Entrance Pathway of Collision Involving Oriented Molecules

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In this paper we consider the entrance pathway of a collision between an atom and a polar molecule oriented by a strong electric field. This orientation technique, developed by Loesch and co-workers, can be applied to a large manifold of molecules to study the stereodynamics of their reactive collisions. As the atom is approaching the oriented molecule, a competition between the molecule−external field and atom−molecule interactions takes place and a reorientation of the molecule may occur. The intense external field may also change the dynamics of the collision process. These two questions are discussed on a general basis, and this discussion is illustrated in the case of the K + ICl reactive collision.

(1) Introduction

The dependence of the reaction probability on the orientation of the reagents plays a central role in stereodynamics. The possibility of such studies with molecular beam methods was discovered by Kramer and Bernstein[1] in 1965. The reaction Rb + oriented CH_3I was studied independently by Brooks and Jones[2] and by Beuhler et al.[3] But the hexapole focusing technique used at that time could only be applied to symmetric top molecules such as CH_3I, CF_3I.

Since 1991, a new orientation technique has been introduced by Loesch and Remscheid[4] and also by Friedrich and Herschbach.[5] This technique relies on the application of an intense electric field on rotationally very cold polar molecules, and it can be applied to a large variety of polar molecules.[6] Several reaction dynamics studies have been produced by Loesch and co-workers concerning the reactions K + oriented CH_3I, ICl, CH_3Br, and C_6H_5I, etc.[7−9]

With both techniques, the question of a possible reorientation of the molecular axis during collision must be discussed. In particular for the experiments with hexapole selected CH_3I beams, the analysis of the observations appeared to be somewhat puzzling.[10,11]

In this paper, we are going to analyze the entrance pathway of a collision between an atom A and an oriented molecule BC. Initially, the molecular axis of BC undergoes a precession motion around the external field $\vec{E}$. When atom A approaches, molecule BC starts feeling its presence through their long-range interaction, which will ultimately dominate the rotational dynamics of BC. We are going to discuss how and when the transition between the two regimes occurs. We will also discuss the perturbation of the intense electric field applied in the new orientation technique[4] on the collision dynamics of the A + BC reaction.

The content of the present paper is organized as follows: the basic notations are introduced in section 2; the electrostatic expansion of the interaction potential between an atom and a molecule is recalled in section 3; the dynamics of the transition is discussed in section 4. In section 5, these ideas are illustrated in the cases of the K + ICl reactive collision.

(2) The Problem

We consider the simplest collision involving an oriented molecule, i.e. an atom A colliding with an oriented molecule BC. $\vec{R}$ denotes the vector joining the center of mass of BC to the atom A (see Figure 1). We define the main regions of the R values:

When R is large, the interaction potential V_{A-BC} is negligible and the dipole $\vec{\mu}_{BC}$ of BC is only coupled to the external field $\vec{E}$ by the Stark term

$$V_{Stark} = -\vec{\mu}_{BC}\vec{E} \qquad (1)$$

$$V_{A-BC} \ll V_{Stark} \qquad (2)$$

In this first case, the molecule is coupled only to the electric field and its rotation is described by the ordinary Stark eigenstates. When R is small enough, the opposite becomes true:

$$V_{A-BC} \gg V_{Stark} \qquad (3)$$

This second case can further be divided in two subregions. In the first one, A and BC can still be considered as almost free. In the second subregion, the A−BC interaction is strong and electron transfer may take place at some critical distance R_H, e.g. by a harpooning process. When atom A approaches molecule BC, R decreases and these three regions are successively crossed. Our discussion will treat what occurs in each of these three regions. In the first of these regions (large R values), the dynamics of the molecular axis of BC is well-understood. J is the total angular moment quantum number and M, K its projections on the laboratory z-axis and the molecular axis, respectively. In the case of hexapole focusing, one $|JKM\rangle$ state is selected,[12] while in the case of the strong field technique, the molecular population is spread on the many "pendular states",[13] produced by the Stark mixing of the $|JKM\rangle$ (or $|J\Omega M\rangle$ for a diatomic molecule) states. These two techniques are compared with respect to the produced molecular axis orientation in the work of Bulthuis *et al.*[14]

In the second region (small R values), the dipole motion occurs in the V_{A-BC} potential which is anisotropic and varies rapidly due to the decreasing R distance. Finally, in the third region, the collision dynamics is governed by the strong range interactions and it is no longer possible to consider separately the rotational dynamics of BC.

