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Polarization of molecular angular momentum in the chemical reactions $\text{Li} + \text{HF}$ and $\text{F} + \text{HD}$

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The quantum mechanical approach to vector correlation of angular momentum orientation and alignment in chemical reactions [G. Balint-Kurti and O. S. Vasyutinskii, *J. Phys. Chem. A* **113**, 14281 (2009)] is applied to the molecular reagents and products of the $\text{Li} + \text{HF}$ [L. Gonzalez-Sanchez, O. S. Vasyutinskii, A. Zanchet, C. Sanz-Sanz, and O. Roncero, *Phys. Chem. Chem. Phys.* **13**, 13656 (2011)] and $\text{F} + \text{HD}$ [D. De Fazio, J. Lucas, V. Aquilanti, and S. Cavalli, *Phys. Chem. Chem. Phys.* **13**, 8571 (2011)] reactions for which accurate scattering information has become recently available through time-dependent and time-independent approaches. Application of the theory to two important particular cases of the reactive collisions has been considered: (i) the influence of the angular momentum polarization of reactants in the entrance channel on the spatial distribution of the products in the exit channel and (ii) angular momentum polarization of the products of the reaction between unpolarized reactants. In the former case, the role of the angular momentum alignment of the reactants is shown to be large, particularly when the angular momentum is perpendicular to the reaction scattering plane. In the latter case, the orientation and alignment of the product angular momentum was found to be significant and strongly dependent on the scattering angle. The calculation also reveals significant differences between the vector correlation properties of the two reactions under study which are due to difference in the reaction mechanisms. In the case of $\text{F} + \text{HD}$ reaction, the branching ratio between HF and DF production points out interest in the insight gained into the detailed dynamics, when information is available either from exact quantum mechanical calculations or from especially designed experiments. Also, the geometrical arrangement for the experimental determination of the product angular momentum orientation and alignment based on a compact and convenient spherical tensor expression for the intensity of the resonance enhanced multiphoton ionization (REMPI $2 + 1$) signal is suggested. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4809992>]

I. INTRODUCTION

Vector correlations in chemical reactions have attracted much attention for decades. Their study provides rich information on the reaction dynamics, which usually cannot be obtained by other methods. In molecular collision dynamics, the intrinsically anisotropic interactions within a collision complex manifest themselves as vector properties such as electronic, or rotational anisotropy in the reaction products, including the polarization of electronic and rotational angular momenta.

The design of experiments where the reactant angular momentum polarization is monitored can give new insight into both the entrance and exit channels of the reaction, providing a way to control the reactivity.¹ Over the years, several methods have been suggested, which allow for the production of anisotropic spatial distributions of the angular momenta of reactant species. As known, polar molecules in a molec-

ular beam can be oriented/aligned by using inhomogeneous electric fields, see Refs. 2–6 and references therein. Also, the absorption of resonant polarized laser radiation provides an efficient method to control the approaching geometry of the reactant molecules in electronically excited states.^{7,8} More, molecules can be aligned by anisotropic collisions in gaseous expansions.^{9–12} Also, the method of alignment and trapping of molecules by off-resonant intense laser field¹³ was found to be very effective in many applications.

Several theoretical approaches have been proposed and used in recent years to study the vector properties in inelastic scattering and molecular dynamics.^{14–28} In the present paper, we apply the full quantum mechanical approach suggested by Balint-Kurti and Vasyutinskii²⁷ to study the angular momentum orientation and alignment of reactants and products in $\text{Li} + \text{HF}$ and $\text{F} + \text{HD}$ chemical reactions. As the treatment^{23,25} mentioned above our approach is based on the spherical tensor formalism, however, the results obtained are presented in somehow different form which provides new insight into the reaction dynamics. The product state

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multipoles are expressed in terms of the anisotropy transforming coefficients $c_{K_i q_k}^K(K_r, L)$, which can be either calculated using quantum mechanical theory, or determined experimentally. The paper presents two alternative forms of the general expressions for the product state multipoles: (i) the angular momenta of both reaction reagents and reaction products are quantized on the direction of the outgoing wave vector $\mathbf{k}$ and (ii) the angular momenta are quantized on laboratory reference frame axis Z . In particular, axis Z can be parallel to the incoming reagent vector $\mathbf{k}_r$.

For the $\text{Li} + \text{HF}$ and $\text{F} + \text{HD}$ chemical reactions, benchmark quantum scattering calculations on highly accurate potential energy surfaces are now available. These reactions have already been under focus of the analysis based on the stereodirected representation of the scattering matrix.^{29–36} The present analysis provides insight into the details of the collision event leading to the reactive encounters with reference to the mutual orientation of approaching reactants. The analysis based on the stereodirected representation^{29–34} provides a complementary view to that presented in this paper.

The aim of this paper is to show two different examples of important chemical reactions examined within the same theoretical treatment. More specifically, we use the scattering matrices to calculate the anisotropy transforming coefficients. Little information at the level of exact quantum mechanics of chemical reactions involving three distinct atoms is available, the processes considered here being unique, as far as we know. They exhibit quite different features: the $\text{Li} + \text{HF}$ reaction is nearly thermo-neutral, with a bent late barrier preceded by a deep well which gives raise to many resonances. On the contrary, the $\text{F} + \text{HD}$ reaction is highly exothermic presenting the prevalence of a direct mechanism. Moreover, the $\text{F} + \text{HD}$ reaction offers an opportunity to study the isotope effect in the $\text{HF} + \text{D}$ or $\text{DF} + \text{H}$ product channels using exact quantum dynamical calculations.

Analysis based on simple symmetry arguments of the product angular momentum orientation and alignment is also presented. As shown, in the case of isotropic distribution of the reactant angular momentum, the product angular momentum can be orientated only along the direction perpendicular to the reaction scattering plane, in agreement with Refs. 25 and 26. The obtained results can be used by the experimentalists for extracting dynamical information from vector correlation scattering experiment. We also describe the experimental geometries which can be used for detection of the product angular momenta orientation and alignment using REMPI $2 + 1$ technique.

The paper is organized as follows. Section II contains general information on the state multipole approach which describes angular momentum polarization in chemical reactions based on the theory of Balint-Kurti and Vasyutinskii.²⁷ In Subsection II A, the anisotropy transforming coefficients $c_{K_i q_k}^K(K_r, L)$ are described and compared with coefficients used by other authors. In Subsections II B and II C, two important particular cases of the general expression are discussed: differential cross section of bimolecular chemical reaction and reaction between unpolarized particles. Sections III and IV contain the results of our calculations and the analysis of the results obtained for the $\text{Li} + \text{HF}$ and

$\text{F} + \text{HD}$ chemical reactions. A brief discussion of the experimental geometries which can be used for determination of the product angular momentum polarization from experiment using REMPI $2 + 1$ technique is given in the appendix.

II. GENERAL THEORY

A. State multipole formalism

We consider a bimolecular chemical reaction between the molecule BC , and the atom A ,

where v_r, j_r and v, j are the vibrational and rotational quantum numbers for reactants and products, respectively. In the present application, both the molecule BC and the molecule AB can possess angular momenta, while the atoms A and C are considered as spin-less particles. The reference frames used throughout the paper are shown in Fig. 1. In molecular collision applications, it is useful to transform from the laboratory frame denoted by the uppercase letters X, Y, Z to the reactant and product reference frames denoted by the lowercase letters x, y, z and x', y', z' , respectively where the calculations are often simpler. In the reactant frame, the quantization axis z lies along the reactant wave vector $\mathbf{k}_r$, while in the product frame, the z' axis is parallel to the recoil wave vector $\mathbf{k}$. The orientation of the frames x, y, z and x', y', z' with respect to the laboratory frame X, Y, Z , is specified by the Euler angles $\varphi, \vartheta, \gamma$ and ϕ, θ, ξ , respectively. The angles ϕ_k, ϑ_k define the direction of the wave vector $\mathbf{k}_r$ in the product frame.

