The dynamics of the $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl}(v',j') + \text{C}_2\text{H}_5$ reaction at 0.24 eV: Is ethyl a spectator?

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The hydrogen atom abstraction reaction between Cl($^2P_{3/2}$) and ethane has been studied at a mean collision energy of 0.24 eV. The experiments were performed in a coexpansion of molecular chlorine and ethane, with the atomic Cl reactants generated by laser photodissociation of Cl$_2$ at 355 nm. HCl($v',j'$) products were detected quantum state selectively using (2 + 1) resonantly enhanced multiphoton ionization, coupled with velocity-map ion imaging. The ion images were used to determine center-of-mass angular and kinetic energy release distributions. Several analysis methods were employed and have been carefully assessed. It is shown that the single beam experiments can be used with confidence to determine both center-of-mass angular and energy release distributions. For the title reaction the angular distribution is found to be forward peaking, with on average 22% of the available energy channeled into internal excitation of the ethyl coproducts. Possible sources of this internal excitation are discussed. © 2003 American Institute of Physics.

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I. INTRODUCTION

The use of laser pump–probe methods to study the dynamics of elementary bimolecular reactions has a long history. These experiments can be represented by the following sequence of processes:

$$h\nu \rightarrow AX \rightarrow A + X,$$

$$A + BC \rightarrow AB(v',j') + C.$$  \hspace{1cm} (1)

Molecular photodissociation is used to generate fast (usually atomic) reactants with well-defined velocities, which then react with molecular target molecules (represented here as BC). The $AB(v',j')$ products of the reaction are probed quantum state selectively at sufficiently short pump–probe delay times to ensure single collision conditions.

Such hot atom experiments have been used to great effect to study quantum state population distributions\(^5\) and reaction cross sections.\(^2\) However, the photon-initiated scheme also offers a route to the center-of-mass (CM) angular distribution of the scattered products\(^3,4\) [proportional to the differential cross section (DCS)] and, through the use of polarized pump and probe radiation, their angular momentum polarization\(^5,6\) [characterized by a set of polarization dependent differential cross sections (PDDCSs)\(^3\)]. The principle of these experiments lies in the fact that, under certain limiting conditions, there is a simple law-of-cosines relationship between the laboratory (LAB) frame speed distribution and the CM frame angular distribution.\(^3,4\) leading Zare and co-workers to coin the acronym PHOTOLOC (photo law-of-cosines)\(^5\) to describe the technique. Experiments of this type have fallen into two distinct classes, those performed under single molecular beam (coexpansion) conditions,\(^7–9\) and those performed under room temperature bulb conditions.\(^6,10–16\)

An important feature of the PHOTOLOC technique is that it allows product state-resolved CM angular distributions to be obtained from bulb or single beam (coexpansion) experiments, which provide much higher product number densities than can be achieved in crossed molecular beams. A second advantage is that the transformation between density and flux is comparatively straightforward, provided that the pump–probe delay times employed are sufficiently short to avoid problems with fly-out.\(^6,14\) This could be an advantage over the parallel beam technique,\(^17\) for example, recently used by Suits and co-workers to study the reactions of O with alkanes,\(^18\) and by Toomes and Kitsopoulos to study the reactions of Cl with ethane and butane.\(^19\) In the latter experiments, the photolysis precursor and target molecules are entrained in two separate, parallel molecular beams. This method overcomes the problems of unwanted background reaction between precursor and reactant inherent in single beam techniques, but is complicated by the requirement for carrying out careful simulations in order to extract the CM angular distribution.\(^18\)

A major issue with the PHOTOLOC method concerns the question of whether or not it can be used to extract the full product flux distribution in both CM speed, $w$, and scattering angle, $\theta$, when the coproduct C in Eq. (1) possesses internal structure, as is necessarily the case when C is a molecule. A number of PHOTOLOC studies have presented CM angular distributions derived by neglecting...
the internal excitation of the molecular coproduct entirely.\textsuperscript{8,20} However, information about the kinetic energy release of the reaction is contained in the LAB frame speed distribution, $P(v)$, and the LAB speed-dependent translational anisotropy, $\beta(v)$.\textsuperscript{15,20–22} The latter is equivalent to the translational anisotropy parameter familiar from molecular photodissociation.\textsuperscript{23} Both $P(v)$ and $\beta(v)$ can readily be obtained experimentally from the variation in product signal intensity with photolysis laser polarization. Compared with a crossed molecular-beam experiment, which determines the CM distribution, $P(w, \theta)$, via transformation of the full LAB frame angular distribution, $P(v, \theta_v)$, the PHOTOLOC experiment attempts to reconstruct the CM angular distribution using just the first two even (speed dependent) moments of the LAB angular distribution, $P(v)$ and $\beta(v)$. A variety of alternative methods have been proposed for using this information to extract the CM angular distribution of interest. These methods (described more fully in Sec. II B) rely either on inversion of the LAB speed distribution and speed-dependent anisotropy,\textsuperscript{20,21} or on fitting the experimental data using a set of basis functions which accommodate a distribution of product speeds, or fractional kinetic energy releases ($f_j$).\textsuperscript{13,15} The latter method has been used traditionally to fit Doppler-resolved laser induced fluorescence (LIF) signals from photon-initiated reactions studied under bulb conditions,\textsuperscript{3,6} while the former inversion method has been applied to the core extraction experiments by Zare and co-workers.\textsuperscript{4,5}

