



HAL
open science

I.Theory of the relaxation by collision of molecular multipole moments : impact approximation with long range electrostatic interactions

M.A. Mélières-Maréchal, M. Lombardi

► **To cite this version:**

M.A. Mélières-Maréchal, M. Lombardi. I.Theory of the relaxation by collision of molecular multipole moments : impact approximation with long range electrostatic interactions. *Journal de Physique*, 1977, 38 (6), pp.527-546. 10.1051/jphys:01977003806052700 . jpa-00208614

HAL Id: jpa-00208614

<https://hal.science/jpa-00208614>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LE JOURNAL DE PHYSIQUE

I. THEORY OF THE RELAXATION BY COLLISION OF MOLECULAR MULTIPOLE MOMENTS : IMPACT APPROXIMATION WITH LONG RANGE ELECTROSTATIC INTERACTIONS

M. A. MÉLIÈRES-MARÉCHAL and M. LOMBARDI

Laboratoire de Spectrométrie Physique (*), Université Scientifique et Médicale de Grenoble,
B.P. 53, 38041 Grenoble cédex, France

(Reçu le 5 octobre 1976, accepté le 10 février 1977)

Résumé. — Un traitement théorique de la relaxation et du transfert de moments multipolaires de molécules lors des collisions intermoléculaires est présenté, basé sur l'approximation d'impact. Les expressions générales des sections efficaces de collision relatives aux différentes interactions multipôle-multipôle sont obtenues au premier et second ordre des perturbations en considérant un potentiel électrostatique à longue distance. La généralisation à un potentiel à courte distance est discutée. Les effets des structures fines et hyperfines sont traités dans les cas de couplage de Hund a et b.

Abstract. — A theoretical treatment of the relaxation and transfer of molecular multipole moments due to intermolecular collisions is presented assuming the impact approximation. General expressions for the collision cross section are obtained for any multipole-multipole interaction, to first and second order of perturbation assuming a long range electrostatic potential. The generalization to short range potential is discussed. Effects of fine and hyperfine structure in Hund's cases a and b are sketched.

1. Introduction. — The effect of collisions between molecules or neutral atoms in the gaseous state on the lineshapes of optical emission lines has been studied for a long time. The most widely used method of calculation uses the semi-classical impact theory of Anderson [1] and its various improvements and extension. A recent review of the relaxation calculations, discussing in particular the validity of the Anderson approximation has been recently made by Rabitz [2] for the rotation and rotation-vibration lineshapes, where the reader can find numerous references to the previous literature. To take into account the isotropy of the collision processes, it is useful to use tensor operator formalism, this has been done in the standard reference works of Tsao and Curnutte [3], and more recently by Ben Reuven [4]. These works study optical linewidth and displacement, but this tensor operator formalism is also particularly well adapted to study the relaxation processes of *polarization* dependant phenomena, which were not studied in previous works, owing to the fact that the polariza-

tion of emitted light is easily related to the tensorial components of the density matrix. This theoretical framework [3, 4] has been used by Omont [5], D'Yakov and Perel [6] to study relaxation processes of polarization-dependant phenomena in atoms (Hanle effect [7], magnetic resonance, etc...) and extended by Carrington, Stacey and Cooper [8] to atoms with any angular momenta. More recently this kind of polarization-dependant studies has been extended to diatomic molecules. It is then useful to adapt the preceding theories to this case. In this paper we present the equations needed to study the effect of collision on various characteristic quantities of the upper molecular state of the optical transition studied : total intensity, polarization, etc... We limit ourselves explicitly to measurements integrated over the linewidth of the optical line, i.e. we do not study the line shape of the optical emission line, since this work has already been done by Tsao and Curnutte. On the other hand we develop fully the theory for the case where a long distance potential gives the main contribution to the relaxation (but some intermediate formulae give useful angular momentum averaged expressions valid also in case of short distance interactions). This

(*) Laboratory associated with the Centre National de la Recherche Scientifique.

approximation is likely to be much more valid for relaxation of polarization than for transfers.

In paper II [9], we apply this theory to a particular example : relaxation of the polarization of light emitted by the $(1s\ 3p)^3\Pi_u$ state of the hydrogen molecule.

2. Model of collision. — The collision model is exactly the same as the one used by Omont for the atomic case. For the sake of clarity we write down the various hypotheses and approximations made :

— Binary impact approximation : the interaction between atoms can be represented by two body collisions well separated in time : the duration of a collision τ_c , is short as compared to the time between two collisions, T_c .

— Semi-classical approximation : the motion of the centre of mass of the two interacting systems is treated classically (in fact, in explicit calculations, we limit ourselves to the straight line trajectory approximation). The internal state of these two systems is treated quantum mechanically : it evolves under the effect of the interaction potential V .

— *Sudden* approximation : during the time τ_c of the collision, the influence of external phenomena can be neglected : applied fields, spontaneous emission, excitation.

— Adiabatic approximation : in principle, to study the evolution of the internal states of the atoms under the effect of the interaction potential V , one has to take into account an infinite number of levels. To reduce this number, we separate the levels of the combined system into two groups. The first group is composed of the levels differing in energy from the initial one by an energy of the order of $1/\tau_c$ or less (we use $\hbar = 1$) : according to Heisenberg's principle of uncertainty there can be appreciable real transition between these states. The second group is composed of the more distant levels. There cannot be appreciable real transitions to these levels at the end of the collision, but virtual transitions to these states can exist during the collision. We take into account the effect of these distant levels by the perturbation theory. The effective potential, V_{eff} , that we take into account during the collision is not limited to the projection of the interaction potential V into the first group of levels, but is given by the Rayleigh Schrödinger perturbation theory

$$V_{\text{eff}} = PVP + PV \frac{Q}{E - \mathcal{H}_0} VP + \dots \quad (1)$$

where P is the projection operator into the first group of states (nearby levels) and $Q = 1 - P$ the projection operator on distant levels; \mathcal{H}_0 is the hamiltonian of the two non-interacting molecules, E is the energy of the initial state. Explicit calculations will be made only for the first two terms in the development of V_{eff} .

— *Long range approximation.* The formula (42) does not depend on this approximation and is valid for any kind of potential V (see § 3.4.2) : it incorporates all the angular momentum recoupling calculations but needs a numerical integration. We also give explicit calculations in the usual case in which it is supposed that the interaction V may be described by an electrostatic potential expanded in powers of $1/R$ (R distance between the two molecules), and limited to the first few terms : this supposes essentially that the measured cross-section is greater than the geometric cross-section, i.e. no overlap of the two molecules during the collision.

— Effect of spins :

a) Nuclear spins. — The hyperfine interaction being negligible as compared both to the electrostatic interaction potential V and to the reciprocal of the collision time $1/\tau_c$, we suppose that the nuclear spins *stand still* during the collision and are not taken into account during the calculation of the collision process. The recoupling after the collision is studied in § 4.

b) Electronic spins. — We treat separately the molecular Hund's case b and a or c. In case b the electronic spin S is weakly coupled to the total orbital angular momentum N . It is treated as above for the nuclear spins. Paragraph 3 gives the formula neglecting the electronic spin during the collision and paragraph 4 gives the recoupling after collision. In case a or c the spin orbit interaction is much larger than the rotational separation and usually larger than the reciprocal of the collision time $1/\tau_c$. The main paragraph 3 is then also valid directly for case a, the *electronic* part of the wave function including the electronic spin in the molecular frame; the other spin components of the same multiplet are treated as other *electronic levels* of the second group (distant levels). In the case in which the spin orbit interaction is of the same order of magnitude as $1/\tau_c$, these other spin components are merely included in the first group (near levels).

3. Relaxation of the density matrix : orbital case. —

As indicated in § 2 this part includes both the effect of the collision on the orbital angular momentum N in case b (with neglect of spin) and the effect of the collision on the total electronic momentum J in case a or c : in the following formulae we always write N for simplicity, but it must be understood that N has to be replaced by J in case a or c.

In § 3.1 we note the various averaging and intermediate steps needed to relate the evolution of the mean density matrix to the description of a particular collision with definite impact parameter and velocity, modulus and direction : this evolution is defined by a Γ matrix.

In § 3.2 we relate this Γ matrix to the usual S matrix of collision theory, written in ordinary wave function space. In § 3.3 we calculate explicitly the S matrix as a function of the interaction potential

V_{eff} . In § 3.4 we give the final formulae for the Γ matrix, and in § 3.5 we give the useful cross sections as a function of Γ .

3.1 DESCRIPTION OF THE COLLISION BY A Γ MATRIX.

— 3.1.1 *Collision parameters.* — The collision is described in the following manner : The entire system under study is composed at time t of two molecular systems separated by a distance $R(t)$. One of them (molecule A) is in the excited state and is considered to be fixed at O_A ; the other (molecule B) is in the ground state and moves at a uniform relative velocity \mathbf{v} (we do not take into account the case of exchange of excitation). The impact parameter, \mathbf{b} (Fig. 1) completes the geometrical description of the collision. If the time between two successive collisions is T_c , the two molecules A and B are infinitely distant and have no interaction at $t - T_c/2$, while they are again infinitely distant at $t + T_c/2$, having undergone collision in between.

The state of the molecule will be described in Dirac notation by $|\alpha N\rangle$, α indicating the group of the other quantum numbers for the excited molecule and $|\beta \nu\rangle$ for the ground state molecule; in general (except for the α and β) the Roman letters are associated with the excited molecule A, and Greek letters with the ground state molecule B.

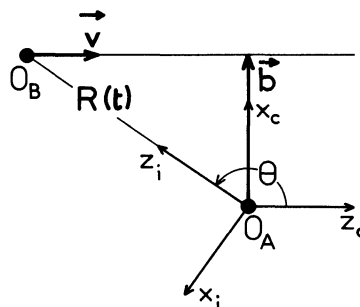


FIG. 1.

3.1.2 *Definition of Γ matrix in the subspace of the excited molecule A.* — The density matrix ρ_A of the excited molecule A is a stationary solution of the equation in the impact approximation :

$$\frac{d\rho_A}{dt} = -i[\mathcal{H}_e, \rho_A] + \frac{\delta\rho_A}{\delta t} - \frac{\rho_A}{\tau} + \rho_A^{\text{exc.}}$$

where \mathcal{H}_e is the Hamiltonian representing external perturbations to which the molecule is subjected other than the collisions (in general the external applied fields), τ the radiation lifetime of the excited state considered, $\rho^{\text{exc.}}$ the excitation term, and $\delta\rho_A/\delta t$ is the change in the density matrix per unit time under the action of the collisions. We only consider isotropic collisions : the relative velocity of the two interacting molecules is completely random; we then expand ρ_A according to its components in the irreducible tensor base defined by Omont [5] :

$$\rho_A = \sum_{\alpha N \alpha' N'} \alpha N \alpha' N' \rho = \sum_{\alpha N \alpha' N' k q} \alpha N \alpha' N' \rho_q^k \alpha N \alpha' N' T_q^k. \tag{2}$$

In what follows only the quantum number N is of interest and accordingly we now drop the index α . T_q^k is the q th standard component of the irreducible tensor of k order defined in the $|\alpha N\rangle$ space with the normalization

$$\text{Tr} ({}^{NN'} T_q^k {}^{N_1 N_1'} T_{q_1}^{k_1+}) = \delta_{NN_1} \delta_{N'N_1'} \delta_{kk_1} \delta_{qq_1} \tag{3}$$

and

$$\langle N_1 \parallel {}^{NN'} T_q^k \parallel N_1' \rangle = (2k + 1)^{1/2} \delta_{NN_1} \delta_{N'N_1'}. \tag{4}$$

Each tensorial component ${}^{NN'} \rho_q^k$ is then a stationary solution of an equation

$$\frac{d}{dt} {}^{NN'} \rho_q^k = -i \sum_{k' q'} \text{Tr} ([\mathcal{H}_e, {}^{NN'} T_q^k] T_q^{k'+} {}^{NN'} \rho_q^{k'}) + \frac{\delta}{\delta t} {}^{NN'} \rho_q^k - \frac{1}{\tau} {}^{NN'} \rho_q^k + {}^{NN'} \rho_q^{\text{exc. } k}. \tag{5}$$

The term $\frac{\delta}{\delta t} {}^{NN'} \rho_q^k$ represents the change per unit time undergone by the component ${}^{NN'} \rho_q^k$ under the average effect of the collisions. The isotropy of the collision direction implies (cf. Omont's proof [5]) that tensorial orders of different k are not linked :

$$\frac{\delta}{\delta t} {}^{NN'} \rho_q^k(t) = \sum_{N_0 N_0'} {}^{NN' N_0 N_0'} \overline{\Delta \Gamma}^k {}^{N_0 N_0'} \rho_q^k(t) \tag{6}$$

where ${}^{NN'}N_0N_0\overline{\Delta\Gamma}^k$ represents the transfer of the quantity ${}^{N_0N_0}\rho_q^k$ from the level N_0 to the level N ; its expression is obtained as follows :

We consider first a single collision characterized by the two parameters \mathbf{b} and \mathbf{v} . The collision, occurring between the instants $t - \frac{T_c}{2}$ and $t + \frac{T_c}{2}$, may be described by a $\Gamma(\mathbf{b}, \mathbf{v})$ matrix related to the molecule A :

$${}^{NN'}\rho_q^k\left(t + \frac{T_c}{2}\right) = \sum_{N_0N_0k_0q_0} {}^{NN'}N_0N_0\Gamma_{qq_0}^{kk_0} {}^{N_0N_0}\rho_{q_0}^{k_0}\left(t - \frac{T_c}{2}\right). \quad (7)$$

The change in the density matrix under the influence of this collision is :

$${}^{NN'}\Delta\rho_q^k = {}^{NN'}\rho_q^k\left(t + \frac{T_c}{2}\right) - {}^{NN'}\rho_q^k\left(t - \frac{T_c}{2}\right).$$

According to the assumptions made, T_c is large compared with the duration of the collision and is therefore allowed to tend to infinity.