It is convenient to describe the angular momentum polarization of the molecules in the reaction (1) in terms of the spherical tensors (state multipoles) $\rho_{Kq}^{(j)}$ which are the irreducible *covariant* components of the molecular density matrix defined as³⁷

$$\rho_{Kq}^{(j)} = \sum_{m, m'} (-1)^{j-m'} C_{jm \ j-m'}^{Kq} \rho_{jm' \ jm}, \quad (2)$$

where $C_{jm \ j-m'}^{Kq}$ are Clebsch-Gordan coefficients.^{38,39}

FIG. 1. Reference frames used.

The indices K and q are the multipole rank and its component on the quantization axis, respectively. The multipole rank K in Eq. (2) ranges from 0 to $2j$ and the component q ranges from $-K$ to K . The state multipoles $\rho_{Kq}^{(j)}$ with different ranks K have clear physical meaning.⁴⁰ For instance, the zeroth-rank state multipole where $K = 0$ and $q = 0$ is proportional to the trace of the density matrix $\rho_{jm'jm}$, or alternatively, to the total population of all m -sublevels of the quantum state with angular momentum j and can be chosen as²⁷

$$\rho_{00}^{(j)} = \frac{1}{(2j+1)^{1/2}\sigma_0} \frac{d\sigma_{v_r, j_r \rightarrow v, j}}{d\Omega}, \quad (3)$$

where σ_0 is the total reaction cross section calculated for the case of unpolarized reagents and $\frac{d\sigma_{v_r, j_r \rightarrow v, j}}{d\Omega}$ is the conventional differential reaction cross section.

All odd-rank state multipoles $K = 1, 3, \dots$ characterize angular momentum *orientation*. In particular, three components of the first-rank state multipole $\rho_{1q}^{(j)}$ are proportional to the mean values of the angular momentum spherical components^{27,37,40}

$$\rho_{10}^{(j)} = \frac{\sqrt{3}}{\sqrt{j(j+1)(2j+1)}} \langle j_z \rangle, \quad (4)$$

$$\rho_{1\pm 1}^{(j)} = \mp \frac{\sqrt{3}}{\sqrt{2j(j+1)(2j+1)}} \langle j_x \pm ij_y \rangle. \quad (5)$$

All even rank state multipoles $K = 2, 4, \dots$ characterize angular momentum *alignment*. In particular, five components of the second-rank state multipole $\rho_{2q}^{(j)}$ are proportional to the mean values of the angular momentum quadrupole components and can be written as⁴⁰

$$\rho_{20}^{(j)} = \frac{C_1}{\sqrt{6}} \langle 3j_z^2 - \mathbf{j}^2 \rangle, \quad (6)$$

$$\rho_{2\pm 1}^{(j)} = \mp \frac{C_1}{2} \langle (j_x j_z + j_z j_x) \pm i(j_y j_z + j_z j_y) \rangle, \quad (7)$$

$$\rho_{2\pm 2}^{(j)} = \frac{C_1}{2} \langle (j_x^2 - j_y^2) \pm i(j_x j_y + j_y j_x) \rangle, \quad (8)$$

where $C_1 = \sqrt{30}/\sqrt{j(j+1)(2j+1)(2j-1)(2j+3)}$.

In general, some of the state multipoles in Eqs. (2)–(8) are complex. In order to define real quantities which are directly proportional to the mean values of Cartesian components of the angular momentum $\mathbf{j}$, the complex multipole moments in Eq. (2) can be combined with each other. Following Hertel and Stoll⁴¹ (see also Ref. 24), we will use the renormalized real state multipoles in the form

$$\rho_{Kq}^+ = \frac{1}{\sqrt{2}\rho_{00}^{(j)}} [(-1)^q \rho_{Kq}^{(j)} + \rho_{K-q}^{(j)}], \quad (9)$$

$$\rho_{Kq}^- = -\frac{i}{\sqrt{2}\rho_{00}^{(j)}} [(-1)^q \rho_{Kq}^{(j)} - \rho_{K-q}^{(j)}], \quad (10)$$

$$\rho_{K0} = \frac{\rho_{K0}^{(j)}}{\rho_{00}^{(j)}}. \quad (11)$$

Note that the rank $K = 1$ and $K = 2$ state multipoles in Eqs. (9)–(11) differ from the state multipoles tabulated by de Miranda *et al.*²⁵ by the factors $\sqrt{3}$ and $\sqrt{5}$, respectively. The extrema values of the state multipoles $\rho_{1q}^{\pm}$ and ρ_{20} in Eqs. (9)–(11) at arbitrary j -value can be obtained directly using Eq. (2). They are: $\pm\sqrt{3j/(j+1)}$ for the state multipoles $\rho_{1q}^{\pm}$ and $-\sqrt{5j(j+1)/(2j-1)(2j+3)}$; $+\sqrt{5j(2j-1)/(j+1)(2j+3)}$ for the state multipole ρ_{20} which is in agreement with the data given in Table II in Ref. 25. The range of other state multipoles can be obtained for any particular j -value by using standard spherical tensor transformation properties under rotation of coordinate frame. For instance, at $j = 2$ both state multipoles $\rho_{21}^{\pm}$ and $\rho_{22}^{\pm}$ can range within $\pm\sqrt{15/14}$.

As shown by Balint-Kurti and Vasyutinskii,²⁷ the state multipole $\rho_{Kq_k}^{(j)}$ describing the angular momentum polarization of the AB molecule in the reaction (1) can be presented in the product reference frame as an expansion over the spherical tensors $R_{K_i q_k}^{K_r L}(\vartheta_k, \varphi_k)$,

$$\rho_{Kq_k}^{(j)} = N \sum_{K_i} \sum_{L K_r} c_{K_i q_k}^{K_r L}(K_r, L) R_{K_i q_k}^{K_r L}(\vartheta_k, \varphi_k), \quad (12)$$

where the rank K of state multipole $\rho_{Kq_k}^{(j)}$ refers to the polarization of the product angular momentum j , the rank L relates to the anisotropy of the relative motion of the reactants, the rank K_r relates to the polarization of the reactant angular momentum j_r , and the rank K_i relates to the total reactant anisotropy, see Eq. (13).

In fact, Eq. (12) is very general. As shown by Balint-Kurti and Vasyutinskii,²⁷ it is valid not only for the case of the atom-diatom chemical reaction (1) but also for the case when A, B, and C are arbitrary molecules each possessing angular momenta. It describes the angular momentum polarization of the reaction product AB under condition that averaging over all quantum numbers of the second (undetected) product C has been performed.

The spherical tensor $R_{K_i q_k}^{K_r L}(\vartheta_k, \varphi_k)$ in Eq. (12) with the rank K_i and component q_k describes the initial anisotropy of the reactants before the reaction. It can be presented as an irreducible product of the spherical harmonic $Y_{Lq_L}(\vartheta_k, \varphi_k)$ and the reagent state multipole moment $\rho_{K_r q_r}^{(j_r)}$,

$$R_{K_i q_k}^{K_r L}(\vartheta_k, \varphi_k) = \sum_{q_L, q_r} C_{Lq_L K_r q_r}^{K_i q_k} Y_{Lq_L}(\vartheta_k, \varphi_k) \rho_{K_r q_r}^{(j_r)}. \quad (13)$$

The spherical harmonics $Y_{Lq_L}(\vartheta_k, \varphi_k)$ in Eq. (13) take into consideration the anisotropy of the reactant relative motion, while the state multipole moments $\rho_{K_r q_r}^{(j_r)}$ describe the reactant angular momentum polarization. The indices q_r and q_L in Eq. (13) are the components of the corresponding ranks onto the direction of the product relative wave vector $\mathbf{k}$.

