

## **A simplified approach to the vibrational self-relaxation of simple molecules through convolution of their velocities\***

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A theoretical approach has been developed for computing collisional self-relaxation probabilities of the first excited level in the lowest vibrational mode of simple molecules. The bending ( $\nu_2$ ) vibration in triatomic molecules, in which the average translational and rotational velocities are of the same order of magnitude, was examined. The approach was based on the assumption that both the velocities should be taken into account as a convolution of the corresponding Maxwell's distribution functions. The model was checked for the SO<sub>2</sub> molecule in the temperature range from 130–1100 K. The calculated temperature dependence curve (the Landau-Teller plot) exhibits a minimum at about 150 K. The data obtained is discussed in relation to some experimental results. The comparison indicates that the problem was treated in correct manner. Some additional aspects of the relaxation, like intermolecular interactions and the steric factor, are also briefly considered. It is believed that this approach offers quite a good basis for further improvements of theoretical treatments.

**Keywords:** vibrational relaxation, molecular collisions, convolution, velocity distribution, SO<sub>2</sub>.

### INTRODUCTION

Vibrational energy transfer in molecular collisions is often the essential step in excitation or deactivation of molecules. It is important both for understanding reaction kinetics and for planning energy pumping into a molecule in order to excite it up to a certain level.

This work deals with the self-relaxation of the lowest vibrational fundamental in small and simple molecules, mostly from the theoretical point of view. The intention is to highlight some specific aspects of energy transfer among molecules in collisions, which are not so often taken into account.

Several years ago we developed an approach to the problem of collisional energy transfer<sup>1</sup> which was based on the assumption of a vibration-rotation ( $V \rightarrow R$ )

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mechanism. It started from the treatment given by Cottrell *et al.*<sup>2</sup> It is basically a vibration-translation (V→T) approach. The relative translational velocity and reduced mass of the colliding pair in that model were substituted by the corresponding rotational parameters –  $\omega d$  and  $I/d^2$  ( $\omega$  – angular velocity,  $I$  – moment of inertia,  $d$  – distance from the axis of rotation to the rotating atom), respectively, see Fig. 1(ii)). This idea gave a simple model, with a potential function which includes both attraction and repulsion between the colliding partners. It was further applied for the calculation of vibrational self-relaxation probabilities for water-like molecules (group VI hydrides and deuterides). The method enabled the prediction of temperature dependence, isotope effects, *etc.*<sup>3</sup> However, this model was still limited to encounters in which a translationally slow vibrator was colliding with a light rotator, *e.g.*, where the rotational velocity of the colliding partner is larger than the relative translational velocity of the pair.\*

A qualitatively new problem appears when the colliding partners have similar values of rotational and translational velocities, neither of which can be neglected. Both velocities contribute to the duration of the encounter and, thus, to the relaxation probability. Such molecules will in the following be called "intermediate" relaxants. An analysis of some aspects of their self-relaxation is the main aim of the present work. A typical example of an "intermediate" relaxant is the SO<sub>2</sub> molecule. The self-relaxation probability of the lowest vibrational (bending,  $\nu_2$ ) fundamental of the SO<sub>2</sub> molecule, which is a general indicator for the overall relaxation of a molecule, will be considered in this work. Sulphur dioxide is a triatomic, non-linear asymmetric top molecule, similar to water, with three different moments of inertia. Due to its molecular mass, moments of inertia and dimensions, the ratio of the rotational velocity of any degree of freedom and the relative translational velocity of a colliding pair in an encounter at the maxima of the corresponding Maxwell's distribution functions are around unity, Table I. As can be seen from the Table these ratios for water, which is a "light rotator", are above 2.

#### THEORY

The theory of Cottrell *et al.*,<sup>2</sup> as mentioned earlier, was adapted for the calculation of the relaxation probabilities of water-like molecules (H<sub>2</sub>O, D<sub>2</sub>O, H<sub>2</sub>S, ...). The results of the calculation were in good agreement with the experimental values, especially in treating the temperature dependence of the probabilities, isotope effects and the relative ratios between the absolute values. However, when that method was applied to the relaxation of SO<sub>2</sub>, which is by structure similar to the above hydrides, deviations from the experimental points by at least six orders of magnitude were observed (if results are presented as Landau-Teller plots –  $\ln P = f(T^{1/3})$  in either the V–R or V–T version). It was, thus, necessary to improve the approach by taking both kinds of velocities into account. This is the main focus of this work.