The average term $\frac{\delta}{\delta t} {}^{NN'}\rho_q^k$ is then obtained

— by averaging ${}^{NN'}\Delta\rho_q^k$ over the directions of \mathbf{v} and \mathbf{b} (Euler angles of the collision frame relative to the laboratory frame); Omont has shown that for isotropic collisions this average is of the form :

$$\langle {}^{NN'}N_0N_0\Gamma_{qq_0}^{kk_0}(\mathbf{b}, \mathbf{v}) \rangle_{\text{dir. } \mathbf{v}, \mathbf{b}} = {}^{NN'}N_0N_0\Gamma^k(b, v) \delta_{kk_0} \delta_{qq_0}$$

with

$${}^{NN'}N_0N_0\Gamma^k(b, v) = \frac{1}{2k+1} \sum_q {}^{NN'}N_0N_0\Gamma_{qq}^{kk}(b\mathbf{e}_{x_c}, v\mathbf{e}_{z_c}) \quad (8)$$

\mathbf{e}_{x_c} and \mathbf{e}_{z_c} being the unit vectors in the collisions frame (Fig. 1);

— by weighting the preceding term by the number of collisions (b, v) per unit time (i.e. $nvP(v) 2\pi b db dv$ where n is the number of relaxing molecules per unit time) and integrating over b and v .

We finally obtain :

$${}^{NN'}N_0N_0\overline{\Delta\Gamma}^k = n \int_v \int_b \sum_{N_0N_0} {}^{NN'}N_0N_0\Delta\Gamma^k P(v) v 2\pi b db dv \quad (9)$$

with

$${}^{NN'}N_0N_0\Delta\Gamma^k = ({}^{NN'}N_0N_0\Gamma^k - \delta_{NN_0} \delta_{N'N'_0}) \delta_{kk_0} \delta_{qq_0}. \quad (10)$$

3.1.3 Relation between ρ_A and ρ_{AB} . — Let ρ_A , ρ_B and ρ_{AB} be the density matrices respectively representing the states of the molecule A, the molecule B, and the two molecules together; they are respectively defined in the two spaces subtended by $|\alpha N\rangle$ and $|\beta v\rangle$ and in the product space subtended by $|\alpha\beta Nv\rangle$. As previously (2), these matrices can be expanded in terms of irreducible tensors defined by relation (3) and (4) : ρ_A is related to ρ_{AB} by the relation $\rho_A = \text{Tr}_B(\rho_{AB})$ which implies, when taking into account the isotropy of the ground state :

$${}^{NN'}\rho_q^k = \sum_{vv'} (2v+1)^{1/2} {}^{vv'}\rho_{q_0}^{k_0} \delta_{vv'}. \quad (11)$$

In the same way as to the Γ_A matrix, the Γ_{AB} matrix connects the tensorial components of ρ_{AB} after and before collision :

$${}^{NN'}\rho_{q\sigma}^{k\kappa}(+\infty) = \sum_{\substack{k_0q_0 \\ \kappa_0\sigma_0}} {}^{NN'}N_0N_0\Gamma_{q\sigma q_0\sigma_0}^{k\kappa k_0\kappa_0} {}^{N_0N_0}\rho_{q_0\sigma_0}^{k_0\kappa_0}(-\infty). \quad (12)$$

In order to obtain the components of Γ_A in terms of Γ_{AB} we replace on the left hand side of (7) the components of $\rho_A(+\infty)$ as a function of those of $\rho_{AB}(+\infty)$ using relation (11) then we express the latter as a function of the components of $\rho_{AB}(-\infty)$ using (12). By identification, Γ_A and Γ_{AB} can be related using two of the assumptions made to describe the collision :

(i) absence of correlation between the two molecules before collision :

$${}^{N_0N_0}\rho_{q_0\sigma_0}^{k_0\kappa_0}(-\infty) = {}^{N_0N_0}\rho_{q_0}^{k_0}(-\infty) {}^{v_0v_0}\rho_{\sigma_0}^{\kappa_0}(-\infty);$$

(ii) the incident molecule B is in an isotropic ground state :

$${}_{v_0 v_0'} \rho_{\sigma_0}^{\kappa_0}(-\infty) = \frac{\Pi(\beta v_0)}{(2v_0 + 1)^{1/2}} \delta_{v_0 v_0'} \delta_{\kappa_0 0} \delta_{\sigma_0 0}$$

where $\Pi(v_0)$ represents the total population of the level v_0 including the nuclear spin degeneracy ; $\sum_{\beta v_0} \Pi(\beta v_0) = 1$.

Identification of terms gives :

$${}_{NN' N_0 N_0'} \Gamma_{qq_0}^{kk_0} = \sum_{\substack{v_0 \\ v_0' v_0'}} \Pi(v_0) \left(\frac{(2v_0 + 1)}{(2v_0 + 1)} \right)^{1/2} {}_{vv' v_0 v_0'} \Gamma_{q_0 q_0 0}^{k_0 k_0 0} \delta_{vv'} \delta_{v_0 v_0'}$$

and Γ^k , given by (8), becomes :

$${}_{NN' N_0 N_0'} \Gamma^k = \frac{1}{2k + 1} \sum_{v_0 q} \Pi(v_0) \left(\frac{2v_0 + 1}{2v_0 + 1} \right)^{1/2} {}_{vv' v_0 v_0'} \Gamma_{q_0 q_0}^{k_0 k_0} \quad (13)$$

3.2 Γ MATRIX AS A FUNCTION OF THE \tilde{S} MATRIX. — The state of the system composed of the two molecules A and B at time t is related to the preceding instant of time, t_0 , by the evolution operator $U(t, t_0)$ which is the solution of the equation, in the interaction representation :

$$i \frac{d\tilde{U}(t, t_0)}{dt} = \exp(i\mathcal{H}_0 t) V_{\text{eff}}(t) \exp(-i\mathcal{H}_0 t) \tilde{U}(t, t_0) \quad (14)$$

$\tilde{\rho}(t)$ is then related to $\rho(t_0)$ by :

$$\tilde{\rho}(t) = \exp(i\mathcal{H}_0 t) \rho(t) \exp(-i\mathcal{H}_0 t) = \tilde{U}(t, t_0) \tilde{\rho}(t_0) \tilde{U}^+(t, t_0) \quad (15)$$

We consider only the projections of ρ in the given subspaces N (we do not study the coherences between N and N'); within such a subspace $\rho(t) = \tilde{\rho}(t)$. In the present particular case of the collision, where the states after ($t = +\infty$) and before ($t_0 = -\infty$) the collision are designated respectively by the quantum numbers $(\alpha N, \beta v)$ and $(\alpha N_0, \beta v_0)$, we set $\tilde{U}(+\infty, -\infty) = \tilde{S}$ so that we have from (15)

$${}_{vv'} \tilde{\rho}(+\infty) = {}_{vv_0} \tilde{S} {}_{v_0 v_0'} \tilde{\rho}(-\infty) {}_{v_0 v'} \tilde{S}^+ \quad (16)$$

Replacing $\tilde{\rho}$ and \tilde{S} in eq. (16) by their corresponding expansions in tensorial components and taking the trace, one obtains the relation :

$${}_{vv'} \tilde{\rho}_{q\sigma}^{k\kappa}(+\infty) = \sum_{\substack{N_0 v_0 \kappa_0 \kappa_0' \\ N_0' v_0' \kappa_0' \kappa_0'}} {}_{vv_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} {}_{v_0 v_0'} \tilde{S}_{q_j \sigma_j}^{k_j \kappa_j +} \times \text{Tr} ({}_{NN_0} T_{q_i}^{k_i} {}_{N_0 N_0'} T_{q_0}^{k_0} {}_{N' N_0'} T_{q_j}^{k_j +} {}_{NN'} T_q^{k+}) \\ \times \text{Tr} ({}_{v_0 v_0'} T_{\sigma_i}^{k_i} {}_{v_0 v_0'} T_{\sigma_0}^{k_0} {}_{v_0 v_0'} T_{\sigma_j}^{k_j +} {}_{vv'} T_{\sigma}^{k+}) {}_{v_0 v_0'} \tilde{\rho}_{q_0 \sigma_0}^{k_0 \kappa_0}(-\infty) \quad (17)$$

By identification of the expressions (17) and (12), the tensorial components of the Γ_{AB} matrix can be obtained as a function of the operator \tilde{S} . We shall express the result of this identification in the particular case that interest us, i.e. for the components of Γ which arise in (13) (i.e. with $k = k_0, q = q_0, \kappa = \kappa_0, \sigma = \sigma_0 = 0, v = v', v_0 = v_0'$); the $\{ \}$ symbol represents the « 6j » symbol of Wigner; we obtain :

$$\sum_q {}_{vv' v_0 v_0'} \Gamma_{q_0 q_0}^{k_0 k_0} = \sum_{k_i \kappa_i q_i \sigma_i} (-)^{(N' + N_0 + k_i + k)} \frac{(2k + 1)}{(2v + 1)^{1/2} (2v_0 + 1)^{1/2}} \times \left\{ \begin{matrix} k_i & N_0 & N \\ k & N' & N_0' \end{matrix} \right\} {}_{vv_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} {}_{v_0 v_0'} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i +}$$

This expression permits us to relate the Γ^k given by (13), and thence the $\Delta\Gamma^k$ given by (10), to the \tilde{S} matrix

$${}_{NN' N_0 N_0'} \Gamma^k = \sum_{v_0 k_i \kappa_i} \frac{\Pi(v_0)}{(2v_0 + 1)} (-)^{(N' + N_0 + k_i + k)} \left\{ \begin{matrix} k_i & N_0 & N \\ k & N' & N_0' \end{matrix} \right\} \times \sum_{q_i \sigma_i} {}_{vv_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} {}_{v_0 v_0'} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i +} \quad (18)$$

In the remainder of the calculation we shall retain only the terms which do not involve coherence i.e. $N = N'$ and $N_0 = N_0'$, owing to the fact that the present calculation is concerned with optical transitions emitted by the levels N , and not with transitions between N and N' .

We give the following expression for $\Delta\Gamma^k$, obtained from (18) but written in a different form (appendix A); we thus obtain two expressions for $\Delta\Gamma^k$ according to the relative values of N and N_0 :

$$N = N_0$$

$${}^{NNNN}\Delta\Gamma^k = \sum_{\nu\nu_0} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} \sum'_{k_i\kappa_i} \sum_{q_i\sigma_i} \left((-)^{(2N+k_i+k)} \begin{Bmatrix} k_i & N & N \\ k & N & N \end{Bmatrix} \left| \begin{smallmatrix} NN \\ \nu\nu_0 \end{smallmatrix} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \right|^2 - \frac{1}{(2N+1)} \sum_{N'} \left| \begin{smallmatrix} N'N \\ \nu\nu_0 \end{smallmatrix} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \right|^2 \right) \quad (19a)$$

$$N \neq N_0$$

$${}^{NNN_0N_0}\Delta\Gamma^k = \sum_{\nu\nu_0} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} \sum'_{k_i\kappa_i} \sum_{q_i\sigma_i} (-)^{(N+N_0+k_i+k)} \begin{Bmatrix} k_i & N_0 & N \\ k & N & N_0 \end{Bmatrix} \left| \begin{smallmatrix} NN_0 \\ \nu\nu_0 \end{smallmatrix} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \right|^2. \quad (19b)$$

In these expressions \sum' signifies that k_i and κ_i are not simultaneously zero. We note that when $k = 0$, expression (19a) reduces to

$${}^{NNNN}\Delta\Gamma^0 = - \sum_{\nu\nu_0} \sum'_{k_i\kappa_i} \sum_{q_i\sigma_i} \sum_{N' \neq N} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} \frac{1}{(2N+1)} \left| \begin{smallmatrix} N'N \\ \nu\nu_0 \end{smallmatrix} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \right|^2$$

i.e.

$$(2N+1)^{1/2} {}^{NNNN}\Delta\Gamma^0 = - \sum_{N' \neq N} (2N'+1)^{1/2} {}^{N'N'NN}\Delta\Gamma^0.$$

This relation means that the change (departure) in population of the level N is equal to the change (arrival) in population of all the states with $N' \neq N$. (The population of N is given by $\text{Tr}(\rho \times {}^{NN}1)$; from the definition of normalization of the tensor \mathbf{T} , (3), we have ${}^{NN}1 = {}^{NN}T^0(2N+1)^{1/2}$ and therefore the population is proportional to :

$$(2N+1)^{1/2} \text{Tr}(\rho \times {}^{NN}T^0) \quad \text{i.e.} \quad (2N+1)^{1/2} \rho^0.$$

We note that this kind of equality ceases to hold for $k \neq 0$, since part of the internal angular momentum of the molecule is transferred to the relative angular momentum of the molecules.

