Dependence of Calculated Product Rotational Polarizations on the Scattering Angle for the $O(^1D) + HCl$ Reaction

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Received: February 18, 1998; In Final Form: September 14, 1998

To investigate the effect of the structure of the potential energy surface on the vector properties of the $O(^1D) + HCl$ reaction, we carried out a quasiclassical trajectory study of some two and three vector correlations. The analysis of the allocation of the angular momentum and of the variation with the scattering angle of the second Legendre moment related to the distribution of the product rotational angular momentum with respect to relative velocity indicated that the formation of an intermediate complex is responsible for deviations from the kinematic limiting behavior. The complex formation explains also the agreement of trajectory results with those of a statistical model reaction proposed by Herschbach (Case, D. A.; Herschbach, D. R. *Mol. Phys.* **1975**, *30*, 1537).

1. Introduction

Owing to their relevance to atmospheric studies,[1] $O(^1D) + HCl \rightarrow OH + Cl$ (R1) and $\rightarrow ClO + H$ (R2) reactions have been extensively investigated both experimentally and theoretically in recent times. On the experimental side, scalar properties of reaction R2 have been succesfully determined using beam techniques both by Balucani et al.,[2] and by Matsumi et al.[3,4] In addition, the Perugia group has also measured the product angular distribution of R2.[2] Recently, Alexander et al.[5] obtained state-to-state information for the product angular distribution of reaction R1.

The first theoretical work on these reactions dates back to 1984.[6] More recently, ab initio calculations have been performed and a potential energy surface (PES) has been constructed.[7] On this PES quasiclassical trajectories (QCT) were run to compare calculated scattering data with measured ones. Most of the available experimental data were reproduced by the calculations despite the fact that, as pointed out in a recent study of Bowman and collaborators,[8] the PES is not of spectroscopic accuracy.

The interest for vector properties of reactive processes has enormously increased in recent years. In this field, important experimental results have been obtained by combining beam apparatuses and polarized lasers or electric and magnetic fields[9] as well as by adopting polarized laser pump−probe strategies when using the so-called photoloc[10] or bulb[11] experimental arrangements.

The whole topic of stereodynamics in bimolecular reactions has been recently reviewed.[10] Seminal papers on both experimental and theoretical aspects of vector correlations and reaction dynamics stem from Herschbach's group in the seventies (starting with refs 12 and 13) and from several other papers presented in a series of workshops on reactive stereodynamics.[14] Recently, some papers[15,16] have been devoted to the illustration of the theoretical tools necessary to extract fundamental parameters of two- and three-vector correlations from (especially QCT) dynamical calculations and recent experiments.[11,17] More recently, reactive stereodynamics has driven also the attention of quantum dynamicists.[18,19]

Interest for extending stereodynamic theoretical studies to the title reaction was also fueled by the structure of the PES of the $O(^1D) + HCl$ system. The PES of this reaction, in fact, has a deep intermediate well and branches into two exoergic product channels having opposite mass combinations. In general, reactive trajectories access either the R1 or the R2 product valley only after spending a certain amount of time inside the region of the intermediate complex well. It is, therefore, important, for reactive stereodynamic studies, to investigate the effect on vector properties of this phase of the reactive process and its relationships with the mass combinations of the two product channels.

These questions have motivated the present paper. The paper is divided as follows: in section 2, findings of a quasiclassical analysis of two vector correlations are compared with kinematic limits. In section 3, the comparison is extended to some aspects of three vector correlations and to a statistical model reaction.[2]

2. Quasiclassical Trajectory Calculations and Relevant Stereodynamic Quantities

QCT calculations were carried out by running in parallel large batches of trajectories on the PES of ref 7. To this end a parallelized version of the QCT program was used, and a batch of one million trajectories was integrated on a cluster of

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10.1021/jp9812029 CCC: $15.00

