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On the key factors of angular correlations in complex-forming elementary reactions*

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Abstract. In the mid-seventies, Case and Herschbach argued that for complex-forming three-atom reactions governed by long-range forces and performed in supersonic molecular beam experiments, vectorial properties are determined by a single parameter $\Lambda' = \langle L'/(L'+j')\rangle$, L' and j' being respectively the moduli of the orbital and rotational angular momenta of the products. A simple mathematical relation between vectorial properties and Λ' was then proposed. However, Λ' must be determined beforehand by phase space theory calculations. Besides, we have recently shown that scalar properties are mainly controled by two factors ρ'_1 and ρ'_2 respectively called *angular excitation* and *diatomic inertial contribution*. We show here that these factors control also vectorial properties. Moreover, the way they control them is summarized in a set of four figures. The advantage of our method is that ρ'_1 and ρ'_2 are related to the mechanical parameters of the reaction by very simple formulas, contrary to Λ'. Last by not least, our parameters appear to be mostly independent, so that vectorial properties cannot be said to strictly depend on Λ'. Nevertheless, it turns out that the rule proposed by Case and Herschbach is reasonable in many realistic situations.

PACS. 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 34.50.Lf Chemical reactions, energy disposal, and angular distribution, as studied by atomic and molecular beams – 82.20.Bc State selected dynamics and product distribution – 82.20.Db Transition state theory and statistical theories of rate constants

1 Introduction

The experimental data providing detailed information about the dynamics of elementary reactions of the type A + BC → AB + C (A, B and C are three atoms) are energy, angular and rotational polarization distributions, all of them measurable in the products [1,2]. Energy distributions show how the energy available to the products is partitioned among translation, vibration and rotation motions. The angular distribution shows how the angle between the reagent and product relative velocity vectors is distributed. Finally, the rotational polarization distribution shows how the angle between the reagent relative velocity vector and the rotational angular momentum of AB is distributed. Though these scalar and vectorial data do not provide direct information about nuclear motions in the strong coupling region (SCR) where the process of bond-breaking/bond-forming takes place, they contribute strongly to the validation of theoretical models describing the entire dynamics from the reagents onto the products.

In the seventies, Case and Herschbach [3,4] showed that for complex-forming elementary reactions governed by long-range forces, vectorial properties are determined by only two parameters, $\Lambda = \langle L/(L+j)\rangle$ and $\Lambda' = \langle L'/(L'+j')\rangle$. L and j are respectively the moduli of the orbital and rotational angular momenta of the reagents. L' and j' are the analogous quantities in the products. Actually, in the supersonic crossed beam experiments performed nowadays, j is almost zero so that $\Lambda \approx 1$. Therefore, according to Case and Herschbach, vectorial properties are determined by only one parameter, i.e. Λ'.

Besides, the authors derived some years ago a simple model — the partial angular constraint model (PACM) — in order to provide some conceptual and technical tools helpful for the understanding of the global shape of energy distributions in the products of the same processes [5]. This model was obtained by simplifying Phase space theory (PST), then arriving at an analytical expression of the translational energy distribution in which two major factors of the dynamics appear explicitly. These factors

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are the *angular excitation* ρ'_1 and the *diatomic inertial contribution* ρ'_2 .

ρ'_1 is defined by

$$\rho'_1 = \frac{J_M}{J'_M} \tag{1.1}$$

and

$$J_M = \min(L_M; J'_M) \tag{1.2}$$

where L_M is the maximum value of the reagent orbital angular momentum consistent with complex formation and J'_M is the maximum value of the total angular momentum J compatible with the available energy E' in the products. J_M is thus the maximum value of the total angular momentum consistent with the reaction.

ρ'_2 is defined by

$$\rho'_2 = \frac{I_{AB}}{I_{AB} + I^{\ddagger}_{AB-C}} \tag{1.3}$$

where I_{AB} is the moment of inertia of AB and $I^{\ddagger}_{AB-C}$ may be roughly viewed as the moment of inertia of C with respect to AB at the orbiting transition state ABC‡ between the intermediate well and the products. In other words, ρ'_2 is the contribution of the diatomic AB to the total moment of inertia of the activated complex ABC‡. Both parameters belong to the range $[0, 1]$. More details on these parameters are given in Sections II.C.3, II.D.1 and II.D.2 of reference [5].

As long as ρ'_1 is lower than $\sim 2/3$, ρ'_1 and ρ'_2 are the determining factors of the energy partitioning. On the other hand, when ρ'_1 is larger than $\sim 2/3$, a third factor turns out to play a role, namely, the J-dependence of the reaction probability that we shall call $R_\gamma(\boldsymbol{J})$ in the followings (see Sect. II.E of Ref. [5]).

Our goal in this work is to prove that in the framework of PST, vectorial properties are mainly determined by the same independent parameters as scalar properties, i.e. ρ'_1, ρ'_2 and the shape of $R_\gamma(\boldsymbol{J})$ (to a less extent, however). Moreover, we compare our approach with the one of Case and Herschbach.

The paper is organized as follows. We pinpoint the key factors evoked above (Sect. 2). We apply some results of the previous section to the description of angular and rotational polarization distributions (Sect. 3), and repeat the same work for Λ' (Sect. 4). We then study the dependence of these quantities on the factors pointed out in Section 2 (Sect. 5). We finally conclude (Sect. 6).

2 Evidencing the key factors

2.1 Defining the system

The collisional process of interest is

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{ABC} \rightarrow \mathrm{A} + \mathrm{BC} \text{ channel } \alpha \tag{2.1}$$

$$\rightarrow \mathrm{AC} + \mathrm{B} \text{ channel } \beta \tag{2.2}$$

$$\rightarrow \mathrm{AB} + \mathrm{C} \text{ channel } \gamma. \tag{2.3}$$

ABC is a long-lived complex due to the existence of a deep well in the strong coupling region (SCR) and α, β and γ are the three possible exit-channels leading respectively to one inelastic and two reactive collisions.

