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Studies of Rotational Energy Transfer (RET) in long-range $\text{NH}_3\text{-NH}_3$ collisions in the gas phase (*)

M. Kaźmierczak

Nonlinear Optics Department, Institute of Physics,
A. Mickiewicz University, 60-780 Poznań, Poland

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Résumé. — Le champ du dipôle électrique, induit dans une molécule par un faisceau laser, crée un moment dipolaire dans une autre molécule *via* le mécanisme de polarisation non linéaire (en mettant en jeu, uniquement, l'hyperpolarisabilité b_{ijk}).

De la partie dispersionnelle de l'énergie totale d'interaction, l'auteur extrait la contribution TER. Le spectre TER est obtenu pour $\Delta J_1 = 1$. Plusieurs nouveaux traits du processus TER sont considérés.

Abstract. — The field of the laser-light induced electric dipole in a molecule creates, in another molecule, a dipole moment *via* the nonlinear polarization mechanism (including the b_{ijk} hyperpolarizability, only). From the dispersional part of the total interaction energy, we extract the RET contribution. The RET spectrum is obtained for $\Delta J_1 = 1$ and some new features of the RET process are discussed.

Recently, transfer processes have been the subject of intensive theoretical and experimental investigations. Their importance resides in the fact that various interaction-induced (JJ) effects originate in energy (charge) transfer during the interaction. Lees and Retallack found a strong dependence of the RET signal intensity on the rotational states degeneracy [1].

The collisional charge transfer model has been recently proposed for the calculation of the atomic pair polarizability anisotropy [2]. Studies of the collisional cross-sections [3] and the dependence of RET on the collision energy [4] and the rotational-to-translational molecular motion energy transfer [5] have been also performed.

In the present report we consider the excitation energy transfer which occurs in long-range molecular interactions accounting for the JJ spectra. The method of comparison between relative line intensities [6], obtained from laser-light induced Raman and JJ hyperRaman polarized spectra, is applied.

From the molecular dispersion interaction energy, the RET part is then extracted.

1. Outline of the theory. — We assume the molecules to be in their ground vibrational state. The sample is illuminated by a laser beam of frequency ω . The radiation induces in the individual

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molecules an oscillating electric multipole moment. The anisotropic dipole interaction Hamiltonian is written for the N -molecule system applying the spherical tensor formalism :

$$H = \sum_{ij}^N H_{ij} = - \sum_{ij}^N \sum_{\alpha} ({}^i\mathbf{M}^{(1)}(\mathbf{R}_{ij}) \otimes {}^j\mathbf{m}^{(1)}_{\alpha}^{(2)}) T_{\alpha}^{(2)}(\mathbf{R}_{ij}). \quad (1)$$

The electric-dipole moment ${}^i\mathbf{M}^{(1)}(\mathbf{R}_{ij})$ oscillates at twice the laser beam frequency modified by the frequency of rotational Raman transitions. It is assumed in the general form : $\mathbf{M} = \frac{1}{2} \mathbf{b} : \mathbf{E} \mathbf{F}$, wherein $\mathbf{b}$ is the hyperpolarizability tensor, $\mathbf{E}$ is the laser-light electric vector and $\mathbf{F}$ is a molecular field. Its origin will be determined further on. An electric-dipole moment ${}^i\mathbf{m}^{(1)}$ is induced at the molecule i by the laser field by way of the linear polarization mechanism. $\mathbf{T}^{(2)}(\mathbf{R}_{ij})$ is the well-known dipole-dipole interaction tensor. In second-order Rayleigh-Schrödinger perturbation theory, the interaction energy is given by :

$$U_{n_1 n_2} = \langle n_1 n_2 | H_{12} | n_1 n_2 \rangle - \sum_{n'_1 n'_2} (E_{n_1 n_2} - E_{n'_1 n'_2})^{-1} | \langle n'_1 n'_2 | H_{12} | n_1 n_2 \rangle |^2. \quad (2)$$

The initial and excited double states $|n_1 n_2\rangle$, $|n'_1 n'_2\rangle$ have unperturbed energies $E_{n_1 n_2}$ and $E_{n'_1 n'_2}$, respectively. The symbol n_i denotes the set of rotational quantum numbers $\{JKM\}$ for the i -th molecule.

