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Using quantum rotational polarization moments to describe the stereodynamics of the $\text{H} + \text{D}_2(\nu=0, j=0) \rightarrow \text{HD}(\nu', j') + \text{D}$ reaction

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We present results of quantum calculations we have performed on the title reaction in order to study its stereodynamics at collision energies of 0.54 and 1.29 eV. Our theoretical model is based on a representation where directional properties are expressed in terms of real rotational polarization moments instead of magnetic quantum numbers. We analyze the physical meaning of rotational polarization moments and show that, when defined as in the present work, these quantities directly describe the reaction stereodynamics in terms of intuitive chemical concepts related to preferences in the reaction mechanism for particular planes and senses of molecular rotation. Using this interpretation, we identify two distinct regimes for the stereodynamics of the title reaction, observed when HD is formed with low or high rotational excitation. We also identify relevant characteristics of both regimes: (i) the existence and location of preferred planes and senses of molecular rotation, (ii) correlations between these preferences, the scattering angle and the reaction probability, and (iii) their dependence on the collision energy. © 1998 American Institute of Physics. [S0021-9606(98)02407-6]

I. INTRODUCTION

When two atoms or molecules collide, the chances that they react are determined not only by their internal states and collision energy, but also by their relative orientations and their relative directions of motion: the reaction probability can be enhanced or diminished when the reagents approach along particular directions or when the molecules rotate with particular senses in particular planes. The same reasoning applies to reaction products. If we want to define sharply the outcome of a reactive collision we have to identify not only the products formed, their internal states and recoil energy, but also their relative directions of motion. Chemical reactions are intrinsically anisotropic; their dynamics depends on directions in space. Understanding the stereodynamics of chemical reactions (i.e., the directional aspects of their dynamics) is important for the study of reaction properties in general and for the elucidation of their molecular mechanisms in particular.¹⁻¹⁰

Today there are several strategies one can use to study the stereodynamics of chemical reactions. The various review articles¹⁻¹⁰ and special issues of journals¹¹⁻¹⁶ dedicated to this subject constitute invaluable sources of information. Experimentally there are now different techniques that can probe the stereodynamics of chemical reactions, and measurements are revealing details about reaction mechanisms that show not only how the reactions depend on the relative motion of reactants, but also what is the relative motion of the products.^{6-10,16-19} The ultimate goal is to perform a

“complete” experiment correlating all directions of motion on the reactants’ and products’ sides of chemical reactions.²⁰ Such an experiment would provide rich dynamical information otherwise lost by averaging over the random azimuthal orientation of the impact parameters.

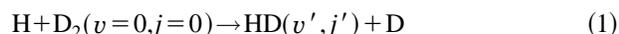
Significant progress has also been made on the theoretical side. In principle, complete descriptions of the stereodynamics can be obtained whenever one performs unconstrained three-dimensional quasiclassical or quantum scattering calculations. The full exploitation of the completeness of these calculations, however, is only beginning (see, for instance, Refs. 21-24). Most of the quantum scattering or quasiclassical trajectories data published to date correspond to results that are averaged or summed over the quantities related to the stereochemical aspects of the reaction dynamics. This underexploitation of theoretical data is due on one hand to the lack of experimental results enabling a detailed comparison between theory and experiment, and on the other hand to a lack of chemically appealing tools of analysis. For example, in quantum scattering studies the directional dependence is traditionally expressed in terms of scattering angles and magnetic quantum numbers. It is not easy for the chemist to use this information to produce simple, easy-to-rationalize pictures of the stereodynamics of chemical reactions.

Two of us have recently presented rigorous equations necessary to transform the usual quantum description of the dynamics of atom-diatom reactions to a representation where

the directional dependence is expressed not in terms of scattering angles and magnetic quantum numbers, but in terms of scattering angles and rotational polarization moments.²¹ As we will show in this paper, this last representation is ideally suited for the complete quantum-mechanical description of the stereodynamics of chemical reactions. Rotational polarization moments are attractive from a chemical perspective, being intrinsically associated with intuitive chemical concepts such as in-plane versus out-of-plane reactions.

The use of polarization moments to describe reaction dynamics is not new; they were used long ago to describe angular correlations in nuclear reactions.^{25–32} More recently, they have also been used in studies of photodissociation,^{33–37} photoionization,^{38–42} and inelastic molecular collisions.^{43–48} Their application to chemical reactions has followed the pioneering work of Herschbach *et al.*^{20,49–52} and now spreads to a variety of problems including their determination with classical or experimental methods.^{6–9,16–19,22,23,53,54}

This article presents the first exact, quantum-mechanical calculation of rotational polarization moments for a chemical reaction. We have applied the equations derived in Ref. 21 to the benchmark reaction



at the experimentally accessible collision energies of 0.54 and 1.29 eV, and obtained a detailed and quantitative account of its stereodynamics. We have chosen reaction (1) for this study for its importance (along with its isotopical variants) as the simplest prototypical chemical reaction,^{55,56} for its status as a primary test case in the development of new dynamical theories and experiments,^{55–65} and for being a promising system with regard to the experimental determination of the quantities we have calculated. One of our purposes in this paper is to show that even for a reaction as thoroughly studied as (1) the analysis of the rotational polarization moments reveals rich dynamical information that is lost when the reaction's directional properties are not explicitly considered.

The paper is organized as follows. In section II we present the mathematical expressions used in the calculation of the quantum rotational polarization moments. Then in section III we discuss their physical meanings and how they compare to their classical counterparts. Section IV is dedicated to the application of these methods to reaction (1), and is divided in two parts. In section IV A we give details of our scattering calculations, while in IV B we present and discuss the results we obtained. The main results and conclusions are then summarized in section V.

II. COMPLEX AND REAL ROTATIONAL POLARIZATION MOMENTS

If nuclear and electronic spins are ignored, an atom-diatom reaction



has four vectors that can be specified or measured experimentally. These are the vectors that describe the relative motions of the reacting species: the relative velocities of reagents and products (\mathbf{k} and \mathbf{k}' , respectively) and the

rotational angular momenta of the reagent and product diatomic molecules (\mathbf{j} and \mathbf{j}'). Knowledge of the correlations between these four vectors is all one needs to completely describe the stereodynamics of atom-diatom reactions.^{20,21}

The spatial distributions of the \mathbf{k} and \mathbf{k}' vectors can be specified simply by the probabilities that they point along any particular directions. As for the quantized \mathbf{j} and \mathbf{j}' vectors, it is convenient to expand their spatial distributions as sums of multipolar distributions.^{6,32,66,67} For a fixed j value, for instance, the monopole moment (the coefficient of the monopolar distribution in the expansion series) gives the total population of that rotational level, while the other multipole moments (dipole, quadrupole, octopole, and so on) give the relative contributions of each multipolar distribution, or, in other words, the relative contributions of different polarizations of \mathbf{j} .^{6,66,67} The operators associated with the multipole moments are the state multipoles $T^{(K_j)}$, also called Fano polarization operators. Non-vanishing multipole moments must have $0 \leq K_j \leq 2j$.⁶⁶ The use of state multipoles allows us to rewrite an arbitrary \mathbf{j} distribution as a sum of a finite number of terms, each one of them having a precise and well-known physical meaning.^{32,66,67} This gives physical insight into the arbitrary \mathbf{j} distribution and provides criteria for comparing different distributions. Furthermore, as we will show, the multipole moments can be combined to form quantities that directly describe the relative contributions to the reaction mechanism of particular planes and senses of rotation.

As mentioned above, the \mathbf{k} - \mathbf{j} - \mathbf{k}' - \mathbf{j}' vector correlation completely describes the stereodynamics of atom-diatom reactions. It can be expressed as the joint probability function that \mathbf{k} and \mathbf{k}' point along any particular directions when \mathbf{j} and \mathbf{j}' have particular multipolar moments. Quantum-mechanical expressions for this probability function have been derived and discussed in detail in Ref. 21, where we presented formulas adapted to both the orbital angular momentum and the helicity representations of the scattering problem, with either space-fixed or body-fixed reference frames. In the present article we extend that formalism by introducing real rotational polarization moments, observable quantities that can be easily calculated once the (complex) multipolar moments have been obtained. As will become clear in the next section, this extension of the formalism presented in Ref. 21 maximizes its usefulness from a chemical point of view.