The scalar expansion coefficients $c_{K_i q_k}^{K_r L}(K_r, L)$ in Eq. (12) are *anisotropy transforming coefficients* which contain all information about the reaction dynamics. The coefficients can be either determined from experiment (at least in certain experimental geometries²⁷), or calculated using quantum mechanical theory. The explicit general expression for the anisotropy transforming coefficients in terms of the reaction scattering matrix elements is given in Ref. 27. The

coefficients depend on the quantum numbers K , K_i , K_r , L , and q_k , where q_k is the coherent quantum number²⁷ which is the component of the ranks K and K_i onto the recoil direction $\mathbf{k}$. The coefficients are the elements of a matrix that performs transformation between the initial anisotropy of the reactants, described by the spherical tensor $R_{K_i q_k}^{K_r L}(\vartheta_k, \varphi_k)$, and the anisotropy in the reaction product described by the spherical tensor $\rho_{K q_k}^{(j)}$, as expressed in Eq. (12). Although the anisotropy transforming coefficients are in general complex values, all measurable variables, like reaction cross sections and the intensity of the probe light absorption are always real, because they contain only real, or imaginary parts of the coefficients.

As can be seen from Eq. (12), the component q_k onto the recoil axis $\mathbf{k}$ is the same in the *lhs* and *rhs* which means that this component is preserved in the chemical reaction. This vector property manifests a new conservation law underlying many vector correlation effects in reaction dynamics. As can be shown, this conservation law is in general based on the conservation of the projection of the total angular momentum of the molecular system onto the recoil axis.

The physical meaning of the projection q_k is as follows. It can take the values $q_k = 0, \pm 1, \pm 2, \dots$, as long as $|q_k| \leq |K|$ and $|q_k| \leq |K_i|$. Using the symmetry property of the Clebsch-Gordan coefficient in Eq. (13), it is easy to conclude that $q_k = q_r + q_l$ arises from a coupling of the reactant polarization and the relative motion of the reactants. More, as shown in Ref. 27 $q_k = \Omega - \Omega'$, where Ω and Ω' are helicity quantum numbers related to the angular momentum polarization of the products. The value $\Omega - \Omega'$ relates to the *coherence* in the product angular momentum system. Therefore, the quantum number q_k is related to the coherence superposition of the angular momentum helicities in the reactants and products both defined in the product frame. The conservation of q_k shows up through the fact that the spherical tensors of the rank K in the right and left-hand sides of Eq. (12) transform in the same way under rotation about the vector $\mathbf{k}$ (i.e., the z -component of the rank, q_k , is conserved throughout).

As recently shown by Shternin and Vasyutinskii,⁴² the expression which is similar to Eq. (12) describes the angular momentum polarization of the products of an arbitrary photolysis reaction.

Using the orthogonality of the spherical tensors, the expression for the anisotropy transforming coefficients $c_{K_i q_k}^K(K_r, L)$ can be obtained from Eq. (12) as

$$c_{K_i q_k}^K(K_r, L) = N^{-1} \frac{\langle\langle \rho_{K q_k}^{(j)} R_{K_i q_i}^{K_r L*} \rangle\rangle}{\langle\langle R_{K_i q_i}^{K_r L} R_{K_i q_i}^{K_r L*} \rangle\rangle}, \quad (14)$$

where the double angular brackets denote integration over the angles (ϑ_k, φ_k) , (θ, ϕ) , and the constant N is defined as

$$N = \frac{\sqrt{2j_r + 1}}{\sqrt{4\pi(2j + 1)}}. \quad (15)$$

It is important to compare the theoretical approach used in this paper for description of the vector correlations in chemical reactions with the approaches used by other authors. From the formal mathematical point of view, the main difference between our approach and that developed by de Miranda

et al.^{23–26} is that we project both the entrance and exit channel multipole ranks onto the *same* recoil axis which is parallel to the product relative motion wave vector $\mathbf{k}$, whereas within the de Miranda *et al.* approach the entrance and exit channel multipole ranks are projected on the entrance $\mathbf{k}_r$ and the exit $\mathbf{k}$ directions, respectively. This relatively small formal difference results in certain qualitative advantages in physical interpretation of the results obtained and in the possibility of collecting more detailed vector correlation data from experiment.

In particular, the approach of this paper has led to the formulation of the important new conservation law described above which allows for deeper understanding of the reaction mechanism. Note, that early works on inelastic collisions (see, e.g., Ref. 43) considered an *approximate propensity rule* $M = M'$, which was based on computation results. However, this effect has little similarity with the *exact conservation rule* $q_k = q'_k$ discussed above which is based on the symmetry of the molecular system under rotation about the recoil axis and valid for any inelastic collision and chemical reaction.

Another advantage of the approach deals with the introduction of the set of the anisotropy-transforming coefficients $c_{K_i q_k}^K(K_r, L)$ in Eq. (12) which contain all information about the reaction dynamics. The anisotropy-transforming coefficients $c_{K_i q_k}^K(K_r, L)$ depend explicitly not only on the exit channel quantum numbers K and q_k but also on the entrance channel quantum numbers K_i , K_r , L , q_k which refer to the initial conditions of the chemical reaction: anisotropy of the reactant relative motion and reactant angular momentum polarization.

In their quantum mechanical treatment of the vector correlations in the atom-diatom chemical reaction (1), de Miranda *et al.*^{1,25} introduced polarization parameters $a_q^{(k)}$ where the rank k and its body frame projection q are related to either reactant,¹ or product²⁵ coordinate frames. Unlike the parameters $a_q^{(k)}$, the coefficients $c_{K_i q_k}^K(K_r, L)$ include the quantum numbers which characterize angular momentum and spatial anisotropy of both reactants and products. This feature of the anisotropy-transforming coefficients provides experimentalist with a flexible way to investigate the role of initial conditions in the reaction dynamics. Note that the quantum numbers k and q in Ref. 25 have the same meaning as the quantum numbers K and q_k in Eq. (12) (that is, $k \equiv K$, $q \equiv q_k$). In general, both the set of the polarization parameters $a_q^{(k)}$ and the set of the anisotropy-transforming coefficients $c_{K_i q_k}^K(K_r, L)$ contain the same information on the reaction dynamics.

The expression in Eq. (12) for the product state multipoles can be presented in an alternative form where all spherical tensors are projected onto the arbitrary laboratory Z axis²⁷

$$\rho_{KQ}^{(j)} = N \sum_{K_i, q_k, Q_i} \sum_{L, K_r} c_{K_i q_k}^K(K_r, L) D_{Q q_k}^{K*}(\phi, \theta, \xi) \times D_{Q_i q_k}^{K_i}(\phi, \theta, \xi) R_{K_i Q_i}^{K_r L}(\vartheta, \varphi), \quad (16)$$

where $D_{Q q_k}^K(\phi, \theta, \xi)$ is a Wigner rotation matrix,^{38,39} the Euler angles (ϕ, θ, ξ) describe transformation from the laboratory frame to the product frame, the polar angles (ϑ, φ) describe the position of the reagent wave vector $\mathbf{k}_r$ in the

laboratory frame, and Q, Q_i are the corresponding rank components onto Z axis.

In an important particular case when the laboratory axis Z is parallel to the wave vector $\mathbf{k}_r$ of the reagent relative motion, $\vartheta = \varphi = 0$ and Eq. (16) describes the product angular momentum distribution where all state multipoles are expressed in the reactant reference frame.

Equations (12) and (16) provide a general description of the product space distribution and angular momentum polarization in reaction (1) as function of the reactant relative motion and their angular momentum polarization. In the applications given below both xz -plane and $x'z'$ -plane in Fig. 1 lie in the scattering plane, the polar angles φ_k and γ are equal to zero, and y and y' axes are directed along the vector product $\mathbf{k}_r \times \mathbf{k}$. Particular cases of Eqs. (12) and (16) are discussed in Secs. II B and II C.