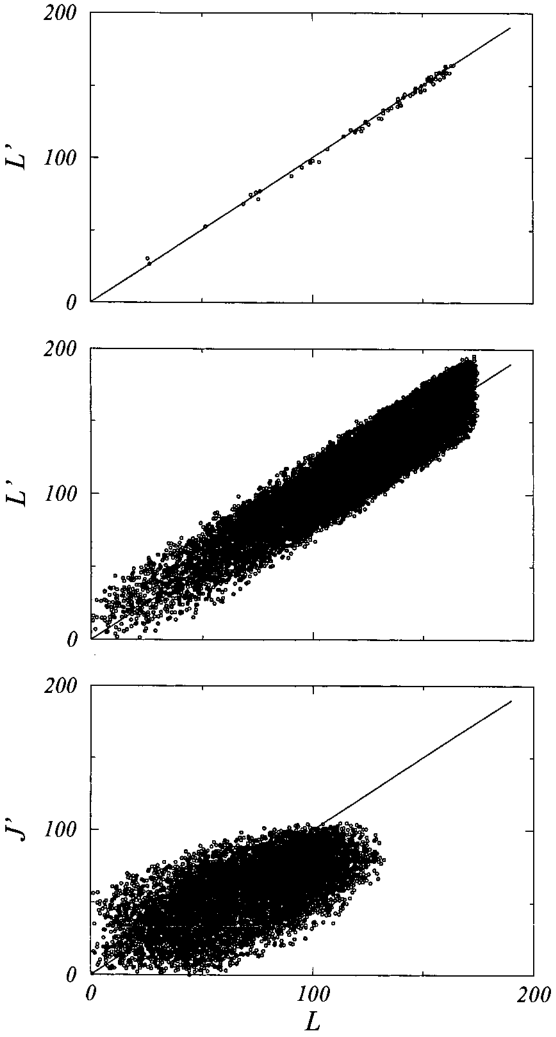

Figure 1. Amount of reactant orbital angular momentum L (in units of $\hbar$) transferred to product rotational angular momentum J' for R2 (lower panel) and to product orbital angular momentum L' for R1 (all trajectories, central panel; direct trajectories, upper panel) plotted as a function of L. Individual trajectories (dots), kinematic limiting behavior (solid line).

workstations. Initial conditions were chosen to be similar to those of the Perugia experiment:[2] the relative collision energy was 12.2 kcal/mol, and the HCl internal energy was that of the ground vibrational state ($v = 0$) and first excited rotational state ($j = 1$).

In our notation primed (unprimed) symbols refer to products (reactants). Boldface lowercase characters refer to unit vectors with $\mathbf{k}'$, $\mathbf{j}'$, $\mathbf{l}'$ ($\mathbf{k}$, $\mathbf{j}$, $\mathbf{l}$) being, respectively, the unit vectors of the collision partners relative velocity, of the rotational angular momentum, and of the orbital angular momentum. Boldface uppercase characters refer to related vectors with $\mathbf{J}'$, $\mathbf{L}'$ ($\mathbf{J}$, $\mathbf{L}$) being, respectively, the rotational angular momentum and the orbital angular momentum. Italic uppercase symbols represent vectors moduli: J', L' (J, L) are the moduli of the rotational and the orbital angular momentum, respectively; italic lowercase symbols represent quantum numbers j', v' (j, v) for rotation and vibration, respectively.

As a first step, the amount of total angular momentum allocated as product rotational angular momentum $\mathbf{J}'$ was analyzed by plotting J' as a function of the modulus L of the reactant orbital angular momentum $\mathbf{L}$. As is apparent from the lower panel of Figure 1, there is a certain tendency for R2 to transfer L into J' (the equation $J' = L$, corresponding to the kinematic limiting behaviour of *heavy heavy−light* (HHL) systems reacting to give heavy−heavy light products, is represented as a solid line).[20] The scatter of trajectory results about the solid line is a measure of the deviation of dynamical calculations from the HHL limiting behavior. Such a deviation is not negligible, and it would be interesting to discorporate the contribution of trajectories entering the region of the intermediate complex well from that of direct trajectories (those not entering the well region). However, since for R2 there are no direct trajectories to compare with, such an analysis could not be made.