The derivation starts with the expression for the \mathbf{k} - \mathbf{j} - \mathbf{k}' - \mathbf{j}' correlation in the helicity representation with body-fixed frames.²¹ The entrance-channel frame xyz has its z axis parallel to \mathbf{k} , while in the exit-channel frame $x'y'z'$ the z' axis is parallel to \mathbf{k}' ; the y and y' axes are both parallel to $\mathbf{k} \times \mathbf{k}'$. The rotational-space density matrices of the entrance and exit channels are respectively expanded in terms of the state multipoles $T^{(K_j)}$ and $T^{(K'_j)}$ as

$$\langle j_1 \Omega_1 | \rho | j_2 \Omega_2 \rangle = \sum_{K_j, Q_j} \rho_{Q_j}^{(K_j)}(j_1 j_2) \langle j_1 \Omega_1 | T_{Q_j}^{(K_j)} | j_2 \Omega_2 \rangle, \quad (3a)$$

$$\langle j'_1 \Omega'_1 | \rho | j_2 \Omega_2 \rangle = \sum_{K'_j, q'_j} \rho_{q'_j}^{(K'_j)}(j'_1 j'_2) \langle j'_1 \Omega'_1 | T_{q'_j}^{(K'_j)} | j_2 \Omega_2 \rangle, \quad (3b)$$

where Ω and Ω' are the helicity quantum numbers in the entrance and exit channels (respectively, projections of \mathbf{j} on \mathbf{k} and of \mathbf{j}' on \mathbf{k}'), and $\rho_{Q_j}^{(K_j)}(j_1 j_2)$ and $\rho_{q'_j}^{(K'_j)}(j'_1 j'_2)$ are the expansion coefficients — the multipolar rotational polarization moments. K_j ranges from $|j_1 - j_2|$ to $j_1 + j_2$, while Q_j ranges from $-K_j$ to K_j , and similarly for K'_j and q'_j . Note that the components of the entrance- and exit-channel state multipoles are indicated by different symbols (Q_j and q'_j); this is because they are referred to different frames.

Given the expansions (3a) and (3b), the $\mathbf{k}\text{-}\mathbf{j}\text{-}\mathbf{k}'\text{-}\mathbf{j}'$ correlation formula reads²¹

$$\begin{aligned} & \rho_{q'_j}^{(K'_j)}(v', j'_1, j'_2, \theta) \\ &= (-1)^{j_1 + j_2 + j'_1 + j'_2} \sum_{K_j, Q_j} \rho_{Q_j}^{(K_j)}(v, j_1, j_2) \\ & \quad \times c_{K_j Q_j K'_j q'_j}(v, j_1, j_2, v', j'_1, j'_2, \theta), \end{aligned} \quad (4)$$

where θ is the scattering angle between \mathbf{k} and \mathbf{k}' . The correlation coefficient c is given by

$$\begin{aligned} & c_{K_j Q_j K'_j q'_j}(v, j_1, j_2, v', j'_1, j'_2, \theta) \\ &= \sum_{J_1, J_2, \Omega_1, \Omega_2} (2J_1 + 1) d_{\Omega_1 \Omega'_1}^{J_1}(\theta) S_{v' j'_1 \Omega'_1 \leftarrow v j_1 \Omega_1}^{J_1} \\ & \quad \times (2J_2 + 1) d_{\Omega'_2 \Omega_2}^{J_2}(\theta) S_{v' j'_2 \Omega'_2 \leftarrow v j_2 \Omega_2}^{J_2*} \\ & \quad \times \langle j_1 \Omega_1 | T_{Q_j}^{(K_j)} | j_2 \Omega_2 \rangle \langle j'_1 \Omega'_1 | T_{q'_j}^{(K'_j)} | j'_2 \Omega'_2 \rangle, \end{aligned} \quad (5)$$

where J stands for the total angular momentum, and S^J and $d^J(\theta)$ are respectively the scattering and reduced Wigner rotation matrices.

Apart from its more explicit notation, Eq. (4) differs from the one presented in Ref. 21 in three minor aspects. First, it is presented here in a state-to-state form; the sums over rotational and vibrational quantum numbers were dropped. Second, the normalization constant used when flux normalization is required (see Ref. 21) was eliminated; we will not need flux normalization here. Third, the formula we just presented is written in terms of the multipolar moments and not in terms of the expectation values $\langle T_{Q_j}^{(K_j)} \rangle$ and $\langle T_{q'_j}^{(K'_j)} \rangle$; this choice appears to be preferred in studies of reaction stereodynamics, and we shall adopt it from now on.

The rotational polarization moments defined by Eq. (3) are in general complex quantities. It follows from Eq. (3), however, that they have the symmetry property

$$\rho_{Q_j}^{(K_j)}(j_1 j_2) = (-1)^{j_2 - j_1 - Q_j} [\rho_{-Q_j}^{(K_j)}(j_2 j_1)]^*. \quad (6)$$

This makes it simple to define real rotational polarization moments. Such a definition is particularly useful when we

consider sharply-defined rotational states, $j_1 = j_2 = j$ and $j'_1 = j'_2 = j'$. We follow the Hertel and Stoll scheme^{6,68} and define the real (and renormalized) rotational polarization moments by

$$\begin{aligned} \rho_{Q_j+}^{\{K_j\}}(j) &= \frac{1}{\sqrt{2} \rho_0^{(0)}(j)} [(-1)^{Q_j} \rho_{Q_j}^{(K_j)}(j) + \rho_{-Q_j}^{(K_j)}(j)], \\ 1 &\leq Q_j \leq K_j, \end{aligned} \quad (7a)$$

$$\begin{aligned} \rho_{Q_j-}^{\{K_j\}}(j) &= \frac{i}{\sqrt{2} \rho_0^{(0)}(j)} [(-1)^{Q_j} \rho_{Q_j}^{(K_j)}(j) - \rho_{-Q_j}^{(K_j)}(j)], \\ 1 &\leq Q_j \leq K_j, \end{aligned} \quad (7b)$$

$$\rho_0^{\{K_j\}}(j) = \frac{\rho_0^{(K_j)}(j)}{\rho_0^{(0)}(j)}. \quad (7c)$$

Real polarization moments (and real polarization operators) are also related to expansions of density matrices. In fact, given the definition (7) it is a simple matter to show that considering the restriction $j_1 = j_2 = j$ we can rewrite Eq. (3a) in the form

$$\begin{aligned} \langle j \Omega_1 | \rho | j \Omega_2 \rangle &= \rho_0^{(0)}(j) \sum_{K_j=0}^{2j} \left\{ \rho_0^{\{K_j\}}(j) \langle j \Omega_1 | T_0^{\{K_j\}} | j \Omega_2 \rangle \right. \\ & \quad + \sum_{Q_j=1}^{K_j} \left[\rho_{Q_j+}^{\{K_j\}}(j) \langle j \Omega_1 | T_{Q_j+}^{\{K_j\}} | j \Omega_2 \rangle \right. \\ & \quad \left. \left. + \rho_{Q_j-}^{\{K_j\}}(j) \langle j \Omega_1 | T_{Q_j-}^{\{K_j\}} | j \Omega_2 \rangle \right] \right\}, \end{aligned} \quad (8)$$

where the real operators $T^{\{K_j\}}$ are related to the spherical tensors $T^{(K_j)}$ by

$$T_{Q_j+}^{\{K_j\}} = \frac{1}{\sqrt{2}} [(-1)^{Q_j} T_{Q_j}^{(K_j)}(j) + T_{-Q_j}^{(K_j)}(j)], \quad 1 \leq Q_j \leq K_j, \quad (9a)$$

$$T_{Q_j-}^{\{K_j\}} = \frac{1}{i\sqrt{2}} [(-1)^{Q_j} T_{Q_j}^{(K_j)}(j) - T_{-Q_j}^{(K_j)}(j)], \quad 1 \leq Q_j \leq K_j, \quad (9b)$$

$$T_0^{\{K_j\}} = T_0^{(K_j)}. \quad (9c)$$

Note that (9b) is not strictly analogous to (7b).

