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State-resolved reactive scattering by slice imaging: A new view of the Cl+C$_2$H$_6$ reaction

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We present state-resolved crossed beam scattering results for the reaction Cl+C$_2$H$_6$→HCl+C$_2$H$_5$, obtained using direct current slice imaging. The HCl ($v=0, J=2$) image, recorded at a collision energy of 6.7 ± 0.6 kcal/mol, shows strongly coupled angular and translational energy distributions revealing features of the reaction not seen in previous studies. The overall distribution is mainly forward scattered with respect to the Cl beam, with a translational energy distribution peaking near the collision energy. However, there is a substantial backscattered contribution that is very different. It shows a sharp peak at 8.0 kcal/mol, but extends to much lower energy, implying substantial internal excitation in the ethyl radical coproduct. These results provide new insight into the reaction, and they are considered in terms of alternative models of the dynamics. This work represents the first genuine crossed-beam study in which a product other than the methyl radical was detected with quantum state specificity, showing the promise of the approach generally for high resolution state-resolved reactive scattering. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2150434]

The reactions of chlorine atoms with alkanes have been the subject of intense scrutiny owing both to their important role in atmospheric chemistry and as model systems for the detailed investigation of polyatomic reaction dynamics. In fact, interest in these systems has accelerated in recent years as new experimental methods, such as the *photoloc* and imaging techniques, have provided the means of gaining insight into the reaction with quantum state specificity. Dagdigian *et al.*[1] and Zare and co-workers[2–4] are among the pioneers who studied the detailed state-resolved dynamics of the reaction of chlorine atoms with small hydrocarbons. The *photoloc* technique combined with core extraction has been applied extensively to obtain the HCl product state distribution and differential cross sections for Cl reaction with methane, ethane, and methanol by Zare and co-workers.[2–4] However, even though great care was taken to deconvolute the center-of-mass velocity and angular distributions, accurate extraction of these distributions is difficult and sometimes uncertain owing to blurring by the internal energy spread in the undetected product. Results for the title reaction represent a telling example. The reaction was studied at a collision energy of 5.5 kcal/mol by Kandel *et al.*[2] and later by Bass *et al.*[5] Both groups employed the *photoloc* method and obtained essentially the same laboratory velocity distributions. However, the interpretations of data were quite different because different analysis methods were used by two groups.

Therefore, a direct method is clearly needed to obtain the detailed state-resolved product distributions unambiguously.

Crossed beam ion imaging methods have been successfully applied to inelastic scattering[6] and reactive scattering[7] experiments and can more directly provide the center-of-mass velocity, angular distributions and even the velocity-flux contour map of the products. Suits and co-workers studied the O(^{3}P) and Cl(^{2}P)[7–9]+alkanes reactions with "universal" detection of the alkyl radical using single photon vacuum ultraviolet (VUV) ionization. However, it has proven to be challenging to use state-resolved probes such as resonance-enhanced multiphoton ionization (REMPI) in crossed beam imaging studies due to the low signal levels arising from the small probe volumes associated with multiphoton ionization. In an effort to get adequate signal levels in imaging studies, some compromises have been made, such as the use of unskimmed beams employed by Kitsopoulos and co-workers.[10] Genuine crossed beam state-resolved scattering was first achieved by Liu and co-workers,[11] who reported spectacular results for the reactions F+CH$_4$ and CD$_4$ using a "time-sliced" imaging approach essentially equivalent to the (direct current) (DC) slicing method employed here. In Liu's crossed-beam studies, images of CD$_3$ and CH$_3$ were acquired using 2+1 REMPI detection. With this capability, Liu and co-workers have thoroughly investigated F +CD$_4$(CH$_4$),[12] Cl+CD$_4$(CH$_4$),[13] and OH+CD$_4$(CH$_4$)[14] systems. However, to date the methyl radical remains the only product successfully probed with quantum-state specificity in crossed beam imaging studies, and rotationally resolved re-

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sults have only been reported for the $F+CD_4$[11] reaction (Ref. 11). Here, we present results for DC slice imaging of HCl ($v=0, J=2$) for reaction of Cl with ethane. The results provide new insight even for the well-studied systems such as $Cl+C_2H_6$. Furthermore, they demonstrate sufficient sensitivity to suggest that a wealth of other systems will now be amenable to direct probe using state-resolved DC slice imaging.