In the present work, we shall consider supersonic crossed beam experiments in which the relative collision energy E between A and BC is well controlled [1,2] and BC is mainly prepared in its rovibrational ground state. Scalar and vectorial properties are supposed to be measured in product channel γ. The energies available to reactants and products γ are E and E', respectively (amount of energy above the zero point energy). E' is related to E by the relation $E' = E - Q'$, where Q' is the exoergicity of reaction (2.3). μ is the reduced mass of A with respect to BC and μ' that of C with respect to AB. m', r'_e, ω' and n' are the reduced mass, the equilibrium distance, the vibrational frequency and the vibrational quantum number of AB. The vibrational energy of AB is $E'_n = \hbar\omega' n'$. The maximum value of the classical vibrational action is thus given by $x'_M = E'/\hbar\omega'$ and the maximum value of n' is $N' = \mathrm{Int}(x'_M)$ (Int is for "integer").

In each channel, the dynamics are supposed to be principally governed by isotropic van der Waals forces, a standard approximation. For instance, the potential energy of interaction between fragments A and BC is given by

$$V(R) = -\frac{C_6}{R^6}, \tag{2.4}$$

where C_6 is the sum of the dispersion and induction coefficient of the reagents and R is the distance between A and the center of mass of BC. Analogous expressions hold for channels β and γ, the sum of the dispersion and induction coefficients of products γ being denoted C'_6. For the sake of convenience, only the mechanical parameters involved in the future developments have been specified. A more detailed presentation of the system is given in Section II.A of reference [5].

2.2 The basic density

2.2.1 Generalities

Let $f'_T = E'_T/E'$ be the fraction of E' in the recoil motion. Let θ be the scattering angle, i.e. the angle between the reagent and product relative velocity vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$. Let χ be the product rotational polarization angle, i.e. the angle between $\boldsymbol{k}$ and the rotational angular momentum $\boldsymbol{j}'$ of AB.

We wish now to derive the PST type [6,7] expression of the density of probability $P(f'_T, n', \cos\theta, \cos\chi)$ that the products are formed with f'_T, n', $\cos\theta$ and $\cos\chi$. This density allows the calculation of any distribution or average value of physical quantities measurable by the experimentalist. $P(f'_T, n', \cos\theta, \cos\chi)$ can be derived in the framework of the following statistical assumption; in the interval between the capture and the final dissociation, the dynamical state of ABC is supposed to wander about in the region of the phase space associated with the strong

coupling region (SCR). Consequently, the final fragments are equally likely to be on any trajectory emerging from the SCR, i.e. crossing the orbiting transition state (OTS) delimiting the SCR in the direction of channels α, β and γ. Following reference [5] (see also Refs. [97, 112] therein), it can be shown that such an assumption leads to the following expression for the distribution $P(f'_T, n', \cos\theta, \cos\chi)$:

$$P(f'_T, n', \cos\theta, \cos\chi) \propto \int_0^{J_M} dJ\, J R_\gamma(\boldsymbol{J}) \frac{F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J})}{F_\gamma(\boldsymbol{J})} \quad (2.5)$$

where

$$R_\gamma(\boldsymbol{J}) = \frac{F_\gamma(\boldsymbol{J})}{F_\alpha(\boldsymbol{J}) + F_\beta(\boldsymbol{J}) + F_\gamma(\boldsymbol{J})} \quad (2.6)$$

is the probability of reaction to channel γ. $F_\alpha(\boldsymbol{J})$, $F_\beta(\boldsymbol{J})$ and $F_\gamma(\boldsymbol{J})$ are the fluxes of trajectories emerging from the SCR with a total angular momentum $\boldsymbol{J}$ and leading to channels α, β and γ respectively, and $F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J})$ is the flux of trajectories emerging from the SCR in the direction of channel γ with f'_T, n', $\cos\theta$, $\cos\chi$ and $\boldsymbol{J}$. The maximum value J_M of J consistent with the formation of products γ was specified previously (Eq. (1.2)). It involves the maximum value L_M of the orbital angular momentum consistent with complex formation, related to the collision energy E by

$$L_M = (3\mu)^{1/2}(2C_6)^{1/6}E^{1/3}, \quad (2.7)$$

and J'_M, given explicitly later (Eq. (2.39)). The maximum values of J consistent with the energy disposals E and E_β on channels α and β will be denoted J^α_M and J^β_M.

As shown in reference [5], the reaction probability $R_\gamma(\boldsymbol{J})$ has two limiting dependences on J, referred to as cases I and II in the following. In case I, $R_\gamma(\boldsymbol{J})$ is almost constant, as for instance when

$$J'_M \approx J^\alpha_M \quad \text{and} \quad J'_M \geq J^\beta_M \quad (2.8)$$

(see Fig. 14 of Ref. [5] and the related discussion). In case II, $R_\gamma(\boldsymbol{J})$ is roughly proportional to $F_\gamma(\boldsymbol{J})$ which decreases down to zero over the range $[0, J'_M]$, as for example when,

$$J'_M < \max(J^\alpha_M; J^\beta_M) \quad (2.9)$$

(see Fig. 15 of Ref. [5] and the related discussion). As a consequence, the distribution $P(f'_T, n', \cos\theta, \cos\chi)$ becomes respectively:

$$P(f'_T, n', \cos\theta, \cos\chi) \propto \int_0^{J_M} dJ\, J \frac{F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J})}{F_\gamma(\boldsymbol{J})} \quad (2.10)$$

in case I and

$$P(f'_T, n', \cos\theta, \cos\chi) \propto \int_0^{J_M} dJ\, J F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J}) \quad (2.11)$$

in case II. These two situations of constant and decreasing reaction probabilities were shown to lead to significant differences in the energy partitioning in the case where ρ'_1 is larger than $\sim 2/3$. We shall now prove that in these limiting cases, vectorial properties, like scalar ones, are mainly determined by ρ'_1 and ρ'_2.