On the other hand, the comparison could be carried out for R1 since there is an appreciable batch of direct trajectories ending up into the OH + Cl product channel. However, since the mass combination of R1 is that of the heavy light−heavy (HLH) systems reacting to give heavy−light heavy products, the relevant kinematic limiting relationship is now $L' = L$ and the quantity to be plotted as a function of L is L'. For this reason, the values of the product orbital angular momentum L' obtained from trajectory calculations for the whole batch and for the direct-only reactive events are plotted as a function of L in the central and in the upper panels of Figure 1, respectively. Here, again, the solid line represents the related kinematic limiting behavior. The figure clearly shows the negligible scatter about the solid line of L' values obtained from direct trajectories. The scatter of results obtained from the whole batch of trajectories, though smaller than that obtained in the case of R2, is still fairly large. This indicates that deviations from the corresponding kinematic limiting behavior can be largely ascribed to the effect of experiencing the intermediate well region of the PES.

However, to extend the investigation to vector polarizations one needs to go beyond the analysis of the value of the vector moduli and to consider also vector directions. In other words, to carry out an analysis of product rotational polarizations, one needs to examine vector distributions. Two vector (say $\mathbf{a}$ and $\mathbf{b}$) distributions are formulated as $P(\cos\theta)$ and depend on a single (planar) angle θ, which is the angle formed by the two vectors ($\mathbf{a}\cdot\mathbf{b} = \cos\theta$). The analysis of vector distributions is usually performed by expanding them in terms of Legendre polynomials $P_s(\cos\theta)$[15,16,21]

$$P(\cos\theta) = \sum_s A^{(s)} P_s(\cos\theta) \qquad (1)$$

where $A^{(s)} = \langle P_s(\cos\theta)\rangle$ ($s = 0, 1, 2, ...$) and the averaging is performed over the unobserved (randonmly distributed) angles.[12] The coefficients of the expansion (*polarization parameters*) are Legendre moments measuring *orientation* (odd terms) or *alignment* (even terms).

When considering the alignment of $\mathbf{j}'$ with either $\mathbf{k}$ or $\mathbf{k}'$ (rotational polarization) strict alignment *must* be obtained for achiral systems since the sense of rotation of the diatom with respect to a single axis cannot be distinguished. This implies that odd labeled coefficients of eq 1 are zero ($A^{(2s+1)} = A'^{(2s+1)} = 0$ and, in particular, $A^{(1)} = A'^{(1)} = 0$; primed and unprimed quantities are used for $\mathbf{k}'$ and $\mathbf{k}$, respectively). Accordingly, for completely aligned $\mathbf{j}'$ vectors, the first alignment parameter, $A^{(2)}$ or $A'^{(2)}$, is the leading coefficient of the expansion with its extreme values being −0.5 (a δ function centered on $\cos\theta = 0$) and +1 (a δ function centered on $\cos\theta = \pm 1$). On the other hand, for an isotropic distribution both $s = 1$ and $s = 2$ $A^{(s)}$ parameters of eq 1 are zero ($A^{(1)} = A^{(2)} = A'^{(1)} = A'^{(2)} = 0$).

Our trajectory calculations led to the following results: For R1 a rather isotropic product rotational angular momentum distribution was obtained since the absolute values of both $A^{(1)}$ and $A^{(2)}$ (from $P(\mathbf{k}\cdot\mathbf{j}')$) and $A'^{(1)}$ and $A'^{(2)}$ (from $P(\mathbf{k}'\cdot\mathbf{j}')$) are of the order of 10^{-2}. This can be rationalized in terms of the fact that, since in the HLH kinematic limit the dominant component of the total angular momentum is $\mathbf{L}$ and this is quantitatively allocated into $\mathbf{L}'$, the modulus of $\mathbf{J}'$ results to be small. Therefore, large variations in the direction of $\mathbf{J}'$ are needed for compensating even small variations in $\mathbf{L}'$. For R2, instead, the product rotational polarization with respect to $\mathbf{k}$ was found to be high since while, as it should be, the absolute value of $A^{(1)}$ for $P(\mathbf{k}\cdot\mathbf{j}')$ is smaller than 10^{-2}, that of $A^{(2)}$ significantly differs from 0 ($A^{(2)} < -0.3$). This is not true for the product rotational polarization with respect to $\mathbf{k}'$, which is weak. In this case, in fact, both $A'^{(1)}$ and $A'^{(2)}$ are about zero (in particular, it is $-0.1 < A'^{(2)} < 0$). Again, this can be rationalized in terms of the fact that since in the kinematic HHL limit the dominant component of the total angular momentum $\mathbf{L}$ is quantitatively allocated into $\mathbf{J}'$, and $\mathbf{k}$, which is perpendicular to $\mathbf{L}$, will also be perpendicular to $\mathbf{J}'$. At the same time, nothing can be said about $\mathbf{k}'$ and $\mathbf{J}'$ since there are no relationships between $\mathbf{k}'$ and $\mathbf{L}$.

