferred per collision on the initial energy of a molecule is developed. The validity of the theory is tested for SO_2 and CS_2 molecules in collisions with noble-gas atoms.
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1. Introduction

Collisional energy transfer of highly vibrationally excited molecules is an important part of many chemical reactions. Despite great efforts, theoretical picture of the phenomenon is still far from complete. In particular, it is still unclear why for some molecules the average energy transfer $\langle \Delta E \rangle$ depends linearly on the initial energy E, and for other molecules this dependence is nonlinear. Can the exponent in the relation $\langle \Delta E \rangle \propto E^n$ exceed $n = 2$? To solve this problem, we express transition probabilities $P_{n \to n'}$ in terms of projectors related to the Gottlieb polynomials in the discrete variable n (or n'). Such an approach makes it possible to derive a simple two-parameter dependence of the average energy $\langle \Delta E \rangle$ on the initial energy. One of the parameters of this fitting law is directly related to the mean number of collisions required to attain equilibrium. Another parameter allows for the influence of vibrational anharmonicity on the energy transfer.

2. Theory

Due to theoretical advances in trajectory-based computations, three-dimensional calculations of $\langle \Delta E \rangle$ at collisions

of highly excited molecules become feasible (see, e.g. [1–3] and references therein). Nevertheless, analytical approaches allow the better insight into the process under investigation, to make general conclusions, and to pose correctly problems for computer simulation. In this section we discuss the approximations needed to formulate the analytical model and give the details of the necessary calculations.

2.1. Model assumptions

Consider a polyatomic molecule that undergoes a vibrationally inelastic transition $(n_1 \ldots n_s) \to (n'_1 \ldots n'_s)$ due to a collision with another particle. According to the definition, the average amount of energy transferred per collision is

$$\langle \Delta E(E) \rangle = \sum_{\text{all } n} \left(E_{n'_1 \ldots n'_s} - E_{n_1 \ldots n_s} \right) N_{n_1 \ldots n_s}(E) P_{n_1 \ldots n_s \to n'_1 \ldots n'_s}, \quad (1)$$

where $N_{n_1 \ldots n_s}(E)$ is the probability to find the molecule in the state characterized by quantum numbers $n_1 \ldots n_s$ with the excitation energy equal to E.

Assume that the molecule can be represented as a set of s independent anharmonic oscillators with equal frequencies, ω, in other words, as one s-fold degenerate oscillator. Of course this energy spectrum is far from the true spectrum, however, it allows one to easily calculate the energy trans-

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fer, with the frequency ω not appearing in the final result. So

$$E_{n_1\ldots n_s} = \omega \sum_{\alpha=1}^{s} \left[n_\alpha + \frac{1}{2} + \frac{\xi\omega}{4D}\left(n_\alpha + \frac{1}{2}\right)^2 \right], \qquad (2)$$

where D is the dissociation energy, $\omega/4D$ the anharmonicity constant. In particular, we have for the Morse oscillator $\xi = -1$, for the Pöschl–Teller oscillator $\xi = 1$. In the first case we are concerned with stretching vibrations, while in the second case bending vibrations are modeled. Anharmonic couplings between modes ensure statistical character of energy redistribution in a real molecule. Formally this interaction is postulated by the distribution $N_{n_1\ldots n_s}(E)$ in Eq. (1). A mechanism of this energy redistribution is not considered here and we assume that the molecule enters into each collision as a system of independent oscillators having the given distribution of quantum numbers. By virtue of this assumption, we can approximately write the expression for transition probabilities

$$P_{n_1\ldots n_s \to n'_1\ldots n'_s} = P_{n_1 \to n'_1} \ldots P_{n_s \to n'_s}. \qquad (3)$$