2.2.2 The constant reaction probability case

Within the framework of (i) the rigid rotor harmonic oscillator (RRHO) approximation and (ii) a semiclassical treatment where vibrations are quantized whereas classical mechanics is used for the description of rotation and translation motions, the remaining equations necessary for the calculation of equations (2.10) and (2.11) are:

$$F_\gamma(\boldsymbol{J}) = \sum_{n'=0}^{N'} \int df'_T d\cos\theta d\cos\chi F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J}) \quad (2.12)$$

and

$$F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J}) = \int d\Gamma' k' \Theta(k') \prod_{i=1}^{7} \delta_i. \quad (2.13)$$

The various terms in the above integral are as follows; a suitable set of phase space coordinates for the description of the dynamical state of the products is the distance R' between C and the center of mass of AB, its conjugate momentum P', the distance r' between A and B, its conjugate momentum p', the modulus j' of $\boldsymbol{j}'$, the projection j'_z of $\boldsymbol{j}'$ on a fixed z-axis, the modulus L' of the orbital angular momentum of C with respect to AB, the projection L'_z of $\boldsymbol{L}'$ on the z-axis, and their conjugate angles α'_j, β'_j, α'_L and β'_L. $d\Gamma'$ is the elementary volume of the phase space given by:

$$d\Gamma' = dR' dP' dr' dp' dj' dj'_z dL' dL'_z d\alpha'_j d\beta'_j d\alpha'_L d\beta'_L. \quad (2.14)$$

As stated previously, $k' = P'/\mu'$ is the radial velocity of recoil of AB with respect to C. Θ s the function of Heaviside. The delta functions are:

$$\delta_1 = \delta(R' - R'_\infty), \quad (2.15)$$

$$\delta_2 = \delta\left(f'_T - \frac{H'_T}{E'}\right) \quad (2.16)$$

$$\delta_3 = \delta\left(n' - \frac{H'_V}{\hbar\omega'}\right), \quad (2.17)$$

$$\delta_4 = \delta(\cos\theta - f_\theta(\alpha'_L, \beta'_L, J, L', j')), \quad (2.18)$$

$$\delta_5 = \delta(\cos\chi - f_\chi(\beta'_j, J, L', j')), \quad (2.19)$$

$$\delta_6 = \delta(\boldsymbol{J} - \boldsymbol{j}' - \boldsymbol{L}') \quad (2.20)$$

and

$$\delta_7 = \delta(E' - H'). \quad (2.21)$$

The Hamiltonian functions H'_T, H'_V and H'_R for the translation, vibration and rotation motions are

$$H'_T = \frac{P'^2}{2\mu' R'^2} + \frac{L'^2}{2\mu' R'^2} + V(R'), \tag{2.22}$$

$$H'_V = \frac{p'^2_r}{2m' r'^2_e} + v(r'), \tag{2.23}$$

$$H'_R = \frac{j'^2}{2m' r'^2_e} \tag{2.24}$$

and the total Hamiltonian function H' is

$$H' = H'_T + H'_V + H'_R. \tag{2.25}$$

Moreover, it is shown in Appendix A that

$$f_\theta(\alpha'_L, \beta'_L, J, L', j') = \cos\alpha'_L \sin\beta'_L + Q_\theta \sin\alpha'_L \cos\beta'_L \tag{2.26}$$

with

$$Q_\theta = \frac{J^2 + L'^2 - j'^2}{2JL'} \tag{2.27}$$

and in Appendix B that

$$f_\chi(\beta'_j, J, L', j') = (1 - Q^2_\chi)^{1/2} \cos\beta'_j \tag{2.28}$$

with

$$Q_\chi = \frac{J^2 + j'^2 - L'^2}{2Jj'}. \tag{2.29}$$

In equation (2.13), the first delta function defines the location of a product hypersurface through which the flux is calculated, the second one implies that the fraction of translational energy is f'_T, the third one causes the vibrational action to have the integer value n', the fourth and fifth ones ensure that the cosine of the scattering and rotational polarization angles are equal to $\cos\theta$ and $\cos\chi$ respectively, the sixth one ensures conservation of $\boldsymbol{J}$ and the last one ensures conservation of the total energy. Proceeding as in Appendix B of reference [8], using in particular the following theorem

$$\delta(f(x)) = \sum_{i=1}^{n} \frac{1}{|f'(x_i)|} \delta(x - x_i) \tag{2.30}$$

(with $f(x_i) = 0$ and $f'(x_i) \neq 0$, n being the number of simple roots), it is found after some algebraic steps, that equation (2.13) reduces to

$$F_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{J}) \propto D^{-1} \int dL' d\alpha'_L d\beta'_L \delta_4 \delta_5 \tag{2.31}$$

with

$$D = J\left(1 - \frac{n'}{x'_M} - f'_T\right)^{1/2}. \tag{2.32}$$

δ_4 is still given by equations (2.18), (2.26) and (2.27), while δ_5 is now given by:

$$\delta_5 = \delta(\cos\chi + (1 - Q^2_\chi)^{1/2} \cos\beta'_L). \tag{2.33}$$

The maximum value of L' and the value of j' consistent with f'_T and n' are given by [5,8]

$$L'_M(f'_T) = L'^0_M f'^{1/3}_T \tag{2.34}$$

and

$$j' = j'^0_M \left(1 - \frac{n'}{x'_M} - f'_T\right)^{1/2} \tag{2.35}$$

with

$$L'^0_M = (3\mu')^{1/2} (2C'_6)^{1/6} E'^{1/3} \tag{2.36}$$

and

$$j'^0_M = \left(2m' r'^2_e E'\right)^{1/2}. \tag{2.37}$$

In addition to that, L' in equation (2.31) must satisfy the triangular inequality

$$|J - j'| \leq L' \leq \min(J + j'; L'_M(f'_T)). \tag{2.38}$$

A quite good approximation of J'_M being [5]

$$J'^a_M = \left((j'^0_M)^2 + (L'^0_M)^2\right)^{1/2}, \tag{2.39}$$

the angular excitation ρ'_1 (Eqs. (1.1) and (1.2)) is given by

$$\rho'_1 \approx \frac{J_M}{J'^a_M}. \tag{2.40}$$

Moreover, the diatomic inertial contribution ρ'_2 (Eq. (1.3); see also Eq. (II.C.27) in Ref. [5]) is given by