3. Toward Three Vector Correlations

From the above analysis it can be inferred that kinematic limits are the driving concepts for the rationalization of the reactive behaviour of both HLH and HHL limiting systems. However, for real systems such as O(^{1}D) + HCl, deviations from a quantitative application of kinematic limits were found to be significant. To learn more about the way these limits apply to the title reaction, we extended our analysis to three-vector correlations.

To carry out a three-vector correlation, one needs to measure (or calculate) the angular distribution of one pair of vectors while measuring (or calculating) at the same time the correlation of another pair of vectors. Multivector correlations are a function of several angles. Strictly speaking, to depict a three-vector correlation one needs two planar (say χ and θ) angles and a dihedral (say ϕ) angle. As an example, when considering the three vectors $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{j}'$ of interest for our investigation, the planar angles are χ and θ (defined as $\cos\chi = \mathbf{k}\cdot\mathbf{k}'$, the *scattering angle,* and $\cos\theta = \mathbf{k}\cdot\mathbf{j}'$, the *product rotational polarization angle with respect to reactant velocity)* while the dihedral angle is ϕ, which is the angle formed by the $\mathbf{k} - \mathbf{k}'$ and the $\mathbf{k} - \mathbf{j}'$ planes. By making use of an expansion in (modified) spherical harmonics,[16] or, equivalently, in bipolar harmonics,[15,22] the related distribution function can be expressed as

$$P(\chi, \theta, \phi) = 2\pi \sum_{s,t} \left(\frac{2s+1}{4\pi}\right)^{1/2} \left[\frac{1}{\sigma}\frac{d\sigma_{s,t}(\chi)}{d\Omega}\right] C^{*}_{s,t}(\theta, \phi) \quad (2)$$

where σ is the cross section and $C^{*}_{s,t}(\theta, \phi)$ factors are the spherical harmonics. Square bracketed terms of eq 2 are the so called *polarization-dependent differential cross sections* (PDDCS). The PDDCSs are a measure of the three-vector correlations[15,16] since each (s, t)-PDDCS is the mean value of the corresponding spherical harmonic in the $P(\chi, \theta, \phi)$ distribution integrated over the θ and ϕ angles. Accordingly, the PDDCSs express the dependence on the scattering angle χ of the rotational product polarization, $P(\mathbf{k}\cdot\mathbf{j}')$ or $P(\mathbf{k}'\cdot\mathbf{j}')$.

For the purpose of this paper we confine the analysis to the few lowest order moments ($t = 0$ and $s = 0, 1, 2$). After all, as found also in our case (see below), related PDDCS carry significant stereodynamic information.[19,23] The quantities discussed in the paper are obtained from QCT results by binning $(\mathbf{k}\cdot\mathbf{k}')$ and by evaluating $\langle P_s\rangle$ from the number of trajectories falling in a given box. This gives us the value of $\rho_{s,0}$ *i.e.*, the value of (s, 0)-PDDCS (or *polar* PDDCS) normalized to 5 (0, 0)-PDDCS[15] or, in other words, the value of the coefficients of eq 2 divided by the corresponding differential cross section DCS)

$$\rho_{s,0} = \left[\frac{d\sigma_{s,0}/d\Omega}{d\sigma_{0,0}/d\Omega}\right] \quad (3)$$

The quantity $\rho_{s,0}$ expresses the dependence of the Legendre moments (polarization parameters) on the angle χ, which is no longer unobserved (and, therefore, not randomly distributed). The product polarization can refer either to the initial $\mathbf{k}$ or to the final $\mathbf{k}'$ velocity. Accordingly, one has $\rho_{s,0}$ for the former distribution and $\rho'_{s,0}$ for the latter. Again, for achiral systems, the (1, 0)-PDDCS should be zero by symmetry and this can be used (as we also did) to check for the accuracy of QCT calculations (this should be routinely done for both $A^{(1)}$ and $A'^{(1)}$ of eq 1 in two-vector correlation studies[20]).