We are going to discuss here the two transitions between the three regions. Before discussing the interaction potential V_{A-BC}, we need the order of magnitude of V_{Stark}. The experiments have been made either in low field ($\leq 10^5$ V/m) for hexapole focusing

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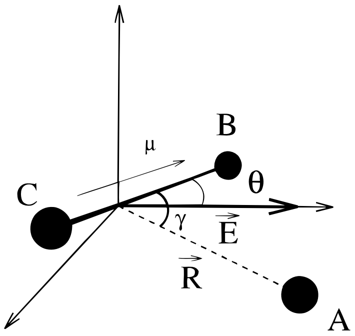

Figure 1. Geometry of the A−BC system in the electric field $\vec{E}$. This figure defines the angle θ between the dipole $\vec{\mu}_{BC}$ of molecule BC and the electric field $\vec{E}$, the vector $\vec{R}$ from the center of mass of BC to A, and the angle γ enclosed by the dipole $\vec{\mu}_{BC}$ and $\vec{R}$.

or intense fields (typically 2×10^6 V/m) for Loesch's orientation technique. With the dipole moments of ICl ($\mu = 1.207 \pm 0.003$ D [15]), CH_3I ($\mu = 1.62$ D [4]), and CH_3Br ($\mu = 1.81$ D [9]), the order of magnitude of V_{Stark} is about 1 cm^{-1} for the intense field case. Considerably larger fields [$(2-5) \times 10^8$ V/m] have been produced in the laboratory with electrode spacing of the order of 0.2 mm.[16,17] The alkali halides have dipole moments close to 10 D, but these strongly bound molecules are the usual products of reactive collisions and are rarely used as reactants. Very large values of V_{Stark} (as large as a few hundred cm^{-1}) might be considered, but here we will assume that V_{Stark} is of the order of 1 cm^{-1} and we must evaluate the interaction V_{A-BC} when it is comparable to this order of magnitude.

(3) Interaction Potential V_{A-BC} at Long Range

The transition region where V_{A-BC} and V_{Stark} have comparable magnitudes occurs at long range. In this range of R values, the electrostatic expansion of V_{A-BC}, limited to the first few terms, should be very accurate. We may obviously neglect the magnetic and retardation effects. This long-range expansion has been used by Luo and Benson[18] and also by Levine and Bernstein[19] to study the effect of molecular orientation on the reaction cross-section. As the collisions occur in an intense electric field, we must consider the particular form of this expansion which is valid when the system is in an external field $\vec{E}$, as discussed by Buckingham[20] (see also refs 21−24). The long-range potential is given by

$$V_{A-BC} = \sum_{i \geq 3} V_i \qquad (4)$$

where V_i depends on the A−BC distance R as R^{-i}. The origins of these terms are the following ones:

(a) V_3 is due to the dipole−dipole interaction. The static dipole of BC interacts with the dipole induced in A by the external electric field $\vec{E}$. This is the only term in the interaction potential solely caused by the external electric field.

(b) V_4 is the dipole−quadrupole interaction made by two contributions. One term comes from the interaction of the molecular dipole with the atomic quadrupole moment. The other one is due to the interaction of the molecular quadrupole moment with the atomic dipole induced by the external field.

(c) V_5 is the quadrupole−quadrupole interaction.

(d) V_6 is the sum of dispersion and induction terms.

(e) V_7 is the interaction of the molecular quadrupole with the atomic dipole induced by the molecular dipole. This term was discussed by Levine and Bernstein[19] as it is the first long-range term which is sensitive to the orientation of BC in zero field (the other terms are sensitive only to the alignment; i.e., they do not distinguish "heads" and "tails"). Its R^{-7} dependence makes that this term is not very important in the present discussion.