3.3 \tilde{S} MATRIX AS A FUNCTION OF $V(t)$. — 3.3.1 *General differential equation for $\tilde{U}(t, t_0)$ as a function of time.* — The evolution operator \tilde{U} satisfies the differential eq. (14). The general solution of such a system (Messiah [10], XVII, (17) (19)) is obtained by integration and set in the form of a series :

$$\tilde{U}(t, t_0) = \tilde{U}^{(0)}(t, t_0) + \sum_{n=1}^{\infty} \tilde{U}^{(n)}(t, t_0)$$

with

$$i \frac{d}{dt} \tilde{U}^{(0)}(t, t_0) = \mathcal{H}_0 \tilde{U}^{(0)}(t, t_0) \quad \text{and} \quad \tilde{U}^{(0)}(t_0, t_0) = 1$$

$$\tilde{U}^{(1)}(t, t_0) = i \int_{t_0}^t \exp(i\mathcal{H}_0(t-\tau)) V_{\text{eff}}(\tau) \exp(-i\mathcal{H}_0(\tau-t_0)) d\tau$$

$$\tilde{U}^{(2)}(t, t_0) = i^2 \int_{t_0}^t \exp(i\mathcal{H}_0(t-\tau)) V_{\text{eff}}(\tau) d\tau \int_{t_0}^{\tau} \exp(i\mathcal{H}_0(t-\tau')) V_{\text{eff}}(\tau') \times \exp(-i\mathcal{H}_0(\tau'-t_0)) d\tau'.$$

(One must not confuse the variable τ , and the lifetime τ .)

That is, symbolically :

$$\tilde{U} = \tilde{U}^{(0)} + \tilde{U}^{(1)}(V_{\text{eff}}) + \tilde{U}^{(2)}(V_{\text{eff}}, V_{\text{eff}}) + \tilde{U}^{(3)}(V_{\text{eff}}, V_{\text{eff}}, V_{\text{eff}}) + \dots$$

A calculation which contains this expansion up to the $(n+1)$ th term, $\tilde{U}^{(n)}$, corresponds to a calculation taken to the n th order of perturbation as a function of time.

We recall that the operator $\tilde{U}(t, t_0)$ acts within the first group of levels as introduced in § 2. The interaction potential, V_{eff} , defined in this space, itself follows from a stationary time-independant Rayleigh-Schrödinger perturbation expansion (1), introduced to take account of the levels of the second group.

The transition from small to large values of the separation ΔE between the studied level and another level (which then goes from the first (near) to the second (distant) group of levels) has been studied in detail by Gay [11] for the case of a dipole-dipole interaction. He has shown that, when ΔE increases, the results with a first order V potential tends continuously towards those of a second order $PV \frac{Q}{\Delta E} VP$ potential, if the time equation is

solved exactly (numerically). If however, one uses, as we do here, a perturbative solution to the time equation, he has shown that the results with the V potential give considerably errors (40 % for relaxation of polarization and orders of magnitude for the probability of transfer of population) if ΔE is greater than the reciprocal of the collision time. However he has also shown that in this case the time perturbative solution with a $PV \frac{Q}{\Delta E} VP$ potential gives a correct result for the relaxation of polarization. The conclusion is then that one must carefully choose the separation between near and distant groups of levels and not think that the results will be better as more levels are included in the near group.

In what follows we shall note $\mathfrak{U}_1 = PVP$ and $\mathfrak{U}_2 = PV \frac{Q}{\Delta E} VP$, and $\mathfrak{U} = \mathfrak{U}_1 + \mathfrak{U}_2$. The calculation of $\tilde{U}(t, t_0)$ will be stopped at the first order by taking \mathfrak{U} as the interaction potential ($\tilde{U}^{(1)}(\mathfrak{U})$).

Our final purpose is to find the tensorial components of the collision operator \tilde{S} . We shall then first write the differential equation satisfied by the matrix elements of $\tilde{U}(\mathfrak{U})$ in the eigenfunction basis of \mathcal{H}_0 ; we shall then transform this equation into one involving the tensor components of \tilde{U} , which will then be solved to first order.

We shall then solve eq. (14) to first order, after replacing V_{eff} by \mathfrak{U} . This equation, taken between the eigenfunctions of \mathcal{H}_0 , $|\alpha\beta N\nu M\mu\rangle$ and $|\alpha_0\beta_0 N_0\nu_0 M_0\mu_0\rangle$ gives :

$$i \frac{d}{dt} \langle N\nu M\mu | \tilde{U}(t, t_0) | N_0\nu_0 M_0\mu_0 \rangle = \sum_{N' M' \nu' \mu'} \exp(i\omega t) \times \\ \times \langle N\nu M\mu | \mathfrak{U}(t) | N' \nu' M' \mu' \rangle \langle N' \nu' M' \mu' | \tilde{U}(t, t_0) | N_0\nu_0 M_0\mu_0 \rangle \quad (20)$$

with

$$\omega = (E_{NM} + E_{\nu\mu} - E_{N'M'} - E_{\nu'\mu'}).$$

In the following calculation the Zeeman splittings are neglected as the corresponding frequencies are very small compared with the reciprocal of the time of collision (sudden approximation). The equation connecting the tensorial components of $\tilde{U}(t, t_0)$ can be deduced from (20) by expanding $\tilde{U}(t, t_0)$ in the same way as \tilde{S} using the Clebsch-Gordan coefficients :

$$i \frac{d}{dt} \overset{NN_0}{\nu\nu_0} \tilde{U}_{q\sigma}^{kk}(t, t_0) = \sum_{N' \nu' k' \kappa' q' \sigma' M' M_0 \mu' \mu_0 \mu'} \exp(i\omega t) \times \\ \times \langle NN_0 M - M_0 | kq \rangle \langle \nu\nu_0 \mu - \mu_0 | \kappa\sigma \rangle \langle N\nu M\mu | \mathfrak{U}(t) | N' \nu' M' \mu' \rangle \\ \times \langle N' N_0 M' - M_0 | k' q' \rangle \langle \nu' \nu_0 \mu' - \mu_0 | \kappa' \sigma' \rangle \overset{N'N_0}{\nu'\nu_0} \tilde{U}_{q'\sigma'}^{k'\kappa'}(t, t_0). \quad (21)$$

The explicit relations between the tensor components of \tilde{U} are obtained from (21) after expanding $\mathfrak{U}(t)$ in tensor form. We shall therefore define the chosen interaction potential, based on long range electrostatic interactions and express successively \mathfrak{U}_1 and \mathfrak{U}_2 in tensor form.

3.3.2 Explicit expressions for \mathfrak{U}_i . — 3.3.2.1 Long range interaction.

i) \mathfrak{U}_1 . We suppose that the interaction energy between the two molecules arises only from long range electrostatic interactions. Molecules A and B are located at time t at distance $R(t)$ from one another, each representing a system of charges defined by two systems of coordinates O_A and O_B ; the charge e_a (algebraic number) is located at \mathbf{r}_a in the reference frame with origin O_A . The energy of interaction between the two systems is :

$$\mathfrak{U}_1 = V = \sum_{ab} \frac{e_a e_b}{|\mathbf{R} + \mathbf{r}_b - \mathbf{r}_a|}.$$

With the assumption that $\mathbf{r}_a + \mathbf{r}_b < \mathbf{R}$ (absence of overlap of the wavefunctions of molecule A and B) V can be expressed using Taylor expansions about O_A and O_B . The following expression was obtained by Fontana [12a], taking the axes $O_A z$ and $O_B z$ to be parallel and directed along \mathbf{R} (we shall call this the intermolecular reference frame (Fig. 1)) :

$$\mathfrak{U}_1 = \sum_{K, \chi=0}^{\infty} \mathfrak{U}_{1K\chi}. \quad (22)$$

$$\mathfrak{U}_{1\chi} = \sum_{ab} \sum_{Q=-K}^K \frac{1}{R^n} \frac{(-)^x 4 \Pi e_a e_b \delta_{Q-\Sigma} \mathfrak{Y}_K^Q(\mathbf{r}_a)^* \mathfrak{Y}_\chi^Q(\mathbf{r}_b)^* (K + \chi)!}{((2K + 1)(2\chi + 1)(K - Q)!(K + Q)!(\chi - \Sigma)!(\chi + \Sigma)!)^{1/2}} \quad (23)$$

with

$$n = K + \chi + 1 \quad \text{and} \quad \mathfrak{Y}_K^Q(\mathbf{r}) = r^K Y_K^Q(\hat{\mathbf{r}}).$$

The $Y_K^Q(\hat{r})$ are the spherical harmonics as defined by (Messiah [10], 1 B (96)) and \hat{r} is a unit vector.

The term $\mathcal{U}_{1K\chi}$ represents the interaction of the 2^K -polar angular momentum of the system A (of the form $\mu_K^Q = \sum_a e_a \mathcal{Y}_K^Q(\mathbf{r}_a)$) with the 2^χ -polar angular momentum of the system B).

This formula is equivalent to the one used in lineshape studies by C. G. Gray and J. Van Kranendonk [12b]. It was also given by M. E. Rose [12c] and Y. N. Chiu [12d]. Using the Clebsch-Gordan coefficients, expression (23) can be written :

$$\mathcal{U}_{1K\chi} = \frac{\beta(K\chi)}{R^n} \sum_Q \langle K\chi Q\Sigma | (K+\chi) 0 \rangle \sum_a e_a \mathcal{Y}_K^{-Q}(\mathbf{r}_a) \sum_b e_b \mathcal{Y}_\chi^{-\Sigma}(\mathbf{r}_b) \delta_{Q-\Sigma} \quad (24)$$

with

$$\beta(K\chi) = (-)^x 4 \Pi \left(\frac{(2(K+\chi))!}{(2K)!(2\chi)!(2K+1)(2\chi+1)} \right)^{1/2}. \quad (25)$$

We abbreviate the set of indices $(1 K\chi)$ by the over-all index s , and we can put (24) into the general form

$$\mathcal{U}_s = \sum_{JQ} \frac{\alpha_{s,J}}{R^{n_s}} \langle K\chi Q\Sigma | J0 \rangle {}^{(s)}\mathcal{U}_Q^K(A) {}^{(s)}\mathcal{U}_\Sigma^\chi(B) \delta_{Q-\Sigma} \quad (26)$$

with

$$\alpha_{1K\chi,J} = (-)^{(K+\chi-J)} \beta(K\chi) \delta_{J,K+\chi}, \quad n_{1K\chi} = K + \chi + 1 \quad (27)$$

and

$${}^{(1-K\chi)}\mathcal{U}_Q^K(A) = \sum_a e_a \mathcal{Y}_K^Q(\mathbf{r}_a).$$

Consequently we have :

$$\mathcal{U}_1 = \sum_s \mathcal{U}_s. \quad (28)$$

ii) $\mathcal{U}_2 = \frac{V^2}{\Delta E}$, we have :

$$V^2 = \sum_{K_1\chi_1=0}^{\infty} V_{1K_1\chi_1} \sum_{K_2\chi_2=0}^{\infty} V_{1K_2\chi_2}. \quad (29)$$

As before we decompose the operator V into a series of terms in which two tensorial operators appear, each one referring to one of the systems A and B. To accomplish this, the operators $\mathcal{Y}_{K_1}^{-Q_1}(\mathbf{r}_{a_1})$ and $\mathcal{Y}_{K_2}^{-Q_2}(\mathbf{r}_{a_2})$, which act on the same molecular system A, are taken together giving the resulting tensor :

$${}^{K_1K_2}\mathcal{G}_Q^K(A) = \sum_{a_1a_2Q_1Q_2} \langle K_1 K_2 - Q_1 Q_2 | KQ \rangle e_{a_1} \mathcal{Y}_{K_1}^{Q_1}(\mathbf{r}_{a_1}) e_{a_2} \mathcal{Y}_{K_2}^{Q_2}(\mathbf{r}_{a_2}). \quad (30)$$

This tensor is of dimension $r^{K_1+K_2}$ and acts in the space A. By expressing V given in (29) as a function of the operator \mathcal{G} defined in (30), then replacing the Clebsch-Gordan coefficients in terms of the « 3j » symbols, and further making use of the relations between the « 3j » and « 9j » symbols (Messiah [10], 2 C (40c)) the expression for \mathcal{U}_2 is obtained

$$\mathcal{U}_2 = \sum_{K_1K_2\chi_1\chi_2} \mathcal{U}_{2K_1K_2\chi_1\chi_2} \quad (31)$$

$$\mathcal{U}_{2K_1K_2\chi_1\chi_2} = \sum_{K=|K_1-K_2|}^{K_1+K_2} \sum_{\chi=|\chi_1-\chi_2|}^{\chi_1+\chi_2} \mathcal{U}_{2K_1K_2\chi_1\chi_2K\chi} \quad (32)$$

$$\mathcal{U}_{2K_1K_2\chi_1\chi_2K\chi} = \sum_J \frac{\gamma}{R^n} \sum_Q \langle K\chi Q\Sigma | J0 \rangle {}^{K_1K_2}\mathcal{G}_Q^K(A) {}^{\chi_1\chi_2}\mathcal{G}_\Sigma^\chi(B) \delta_{Q-\Sigma} \quad (33)$$

where $n = K_1 + K_2 + \chi_1 + \chi_2 + 2$

$$\gamma = \frac{\beta(K_1 \chi_1) \beta(K_2 \chi_2)}{\Delta E} ((2(K_1 + \chi_1) + 1) (2(K_2 + \chi_2) + 1) (2K + 1) (2\chi + 1))^{1/2}$$

$$\times (2J + 1)^{1/2} \begin{pmatrix} K_1 + \chi_1 & K_2 + \chi_2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_1 & \chi_1 & K_1 + \chi_1 \\ K_2 & \chi_2 & K_2 + \chi_2 \\ K & \chi & J \end{Bmatrix}. \quad (34)$$

Term (32) corresponds to the second order interaction of the induced (2^{K_1} polar- 2^{K_2} polar) moment of the molecule A with the induced (2^{χ_1} polar- 2^{χ_2} polar) moment of the molecule B. K and χ are obtained by the coupling of K_1 and K_2 , χ_1 and χ_2 respectively.