2.2. The Gottlieb polynomials

The Gottlieb polynomials turned out to be an effective mathematical tool for the investigation of vibrational relaxation of an ensemble of harmonic oscillators interacting with a heat bath [4]. They are defined on the variation interval of the variable x from zero to infinity with the weighting function

$$w_n(x) = (1 - e^{-x})e^{-nx}. \qquad (4)$$

For our purposes it is convenient to express the Gottlieb polynomials in terms of the hypergeometric function

$$\Psi_k(n,x) = \exp\left(-\frac{kx}{2}\right)F(-k,-n;1;1-e^x). \qquad (5)$$

These polynomials satisfy the orthogonality condition and the completeness property

$$\sum_{n=0}^{\infty} w_n(x)\Psi_k(n,x)\Psi_{k'}(n,x) = \delta_{kk'}, \qquad (6)$$

$$w_n(x)\sum_{k=0}^{\infty} \Psi_k(n,x)\Psi_k(n',x) = \delta_{nn'}. \qquad (7)$$

In particular, n and n^2 can be expressed via the Gottlieb polynomials. From definition (5) we immediately get

$$n = m_1(x)\left[\Psi_0(n,x) - \Psi_1(n,x)e^{x/2}\right], \qquad (8)$$

$$n^2 = m_2(x)\Psi_0(n,x) - m_1(x)[1 + 4m_1(x)]\Psi_1(n,x)e^{x/2}$$
$$\qquad + 2m_1^2(x)\Psi_2(n,x)e^x, \qquad (9)$$

where m_1 and m_2 denote the averages $\langle n \rangle$ and $\langle n^2 \rangle$ calculated with the distribution function $w_n(x)$:

$$m_1(x) = \frac{1}{e^x - 1}, \qquad (10)$$

$$m_2(x) = \frac{e^x + 1}{(e^x - 1)^2}. \qquad (11)$$

2.3. Average energy transfer

First consider an isolated vibrational mode with the frequency ω and introduce the designation $\theta = \omega/k_B T$. Hereafter ω and $k_B T$ are given in cm^{-1}. As a result of collisions the molecule undergoes the inelastic transition between vibrational levels n and n' with the probability $P_{n\to n'}$. Completeness property (7) makes it possible to express these transition probabilities via an appropriate set of projectors

$$P_{n\to n'} = w_{n'}(\theta)\sum_{k=0}^{\infty} p_k \Psi_k(n,\theta)\Psi_k(n',\theta), \qquad (12)$$

where p_k are the expansion coefficients depending on temperature. With the orthogonality condition one gives the inverse transformation

$$p_k = \sum_{n,n'=0}^{\infty} w_n(\theta)\Psi_k(n,\theta)P_{n\to n'}\Psi_k(n',\theta). \qquad (13)$$

Definition (5) shows that $\Psi_0(n,\theta) = 1$, thus we immediately have $p_0 = 1$ from Eq. (13).

After these explanations we proceed to calculate the average energy transferred per collision $\langle \Delta E_n \rangle$ as a function of initial vibrational quantum number. Let us find the first and the second moments of the form ($k = 1, 2$)

$$M_k(n) = \sum_{n'=0}^{\infty} \left(n'^k - n^k\right)P_{n\to n'}. \qquad (14)$$

This problem is easily solved if we express n' and n'^2 in terms of the Gottlieb polynomials according to Eqs. (8) and (9), and make use of the orthogonality property. Simple calculations yield for the first moment

$$M_1(\theta,n) = -(1 - p_1)[n - m_1(\theta)]. \qquad (15)$$

Expression for the second moment is more complicated

$$M_2(\theta,n) = -(1 - p_1)[1 + 4m_1(\theta)][n - m_1(\theta)]$$
$$\qquad - (1 - p_2)\{n^2 + 2m_1^2(\theta) - [1 + 4m_1(\theta)]n\}. \qquad (16)$$

The efficiency of energy transfer is seen to depend on two parameters only. At $p_1 \approx p_2 \approx 1$ the energy transfer becomes extremely inefficient, on the contrary, at $p_1 \approx p_2 \approx 0$ the amount of energy transferred per collision is maximum. In principle, other p_k with $k > 2$ may appear in the theory where the dependence of vibrational energy levels E_n on n must include the terms of the order n^3 and more higher powers.