We are going to limit our discussion to the terms V_i with $i = 3, ..., 6$. Moreover, we will assume that the atom A is in a spherically symmetric S state: this is the case of potassium atoms considered below. The case where the atom A is not in an S state but, for instance, in a P state is more complex. The atomic quadrupole moment is not vanishing, and several potential energy surfaces have to be taken into account, corresponding to various projections Λ of the atomic electronic orbital angular momentum on the vector $\vec{R}$. For atomic S states, the atomic polarizability α_A becomes a scalar (α_A is the polarizability volume noted α' by Atkins[25]) and the dipole $\vec{\mu}_A$ induced by the external electric field $\vec{E}$ is

$$\vec{\mu}_A = 4\pi\epsilon_0 \alpha_A \vec{E} \qquad (5)$$

V_3 is then given by

$$V_3 = \frac{\alpha_A}{R^5}[(\vec{\mu}_{BC}\cdot\vec{E})R^2 - 3(\vec{\mu}_{BC}\cdot\vec{R})(\vec{E}\cdot\vec{R})] \qquad (6)$$

Its order of magnitude is therefore

$$V_3 \approx \frac{\alpha_A}{R^3}\vec{\mu}_{BC}\cdot\vec{E} \approx \frac{\alpha_A}{R^3}V_{Stark} \qquad (7)$$

Even with the very large polarizabilities of alkali atoms in their ground state ($\alpha_K = 292.8\ a_0^3$, $\alpha_{Cs} = 402.2\ a_0^3$ [26]), the term V_3 will be comparable to V_{Stark} only at low R values of the order of 7 a_0, where this expansion is not accurate. We can therefore forget this term induced by the external field as well as the other similar contributions to the higher order terms. Both V_4 and V_5 disappear when atom A has a vanishing quadrupole moment. The only remaining term is V_6, which is the sum of two terms. Both terms are due to the effect of the dipole−dipole interaction calculated at second order perturbation theory.

(a) The induction term is due to the interaction of the permanent molecule dipole $\vec{\mu}_{BC}$ with the related induced dipole in the atom:

$$V_6^{ind} = -\frac{\alpha_A {\mu_{BC}}^2}{4\pi\epsilon_0 R^6}[1 + P_2(\cos\gamma)] \qquad (8)$$

γ is the angle between the vector $\vec{R}$ and the dipole $\vec{\mu}_{BC}$ (see Figure 1).

(b) Usually the dispersion term is considerably larger than the induction term. For a linear molecule BC, this term is given by

$$V_6^{disp} = -\frac{C_6^{disp}}{R^6}[1 + qP_2(\cos\gamma)] \qquad (9)$$

An accurate evaluation of the C_6^{disp} coefficient is not easy, and the anisotropy parameter q is even less well-known. A family of combination rules and approximate formulas for C_6^{disp} was discussed by Kramer and Herschbach[27] and will be used in the next paragraph. The anisotropy parameter q is known for a few systems: q lies in the range 0.22−0.48 for the interaction of NO, TlF, CsF, and Na_2 with rare gases.[28] It is expected to be reasonably well-approximated by the anisotropy parameter κ of the molecular polarizability[19,21] defined by $\kappa = (\alpha_{\|} - \alpha_{\perp})/(\alpha_{\|} + 2\alpha_{\perp})$. This parameter has been measured systematically by Bridge and Buckingham,[29] and as expected, κ is usually

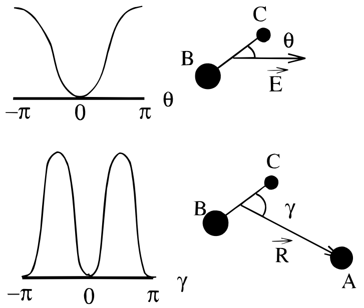

Figure 2. Schematic drawing of the potential governing BC rotational motion: (upper part) when the Stark term is dominant; (lower part) when the A−BC interaction is dominant. Note that these two plots are made as a function of two different angles θ (upper part) and γ (lower part). The definition of these angles is recalled in the right hand part of the figure.

positive for prolate molecules. A rule of thumb[30] is $\alpha_{\|} = 2\alpha_{\perp}$ for linear molecules, corresponding to $\kappa = 0.25$.