Use of complex or real polarization moments is a matter of convenience. In mathematical and computational terms it is more convenient to use the complex moments. They possess a series of symmetry and group-theoretical properties³² that make it easier to express and actually evaluate them. The simple way in which they transform under rotation of coordinate frames is especially handy, since it allows us to compute their values in any coordinate frame with relative ease.⁶⁷ In physical terms it may also be more convenient to use the complex moments, because they give the relative importances of the respective multipolar distributions and such an interpretation may be what one is looking for.

Real rotational polarization moments have lower symmetry than their complex counterparts, and the way they

transform under rotation is not as straightforward. Their physical meaning is also quite different: they are not associated to multipolar distributions, but rather to the linear combinations of multipolar distributions defined by Eqs. (7)–(9). This different physical meaning is precisely what makes it interesting to use them in the description of chemical stereodynamics. Let us now turn our attention to it.

III. PHYSICAL MEANING OF REAL ROTATIONAL POLARIZATION MOMENTS

Complex polarization moments are intrinsically associated with the so-called *spherical* (not to be confused with spherical polar) or *cyclic* coordinates.^{66,67,69} Cyclic coordinates are complex and cannot be visualized in real three-dimensional space. Real polarization moments, on the other hand, are always defined in a way that gives them a precise (and visualizable) meaning in Cartesian space, as done in definition (7).

The best way to get a clear idea of the physical meaning of real rotational polarization moments is to consider them at their classical limit.^{67,70} When j becomes large, the density matrix elements $\langle j\Omega_1|\rho|j\Omega_2\rangle$ approach the coefficients of the Fourier expansion of the classical probability density $\rho_j(\theta_j, \phi_j)$ (where θ_j and ϕ_j are the angles that specify the direction of the \mathbf{j} vector in polar coordinates).^{71,72} It follows from this that if we expand the classical probability density in terms of spherical harmonics $Y_{K_j Q_j}(\theta_j, \phi_j)$,

$$\rho_j(\theta_j, \phi_j) = \sum_{K_j=0}^{\infty} \sum_{Q_j=-K_j}^{K_j} \rho_{Q_j}^{(K_j)}(j) Y_{K_j Q_j}(\theta_j, \phi_j), \quad (10)$$

then in the correspondence principle limit the classical and quantum expansion coefficients become equal.^{67,70}

As in the quantum case, we can expand the classical probability density in terms of real polarization moments and ‘‘real harmonics’’ defined in analogy with Eqs. (7)–(9). In the correspondence principle limit, the classical and quantum real polarization moments must again be the same.

Let us now consider the classical real polarization moments in detail. Because the probability density must be always finite and non-negative, the rotational polarization moments must fall within well-defined ranges.^{6,67} Figures 1 and 2 show angular momentum distributions associated with particular real polarization moments, and also the total distributions when these moments take either their maximum or minimum value and all other moments (except $\rho_0^{(0)}$, which equals 1 by definition) vanish. The question we will now address is the following: what can we learn about the reaction dynamics when the rotational angular momenta of reagents or products are distributed as in Figures 1 and 2?

Consider the real polarization moment $\rho_0^{(1)}$ shown in Figure 1(a). When $\rho_0^{(1)}$ is the only nonvanishing real polarization moment apart from $\rho_0^{(0)}$, the most extreme angular momentum distributions we can have are those depicted in Figures 1(b) and 1(c). Respectively, they are observed when $\rho_0^{(1)}$ takes its maximum or minimum value. The key observation to be made here is that Figures 1(b) and 1(c) show net orientations of the angular momentum vector with regard to the Z axis. In Figure 1(b) (maximum positive $\rho_0^{(1)}$) this vec-

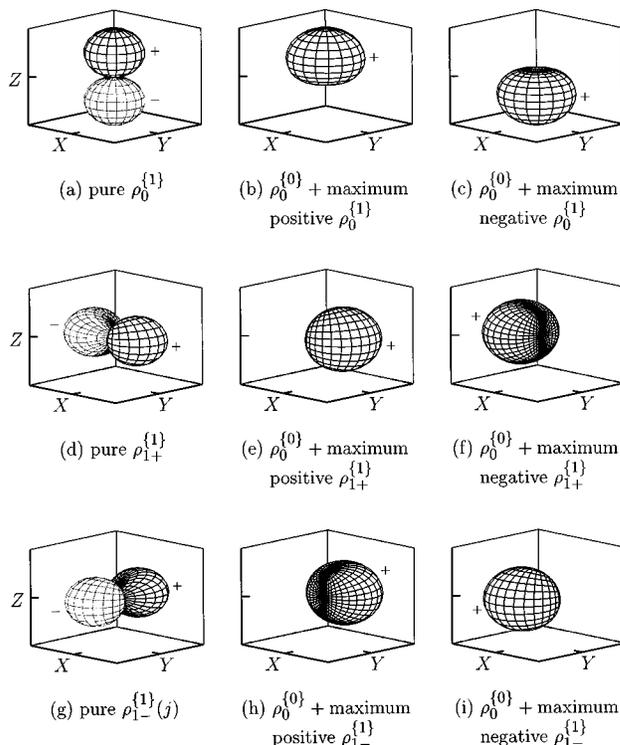


FIG. 1. Spatial distributions of rotational angular momentum vectors associated with real rotational polarization moments of rank 1. The probability functions shown are positive where drawn in black and negative where drawn in gray. Note that distributions containing negative probabilities do not represent a real physical situation ($\rho_0^{(0)}$ can never vanish) and are shown here only for illustration purposes.

tor is preferentially parallel to Z, while in Figure 1(c) it is preferentially anti-parallel to Z. In terms of molecular motion, Figures 1(b) and 1(c) are related to preferred senses of rotation: Figure 1(b) (maximum positive orientation) shows preference for positive (right-handed) rotation with regard to the XY plane, while Figure 1(c) (maximum negative orientation) indicates preference for negative (left-handed) rotation with regard to the XY plane.

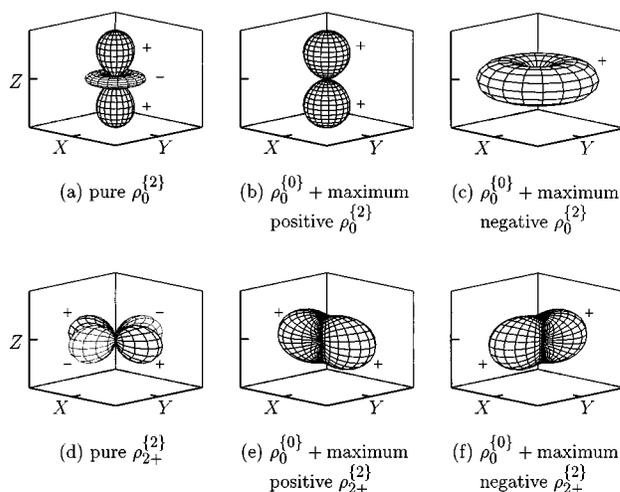


FIG. 2. As in Figure 1, but with real rotational polarization moments of rank 2.

Suppose first that we are looking at the entrance channel of our atom-diatom reaction (2). The angular momentum we consider is \mathbf{j} , and the frame XYZ coincides with xyz as defined in the second paragraph of section II. That is, the approach direction is parallel to Z and the recoil direction lies in the half plane $XZ, X > 0$. The chemical picture that emerges then from Figures 1(b) and 1(c) is that of the atom A approaching the diatomic BC and seeing it rotate like a helix (i.e., in the plane perpendicular to the approach direction). If the reaction probability is larger when the polarization moment $\rho_0^{\{1\}}(j)$ is positive, this means that reaction is more likely to occur when the helix rotates clockwise from the atom's point of view. If the reaction probability increases when $\rho_0^{\{1\}}(j)$ becomes negative, this means that reactions with anticlockwise-rotating helices are preferred.