In the usual case where one has $K_1 = K_2$, $\chi_1 = \chi_2$, we note that the only non zero terms in (32) correspond to even values of K and χ ; then J , obtained by coupling between K and χ , can only take on even values (selection rule for the $3j$ coefficients).

We abbreviate the set of indices ($2 K_1 K_2 \chi_1 \chi_2 K\chi$) by the overall index s , and we can put (33) into the general form \mathcal{U}_s given by expression (26) with :

$$\begin{aligned} \alpha_{2K_1K_2\chi_1\chi_2K\chi,J} &= (-)^{(K+\chi-J)} \gamma, \\ n_{2K_1K_2\chi_1\chi_2K\chi} &= K_1 + K_2 + \chi_1 + \chi_2 + 2 \\ {}_{(2K_1K_2\chi_1\chi_2K\chi)}\mathcal{U}_Q^K(A) &= {}_{K_1K_2}C_Q^K(A). \end{aligned} \tag{35}$$

Thus the term \mathcal{U}_2 given by (42) can be written in the same way as \mathcal{U}_1 given by (39) : $\mathcal{U}_2 = \sum_s \mathcal{U}_s$. It is therefore possible to continue the calculation by decomposing the potential \mathcal{U} into a sum of general terms \mathcal{U}_s :

$$\mathcal{U} = \mathcal{U}_1 + \mathcal{U}_2 = \sum_s \mathcal{U}_s \tag{36}$$

where the index s is successively equal to ($1 K\chi$) and ($2 K_1 K_2 \chi_1 \chi_2 K\chi$) and where \mathcal{U}_s is given by (26).

3.3.2.2 *General case.* — The form (26) for \mathcal{U}_s can be generalized for any order of perturbation theory and even for short distance interaction (in which case the $1/R$ development is no longer valid) as :

$$\mathcal{U} = \sum_{sJQ\Sigma} f_{s,J}(R) \langle K\chi Q\Sigma | J0 \rangle T_Q^K(A) T_{\Sigma}^{\chi}(B) \delta_{Q-\Sigma} \tag{37}$$

where the T_Q^K are normalized tensor operators of the molecules A or B. Indeed the T_Q^K form a complete basis for the electronic operators in the corresponding space (A or B) so that the function $\mathcal{U}(R, \mathbf{r}_a, \mathbf{r}_b)$ can always be decomposed as a sum of the form :

$$\sum_{sJQ\Sigma} g_s(R) T_Q^K(A) T_{\Sigma}^{\chi}(B).$$

On the other hand the transformation between the product $T_Q^K(A) T_{\Sigma}^{\chi}(B)$ and the coupled representation

$$\sum_{Q\Sigma} \langle K\chi Q\Sigma | JQ_J \rangle T_Q^K(A) T_{\Sigma}^{\chi}(B)$$

is an orthonormal one and conserves the completeness. Finally the fact that $Q_J = 0$ in (37) is a mere consequence of the invariance of the interaction \mathcal{U} when one rotates the whole system of the two molecules around the intermolecular axis.

As a consequence, the following formulae could be used even for short distance interaction, by replacing $\alpha_{s,J}/R^n$ and \mathcal{U}_Q^K by respectively $f_{s,J}(R)$ and T_Q^K defined by (37).

3.3.3 *Differential equation for $\tilde{U}(t, t_0)$.* — The differential equation (20) relates the matrix elements of the operator \tilde{U} to those of \mathcal{U} , the matrix elements being taken in the basis $| N\nu M\mu \rangle$ relative to a coordinate system associated with the collision (\mathbf{b}, \mathbf{v}) under study. This *collision* coordinate system (subscript c) is composed of the set of two coordinate systems centered respectively at O_A and O_B , with axes Ox_c, Oy_c, Oz_c parallel; the axis Oz_c is parallel to the relative velocity \mathbf{v} of the two molecules, while the axis Ox_c is parallel to \mathbf{b} (Fig. 1).

Thus in equation (20) the matrix elements of \tilde{U} and \mathcal{U} are taken among the wavefunctions $| N\nu M\mu \rangle_c$ defined in the collision coordinate system. Now the operator \mathcal{U} , given by (36) has been expressed as a function of the variables $\mathbf{R}, \mathbf{r}_a, \mathbf{r}_b$ defined in the intermolecular coordinate system (Fig. 1); therefore the matrix elements of \mathcal{U} will be calculated by using the wave-functions defined in the intermolecular coordinate system (subscript i), $| N\nu M\mu \rangle_i$. It therefore remains for us to express the element $\langle N\nu M\mu | \mathcal{U} | N' \nu' M' \mu' \rangle_c$ in terms of the elements $\langle N\nu M\mu | \mathcal{U} | N' \nu' M' \mu' \rangle_i$. This is done in appendix B by noting that for each molecule the intermolecular coordinate system is obtained from the collision system by a rotation through θ about the axis Oy_c (identical with Oy_i). Then, this rotation, relative to the molecule A, is expressed by the rotation operator $R_{O_A y}(\theta)$:

$$| NM \rangle_i = \sum_{M'} \langle NM' | R_{O_A y}(\theta) | NM \rangle | NM' \rangle_c$$

with the angle θ (Fig. 1) varying from π to 0 between $t_0 = -\infty$ and $t = +\infty$. Using the tensorial decomposition of \tilde{U} in the basis of irreducible tensors as well as that of \mathcal{U} given by (36) and using the properties of the rotation operator, we obtain after a calculation detailed in appendix B, a new form of equation (21) :

$$i \frac{d}{dt} \overset{NN_0}{v\nu_0} \tilde{U}_{q\sigma}^{kk'}(t, t_0) = \sum_{N'v'k'\kappa'q'\sigma'} (-)^{(N_0+N+q+\nu_0+\nu+\sigma)} [(2k+1)(2k'+1)(2\kappa+1)(2\kappa'+1)]^{1/2} \sum_{sJQ\Sigma} \frac{\alpha_{s,J}}{R^{n_s}} \times$$

$$\times \langle N \parallel {}^{(s)}\mathcal{U}^K(\mathbf{A}) \parallel N' \rangle \langle \nu \parallel {}^{(s)}\mathcal{U}^\chi(\mathbf{B}) \parallel \nu' \rangle \begin{pmatrix} k' & K & k \\ q' & Q & -q \end{pmatrix} \begin{Bmatrix} k' & K & k \\ N & N_0 & N' \end{Bmatrix}$$

$$\times \begin{pmatrix} \kappa' & \chi & \kappa \\ \sigma' & -\Sigma & -\sigma \end{pmatrix} \begin{Bmatrix} \kappa' & \chi & \kappa \\ \nu & \nu_0 & \nu' \end{Bmatrix} \sum_M \langle K\chi Q\Sigma \mid JM \rangle r_{M0}^J(\theta) \exp(i(E_N - E_{N'} + E_\nu - E_{\nu'})t) \overset{N'N_0}{v'\nu_0} \tilde{U}_{q'\sigma'}^{k'\kappa'}(t, t_0) \quad (38)$$

where, using the convention of (Messiah [10], 2 C (55)) $r_{M0}^J(\theta) = R_{M0}^J(000)$.

3.3.4 *Solution of the equation for $\tilde{U}(t, t_0)$ in the first order.* — The S matrix has the form, if one considers only one s value,

$$S = S^{(0)} + S^{(1)} + S^{(2)} + \dots$$

where $S^{(1)}$, $S^{(2)}$ are functions of $1/R^{n_s}$, $1/R^{2n_s}$. The calculation of $\Delta\Gamma$ introduces the product SS^+ . $S^{(1)}$ being purely imaginary, the first order terms in $\Delta\Gamma$ vanish. The second order term in $\Delta\Gamma$ can come either from the square of the first order term in S , $(S^{(1)})^2$, or from the cross product between zero order and second order terms in S : $S^{(0)}S^{(2)+} + S^{(0)+}S^{(2)}$.

It can be shown [13] that, since in expansion (19) the summation over the term component excludes the case where $K_i = \chi_i = 0$, the cross products $S^{(0)}S^{(2)+} + S^{(0)+}S^{(2)}$ vanish. It is then only necessary to calculate S up to first order; and this gives an expression of $\Delta\Gamma$ valid up to second order.

In the limiting case for $t = +\infty$ and $t_0 = -\infty$, and remembering that

$$\tilde{U}(-\infty, -\infty) = 1 = \sum_{NN_0\nu\nu_0} \overset{NN_0}{v\nu_0} \tilde{U}_{00}^{00}(-\infty, -\infty) \overset{NN_0}{T_0^0} \overset{v\nu_0}{T_0^0}$$

which implies

$$\overset{NN_0}{v\nu_0} \tilde{U}_{q\sigma}^{kk'}(-\infty, -\infty) = (2N+1)^{1/2} (2\nu+1)^{1/2} \delta_{NN_0} \delta_{\nu\nu_0} \delta_{k0} \delta_{\kappa 0},$$

the first order solution of the differential equation (38) is

$$\overset{NN_0}{v\nu_0} \tilde{S}_{q\sigma}^{kk'} \left(\sum_s \mathcal{U}_s \right) = (2N+1)^{1/2} (2\nu+1)^{1/2} \delta_{NN_0} \delta_{\nu\nu_0} \delta_{k0} \delta_{\kappa 0} - \left(i \int_{-\infty}^{+\infty} dt \times \right.$$

$$\times \exp(i\omega t) \sum_{sJ} \frac{\alpha_{s,J}}{R^{n_s}} \frac{\langle N \parallel {}^{(s)}\mathcal{U}^K(\mathbf{A}) \parallel N_0 \rangle \langle \nu \parallel {}^{(s)}\mathcal{U}^\chi(\mathbf{B}) \parallel \nu_0 \rangle}{(2K+1)^{1/2} (2\chi+1)^{1/2}} \sum_{Q\Sigma M} \langle K\chi Q\Sigma \mid JM \rangle r_{M0}^J(\theta) \delta_{Kk} \delta_{\chi\kappa} \delta_{Qq} \delta_{\Sigma\sigma} \left. \right) \quad (39)$$

with $\omega = (E_N - E_{N_0} + E_\nu - E_{\nu_0})$.

3.4 EXPRESSION FOR THE $\Delta\Gamma$ MATRIX. — 3.4.1 *Long range interaction.* — The expression of the \tilde{S} matrix is then given by (39) and we can express the summation over q_i and σ_i which occurs in the relation (19) for $\Delta\Gamma^k$ so that k_i and κ_i are not simultaneously zero. The evaluation of these terms is developed in appendix C. This gives :

$$\sum_{q_i\sigma_i} \overset{NN_0}{v\nu_0} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \left(\sum_s \mathcal{U}_s \right) \overset{NN_0}{v\nu_0} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \left(\sum_{s'} \mathcal{U}_{s'} \right)^* = \sum_{ss'J_s} \alpha_{s,J_s} \alpha_{s',J_s}^* \times$$

$$\times \frac{\langle N \parallel {}^{(s)}\mathcal{U}^{k_i}(\mathbf{A}) \parallel N_0 \rangle \langle N \parallel {}^{(s')} \mathcal{U}^{k_i}(\mathbf{A}) \parallel N_0 \rangle^*}{(2k_i+1)} \frac{\langle \nu \parallel {}^{(s)}\mathcal{U}^{\kappa_i}(\mathbf{B}) \parallel \nu_0 \rangle \langle \nu \parallel {}^{(s')} \mathcal{U}^{\kappa_i}(\mathbf{B}) \parallel \nu_0 \rangle^*}{(2\kappa_i+1)}$$

$$\times \frac{\alpha_{n_s, n_{s'}}^{J_s}(\omega b/v)}{v^2 h^{(n_s+n_{s'}-2)}} \delta_{J_s J_{s'}} \delta_{k_i K_s} \delta_{k_i K_{s'}} \delta_{\kappa_i \chi_s} \delta_{\kappa_i \chi_{s'}} \quad (40)$$

distinguishing the $(K\chi J)$ corresponding to \mathcal{U}_s from those corresponding to $\mathcal{U}_{s'}$ by the indices s and s' . The function $\alpha(\omega b/v)$ is a cut-off function defined by

$$\frac{\alpha_{n_s, n_{s'}}^{J_s, J_{s'}}(\omega b/v)}{v^2 b^{(n_s + n_{s'} - 2)}} = \int_{-\infty}^{+\infty} dt' \int_{-\infty}^{+\infty} dt \frac{\exp(i\omega(t - t'))}{R^{n_s}(t) R^{n_{s'}}(t')} r_{00}^{J_s}(\theta - \theta'). \quad (41)$$

The physical meaning of the cut-off function is the following : it represents, roughly speaking, the Fourier transform at reduced frequency $(\omega b/v)$ of the time varying interaction between the two molecules. This function tends to zero when $(\omega b/v) \gg 1$, i.e. when the frequency of the transition between initial and final bimolecular states is higher than the Fourier spectrum of the interaction. The width of this function is called the adiabatic cut-off frequency corresponding to a collision (b, v) . Specific calculations for a few cases will be given in a paper to follow concerning the relaxation of H_2 .