Finally, under the assumption of a vanishing atomic quadrupole, the significant terms of $V_{\mathrm{A-BC}}$ at long range are limited to the R^{-6} contributions:

$$V_{\mathrm{A-BC}} \approx -\frac{C_6}{R^6}(1 + q'P_2(\cos\gamma)) \tag{10}$$

with $C_6 = C_6^{\mathrm{disp}} + C_6^{\mathrm{ind}}$ and $q' = (C_6^{\mathrm{disp}}\kappa + C_6^{\mathrm{ind}})/C_6$.

(4) Transition Dynamics

The potential governing the rotation of the molecule BC is given by

$$V = V_{\mathrm{Stark}} + V_{\mathrm{A-BC}} \tag{11}$$

$$V = -\mu_{\mathrm{BC}}E\cos\theta - \frac{C_6}{R^6}[1 + q'P_2(\cos\gamma)] \tag{12}$$

The anisotropic terms depend on two different angles θ (enclosed by $\vec{\mu}_{\mathrm{BC}}$ and $\vec{E}$) and γ ($\vec{\mu}_{\mathrm{BC}}$, $\vec{R}$) (see Figure 2). The Stark term and the anisotropic part of $V_{\mathrm{A-BC}}$ are comparable when

$$\mu_{\mathrm{BC}}E = \frac{C_6 q'}{{R_{\mathrm{T}}}^6} \tag{13}$$

This equation fixes the transition value R_{T}. We can also evaluate the range ΔR in which the transition occurs. If the limits of this zone is given by $\mu_{\mathrm{BC}}E = (2 \text{ or } {}^1/_2)C_6q'/R^6$, we get

$$\Delta R = 0.23R_{\mathrm{T}} \tag{14}$$

The transition has a duration $\tau_{\mathrm{T}} = \Delta R/v_{\mathrm{r}}$ where v_{r} is the relative velocity A/BC assumed to be almost purely radial.

The pendular motion of the dipole BC in an intense electric field is characterized by the angular frequency ω_{P} given by the expression

$$\hbar\omega_{\mathrm{P}} = [2B_{\mathrm{BC}}\mu_{\mathrm{BC}}E]^{1/2} \tag{15}$$

where B_{BC} is the rotational constant of the molecule BC assumed to be diatomic: $B_{\mathrm{BC}} = \hbar^2/2\mu {r_{\mathrm{e}}}^2$ (μ, reduced mass of B and C; r_{e}, internuclear distance). As one can see, ω_{P} does not depend on $\hbar$. This is expected because the pendular oscillation of a dipole in an external electric field is a classical phenomena. The evaluation of the product $\omega_{\mathrm{P}}\tau_{\mathrm{T}}$ will tell us if the transition is sudden (if $\omega_{\mathrm{P}}\tau_{\mathrm{T}} \ll 1$) or adiabatic (if $\omega_{\mathrm{P}}\tau_{\mathrm{T}} \gg 1$). An adiabatic transition would induce an important reorientation: for instance, the lower pendular state (which is the best oriented state) will be transformed in the lowest state of the $V_{\mathrm{A-BC}}$ potential. If q' is positive, there are two quasi degenerate states located near $\gamma = 0$ and $\gamma = \pi$; their quasi degeneracy is lifted by the tunnel effect, the Stark Hamiltonian, and higher order terms like V_7. We think that these terms have a larger effect than the tunnel effect and the symmetry is broken. Then, the eigenstates are localized near $\gamma = 0$ or $\gamma = \pi$, and they are not the symmetric and antisymmetric combinations of the localized states. But just because $\theta = 0$ and $\gamma = 0$ represent different regions of phase space, the adiabatic transfer would possibly induce a large reorientation of the BC axis.