Suppose now that we are examining the products' side of the reaction. We consider the angular momentum \mathbf{j}' , and the frame XYZ coincides with $x'y'z'$: Z is parallel to the recoil direction, and the approach direction lies in the half plane $XZ, X < 0$. The situation then is the following: the atom C recoils from the molecule AB along a direction that is perpendicular to AB 's plane of rotation; if $\rho_0^{\{1\}}(j')$ is positive, this is so because our reaction is forming AB molecules that preferably rotate in the positive direction (i.e., \mathbf{j}' parallel to the recoil direction is preferred), and the other way round for negative $\rho_0^{\{1\}}(j')$.

Before moving on to the meanings of other polarization moments, we must make two comments about the considerations above. The first one is that the axes of our "helices" may not be perfectly parallel to the approach or recoil directions. That is, \mathbf{j} and \mathbf{j}' may not be perfectly parallel or antiparallel to \mathbf{k} and \mathbf{k}' ; this is indeed the case when they are distributed as in Figure 1(b) or 1(c). The second comment is that a brief reflection over the symmetry of the problem shows that reactions with helices that rotate clockwise cannot be preferred over reactions with helices that rotate anticlockwise. Although the preparation of the reagent diatomic with nonvanishing $\rho_0^{\{1\}}(j)$ can change the rotational polarization of the product diatomic AB , it cannot change the probability that AB is produced. And if the reagents are unpolarized, the $\rho_0^{\{1\}}(j')$ polarization moment of the products must necessarily vanish. This is so because the $\rho_0^{\{1\}}$ polarization moments are related to rotations that are not symmetric with regard to reflection in the scattering \mathbf{k}, \mathbf{k}' plane. A mathematical confirmation of these observations can be obtained by an analysis of the symmetry properties of the correlation coefficients defined in Eq. (5).

Consider now the polarization moment $\rho_{1+}^{\{1\}}$, shown in Figure 1(d). As comparison with Figure 1(a) shows, this polarization moment is similar to the $\rho_0^{\{1\}}$ moment discussed above, except that it describes orientation along the X axis and not along Z as in the previous case. On the reagents' side, we have to think about the atom A approaching the molecule BC along a direction that is parallel to its plane of rotation and leading to a reaction in which the recoil direction is not parallel to BC 's plane of rotation. Positive or negative values of $\rho_{1+}^{\{1\}}(j)$ are related to reactions where BC rotates in one sense or another. On the products' side the

situation is analogous, except that then we have the recoil direction lying parallel to the plane in which the product diatomic AB rotates while the approach direction is not parallel to it. As above, an analysis of symmetry with regard to reflection in the scattering plane shows that $\rho_{1+}^{\{1\}}(j')$ must necessarily vanish unless the reagent molecule BC is prepared with some handedness in its rotational motion, and that nonvanishing $\rho_{1+}^{\{1\}}(j)$'s cannot contribute to reactions leading to unoriented product rotational angular momenta and cannot affect the reaction cross sections.

The last polarization moment of rank 1 to be considered is $\rho_{1-}^{\{1\}}$, shown in Figure 1(g). This polarization moment describes orientation along the $\mathbf{k} \times \mathbf{k}'$ axis. The reagents' polarization moment $\rho_{1-}^{\{1\}}(j)$ is related to reactions where the plane of rotation of the reagent diatomic BC is parallel to the scattering plane (i.e., parallel to both the approach and recoil directions), while the products' polarization moment $\rho_{1-}^{\{1\}}(j')$ is related to reactions where it is the product diatomic AB that rotates in a plane parallel to \mathbf{k} and \mathbf{k}' . Positive or negative values of $\rho_{1-}^{\{1\}}$ mean in either case that there is a preferred sense of rotation. In contrast to the cases above, a nonvanishing reagents' $\rho_{1-}^{\{1\}}(j)$ polarization moment can (and most probably will) enhance or diminish the reaction probability regardless of the polarization of the products. Similarly, the probabilities that the product diatomic rotates clockwise or anticlockwise with regard to the scattering plane will in general be different, even when the reagents are completely unpolarized; the products' polarization moment $\rho_{1-}^{\{1\}}(j')$ gives a quantitative measure of how different these probabilities actually are.

The discussion above concerns polarization moments of rank 1. As we have just shown, rotational polarization moments of rank 1 correlate reaction probabilities to particular senses of molecular rotation. In other words, they are *orientation* moments.^{6,73} We will now turn our attention to polarization moments of rank 2, the so-called *alignment* moments. They correlate reaction probabilities to particular planes of molecular rotation without regard for the sense of rotation in that plane.^{6,73}

There are five polarization moments of rank 2. Two of those ($\rho_0^{\{2\}}$ and $\rho_{2+}^{\{2\}}$) describe alignment with regard to the X, Y and Z axes. The other three ($\rho_{1+}^{\{2\}}$, $\rho_{1-}^{\{2\}}$ and $\rho_{2-}^{\{2\}}$) describe alignment with regard to transversal directions ($X+Y, X-Z, Y+Z$, etc.). Our analysis of their physical meanings has convinced us that the most useful dynamical information is to be obtained from the moments related to the X, Y , and Z axes, and for that reason we will restrict our discussion to $\rho_0^{\{2\}}$ and $\rho_{2+}^{\{2\}}$.

The angular distribution function associated with $\rho_0^{\{2\}}$ is shown in Figure 2(a). When this polarization moment is the only one with $K_j \neq 0$ not to vanish and its value is maximum or minimum, the corresponding probability functions for the spatial distribution of the rotational angular momentum vector are those plotted in Figures 2(b) and 2(c). In Figure 2(b) the rotational angular momentum vector is aligned along Z , which relates to molecules rotating in planes parallel to XY but without preference for clockwise or anticlockwise rotations. On the other hand, Figure 2(c) corresponds to a situa-

tion where the rotational angular momentum vector is preferably parallel to the XY plane but has no net orientation or alignment with regard to any axis in this plane. In terms of the entrance-channel dynamics, Figure 2(b) [positive $\rho_0^{\{2\}}(j)$] corresponds to reagents approaching along a direction perpendicular to the plane in which BC rotates, while Figure 2(c) [negative $\rho_0^{\{2\}}(j)$] represents a case where the approach direction is parallel to BC 's plane of rotation. In terms of the products' side of the reaction, positive and negative values of $\rho_0^{\{2\}}(j')$ describe situations where the recoil direction is respectively perpendicular or parallel to the plane where the product diatomic rotates.

The polarization moment that describes alignment relative to the X and Y axes is $\rho_{2+}^{\{2\}}$ [Figure 2(d)]. Probability distributions obtained when other polarization moments vanish and $\rho_{2+}^{\{2\}}$ is maximum or minimum are shown in Figures 2(e) and 2(f). When $\rho_{2+}^{\{2\}}$ is positive one has alignment along the X axis; when it is negative the alignment is along Y . Let us first consider the entrance channel. The approach direction being parallel to the plane where the reagent diatomic rotates, positive/negative values of $\rho_{2+}^{\{2\}}(j)$ respectively indicate preference for recoil directions not parallel/parallel to that same plane. In other words, positive/negative values of $\rho_{2+}^{\{2\}}(j)$ respectively indicate preference for planes of BC rotation perpendicular/parallel to the scattering plane; we will use the terms "out-of-plane"/"in-plane" to refer to these preferences. In the exit channel we have to think about reactions in which the recoil direction is parallel to the plane of rotation of the product diatomic while the approach direction is or is not parallel to that plane. Positive values of $\rho_{2+}^{\{2\}}(j')$ indicate preference for out-of-plane reactions (in which the scattering plane is preferentially perpendicular to the plane of AB rotation), while negative values show that in-plane mechanisms (where the two planes are preferentially parallel) dominate.

In this article our attention will be restricted to rotational polarization moments of rank 1 and 2. These are the only polarization moments that can be related to particular planes of molecular rotation, and for that reason they are the most useful when one wants to describe the reaction mechanism in terms of intuitive chemical concepts such as in-plane versus out-of-plane reactions and so on. Note, however, that this does not mean that the information contained in the higher-rank polarization moments is uninteresting. Those moments describe correlations between different planes of rotation. For instance, $\rho_{1-}^{\{3\}}$ describes the probability that the rotational angular momentum is aligned with regard to Z and simultaneously oriented along Y , while $\rho_{4+}^{\{4\}}$ is related to simultaneous alignment relative to X and Y . This correlated information can be useful in sharpening the description of the reaction stereodynamics given by the (uncorrelated) polarization moments of rank 1 and 2.