\* In this sense translational or rotational velocity means average values of those velocities according to the corresponding Maxwell's distribution functions

*General.* According to the *Ehrenfest's adiabatic principle*, expressed through the adiabaticity parameter,<sup>4</sup>  $\xi = \tau/t_v$ , where  $\tau$  is the duration of the collision and  $t_v$  is the period of the vibration for a vibrating molecule, a collisional process will be non-adiabatic (efficient transfer of energy) if  $\xi < 1$ , *e.g.*, if the duration of the encounter is shorter than the period of vibration,  $\tau < t_v$ . The duration of the encounter can be expressed as  $\tau = a/v$ , where  $a$  is the range of the intermolecular interaction and  $v$  the average value of the relative velocity of approach. This means: the higher the relative velocity of approach of a colliding pair *in a single collision*, the higher the efficiency of energy transfer. Accordingly, the lower the velocity of the atoms moving along the corresponding chemical bond within the oscillator (smaller vibrational frequency,  $t_v = v^{-1}$ ), the higher the efficiency of transition. Thus, for an efficient transfer we can write  $v > av$ . The velocity is generally a function of absolute temperature and molecular mass,  $v = (8kT/\pi m)^{1/2}$ . A steep intermolecular potential (small  $a$ ) also has a positive contribution to the efficiency of the transfer. If the attraction between the partners is significant, *i.e.*, if the potential function has a deep well, it will strongly accelerate those partners during the collision and contribute to the overall velocity. Another contribution might come from rotation (see Fig. 1(i)), in cases where it must not be neglected.

*The idea.* The idea is based on the assumption that the probability of relaxation in a single collision, as a function of velocity of approach of the colliding pair, should be averaged over the thermal distribution of velocities to obtain the macroscopic probability. This value can further be compared to experimental data.

The corresponding equation, based on the expressions published earlier<sup>1,3</sup> is

$$P_{10}Z_0 = \int_0^{\infty} p_{10}(v)R(v)dv \quad (1)$$

where  $P_{10}$  is the average macroscopic relaxation probability of level 1 in a certain vibrational mode;  $p_{10}$  is the relaxation probability in a single collision;  $v$  is the relative velocity of approach of the colliding partners at an infinite distance apart (in the basic theory<sup>1</sup> it was understood to be purely translational);  $R$  is the distribution function of velocities  $v$  at a certain temperature;  $Z_0$  is a so called steric factor (introduced into the theory to account for non head-on collisions).

Here  $p_{10}$  is taken to be<sup>2</sup>

$$p_{10} = \frac{32\pi^4 m^2 v}{h\mu\alpha^2} \exp \left\{ -4\pi v \left[ \pi - 2\arctan \left( \frac{\gamma^2}{2mv^3\lambda} \right)^{1/2} \right] (\alpha v)^{-1} \right\} \quad (2)$$

where  $m$  is the reduced mass of the colliding pair (used here associated with the relative velocity  $v$ ),  $v$  is the frequency of the  $(1 \rightarrow 0)$  transition,  $h$  is Planck's constant,

$\mu$  is the effective mass of the relaxing harmonic oscillator and  $\alpha$ ,  $\lambda$  and  $\gamma$  are parameters of the potential function describing the intermolecular interaction (Morse type equation,  $V(r) = \lambda \exp(-\alpha r) - \gamma \exp(-\alpha r/2)$ ). Equation (2) is obtained from a semi-classical treatment: the translational motion was calculated classically,<sup>5</sup> the transition probability was treated quantum-mechanically. The model is a simplification with respect to a full quantum-mechanical approach, as the dynamics of the encounter are not regarded separately.

The above expression was derived under the conditions: (i) transfer of energy takes place in a head-on encounter from a harmonic oscillator to a colliding partner; (ii) the dynamics of the encounter are considered unaffected by the energy transfer – transferred vibrational energy is much lower than the mutual kinetic energy of the colliding pair.

There are two crucial questions relevant to the relaxation of "intermediate" molecules: (i) what is the real velocity in the case where neither translation nor rotation can be neglected; (ii) what should be the corresponding velocity distribution function (we shall call it the "generalized" distribution –  $R(v)$ ). The velocity of approach in a collision should not be the simple sum of the translational and rotational components, since these components, in principle, can take any value from 0 to  $\infty$  at a temperature, according to their own distribution functions. To obtain the velocity expressions necessary for the new treatment we developed a unique procedure.<sup>6</sup> We concluded that the "generalized" distribution is an ordinary convolution of the two functions, translational and rotational, which is given as the convolution integral

$$R(v) = \frac{dN(v)}{Nd v} = \int_0^v \frac{m v_t}{kT} e^{-\frac{m v_t^2}{2kT}} \frac{I(v - v_t)}{d^2 kT} e^{-\frac{I(v - v_t)^2}{d^2 kT}} dv_t \quad (3)$$

Where  $dN$  is the number of molecules with generalized velocities between  $v$  and  $(v + dv)$ ,  $N$  is the total number of molecules,  $m$  is the reduced mass of the molecules in collision,  $k$  is Boltzmann's constant,  $T$  is absolute temperature.