$$\rho'_2 = \frac{(j'^0_M)^2}{(J'^a_M)^2}. \tag{2.41}$$

Setting

$$u = \frac{J}{J'^a_M}, \tag{2.42}$$

$$v = \frac{L'}{L'^0_M} \tag{2.43}$$

and

$$w = \frac{j'}{j'^0_M} = \left(1 - \frac{n'}{x'_M} - f'_T\right)^{1/2} \tag{2.44}$$

and substituting them to J, L' and j' in equations (2.10), (2.12) and (2.31), we arrive at

$$P(f'_T, n', \cos\theta, \cos\chi) \propto \int_0^{\rho'_1} duu \frac{G_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{u})}{G_\gamma(\boldsymbol{u})} \tag{2.45}$$

where

$$G_\gamma(\boldsymbol{J}) = \sum_{n'=0}^{N'} \int df'_T d\cos\theta d\cos\chi G_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{u}) \tag{2.46}$$

$$G_\gamma(f'_T, n', \cos\theta, \cos\chi|\boldsymbol{u}) \propto D^{-1} \int dv d\alpha'_L d\beta'_L \delta_4 \delta_5 \tag{2.47}$$

and the two quantities Q_θ and Q_χ present in δ_4 (Eqs. (2.18) and (2.26)) and δ_5 (Eq. (2.33)) read

$$Q_\theta = \frac{u^2 + (1-\rho_2')v^2 - \rho_2' w^2}{2uv(1-\rho_2')^{1/2}} \tag{2.48}$$

and

$$Q_\chi = \frac{u^2 - (1-\rho_2')v^2 + \rho_2' w^2}{2uw\rho_2'^{1/2}}. \tag{2.49}$$

In addition to that, the triangular inequality (Eq. (2.38)) transforms to

$$v_{min} \leq v \leq v_{max} \tag{2.50}$$

with

$$v_{min} = \left| \frac{u}{(1-\rho_2')^{1/2}} - \left(\frac{\rho_2'}{(1-\rho_2')} \right)^{1/2} w \right| \tag{2.51}$$

and

$$v_{max} = \min \left(\frac{u}{(1-\rho_2')^{1/2}} + \left(\frac{\rho_2'}{(1-\rho_2')} \right)^{1/2} w ; f_T'^{1/3} \right). \tag{2.52}$$

After a careful inspection inspection of equations (2.44–2.52), we arrive at the following key conclusion: in the present case where the reaction probability is a constant, the only independent parameters appearing in $P(f_T', n', \cos\theta, \cos\chi)$ are the angular excitation ρ_1', the diatomic inertial contribution ρ_2' and the maximum value x_M' of the vibrational action (we recall that N' in Eq. (2.46) is the integer part of x_M'). Therefore, they fully determine both the scalar and vectorial properties of the chemical reaction. As far as angular correlations are concerned, we shall see in the following that x_M' does not play a significant role.

2.2.3 The decreasing reaction probability case

From equation (2.11), $P(f_T', n', \cos\theta, \cos\chi)$ is now given by

$$P(f_T', n', \cos\theta, \cos\chi) \propto \int_0^{\rho_1'} du\, u G_\gamma(f_T', n', \cos\theta, \cos\chi | \boldsymbol{u}). \tag{2.53}$$

Therefore, we arrive at the same conclusion as previously, for exactly the same reasons.

3 Description of vectorial properties

3.1 On the calculation of $\langle \cos^2\theta \rangle$

The average value of $\cos^2\theta$ is given by

$$\langle \cos^2\theta \rangle = \int_{-1}^{1} d\cos\theta P(\cos\theta) \cos^2\theta \tag{3.1}$$

where $P(\cos\theta)$ is the distribution of $\cos\theta$. Following Section 2, we have

$$P(\cos\theta) \propto \int_0^{J_M} dJ J \frac{F_\gamma(\cos\theta|\boldsymbol{J})}{F_\gamma(\boldsymbol{J})} \tag{3.2}$$

in case I and

$$P(\cos\theta) \propto \int_0^{J_M} dJ J F_\gamma(\cos\theta|\boldsymbol{J}) \tag{3.3}$$

in case II. $F_\gamma(\cos\theta|\boldsymbol{J})$ is the flux of trajectories emerging from the SCR in the direction of channel γ with $\cos\theta$ and $\boldsymbol{J}$, quantity given by

$$F_\gamma(\cos\theta|\boldsymbol{J}) = \sum_{n'=0}^{N'} \int d\Gamma' k' \Theta(k') \delta_1 \delta_3 \delta_4 \delta_6 \delta_7. \tag{3.4}$$

After some algebraic steps, we arrive at

$$F_\gamma(\cos\theta|\boldsymbol{J}) \propto J^{-1} \sum_{n'=0}^{N'} \int dL' dj' d\alpha_L' d\beta_L' \delta_4 \tag{3.5}$$

where the angular momenta must satisfy equation (2.38). Moreover,

$$\begin{aligned} F_\gamma(\boldsymbol{J}) &= \int_{-1}^{1} d\cos\theta F_\gamma(\cos\theta|\boldsymbol{J}) \\ &\propto J^{-1} \sum_{n'=0}^{N'} \int dL' dj' d\alpha_L' d\beta_L'. \end{aligned} \tag{3.6}$$

Using the same change of variables as in Section 2 (Eqs. (2.42–2.44)) leads to

$$P(\cos\theta) \propto \int_0^{\rho_1'} du\, u \frac{G_\gamma(\cos\theta|\boldsymbol{u})}{G_\gamma(\boldsymbol{u})} \tag{3.7}$$

in case I and

$$P(\cos\theta) \propto \int_0^{\rho_1'} du\, u G_\gamma(\cos\theta|\boldsymbol{u}) \tag{3.8}$$

in case II with

$$G_\gamma(\cos\theta|\boldsymbol{u}) \propto u^{-1} \sum_{n'=0}^{N'} \int dv\, dw\, d\alpha_L' d\beta_L' \delta_4 \tag{3.9}$$

and

$$\begin{aligned} G_\gamma(\boldsymbol{u}) &= \int_{-1}^{1} d\cos\theta G_\gamma(\cos\theta|\boldsymbol{u}) \\ &\propto u^{-1} \sum_{n'=0}^{N'} \int dv dw d\alpha_L' d\beta_L'. \end{aligned} \tag{3.10}$$

The triangular inequality is given by equations (2.50–2.52) with

$$f_T' = 1 - \frac{n'}{x_M'} - w^2. \tag{3.11}$$

As far as the numerical calculation of $\langle \cos^2\theta \rangle$ is concerned, the Dirac distribution δ_4 is conveniently replaced by any approximate function (Gaussian, Lorentzian, etc.).