We would also like to stress that although the discussion above is centered on the classical limit of the quantum rotational polarization moments, the reasoning we developed also applies in the quantum regime. The quantum and classical real rotational polarization moments describe the reaction stereodynamics in the same manner.^{67,70} Note, however,

that we have restricted our discussion of real polarization moments to well-defined j and j' . Real polarization moments can also be defined when different angular momentum eigenstates get coherently superposed (i.e., when $j_1 \neq j_2$ or $j'_1 \neq j'_2$), but in that case the discussion about the quantum-classical transition gets more involved than the one we just presented. Another noteworthy point is that, just like their classical counterparts, the numerical values of the quantum polarization moments are restricted to well defined ranges. This is so because of the properties of the density matrix (it is Hermitian, positive definite and has unit trace²⁹) and because of the restricted values of the magnetic quantum numbers. The quantum ranges, however, are not fixed: they depend on the values of j and j' and tend to the classical ranges in the correspondence principle limit. Explicit expressions for the allowed ranges of quantum rotational polarization moments of rank 0, 1 and 2 are presented along with their classical limits in Table I.

Before we close this section, it may be useful to say a few words about the specification of angular momentum distributions with regard to different directions in space. At first sight this may seem to be in conflict with the uncertainty principle, which says that if we know the angular momentum projection on the quantization axis Z we cannot simultaneously obtain information about its projection along the X or Y directions. In our case we can obtain information about angular momentum projections with regard to different directions because we are not dealing with pure angular momentum eigenstates but rather with coherent superpositions of them.^{67,70} For instance, the polarization moment $\rho_{1-}^{\{1\}}(j)$ is related to coherent superpositions of eigenstates with different magnetic quantum numbers: $|j\Omega\rangle$ and $|j\Omega+1\rangle$. The fact that the magnetic quantum numbers differ brings uncertainty into j_z , and this is what allows us to obtain \mathbf{j} distributions that are localized in the xy plane.⁷⁰ The situation is different when we consider polarization moments of component 0, such as $\rho_0^{\{1\}}(j)$ and $\rho_0^{\{2\}}(j)$. Then both j and its projection on z are well defined. As Figures 1(a)–1(c) and 2(a)–2(c) show, in such cases the \mathbf{j} distributions we obtain are not localized in any way in the xy plane. They have cylindrical symmetry around the z axis, as required by the uncertainty principle.

IV. APPLICATION TO $\text{H}+\text{D}_2 \rightarrow \text{HD}+\text{D}$

The main results of our application of the methods discussed in sections II and III to reaction (1) are the numerical values of the quantum real rotational polarization moments. Once the scattering matrix has been obtained, calculation of the quantum polarization moments is a simple task that can be easily done by a straightforward implementation of formulas (4), (5) and (7). Calculation of the scattering matrix, on the other hand, is not as simple. For this reason we start this section with a description of the methods and parameters we used in our scattering calculations.

A. Quantum scattering calculations

The present $\text{H}+\text{D}_2$ quantum reactive scattering calculations were performed on the LSTH potential energy

TABLE I. Physical meanings and allowed quantum and classical ranges of rotational polarization moments of rank 0, 1 and 2.

Polarization moment	Physical meaning: proportional to	Quantum range	Classical range
$\rho_0^{(0)}$	Population	Fixed: $\frac{\text{Pop}(j)}{\sqrt{2j+1}}$	Fixed: $\frac{\text{Pop}(j)}{\sqrt{4\pi}}$
$\rho_0^{(1)}$	$\langle j_z \rangle$	$\left[-\sqrt{\frac{3j}{j+1}}, \sqrt{\frac{3j}{j+1}} \right]$	$[-\sqrt{3}, \sqrt{3}]$
$\rho_{1+}^{(1)}$	$\langle j_x \rangle$	$\left[-\sqrt{\frac{3j}{j+1}}, \sqrt{\frac{3j}{j+1}} \right]$	$[-\sqrt{3}, \sqrt{3}]$
$\rho_{1-}^{(1)}$	$\langle j_y \rangle$	$\left[-\sqrt{\frac{3j}{j+1}}, \sqrt{\frac{3j}{j+1}} \right]$	$[-\sqrt{3}, \sqrt{3}]$
$\rho_0^{(2)}$	$\langle 3j_z^2 - \mathbf{J}^2 \rangle$	$\left[-\sqrt{\frac{5j(j+1)}{(2j-1)(2j+3)}}, \sqrt{\frac{5j(2j-1)}{(j+1)(2j+3)}} \right]$	$\left[-\frac{\sqrt{5}}{2}, \frac{\sqrt{5}}{2} \right]$
$\rho_{1+}^{(2)}$	$\langle j_x j_z + j_z j_x \rangle$	$\left[-\sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}}, \sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}} \right]$	$\left[-\frac{\sqrt{15}}{2}, \frac{\sqrt{15}}{2} \right]$
$\rho_{1-}^{(2)}$	$\langle j_y j_z + j_z j_y \rangle$	$\left[-\sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}}, \sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}} \right]$	$\left[-\frac{\sqrt{15}}{2}, \frac{\sqrt{15}}{2} \right]$
$\rho_{2+}^{(2)}$	$\langle j_x^2 - j_y^2 \rangle$	$\left[-\sqrt{\frac{15j^3}{(j+1)(2j-1)(2j+3)}}, \sqrt{\frac{15j^3}{(j+1)(2j-1)(2j+3)}} \right]$	$\left[-\frac{\sqrt{15}}{2}, \frac{\sqrt{15}}{2} \right]$
$\rho_{2-}^{(2)}$	$\langle j_x j_y + j_y j_x \rangle$	$\left[-\sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}}, \sqrt{\frac{15j(j+1)}{(2j-1)(2j+3)}} \right]$	$\left[-\frac{\sqrt{15}}{2}, \frac{\sqrt{15}}{2} \right]$

surface,⁷⁴ using the same coupled-channel hyperspherical coordinate reactive scattering method as was used in our recent study of F+H₂.⁷⁵

The parameters employed in the calculations were $E_{\text{max}} = 2.65$ eV (measured from the bottom of the H+D₂ reactant valley) and $j_{\text{max}} = 16$. The definition of these parameters is such that all reactant and product rovibrational states with energies less than or equal to j_{max} were retained in the calculations, in addition to one extra vibrational function for each value of j that was included to give a better description of the exchange region. The resulting coupled-channel basis set for total angular momentum $J=0$ contained 73 rovibrational functions with vibrational quantum numbers up to $v=8$ in the H+D₂ arrangement and 110 rovibrational functions with vibrational quantum numbers up to $v'=7$ in the HD+D arrangement. This basis set was found in preliminary convergence tests to give all relevant $J=0$ S -matrix elements accurate to better than 1% at the higher of the two collision energies (1.29 eV) considered in the calculations.

For higher total angular momenta, a truncated body-frame angular momentum basis set was used as described in our earlier work on F+H₂,⁷⁵ with projection quantum numbers up to and including $|\Omega|=6$ retained in each arrangement. Preliminary convergence tests for total angular momentum $J=10$ suggested that this value of Ω_{max} would be sufficient to give accurate rotational polarization moments for the present (collinearly-constrained) reaction, and this was confirmed once the calculations had been completed by repeating them with $\Omega_{\text{max}}=5$. (Rotational polarization mo-

ments and differential cross sections calculated with the two values of Ω_{max} are shown for comparison in Figs. 5–7).

Finally, as in the earlier quantum reactive scattering calculations for the H+D₂ reaction by D'Mello, Manolopoulos and Wyatt,⁷⁶ the geometric phase effect^{64,65} was not incorporated in the present calculations. The latest experimental evidence suggests that the errors so introduced will not be important at the collision energies considered here.^{63,77} Indeed, our calculated rotationally-resolved differential cross sections are in excellent agreement with the recent experimental results of Wrede and Schnieder, obtained at the higher collision energy of 1.29 eV.⁷⁷ The theoretical and experimental differential cross sections are plotted in Fig. 3 ($v'=0$, $j'=0-11$) and Fig. 4 ($v'=1$, $j'=0-11$). The agreement with the state-to-state experimental differential cross sections is very good, and we expect our predictions of other stereodynamical properties to be similarly reliable.