In the case of (2, 0)-PDDCSs, there is no symmetry constraint and, therefore, the shape of both $\rho_{2,0}$ and $\rho'_{2,0}$ must exhibit dynamic and kinematic features specific of the two reaction channels.[13] For the R1 channel producing OH + Cl, we found both $\rho_{2,0}$ and $\rho'_{2,0}$ to be about zero at all values of the scattering angle. This implies that the process is essentially isotropic regardless of the value of the scattering angle and that, apart from a possible correlation between the $\mathbf{k} - \mathbf{k}'$ and $\mathbf{k} - \mathbf{j}'$ planes (given by the distribution of the dihedral angle ϕ, not considered in our work), the three vectors are uncorrelated when the product is OH + Cl. On the contrary, for the R2 channel producing ClO + H, the three-vector correlation expressed by $\rho'_{2,0}$ (solid line of the upper panel of Figure 2) is strong. In fact, from the plot given in the figure, it is apparent that the $\mathbf{k}'\cdot\mathbf{j}'$ alignment, which is large for the forward and backward scattering (the value of $\rho'_{2,0}$ in both forward and backward limits is close to -0.5) becomes negligible for sideways scattering. This result deviates from the kinematic HHL limiting behavior worked out by Case and Herschbach (Figure 2 of ref 13) and plotted here for comparison in the upper panel of Figure 2 as a dotted line. It rather well agrees with values obtained by the same authors (see Figure 6 of ref 13) for a realistic model of the K + HBr reaction based on statistical assumptions[26] (this has been also plotted for comparison in the upper panel of Figure 2 as a dashed line).

A close similarity was also found when comparing $\rho_{2,0}$ values obtained from our trajectory calculations (solid line of the lower panel of Figure 2) with corresponding results of the statistical model (dashed line of the same panel). The curvature of both plots is less pronounced than that of $\rho'_{2,0}$ plots given in the upper panel. This is due to the fact that, as already mentioned, the mean value $A^{(2)}$, is quite negative. In this case, the deviation from the HHL kinematic asymptotic limit, which is (constantly) -0.5 at all values of the scattering angle, is large.

The deviation of QCT results from the kinematic asymptotic limiting behavior is not surprising. This agrees well with the fact that, as already seen for two-vector corrrelations, trajectories experiencing the intermediate complex well were found to be responsible for deviation from the kinematic limit. For the same reason it is not surprising that QCT results agree with those obtained from the statistical model. The experiencing of the well and the formation of an intermediate complex is not only

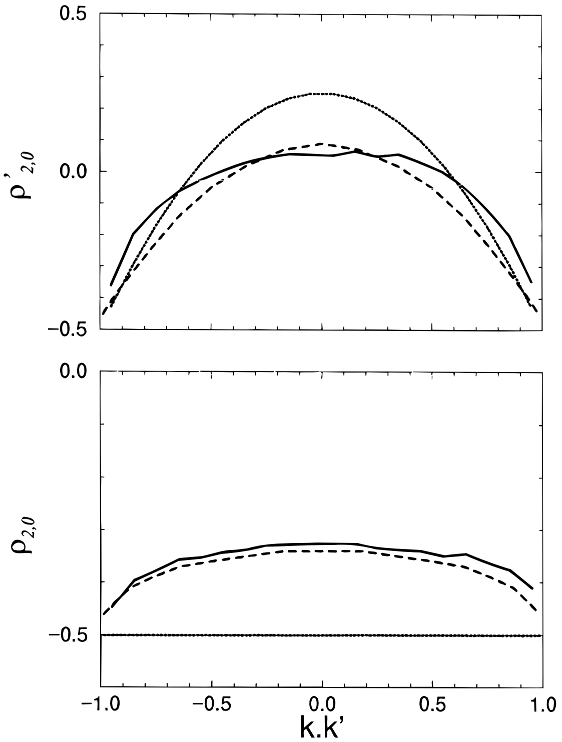

Figure 2. Normalized polarization dependent differential cross sections $\rho'_{2,0}$ (upper panel) and $\rho_{2,0}$ (lower panel) plotted as a function of the scattering angle, cos $\chi = (\mathbf{k}\cdot\mathbf{k}')$ for R2. Trajectory results (solid line) are compared with results from a statistical complex theory for the HHL kinematic limiting system (dotted line)[13] and for a realistic model of the K + HBr reaction (dashed line).[13]