B. Differential cross section for bimolecular chemical reaction between polarized particles

The differential cross section of the reaction (1) in the center-of-mass frame can be obtained from Eq. (16) as particular case $K = Q = q_k = 0$ which relates to the $\mathbf{j}_r - \mathbf{k}_r - \mathbf{k}$ vector correlation

$$\begin{aligned} \frac{d\sigma_{v_r, j_r \rightarrow v, j}}{d\Omega} &\propto (2j+1)^{1/2} \rho_{00}^{(j)}(\theta, \phi) \\ &= \left(\frac{2j_r+1}{4\pi} \right)^{1/2} \sum_{K_i, Q_i} \sum_{L, K_r} c_{K_i 0}^0(K_r, L) (-1)^{K_r+Q_r} \\ &\quad \times C_{K_i-Q_i, K_r, Q_r}^{L0} Y_{K_i Q_i}^*(\theta, \phi) \rho_{K_r Q_r}^{(j_r)}. \end{aligned} \quad (17)$$

It is easy to see using the symmetry of the Clebsch-Gordan coefficient in Eq. (17) that $Q_i = Q_r$. In the case of unpolarized reagents, $K_r = Q_r = 0$ and Eq. (17) becomes equivalent to the conventional differential cross section expression, see for instance Ref. 44 which describes correlation between the vectors $\mathbf{k}_r$ and $\mathbf{k}$.

Note that reflection in the scattering plane, σ_v , does not change the *lhs* in Eq. (17). At the same time the spherical tensor $\rho_{K_r Q_r}^{(j_r)}$ and the spherical harmonic $Y_{K_i Q_i}^*(\theta, \phi)$ in the *rhs* of Eq. (17) are transformed under reflection as: $\sigma_v \rho_{K_r Q_r}^{(j_r)} = (-1)^{K_r+Q_r} \rho_{K_r-Q_r}^{(j_r)}$ and $\sigma_v Y_{K_i Q_i}^*(\theta, \phi) = Y_{K_i Q_i}^*(\theta, -\phi) = (-1)^{Q_i} Y_{K_i-Q_i}^*(\theta, \phi)$, respectively.³⁸ Therefore, the coefficients $c_{K_i 0}^0(K_r, L)$ obey the following symmetry rule:

$$c_{K_i 0}^0(K_r, L) = (-1)^{K_i+L} c_{K_i 0}^0(K_r, L). \quad (18)$$

As can be seen from Eq. (18), the coefficients $c_{K_i 0}^0(K_r, L)$ can differ from zero only if the sum $K_i + L$ has an even value. Therefore, using the symmetry of the Clebsch-Gordan coefficient in Eq. (17), one can see that in case $Q_r = 0$ the differential cross section can differ from zero only when the rank K_r is also even. This feature nicely fits with the known fact⁴⁵ that only the component of the reactant angular momentum orientation perpendicular to the reaction plane can contribute to the differential reaction cross section, see Eq. (17).

As can be shown by integration of Eq. (17) over the angles θ, ϕ , the total reaction cross section depends only on the $Q_r = 0$ state multipole components. The corresponding expression for the total reaction cross section can be written as

$$\sigma_{v_r, j_r \rightarrow v, j} = (2j_r+1)^{1/2} \sum_{K_r} c_{00}^0(K_r) \rho_{K_r 0}^{(j_r)}, \quad (19)$$

where K_r can take only even values and the state multipole $\rho_{K_r 0}^{(j_r)}$ describes the reactant angular momentum alignment.

C. Reaction between unpolarized particles

In case of the chemical reaction between unpolarized particles the indices K_r and q_r in Eq. (12) should be both set to zero: $K_r = q_r = 0$ and Eq. (12) can be written as

$$\rho_{K q_k}^{(j)}(\vartheta_k) = \frac{1}{\sqrt{4\pi(2j+1)}} \sum_{L=0}^{\infty} c_{L q_k}^K Y_{L q_k}(\vartheta_k, 0), \quad (20)$$

where $c_{L q_k}^K = c_{L q_k}^K(0, L)$ are anisotropy-transforming coefficients describing correlation between the anisotropy of relative motion of reagents and product angular momentum polarization of AB products.

Equation (20) describes correlation between three vectors $\mathbf{j}, \mathbf{k}_r$, and $\mathbf{k}$ in the chemical reaction (1). Using reflection symmetry in the scattering plane in Eq. (20), one can come to the following known conclusions about the state multipole values:^{40,45}

- (i) odd rank K state multipoles $\rho_{K q_k}^{(j)}$ are all pure imaginary (in the mathematical sense);
- (ii) even rank K state multipoles $\rho_{K q_k}^{(j)}$ are all pure real;
- (iii) the state multipole moments $\rho_{K 0}^{(j)}$ with odd K values and $q_k = 0$ are all equal to zero.

The conclusion (iii) means that in the case of isotropic distribution of the reactant angular momenta, the product angular momenta cannot be orientated in the scattering plane.

III. Li + HF CHEMICAL REACTION

Chemical reactions between alkali atoms and hydrogen halides are excellent candidates for studying vector properties⁴⁶ because the reactant and product molecules possess strong permanent dipole moments. Among these systems, the reaction $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ is a prototype which has already been a subject of several stereodynamic studies.^{25,47-49} Loesch and co-workers excited HF from the ground vibrational state to the $v_r = 1, j_r = 1$ state using linearly polarized laser within the condition of crossed-beam experiment.^{8,49-52} By changing the laser beam polarization, the molecular orbital angular momenta $j_r = 1$ were aligned either parallel, or perpendicular to the relative velocity vector $\mathbf{k}$. The integral (ICS) and differential (DCS) cross sections obtained have shown important steric effects, favoring a side attack. More ICS experiments have been carried out by Lee *et al.*⁵³ and by Loesch *et al.*^{47,54-56}

Theoretically, the steric effect has been analyzed for the case of initially ro-vibrational excited HF molecules, $\text{HF}(v_r = 1, j_r = 1)$ using quantum⁴⁸ and quasi-classical approaches (QCT).^{25,49,56,58} The results obtained were in good agreement with experiment.^{8,50,52} Both experiments and calculations have shown that the initial vibrational excitation of HF increases the reactivity^{8,48–50,59} enormously, because of the late character of the reaction barrier. This is also the reason why simulations indicate that the reaction cross section depends strongly on the rotational alignment of HF reagents in their ground $v_r = 0$ vibrational state, because collinear collisions favor the excitation of the vibrational stretch needed to overpass the late barrier. For $v_r = 1$, however, vibrational excitation is already enough and the rotational alignment does not play a significant role.

The product and reactant angular momentum orientation and alignment have recently been studied using quantum wave packet calculations.^{28,57} The studies were focused onto the $q_k = 0$ case which refers to the angular momenta orientation and alignment in the reaction plane and parallel either to the $\mathbf{k}$, or $\mathbf{k}_r$ directions. The calculations have shown that the $K = 1, q_k = 0$ component of the product LiF angular momentum orientation can only be obtained from the oriented HF molecules, as expected. The product angular momentum orientation component which is perpendicular to the reaction plane was found to be large.

This finding was explained considering the bent geometry of the reaction barrier which is created by a covalent/ionic crossing⁶⁰ where an electron “jumps” from the Li atom to the F atom within the harpoon mechanism forming the bent $\text{Li}^+\text{F}^-\text{H}$ transition state. Within this model, the HF^- transient is generated in an unbound state with dissociative well-less potential. That is, at the equilibrium distance corresponding to the neutral HF molecule the ionic HF^- system is localized on a highly repulsive PES region. Once the barrier is overcome, the HF^- complex quickly dissociates producing fast H-fragments which fly away and leave the Li^+F^- products in a strongly attractive quantum state. This so-called direct interaction with product repulsion (DIPR) mechanism has recently been reviewed by Mestdagh *et al.*⁶¹ The mechanism is typical for metal atom (M) – hydrogen halide (HX) reactions: the electron jumps from M forming HX^- transient, which is unstable and dissociates rapidly leaving the M^+X^- ionic products. Within this mechanism the product distribution is formed by the transition state region under the condition of fast dissociation.