B. Results

Since in reaction (1) the D₂ molecule is in its $j=0$ state, all polarization moments we have to consider here concern the diatomic product HD. The reaction can be described as follows. The reagents H and D₂ approach along the direction \mathbf{k} (defined as the velocity of H relative to D₂ in the center-of-mass frame), with the nonrotating D₂ having its interatomic axis isotropically distributed in space. They collide, react and the products D and HD recoil along the direction \mathbf{k}' (defined as the velocity of HD relative to D in the center-

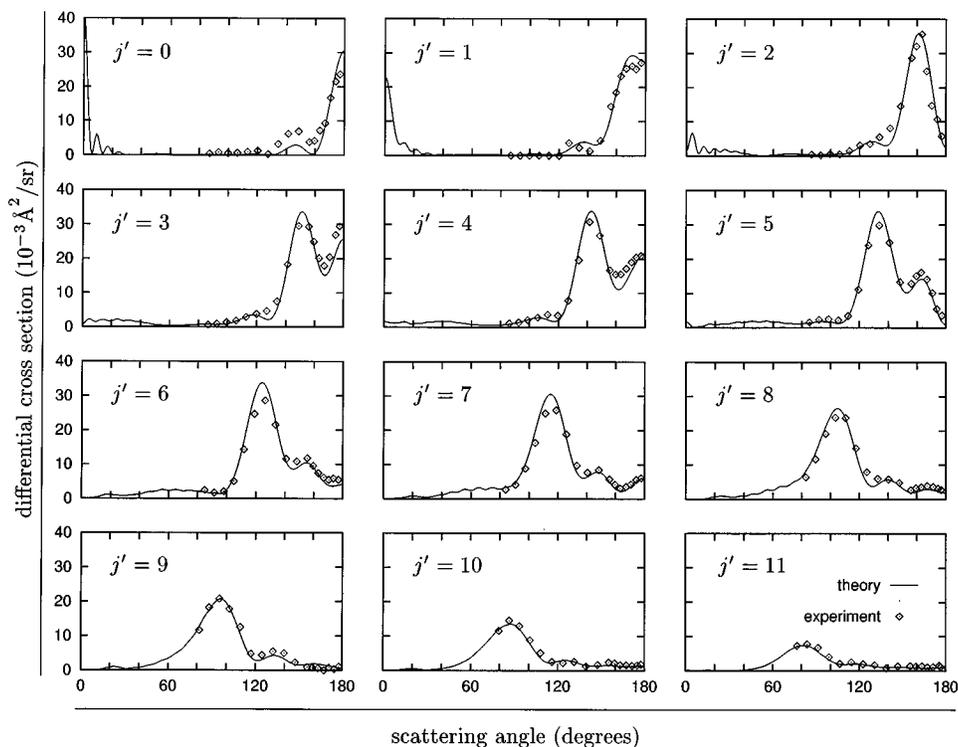


FIG. 3. Theoretical (this work) and experimental (Ref. 77) state-to-state differential cross sections for the $\text{H}+\text{D}_2(v=0, j=0) \rightarrow \text{HD}(v'=0, j') + \text{D}$ reaction at $E_{\text{col}} = 1.29$ eV.

of-mass frame) with HD being in the rotational level j' and having real polarization moments with K'_j up to $2j'$. What we want to know is whether there are correlations tying the scattering angle to the rotational level in which HD is produced, to the plane where it rotates and to the direction of its

rotational motion. We will now show that there are, and that even restricting our analysis to real polarization moments with $K'_j \leq 2$ we can describe them quantitatively and in detail.

Figures 5–7 show our results for the experimentally ac-

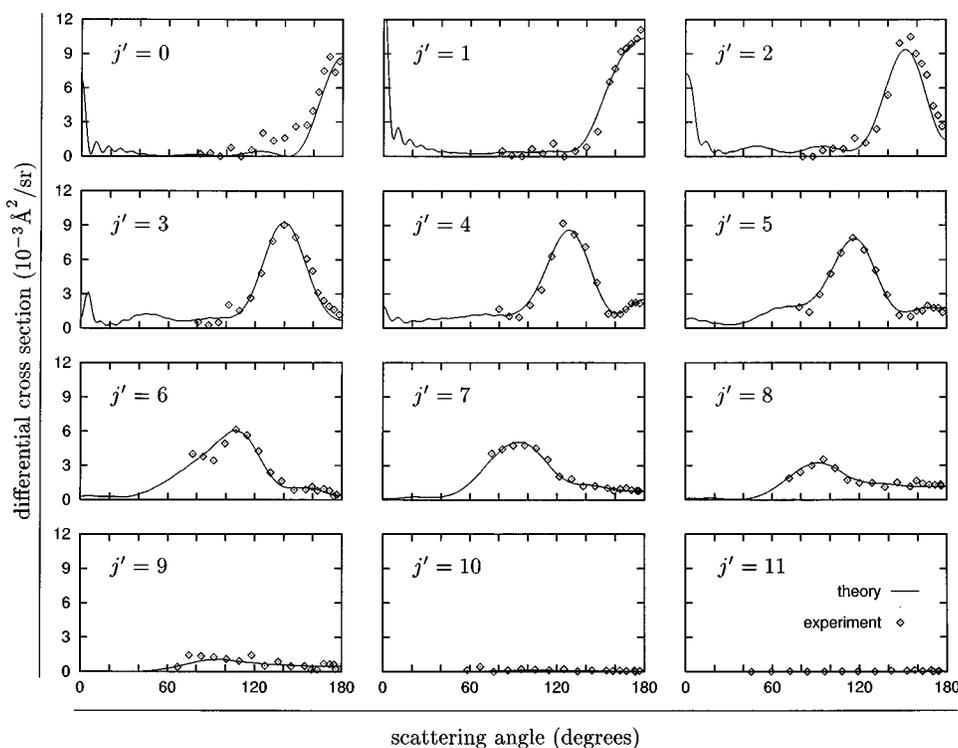


FIG. 4. As in Figure 3, but with $v' = 1$.

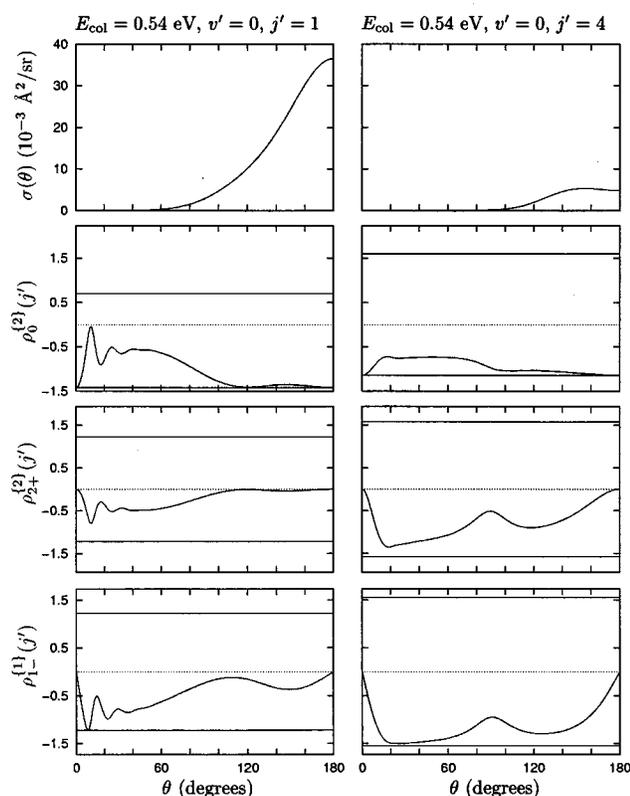


FIG. 5. Stereodynamical data for the $\text{H}+\text{D}_2(v=0,j=0)\rightarrow\text{HD}(v'=0,j')+\text{D}$ reaction at a collision energy $E_{\text{col}}=0.54$ eV. Left column corresponds to $j'=1$, right column to $j'=4$. From top to bottom, data presented correspond to differential cross sections $\sigma(\theta)$ and real rotational polarization moments $\rho_0^{(2)}(j')$, $\rho_{2+}^{(2)}(j')$ and $\rho_{1-}^{(1)}(j')$ referred to the $x'y'z'$ frame. Data represented with solid lines were obtained with $\Omega_{\text{max}}=6$ in the scattering calculations, while data represented with dashed lines were obtained with $\Omega_{\text{max}}=5$. The agreement between the two sets of data illustrates the degree of convergence. Solid horizontal lines in the panels showing polarization moments indicate the limits of their allowed ranges.