Thus the $\Delta\Gamma^k$, relating to the collision (b, v) , which we write as $\Delta\Gamma^k\left(\sum_s \mathcal{U}_s, \sum_{s'} \mathcal{U}_{s'}\right)$ to indicate that the expression for it is obtained for the most general case where all the multipolar electrostatic interactions are included to the first two orders of perturbation, becomes :

$$N = N_0$$

$$\begin{aligned} {}^{NNNN}\Delta\Gamma^k\left(\sum_s \mathcal{U}_s, \sum_{s'} \mathcal{U}_{s'}\right) &= \sum_{ss'v_0N'} \sum_{k_i\kappa_i'} \frac{\Pi(v_0)}{(2v_0 + 1)} \times \\ &\times \frac{\langle N' \parallel {}^{(s)}\mathcal{U}^{k_i}(\mathbf{A}) \parallel N \rangle \langle N' \parallel {}^{(s')}\mathcal{U}^{k_i}(\mathbf{A}) \parallel N \rangle^*}{(2k_i + 1)} \frac{\langle v \parallel {}^{(s)}\mathcal{U}^{k_i}(\mathbf{B}) \parallel v_0 \rangle \langle v \parallel {}^{(s')}\mathcal{U}^{k_i}(\mathbf{B}) \parallel v_0 \rangle^*}{(2\kappa_i + 1)} \\ &\times \sum_{J_s} \frac{\alpha_{s, J_s} \alpha_{s', J_{s'}}^*}{v^2 b^{(n_s + n_{s'} - 2)}} \delta_{J_s J_{s'}} \alpha_{n_s, n_{s'}}^{J_s, J_{s'}}(\omega b/v) \left((-)^{(2N+k+k_i)} \begin{Bmatrix} k_i & N & N \\ k & N & N \end{Bmatrix} \delta_{N'N} - \frac{1}{2N+1} \right) \\ &\times \delta_{k_i K_s} \delta_{k_i K_{s'}} \delta_{\kappa_i \chi_s} \delta_{\kappa_i \chi_{s'}} \end{aligned} \quad (42a)$$

$$\text{with } \omega = E_{N'} - E_N + E_v - E_{v_0}.$$

This quantity, ${}^{NNNN}\Delta\Gamma^k(b, v)$, corresponds to the evolution of the ${}^{NN}\rho_q^k$ component under the effect of the (b, v) collisions inside the N state. In this expression, N (and v_0) represent the initial state (i.e. before the (b, v) collision) of molecule A (and B); N' (and v) the final states. Selection rules connect N and N' (v_0 and v). Terms with $N' = N$ correspond to the evolution of ${}^{NN}\rho_q^k$ inside the N state and terms with $N' \neq N$ to the transfer of part of ${}^{NN}\rho_q^k$ from the level N to N' .

$$N \neq N_0$$

$$\begin{aligned} {}^{NNN_0N_0}\Delta\Gamma^k\left(\sum_s \mathcal{U}_s, \sum_{s'} \mathcal{U}_{s'}\right) &= \sum_{ss'v_0} \sum_{k_i\kappa_i'} \frac{\Pi(v_0)}{(2v_0 + 1)} \times \\ &\times \frac{\langle N \parallel {}^{(s)}\mathcal{U}^{k_i}(\mathbf{A}) \parallel N_0 \rangle \langle N \parallel {}^{(s')}\mathcal{U}^{k_i}(\mathbf{A}) \parallel N_0 \rangle^*}{(2k_i + 1)} \frac{\langle v \parallel {}^{(s)}\mathcal{U}^{k_i}(\mathbf{B}) \parallel v_0 \rangle \langle v \parallel {}^{(s')}\mathcal{U}^{k_i}(\mathbf{B}) \parallel v_0 \rangle^*}{(2\kappa_i + 1)} \\ &\times \sum_{J_s} \frac{\alpha_{s, J_s} \alpha_{s', J_{s'}}^*}{v^2 b^{(n_s + n_{s'} - 2)}} \delta_{J_s J_{s'}} (-)^{(N+N_0+k+k_i)} \begin{Bmatrix} k_i & N_0 & N \\ k & N & N_0 \end{Bmatrix} \alpha_{n_s, n_{s'}}^{J_s, J_{s'}}(\omega b/v) \\ &\times \delta_{k_i K_s} \delta_{k_i K_{s'}} \delta_{\kappa_i \chi_s} \delta_{\kappa_i \chi_{s'}} \end{aligned} \quad (42b)$$

with

$$\omega = (E_N - E_{N_0} + E_v - E_{v_0}).$$

This quantity corresponds to the transfer of ${}^{N_0N_0}\rho_q^k$ from level N_0 to N . We recall that in these expressions the operator $\mathcal{U}(\mathbf{A})$ depends on the spatial coordinates \mathbf{r}_a of the charged particles constituting the molecule A, and that the coordinates are defined in the intermolecular frame of reference figure 1. The expressions for the reduced matrix elements of this operator are given in appendix D for diatomic molecules (the general formulae are applied to the particular case of multipole-multipole interaction considered to first ($\mathcal{U} = \mathcal{Y}$) or to second ($\mathcal{U} = \mathcal{C}$) order of perturbation).

3.4.2 *Short range interactions.* — The expression of the S matrix can be deduced from (39) by replacing $\alpha_{s,J}/R^n$ by $f_{s,J}(R)$ defined by (37). It follows that the expressions (42) are always valid when replacing \mathcal{U} by T defined by (37) and

$$\alpha_{s,J_s} \alpha_{s',J_{s'}} \frac{\alpha_{n_s,n_{s'}}^{J_s}(\omega b/v)}{v^2 b^{(n_s+n_{s'}-2)}}$$

by

$$\int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt' f_{s,J}(R) f_{s',J_{s'}}(R') \exp(i\omega(t-t')) r_{00}^J(\theta-\theta').$$

3.4.3 *Particular cases.* — We have thus obtained the expression for the $\Delta\Gamma$ matrix relating to the collision (b, v) in the general case of a calculation to the first two orders of perturbation, where the interaction potential causing the collision is a long range electrostatic potential expanded to all multipole orders. Frequently it is of interest to evaluate the contribution to the collision of a particular multipolar interaction of the 2^a -polar moment of the given molecule with the 2^b -polar moment of the relaxing molecule. Below we set out explicitly the simplified form then taken by $\Delta\Gamma^k$ when this interaction occurs.

i) In first order of perturbation \mathcal{U}_1 , given by (22), reduces to the term $\mathcal{U}_{1K\chi}$ with $K = a$ and $\chi = b$, and $\mathcal{U}_2 = 0$. Then $\mathcal{U} = \mathcal{U}_{1K\chi}$ and for example the expression (42a) for $\Delta\Gamma^k$ simplifies to

$$\begin{aligned} {}^{NNN}\Delta\Gamma^k(\mathcal{U}_{1K\chi}, \mathcal{U}_{1K\chi}) &= \sum_{v_0 N'} \frac{\Pi(v_0)}{(2v_0+1)} \times \frac{|\langle N' \| \mathcal{Y}_K(\mathbf{A}) \| N \rangle \langle v \| \mathcal{Y}_\chi(\mathbf{B}) \| v_0 \rangle|^2}{(2K+1)(2\chi+1)} \times \\ &\times \frac{\beta^2}{v^2 b^{2(n-1)}} \alpha_{n,n}^{K+\chi}(\omega b/v) \left((-)^{(2N+k+\chi)} \begin{Bmatrix} K & N & N \\ k & N & N \end{Bmatrix} \delta_{NN'} - \frac{1}{2N+1} \right) \end{aligned} \quad (43)$$

with $\omega = E_{N'} - E_N + E_v - E_{v_0}$.

In this expression $n = K + \chi + 1$ and the function β is defined by (25).

ii) In second order of perturbation \mathcal{U}_2 given by (31) reduces to the term $\mathcal{U}_{2K_1K_2\chi_1\chi_2}$ with $K_1 = K_2 = a$ and $\chi_1 = \chi_2 = b$, and $\mathcal{U}_1 = 0$. Then $\mathcal{U} = \mathcal{U}_{2K_1K_2\chi_1\chi_2}$ and $\Delta\Gamma^k$ given by (42a) becomes :

$$\begin{aligned} {}^{NNN}\Delta\Gamma^k(\mathcal{U}_{2K_1K_2\chi_1\chi_2}, \mathcal{U}_{2K_1K_2\chi_1\chi_2}) &= \sum_{v_0 N'} \sum_{K\chi} \sum_J \frac{\Pi(v_0)}{(2v_0+1)} \times \\ &\times \frac{|\langle N' \| \mathcal{C}^K(\mathbf{A}) \| N \rangle \langle v \| \mathcal{C}^\chi(\mathbf{B}) \| v_0 \rangle|^2}{(2K+1)(2\chi+1)} \frac{\gamma^2}{v^2 b^{2(n-1)}} \alpha_{n,n}^J(\omega b/v) \\ &\times \left((-)^{(2N+k+\chi)} \begin{Bmatrix} K & N & N \\ k & N & N \end{Bmatrix} \delta_{NN'} - \frac{1}{2N+1} \right) \end{aligned} \quad (44)$$

with $\omega = (E_{N'} - E_N + E_v - E_{v_0})$.

In this expression $n = 2(K_1 + \chi_1 + 1)$ and the function γ is defined by (34). We recall that K varies from zero to $2K_1$, χ from zero to $2\chi_1$ and J from $|K - \chi|$ to $K + \chi$, and also that the summation \sum' means that K and χ cannot simultaneously be zero.

iii) Two interactions must sometimes be considered at the same time, one in first order, $\mathcal{U}_{1K\chi}$, and the other in second order ($\mathcal{U}_{2K_1K_2\chi_1\chi_2}$). An example might be the quadrupole-quadrupole interaction in first order ($K = \chi = 2$) which varies as R^{-5} and the dipole-dipole interaction in second order ($K_1 = K_2 = 1, \chi_1 = \chi_2 = 1$) which varies as R^{-6} . In this case several cross terms appear in $\Delta\Gamma^k$: we have $\mathcal{U} = (\mathcal{U}_{1K\chi} + \mathcal{U}_{2K_1K_2\chi_1\chi_2})$ and from (42) :

$$\begin{aligned} \Delta\Gamma^k(\mathcal{U}_{1K\chi} + \mathcal{U}_{2K_1K_2\chi_1\chi_2}, \mathcal{U}_{1K\chi} + \mathcal{U}_{2K_1K_2\chi_1\chi_2}) &= \Delta\Gamma^k(\mathcal{U}_{1K\chi}, \mathcal{U}_{1K\chi}) + \\ &+ \Delta\Gamma^k(\mathcal{U}_{2K_1K_2\chi_1\chi_2}, \mathcal{U}_{2K_1K_2\chi_1\chi_2}) + 2 \Delta\Gamma^k(\mathcal{U}_{1K\chi}, \mathcal{U}_{2K_1K_2\chi_1\chi_2}). \end{aligned} \quad (45)$$

3.5 CROSS-SECTION. — The collision term, $\frac{\delta}{\delta t} {}^{NN} \rho_q^k$, occurring in the density matrix eq. (5), can now be evaluated using expressions (6), (9) and (42).

We consider here only the case where the contribution of the components ${}^{N_0 N_0} \rho_q^k$ coming from the level N_0 to the level N are neglected. In the density matrix equation there only appear terms relating to the level N ;

the differential equations giving the different components ${}^{NN}\rho_q^k$ and ${}^{N_0N_0}\rho_q^k$ are no longer coupled and the term relating to the collision reduces to the classical expression defining the collision cross-section σ^k :

$$\frac{\delta}{\delta t} {}^{NN}\rho_q^k = \left(n \int_0^\infty \int_0^\infty {}^{NNNN}\Delta\Gamma^k(b, v) P(v) v dv 2 \Pi b db \right) {}^{NN}\rho_q^k \tag{46}$$

$$= - \sigma^k n\bar{v} {}^{NN}\rho_q^k . \tag{47}$$

We shall now, for this case, detail the calculation of σ^k starting from $\Delta\Gamma^k$. The collision cross-section obtained by identification of (46) and (47) requires the integration over the impact parameter b between zero and infinity. Now the present calculation, based on the predominance of long range electrostatic interactions, is no longer valid at short distances (small values of b). In order to exclude these small values we shall make the cut-off approximation of Anderson, studied and justified by Omont, which consists of saying that the destruction of the component ρ_q^k is complete ($\Delta\Gamma^k(b) = 1$) for all collisions with small impact parameter ($b < b_0$). The cut-off parameter, b_0 , is determined by the relation $\Delta\Gamma^k(b_0) = 1$.

We recall that Gay [11] has studied in detail the validity of this procedure for studying relaxation processes and its non validity for studying the transfers when the separation ΔE of levels is larger than $1/\tau_c$ (where all the contribution comes from short range collisions).

The cross-section corresponding to the level N is then given by

$$- \sigma^k = \Pi b_0^2 + \frac{1}{v} \int_{b_0}^\infty \int_0^\infty {}^{NNNN}\Delta\Gamma^k(b, v) P(v) v dv 2 \Pi b db . \tag{48}$$

We remark that frequently the average over v is not performed numerically, and the usual approximation consists of replacing v by its average \bar{v} .