The average energy transferred per collision as a function of initial vibrational state is

$$\langle \Delta E_n \rangle = \omega\left(1 + \frac{\xi\omega}{4D}\right)M_1(\theta,n) + \frac{\xi\omega^2}{4D}M_2(\theta,n). \qquad (17)$$

Let us discus this expression. The vibrational anharmonicity has a pronounced effect on vibrational relaxation near the dissociation threshold, thus taking it into account is a key condition for proper determination of the energy dependence of $\langle \Delta E \rangle$. For this reason we consider vibrational modes as anharmonic oscillators. On the other hand,

for polyatomic molecules the proportion of phase space associated with dissociation is so small, and the number of degrees of freedom is so large, that energy is primarily transferred from states with just a few quanta of vibrational excitation per mode. Thus, the harmonic approximation is quite sufficient for the evaluation of the first and the second moments in Eq. (17). This close approximation is appropriate in many cases, though not always. It is inapplicable when a leveling-off (energy independent $\langle \Delta E \rangle$) at high excitation energies is observed.

The probability of finding the molecule in the state $(n_1 \ldots n_s)$ with the excitation energy E is given by the microcanonical distribution

$$N_{n_1 \ldots n_s}(E) = C\delta\left[E - \omega\left(n_1 + \cdots + n_s + \frac{s}{2}\right)\right]. \tag{18}$$

With Eq. (18), the average energy transfer takes the form

$$\langle \Delta E \rangle = s \sum_{n_1 \ldots n_s} N_{n_1 \ldots n \ldots n_s}(E)\langle \Delta E_n \rangle. \tag{19}$$

Different methods have been proposed for the determination of the normalization factor C. Here we consider the first-order steepest-descent method [5]. It can be used for a concrete series summation in (19). Since all the necessary computational technique can be found in [5], here we shall just outline the essentials. The normalization factor in the case of s harmonic oscillators is given by

$$C = \sqrt{2\pi f''(\beta)}\exp[-f(\beta)] \tag{20}$$

with the standard expressions for the function $f(\beta)$ and its second derivative

$$f(\beta) = \beta E - \ln\left[\prod_{m=1}^{s} 2\sinh\left(\frac{\beta\omega_m}{2}\right)\right], \tag{21}$$

$$f''(\beta) = \frac{1}{\beta^2}\sum_{m=1}^{s}\frac{(\beta\omega_m/2)^2}{\sinh^2(\beta\omega_m/2)}. \tag{22}$$

The parameter $\beta(E)$ is determined by the inversion of the relation

$$E = \sum_{m=1}^{s}\frac{\omega_m}{2}\coth\left(\frac{\beta\omega_m}{2}\right). \tag{23}$$

This equation is easily solved for the s-fold degenerate oscillator. Instead of Eq. (23) we have

$$E = \left(\frac{s\omega}{2}\right)\frac{\exp(\beta\omega/2) + \exp(-\beta\omega/2)}{\exp(\beta\omega/2) - \exp(-\beta\omega/2)}. \tag{24}$$

It follows that

$$\exp(\beta\omega) = \frac{2E + s\omega}{2E - s\omega}. \tag{25}$$

The developed technique [5] for evaluating C can be used here to find $\langle \Delta E \rangle$ from Eq. (19). The resulting expression is

$$\langle \Delta E \rangle = s\left[\frac{f''(\beta)}{2\pi}\right]^{1/2}\int_{-\infty}^{+\infty}\exp\left[-\frac{1}{2}f''(\beta)y^2\right]$$
$$\times \langle \Delta E(\beta + iy)\rangle \, dy. \tag{26}$$

The energy $\langle \Delta E(\beta + iy)\rangle$ is given by expression (17) where n and n^2 should be replaced by $m_1[(\beta + iy)\omega]$ and $m_2[(\beta + iy)\omega]$, respectively.

