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Energy transfer in near-resonant molecular collisions from diatomic to symmetric top molecules

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Résumé. — Nous avons étendu une théorie du transfert d'énergie vibrationnelle, basée sur l'interaction multipolaire à grande distance, au cas où l'une des molécules est une toupie symétrique. Nous avons calculé la valeur de la probabilité d'échange en fonction de la température pour cinq réactions d'échange entre $D_2(v = 1)$ et CH_3Cl , CH_3CCH ou NH_3 . Les valeurs obtenues sont assez faibles, à cause du grand nombre de niveaux de rotation dans les toupies symétriques.

Abstract. — A theory of vibrational energy transfer using long-range multipolar interaction has been extended to the case of a transfer between a diatomic and a symmetric top molecule. Energy transfer probabilities *versus* temperature were calculated for five energy-exchange reactions between $D_2(v = 1)$ and CH_3Cl , CH_3CCH or NH_3 . Due to the great number of rotational levels in symmetric top molecules, the values obtained are rather low.

1. Introduction. — Up to now, vibration-to-vibration (V-V) energy transfer calculations based on long-range interaction forces have been mainly applied to the case of energy transfer between diatomic or linear polyatomic molecules. The theory of these calculations was first derived by Sharma and Brau [1, 2]. Assuming long-range multipolar interaction, non or weakly polar molecules and near-resonant collisions, these calculations have given results which are most

often in rather good agreement with experiment below 1 000 K. To our knowledge Preses and Flynn [3] mentioned the only application of Sharma's theory to V-V energy transfer reactions involving symmetric top molecules, but their formalism was not developed. The present paper extends Sharma's theory for energy exchange reactions between a diatomic and a symmetric top molecule.

2. Theory. — Consider the binary collision of energy defect ΔE :

$$D_2(v = n_2 + 1, J_2, M_2) + X(v_i = n_1, J_1, K_1, M_1) \rightleftharpoons D_2(v = n_2, J'_2, M'_2) + X(v_i = n_1 + 1, J'_1, K'_1, M'_1) + \Delta E$$

D_2 being a diatomic molecule, and X a symmetric top. J_1, K_1, M_1, J_2, M_2 are the initial rotational quantum numbers, $J'_1, K'_1, M'_1, J'_2, M'_2$ the final ones and n_1 and n_2 the vibrational quantum numbers of both molecules. Using first-order perturbation theory, the probability P of such a collision is given by :

$$P_{J_1 J_2 K_1 M_1 M_2}^{J'_1 J'_2 K'_1 M'_1 M'_2} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} e^{i\omega t} \langle n_2 n_1 + 1 J'_1 J'_2 K'_1 M'_1 M'_2 | V(t) | n_2 + 1 n_1 J_1 J_2 K_1 M_1 M_2 \rangle dt \right|^2$$

where $\omega = \Delta E/\hbar$, and $V(t)$ is the intermolecular potential. $V(t)$ can be expanded in terms of multipole series [4, 5] :

$$V(t) = (4\pi)^{3/2} \sum_{l=l_1+l_2} \frac{(-1)^{l_2}}{\sqrt{2l+1}} \sqrt{\frac{(2l_1+2l_2)!}{(2l_1+1)!(2l_2+1)!}} R^{-(l+1)} \sum_{\substack{m_1, m_2 \\ m_l = m_1 + m_2}} \sum_{k_1, k_2} Y_{l, m_l}^*(\Omega_r) \times \\ \times C(l_1 l_2 l | m_{l_1} m_{l_2} m_l) D_{m_{l_1}, k_1}^{l_1}(\Omega_1) D_{m_{l_2}, k_2}^{l_2}(\Omega_2) \bar{Q}_{l_1, k_1}^{(1)}(\theta'_{l_1}, \varphi'_{l_1}) \bar{Q}_{l_2, k_2}^{(2)}(\theta'_{l_2}, \varphi'_{l_2})$$

where superscript (1) refers to D_2 , (2) to X ; (R, Ω_r) is the vector distance between the two molecules, Ω_r indicating the orientation of this vector in space-fixed axes XYZ ; C and D denote the Clebsch-Gordan coefficients and the rotation matrices; Ω_1 and Ω_2 represent the set of Euler angles between convenient molecule-fixed axes and XYZ ; $\bar{Q}_{l_i, k_{l_i}}^{(i)}(\theta'_{l_i}, \varphi'_{l_i})$ is the multipole moment of molecule (i) ($l_i = 1$: dipole moment; $l_i = 2$: quadrupole moment...), defined by :

$$\bar{Q}_{l_i, k_{l_i}}^{(i)}(\theta'_{l_i}, \varphi'_{l_i}) = \sum_{\beta} l_{\beta} r_{\beta}^{l_i} Y_{l_i, k_{l_i}}(\theta_{\beta}, \varphi_{\beta})$$

θ_{β} and φ_{β} denoting the orientation of the charge β in the molecule-fixed axes of molecule (i). It can be shown that, for a diatomic molecule, the non-vanishing terms of $V(t)$ correspond to $k_{l_i} = 0$.