4. Spin recoupling. — So far we have studied the evolution of the tensorial components ${}^{\alpha N \alpha' N'}\rho_{qN}^{kN}$ of the density matrix under the effect of the collision in the level $|\alpha N\rangle$ of the molecule under examination. This evolution was characterized by the quantity ${}^{\alpha N \alpha' N' \alpha_0 N_0 \alpha_0' N_0'}\Delta\Gamma^{kN}$ defined by relation (6) and expressed by use of (9), (10) and (42) in the case where $N = N'$, $N_0 = N_0'$ (we shall give the index k_N so as to recall that this quantity is relative to the kinetic momentum N). This is valid for singlet Hund's case b and Hund's case a or c molecules with no nuclear spin. We shall now introduce the effect of an electronic spin S in Hund's case b. (The effect of a nuclear spin I in Hund's case a, b or c would be identical, replacing S by I).

When spin S exists, it couples with the kinetic momentum N and the level $|\alpha N\rangle$ splits into fine structure levels $|\alpha J\rangle$ with $J = N + S$. In the same way as previously (§ 3) the density matrix is decomposed according to its tensorial components :

i) either in the coupled space $|\alpha NJ\rangle$ (we now drop index α to simplify the notation) :

$$\rho = \sum_{NJ, N'J'} {}^{NJN'J'}\rho_q^k {}^{NJN'J'}T_q^k \tag{49}$$

the evolution of these components under the effect of collision is then expressed by :

$$\frac{\delta}{\delta t} {}^{NJN'J'}\rho_q^k = \sum_{J_0J_0'} {}^{NJN'J'N_0J_0N_0'J_0'}\overline{\Delta\Gamma}^{kN} {}^{N_0J_0N_0'J_0'}\rho_q^k ; \tag{50}$$

ii) or in the uncoupled space $|\alpha NS\rangle$

$$\rho = \sum_{NN'k_Nq_Nk_Sq_S} {}^{NN'SS}\rho_{q_Nq_S}^{k_Nk_S} {}^{NN'}T_{q_N}^{k_N} {}^{SS}T_{q_S}^{k_S} . \tag{51}$$

Taking into account that the electrostatic interaction which is responsible for the collision does not act upon the spins and thus reduces to the identity operator in this space, the evolution of these components under the influence of the collisions is noted as

$$\frac{\delta}{\delta t} {}^{NN'SS}\rho_{q_Nq_S}^{k_Nk_S} = \sum_{N_0N_0'} {}^{NN'N_0N_0'}\overline{\Delta\Gamma}^{k_N} {}^{N_0N_0'SS}\rho_{q_Nq_S}^{k_Nk_S} . \tag{52}$$

In order to express $\overline{\Delta\Gamma}^k$ defined by (50), we shall link the components defined by (49) to those defined by (51)

$${}^{NN'SS}\rho_{q_N q_S}^{k_N k_S} = \sum_{kqJJ'} {}^{NJN'J'}\rho_q^k ((2k_N + 1)(2k_S + 1)(2J + 1)(2J' + 1))^{1/2} \times \\ \times \begin{Bmatrix} N & N' & k_N \\ S & S & k_S \\ J & J' & k \end{Bmatrix} \langle k_N k_S q_N q_S | kq \rangle. \quad (53)$$

Then by replacing ${}^{NN'SS}\rho_{q_N q_S}^{k_N k_S}$ by its expression (53) in relation (52), we obtain by identification with (50)

$${}^{NJN'J'N_0J_0N_0J_0}\overline{\Delta\Gamma}^k = \sum_{k_N k_S} (2k_N + 1)(2k_S + 1)((2J + 1)(2J' + 1)(2J_0 + 1)(2J'_0 + 1))^{1/2} \times \\ \times \begin{Bmatrix} N_0 & N'_0 & k_N \\ S & S & k_S \\ J_0 & J'_0 & k \end{Bmatrix} \begin{Bmatrix} N & N' & k_N \\ S & S & k_S \\ J & J' & k \end{Bmatrix} {}^{NN'N_0N_0}\overline{\Delta\Gamma}^{k_N} \quad (54)$$

where k_N varies from $|N - N_0|$ to $N + N_0$ and k_S from 0 to $2S$. Numerical calculations can use the formula (54) with $\overline{\Delta\Gamma}^{k_N}$ defined by equation (6). Note that in equation (54) one has different cut off parameters b_0 for the various k values defined by $\Delta\Gamma^k(b_{0k}) = 1$, i.e. total destruction of the k th multipole.

Another equivalent expression which does not use $9j$ symbols is the following (see appendix E) :

$$N = N_0$$

$${}^{NJNJ'NJ_0NJ_0}\Delta\Gamma^k = \sum_{\nu\nu_0} \sum'_{k_i \kappa_i} \sum_{q_i \sigma_i} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} \left(((2J + 1)(2J' + 1)(2J_0 + 1)(2J'_0 + 1))^{1/2} \times \right. \\ \times (-)^{(J'+J+k+\kappa_i)} \begin{Bmatrix} k_i & J & J_0 \\ S & N & N \end{Bmatrix} \begin{Bmatrix} k_i & J' & J'_0 \\ S & N & N \end{Bmatrix} \begin{Bmatrix} J & J_0 & k_i \\ J'_0 & J' & k \end{Bmatrix} \\ \left. \times \left| \frac{NN}{\nu\nu_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2 - \frac{1}{2N + 1} \delta_{J_0 J} \delta_{J'_0 J'} \sum_{N'} \left| \frac{N'N}{\nu \nu_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2 \right). \quad (55a)$$

$$N \neq N_0$$

$${}^{NJNJ'N_0J_0N_0J_0}\Delta\Gamma^k = \sum_{\nu\nu_0} \sum'_{k_i \kappa_i} \sum_{q_i \sigma_i} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} ((2J + 1)(2J' + 1)(2J_0 + 1)(2J'_0 + 1))^{1/2} \times \\ \times (-)^{(J'+J_0+k+\kappa_i)} \begin{Bmatrix} k_i & J & J_0 \\ S & N_0 & N \end{Bmatrix} \begin{Bmatrix} k_i & J' & J'_0 \\ S & N_0 & N \end{Bmatrix} \begin{Bmatrix} J & J_0 & k_i \\ J'_0 & J' & k \end{Bmatrix} \left| \frac{NN_0}{\nu\nu_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2. \quad (55b)$$

With this second method, one has to be careful with the cut off impact parameter b_0 (see § 3.4.1) : in equation (55) the spin S always conserves some memory of the value of the k th multipole before collision, and the cut off does not correspond to total destruction of the orbital part of it. The corresponding cut off value has been given by Omont [5]. Serious difficulties can occur when the cut off parameters are very different.

Appendix A. — We shall evaluate explicitly the term ${}^{\nu\nu_0} \tilde{S}_{00}^{NN_0}$ in equation (18) in order to simplify (cf. § 3.2) the solution in first order for \tilde{S} .

The term ${}^{\nu\nu_0} S_{00}^{NN_0}$ appears in (18) only when $N = N_0$, and $\nu = \nu_0$ due to triangle rules in (N, N_0, k_i) and (ν, ν_0, κ_i) . In equation (18) we split off the term containing $|S_{00}^{00}|^2$:

$${}^{NNN_0N_0}\Delta\Gamma^k = \sum_{\nu\nu_0} \frac{\Pi(\nu_0)}{(2\nu_0 + 1)} \left((-)^{(N+N_0+k)} \begin{Bmatrix} 0 & N & N_0 \\ k & N_0 & N \end{Bmatrix} \left| \frac{NN_0}{\nu\nu_0} S_{00}^{00} \right|^2 \delta_{NN_0} \delta_{\nu\nu_0} + \right. \\ \left. + \sum'_{k_i \kappa_i} \sum_{q_i \sigma_i} (-)^{(N+N_0+k_i+\kappa_i)} \begin{Bmatrix} k_i & N & N_0 \\ k & N_0 & N \end{Bmatrix} \left| \frac{NN_0}{\nu\nu_0} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2 \right) - \delta_{NN_0}. \quad (56)$$

In this expression \sum' represents the sum over k_i and κ_i when they are not simultaneously equal to zero. $\Delta\Gamma^k$ then takes two different forms depending on the relative values of N and N_0 .

i) $N = N_0$. We shall express the term ${}^{NN}S_{00}^{00}$ starting from the tensor relations which describe the unitarity of \tilde{S} : $1 = \tilde{S}^+ S$:

$$1 = \sum_{\text{all indices}} {}^{NN'}_{vv'} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} {}^{N_1 N'_1}_{v_1 v'_1} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} {}^{NN'} T_{q_i}^{k_i} {}^{N_1 N'_1} T_{q_i}^{k_i} {}^{vv'} T_{\sigma_i}^{k_i} {}^{v_1 v'_1} T_{\sigma_i}^{k_i}.$$

Taking the trace we obtain :

$$(2N + 1)(2v + 1) = \sum_{N' v' k_i \kappa_i q_i \sigma_i} \left| {}^{N' N}_{v' v} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2.$$

Hence

$$\left| {}^{NN}_{vv} \tilde{S}_{00}^{00} \right|^2 = (2N + 1)(2v + 1) - \sum_{N' v'} \sum_{k_i \kappa_i} \sum_{q_i \sigma_i} \left| {}^{N' N}_{v' v} \tilde{S}_{q_i \sigma_i}^{k_i \kappa_i} \right|^2$$

and the expression for ${}^{NNNN} \Delta \Gamma^k$, on replacing ${}^{NN}_{vv} \tilde{S}_{00}^{00}$ in (56), is then given by (19a).

ii) $N \neq N_0$: ${}^{NNN_0 N_0} \Delta \Gamma^k$ is given by (19b).

Appendix B. — The notation used here is that employed by Messiah [10]. The wavefunction $|NM\rangle_i$ defined in the intermolecular frame (Fig. 1) may be deduced from the $|NM\rangle_c$ defined in the collision frame through the rotation operator $R_{O_{A'Y}}(\theta)$ defined by (Messiah [10], 2 C (46)) :

$$|N' M'_1\rangle_i = \sum_{M'} \langle N' M' | R_{O_{A'Y}}(\theta) | N' M'_1\rangle | N' M'\rangle_c = \sum_{M'} R_{O_{A'Y}}(\theta)_{M' M'_1}^N | N' M'\rangle_c.$$

Conversely, by use of the unitary and orthogonality properties of the rotation operator (Messiah [10], 2 C (57) (60)) we obtain :

$$|N' v' M' \mu'\rangle_c = \sum_{M'_1 \mu'_1} R_{O_{A'Y}}(-\theta)_{M'_1 M'}^{N'} R_{O_{B'Y}}(-\theta)_{\mu'_1 \mu'}^{v'} | N' v' M'_1 \mu'_1\rangle_i.$$

The matrix element of \mathcal{U} in the collision frame is then obtained as a function of the corresponding element in the intermolecular frame

$$\langle NvM\mu | \mathcal{U} | N' v' M' \mu'\rangle_c = \sum_{M_1 M'_1 \mu_1 \mu'_1} R_{O_{A'Y}}(\theta)_{M M_1}^N R_{O_{B'Y}}(\theta)_{\mu \mu_1}^v \times \langle NvM_1 \mu_1 | \mathcal{U} | N' v' M'_1 \mu'_1\rangle_i R_{O_{A'Y}}^+(\theta)_{M'_1 M'}^{N'} R_{O_{B'Y}}^+(\theta)_{\mu'_1 \mu'}^{v'}. \quad (57)$$

Replacing \mathcal{U} by its expression (36), and expressing the operators \mathcal{U} in terms of their reduced matrix elements

$$\langle NM_1 | {}^{(s)q}U_Q^K(A) | N' M'_1\rangle_i = \frac{\langle N || {}^{(s)q}U^K(A) || N'\rangle}{(2K + 1)^{1/2}} \langle NM_1 | {}^{NN'} T_Q^K | N' M'_1\rangle$$

and performing the summation over the indices $M_1 M'_1 \mu_1 \mu'_1$, expression (57) becomes

$$\begin{aligned} \langle NvM\mu | \mathcal{U} | N' v' M' \mu'\rangle_c &= \sum_{sJQ} \frac{\alpha_{s,J}}{R^{n_s}} \langle K\chi Q\Sigma | J0\rangle \times \\ &\times \frac{\langle N || {}^{(s)q}U^K(A) || N'\rangle \langle v || {}^{(s)q}U^\chi(B) || v'\rangle}{(2K + 1)^{1/2} (2\chi + 1)^{1/2}} \langle NM | R_{O_{A'Y}}(\theta) {}^{NN'} T_Q^K R_{O_{A'Y}}^+(\theta) | N' M'\rangle \\ &\times \langle v\mu | R_{O_{B'Y}}(\theta) {}^{vv'} T_\Sigma^\chi R_{O_{B'Y}}^+(\theta) | v' \mu'\rangle \delta_{Q-\Sigma}. \end{aligned}$$