Finally, introducing velocity symmetrization into Eq. (1) and combining with the convolution integral, the expression used in all calculations of self-relaxation probabilities is obtained:

$$P_{10} Z_0 = e^{\frac{h\nu}{kT}} \left( \frac{32\pi^4 m^2 v}{h\mu\alpha^2} \right) \int_0^\infty e^{-4\pi v} \left[ \pi - 2 \arctan \left( \frac{\gamma^2}{2m v^2 \lambda} \right) \right] dv \int_0^v \frac{v}{kT} e^{-\frac{m v}{2kT}} \cdot \frac{I(v - v_t)}{d^2 kT} \cdot e^{-\frac{I(v - v_t)}{2d^2 kT}} dv_t \quad (4)$$

#### CALCULATIONS, RESULTS AND DISCUSSION

The calculations were made by performing the integration of the convolution integral  $R(v)$  within Eq. (4) first by the argument  $v_t$ , and then by numerical

integration of the generalized velocity  $v$  from 0 to  $\infty$ . We succeeded in obtaining an analytical solution of the convolution integral.<sup>6</sup> Most of the integrations were performed using Simpson's method.

A value of 3 for the steric factor  $Z_0$  as a good approximation for  $\text{SO}_2$  was assumed, as suggested in literature.<sup>7</sup> The value actually depends on the type and size of the molecules in the encounter, as small and strongly interacting molecules can be more easily reoriented during the collision, and, accordingly, deviate less from linear geometry. A detailed investigation of the role of  $Z_0$  was beyond the central scope of the present work.

To perform the calculation it is necessary to supply Eq. (4) with numerical values of corresponding parameters and constants. The fundamental vibrational bending frequency ( $\nu_2$ ) was taken to be 518 wavenumbers,<sup>8</sup> the reduced mass of the colliding pair  $m = M/2$  (Table I); the effective mass of the harmonic oscillator was obtained as  $\mu = f/(4\pi^2\nu^2) = 3.4098 \times 10^{-23}$  g, where  $f = 324 \text{ N m}^{-1}$  is the force constant for the "O—O bond" in  $\text{SO}_2$  assuming central forces.<sup>9</sup> The moments of inertia and the distances from the center of the masses to the rotating atoms for all three degrees of rotational freedom are presented in Table I, along with the corresponding data for  $\text{H}_2\text{O}$ , for comparison.

TABLE I. Moments of inertia —  $I$ , structural parameters (molecular mass —  $M^a$ , angle between chemical bonds —  $\beta$  and bond lengths —  $r$ ), distances<sup>b</sup> from the molecular center of mass to the peripheral rotating atom —  $d$ , and the ratios of the rotational and translational velocities<sup>c</sup> at the maxima of the corresponding Maxwell's distribution functions —  $\omega d/v_t$  for the  $\text{SO}_2$  and  $\text{H}_2\text{O}$  molecules

Quantity		$\text{SO}_2$	Ref.	$\text{H}_2\text{O}$	Ref.
$I_A$	(g cm <sup>2</sup> )	$1.3804 \times 10^{-39}$	10	$1.0220 \times 10^{-40}$	11
$I_B$	(g cm <sup>2</sup> )	$8.13067 \times 10^{-39}$	"	$1.9187 \times 10^{-40}$	"
$I_C$	(g cm <sup>2</sup> )	$9.53376 \times 10^{-39}$	"	$2.9376 \times 10^{-40}$	"
$M$	(g)	$1.0636 \times 10^{-22}$		$2.9912 \times 10^{-23}$	
$\beta$	(°)	119.53	8	104.45	8
$r$	(cm)	$1.4321 \times 10^{-8}$	"	$0.958 \times 10^{-8}$	"
$d_A$	(cm)	$0.361 \times 10^{-8}$		$0.522 \times 10^{-8}$	
$d_B$	(cm)	$1.237 \times 10^{-8}$		$0.756 \times 10^{-8}$	
$d_C$	(cm)	$1.288 \times 10^{-8}$		$0.919 \times 10^{-8}$	
$\omega d/v$	A	0.71		2.00	
	B	1.00		2.11	
	C	0.96		2.07	