3.2 On the calculation of $\langle \cos^2 \chi \rangle$

The mathematical developments are exactly the same as in the previous section with $\cos\theta$ and δ_4 replaced by $\cos\chi$ and δ_5 respectively.

4 Description of the parameter Λ'

Λ' is the average value of

$$\Omega' = \frac{L'}{L' + j'}. \tag{4.1}$$

It is thus given by

$$\Lambda' = \int_0^1 d\Omega' P(\Omega') \Omega' \tag{4.2}$$

where $P(\Omega')$ is the normalized distribution of Ω'. $F_\gamma(\Omega'|\boldsymbol{J})$ being the flux of trajectories emerging from the SCR in the direction of channel γ with Ω' and $\boldsymbol{J}$, we have

$$P(\Omega') \propto \int_0^{J_M} dJ\, J \frac{F_\gamma(\Omega'|\boldsymbol{J})}{F_\gamma(\boldsymbol{J})} \tag{4.3}$$

in case I and

$$P(\Omega') \propto \int_0^{J_M} dJ J F_\gamma(\Omega'|\boldsymbol{J}) \tag{4.4}$$

in case II. $F_\gamma(\Omega'|\boldsymbol{J})$ is given by

$$F_\gamma(\Omega'|\boldsymbol{J}) = \sum_{n'=0}^{N'} \int d\Gamma' k' \Theta(k') \delta_1 \delta_3 \delta_6 \delta_7 \delta_8 \tag{4.5}$$

with

$$\delta_8 = \delta\left(\Omega' - \frac{L'}{L' + j'}\right). \tag{4.6}$$

After some steps of algebra, it is found that

$$F_\gamma(\Omega'|\boldsymbol{J}) \propto J^{-1} \sum_{n'=0}^{N'} \int dj' \frac{j'}{(1-\Omega')^2}. \tag{4.7}$$

Moreover,

$$F_\gamma(\boldsymbol{J}) = \int_0^1 d\Omega' F_\gamma(\Omega'|\boldsymbol{J}) \propto J^{-1} \sum_{n'=0}^{N'} \int dj' dL'. \tag{4.8}$$

j' must satisfy the triangular inequality (2.38) which becomes in the present case

$$|J - j'| \leq \frac{\Omega'}{1-\Omega'} j' \leq \min(J + j'; L'_M(j', n')) \tag{4.9}$$

with

$$L'_M(j', n') = L'^0_M \left(1 - \frac{n'}{x'_M} - \left(\frac{j'}{j'^0_M}\right)^2\right)^{1/3}. \tag{4.10}$$

Using the same change of variables as in Section 2 (Eqs. (2.42–2.44)) leads to

$$P(\Omega') \propto \int_0^{\rho'_1} du\, u \frac{G_\gamma(\Omega'|\boldsymbol{u})}{G_\gamma(\boldsymbol{u})} \tag{4.11}$$

in case I and

$$P(\Omega') \propto \int_0^{\rho'_1} du\, u G_\gamma(\Omega'|\boldsymbol{u}) \tag{4.12}$$

in case II with

$$G_\gamma(\Omega'|\boldsymbol{u}) \propto u^{-1} \sum_{n'=0}^{N'} dw\, d\alpha'_L d\beta'_L \frac{w}{(1-\Omega')^2} \tag{4.13}$$

and

$$G_\gamma(\boldsymbol{u}) = \int_0^1 d\Omega' G_\gamma(\Omega'|\boldsymbol{u}) \propto u^{-1} \sum_{n'=0}^{N'} \int dv dw. \tag{4.14}$$

The triangular inequality is given by equations (2.50–2.52) with

$$v = \frac{\Omega'}{1-\Omega'} \left(\frac{\rho'_2}{1-\rho'_2}\right)^{1/2} w \tag{4.15}$$

and

$$f'_T = 1 - \frac{n'}{x'_M} - w^2 \tag{4.16}$$

(Eq. (4.15) is deduced from Eqs. (2.39), (2.41), (2.43), (2.44) and (4.1)).

From equations (4.11–4.16) and (2.50–2.52), we arrive at the same conclusion as previously: in the limiting cases I and II, the only independent parameters appearing in $P(\Omega')$ are the angular excitation ρ'_1, the diatomic inertial contribution ρ'_2 and the maximum value x'_M of the vibrational action.

5 Results and discussion

$\langle \cos^2\theta \rangle$ is represented in terms of ρ'_1 and ρ'_2 in Figures 1 and 2. Figure 1 corresponds to case I and $N' = 0$ and Figure 2 to case II and $N' = 0$. The same average quantity has also been calculated for both cases I and II but for $N' = 5$ instead of 0. Since there is no significant difference with the situation $N' = 0$, these graphs are not shown. From these calculations, both the number $N' = \mathrm{Int}(x'_M)$ of available vibrational states and the shape of $R_\gamma(\boldsymbol{J})$ have a weak influence on $\langle \cos^2\theta \rangle$ (except for ρ'_1 approaching 1). For small values of the angular excitation ρ'_1, $\langle \cos^2\theta \rangle$ is close to 1/3. The reason is as follows: when J is zero, which corresponds to $\rho'_1 = 0$, $\boldsymbol{L}'$ and $\boldsymbol{j}'$ have same modulus and opposite direction. This direction is however random. As is well-known, the angular distribution $P(\theta)$ in the whole space is then proportional to $\sin\theta$ (whereas the analogous distribution in the collision plane is a constant) [3,4,9]. Given that $P(\cos\theta) d\cos\theta = P(\theta) d\theta$, it is a simple matter to show from equation (3.1) that $\langle \cos^2\theta \rangle = 1/3$. For