Making use of the tensor decomposition properties of the operator R (Messiah [10], 2 C (81)) and writing the matrix element of the tensor \mathbf{T} in terms of its reduced matrix element

$$\begin{aligned} \langle NvM\mu | \mathcal{U} | N' v' M' \mu'\rangle_c &= \sum_{sJQ\Sigma} \frac{\alpha_{s,J}}{R^{n_s}} \sum_{Q_1} \langle K\chi Q_1 \Sigma_1 | J0\rangle \langle N || {}^{(s)q}U^K(A) || N'\rangle \times \\ &\times \langle v || {}^{(s)q}U^\chi(B) || v'\rangle r_{Q_1}^K(\theta) r_{\Sigma_1}^\chi(\theta) (-)^{(N-m+v-\mu)} \begin{pmatrix} N & K & N' \\ -M & Q & M' \end{pmatrix} \begin{pmatrix} v & \chi & v' \\ -\mu & \Sigma & \mu' \end{pmatrix} \delta_{Q_1-\Sigma_1} \end{aligned}$$

where $r(\theta) = R(0\theta 0)$. We obtain the final form of the differential equation relating the tensor components of the operator \tilde{U} by replacing in (21) the matrix element of \mathcal{U} ; taking account of $\delta_{Q-\Sigma}$ and by summing over $MM' M_0$ and $\mu\mu' \mu_0$ with the help of (Messiah [10], 2 C (33)) we have :

$$i \frac{d}{dt} \overset{NN_0}{v\nu_0} \tilde{U}_{q\sigma}^{kk}(t, t_0) = \sum_{N'v'k'\kappa'q'\sigma'} (-)^{(N_0+v_0+N+v+q+\sigma)} \times \\ \times ((2k+1)(2k'+1)(2\kappa+1)(2\kappa'+1))^{1/2} \sum_{sJQ\Sigma} \frac{\alpha_{s,J}}{R^{n_s}} \langle N \| {}^{(s)}\mathcal{U}^K(\mathbf{A}) \| N' \rangle \\ \times \langle v \| {}^{(s)}\mathcal{U}^\chi(\mathbf{B}) \| v' \rangle_i \begin{pmatrix} k' & K & k \\ q' & Q & -q \end{pmatrix} \begin{Bmatrix} k' & K & k \\ N & N_0 & N' \end{Bmatrix} \begin{pmatrix} \kappa' & \chi & \kappa \\ \sigma' & -\Sigma & -\sigma \end{pmatrix} \begin{Bmatrix} \kappa' & \chi & \kappa \\ v & \nu_0 & v' \end{Bmatrix} \\ \times \sum_{Q_1} r_{Q_1}^K(\theta) r_{\Sigma-Q_1}^\chi(\theta) \langle K\chi - Q_1 \ Q_1 | J0 \rangle \exp(i(E_N - E_{N'} + E_v - E_{v'}) t) \overset{N'N_0}{v'\nu_0} \tilde{U}_{q'\sigma'}^{k'\kappa'}(t, t_0). \quad (58)$$

Part of this expression can be simplified by expressing the product of the rotation operators (Messiah [10], 2 C (69)) :

$$r_{Q_1}^K(\theta) r_{\Sigma-Q_1}^\chi(\theta) = \sum_{FM} \langle K\chi Q\Sigma | FM \rangle r_{M_0}^F(\theta) \langle K\chi Q_1 - Q_1 | F0 \rangle.$$

Upon summing over Q_1 and thus introducing δ_{FJ} we obtain :

$$\sum_{Q_1} r_{Q_1}^K(\theta) r_{\Sigma-Q_1}^\chi(\theta) \langle K\chi - Q_1 \ Q_1 | J0 \rangle = \sum_M \langle K\chi Q\Sigma | JM \rangle r_{M_0}^J(\theta).$$

Replacing this quantity by its simplified form in (58) we obtain the final expression (38).

Appendix C. — We want to express the summation over q_i and σ_i of the \tilde{S} components product, which appears in (19), taking into account the fact that k_i and χ_i are not simultaneously zero. Starting from (39) we have :

$$\sum_{q_i\sigma_i} \left(\overset{NN_0}{v\nu_0} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \left(\sum_s \mathcal{U}_s \right) \right) \left(\overset{NN_0}{v\nu_0} \tilde{S}_{q_i\sigma_i}^{k_i\kappa_i} \left(\sum_{s'} \mathcal{U}_{s'} \right) \right) = \\ = \sum_{ss'JJ'} \alpha_{s,J} \alpha_{s',J'} \frac{\langle N \| {}^{(s)}\mathcal{U}^K(\mathbf{A}) \| N_0 \rangle \langle v \| {}^{(s)}\mathcal{U}^\chi(\mathbf{B}) \| v_0 \rangle}{(2K+1)^{1/2} (2\chi+1)^{1/2}} \delta_{Kk_i} \delta_{\chi\kappa_i} \times \\ \times \frac{\langle N \| {}^{(s')} \mathcal{U}^{K'}(\mathbf{A}) \| N_0 \rangle \langle v \| {}^{(s')} \mathcal{U}^{\chi'}(\mathbf{B}) \| v_0 \rangle}{(2K'+1)^{1/2} (2\chi'+1)^{1/2}} \delta_{K'k_i} \delta_{\chi'\kappa_i} \sum_{q_i\sigma_i} \tilde{\gamma} \tilde{\gamma}' \quad (59)$$

with :

$$\tilde{\gamma} = \int_{-\infty}^{+\infty} dt \exp(i\omega t) \frac{1}{R^{n_s}} \sum_{Q\Sigma M} \langle K\chi Q\Sigma | JM \rangle r_{M_0}^J(\theta) \delta_{Qq_i} \delta_{\Sigma\sigma_i}.$$

We then express the quantity $\sum \tilde{\gamma} \tilde{\gamma}'$ using the fact that K and χ are respectively equal to K' and χ' in (59) : this allows us to use the closure relation :

$$\sum_{q_i\sigma_i} \langle K\chi q_i \sigma_i | JM \rangle \langle K' \chi' q_i \sigma_i | J' M' \rangle^* = \delta_{MM'} \delta_{JJ'}$$

and therefore to simplify the r product. We finally obtain :

$$\sum_{q_i\sigma_i} \tilde{\gamma} \tilde{\gamma}' = \iint_{-\infty}^{+\infty} dt dt' \exp(i\omega(t-t')) \frac{1}{R^{n_s} R^{n_{s'}}} r_{M_0}^J(\theta - \theta') \delta_{JJ'}.$$

In this expression $R = (v^2 t^2 + b^2)^{1/2}$ and $\text{tg } \theta = b/vt$. Introducing the reduced time variables vt/b and vt'/b , we factor out a cut off function α expressed by relation (41), and expression (59) simplifies to (40). In this last expression, in order to make clear that $K\chi J$ and $K' \chi' J'$ refer respectively to \mathcal{U}_s and $\mathcal{U}_{s'}$, we write them as $K_s \chi_s J_s$ and $K_{s'} \chi_{s'} J_{s'}$.

Appendix D. — We want to express the reduced matrix elements of the operators $^{(s)}\mathcal{U}(A)$. These operators, defined by (27) and (35) are function in expression (42) of the spatial electronic and nuclear coordinates of particles, defined in the intermolecular frame (Fig. 1). We first express the molecular wavefunctions, then we give the reduced matrix element, considering separately the electronic and nuclear contributions.

1. WAVEFUNCTIONS. — In this paragraph we shall give our conventions for the molecular wavefunctions $|\alpha p | A | vNM \rangle$ (short hand notation $\Psi_{|A|}$) since these conventions differ widely from author to author.

We consider the general case of diatomic molecules corresponding to Hund's case b or a. In Hund's case b, A is the projection of the total orbital electronic angular momentum (and is therefore integral), the spin coupling giving rise to a fine structure much smaller than the rotational structure. On the contrary, in Hund's case a, where the fine structure is much larger than the rotational one, the total orbital electronic angular momentum is coupled to the spin, to give the total electronic angular momentum whose projection on the internuclear axis is Ω ; Ω is therefore integral or half-integral.

In the following we use the notation of case b where A , the projection of the total orbital electronic angular momentum, can be integral or half-integral, to allow treatment of the general case of coupling; N can also be half-integral (note that in case a A and N must be replaced by Ω and J).

We define then $|\alpha p | A | vNM \rangle$ a basis vector of the eigenstates of molecule A where : p is the parity through an inversion $\bar{\gamma}$ of the spatial coordinates of all the particles forming the molecule :

$$\bar{\gamma} |\alpha p | A | vNM \rangle = (-)^p |\alpha p | A | vNM \rangle \quad (60)$$

v is the vibrational number, N and M are the quantum numbers characterizing respectively the total kinetic momentum and its projection on the magnetic field; α covers all the other quantum numbers.

The orthonormalized wavefunction $\Psi_{|A|}$ is expressed as a linear combination of the orthonormalized function Φ_A

$$\Psi_{|A|} = A(\Phi_A + c\Phi_{-A}) \quad (61)$$

when $A = 1/\sqrt{2}$ if $A \neq 0$ and $A = 1/2$ if $A = 0$. The functions Φ_A , assuming the Born Oppenheimer approximation, are given by

$$\Phi_A(\dots(\mathbf{r}_{ae})_m, s_{ae}; \rho) = \psi_A(\dots(\mathbf{r}_{ae})_m, s_{ae}) f_{av}(\rho) \chi_{MA}^N(\beta\alpha) \quad (62)$$

with :

i) $\psi_A(\dots(\mathbf{r}_{ae})_m, s_{ae})$: the electronic part which is function of the spatial coordinates, \mathbf{r}_{ae} (and, in case a only, of the spin s_{ae}) of the ae th electron, in the molecular frame (index m) (Fig. 2).

ii) $f_{av}(\rho)$: the vibrational nuclear part with ρ the internuclear distance.

iii) $\chi_{MA}^N(\beta\alpha)$: the rotational nuclear part; the α and β angles ⁽¹⁾ determine the rotation $R(\alpha\beta 0)$ through which the intermolecular frame superposes the molecular one (Fig. 2) (the third arbitrary angle, γ , has been fixed at zero : it is this convention that leads our formulae to be somewhat different in form but equivalent, to the ones of Carrington *et al.* [14] and Chiu [15]).

We have the following expression where the rotation matrix R is that of Messiah [10] :

$$\chi_{MA}^N(\beta\alpha) = \left(\frac{2N+1}{4\pi} \right)^{1/2} R_{MA}^N(\alpha\beta 0).$$

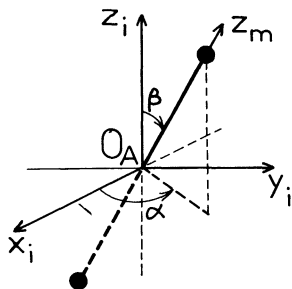


FIG. 2.

⁽¹⁾ The angle α , and the subscript α , which covers all the undefined quantum numbers, must not be confused.

In order to express $\Psi_{|A|}$ we want to determine the constant c in (61) by noting how Φ_A and $\Psi_{|A|}$ transform in inversion \mathcal{J} . This operator is equivalent to the product of a reflexion $S(\text{Ox}_m)$ through the plane $\text{Oy}_m z_m$ (molecular frame) of the electronic coordinate \mathbf{r}_{ae} (and possibly s_{ae}) and of an inversion $I(\alpha \rightarrow \Pi + \alpha, \beta \rightarrow \Pi - \beta)$ of the internuclear axis (Chiu [15]). If we choose the phase of ψ_A so that ⁽²⁾

$$S(\text{Ox}_m) \psi_A = \psi_{-A} \quad (63)$$

which implies $S(\text{Ox}_m) \psi_{-A} = (-)^{2A} \psi_A$ (the dissymmetry comes from $R(2\pi) = (-)^{2A}$), we have :

$$\mathcal{J}\Phi_A = f_{av} S(\text{Ox}_m) \psi_A I\chi_{MA}^N = f_{av} \psi_{-A} (-)^{-N} \chi_{M-A}^N = (-)^{-N} \Phi_{-A}.$$

With (60) and (61) we finally get

$$\Psi_{|A|} = A(\Phi_A + (-)^{p-N} \Phi_{-A}). \quad (64)$$

2. REDUCED MATRIX ELEMENT. — The matrix element of \mathcal{U}_Q^K in the intermolecular frame is, using (64), and taking into account that $((-)^{-N})^* = (-)^N$

$$\begin{aligned} \langle \alpha p | A | vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' | A' | v' N' M' \rangle &= A^2 (\langle \alpha p A vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' A' v' N' M' \rangle + \\ &+ (-)^{p'-N'} \langle \alpha p A vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' - A' v' N' M' \rangle \\ &+ (-)^{p+N} \langle \alpha p - A vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' A' v' N' M' \rangle \\ &+ (-)^{p+N+p'-N'} \langle \alpha p - A vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' - A' v' N' M' \rangle). \quad (65) \end{aligned}$$

In this expression, the wavefunctions being expressed in the molecular frame, the \mathcal{U}_Q^K in the intermolecular frame have to be related to the \mathcal{U}_Q^K in the molecular frame by :

$$\mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) = \sum_{Q'} \mathcal{U}_{Q'}^K(\dots(\mathbf{r}_a)_m) R_{Q'Q}^{K*}(\alpha\beta 0). \quad (66)$$

We shall now express the general term t

$$t = \langle \alpha p A vNM | \mathcal{U}_Q^K(\dots(\mathbf{r}_a)_i) | \alpha' p' A' v' N' M' \rangle$$

by considering separately the electronic ($a = ae$) and nuclear ($a = an$) part of \mathcal{U}_Q^K .

a) Electronic reduced matrix elements. By use of (64), (62), (66) we obtain a sum of products of three integrals :

$$t = \sum_{Q'} \mathcal{L}_1 \mathcal{L}_2 \mathcal{L}_3$$

with

$$\mathcal{L}_1 = \int \dots d^3(\mathbf{r}_{ae})_m \psi_A^*(\dots(\mathbf{r}_{ae})_m, s_{ae}) \mathcal{U}_{Q'}^K(\dots(\mathbf{r}_{ae})_m) \psi_A(\dots(\mathbf{r}_{ae})_m, s_{ae})$$

expression that we shall note $\mathcal{L}_1(A, Q', A')$;

$$\mathcal{L}_2 = \int d\rho \rho^2 f_{av}(\rho) f_{a'v'}(\rho) = F_{av,a'v'}; \text{ the Franck Condon factor ;}$$

$$\mathcal{L}_3 = \frac{1}{4\Pi} ((2N+1)(2N'+1))^{1/2} \int d\alpha d\beta \sin \beta R_{MA}^N(\alpha\beta 0) R_{Q'Q}^{K*}(\alpha\beta 0) R_{M'A'}^{N'*}(\alpha\beta 0).$$

The integration over azimuthal angle in \mathcal{L}_1 implies that $A = A' + Q'$. One has then :

$$1 = \frac{1}{2\Pi} \int_0^{2\Pi} \exp(i(A - A' - Q')\gamma) d\gamma.$$

⁽²⁾ If ψ_A were an atomic wavefunction of parity $(-)^p$ and orbital momentum L , one would have $S(\text{Ox}_m) \psi_A = (-)^p e^{-i\pi L} \psi_A$ which would correspond to our definition for a mono-electronic atom. In the case in which L is no longer a good quantum number, one has to choose arbitrarily a phase. We have chosen here this phase equal to zero but other authors (Carrington, A., *et al.* [14], Chiu [15]) choose different conventions, which explains the formal difference between their formulae and ours.