The second term in equation (2) comprises inductional and dispersive interactions and is the main subject of our concern. The case of $n'_1 = n_1$, $n'_2 = n_2$ is excluded here. Usually, in calculations of the energy U , the matrix element $\langle n'_1 n'_2 | \dots | n_1 n_2 \rangle$ is factorized into $\langle n'_1 | \dots | n_1 \rangle$ and $\langle n'_2 | \dots | n_2 \rangle$. By this, the permanent-induced and induced-induced multipole interaction are described. However, due to mutual interaction, molecules undergo rotational transitions which are associated with the RET process. The form of the latter, for dipole-induced dipole interaction (DID), may be obtained by Racah algebra methods yielding :

$$\begin{aligned} \langle n'_1 n'_2 | H_{12} | n_1 n_2 \rangle = & - \sum_{N_2} \sum_{\alpha \nu \delta} [1 \nu 1 \delta | 2 \alpha] \langle n'_1 n'_2 | {}^1M_{\nu}^{(1)}(R_{12}) | n_1 N_2 \rangle \times \\ & \times \langle N_2 | {}^2m_{\delta}^{(1)} | n_2 \rangle T_{\alpha}^{(2)}(R_{12}). \end{aligned} \quad (3)$$

Here the Clebsch-Gordan coefficients are denoted by $[a\alpha b\beta | c\gamma]$.

Thus, the molecule 2, affected by an external field, is pumped to the state $|N_2\rangle$, related to the initial state $|n_2\rangle$ by way of dipole selection rules. The interaction between both molecules causes the transition of the molecule 2 to the final state $|n'_2\rangle$ while the molecule 1 is removed from the initial state $|n_1\rangle$ to the state $|n'_1\rangle$ (energy absorption). Now, the selection rules are more complicated because of interference with the rules which originate in the existence of intermediate states $|N_2\rangle$ (Fig. 1).

Fig. 1. — The excitation-collision induced deexcitation scheme. The state 3_1 is assumed to be the initial one. Pumping — empty arrows; deexcitation — solid line arrows.

The electric-dipole moment ${}^1\mathbf{M}^{(1)}(\mathbf{R}_{12})$ oscillating at a frequency $2\omega \pm \omega_{n_1n'_1}$ ($\omega_{n_1n'_1}$ is the transition frequency between the states $|n_1\rangle$ and $|n'_1\rangle$) is taken in the form :

$${}^1M_v^{(1)}(\mathbf{R}_{12}) = \frac{1}{4} \sum_{Tb} (2T+1)^{1/2} (\mathbf{A}^{(b,T)}(\mathbf{R}_{12}) \otimes \mathbf{E}^{(b)}_v)^{(1)}, \quad (4)$$

where $\mathbf{E}^{(b)}$ represents the external electric field tensor :

$$E_\gamma^{(b)} = (\mathbf{E}^{(1)} \otimes \mathbf{E}^{(1)})_\gamma^{(b)} = \sum_{\alpha\beta} [1 \alpha 1 \beta | b \gamma] E_\alpha^{(1)} E_\beta^{(1)},$$

while the third-rank $\mathfrak{J}\mathfrak{J}$ polarizability tensor is described by the relation [7] :

$$A_\omega^{(b,T)}(\Omega_1 \Omega_2 R_{12}) = \sum_{kl} (-1)^{l-k+\omega} [(2k+1)(2l+1)(2T+1)]^{1/2} \begin{Bmatrix} l & k & T \\ 1 & b & 1 \end{Bmatrix} \times \\ \times (\mathbf{b}^{(b,l)}(\Omega_1) \otimes \mathbf{L}^{(k)}(\Omega_2 \mathbf{R}_{12}))_\omega^{(T)}. \quad (5a)$$

Here, $\mathbf{b}^{(b,l)}(\Omega)$ is the orientation-dependent first-order Raman hyperpolarizability of the single molecule, $\mathbf{L}^{(k)}$ is the Kirkwood-Yvon oscillating molecular field derivative with respect to the variations in the initial electric field :

$$L_\sigma^{(k)} = - \sum_{rs} (-1)^{r-s} [(2r+1)(2s+1)]^{1/2} \begin{Bmatrix} r & s & k \\ 1 & 1 & 1 \end{Bmatrix} (\mathbf{T}^{(r)}(\mathbf{R}_{12}) \otimes \mathbf{a}^{(s)}(\Omega_2))_\sigma^{(k)}. \quad (5b)$$

The symbol $\mathbf{a}^{(s)}$ denotes the spherical s -rank linear polarizability and $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ is the 6 j coefficient.

