Differential Cross Sections from Quantum Calculations on Coupled *Ab Initio* Potential Energy Surfaces and Scattering Experiments for $Cl(^2P) + H_2$ Reactions

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To assess the relative reactivity of the spin-orbit excited state of atomic Cl with molecular hydrogen, we have measured differential cross sections using an atomic Cl beam with a known concentration of the ground and excited spin-orbit states. These are compared with the first determination of the cross sections from quantum mechanical scattering calculations on a set of coupled *ab initio* potential energy surfaces. The comparison suggests that these surfaces may underestimate the degree of rotational excitation of the HCl products and that the excited spin-orbit state plays a minor role in the reaction.

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In the theoretical study of chemical reactions it is common to invoke the Born-Oppenheimer (BO) approximation. Within this approximation the motion of the nuclei occurs adiabatically, governed by the electronic energy of a single electronic state. Transitions between different electronic states are not allowed. This leads to a considerable simplification in the complex calculations. For bimolecular reactions in the electronic ground state the BO assumption is supported by the majority of prior experimental work [1,2] which indicates that nonadiabatic (BO forbidden) reactive pathways play only a minor role. This "adiabatic correlation rule" has been challenged by recent experiments on the reaction of chlorine atoms with molecular hydrogen [3,4]. Here the spin-orbit (SO) excited state of atomic chlorine (Cl^*, $^2P_{1/2}$) was inferred to be more reactive than the SO ground state, (Cl, $^2P_{3/2}$), although only atoms in the ground SO state correlate adiabatically with the observed products in their ground electronic state, $HCl(X^1\sum^+) + H(^2S)$. Such a striking and unexpected result forces us to go beyond the BO approximation and consider nonadiabatic effects in the dynamics of this exemplary reaction.

The theoretical study of nonadiabaticity in the reactions of halogens with molecular hydrogen goes back to the early work of Tully [5]. In 1995 Schatz [6] used previous work of Rebentrost and Lester [7] to develop the framework for the quantum mechanical (QM) treatment of reactive collisions involving multiple electronic states, using an expansion in hyperspherical coordinates and a close-coupled solution of the Schrödinger equation. Truhlar and co-workers [8] have presented a related treatment based on a variational solution. However, only in the past few years have calculations of full cross sections (rather than reaction probabilities) appeared for the reactions of $Cl(^2P) + HCl$ [9] and $F(^2P) + H_2$ [10]. As previously described [10], the exact treatment of these reactions involves six three-dimensional hypersurfaces: four diabatic electronic potential energy functions, and two coordinate-dependent SO couplings. All these six can be determined by multireference, configuration-interaction calculations. The scattering is then treated fully quantum mechanically, explicitly including all Coriolis coupling between the nuclear and electronic angular momenta. For the $F + H_2$ reaction, except at the lowest collision energies, calculated integral cross sections (ICSs) for the adiabatically forbidden reaction of the excited SO state were no more than 10% of those for the BO allowed reaction of the ground state [10]. In this Letter "collision energy" (E_c) designates the initial relative translational energy of the reactants.

Stimulated by Liu's recent experiments, a similar treatment has been applied to the title reaction [11] on a set of new *ab initio* potential energy surfaces (PES) [12]. There are several major differences between the $F + H_2$ and $Cl + H_2$ reactions: (i) the SO splitting of the Cl atom is larger than that of the F atom (2.52 as compared to 1.05 kcal/mol). This should imply that nonadiabatic effects will be less important in the $Cl + H_2$ reaction. However, (ii) the barrier height is much higher for the $Cl + H_2$ reaction (8.45 kcal/mol). Consequently, at low E_c the internal SO energy could help to overcome the barrier. Finally, (iii) the reaction of Cl with H_2 is nearly thermoneutral [reaction of the Cl is slightly endothermic ($\Delta H_0^\circ = +1.03$ kcal/mol) while reaction of Cl^* is slightly exothermic ($\Delta H_0^\circ = -1.49$ kcal/mol)], while the reactions of both SO states of F with H_2 are strongly exothermic. Despite the differences, the general trend predicted by recent QM calculations [11] is substantially similar to

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what was found for F + H_2: the ICSs for the BO allowed reaction of Cl are much larger than that of the BO forbidden reaction of Cl*. The latter reaction is important only at very low E_c, where the ground SO state does not have enough energy to overcome the barrier. As the collision energy increases, the reactivity of the ground SO state rapidly dominates. These results do not support the experimental observations of Liu and co-workers [4] who found that the reactivity of Cl* increasingly dominates as the collision energy increases.