Thus, neglecting vibration-rotation interaction, as :

$$\begin{aligned} \langle J'_1 K'_1 M'_1 | D_{m_{l_1}, k_{l_1}}^{l_1}(\Omega_1) | J_1 K_1 M_1 \rangle &= \sqrt{\frac{2J_1 + 1}{2J'_1 + 1}} C(J_1 l_1 J'_1 | K_1 k_{l_1} K'_1) C(J_1 l_1 J'_1 | M_1 m_{l_1} M'_1) \\ \langle J'_2 M'_2 | D_{m_{l_2}, 0}^{l_2}(\Omega_2) | J_2 M_2 \rangle &= \sqrt{\frac{2J_2 + 1}{2J'_2 + 1}} C(J_2 l_2 J'_2 | 0 0 0) C(J_2 l_2 J'_2 | M_2 m_{l_2} M'_2). \end{aligned}$$

We have :

$$\begin{aligned} P_{J'_1 J'_2 K'_1 M'_1 M'_2}^{J_1 J_2 K_1 M_1 M_2} &= \frac{(4\pi)^3}{\hbar^2} \left| \int_{-\infty}^{+\infty} e^{i\omega t} \sum_{l_1, l_2} \frac{(-1)^{l_2}}{\sqrt{2l+1}} \sqrt{\frac{(2l)!}{(2l_1+1)!(2l_2+1)!}} R^{-(l+1)} \times \right. \\ &\times \sum_{m_{l_1}, m_{l_2}} \sum_{k_{l_1}} C(l_1 l_2 l | m_{l_1} m_{l_2} m_l) C(J_1 l_1 J'_1 | K_1 k_{l_1} K'_1) C(J_1 l_1 J'_1 | M_1 m_{l_1} M'_1) \\ &\times C(J_2 l_2 J'_2 | 0 0 0) C(J_2 l_2 J'_2 | M_2 m_{l_2} M'_2) \sqrt{\frac{2J_1 + 1}{2J'_1 + 1}} \times \frac{2J_2 + 1}{2J'_2 + 1} \langle n_2 | \bar{Q}_{l_2, 0}^{(2)}(\theta'_{l_2}, \varphi'_{l_2}) | n_2 + 1 \rangle \\ &\left. \times \langle n_1 + 1 | \bar{Q}_{l_1, k_{l_1}}^{(1)} | n_1 \rangle dt \right|^2. \end{aligned}$$

Following Tsao's way of calculation, [6] assuming straight line trajectories and weighting over initial rotational states by a Maxwell Boltzmann distribution, we finally get :

$$\begin{aligned} P_{J'_1 J'_2 K'_1}^{J_1 J_2 K_1} &= \sum_{l_1, l_2} \frac{(4\pi)^2}{(2l_1+1)(2l_2+1)} \frac{4(2l)!}{(2l_1+1)!(2l_2+1)!} \sum_{k_{l_1}} |Q_{l_1, k_{l_1}}|^2 |Q_{l_2}|^2 \times \\ &\times C^2(J_1 l_1 J'_1 | K_1 k_{l_1} K'_1) C^2(J_2 l_2 J'_2 | 0 0 0) \frac{G_l(\omega b/v)}{\hbar^2 v^2 b^{2l}} P_{J_1, K_1} P_{J_2} \end{aligned}$$

$Q_{l_1, k_{l_1}}$ and Q_{l_2} being the vibrational multipole matrix elements of molecules (1) and (2), b the impact parameter, P_{J_1, K_1} and P_{J_2} the distribution of rotational populations in the initial states $|n_1 J_1 K_1\rangle$ and $|n_2 + 1 J_2\rangle$ and G_l the function :

$$G_l(x) = \sum_{\mu=-l}^l [(l+\mu)!(l-\mu)!]^{-1} x^{2l} K_{\mu}^2(x)$$

where K_{μ} is the modified Bessel function of order μ .