In this paper we apply the PHOTOLOC method to a new ion-imaging study of the photon-initiated reaction

$$
\begin{align*}
\hbar \nu &
\quad \text{Cl}_2 \rightarrow \text{Cl}(^2P_{3/2}) + \text{Cl}(^2P_{3/2}), \\
\text{Cl}(^2P_{3/2}) + \text{C}_2\text{H}_6 &\rightarrow \text{HCl}(v', j') + \text{C}_2\text{H}_5,
\end{align*}
$$

(2)

where atomic Cl reactants were generated preferentially in their ground electronic state by photodissociation of molecular chlorine at 355 nm. The new data have been analyzed using the basis function method to obtain angular and kinetic energy release distributions. Alternative analysis methods, which either (i) neglect the ethyl internal excitation altogether, (ii) use $\beta(v)$ to attempt an inversion of the data, or (iii) treat the internal excitation as a delta function at some fixed nonzero value of $f_j$, are also employed and carefully assessed. We show that the basis function analysis allows the fewest number of assumptions to be made about the nature of the energy release, and provides a clear indication of the CM angular and speed resolution of the experiments.

Reaction (2) has been the focus of several previous experimental investigations, having been studied using both the core extraction PHOTOLOC technique of Zare and co-workers,\textsuperscript{20,21,24} and the velocity map\textsuperscript{25} ion-imaging\textsuperscript{26} technique by Kitsopoulos and co-workers.\textsuperscript{9} The data from HCl resonantly enhanced multiphoton ionization (REMPI) core extraction experiments were first analyzed on the assumption that the ethyl coproduct takes away no internal excitation.\textsuperscript{20} The assumption of internally cold coproducts was supported by measurements of $\beta(v)$, which suggested that on average the ethyl products were born internally cold.\textsuperscript{20} Further evidence for this was provided by probing the LAB velocity distribution of the ethyl products non-state-selectively using multiphoton ionization.\textsuperscript{21} These experiments were analyzed using the inversion method mentioned above, which yielded CM angular distributions consistent with those derived from the state-resolved HCl experiments when reanalyzed using the same inversion procedure.\textsuperscript{21} Unlike the present experiments and the previous studies by Zare and co-workers, the ion-imaging experiments of Kitsopoulos and co-workers\textsuperscript{9} used 308 nm radiation to photolyze Cl\textsubscript{2} (as opposed to radiation at 355 nm). The data were analyzed by inverting $P(v)$ and $\beta(v)$, but the differences in collision energy ($\sim 0.36$ eV as opposed to 0.24 eV) meant that direct comparison between the results of the two sets of experiments was not possible.

The paper is structured as follows: The following section describes the experimental details of the ion-imaging experiments, while details of the various analysis procedures employed are outlined in Sec. II B. The results are presented and analyzed in Sec. III and are critically assessed and discussed in Sec. IV.

II. METHOD

A. Experimental procedures

The experiments were performed using the ion imaging apparatus at the Institute for Electronic Structure and Laser in Crete, which has been described in detail elsewhere.\textsuperscript{9,27} A 1:1 mixture of Cl\textsubscript{2} and ethane stored in a glass bulb at a backing pressure of $\sim 600$ Torr was coexpanded in a pulsed molecular beam using a homemade piezoelectric nozzle with a 1 mm orifice operating at 10 Hz. Standard velocity-mapping ion optics\textsuperscript{25} were mounted directly in front of the nozzle, with the nozzle and the repeller plate maintained at the same voltage to avoid electrical discharging during the gas pulse.

Mid-way between the repeller and extractor plates the molecular beam was intersected at right angles by two counter-propagating laser beams. Photolysis of Cl\textsubscript{2} at 355 nm using the third harmonic output of a Nd:YAG laser ($\sim 20$ mJ per pulse) afforded nearly monoenergetic ground state Cl($^2P_{3/2}$) atoms travelling at 1675 ms$^{-1}$. Assuming that the relative motion between the molecular chlorine precursor and ethane is small, due to efficient translational cooling in the jet expansion, the photolysis defines the relative motion of the chlorine atom and the ethane molecule yielding a mean collision energy of 0.24 eV with a full-width-at-half-maximum of 0.05 eV. The spread is due to residual thermal motion of the precursor and reagent, and was calculated using an estimated translational temperature of 50 K based on probe-only images of background HCl\textsuperscript{3} (see below).