On the contrary, a sudden transition means that the initially oriented state does not suffer any evolution during the transition period. This is precisely what is wanted in collision experiments with oriented targets. We will see that in an intense electric field and for a heavy molecule BC (i.e. a small rotational constant B_{BC}) the experimental parameters fulfill well the conditions for a sudden transition.

We can apply the same type of analysis to the second period of the entrance pathway, when the distance R is smaller than R_{T} but still large enough so that the long-range expansion of $V_{\mathrm{A-BC}}$ remains a reasonable approximation. The angle dependent potential can be approximated by a harmonic potential in γ at $\gamma = 0$ ($\gamma = \pi$) for a positive value of the anisotropy parameter q'. Then at fixed R value the angular motion would be also pendular with a new angular frequency:

$$\hbar\omega'_{\mathrm{P}} = \left[6B_{\mathrm{BC}}\frac{C_6q'}{R^6}\right]^{1/2} \tag{16}$$

Taking the example of K + ICl, we will see that the value of ω'_{P} is small so that a sudden approximation also applies:

$$\omega'_{\mathrm{P}}\tau' \ll 1 \tag{17}$$

where τ' is the time necessary to travel from R_{T} to the beginning of the collision chosen at the harpooning radius R_{H}. In practice, ω'_{P} varies rapidly with R, and consequently the evaluation of the time integral $\int_0^{\tau'}\omega'_{\mathrm{P}}\,\mathrm{d}t$ is more appropriate for testing the sudden approximation.

Condition 17 may seem to be to strong if one performs a discussion on the reorientation on the basis of classical mechanics arguments. This point was raised by one of the reviewers, and we add the following discussion to clarify this question. We start with the differential equation for classical particles:

$$I_{\mathrm{BC}}\frac{\mathrm{d}^2\gamma}{\mathrm{d}t^2} = -\frac{\partial V}{\partial\gamma} = \frac{3C_6q'}{2R^6}\sin(2\gamma) \tag{18}$$

where I_{BC} is the moment of inertia of BC. This equation can be integrated, with two approximations: negligible initial angular velocity $\mathrm{d}\gamma/\mathrm{d}t$ is assumed; in order to get the maximum possible rotation $\Delta\gamma$, one assumes that $\sin(2\gamma)$ is equal to its maximum value 1. During the time τ the molecular axis undergoes a maximal rotation of $\Delta\gamma$ given by

$$\Delta\gamma = \left|\frac{3C_6q'}{4R^6}\tau^2\right| = (\omega'_{\mathrm{P}}\tau)^2 \tag{19}$$

In contrast to relation 17, the condition of $\Delta\gamma \ll 1$ is related to the square of the product $\omega'_{\mathrm{P}}\tau$ and is therefore less strong. This difference has two origins:

TABLE 1: Polarizability Values for Cl_2, I_2, and ICl

molecule	Cl_2	I_2	ICl
α (au)	30.91[a]	79.23[b]	55[c]
$\alpha_{\parallel} - \alpha_{\perp}$	16.83[a]	45.15 ± 2.30[b]	
κ	0.181	0.19	0.185[c]

[a] Calculated values from ref 36. [b] From ref 37 The value of α is calculated using the empirical rules developed in ref 38 while $\alpha_{\parallel} - \alpha_{\perp}$ is measured. [c] Obtained by interpolation between I_2 and Cl_2.

(a) The assumption on the initial values of $d\gamma/dt$ obviously diminishes the reorientation effect, and this assumption is not easy to release in a classical treatment. In fact, this approximation is not correct in our case, as the strong electric field causes a pendular motion around the field vector and consequently the angular velocity $d\gamma/dt$ is in general not vanishing and its value depends on the electric field strength.