In this work, we focus on the $q_k \neq 0$ multipole components of the reaction products. The wave packet calculations have been performed for $\text{Li} + \text{HF}(v_r = 0, j_r = 3) \rightarrow \text{LiF}(v, j) + \text{H}$ for $J = 0, 1, 2, \dots, 45$ for $\Omega_r = 0, \dots, \min(j, J)$ and the two parities under coordinate inversion, $P = \pm 1$.²⁸ The propagation in time has been done using a modified Chebyshev integrator using reactant Jacobi coordinates in a body-fixed frame.⁶² The MAD-WAVE3 program has been used for doing the calculations.⁵⁷ The parameters utilized in the wave packet propagation are the same as those used in Ref. 57 for the initial case of $j = 0$. The number of helicity components is set to a maximum of 16 functions ($\Omega_{\max} = \min(J, 15)$), yielding DCSs which are in good agreement with the same re-

sults obtained with 32 functions (better than 0.1%), as studied for $\text{Li} + \text{HF}(v_r = 0, j_r = 0)$. Finally, the number of Chebyshev iterations used was of the order of 20 000. This number was checked to yield convergence of the rotational average state-to-state probabilities to values better than 1%, in most of the energy intervals considered. The APW PES by Aguado *et al.*⁶³ has been used.

The reaction presents many resonances at low energies,⁵⁷ which were expected to lower down polarization effects significantly. For this reason, in this paper we consider the highest converged collision energy analyzed used in Ref. 28 and coincide with a collision energy measured in the experiment.⁵⁶ Higher energies would imply the calculations for $J > 45$ total angular momentum which are out the scope of this paper. The rotational excitation of the reactants was found to have a significant effect on the reaction (see also Ref. 28). The increasing of the reactant initial rotation energy from the $j_r = 0$ state to the $j_r = 3$ state significantly increases the product vibrational excitation. In particular, while at the collision energy of 300 meV nearly 70% of the reactants are in their $v = 0$ for $j_r = 0$, for $j_r = 3$ this fraction reduces to less than 1/2. This is already an indication that as rotational excitation increases, the reaction dynamics becomes more complex.

Also, for $j_r = 1$ the reaction ICS for $\Omega_r = 0$ was found to be about three times larger than that for $\Omega_r = 1$,^{28,48} indicating that head-on collisions yield to products more efficiently than side collisions. This finding was interpreted as follows:⁴⁸ to overpass the late barrier some vibrational excitation is needed, and this is obtained more efficiently in collinear collisions than in side conditions. As initial j_r increases, this situation becomes more complex, and the ICS increases for high Ω_r . Thus, for $j_r = 2, 3$, the ICSs for $\Omega_r = 0$ and 1 are of the same magnitude (see Fig. 5 in Ref. 28). This means that the initial rotation of the HF reactant reduces significantly the strong alignment effect described above for $j_r = 1$, simply because the system can reorient during the approach of the two reactants. It is therefore interesting to analyse the polarization of products to check the effect of the model. The LiF fragments are produced in a high rotational state. This is explained by the DIPR mechanism described above: when H departs rapidly from the bent transition state, it “hits” LiF producing a high rotational excitation.

According to our calculations, for initial $v_r = 0, j_r = 3$ the maximum values of the DCS are achieved for the following $\text{LiF}(v, j)$ states: $v = 0, j = 40, v = 1, j = 34$, and $v = 2, j = 25$, which is mostly due to the energy conservation requirement. The DCS for $\text{Li} + \text{HF}(v_r = 0, j_r = 3) \rightarrow \text{LiF}(v, j) + \text{H}$ reaction at 317 meV has been calculated using Eq. (17) and are shown in Fig. 2. Two different initial distributions of reagents are presented: isotropic, where all initial Ω_r states (where Ω_r is a projection of the reagent angular momentum j_r onto the wave vector $\mathbf{k}_r$) are equally populated with a weight of $1/(2j_r + 1)$ and aligned, where only the initial $\Omega_r = 0$ state is populated which implies that the initial angular momentum $\mathbf{j}_r$ is perpendicular to the direction $\mathbf{k}_r$. The particular alignment geometry chosen was used because it is known to give the maximum negative alignment value⁴⁰ which was expected to achieve maximum effect in DCSs.

FIG. 2. DCSs in reaction $\text{Li} + \text{HF}(v_r = 0, j_r = 3) \rightarrow \text{LiF}(v, j) + \text{H}$ at 317 meV.

Data presented in Fig. 2 manifest a complex behavior as function of the scattering angle which depends on the v, j values, in many cases forward and backward scattering is significant. It seems that as the vibrational quantum num-

ber v increases the DCS shifts towards higher angles, as a consequence of the reduction of the energy disposal. For $j_r = 3$, the isotropic and aligned reagents (AR) DCSs have comparable magnitudes in contrast to what happens for $j_r = 1$. For $j_r = 1$ and $\Omega_r = \Omega'_r$, one can only distinguish between head-on or side collisions, while for $j_r = 3$ this is no longer the case. This and the fact that the dynamics for $j_r = 3$ becomes more complex seems to indicate that a more complex linear combination of Ω should be considered in order to enhance, or control the reactivity. In the AR case, reagent state multipoles are different from zero when $K_r = 0, 2, 4, 6$ and numeric values of these multipoles are equal to $1, -2/\sqrt{15}, \sqrt{2/11}, -10/\sqrt{429}$, respectively. The DCSs related to any other state multipole values can be readily calculated using Eq. (17).

The state multipoles $\rho_{Kqk}^\pm$ describing the angular momentum orientation and alignment of the reaction products $\text{LiF}(v = 0, j = 40)$, $\text{LiF}(v = 1, j = 34)$, $\text{LiF}(v = 2, j = 25)$ were calculated using Eqs. (14) and (16) assuming that the reaction reagents are unpolarized. The results obtained are shown in Fig. 3.

The dependence of the state multipole $\rho_{11}^- \approx \langle j_Y \rangle$ of the reaction products on the scattering angle θ is shown in Fig. 3(a) for several rovibrational states of the products. At the scattering angles 0° and 180° the state multipole is equal to zero. This fact is well known⁴⁵ and can be explained referring to the reflection symmetry of the molecular complex. For intermediate scattering angles, the dependence is rather complicated, showing oscillations. The maxima of the angular momentum orientation are in the order of 0.5–0.6, which is about a half of their theoretical limits.

The dependence of the state multipoles $\rho_{20}, \rho_{21}^+, \rho_{22}^+$ on the scattering angle is shown in Figures 3(b)–3(d). As can be seen from these figures, the alignment component ρ_{20} always has negative values indicating that the product angular momenta are directed preferably perpendicular to the product wavevector $\mathbf{k}$. This behavior is mostly pronounced for small and large scattering angles where the alignment value takes its minima equal to -1 , as already been found in Ref. 28. More, relatively small values of the alignment component ρ_{21}^+ and relatively large and negative values of the alignment component ρ_{22}^+ indicate (see Eqs. (7) and (8)) that the angular momenta j are aligned preferably perpendicular to the scattering plane.

The features obtained show that the product angular momentum orientation is very sensitive to the scattering angle and to the angular momentum value. Therefore, further comparison with experiment can be used as a sensitive tool for proving the accuracy of the theoretical methods and PES used.