Now we make the necessary estimations. The approximate solution of Eq. (23) at high energies can be written as $\beta \approx s/E$, i.e., it is seen that this parameter is small. At small β Eq. (22) immediately gives $f''(\beta) \approx s/\beta^2$, i.e., it is a very large parameter. For example, at $E = 3000$ cm^{-1} and $s = 3$ we have $f''(\beta) = 3 \times 10^6$ (cm^{-1})^2. With such numerical values of this parameter, it is actually a delta function enters into the integrand (26)

$$\delta(y) = \lim_{x \to \infty}\sqrt{\frac{x}{\pi}}e^{-xy^2}. \tag{27}$$

We can apply this equation to give $\langle \Delta E \rangle = s\langle \Delta E(\beta)\rangle$. Rewrite this relation once again rearranging properly the terms and taking into consideration that the moment m_2 is equal to $2m_1^2 + m_1$. This gives the dependence

$$\langle \Delta E \rangle = -(1 - p_1)s\omega[m_1(\beta\omega) - m_1(\theta)]$$
$$- \frac{\xi s\omega^2(p_1 - p_2)}{2D}[m_1(\beta\omega) - m_1(\theta)]^2$$
$$- \frac{\xi s\omega^2(1 - p_1)}{2D}[m_1(\beta\omega)(1 + m_1(\beta\omega))$$
$$- m_1(\theta)(1 + m_1(\theta))]. \tag{28}$$

Let us find the explicit form of the dependence $\langle \Delta E \rangle$ on E. With this aim, $e^{\beta\omega}$ from (25) is substituted in $m_1(\beta\omega)$ from (10). Similarly one can express e^θ in terms of the mean thermal energy E_T (see Eq. (24) with $1/k_BT$ instead of β). The final result is then the following simple fitting law:

$$\langle \Delta E \rangle = -(1 - p_1)(E - E_T) - \frac{\xi(p_1 - p_2)}{2sD}(E - E_T)^2$$
$$- \frac{\xi(1 - p_1)}{2sD}(E^2 - E_T^2). \tag{29}$$

It is interesting that the effective frequency ω does not appear in Eq. (29) explicitly. This allows us to treat E and E_T as the quantities corresponding to a real molecule irrespective of the particular derivation (29). Careful examination [6] shows that this conclusion will be preserved in a more realistic model, but the expressions for anharmonic terms will be valid just approximately. To write them in the form (29), the excitation energy should exceed the zero-point one. The value $\xi = -1$ means that the main contribution into $\langle \Delta E \rangle$ is made by stretching vibrations, while $\xi = 1$ means that the predominant contribution is made by bending vibrations. In principle, ξ can be considered as one more adjustable parameter of the model $-1 \leqslant \xi \leqslant 1$. Particular calculations with triatomic molecules SO_2, CS_2 show that this just slightly improves the quality of the fit. For our applications we put $\xi = 1$. This choice is governed by comparison with the experiments [7–9], since only at positive ξ, the numerical values of parameters p_1 and p_2 obtained by fitting are less than unity. This conclusion is in agreement with a common opinion that the main

contribution into vibrational relaxation is made by low-frequency modes [10] belonging to bending vibrations in the case of SO_2 and CS_2 molecules.

In Eq. (29), p_1 and p_2 are the fitting parameters of the model depending on collision dynamics: $0 \leqslant p_1 \leqslant 1$ and $0 \leqslant p_2 \leqslant 1$. Note that inequality $p_k \leqslant 1$ follows immediately from definition (13). Making use of the relation $\sum p_k = Tr(P)$ gives

$$\lim_{N \to \infty} \frac{1}{N} \left(1 + \sum_{k=1}^{N} p_k \right) = \lim_{N \to \infty} \frac{1}{N} \sum_{n=0}^{N} P_{n \to n} \leqslant 1. \quad (30)$$

It is obvious that all positive p_k must be less than or equal to 1.

Particular attention should be given to the role of the parameter p_2 in the creation of nonlinear dependence $\langle \Delta E \rangle$ on E. At $p_2 = 1$ the energy transfer ceases to depend on n^2, hence, the energy $\langle \Delta E \rangle$ is only linearly dependent on E. It should be emphasized that this parameter appears in the theory owing to the vibrational anharmonicity.

As is easy to see, the dependence $\langle \Delta E \rangle \propto E$ occurs for polyatomic molecules in the limit $s \gg 1$. Therefore, the linear energy dependence results from a large number of vibrational degrees of freedom. Indeed, triatomic molecules, such as CS_2 and SO_2, show the energy dependence $\langle \Delta E \rangle \propto E^2$ [7–9], while large molecules, such as azulene, show the linear behavior [11,12]. SF_6 may be considered a medium-sized molecule [13,14]. Now, to elucidate the physical meaning of the parameter p_1, consider the characteristic time of vibrational relaxation.