ossible collision energies of 0.54 eV (Figure 5) and 1.29 eV (Figures 6 and 7) and the final HD vibrational levels $v'=0$ (Figures 5 and 6) and $v'=1$ (Figure 7). Each one of Figures 5–7 shows, from top to bottom, the calculated differential cross sections and rotational polarization moments $\rho_0^{(2)}(j')$, $\rho_{2+}^{(2)}(j')$ and $\rho_{1-}^{(1)}(j')$ as functions of the scattering angle θ . Solid lines correspond to results obtained with $\Omega_{\text{max}}=6$ in the scattering calculations, while dashed lines correspond to results obtained with $\Omega_{\text{max}}=5$ (see section IV A). The left column displays results for $j'=1$, while the right column shows results for a higher j' . In our examination of the stereodynamical data we have noticed that at the collision energies considered here there are two clearly distinguishable regimes under which reaction (1) proceeds, namely when j' is low or high. Intermediate j' levels show intermediate behavior that tends progressively to one of those limits as j' gets lower or higher. For this reason we restrict our presentation to data corresponding to $j'=1$ and to the highest j' level with a significant cross section compared to the $j'=1$ level at the same collision energy and final HD vibrational state. Finally, we would like to note that Figures 5–7 also show the allowed ranges for the rotational polarization moments displayed in them. These ranges are limited by the

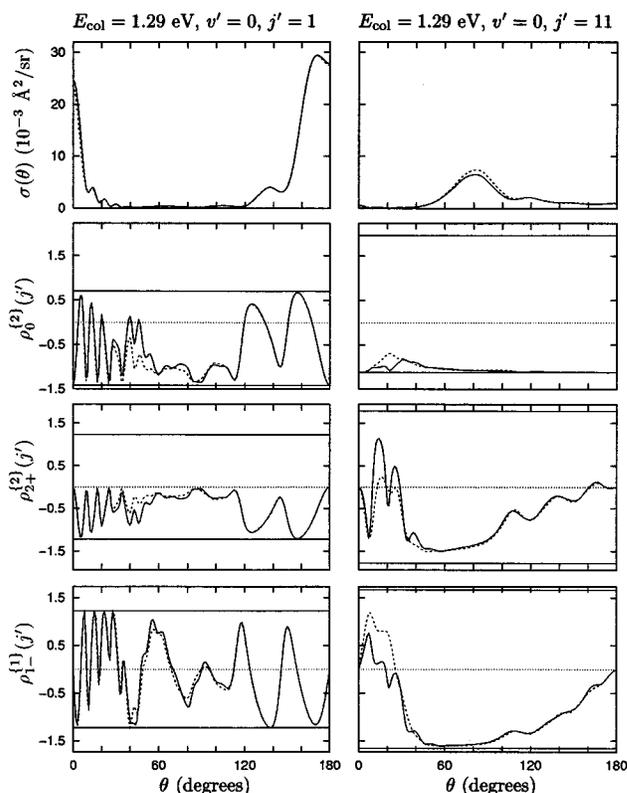


FIG. 6. As in Figure 5, but with $E_{\text{col}}=1.29$ eV, $v'=0$ and $j'=1$ (left column) or $j'=11$ (right column). Note that the difference between the $\Omega_{\text{max}}=5$ (dashed) and $\Omega_{\text{max}}=6$ (solid) results is only significant where the differential cross section $\sigma(\theta)$ (top panel) is very small.

solid horizontal lines shown in the corresponding panels.

Let us now turn to the analysis of the calculated data. We start with Figure 5 ($E_{\text{col}}=0.54$ eV, $v'=0$, $j'=1$ or 4). The differential cross section for production of the $j'=1$ level is maximum at the backward direction ($\theta=180^\circ$) while that for $j'=4$ peaks at $\theta=155^\circ$, but in both cases the reaction probability is largely dominated by scattering with $\theta>100^\circ$. At scattering angles larger than 100° the rotational polarization moment $\rho_0^{(2)}(j')$ is in both cases very close to its maximum negative value. That is, in both cases the recoil direction lies preferentially parallel to the plane where HD rotates (see Figure 2). Marked differences between $j'=1$ and $j'=4$ appear, however, when one compares the results for other polarization moments. While $\rho_{2+}^{(2)}(j')$ is practically zero for $j'=1$, it is clearly negative for $j'=4$; on the other hand, $\rho_{1-}^{(1)}(j')$ is negative both for $j'=1$ and $j'=4$, but much more strongly so for the higher rotational level. This leads to the following picture of the stereodynamics of reaction (1) at a collision energy of 0.54 eV. In nearly every case the HD molecule is ejected in the backward hemisphere ($\theta>100^\circ$) with a recoil direction that is approximately parallel to its plane of rotation ($\rho_0^{(2)}(j')$ close to its most negative allowed value). The characteristic properties of reactions leading to HD molecules in the $j'=1$ level are: they have $\theta=180^\circ$ as the most probable scattering angle, they do not depend on the dihedral angle between the scattering and HD's rotation planes ($\rho_{2+}^{(2)}(j')$ close to zero), but they do show some handedness with regard to HD rotation relative to

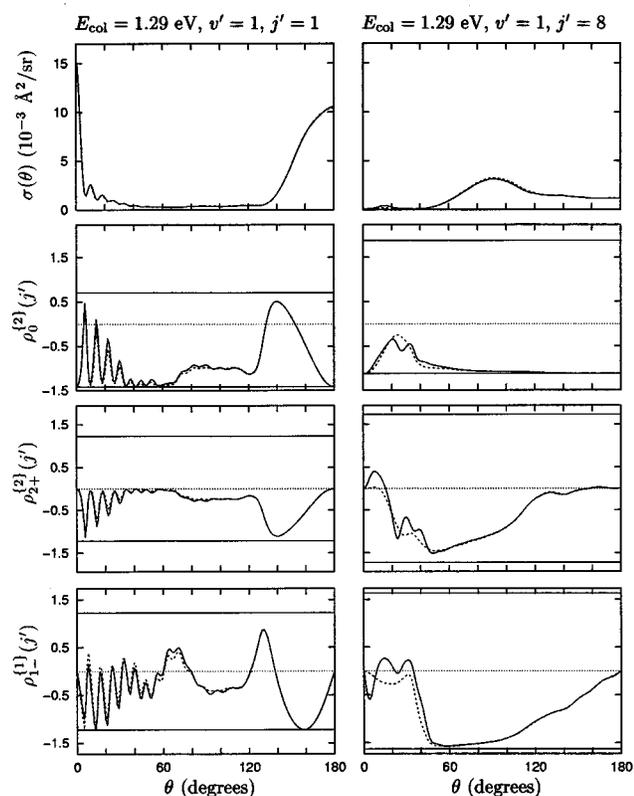


FIG. 7. As in Figure 6, but with $E_{\text{col}} = 1.29$ eV, $v' = 1$ and $j' = 1$ (left column) or $j' = 8$ (right column).

the scattering plane [negative $\rho_{1-}^{(1)}(j')$]. As j' increases, the reaction stereodynamics changes: it gets increasingly dominated by in-plane mechanisms where the scattering and HD's rotation planes are preferentially parallel ($\rho_{2+}^{(2)}(j')$ increasingly negative); the most probable scattering angle progressively shifts from backwards to sideways directions; the handedness in HD's rotational motion gets more pronounced, with \mathbf{j}' privileging orientations antiparallel to the $\mathbf{k} \times \mathbf{k}'$ vector [more strongly negative $\rho_{1-}^{(1)}(j')$].