IV. F + HD CHEMICAL REACTION

Another interesting system from the stereodynamical point of view is F + HD. Several theoretical^{64–66} and experimental studies^{67–69} in a wide range of collision energies have been performed in the last few years to investigate the reactive cross sections behavior, supplying a wealth of information about the main reactive mechanisms acting on this system. Large differences have been found for the two product

FIG. 3. Product state multipoles in reaction $\text{Li} + \text{HF}(v_r = 0, j_r = 3) \rightarrow \text{LiF}(v, j) + \text{H}$ at 317 meV in case of isotropic reagents. Limits along Y axes in panels (a)–(d) are equal to the possible extremum values of the corresponding state multipoles calculated at the classical limit.²⁵

reactive channels. In particular, the HF channel has been extensively studied because prominent resonances, mainly related to the $v = 2$ manifold of the product, have been clearly revealed both in crossed molecular beam experiments and in theoretical quantum mechanical calculations.⁷⁰ The integral cross sections in the neighborhood of these features have been shown to be a prototypical example for obtaining quantum coherent control in collision processes.⁷¹

However, studies of the stereodynamics and of its relationship with the reaction mechanisms are relatively scarce^{34,72} and mainly performed using the Stark and Werner (SW) PES⁷³ or its spin-orbit corrected variants.⁷⁴ A deep quantum stereodynamical analysis of the HF($v = 2$) channel in the range of energies of the resonance feature mentioned above using SW PES has been recently reported.⁷⁵ In Ref. 76, close coupling quantum integral cross sections and rate constants for both reactive channels calculated with a new *ab initio* PES recently published⁷⁷ by Fu, Xu, and Zhang (FXZ) were compared with several sets of experimental data. The vibrationally selected integral cross sections for the HF channel were shown for the first time in excellent agreement

with experiments,⁷⁸ notably for the HF($v = 3$) channel, where the presence of a broad maximum has revealed the role of a new direct mechanism acting selectively on the FXZ PES. The state-to-state ICS presented in Fig. 7 in Ref. 76 facilitates the reading of the article.

As discussed in Ref. 76, the HF($v = 3$) channel is also very interesting by the resonance point of view. Narrow resonance features in the neighborhood of the HF($v' = 3, j' = 0$) threshold are clearly shown in the ICS especially in the state-to-state ICS of the lower product rotational states. These resonance features (also present in SW PES) were deeply analyzed in Ref. 64 and clearly assigned to high excited bending vibrational modes of long living resonance metastable states trapped in the van der Waals well of the product. At higher collision energies broader Regge oscillations⁷⁹ coming from the short living transition state resonance (called A in Ref. 64) responsible of the total ICS maximum studied in Ref. 70 are also clearly manifested. Note also, that this PES has shown to reproduce with high accuracy the experimental fingerprints of this resonance in HF($v' = 2$) rotational resolved ICS.^{68,69}

FIG. 4. DCSs in reaction $F + HD(v_r = 0, j_r = 0)$. (a) $H + DF(v = 3, j = 2)$ channel (b) $HF(v = 3, j = 2) + D$ channel.

Regarding the DF channel, detailed vibrational (and partially rotational) resolved experimental data are available at several collision energies.^{80,81} The reaction dynamics for this channel is much more classical than that for the other isotopic channel⁷⁰ and no significant resonance patterns appear in the reactive observables. However, the stereodynamics of this channel has been predicted⁸⁰ to be relevant to explain the behavior of the differential cross section, where for high final vibrational states a sideways maximum was observed.^{80,81} The effect was shown to increase at higher collision energies. Classical trajectories⁸² and stereodynamical quantum studies³⁴ have shown that at higher collision energies and for high vibrational states a migratory mechanism, where the incoming F atom crosses the transition state from the H end, becomes relevant in the reaction dynamics.

To obtain further physical insight into these aspects, within the present theoretical framework we focus on two prototypical state-to-state processes, namely, the reactions $F + HD(v_r = 0, j_r = 0) \rightarrow HF(DF)(v = 3, j = 2) + D(H)$, at two different collision energies (78.15 and 118.15 meV), deserving to further study a more complete analysis involving more reactive transitions. The lower collision energy is close to that studied in Ref. 34 (76.0 meV) and just above the threshold of the $HF(v = 3, j = 2)$ channel but out of the long living resonances energy range. The higher energy is in the range of collision energies where the sideways broad peak starts to appear in the experiment of Ref. 80. At this energy, the $HF(v = 3, j = 2)$ state is a relevant product channel of the $v = 3$ manifold. Note that at this energy, the Regge oscillations coming from the A resonance are present although with smaller intensity with respect to the lower rotational states, also in the ICS of the $j = 2$ channel, suggesting some resonance contribution also in this particular reactive transition.

In this paper, quantum scattering calculations have been carried out using a modified and parallelized version of the ABC code⁸³ (for details of the changes performed and the parallelization strategy implemented see Refs. 76 and 84). State-to-state differential cross sections shown in the present article require more stringent values of the input parameters with respect to the ones given in Ref. 76, in order to obtain

convergent results within 1%. Also, an enhanced Numerov propagator⁸⁵ was used to propagate the hyperradial equations. Specifically, the value of the Ω_{max} parameter (k_{max} in Ref. 76) turned out to be crucial in order to obtain convergent S-matrix elements for the DF channel (see Sec. III of Ref. 76) at the higher collision energy: the chosen value was $\Omega_{max} = \min(J, 10)$. The parameters j_{max} and e_{max} were the same as in Ref. 76 (25 and 2.0 eV, respectively), while the implementation of the improved propagator permits to reduce significantly (by about a factor 6) the number of the hyperradial sectors ($r_{max} = 12.0$ a.u. and $d\rho = 0.1$ a.u. were employed) extending the accuracy requirement at the state-to-state observables. The number of partial waves employed was 29.

The state-to-state differential cross sections at the two collision energies are shown in Figure 4 in panels (a) and (b) for the production of DF and HF, respectively. The integral cross sections at the two energies are 0.0271 and $0.0432 \text{ \AA}^2$ for HF and 0.0709 and $0.0716 \text{ \AA}^2$ for DF. As already known from quantum reactive scattering calculations⁷⁰ and experiments,^{80,81} the angular distribution of the DF product is mainly concentrated in the backward hemisphere at all the collision energies, as a consequence of a dominating rebound mechanism. However, at the higher collision energy a broad peak at scattering angles around 110° – 120° shows the enhancement of sideways reactivity. The intensity of the sideways peak grows as the DF rotational quantum number increases. For higher rotational states, the backward peak becomes broader and more extended towards the sideways angular range. This agrees with the observation of just one peak (given by the overlap of the two features) around 150° in the experimentally measured $v = 3$ vibrationally resolved differential cross sections.⁸⁰

The differential cross sections of the HF channel exhibit a completely different behavior. The products are mainly forward scattered with remarkable nearside-farside oscillations^{86,87} in the full range of angles, suggesting again resonance contribution⁸⁸ especially at the higher collision energy. As will be shown in Ref. 89, the forward scattering markedly increases near the maximum of the $HF(v = 3)$ integral cross sections, producing narrow peaks in the forward

FIG. 5. Product state multipoles in reaction $F + HD(v_r = 0, j_r = 0) \rightarrow DF(v = 3, j = 2) + H$. Only the scattering angles where DCSs notably differ from zero are represented. Limits along Y axes in panels (a)–(d) are equal to the possible extremum values of the corresponding state multipoles at $j = 2$.

direction as a function of the collision energy. As described in Ref. 76, the $HF(v = 3)$ broad maximum appearing in the ICS shows the typical features of the peripheral stripping dynamics,^{90,91} where the atom H is abstracted by the incoming heavy fluorine atom remaining nearly unperturbed in its trajectory. The driving force of the stripping mechanism is the presence, at the collinear configuration, of a van der Waals well in the exit channel of the reaction that favors the transfer of the H atom by tunneling thus enhancing the reactivity. The role of the long-range forces and of their anisotropy in the peripheral mechanism is well documented in Ref. 92. A clear propensity for a collinear crossing for the $HF(v = 3)$ channel was also noted in the stereodirected analysis of Ref. 34 although the PES there employed (using the exit channel of the SW PES) underestimates this mechanism. In fact, as shown in Fig. 1 in Ref. 76, the exit van der Waals well in the FXZ PES is deeper than in SW PES and it is more extended in its angular range so that the acceptance cone of the reaction is larger.