To resolve this outstanding discrepancy, further theoretical and experimental studies are needed. Differential cross sections (DCSs) are a far more detailed probe of the dynamics than the ICSs. In this Letter we report a combined experimental and theoretical determination of the DCSs of the title reaction at three collision energies (3.85, 4.25, and 5.85 kcal/mol). More specifically, we have carried out crossed molecular beam (CMB) experiments using an atomic Cl beam with a defined population of the two SO states. We have also calculated DCSs for reaction of each SO state using the same PESs as in our earlier ICS calculations. Calculations have also been done at $E_c = 5.2$ kcal/mol, to simulate the DCS measurement of Lee and Liu at this energy [3]. This is the first time ever that reactive QM DCSs have been reported for a set of coupled *ab initio* PESs.

The scattering calculations have been performed using the six *ab initio* PESs of Capecchi and Werner [12]. In the entrance channel these correspond asymptotically to linear combinations of the six components of the ^2P state of the Cl atom, in particular, the four projection states of the $j = 3/2$ atomic angular momentum vector of the $^2P_{3/2}$ state and the two projection states of the $j = 1/2$ angular momentum of the $^2P_{1/2}$ state.

The definition of the states and matrix elements of the electronic Hamiltonian in this basis of six states are contained in Ref. [10]. The reactive DCS is determined in the helicity representation with the scattering amplitude given by [13]

$$f_{v\, j_t\, k_t \to v' j'_t\, k'_t}(\theta) = \frac{1}{2ik}\sum_J (2J+1)\, d^J_{k'k}(\pi-\theta) \times S^J(v\, j_t\, k_t, v' j'_t\, k'_t). \quad (1)$$

Here v and v' are the vibrational quantum numbers of the H_2 and HCl molecules and j_t, k_t and j'_t, k'_t are the total internal angular momenta and their projections along the separation coordinate $\vec{R}$ in the reactant and product arrangements, respectively. This total internal angular momentum is the vector sum of the rotational angular momentum of the diatomic moiety $\vec{j}$ and the total electronic angular momentum of the atom $\vec{j}_a$. The quantity $d^J_{k'k}$ is a reduced rotation matrix element and the quantity k in the denominator is the reactant wave vector. In the scattering calculations the S matrix is determined in a "partially coupled" basis in which the states are defined in terms of the quantum numbers v, j, k, j_a, and k_a [10], where j and k are the rotational angular momentum of the diatomic fragment (HCl or H_2) and its projection, and j_a and k_a are the total electronic angular momentum of the atomic fragment (H or Cl) and its projection. Since $\vec{j}_t = \vec{j} + \vec{j}_a$, the S-matrix elements in Eq. (1) can be obtained from the partially coupled S-matrix elements by a double Clebsch-Gordan orthogonal transformation. We assume that there is no selection of the projection quantum numbers k and k_a in the incident beam and that the product detection is independent of projection quantum number. Consequently, the physically relevant reactive DCS is proportional to the square modulus of the scattering amplitude in the partially coupled basis, summed over the final (and averaged over the initial) projection quantum numbers. The scattering calculations were done using the time-independent ABC scattering code [14], extended to include the internal spin and electronic orbital angular momenta [10]. Figure 1 shows the calculated DCSs summed over the final j' for different values of j and for both values of j_a at $E_c = 4.25$ kcal/mol. In Fig. 2 the ICSs as a function of the final rotational state of HCl products are shown, again for different values of j and for both values of j_a. The theoretical DCSs for the other collision energies investigated (not shown here) are essentially similar [15].

The experiments were done with a CMB apparatus with mass spectrometric detection and product time-of-flight (TOF) analysis, as described in detail in previous papers which presented experimental results at $E_c = 5.85$ kcal/mol [16,17]. Our theoretical calculations predict reactivity of Cl* to be most significant, as compared to the reactivity of Cl, at low collision energies. Consequently, we have extended our previous study to two additional collision energies (3.85 and 4.25 kcal/mol) which are below the dynamical threshold for the reaction $Cl(^2P_{3/2}) + H_2(v = 0, j = 0)$. Unfortunately, for favorable kinematics we were forced to use a slow atomic