The experiment was carried out in a crossed beam imaging apparatus described elsewhere.[15] Recent modifications to the apparatus will be described in detail in a forthcoming paper.[16] Here a brief description of the essential experimental components will be provided. The chlorine atom beam is generated by photolyzing a 10% Cl_2/He mixture using 308 nm laser (typical power 40 mJ/pulse) at the nozzle of a piezoelectric pulsed valve, with the resulting atomic beam entrained in the jet. Less than 1% fluorine was also added to the Cl_2/He mixture to suppress the HCl contamination. The beam was then skimmed before entering a separate interaction chamber. The ethane beam, seeded 40% in helium, was expanded from 5 bar in a piezoelectric valve, skimmed, then intersected the chlorine beam at an angle of 90°. The collision energy was 6.7±0.6 kcal/mol (quoted uncertainty is full-width half-maximum spread in the collision energy based on measured beam velocity distributions). The product HCl ($v=0, J=2$) was ionized using 2+1 REMPI through $F\ ^1\Delta_2$ state. In order to efficiently ionize and collect all the product molecules, we used the fundamental output of a 532 nm-pumped Sirah dye laser which was sum frequency mixed with the third harmonic of the injection-seeded pump laser at 355 nm. This gave about 8–9 mJ/pulse at 241.16 nm. The high power of the probe laser was a major factor contributing to the improved sensitivity. An $f=50$ cm spherical lens was employed and the probe laser was loosely focused at the interaction region. The slice imaging detection scheme[17] and IMACQ Megapixel acquisition program[18] were used to accumulate the raw images. The associated IMAN program was used to analyze the data.

The raw image of HCl ($v=0, J=2$), obtained with about four hours of data accumulation, is shown in Fig. 1. This image has not been processed in any way. From the image, it is apparent that the number density to flux correction is small. This correction was performed by scaling the pixel intensity by the lab velocity at each point. In the right side of the image, there is also a small amount of enhancement due to Doppler selection. This distortion was also corrected before analyzing the results. After making these corrections, the resulting image represents a direct measurement of the velocity-flux contour map. In the present case, because these are modest and roughly opposing corrections, the raw image itself is a close approximation to the contour map.

The angular distribution extracted from the image is shown for several different velocity ranges of the product in Fig. 2. It can be seen that the fast product has a near-forward peaking trend while the slower products are mainly backward and sideways scattered (defined with respect to the Cl beam direction). In the backward direction, both slow and fast products show ringlike structure, which means they have well defined translational energy release. It is clear that trans-
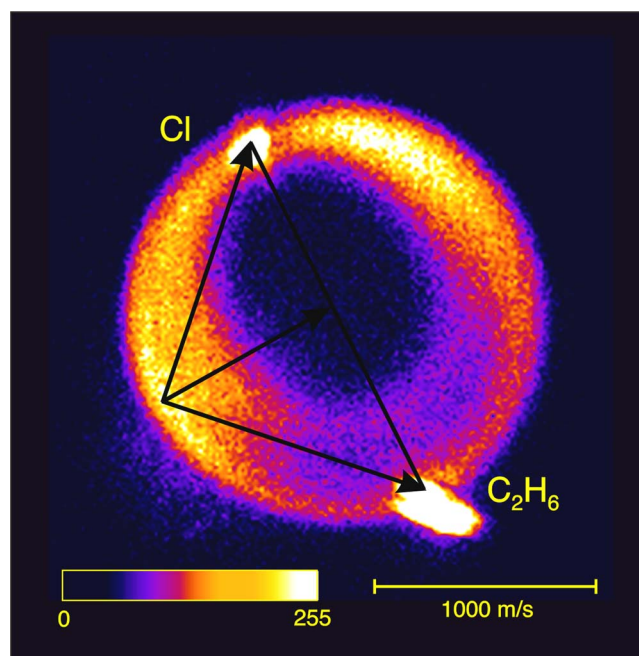

FIG. 1. Raw image of HCl ($v=0, J=2$) with Newton diagram superimposed.

lational energy and the angular distributions are very strongly coupled. In the translational energy spectrum (Fig. 3), the dot-dashed line was obtained by integrating the signal in the backward direction. A sharp peak is seen at high energy, with a very broad shoulder and the suggestion of a second peak at lower energy. The peaks correspond to 8.0 and 3.2 kcal/mol. Considering the total available energy 9.4 kcal/mol and the HCl ($J=2$) rotational energy, the ethyl radical was found to have 1.2 and 6.0 kcal/mol deposited to its internal degrees of freedom at these peaks. These represent 15% and 66% of the total available energy. Figure 3 also shows that the slow product becomes weaker in the sideways direction and completely disappears in the forward direction, while the fast product becomes stronger toward the forward hemisphere. This detail of the coupling between translational energy and angular distribution was not available from single
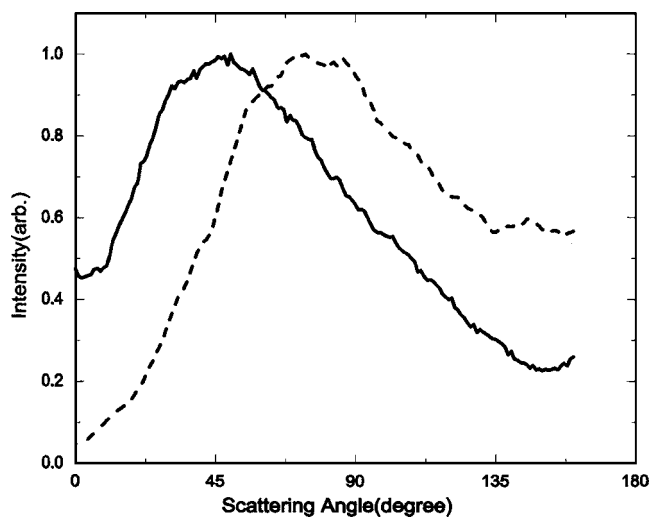