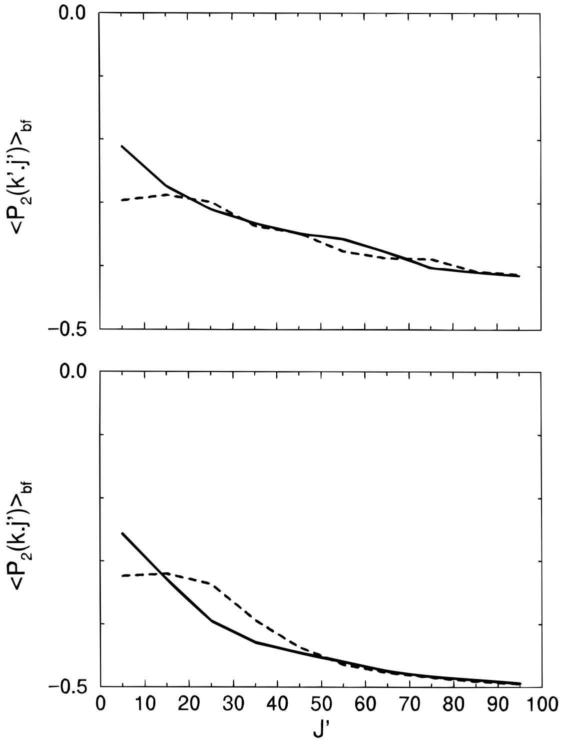

Figure 3. Forward cos $\chi = \mathbf{k}\cdot\mathbf{k}' = 1$ (solid line) and backward cos $\chi = \mathbf{k}\cdot\mathbf{k}' = -1$ (dotted line) components of the (2, 0)-PDDCSs for R2 plotted as a function of J' (in units of $\hbar$). Values of $\rho'_{2,0}$ are given in the upper panel; values of $\rho_{2,0}$ are given in the lower panel.

evidenced by our graphical study of calculated trajectories, but it is also discussed in references 27−29 for the O(^{1}D) + HD → OH + D and the O(^{1}D) + H_2 → OH + H reactions having a PES showing a similar structure. The authors of those papers, however, point out that the formed complex is rather short-lived. For the title reaction, this was pointed out by us in ref 7, where it is also shown that, on the average, the system spends less than 50 fs in the well region.

Usually, to be considered statistical, a molecular aggregate has to undergo more than one rotation.[30] To set a convenient reference time for the rotation period of the OHCl triatom, we assume that, during its rotation around an axis of inertia, the system behaves as a rigid body (or, equivalently, that its oscillations around the equilibrium geometry are small). Under this assumption, the rotation period can be approximated as $\tau_r = 2\pi I/L$. The HOCl triatom can be assimilated with a prolate top having two nearly identical largest moments of inertia[31] ($I_a = 8.60 \times 10^{-47}$ kg m^2 and $I_b \approx I_c = 3.58 \times 10^{-45}$ kg m^2). To estimate the shortest rotational period, one can take the value of L obtained from trajectory calculations. From the most probable value of L ($L = 30\ \hbar$) it turns out that even the fastest rotation (the one around the a axis which almost coincides with the ClO axis) has a rotational period $\tau_r(a)$ of about 200 fs. This time is about four times longer than the average residence time of trajectories inside the well, implying that the system spends in the well a too short time to be considered truly statistical. This also means that the assumption made by the model that *the system spends in the well region a time long enough to be considered statistical* could be weakened.

Further details on vector properties of this reaction can be obtained from $\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle$ when restricting the analysis to (exact) forward and backward directions (indicated by subindex bf). In this case, **k** and **k′** lie along the same line, or, in other words, the ($\mathbf{k} - \mathbf{k}'$) scattering plane collapses into a line. Therefore, the projections of **J** and **J′** onto **k** and **k′**, respectively, satisfy the relationships $m_j = \pm m_{j'}$ and it is

$$\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle_{bf} = -0.5 + 1.5\left\langle\left(\frac{m_j}{J'}\right)^2\right\rangle \tag{4}$$

as can be easily obtained from geometrical considerations. Since $\mathbf{k} = \pm\mathbf{k}'$, same considerations (and in particular eq 4) apply also to **k′**.