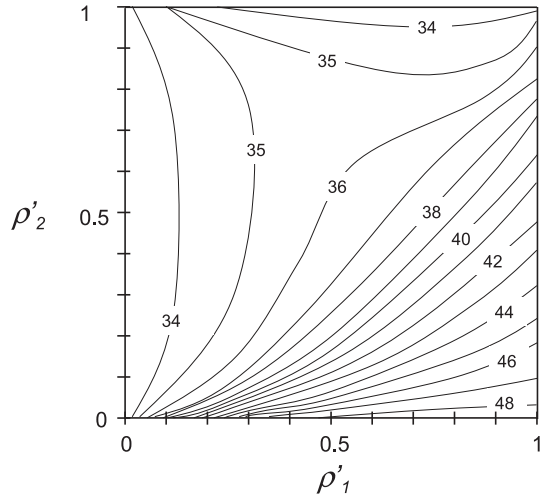

Fig. 1. $\langle\cos^2\theta\rangle$ in terms of ρ'_1 and ρ'_2 in case I and $N'= 0$. Contour numbers correspond to a percentage. They must be divided by 100 to represent a cosine value (idem for the next five figures).

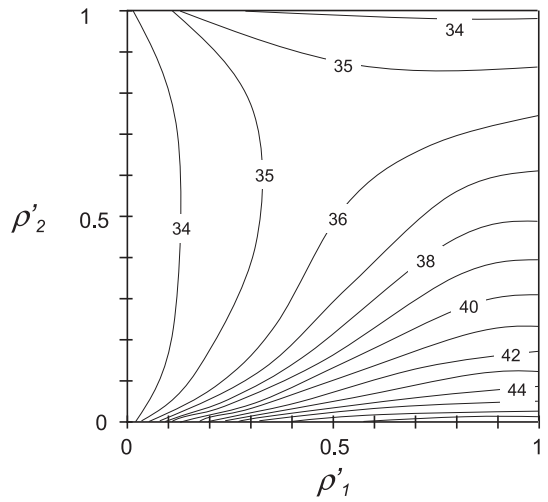

Fig. 2. $\langle\cos^2\theta\rangle$ in terms of ρ'_1 and ρ'_2 in case II and $N' = 0$.

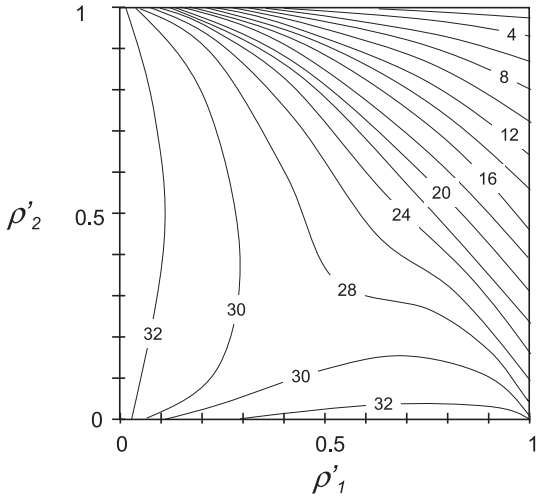

Fig. 3. $\langle\cos^2\chi\rangle$ in terms of ρ'_1 and ρ'_2 in case I and $N'= 0$.

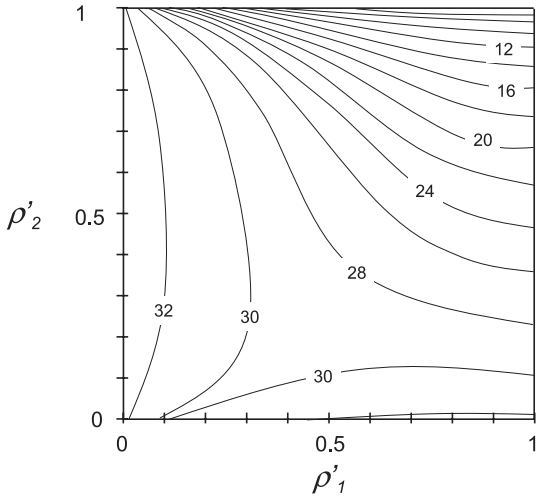

Fig. 4. $\langle\cos^2\chi\rangle$ in terms of ρ'_1 and ρ'_2 in case II and $N'= 0$.

values of the inertial contribution ρ'_2 very close to 1, $\boldsymbol{j}'$ is almost equal to $\boldsymbol{J}$. $\boldsymbol{L}'$ has a very small modulus and its orientation is random. For the same reason as previously, $\langle\cos^2\theta\rangle$ is close to 1/3. On the other hand, for values of ρ'_2 very close to 0, $\langle\cos^2\theta\rangle$ is close to 1/2. This is because $\boldsymbol{L}'$ is almost equal to $\boldsymbol{J}$. The angular distribution $P(\theta)$ in the whole space is then a constant (whereas the analogous distribution in the collision plane is proportional to $1/\sin\theta$) [3,4,9]. The value of 1/2 of $\langle\cos^2\theta\rangle$ is then recovered from equation (3.1).

$\langle\cos^2\chi\rangle$ is represented in terms of ρ'_1 and ρ'_2 in Figures 3 and 4. Figure 3 corresponds to case I and $N' = 0$ and Figure 4 to case II and $N' = 0$. For the same reason as previously, we do not display the graphs for cases I and II with $N' = 5$ and we conclude that both the number $N' = \mathrm{Int}(x'_M)$ of available vibrational states and the shape of $R_\gamma(\boldsymbol{J})$ have a weak influence on $\langle\cos^2\chi\rangle$ (except again, for ρ'_1 approaching 1). For small values of ρ'_1 and ρ'_2, $\langle\cos^2\chi\rangle$ is close to 1/3; since $\boldsymbol{j}'$ has a very small modulus and a random orientation, the polarization angle distribution $P(\chi)$ in the whole space is proportional to $\sin\chi$ [3, 4,9]. Following the same reasoning as for the angle θ, the value of 1/3 of $\langle\cos^2\chi\rangle$ is justified. For values of ρ'_2 very close to 1, $\boldsymbol{j}'$ is almost equal to $\boldsymbol{J}$. It is thus orthogonal to $\boldsymbol{k}$ so that $\langle\cos^2\chi\rangle$ is negligible [3,4,9].