<sup>a</sup>Calculated as the ratio of the relative molecular mass and Avogadro's number. <sup>b</sup>Calculated using the necessary molecular parameters given above. <sup>c</sup>Calculated as  $\frac{\omega d}{v} = \left[ \frac{m}{I/d^2} \right]^{1/2}$

The distances  $d$  were computed by the methods of classical mechanics using the geometry shown in Fig. 1(ii) and the necessary data for bond lengths ( $r$ ) and angles between them ( $\beta$ ). The Morse potential function parameters are usually not

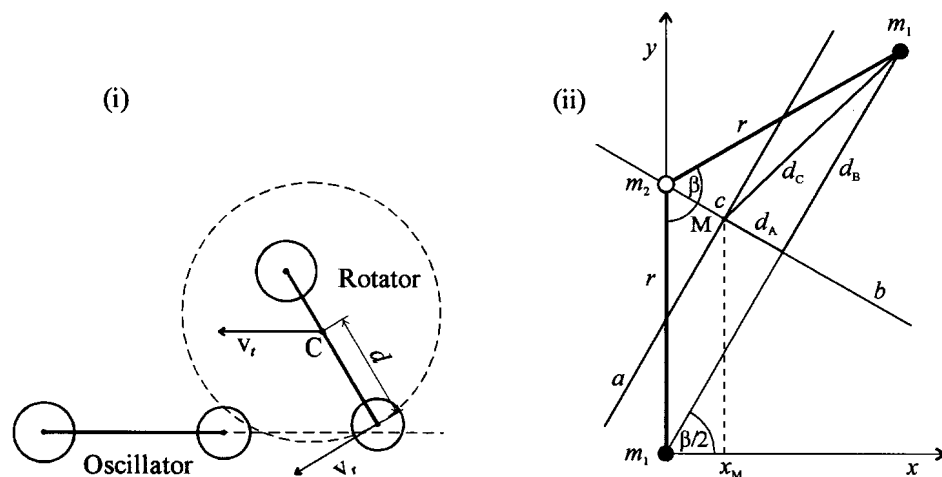


Fig. 1. (i) Collision between a stationary oscillator and an approaching rotator. The velocity of approach is  $v_t$ . The peripheral velocity of rotation is  $v_r$ . Its vector at the moment of collision is parallel to the axis of approach. (ii) Geometry of the  $\text{SO}_2$  molecule with the three main axes of rotation ( $a$ ,  $b$  and  $c$ ).

available in the literature for the majority of molecules. We had to extract them from those given for the Krieger potential,<sup>12</sup> which is commonly used for simple and polar molecules, by fitting one function to another. The least squares criterion was used in a method taking points to be equally distant along the potential curve. The data obtained are:  $\lambda/k = 3.389 \times 10^7$  K,  $10^{-10} \alpha = 2.363 \text{ m}^{-1}$ ,  $\gamma/k = 2.740 \times 10^5$  K.

*Calculation of relaxation probabilities.* Fig. 2 shows some of the results obtained with the described procedure, along with some available experimental data. All the calculated probabilities are mean values for three degrees of rotational freedom. The calculated probabilities for the "pure" V-T or V-R transfer are also included. The computing is based on the procedure given in Ref. 1. This approach generated temperature dependence curves which showed the most important disadvantage of the method: the "pure curves" are situated many orders of magnitude below the experimentally indicated level. They are not sensitive enough to the method of fitting the potential function to the empirical one. In this sense, our investigation showed that no significant help in reaching the area of the experimental points can be expected from either the potential function or the value of the steric factor, although all of these factors have an evident influence on the above curves. Only a proper treatment of the velocity of approach in a collision can ensure great progress in the entire theory. As mentioned in the introduction, this fact determined the aim of this work.

The employed method of fitting the potential function ("equally distant points along the curve") has shown itself to be superior to the other method used ("along the  $r$ -axis") because it does not underestimate the steep parts of the potential func-