(b) In the quantum treatment, which does not suffer from this weakness, the angular motion is approximated by a quasi harmonic oscillator with an angular frequency ω'_P. If one looks at the quantum average of γ considering a wave packet with an angular frequency ω'_P, the evaluation can be written as

$$\langle\gamma\rangle(t) = \gamma_0 \sin(\omega'_P t + \varphi) \tag{20}$$

where φ is related to the choice of initial conditions. After time τ, the maximal $\Delta\gamma$ can be written as

$$\Delta\gamma \leq \gamma_0 \omega'_P \tau \tag{21}$$

and within the quasi harmonic assumption ($\gamma_0 \leq 1$) the condition of negligible reorientation $\Delta\gamma \ll 1$ becomes equivalent to relation 17.

(5) Example: K + ICl Reactive Collision

This reactive collision has been studied in great detail by Loesch and Moller at two elevated collision energies (1.64 and 3.03 eV) with oriented ICl molecules.[8,31] The observed orientation effect presents some surprising features (the formation of the fast KCl product is favored when the I end of ICl is pointing toward the incoming K atom) which are very well explained by a DIPR model.[8.31]

We are going to evaluate the long-range potential along the lines of section 3. To evaluate the C_6^{disp}(K−ICl), we need the polarizability of ICl and its anisotropy parameter. We have not found these quantities in the literature, and we have used interpolation between I_2 and Cl_2 for which data are available. Table 1 summarizes these constants. Knowing α_K [26] and α_{ICl}, we estimated C_6^{disp}(K, ICl) with the following combination rule:[27]

$$C_6(\text{K,ICl}) = \frac{3}{2}\alpha_K \alpha_{ICl} \frac{w_K w_{ICl}}{w_K + w_{ICl}} \tag{22}$$

where w_K and w_{ICl} are the mean excitation energies of the species K and ICl.

The values[26] of α_K and C_6(K, K) are used to get $w_K = 0.0593$ au. This formula has a low sensitivity to the exact value of w_{ICl} because $w_{ICl} \gg w_K$. We have taken w_{ICl} as the first ionization potential of ICl (10.10 eV = 0.371 au.) as measured experimentally.[32] We thus get $C_6^{\text{disp}} = 1235$ au. The calculation of C_6^{ind} is very easy: $C_6^{\text{ind}} = \alpha_K \mu_{ICl}^2 = 66.1$ au. It is clear that the contribution of the induction term to the anisotropy of the complete R^{-6} term is not negligible:

$$V_6 \approx -\frac{1301}{R^6}(1 + 0.226 P_2(\cos\gamma)) \tag{23}$$

With the electric field used in the experiments $E = 2$ MV/m, we calculate a transition radius of $R_T = 23.3$ au. $= 12.3$ Å.

The transition time τ_T is deduced from the value of $\Delta R = 2.83$ Å and the relative velocity $v_r \approx 3500$ m/s (3150 m/s for one experiment, 4300 m/s for the other one). It is very short: $\tau_T = 0.81 \times 10^{-13}$ s. We may evaluate the pendular angular frequency $\omega_P = 0.57 \times 10^{11}\ \text{s}^{-1}$ and the product $\omega_P \tau_T$ which defines the nature of the transition dynamics to be

$$\omega_P \tau_T \approx 0.46 \times 10^{-2} \ll 1 \tag{24}$$

The transition is very well described as sudden, and as a consequence the associated reorientation effect is fully negligible. We have also evaluated the harpooning radius R_H given by

$$\frac{1}{4\pi\epsilon_0}\frac{1}{R_H} = \text{IP(K)} - \text{EA(ICl)} \tag{25}$$

The vertical electron affinity of ICl, EA(ICl), is obtained from the electron affinity of chlorine (3.6127 eV [33]), the dissociation energy of ICl (2.177 eV [34]), and the ground state potential curve of ICl^- (1.23 eV, above discussion threshold[35]). We thus get $EA_{\text{vert}}(ICl) = 0.48$ eV and $R_H = 6.6$ au $= 3.45$ Å. Following our discussion in section 4, we calculate the time integral $\int_0^{\tau'} \omega'_P\, dt$, by using eq 16 and assuming the velocity as purely radial and constant (3500 m/s). We finally obtain a value of $\int_0^{\tau'} \omega'_P\, dt = 0.205$. This means that reorientation of ICl is not very important during this second period, before strong chemical forces begin playing a role. But, this estimation is crude, and a more sophisticated calculation may show some reorientation effect.