Following Sharma's formulation [2], we can then integrate over v , and summing over J_1 , K_1 and J_2 gives :

$$\begin{aligned} P &= \frac{M}{kT} \sum_{l_1, l_2} \frac{4(2l)!}{(2l_1+1)!(2l_2+1)!} \frac{(4\pi)^2}{(2l_1+1)(2l_2+1)} \sum_{k_{l_1}} |Q_{l_1, k_{l_1}}|^2 |Q_{l_2}|^2 \times \\ &\times \sum_{J'_1 J'_2} \sum_{K'_1} C^2(J_1 l_1 J'_1 | K_1 k_{l_1} K'_1) C^2(J_2 l_2 J'_2 | 0 0 0) \frac{\bar{I}_l(b, \omega, T)}{\hbar^2 b^{2l}} P_{J_1, K_1} P_{J_2} \end{aligned}$$

where M is the reduced mass of the colliding particles, and

$$\bar{I}_l(b, \omega, T) = \frac{M}{2kT} \int_0^{\infty} \frac{1}{v^2} G_l\left(\frac{\omega b}{v}\right) \exp\left(-\frac{Mv^2}{2kT}\right) v^3 dv.$$

We can finally derive $\langle P \rangle$ by integrating over b , following Sharma [2].

3. **Applications.** — We have applied this theory to calculate $\langle P \rangle$ for the following energy-exchange reactions :

Reactions (1), (3) and (5) correspond to a parallel band, i.e., $l_1 = 1, l_2 = 2$ and $k_{l_1} = 0$; reactions (2) and (4) correspond to a perpendicular band, i.e. $l_1 = 1, l_2 = 2$ and $k_{l_1} = \pm 1$. We have used the numerical values listed in Table I for the symmetric top molecules, with for D_2 : $\omega_e = 3\,118.5 \text{ cm}^{-1}$; $\omega_e x_e = 64.1 \text{ cm}^{-1}$; $B = 30.43 \text{ cm}^{-1}$; $|Q_2|^2 = 1.1 \times 10^{-54} \text{ e.s.u.}$

Table I. — Symmetric top molecules : numerical values used in the calculation.

Molecule	CH ₃ Cl	CH ₃ Cl	CH ₃ CCH	CH ₃ CCH	NH ₃
Mode	v_1	v_4	v_2	v_6	v_1
Band centre (cm ⁻¹)	2 966.2 [7]	3 041.8 [7]	2 930 [9]	2 981 [9]	3 337 [7]
A (cm ⁻¹)	5.09	5.09	5.4 [10]	5.4	6.3
B (cm ⁻¹)	0.49	0.49	0.285	0.285	9.94
$ Q_{1,1} ^2$ (e.s.u.)	3.6×10^{-39} [8]	1.4×10^{-39} [8]	6.1×10^{-39} [9]	5.9×10^{-39} [9]	5.9×10^{-40} [11]
$\langle P \rangle$ for $T=300 \text{ K}$	1×10^{-4}	2.8×10^{-5}	1.5×10^{-5}	3.4×10^{-5}	2.5×10^{-6}

4. **Results.** — Figure 1 shows the variations of $\langle P \rangle$, summed over the initial rotational quantum numbers up to $J_1 = 50, J_2 = 10$ and $K_1 = 13$, for $T = 200 \text{ K}$ to $1\,000 \text{ K}$. It can be seen that the transfer probability is quite small as compared for example with $\text{D}_2(v = 1)\text{-HCl}(v = 0)$ V-V energy-exchange reaction for which $\langle P \rangle = 2.8 \times 10^{-4}$ [12] at 296 K . This is mainly due to the larger number of rotational levels in symmetric top molecules as compared with linear molecules. However, reaction (5) being very off-resonant, the theory must greatly underestimate $\langle P \rangle$. This explains the initial increase of $\langle P \rangle$ for reaction (5), whilst the initial increase for reaction (3) is not clear. Sharma's theory has already given good results for much more off-resonant processes than reaction (3) ($\Delta E/kT = 0.43$ for $T = 200 \text{ K}$) such as HCl-D_2 energy exchange reaction ($\Delta E/kT = 0.78$ for $T = 200 \text{ K}$) [12]. The inclusion of quadrupole-quadrupole effects, resulting in an increase of $\langle P \rangle$ for low T , might suppress this initial increase.

One must also point out that Sharma's theory doesn't satisfy the detailed rate balance, by a factor $\exp(-\Delta E_v/kT)$, where ΔE_v is the vibrational energy mismatch. It has sometimes been suggested to multiply $\langle P \rangle$ by $\alpha = \exp(-\Delta E_v/2kT)$, thus leading to the detailed balancing. By the way, for processes (1) to (4), α is close to unity. Only for process (5) is α very different from unity, thus lowering $\langle P \rangle$.

Fig. 1. — V-V energy-exchange probabilities as a function of temperature.

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