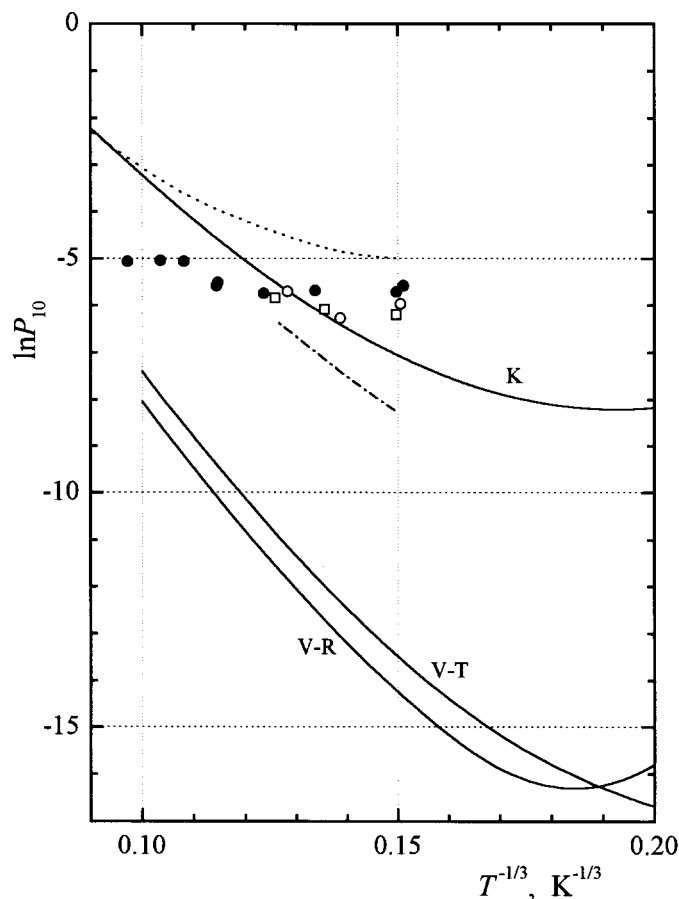


Fig. 2. Temperature dependence of  $\text{SO}_2$  ( $v_2$ ) self-relaxation probabilities (Landau-Teller plots): ( $\bullet$ ) – measured values, Bass *et al.*<sup>13</sup>; ( $\square$ ) – measured values Shield<sup>14</sup>; ( $\circ$ ) – measured values, Lambert *et al.*<sup>15</sup>; (–•–) – calculated values, Rao<sup>17</sup>; (••••) – calculated values, Shin<sup>16</sup>; (V–T) – calculated using the "pure" vibration-translation approach (this work); (V–R) – calculated using the "pure" vibration-rotation approach (this work); K – calculated using the generalized approach (this work).

tions. Colliding particles exhibit the strongest changes of relative velocities exactly in these parts. The investigation also showed that the calculated probabilities are extremely sensitive to the position of the limits of the domain in which the approximation is carried out. It can be a useful tool, especially when studying the dynamics of a collision at low energy, *i.e.*, at low temperatures, where the existence of long-range intermolecular attraction can be very important, and is often neglected in studies.

The K-curve in Fig. 2 is an example that represents the validity of the whole method for several reasons. Firstly, it passes through the region of experimental points,<sup>13–15</sup> although its slope is a little steeper than that of a line which could be drawn to fit these points. Secondly, it predicts the existence of a minimal probability of energy transfer. It is unlike the curve calculated by Shin<sup>16</sup> (also shown in Fig. 2),

which shows no minimum in the specified domain. In addition, a conclusion of his work was that vibrational de-excitation in  $\text{SO}_2\text{--SO}_2$  can be explained in terms of the mechanism of vibration-to-translation energy transfer. Another statement was that all the atoms involved in the collision are heavy and the V–R transfer is not expected to be an important process for the deactivation (!). In contrast to this, we found that the V–R step is as important as the V–T channel. Sulphur dioxide is a typical example where neither the translational nor the rotational mechanism can be neglected. Similarly, another calculation (Rao<sup>17</sup>), also included in the Figure, was performed according to the SSH breathing sphere theory, using Lennard-Jones potential function parameters. Only the V–T mechanism was considered. The obtained curve is below our one, having roughly the same slope. It has no minimum within the region of the calculations.

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#### ИЗВОД

#### УПРОШЋЕНИ ТРЕТМАН ВИБРАЦИОНЕ САМОРЕЛАКСАЦИЈЕ ЈЕДНОСТАВНИХ МОЛЕКУЛА ПРЕКО КОНВОЛУЦИЈЕ ЊИХОВИХ БРЗИНА

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Развијен је теоријски приступ за рачунање вероватноћа сударне саморелаксације првог побуђеног вибрационог нивоа ( $v_2$ ) једноставних молекула, у којима су средње транслационе и ротационе брзине истог реда величине. Приступ је заснован на претпоставци да би обе брзине требало узети у обзир као конволуцију одговарајућих Максвелових функција расподеле. Модел је проверен на примеру молекула  $\text{SO}_2$ . Израчуната крива температурске зависности (Ландау-Телеров дијаграм) показује минимум на око 150 K. Добивени резултати су дискутовани у односу на постојеће експерименталне податке. Поређење показује да је проблем третиран на исправан начин. Овакав приступ представља добру основу за даља побољшања метода за теоријске интерпретације.

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