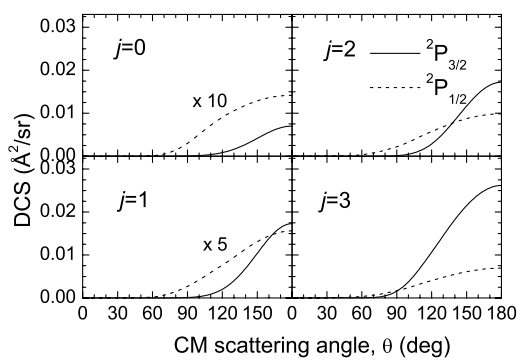

FIG. 1. QM CM DCSs for the different initial j of H_2 relevant in the crossed beam experiment (the $j = 4$ DCS was also calculated and used in the simulation, see text). The multiplication by 10 and by 5 on the left-hand-side panels refers to both curves (solid and dashed).

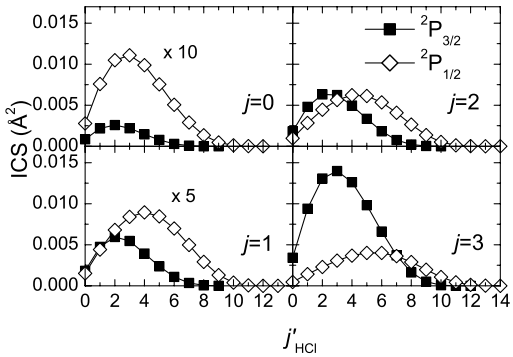

FIG. 2. QM ICSs as a function of final HCl j' for the different initial j of H_2.

beam (seeded in Ne) and fast molecular hydrogen beams, which were achieved by heating the gas, thus altering the H_2 rotational population (for a discussion on the effect of the kinematics for this reaction, see Ref. [17]). We have estimated the relative H_2 rotational state populations by extrapolating the experimental determination of Pollard *et al.* [18] for beams obtained under similar expansion conditions [19]. Since levels up to $j = 4$ are populated, the QM calculations were performed for $j = 0$–4. Unfortunately, the presence of excited H_2 rotational levels in the beams counteracts the advantage of working at low E_c, since H_2 rotational excitation strongly promotes the reaction of the SO ground state [17,20].

The characteristics of the radio frequency discharge source used to produce continuous beams of atomic chlorine are given in Ref. [21]. The ratios of the $^2P_{1/2}$ to $^2P_{3/2}$ populations were determined to be 0.22 ± 0.03 when using Ne as seeding gas ($E_c = 3.85$ and 4.25 kcal/mol) and 0.15 ± 0.03 when using He ($E_c = 5.85$ kcal/mol). For the experiments at $E_c = 3.85$ and 4.25 kcal/mol, the Cl beam velocity was 1615 m/s [speed ratio (SR) = 6.9]; the peak velocity of the H_2 beams was 3820 m/s (SR = 12) and 4020 m/s (SR = 11), respectively. For better sensitivity (see Ref. [17]) the reaction of ^{37}Cl was used to determine the laboratory angular distributions (LAD) shown in Fig. 3. The TOF spectra, also measured in our experiment, will be shown in a future paper [15].

To compare the QM calculations with the measured LADs in the most straightforward way, we have carried out a forward simulation by transforming the theoretical DCSs from the center-of-mass (CM) frame into the laboratory frame. In doing so we included an averaging over the experimental conditions (beam velocity distributions and angular divergences, detector aperture) as well as the relative populations in each $\{j, j_a\}$ initial state and their relative reactivity. Also, the translational energy distributions as predicted by QM calculations for each initial j were used in the simulation [the j' rotational distributions obtained in the calculations have been converted into final relative translational energy distributions, $P_j(E'_t)$, using the endothermicity predicted by the *ab initio* calculations [12]]. The energy dependence of the ICS predicted by the QM calculations for each j was also explicitly included in the convolution routine.

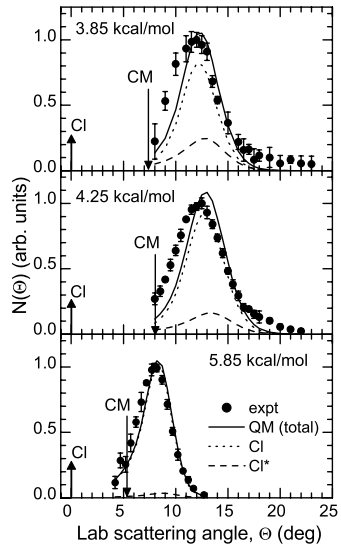

FIG. 3. HCl product laboratory angular distributions at the investigated E_c. The solid lines represent the LADs obtained from QM calculations. The separate contributions from the reactions of the two spin-orbit states of Cl are shown.