Λ' is represented in terms of ρ'_1 and ρ'_2 in Figures 5 and 6. Figure 5 corresponds to case I and $N' = 0$ and Figure 6 to case II and $N' = 0$. Similar representations are obtained for both cases I and II and $N'= 5$ (not shown). There are only tiny differences between these two figures.

Last but not least, $\langle\cos^2\theta\rangle$ is also represented in terms of Λ' in Figures 7 and 8 for randomly chosen values of ρ'_1 and ρ'_2. Figure 7 corresponds to case I and Figure 8 to case II. As a matter of fact, several values of $\langle\cos^2\theta\rangle$ are consistent with a given value of Λ', i.e., $\langle\cos^2\theta\rangle$ is not a function of the single parameter Λ', in contrast with the conclusion of Case and Herschbach. However, the curve corresponding to the Case and Herschbach rule remains relatively close to our predictions.

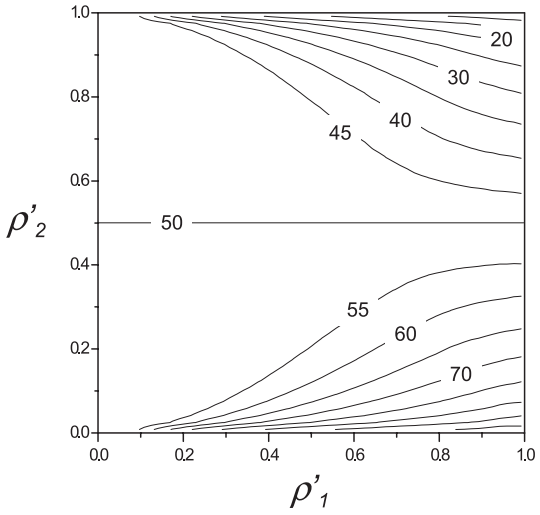

Fig. 5. Λ' in terms of ρ'_1 and ρ'_2 in case I and $N'= 0$.

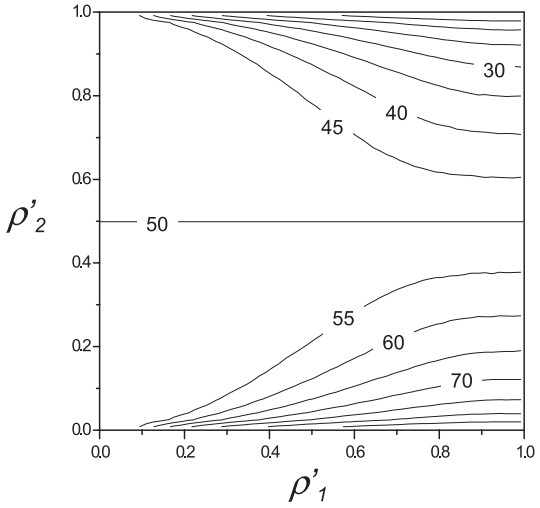

Fig. 6. Λ' in terms of ρ'_1 and ρ'_2 in case II and $N'= 0$.

6 Conclusion

We have shown that vectorial properties of triatomic bimolecular reactions governed by long-range forces are mainly controled by two factors ρ'_1 and ρ'_2 respectively called angular excitation and diatomic inertial contribution. These factors are related to the mechanical parameters of the system (atomic masses, collision energy, dispersion coefficients, etc.) by very simple formulas. In the case of strong angular excitation, however, a third quantity appears to play a role, i.e., the total angular momentum dependence of the reaction probability. In the limiting cases where this probability is a constant (case I) or decreases (case II), $\langle\cos^2\theta\rangle$ and $\langle\cos^2\chi\rangle$ where θ and χ are the scattering and rotational polarization angles respectively, can be straightforwardly estimated in terms of ρ'_1 and ρ'_2 with the help of Figures 1–4.

This work is to be compared with the one of Case and Herschbach which argued in the mid-seventies that vectorial properties are determined by the parameter $\Lambda' = \langle L'/(L'+j')\rangle$, L' and j' being respectively the moduli of the orbital and rotational angular momenta of the products. A simple mathematical relation between $\langle\cos^2\theta\rangle$ and $\langle\cos^2\chi\rangle$ and Λ' was then proposed. However, Λ' must be determined beforehand by phase space theory (PST) calculations, contrary to ρ'_1 and ρ'_2 . In addition to that, ρ'_1 and ρ'_2 appear to be somewhat independent so that vectorial properties cannot be said to strictly depend on Λ'. However, Figures 7 and 8 demonstrate that the rule proposed by Case and Herschbach is reasonable in many situations.

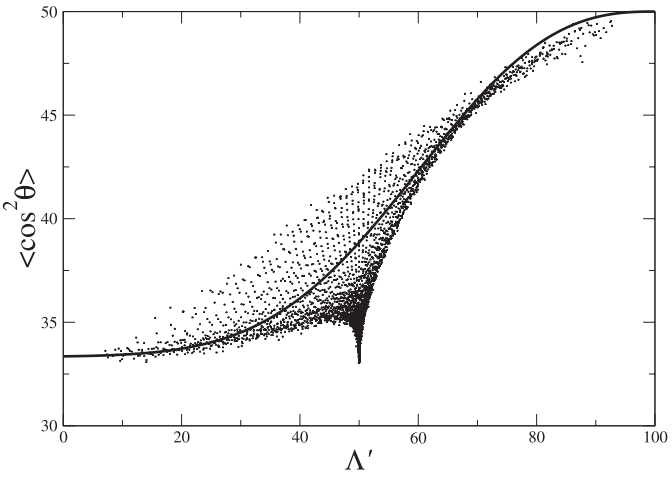

Fig. 7. $\langle\cos^2\theta\rangle$ in terms of Λ' for a uniform distribution of ρ'_1 and ρ'_2 in the "unit square". The figure corresponds to case I and $N' = 0$. The values of Λ' and $\langle\cos^2\theta\rangle$ must be divided by 100, since they are expressed in this figure as a percentage.