Real state multipoles $\rho_{Kqk}^\pm$, which characterize orientation and alignment of reactive products at the two collision energies investigated, have been calculated using Eqs. (21) and (B6) in Ref. 27 under the assumption of unpolarized

reagents. The dependence on the scattering angle, i.e., the so-called $\mathbf{k}_r - \mathbf{k} - \mathbf{j}$ correlation for the $DF(v = 3, j = 2)$ and $HF(v = 3, j = 2)$ products are presented in Figures 5 and 6, respectively. To compare the polarization properties of the two state-to-state channels the different relevance of the kinematic constrain⁹³ must be taken into account. The conservation of the total angular momentum for un-polarized reactants ($j_r = 0$) can be written as:⁹⁴ $\mathbf{j} = \mathbf{L}_r \sin^2 \beta + \mathbf{d} \cos^2 \beta$ and $\mathbf{L} = \mathbf{L}_r \cos^2 \beta - \mathbf{d} \cos^2 \beta$, where $\mathbf{L}(\mathbf{L}_r)$ is the orbital quantum momentum vector of the products (reactants), β is the skewing angle of the reaction and $\mathbf{d}$ is a vector depending on the reaction mechanism and energetics. When $\cos^2 \beta$ is small, it can be assumed that the orbital quantum momentum is fully transformed in rotational energy during the reactive process conserving its directional properties. This effect, known as kinematic constraint, is responsible of the stereodynamical properties observed in several chemical systems disregarding the characteristics of the potential energy surface and the reaction mechanism involved.⁹³ Comparison among classical trajectories stereodynamical properties of different isotopic variants of the $F + H_2$ reaction at very high collision energies⁹⁵ has also shown for this system an important effect on the alignment properties. For the reactions of the $F + HD$ system,

FIG. 6. Product state multipoles in reaction $F + HD(v_r = 0, j_r = 0) \rightarrow HF(v = 3, j = 2) + D$. Limits along Y axes in panels (a)–(d) are equal to the possible extremum values of the corresponding state multipoles at $j = 2$.

$\cos^2\beta$ is about 0.3 for the DF channel and about 0.63 for the HF channel so that from the kinematic point of view, larger polarization properties are expected for the DF product.

In Figure 5, real state multipoles are shown for the DF product in the range of angles where DCS notably differs from zero. As noted in Sec. II, odd state multipoles define the orientation of the angular momentum of the product and in particular ρ_{11}^- is proportional to the average value of the angular momentum projection on the Y axis. From panel (a) of Figure 5, we can observe that ρ_{11}^- is mainly positive in the backward hemisphere and has a large maximum in the 100–140 range for the higher collision energy, to be viewed in relationship with the broad sideways peak in the differential cross sections of Figure 4(a). The ρ_{11}^- state multipole reaches the highest value of about 0.9 to be compared to the maximum allowed value $\sqrt{2}$. This indicates that for these scattering angles most rotational angular momenta are oriented along the positive direction of the Y axis. At the lower collision energy, the maximum appears shifted towards a higher scattering angle, and the migratory mechanism feature in the DCS is presumably hidden by the backward rebound mechanism that exhibits less relevant orientation properties.

Positive orientation of the product was also found in classical trajectories analysis of the $F + H_2$ reaction.⁹⁶ The effect

of the orientation was more evident in the $HF(v = 0)$ product dominated by rebound mechanism. We remark here that this result can be also expected by simple considerations on the magnitude of the angular momenta involved. In fact, the exothermicity of the DF($v = 3$) channel (and of HF($v = 0$) channel in the $F + H_2$ reaction) compensates the decreasing of reduced mass of the product, μ . Since in a rebound mechanism low values of the impact parameter, b_r , are involved, the orbital angular momentum of the product L (of modulus $\hbar\mu kb$) is larger than L_r . The classical trajectories analysis of Ref. 96 shows that $\mathbf{L}$ and $\mathbf{L}_r$ are strongly aligned along the Y axis and point towards the same (negative) direction. For the present reactive transition, the low value of j suggests that also in this case $\mathbf{L}$ and $\mathbf{L}_r$ point to the same negative direction. Therefore, j has to be directed anti-parallel to $\mathbf{L}$ and $\mathbf{L}_r$ with a positive orientation.

In the interval 100°–140°, the multipole ρ_{22}^+ multipole (panel (d) of Figure 5) has broad oscillations in the negative range with minima slightly shifted with respect to the maxima of ρ_{11}^- . From Eq. (8), we can see that being ρ_{22}^+ proportional to $j_X^2 - j_Y^2$, the negative values indicate that the rotational angular momentum aligns preferentially along Y rather than along the X axis. The ρ_{20}^+ is proportional to $(3j_Z^2 - j^2)$. For randomly aligned angular momenta $j_Z^2 = j^2/3$ and ρ_{20}^+ is

equal to zero. From the results of the panel (b) of Figure 5, we can observe that ρ_{20}^+ is negative in the full range of the considered scattering angle, indicating that the angular momentum of the products is not aligned along the product relative velocity vector. Moreover, ρ_{20}^+ becomes more negative increasing the scattering angle attaining the lowest permitted value.

In Figure 6, we present real state multipoles for the HF($v = 3, j = 2$) channel. Regular oscillations with the same frequency are observed for all the multipoles. The amplitude of the oscillations is larger at the higher collision energy where the intense forward scattering is shown (see panel (b) in Figure 4). In the angular range where the forward peak appears in the DCS, a marked orientation in the negative direction of the Y axis is observed, as indicated by a minimum value of ρ_{11}^- around to -0.5 which is obtained in the neighborhood of 10° (panel (a)). However, at 0° ρ_{11}^- is zero as required by the geometrical constraint (see Sec. III).

To understand the polarization properties of the forward peak of the HF channel, we consider its mechanistic origin, as alluded to above. In this case, the incoming fluorine atom attacks the peripheral region of the HD molecule from the H end nearly conserving its initial velocity. In the neighborhood of collinear configurations, the van der Waals well in the exit channel increases locally the kinetic energy thus favouring the crossing of the barrier by tunneling. The ejected H atom is attracted by the fluorine atom forming the new HF bond and the products slowly depart from each other. It is interesting, a comparison with the DIPR model discussed in Sec. III, where the kinetic energy required to break the reactant's bond is supplied by the antibonding character of the HF^- ion formed by the harpooning mechanism: in this case, the kinetic energy of the H atom transferred is much lower, and accordingly the HF product is formed mainly with low rotational energy. It is the small impulse coming from the H atom that changes the direction of the motion of the incoming F atom. Small displacement from the collinear configuration generates the moment which is responsible for the rotation motion of the product. Because this impulse is in the direction of the old HD bond, it produces a rotational angular momentum perpendicular to $\mathbf{k}$. Moreover because the reaction occurs preferentially at a nearly collinear configuration, the new bond will be formed mainly from behind with respect to the motion of the incoming atom producing a preferentially clockwise rotation. The product rotational angular momentum is therefore oriented in the same direction as the reactant orbital momentum.

A further confirmation of these observations can also be obtained by considerations on the angular momenta involved as for the case of DF. In this case, the endothermicity of the channel (about 71 meV) and the reduction of the reduced mass suggest that the orbital angular momentum strongly decreases during the reactive process. To compensate this reduction, the rotational angular momentum of the product must be parallel to $\mathbf{L}$ and $\mathbf{L}_r$ and point on the negative Y direction. Again, the results agree with the results obtained in Ref. 96 for the production of HF($v = 3$). This agreement suggests that the production of the HF molecule in the third excited vibrational state has similar mechanistic origin in both the $\text{F} + \text{H}_2$ and $\text{F} + \text{HD}$ reactions and that the result obtained has essentially a classical origin.