Insertion of equations (4, 5a, b) into equation (3) and then into equation (2) gives an approximate formula for the energy U in DID interaction regime. Additionally, some restrictions on the rotational selection rules must be imposed. The intrinsic polarizability tensor $\tilde{\alpha}_\tau^{(t)}$ appearing in the laser-field induced dipole formula $m \sim \tilde{\alpha}_\tau^{(t)} E^{(1)}$, when calculated in the frame of NH_3 molecule principal axes, is nonzero for $t = 0$ and 2 and for $\tau = 0$ only. Thus, the admissible selection rules are : $\Delta j = 0, \pm 1, \pm 2$, and the positive values of Δj only are accepted for the description of the pumping process, whereas the negative ones indicate spontaneous emission effects due to rotational transitions.

Let us consider the factor $(E_{n_1n_2} - E_{n_1n'_2})^{-1}$ which we rewrite, according to [8], as :

$$(E_{n_1n_2} - E_{n_1n'_2})^{-1} \simeq \frac{E_1 E_2}{E_1 + E_2} [(E_{n_1} - E_{n'_1})(E_{n_2} - E_{n'_2})]^{-1}, \quad (6)$$

where E_1 and E_2 are the excitation energies of the two molecules.

Denoting the $\mathfrak{J}\mathfrak{J}$ transitions by ΔJ , one finds that $n'_2 - n_2 = \Delta j + \Delta J$ which leads to $\Delta j \neq |\Delta J|$ (otherwise Eq. (6) becomes indefinite). The form of the nonzero linear polarizability components determines the rules for transitions between K substates ; for all transitions we have $\Delta K = 0$.

The hyperpolarizability tensor $\tilde{b}^{(1)}$ of the ammonia molecule in its completely symmetric representation has, in the ground vibrational state, four nonzero components : $\tilde{b}_0^{(1)}, \tilde{b}_0^{(3)}, \tilde{b}_{\pm 3}^{(3)}$. Hence, the selection rules for the transitions of molecule 1 are : $\Delta J_1 = 0, \pm 1, \pm 2, \pm 3$ and $\Delta K_1 = 0, \pm 3$. The total change in rotational energy during the $\mathfrak{J}\mathfrak{J}$ initial-to-final state transition ($|N_2\rangle$ is thus the initial state of molecule 2) is given by :

$$\Delta E_1 = B \Delta J_1 (2J_1 + \Delta J_1 + 1) + A \Delta K_1 (2K_1 + \Delta K_1), \quad (7a)$$

$$\Delta E_2 = B \Delta J (2J_2 + 2\Delta j + \Delta J + 1) + A \Delta K (2K_2 + 2\Delta K_2 + \Delta K), \quad (7b)$$

where A and B are the rotational constants.

The total energy absorbed by molecule 1 during interaction is postulated to be equal to the energy emitted by molecule 2, i.e. $\Delta E_1 = |\Delta E_2|$. This fitting formula is a control test for the adequate choice of transfer-active states, so taking into account the state $|n_1\rangle$ we can find the transfer-active states $|n_2\rangle$. It has been confirmed that $\Delta K = \Delta K_2 = 0$ which, due to the adjustment relation, entails $\Delta K_1 = 0$ and $\Delta J_1 > 0$. The above selection rules enable us to extract from equation (2) the component related with RET calculated further on under rejection of all but the two-molecule radial correlations, performing unweighted averaging over orientations. The final formula is split into two components to obtain :

$$|\langle |H_{12}| \rangle|^2 = \frac{16}{140\,625} \langle R_{12}^{-12} \rangle (2J'_1 + 2\Delta J + 1) \sum_{\Delta J} (2J_2 + 2\Delta J + 1) \times \\ \times \left[\frac{989}{81} (J'_1 - K'_1 10 |J_1 K_1|^2 |\tilde{b}_0^{(1)}|^2 + \frac{38}{7} (J'_1 - K'_1 30 |J_1 K_1|^2 |\tilde{b}_0^{(3)}|^2 \right] \\ \times (J_2 + \Delta J - K 20 |J_2 K_2|^2 |\tilde{a}_0^{(2)}|^2 |\tilde{a}_0^{(0)}|^2 I^3, \quad (8a)$$