The comparison of this simulation with experiment is shown in Fig. 3. The QM calculations are able to reproduce the general features of the LADs, such as the pronounced backward scattering propensity, but fail to reproduce the detailed shape. At each E_c the simulations predict the peak in the LAD to occur at too large an angle. Also, for scattering at angles close to the CM position vector (which corresponds to sideways scattered and low recoil speed products) the predicted intensities are too small, even when the experimental uncertainties are taken into account.

We observe in Fig. 3 that the Cl* LADs are only a fraction of those of the ground SO state. In view of Liu's experiments, one might wonder whether the discrepancy between theory and experiment is due to an underestimation of the relative reactivity of Cl*. However (see Fig. 3), the peaks of the predicted Cl* LADs always occur at angles larger than those for the ground SO state. This is because, for an initial E_c, the products of the Cl* reaction will always have a greater translational energy, due to the internal (relatively large) SO energy of Cl*. Thus, were we to increase the weight of the Cl* contribution, the peak of the QM distributions would be shifted even more in the wrong direction. An increase in the Cl* contribution would help resolve the observed discrepancy only if the DCSs and energy release associated with reaction of Cl* were dramatically different than those associated with reaction of Cl. This appears to be unreasonable, since a single PES describes the exit channel for reaction of both SO states [12].

A detailed comparison of QM results with Liu's experiment will be the subject of a future paper. The QM results at $E_c = 5.2$ kcal/mol (not shown here) resemble, very closely, those shown in Figs. 1 and 2 (in Liu's experiments, the H_2 beam was cold, so that only $j = 0$ and 1 have appreciable populations). Notably, the QM DCS at $E_c = 5.2$ kcal/mol for the reaction of Cl is very similar to that derived from Liu's experiment with photolytic production of Cl beams. However, the QM DCS for reaction of Cl^* is more sideways peaked and the Cl^* contribution is much less significant than that derived by Liu from the experiment with the discharge Cl/Cl^* source. A significant discrepancy occurs also for the product rotational distributions: the QM distributions are peaked at $j' = 2$–3 and $j' = 5$ for reaction of Cl and Cl^*, respectively. In contrast, Liu's experimental distributions are peaked at $j' = 4$ and $j' > 7$. Unfortunately, a direct comparison between the present experimental results and Liu's is not possible, because in his experiment the H_2 beam contains only $j = 0, 1$ and the collision energy is different. Notwithstanding, as we have already noted, increasing the contribution of the excited SO reaction, as suggested by Liu, will lead to a poorer agreement with our experimental results, unless the dynamics of the reaction of Cl and Cl^* were to differ dramatically. This is not supported from the experimental data themselves, since Liu's CM DCSs show a clear propensity for backward scattering in both reactions.

In summary, for the reaction of Cl with H_2 QM scattering calculations lead to LADs which differ somewhat with the present CMB results. It is possible that the calculations predict: (i) too large an increase in reactivity with the increase in initial H_2 rotation, (ii) a DCS which is peaked at too large an angle, or (iii) too little energy released as final HCl rotation. The last possibility would be also consistent with the energy release of the ground SO state reaction derived by Liu and could be due to residual imperfections in the topology of the product channel of the *ab initio* PES.

The scattering calculations based on coupled electronic PESs allow us to assess the contribution of the excited SO state of Cl to the DCS of the overall reaction. The calculations suggest that (a) the magnitude of the DCSs for the SO excited state reaction are much smaller than those of the ground state reaction and (b) the calculated LADs are shifted to a larger angle than those for the ground state reaction. Consequently, the discrepancy between the calculations and the experiments described here would not be resolved by invoking a greater relative reactivity of the excited SO state, provided that the theoretically predicted DCSs are at least qualitatively correct. It should also be noted that the use of the experimental value of the reaction endothermicity in transforming $P(j)$ into $P_j(E_t')$ would make the agreement slightly worse, since the calculated LADs would be shifted further towards larger angles as a consequence of more energy (0.4 kcal/mol) available for translation.

We conclude that crucial features of the $Cl + H_2$ reaction are not yet fully understood, in particular, the details of the product internal energy release and the relative reactivity of the excited SO state.

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