As far as high rotational levels are concerned, the situation does not change much when the collision energy is increased to 1.29 eV (Figures 6 and 7). Regardless of the final vibrational level of HD, we found again that, for scattering angles where the differential cross section is larger, reactions leading to high j' levels are dominated by in-plane mechanisms similar to those observed for the lower collision energy (scattering and HD's rotation planes preferentially parallel, negative orientation of \mathbf{j}' with regard to $\mathbf{k} \times \mathbf{k}'$, shift towards sideways scattering with increasing j').

The stereodynamics of reactions leading to low HD rotational levels, on the other hand, changes significantly when the collision energy is increased from 0.54 to 1.29 eV. This is clear in each one of the vector properties displayed in Figures 6 and 7. The differential cross sections show pronounced peaks for forward scattering with $\theta < 30^\circ$, and the rotational polarization moments show a highly oscillating behavior that is strikingly different from the behavior observed at $E_{\text{col}} = 0.54$ eV.

Let us take a close look at the oscillations found for the

rotational polarization moments when $j' = 1$ and $E_{\text{col}} = 1.29$ eV. For $v' = 0$ (Figure 6) we found extreme behavior at three groups of scattering angles. The first of these ($\theta = 0, 9, 17, 25, 113, 145$ and 180°) is associated with a maximum negative value for $\rho_0^{(2)}(j')$ and vanishing or nearly vanishing values for $\rho_{2+}^{(2)}(j')$ and $\rho_{1-}^{(1)}(j')$. In terms of reaction mechanisms, this situation corresponds to the product diatomic rotating in a plane parallel to the recoil direction but without preference for any particular handedness or dihedral angle with regard to the scattering plane (note that this behavior is required by symmetry when $\theta = 0$ or 180° , but not when the scattering angle takes other values). Except for the absence of handedness, this behavior is similar to that observed for reactions leading to $j' = 1$ at the lower collision energy $E_{\text{col}} = 0.54$ eV.

The second group of scattering angles with extreme behavior ($\theta = 5, 13, 20, 124$ and 157°) is associated with a maximum positive value for $\rho_0^{(2)}(j')$ correlated with maximum negative $\rho_{2+}^{(2)}(j')$ and vanishing $\rho_{1-}^{(1)}(j')$. The values found for the rotational polarization moments at these scattering angles indicate an absence of handedness in HD's rotation ($\rho_{1-}^{(1)}(j') = 0$) and a preference for \mathbf{j}' lying in the $y'z'$ plane [positive $\rho_0^{(2)}(j')$, negative $\rho_{2+}^{(2)}(j')$]. Note that this preference is stronger where the differential cross section is larger (i.e., at angles close to $\theta = 0$ or 180°), and that there is no clearly preferred plane for HD rotation since there is no privileged direction for \mathbf{j}' , only a privileged plane. In other words, at the scattering angles considered here the product diatomic HD privileges planes of rotation that are parallel to the x' axis but shows no clear preference for any particular angle relative to the recoil direction.

The third group of points with extreme behavior ($\theta = 3, 8, 11, 15, 18, 22, 26, 138, 150$ and 170°) is associated to scattering angles where there is a maximum handedness for HD rotation (i.e., where $\rho_{1-}^{(1)}(j')$ has a local maximum or minimum). One interesting observation is that the maxima of the differential cross sections in the backward hemisphere ($\theta = 170$ and 138°) are at scattering angles where $\rho_{1-}^{(1)}(j')$ is minimum (and very close to its negative limit) but that no correlation of this kind is observed in the forward hemisphere.

When HD is produced in its $v' = 1, j' = 1$ state (Figure 7) the situation resembles the one described above for the $v' = 0, j' = 1$ state except that in the $v' = 1$ case there is no obvious correlation between the maxima of the differential cross sections and those scattering angles where there is some sort of extreme behavior. Note also that for $v' = 1$ we still have the same three groups of scattering angles with extreme stereodynamical behavior. Scattering with maximum negative $\rho_0^{(2)}(j')$ and vanishing or nearly vanishing $\rho_{2+}^{(2)}(j')$ and $\rho_{1-}^{(1)}(j')$ is observed here at $\theta = 0, 10, 18, 26, 121$ and 180° , while scattering with maximum $\rho_0^{(2)}(j')$, minimum $\rho_{2+}^{(2)}(j')$ and vanishing $\rho_{1-}^{(1)}(j')$ is seen at $\theta = 6, 14, 22$ and 140° . Finally, scattering with maximum or minimum $\rho_{1-}^{(1)}(j')$ is found at $\theta = 5, 8, 13, 16, 21, 130$ and 159° [note, however, that we are using the term "maximum" to refer to points where $\rho_{1-}^{(1)}(j')$ nearly vanishes; the preference

for negative orientation of \mathbf{j}' with regard to $\mathbf{k} \times \mathbf{k}'$ is here stronger than in the $v' = 0$ case].

V. CONCLUSION

In this article we have presented results from the first quantum-mechanical calculation of rotational polarization moments for a chemical reaction. We used exact three-dimensional quantum scattering calculations along with the formalism introduced in Ref. 21 to calculate the multipolar moments that describe how the rotational angular momentum \mathbf{j}' of the products of the benchmark reaction $\text{H} + \text{D}_2(v=0, j=0) \rightarrow \text{HD}(v', j') + \text{H}$ is distributed in space, and then combined the multipolar moments to form real rotational polarization moments. As we have shown here, real rotational polarization moments are ideally suited for the complete quantum description of the stereodynamics of chemical reactions. They are intrinsically associated with intuitive chemical concepts such as in-plane or out-of-plane reactions and for this reason describe the directional properties of chemical reactions in a way that from a chemist's point of view is appealing.

The central question in our study concerned the existence and the nature of three-vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlations tying the angle between the reagent-approach and product-recoil directions (i.e., the scattering angle) to the rotational level in which the product molecule HD is formed, to the plane where it rotates and to the sense of its rotational motion. The examination of our calculated data, although restricted to rotational polarization moments of rank 0, 1 and 2, showed not only that such a correlation indeed exists but also that it is quite pronounced, approaching extreme situations under various conditions. By paying due attention to the physical meanings of the rotational polarization moments we could not only quantify the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation but also analyze it in terms of different reaction mechanisms depending on the collision energy, on the scattering angle, and on the relationship between the rotational motion of the product molecule and the location of the scattering plane.

We found that for both collision energies considered (0.54 and 1.29 eV) there is a common limit to which the reaction mechanism tends as HD is formed in increasingly high rotational levels. As j' increases the preference for forward or backward scattering observed for low j' becomes a preference for sideways scattering, and the reaction dynamics gets increasingly dominated by in-plane mechanisms characterized by scattering and HD's rotation planes preferentially parallel and by a definite handedness in HD's rotational motion (\mathbf{j}' privileges antiparallel orientations relative to the $\mathbf{k} \times \mathbf{k}'$ vector).

We have also found that the situation is more complex for reactions forming HD in low rotational levels. We observed that the situation changes quite dramatically as the collision energy is increased from 0.54 to 1.29 eV. For the lower collision energy the reaction stereodynamics looks relatively simple (backward scattering, recoil direction preferentially parallel to the plane where HD rotates, no preference for specific dihedral angles between scattering and HD's rotation planes, relatively weak handedness in HD's

rotation relative to the scattering plane). In the case of the higher collision energy, however, the stereodynamics becomes more complicated. Forward scattering becomes approximately as intense as backwards, and the rotational polarization moments show a rapidly changing behavior. They quickly oscillate among three extreme and qualitatively different situations, and their oscillations show up even in the restricted range of scattering angles for which the reaction probability is relatively large.

Although restricted to polarization moments of rank 0, 1 and 2 and to a single reference frame, the results presented in this article reveal rich information and deepen the description of the H+D₂ reaction dynamics. Measurements of directional properties of the H₃ system and its isotopical variants will clearly be useful in order to verify the validity of our predictions. No other chemical reaction is as promising with regard to a rigorous comparison between theory and experiments on dynamical stereochemistry.

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