In contrast, the high frequency oscillatory pattern in the state multipoles is a pure quantum stereodynamical effect.²⁵ Similar behavior in real state multipoles has been observed already from the first quantum computation of stereodynamical effects for the $\text{H} + \text{D}_2$ reaction in the forward scattering of the low rotational states of HD($v = 0$) product.²⁴ In the present HF($v = 3, j = 2$) case, the rapid oscillations in the multipole states are observed in the full range of the scattering angles suggesting interference with a metastable state living at least for a complete rotations. From the semiclassical point of view, this can be conveniently discussed in terms of nearside-farside interferences⁹⁷ between trajectories with positive and negative values of the classical deflection function. We note here that a change in sign of the classical deflection function produces a different orientations of the axis because of the change in sign of the vectorial product between $\mathbf{k}$ and $\mathbf{k}_r$ leading to the oscillations in the multipole states (see Figure 6). A more rigorous analysis confirming the resonance fingerprints discussed above will be given in Ref. 89.

V. CONCLUSIONS

In this work, we have presented the application of a new approach for the description of the vector correlations to the elementary chemical reactions $\text{Li} + \text{HF}(v_r = 0, j_r = 3) \rightarrow \text{LiF}(v, j) + \text{H}$ at the collision energy 317 meV, and $\text{F} + \text{HD}(v_r = 0, j_r = 0) \rightarrow \text{H} + \text{DF}(v, j), (\text{D} + \text{HF}(v, j))$ at the collision energies 78.15 meV and 118.15 meV. The theoretical approach has been tested on the $\text{Li} + \text{HF}$ and $\text{F} + \text{HD}$ reactions since they are two most relevant case studies analyzed in the stereodynamics literature.

Reaction S-matrices have been computed using a time-dependent approach for the first reaction and a time independent approach for the second reaction. Calculated molecular angular momentum distributions have been presented in terms of the anisotropy-transferring coefficients and then analyzed. It was shown that the reagents with substantial angular momentum orientation and alignment can effectively contribute to chemical reaction cross-sections, moreover this effect depends strongly on the orientation and alignment direction with respect to the reaction scattering plane. The angular momentum orientation and alignment distributions were found to be quite different for the two HF and DF products channels, consistently with the different dynamics in the corresponding reaction channels.

In DF case, we attribute the polarization features found to kinematic and energetic constraints which are well described in terms of classical mechanic. In HF case, these features are likely induced by the reaction mechanism which shows more pronounced quantum behavior.

Rich information obtained from the analysis shows perspectives for deeper understanding of the reaction stereodynamics using accurate theoretical data which become progressively available from reliable quantum mechanical studies. From the experimental viewpoint, geometrical arrangements based on the REMPI(2 + 1) technique have been considered which are suitable for determination of the product orientation and alignment.

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APPENDIX: DETECTION OF THE REACTION PRODUCT ANGULAR MOMENTUM POLARIZATION

REMPI 2 + 1 is widely used for determination of the atomic and molecular angular momentum orientation and alignment from experiment.⁹⁸ A general method for extraction of orientation and alignment information from 2 + 1 REMPI measurements has been developed by Kummel and co-workers.^{99,100} A modification of this method that adapts it to the case of atoms and provides complete separation between the scalar and tensor quantities has been suggested by Bracker *et al.*¹⁰¹ However, both methods result in rather cumbersome expressions.

A compact and convenient spherical tensor expression for the intensity of the REMPI 2 + 1 signal which is valid for the pure linearly, or circularly polarized probe light can be written in the form^{102,103}

$$I = F_0 \sum_K (C_K(\mathbf{n}_{ph}) \cdot \rho_K^{(j)}) P_K, \quad (\text{A1})$$

where F_0 is a constant proportional to the square of the light intensity, the term in parentheses is a scalar product of the modified spherical harmonic $C_K(n_{ph})$ and the product state multipole $\rho_K^{(j)}$, and P_K is the line strength factor.¹⁰²

The vector $\mathbf{n}_{ph}$ in Eq. (A1) is parallel to the direction of the probe light polarization vector if the light is linearly polarized and parallel to the direction of the probe light propagation if the light is circularly polarized. The rank K is limited to the values $K = 0, 2, 4$ in the case of linearly polarized probe light and to the values $K = 0, 1, 2, 3, 4$ in the case of circularly polarized probe light.

Possible detection schemes which can be used for determination of the angular momentum orientation and alignment of the reaction products are presented in Figure 7. The experimental scheme presented in Fig. 7(a) is suitable for determination of the angular momentum orientation which is perpendicular to the scattering plane. As shown in Fig. 7(a), the circularly polarized probe light propagates along the direction of axis Y which is perpendicular to the scattering plane $\mathbf{k}_r - \mathbf{k}$. The expression for the orientation signal is given in Eq. (A2),

$$\begin{aligned} & \frac{I_Y^+(\theta) - I_Y^-(\theta)}{\langle I_Z \rangle + \langle I_X \rangle - 1/3[\langle I_Y^R \rangle + \langle I_Y^L \rangle]} \\ &= \frac{\sqrt{2j+1}}{3} \left[\frac{P_1^C}{P_0} 2\sqrt{2} \Im[\rho_{11}^{(j)}(\theta)] \right. \\ & \quad \left. - \frac{P_3^C}{P_0} (\sqrt{3} \Im[\rho_{31}^{(j)}(\theta)] + \sqrt{5} \Im[\rho_{33}^{(j)}(\theta)]) \right], \quad (\text{A2}) \end{aligned}$$

where $I_Y^+(\theta)$ and $I_Y^-(\theta)$ are two-photon absorption intensities for the right- and left-handed circular polarized probe light, respectively, both propagating along Y axis. The values I_Z and I_X are two-photon absorption intensities for the linearly polarized light with polarization vector parallel to Z and X axes, respectively. The angular brackets mean integration over all

FIG. 7. Experimental schemes for the detection of (a) orientation (b) alignment.

product directions. The symbol $\Im$ denotes the imaginary part of the corresponding state multipoles.

Difference between the intensities $I_Y^+(\theta)$ and $I_Y^-(\theta)$ is used in Eq. (A2) in order to eliminate contributions of the zeroth-rank and all even rank K terms from the experimental signal. The orientation signal in Eq. (A2) is normalized by the combination of absorption signals integrated over all product recoil directions $\mathbf{k}$: $\langle I_Z \rangle + \langle I_X \rangle - 1/3[\langle I_Y^R \rangle + \langle I_Y^L \rangle]$ which is proportional to the total number of the reaction products $\langle \rho_{00} \rangle$ neglecting the rank 4 terms.¹⁰⁴ Alternatively, Eq. (A2) can be normalized by the sum of two-photon absorption intensities with linear polarizations along three Cartesian axes: $\langle I_X \rangle + \langle I_Y \rangle + \langle I_Z \rangle$. However, the normalization form given in Eq. (A2) has an advantage because the determination of the product total population for any angular space distribution can be carried out by changing only the probe laser polarization, without moving the probe beam direction.¹⁰⁴

An experimental scheme which can be used for determination of the product angular momentum alignment is given in Fig. 7(b). In this case, the absorption signal can be written as

$$\begin{aligned} & \frac{I_Z(\theta) - I_Y(\theta)}{\langle I_Z \rangle + \langle I_X \rangle - 1/3[\langle I_Y^R \rangle + \langle I_Y^L \rangle]} \\ &= \frac{\sqrt{2j+1}}{2} \left[\frac{P_2}{P_0} \Re[\rho_{20}^{(j)}(\theta)] + \frac{\sqrt{6}}{3} \Re[\rho_{22}^{(j)}(\theta)] \right] \\ &+ \frac{P_4}{12P_0} \left(5\Re[\rho_{40}^{(j)}(\theta)] - 2\sqrt{10}\Re[\rho_{42}^{(j)}(\theta)] \right. \\ &\quad \left. - \sqrt{70}\Re[\rho_{44}^{(j)}(\theta)] \right), \end{aligned} \quad (\text{A3})$$

where P_2 , P_4 are line strength factors and the symbol $\Re$ denotes the real part of the corresponding state multipoles.

In Eq. (A3), difference between the absorption signals with light polarization along Z and Y axes is used for elimination of the contributions from the zeroth rank and all odd rank state multipoles from the signal.

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