FIG. 2. Center-of-mass angular distribution at different recoil velocities: solid line, 0–670 m/s; dashed line, 670–1046 m/s.
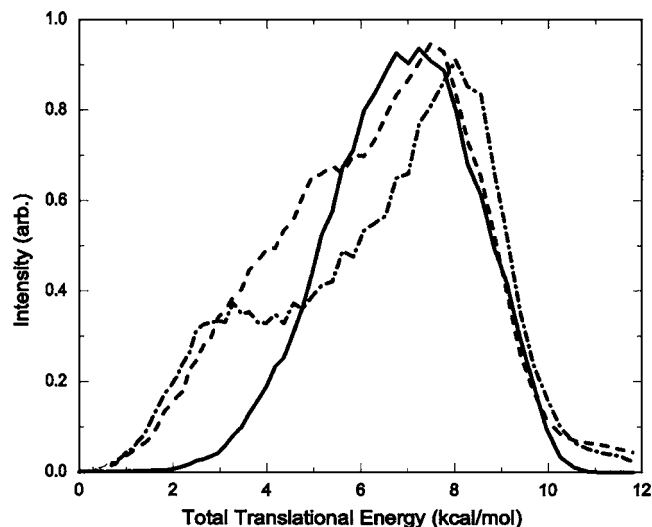
FIG. 3. Translational energy release for the following center-of-mass angular regions: solid line, 5–50°; dashed line, 55–115°; dot-dashed line, 124–175°.

beam *photoloc* experiment. In comparing to previous results, we find the average excitation of the ethyl radical for the dominant fast HCl products is about 23% of the total available energy, which is in agreement with the results by Bass *et al.*[5] The internal energy of the ethyl radical corresponding to the slow HCl product in the backward direction is as high as 66% of the total available energy. Since the signal intensity for this slow HCl feature is small, it is not surprising that previous experiments were unable to detect it.

Now we turn to a discussion of the dynamics. Earlier experiments by Kandel *et al.*[2] and Bass *et al.*[5] offered opposing conclusions about the role of ethyl radical in this reaction. The Zare group[2] found only 7% of the total available energy going to the internal excitation of the ethyl radical and concluded it merely a spectator in the reaction. Bass *et al.* found substantial ($>20\%$) internal excitation in the ethyl radical and concluded it plays a significant role in the dynamics. We find the results of Bass *et al.* in closer agreement with our own. However, our new results provide more detailed dynamical information. The translational energy distributions for the forward and backward scattered products are clearly distinct, and we will consider them separately. In the forward direction, the translational energy distribution peaks at the collision energy and has a significant width. A "stripping" mechanism as proposed by Zare and co-workers[19] for Cl+CH$_4$ can be used to explain this.

In the backward direction, the "rebound" model by Zare and co-workers cannot account for the two-peak feature for two reasons. One is that the backward scattered fast HCl (8.0 kcal/mol) is actually faster than that in the forward direction (7.0 kcal/mol), which is opposite to the prediction of the model. The other reason is that the rebound model cannot explain the 3.2 kcal/mol feature, which has far too much ethyl radical internal excitation. To explain the translational energy distribution in the backward direction, we adapt the kinematic model proposed by Valentini *et al.*[20] This simple limiting model constrains the translational energy of the products to be larger than $E_{col} \cdot \cos^2 \beta$ for exothermic reac-

tions, where β is the skew angle for the reaction and E_{col} is the collision energy. The reaction Cl+C$_2$H$_6$ is a typical heavy-light-heavy reaction, which has small skew angle of 14.2°. The calculated minimum translational energy is thus 6.3 kcal/mol. If we consider the collision energy uncertainty, the distribution for the fast HCl component in the backward direction is quite consistent with this model. However, the slow component represents a profound deviation from it. Nevertheless, the kinematic picture proposed by Valentini may help us to understand this deviation. One fundamental assumption of this model is that the trajectory reflection toward products happens only once in the inner potential wall, and only trajectories that have a sufficient projection of the recoil velocity on the exit coordinate may escape to products. However, multiple reflections between outer and inner potential wall are also likely to take place owing to the small skew angle for the system. For the reactions with these trajectories, H atoms are temporarily trapped in "chattering collisions" and this may enhance coupling of the collision energy into internal excitation of the products.[21] This picture accounts for the fact that this shoulder to low energy only occurs in backward direction where chattering collisions are possible. Dynamical calculations will be useful to investigate this aspect of the dynamics.

In conclusion, we show state-resolved slice imaging in crossed-beams under single collision conditions opens the door to a more detailed understanding of Cl+alkane reaction dynamics. The results also demonstrate the general feasibility of state-resolved REMPI detection in crossed beam slice imaging studies.

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