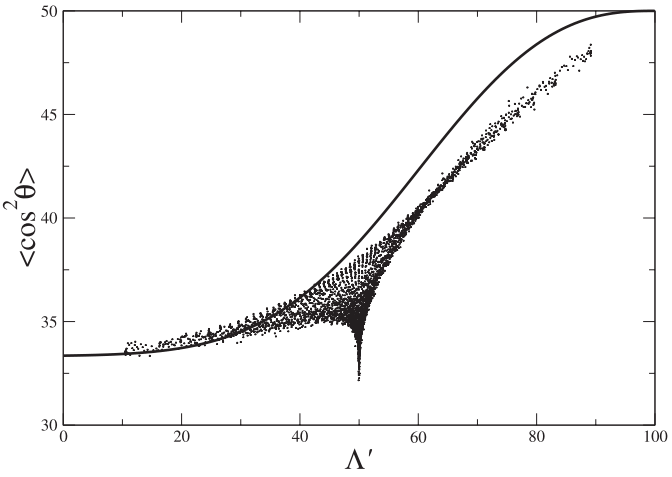

Fig. 8. $\langle\cos^2\theta\rangle$ in terms of Λ' for a uniform distribution of ρ'_1 and ρ'_2 in the "unit square". The figure corresponds to case II and $N'= 0$. Same comment as in Figure 7.

We are grateful to Dr P. Larrégaray for stimulating discussions on angular correlations.

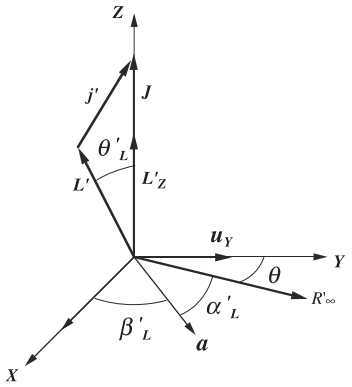

Fig. 9. Some relevant vectors and angles of the problem.

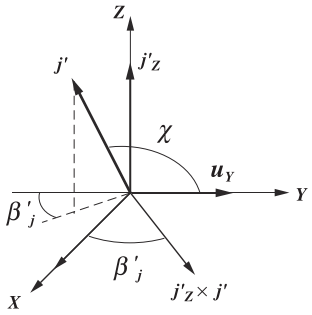

Fig. 10. As in Figure 9.

Appendix A

Consider the following vectors represented in Figure 9:

$$\boldsymbol{a} = \frac{\boldsymbol{L}'_Z \times \boldsymbol{L}'}{L'_Z L' \sin\theta'_L}, \tag{A.1}$$

$$\boldsymbol{b} = \boldsymbol{u}_y, \tag{A.2}$$

$$\boldsymbol{c} = \boldsymbol{a} \tag{A.3}$$

and

$$\boldsymbol{d} = \boldsymbol{R}'_\infty. \tag{A.4}$$

$\boldsymbol{u}_y$ is the unit vector along the Y-axis. The reagent velocity vector $\boldsymbol{k}$ is supposed to be parallel to $\boldsymbol{u}_y$ and the total angular momentum is supposed to be along the Z-axis. Since $\boldsymbol{k}'$ is parallel to $\boldsymbol{R}'$ for large values of its modulus, θ is the angle between $\boldsymbol{d}$ and $\boldsymbol{u}_y$. Using the standard identity

$$(\boldsymbol{a}\times\boldsymbol{b})\cdot(\boldsymbol{c}\times\boldsymbol{d}) = (\boldsymbol{a}\cdot\boldsymbol{c})(\boldsymbol{b}\cdot\boldsymbol{d}) - (\boldsymbol{a}\cdot\boldsymbol{d})(\boldsymbol{b}\cdot\boldsymbol{c}), \tag{A.5}$$

we arrive at

$$\cos\theta = \cos\alpha'_L \sin\beta'_L + \sin\alpha'_L \cos\beta'_L \cos\theta'_L \tag{A.6}$$

with

$$\cos\theta'_L = \frac{L'_Z}{L'}. \tag{A.7}$$

Squaring the equation

$$\boldsymbol{j}' = \boldsymbol{J} - \boldsymbol{L}', \tag{A.8}$$

and given that

$$\boldsymbol{J}\cdot\boldsymbol{L}' = JL'_Z, \tag{A.9}$$

we finally arrive at

$$\cos\theta = \cos\alpha'_L \sin\beta'_L + \sin\alpha'_L \cos\beta'_L \frac{J^2 + L'^2 - j'^2}{2JL'}. \tag{A.10}$$

Appendix B

From Figure 10, the projection of $\boldsymbol{j}'$ on the Y-axis is given by

$$\boldsymbol{j}'\cdot\boldsymbol{u}_y = \cos\chi j'. \tag{B.1}$$

Moreover,

$$\boldsymbol{j}'\cdot\boldsymbol{u}_y = \cos\beta'_j (j'^2 - j'^2_Z)^{1/2}. \tag{B.2}$$

Therefore,

$$\cos\chi = \cos\beta'_j \left(1 - j'^2_Z/j'^2\right)^{1/2}. \tag{B.3}$$

Squaring the equation

$$\boldsymbol{L}' = \boldsymbol{J} - \boldsymbol{j}', \tag{B.4}$$

and given that

$$\boldsymbol{J}\cdot\boldsymbol{j}' = Jj'_Z, \tag{B.5}$$

we finally arrive at

$$\cos\chi = \cos\beta'_j \left(1 - \left(\frac{J^2 + j'^2 - L'^2}{2Jj'}\right)^2\right)^{1/2}. \tag{B.6}$$

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