The present results concern the K + ICl reaction collision. We expect similar orders of magnitude for many other collisions. This is due to the fact that even if the C_6 parameter may vary widely with the system considered, this parameter appears to power $^1/_6$. Another parameter like the pendular frequency ω_P cannot be easily varied in a very wide range because of the limitation on available fields and also because, for light molecules with large B_{BC} values, the pendular regime ($\mu_{BC}E \gg B_{BC}$) cannot be reached. Finally, even the relative velocity v_r is rarely less than 500 m s^{-1} in usual collision experiments so that it spans a limited range.

Finally, we discuss briefly if the applied external field can modify the dynamics of the reactive collision. Two different arguments can be developed:

(a) In a simple way, we can compare the external electric field $E_{\text{ext}} = 2$ MV/m to the electric field created by one unit charge at a distance comparable to $R_H = 6.6$ Å. This internal field is of the order of $E_{\text{int}} = 3$ GV/m. The ratio $E_{\text{ext}}/E_{\text{int}}$ is less than 10^{-3}, and one may think that the external field is fully negligible.

(b) A more refined analysis requires that one can forget the Stark term during the collision, i.e. that the sudden approximation applies to this term:

$$V_{\text{Stark}} \tau_{\text{coll}} \ll \hbar \tag{26}$$

where τ_{coll} is the duration of the collision. The present collision is a direct process, with an expected duration of the order of $\tau_{\text{coll}} = 2R_H/v_r \approx 4 \times 10^{-13}$ s. The magnitude of V_{Stark} is less clear to define, as the dipole moment of the collision complex can be very large, just after harpooning. Taking as an order of magnitude 10 D, we get $V_{\mathrm{Stark}} \approx 7 \times 10^{-23}$ J and $V_{\mathrm{Stark}}\tau_{\mathrm{coll}}/\hbar \approx 0.25$. The sudden approximation condition is almost fulfilled. It may seem surprising that these two ways of thinking lead to such different conclusions. Behind the quantum discussion, there is the fact that different paths may interfere to give products (many such interference effects are known in collision physics, such as rainbow scattering, glory scattering, etc.) and the relative phase of the interfering paths may be modified by the external field. Usually, total scattering has a very small sensitivity to these interference effects. As a consequence, one may expect that an intense field of the order of a few megavolts per meter will have no effects on the gross of the reactive collision features (e.g. total cross-section, average translational and vibrational energies), but, in favorable cases, it could have an effect on some detailed properties (e.g. differential cross-section).

(6) Conclusion

In this paper, we have considered the entrance pathway of a collision involving an atom and a molecule oriented by an intense electric field. We wanted to understand how the transition occurs between the preparation phase (molecule bound to the electric field) and the reaction phase (molecule interacting with the atom). In a first step, we have evaluated the atom–molecule interaction at long range. To simplify this evaluation, we have assumed that the atomic quadrupole vanishes: the opposite case is surely rather complex as then several potential energy surfaces with a priori different reaction dynamics must be considered. In a second step, we have evaluated the adiabatic/sudden character of the transition and also the reorientation of the molecule in the following phase. To put numbers on the obtained formulas, we have studied the case of the K + ICl reactive collision, for which the transition appears to be fully in the sudden regime. The reorientation of the ICl axis is then calculated to be negligible. We expect these results to be rather general: although the various parameters involved can vary widely, the limitations imposed on some parameters by experimental constraints and the low sensitivity to other parameters (like the long-range C_6 coefficient) explain this general character.

Finally, we have verified that the applied electric field has little effect on the reaction dynamics for the K + ICl collision. More precisely, this should be unambiguously verified for integral properties like rates or total cross-section, but this might be wrong if one could look at some quantum interference effects.

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