Inserting this relation in \mathfrak{L}_3 and using relation (Messiah [10], 2 C (66)) and (Edmonds [16], 4, 62) we obtain :

$$\mathfrak{L}_3 = ((2N + 1)(2N' + 1))^{1/2} (-)^{Q-Q'+M'-A'} \begin{pmatrix} N & K & N' \\ M & -Q & -M' \end{pmatrix} \begin{pmatrix} N & K & N' \\ A & -Q' & -A' \end{pmatrix}.$$

The $3j$ selection rules implies $M - Q - M' = 0$ which allows us to replace $(-)^{Q-Q'+M'-A'}$ by $(-)^{(N-M+N-A)}$; the general term becomes :

$$t = (-)^{(N-M)} \begin{pmatrix} N & K & N' \\ -M & Q & M' \end{pmatrix} F_{av,\alpha'v'}((2N + 1)(2N' + 1))^{1/2} \times \sum_{Q'} (-)^{(N-A)} \begin{pmatrix} N & K & N' \\ -A & Q' & A' \end{pmatrix} \mathfrak{L}_1(AQ' A').$$

We now want to show that there are simple relations between first and fourth (and between the second and third) terms in (65), terms which differ by changing the signs of A and A' . Using (63) and its complex conjugate we have :

$$\mathfrak{L}_1(-A, Q', -A') = \int \psi_A^* S^+(Ox) \mathfrak{U}_{Q'}^K S(Ox) \psi_{A'},$$

considering that

$$S^+(Ox) \mathfrak{U}_{Q'}^K S(Ox) = I^+ R_{Ox}^+(\Pi) \mathfrak{U}_{Q'}^K R_{Ox}(\Pi) I = (-)^{(p_u-K)} \mathfrak{U}_{-Q'}^K$$

(p_u being the parity of $\mathfrak{U}_{Q'}^K$) we have $\mathfrak{L}_1(-A, Q', -A') = (-)^{(p_u-K)} \mathfrak{L}_1(A, -Q', A')$. Similarly we have $\mathfrak{L}_1(-A, Q', A') = (-)^{(p_u-K+2N)} \mathfrak{L}_1(A, -Q', -A')$. Then, using (65) and the Wigner Eckart theorem we have :

$$\begin{aligned} \langle \alpha p | A | vN \| \mathfrak{U}^K(\cdot, (\mathbf{r}_{ae})) \| \alpha' p' | A' | v' N' \rangle = \\ = F_{av,\alpha'v'}((2N + 1)(2N' + 1))^{1/2} (1 + (-)^{(p+p'+p_u)}) A^2 (-)^{(N-A)} \times \\ \times \sum_{Q'} \left(\begin{pmatrix} N & K & N' \\ -A & Q' & A' \end{pmatrix} \mathfrak{L}_1(A, Q', A') + (-)^{(p'-N')} \begin{pmatrix} N & K & N' \\ -A & -Q' & -A' \end{pmatrix} \mathfrak{L}_1(A, -Q', -A') \right). \end{aligned} \quad (67)$$

b) Nuclear reduced matrix elements. In the molecular frame, due to invariance of the nuclear coordinates by rotation around the internuclear axis all $\mathfrak{U}_{Q'}^K(\cdot, (\mathbf{r}_{an})) = h_K(\rho) R_{Q'}^{K*}(\alpha\beta 0)$.

Inserting this expression into (65) we obtain : $t = \mathcal{M}_1 \mathcal{M}_2 \mathcal{M}_3$ with :

$$\mathcal{M}_1 = \int d^3(\mathbf{r}_{ae})_m \psi_A^*(\cdot, (\mathbf{r}_{ae})_m, s_{ae}) \psi_{A'}(\cdot, (\mathbf{r}_{ae})_m, s_{ae}) = \delta_{\alpha\alpha'} \delta_{AA'}$$

$$\mathcal{M}_2 = \int d\rho \rho^2 f_{av}(\rho) h_K(\rho) f_{\alpha'v'}(\rho) = \langle h_K(\rho) \rangle_{av,\alpha'v'}$$

$$\mathcal{M}_3 = \frac{1}{4\pi} ((2N + 1)(2N' + 1))^{1/2} \int d\alpha \sin \beta d\beta R_{MA}^N(\alpha\beta 0) R_{Q'}^{K*}(\alpha\beta 0) R_{M'A'}^{N'*}(\alpha\beta 0).$$

\mathcal{M}_3 can be simplified in the same way as \mathfrak{L}_3 ; t becomes

$$t = (-)^{(N-M)} \begin{pmatrix} N & K & N' \\ -M & Q & M' \end{pmatrix} \langle h_K(\rho) \rangle_{av,\alpha'v'} ((2N + 1)(2N' + 1))^{1/2} (-)^{(N-A)} \begin{pmatrix} N & K & N' \\ -A & 0 & A' \end{pmatrix} \delta_{\alpha\alpha'} \delta_{AA'}$$

and the nuclear reduced matrix element is :

$$\begin{aligned} \langle \alpha p | A | vN \| \mathfrak{U}^K(\cdot, (\mathbf{r}_{an})) \| \alpha' p' | A', v' N' \rangle = \langle h_K(\rho) \rangle_{av,\alpha'v'} ((2N + 1)(2N' + 1))^{1/2} \times \\ \times (1 + (-)^{(p+p'+K)}) A^2 (-)^{(N-A)} \begin{pmatrix} N & K & N' \\ -A & 0 & A' \end{pmatrix} \delta_{\alpha\alpha'} \delta_{AA'}. \end{aligned}$$

Appendix E. — We consider the equality obtained from (54) by replacing $\overline{\Delta\Gamma}$ by $\Delta\Gamma$ (i.e. integration over b and v is not performed). By replacing $\Delta\Gamma^{k_N}$ as a function of the S matrix (18) we obtain :

$$\begin{aligned}
 NJNJ'N_0J_0N_0J_0\Delta\Gamma^k &= \sum_{k_N k_S v_0} \frac{\Pi(v_0)}{(2v_0+1)} \sum'_{k_i k_i} \sum_{q_i \sigma_i} (-)^{(N+N_0+k_i+k_N)} \left| \begin{matrix} NN_0 \\ v_0 v_0 \end{matrix} S_{q_i \sigma_i}^{k_i k_i} \right|^2 \left\{ \begin{matrix} k_i & N_0 & N \\ k_N & N & N_0 \end{matrix} \right\} \times \\
 &\quad \times (2k_N+1)(2k_S+1)((2J+1)(2J'+1)(2J_0+1)(2J'_0+1))^{1/2} \\
 &\quad \times \left\{ \begin{matrix} N_0 & N_0 & k_N \\ S & S & k_S \\ J_0 & J'_0 & k \end{matrix} \right\} \left\{ \begin{matrix} N & N & k_N \\ S & S & k_S \\ J & J' & k \end{matrix} \right\} - \delta_{NN_0} \delta_{N'N_0}.
 \end{aligned}$$

In this expression we shall replace the « 6j » by a « 9j » according to

$$\left\{ \begin{matrix} k_i & N_0 & N \\ k_N & N & N_0 \end{matrix} \right\} = \left\{ \begin{matrix} N_0 & N_0 & k_N \\ N & N & k_i \end{matrix} \right\} = ((2k_N+1)(2k_i+1))^{1/2} (-)^{(N_0+N+k_N+k_i)} \left\{ \begin{matrix} N_0 & N_0 & k_N \\ N & N & k_N \\ k_i & k_i & 0 \end{matrix} \right\}.$$

Then we introduce

$$1 = ((2k+1)(2k_N+1))^{1/2} \left\{ \begin{matrix} 0 & k & k \\ k_S & k_N & k_N \end{matrix} \right\} (-)^{(k+k_N+k_S)}$$

in order to obtain, after permutation of the columns of the third « 9j »,

$$\begin{aligned}
 NJN'J'N_0J_0N_0J_0\Delta\Gamma^k &= \sum_{v_0} \frac{\Pi(v_0)}{(2v_0+1)} \sum'_{k_i k_i} \sum_{q_i \sigma_i} \left| \begin{matrix} NN_0 \\ v_0 v_0 \end{matrix} S_{q_i \sigma_i}^{k_i k_i} \right|^2 \times \\
 &\quad \times ((2J+1)(2J'+1)(2J_0+1)(2J'_0+1)(2k+1)(2k_i+1))^{1/2} (-)^{(J_0-J'_0)} \sum_{k_N k_S} (2k_N+1)^2 (2k_S+1) \\
 &\quad \times \left\{ \begin{matrix} 0 & k & k \\ k_S & k_N & k_N \end{matrix} \right\} \left\{ \begin{matrix} k_i & N_0 & N \\ k_i & N_0 & N \\ 0 & k_N & k_N \end{matrix} \right\} \left\{ \begin{matrix} S & J & N \\ S & J' & N \\ k_S & k & k_N \end{matrix} \right\} \left\{ \begin{matrix} S & N_0 & J_0 \\ S & N_0 & J'_0 \\ k_S & k_N & k \end{matrix} \right\} - \delta_{NN_0} \delta_{N'N_0}.
 \end{aligned}$$

Summation over k_N and k_S is simplified by using the relation (Judd [17], 3.28) :

$$\begin{aligned}
 NJN'J'N_0J_0N_0J_0\Delta\Gamma^k &= \sum_{v_0} \frac{\Pi(v_0)}{(2v_0+1)} \sum'_{k_i k_i} \sum_{q_i \sigma_i} \left| \begin{matrix} NN_0 \\ v_0 v_0 \end{matrix} S_{q_i \sigma_i}^{k_i k_i} \right|^2 \times \\
 &\quad \times ((2J+1)(2J'+1)(2J_0+1)(2J'_0+1)(2k+1)(2k_i+1))^{1/2} \\
 &\quad \times \left\{ \begin{matrix} k_i & J & J_0 \\ S & N_0 & N \end{matrix} \right\} \left\{ \begin{matrix} k_i & J' & J'_0 \\ S & N_0 & N \end{matrix} \right\} \left\{ \begin{matrix} k_i & J & J_0 \\ k_i & J' & J'_0 \\ 0 & k & k \end{matrix} \right\} - \delta_{NN_0} \delta_{N'N_0}.
 \end{aligned}$$

After the simplification of the « 9j » coefficient, we obtain the expression (55).

References

- [1] ANDERSON, P. W., *Phys. Rev.* **76** (1949) 647.
- [2] RABITZ, H., *Ann. Rev. Phys. Chem.* **25** (1974) 155.
- [3] TSAO, C. J. and CURNUTTE, B., *J. Quant. Spectros. Radiat. Transfer* **2** (1962) 41.
- [4] BEN REUVEN, A., *Phys. Rev.* **141** (1966) 34; **145** (1966) 7.
- [5] OMONT, A., *J. Physique* **26** (1965) 26.
- [6] D'YAKONOV, M. I. and PEREL, V. I., *Sov. Phys. J.E.T.P.* **21** (1965) 227.
- [7] HANLE, W., *Z. Phys.* **30** (1924) 93.
- [8] CARRINGTON, C. G., STACEY, D. N. and COOPER, J., *J. Phys. B : Atom. Mol. Phys.* **6** (1973) 417.
- [9] MÉLIÈRES-MARÉCHAL, M. A. and LOMBARDI, M., *J. Physique* **38** (1977) 547.
- [10] MESSIAH, A., *Mécanique Quantique*, Vol. 1 and 2 (2nd ed. Dunod, Paris) 1964.
- [11] GAY, J. C., *J. Physique* **35** (1974) 813.
- [12a] FONTANA, P. R., *Phys. Rev.* **123** (1961) 1865.
- [12b] GRAY, C. G. and VAN KRANENDONK, J., *Can. J. Phys.* **44** (1966) 2411.
- [12c] ROSE, M. E., *J. Math. Phys.* **37** (1958) 215.
- [12d] CHIU, Y. N., *J. Math. Phys.* **5** (1964) 283.
- [13] MÉLIÈRES-MARÉCHAL, M. A., Thèse, Grenoble (1973).
- [14] CARRINGTON, A., LEVY, D. M. and MILLER, T. A., *Adv. Chem. Phys.* **18** (1970) 149.
- [15] CHIU, Y. N., *J. Chem. Phys.* **45** (1966) 2969.
- [16] EDMONDS, A. R., *Angular Momentum in Quantum Mechanics* (Princeton N. J. : Princeton University Press) 1960.
- [17] JUDD, B. R., *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, Inc.) 1963.