In the particular case of a rotationless reagent molecule, $j = 0$, $m_j = m_{j'} = 0$ (which, obviously, does *not* necessarily imply that $j' = 0$) this means that (see eq 4) $\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle_{bf} = -0.5$; i.e., the product rotational angular momentum vector is perpendicular to the relative velocity. This applies to all reaction channels and to all product internal states.

The case in which j is not equal to 0 yet is close to 0 is of special relevance to our calculations since they were carried out at $j = 1$. In this case, $\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle$ can still be evaluated from eq 4: a small value of j implies also that its projection m_j is small. One can envisage here two extreme situations valid as limiting models for the R1 and R2 reaction channels. Let us, first, consider the $J' \gg L'$ case, which is a model for the HHL reaction (R2) leading to ClO + H. In this case, the ratio $m_j/J' \rightarrow 0$, and eq 4 predicts that $\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle_{bf} \rightarrow -0.5$ as is for the solid line of Figure 2. Then, let us consider the J' not much greater than L' case, which is a model for the HLH reaction (R1) leading to the OH + Cl product. In this case, m_j/J' does not need to be small. Therefore, as found in our calculations, $\langle P_2(\mathbf{k}\cdot\mathbf{j}')\rangle_{bf}$ is not close to -0.5.

The calculations allowed also an extension of the analysis to the detailed J' dependence of (2, 0)-PDDCSs in the case of exact forward and backward scattering. For R2, values of the related $\langle P_2\rangle_{bf}$ are plotted as a function of J' in the upper panel of Figure 3 for ($\mathbf{k}'\cdot\mathbf{j}'$) and in the lower panel of the same figure for ($\mathbf{k}\cdot\mathbf{j}'$).

As apparent from the figure, the monotonous decrease of the $\langle P_2 \rangle_{bf}$ of R2 toward −0.5 clearly confirms the above analysis. The same is not true for R1 for which forward and backward (2, 0)-PDDCSs (not shown in the figure) are about zero at all values of the OH rotational angular momentum.

4. Conclusions

The development of two- and three-vector correlation indicators via an expansion of vector distributions in Legendre polynomials and spherical harmonics, respectively, has allowed a detailed analysis of the appearance of kinematic features in properties of reactions taking place on potential energy surfaces characterized by a deep well. Such an analysis has been applied to the O(^{1}D) + HCl reaction focusing on the product rotational polarization. To this end, the amount of reactant orbital angular momentum allocated as product rotational angular momentum and polarization-dependent differential cross sections have been estimated using quasiclassical trajectory techniques. Of the two accessible product channels in which this reaction can branch, the heavy light−heavy channel, producing OH + Cl (R1), is found to lead to essentially isotropic rotational distributions. On the contrary, the heavy heavy-light one producing ClO + H (R2) is found to lead to clear product rotational polarization. However, even for R2, both two- and three-vector correlation QCT results show nonnegligible deviations from the limiting HHL kinematic behavior. These deviations were rationalized in terms of the formation of the intermediate complex associated with the potential energy well. The time spent in the region of the PES associated with the well explains also the similarity between QCT results for the title reaction and those of the statistical model proposed by Herschbach for the K + HBr reaction. However, an analysis of the QCT results suggests that one could weaken the assumption of the model requiring that the reaction intermediate is long lived.

Acknowledgment. J.M.A. thanks Javier Aoiz (Universidad Complutense, Madrid) for enlightening discussions and Aurelio Rodríguez (Universidad de Salamanca) for help with part of the calculation. This work has been carried out as a part of the COST in Chemistry european cooperative project D9/0003/98. It has also been financially supported by DGICYT of Spain (Grants PB95-0930), MURST, and CNR (Italy). A.B. acknowledges an Erasmus studentship at Salamanca. A.L. thanks ZiF (Zentrum für Interdisziplinare Forschung, Universitat Bielefeld) for hospitality during the work of the Forschungsgruppen on “Interactions of oriented molecules”.

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