$$|\langle |H_{12}| \rangle|^2 = \frac{16}{28\,125} \langle R_{12}^{-12} \rangle (2J'_1 + 1) \sum_{JK} (2J + 1)(2J'_2 + 1) \times \\ \times \left[\frac{989}{81} (J'_1 - K'_1 10 |J_1 K_1|^2 |\tilde{b}_0^{(1)}|^2 + \frac{38}{7} (J'_1 - K'_1 30 |J_1 K_1|^2 |\tilde{b}_0^{(3)}|^2 \right] \\ \times \left[\frac{1}{5} \left\{ \begin{matrix} J_2 & J'_2 & 0 \\ 2 & 2 & J \end{matrix} \right\}^2 + \frac{2}{7} \left\{ \begin{matrix} J_2 & J'_2 & 2 \\ 2 & 2 & J \end{matrix} \right\}^2 + \frac{2}{315} \left\{ \begin{matrix} J_2 & J'_2 & 4 \\ 2 & 2 & J \end{matrix} \right\}^2 \right] \\ \times (J'_2 - K'_2 20 |JK|^2 (J - K 20 |J_2 K_2|^2 |\tilde{a}_0^{(2)}|^4 I^3, \quad (8b)$$

for $\Delta j = 0$ and $\Delta j \neq 0$, respectively. Herein I is the laser-light intensity, $(\alpha\alpha\beta\beta|c\gamma)$ the 3j coefficient and $J'_m = J_m + \Delta J_m$. Next, these formulae are multiplied by the Boltzmann number of molecules in the given rotational state.

2. Results. — The main purpose of our calculations was to determine the spectral distribution for laser-light induced RET. The one-mole gaseous sample with a density of 150 amagats at 300 K was illuminated by a laser beam of intensity $I = 4 \times 10^{-14} \text{ J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. The total RET cross-section in DID model was found to be proportional to $\langle R_{12}^{-12} \rangle$ (averaged intermolecular separation defined as in [7]). Using the L-J potential and taking the appropriate L-J parameters for NH_3 [9], the region from $R/\sigma = 0.86$ to 2.4 was examined. A narrow transfer maximum was observed at $R/\sigma = 1.06$, while for $R/\sigma > 1.5$ the total RET signal intensity became stabilized (Fig. 2 — SI units). Our conviction is, however, that since our approach used the DID approximation, the transfer contribution determined for distances larger than $R/\sigma = 1.5$ is the most realistic. This results from the known mean separation between the molecules in gas phase media.

RET temperature-dependence investigations show that, for the temperatures under study, the differences in transferred energy values are about 31 % while only about 1.6 to 1.8 % between two neighbouring temperature points (independently of the induced transition — Fig. 3). The effect of temperature on the total RET intensity was found to decrease with increasing number J_1 .

If a given molecule is strongly excited (large J_1) before the collision, then the probability of the $\mathfrak{J}\mathfrak{J}$ transition is negligible and independent on the excitation degree of all other molecules. The decay of the RET intensity is demonstrated on the RET spectrum (Fig. 4).

In reference [10], a strong dependence of the rotational spectra structure (e.g. for NH_3) on the sign of the hyperpolarizability tensor components b_{ijk} given in the literature is proved. Now the approach of reference [10] is extended to the RET spectra calculated with the data of references [11, 12]. In this approach we have dealt with two spectra, the first of which is shown in figure 4. The

Fig. 2. — Total RET vs. intermolecular separation when interaction of the Lennard-Jones type is assumed.

Fig. 3. — Temperature dependence of the rotational energy transferred to the $J_1 = 9$ state of the absorber molecules in the transitions: $\Delta J_1 = 1$ ($U \times 10$) — filled circles; $\Delta J_1 = 2$ ($U \times 10^{11}$) — crosses; $\Delta J_1 = 3$ ($U \times 10^{11}$) — empty circles.

presentation of the second RET spectrum is omitted because of the structural identity of the two. A comparison between the transferred energies related with the corresponding lines within both spectra shows that they differ but imperceptibly. This leads to the conclusion that the RET spectra are not significantly affected by the sign of the hyperpolarizability components. The ratio U_H/U_A of transferred energies, calculated for the two sets of hyperpolarizability component data, ranges from 1.456 1 to 1.640 1 for the $\Delta J_1 = 1$ branch (Fig. 5). With no further calculations, that ratio, with equations (8a, b), has been estimated for $\Delta J_1 = 2$ and 3 to be equal to 0.146 2 which results from the assumed fully symmetric form of b_{ijk} . However, when the $\mathcal{J}\mathcal{J}$ transitions are energetically fitted, it is indispensable to introduce an asymmetric form of that tensor (then U_H/U_A remains unchanged for $\Delta J_1 = 3$, only).

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Fig. 4. — Structure of the RET spectral branch for $\Delta J_1 = 1$.

Fig. 5. — Ratio of transferred energies U_H (data of Ref. [11]) and U_A (data of Ref. [12]). The transition rule is $\Delta J_1 = 1$.

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