2.4. Vibrational relaxation time

According to the formal kinetic theory of molecular gases [15], we express vibrational relaxation time in terms of the mean-squared energy transfer in vibrationally inelastic collisions

$$\frac{1}{\tau_{VT}} = \frac{Z}{2^s} \sum_{\text{all } n} w_{n_1}(\theta) P_{n_1 \to n_1'} \ldots w_{n_s}(\theta) P_{n_s \to n_s'}$$
$$\times \frac{(E_{n_1' \ldots n_s'} - E_{n_1 \ldots n_s})^2}{\langle E^2 \rangle_{\text{eq}} - \langle E \rangle_{\text{eq}}^2}, \quad (31)$$

where Z is the collision frequency. In the harmonic approximation a little manipulation yields

$$\frac{1}{\tau_{VT}} = Z(1 - p_1). \quad (32)$$

Often vibrational relaxation rate is characterized by the effective collision number Z_{vib} which is defined as the product of collision frequency and vibrational relaxation time. Consequently, Eq. (32) gives the desired relation between p_1 and the number of collisions, namely $1 - p_1 = 1/Z_{\text{vib}}$. Returning to Eq. (29), note that for polyatomic molecules with a large number of vibrational degrees of freedom it takes a particularly simple form

$$\langle \Delta E \rangle = -\frac{E - E_T}{Z_{\text{vib}}}. \quad (33)$$

Previously this equation was derived by Forst and Barker [16] in the approximation of simple exponential relaxation. Thus, in the limit $s \gg 1$, the contribution of the terms determined by vibrational anharmonicity becomes small, and the large molecule can be treated as a system of harmonic oscillators attaining equilibrium with the same unique relaxation time.

Finally, we answer the question posed in the Introduction. In principle, the energy dependence $\langle \Delta E \rangle \propto E^k$ with $k > 2$ is possible provided that the energy levels of the low-frequency mode E_n are described by the expression where the terms of the order n^3 cannot be neglected.

3. Results and discussion

To compare the theory and experiment, we have chosen the detailed investigations of relaxation CS_2 [7,8] and SO_2 [9] with noble-gas atoms and hydrogen. The resulting values of the model parameters found by fitting of experimental data are listed in Table 1. Fitting of experimental values by formula (29) has been performed with a statistical goodness-of-fit χ^2/v. In Fig. 1 the fitting law is seen to reproduce the $\langle \Delta E \rangle$ values for SO_2 with rare gases at a level that it consistent within the experimental error at all E. As is also seen, the dependence $\langle \Delta E \rangle \propto E^2$ takes place both for high energies and for low ones. For SO_2 + inert gases the parameter $1 - p_1$ is approximately equal to 5×10^{-5} or, in other words, about 20,000 collisions are required to attain equilibrium. Since the number of vibrational degrees of freedom is rather small, the term $\propto (E - E_T)^2$ makes the main contribution to the energy transfer. Similar results are obtained for CS_2 (see Fig. 2). However, there is an excep-

Table 1
Model parameters obtained by fitting of experimental data [7–9] to Eq. (29) with $\xi = 1$

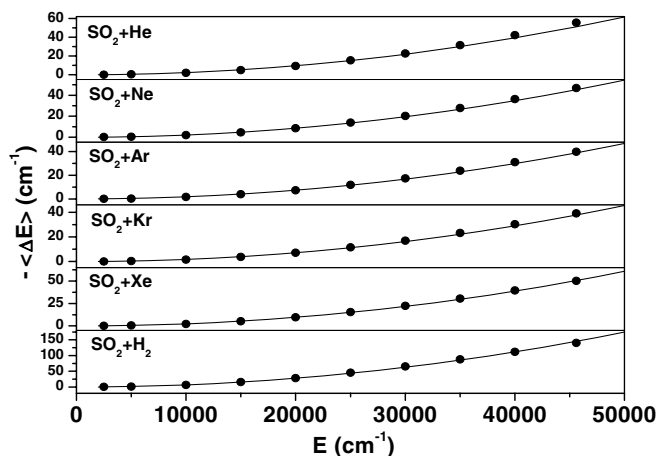| M	$SO_2 + M$			$CS_2 + M$		
	$10^4(1 - P_1)$	P_2	χ^2/v	$10^4(1 - P_1)$	P_2	χ^2/v
He	0.61	0.993	0.99	7.92	0.977	1.22
Ne	0.60	0.994	0.68	1.49	0.992	0.12
Ar	0.52	0.995	0.68	0.86	0.995	0.11
Kr	0.50	0.995	0.68	1.03	0.994	0.11
Xe	0.69	0.993	0.58	0.69	0.996	0.11
H_2	2.18	0.981	0.49	56.5	1.0	0.83

Fig. 1. Comparison of the average energies transferred per collision from [9] (circles) with predictions based on Eq. (29).
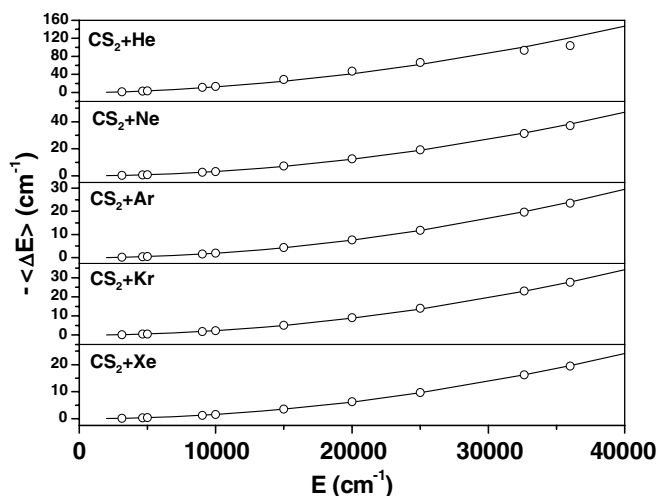

Fig. 2. Comparison of the average energies transferred per collision from [7,8] (circles) with predictions based on Eq. (29).

Fig. 3. Linear behavior of $\langle \Delta E \rangle$ vs. E in $CS_2 + H_2$. The squares are experimental values from [7,8].

our opinion, by the low sensitivity of the method [17] with a small addition of sulfur dioxide to argon.

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tion. For $CS_2 + H_2$ the parameter p_2 is no different from 1 (see Table 1), thus $\langle \Delta E \rangle$ increases linearly with E even in the case where the active molecule is triatomic, Fig. 3. Of course, the phenomenological theory fails to explain why in one case the parameter p_2 is equal to 1, and in the other case, say, 0.996. Trajectory-based calculations are needed for this explanation. The average collision number $Z_{vib} \approx 8000$ for the $SO_2 + Ar$ system is determined from ultrasonic measurements [17]. Our estimate of this value (see Table 1) gives 19,000 collisions. Since in pure sulfur dioxide the value $Z_{vib} = 710$ is in good agreement with ou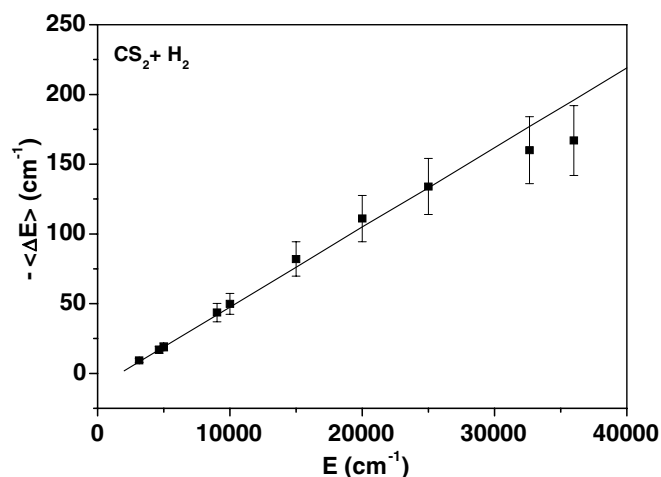r $Z_{vib} = 520$ [6], the discrepancy may be explained, in