The HCl($v' = 0$) products were detected with rotational state-resolution via $(2 + 1)$ resonantly-enhanced multiphoton ionization (REMPI), either through the Q-branch of the $E(1\Sigma^+)$ state\textsuperscript{28} for $j' = 0$, or through the R-branch of the $F(\Delta_2)$ state\textsuperscript{28} for $j' = 1$ and 3. The probe radiation was generated using the frequency-doubled output of a Nd:YAG-pumped optical parametric oscillator (Spectra-Physics Pro
250, MOPO) with a typical pulse energy of \( \sim 1 \text{ mJ} \). For each transition the probe laser was scanned over the Doppler profile of the HCl product. Both photolysis and probe laser beams were linearly polarized in the plane of the detector and were focused using 25 cm focal length lenses. The timing of the experiment was controlled using digital delay pulse generators (SRS DG535). A short delay of between 120 and 150 ns between the photolysis and probe laser pulses allowed sufficient HCl product density to build up prior to detection. Due to the narrow focus of both laser beams, care was taken to ensure that fly-out was avoided (see Sec. III). Suitable electrostatic potentials applied to the repeller and extractor plates of the ion optics effected velocity-mapping\(^{25} \) of the ionized reaction products onto the detector [a pair of matched MCPs (Hamamatsu) coupled to a P46 phosphor anode (Proximtronic)]. \(^{35}\text{Cl}^+ \) ions were detected mass-selectively by pulsing the voltage applied to the MCPs from \(-1100\) to \(-1600 \text{ V}\) at the appropriate time-of-flight. The resulting images were captured using a CCD camera (Cohu 4910) and sent to a PC for signal averaging (EyeSpy Software by k-Space Associates).

As shown in Fig. 1(a), velocity calibration of the ion images was achieved by direct detection of the Cl(\(^{2}P_{3/2}\)) photofragments from Cl\(_2\) photolysis at 355 nm via the \(4p^{2}P_{3/2} \rightarrow 2^{2}P_{3/2}\) transition at 240.46 nm.\(^{29} \) This image, and others like it, was obtained under similar time-delay and molecular beam intensity conditions to those used for the studies of the Cl+C\(_2\)H\(_6\) bimolecular reaction. The radial coordinate of the resulting images could be transformed directly into velocity using the known single velocity of the Cl photofragment.\(^{30} \) Direct Abel inversion of the Cl images allowed determination of the speed resolution of the apparatus, which was found to be \( \sim 6\% \) [see Fig. 1(b)]. The Abel-inverted image yields a translation anisotropy parameter \( \beta_0 \) close to \(-1.0\) for the photodissociation process, suggesting that collisional scrambling of the Cl velocity distribution prior to reaction is unlikely to be a serious problem in the present experiments (see also Sec. III).

Acquisition of ion images of reactively scattered HCl was complicated by the presence of a cold background HCl signal arising from unwanted side-reactions in the gas lines [see Fig. 1(c)]. This background signal was observed as a bright spot in the center of the HCl images, which could be minimized by using fresh gas mixtures approximately every three hours. Probe-only images of the background HCl were obtained after collection of each signal image and were subtracted from the signal images. However, since the background subtraction is imperfect, this central portion of the image was not used in the data analysis. It should be stressed that the region of the image obscured by the cold background signal corresponds to extreme backward scattering of the HCl products with near maximum CM kinetic energy (corresponding to CM scattering angles between 180° and 175°), and thus does not severely impair the analysis.

**B. Data analysis**

The analysis of the images was performed in two separate ways.

**1. Method 1**

In this method, the ion images were first inverted using the inverse-Abel transformation to obtain the full three-dimensional (3D) velocity in the LAB frame (in which the \( z \)-axis lies parallel to the electric vector of the photolysis light, \( \mathbf{E} \)). The analysis then followed the procedure first developed by Kandel *et al.*,\(^{20} \) which neglected any spread of velocities in the reactant Cl atom or target ethane molecules and assumed the ethyl coproduct is produced with a single internal energy. The latter was either chosen to be zero, as employed in the HCl REMPI experiments of Zare and co-workers,\(^{20} \) or alternatively, was estimated by inversion of the speed dependent translational anisotropy, \( \beta(\mathbf{v}) \), where \( \mathbf{v} \) is the LAB frame speed of the HCl product.\(^{20,21} \) We outline the latter procedure below.

The law of cosines may be used to relate the LAB to the CM frame.\(^{3,4} \) In terms of the HCl LAB speed, \( \mathbf{v} \), the velocity of the CM, \( \mathbf{v}_{\text{CM}} \), and the recoil speed of the HCl in the CM frame, \( \mathbf{w} \), one can write

\[
\begin{align*}
\mathbf{v}^2 &= v^2 + v_{\text{CM}}^2 + \mathbf{v}_{\text{CM}} \cdot \mathbf{w} \\
\mathbf{w}^2 &= w^2 + v_{\text{CM}}^2 - 2 v w \cos \theta 
\end{align*}
\]

\[\text{(3)}\]
where
\[
\cos \theta_v = \hat{\mathbf{r}} \cdot \hat{\mathbf{v}}, \quad \cos \theta = \hat{\mathbf{r}} \cdot \hat{\mathbf{w}}
\] (4)
and \(\mathbf{v}_r\) is the relative velocity vector. In this analysis \(\mathbf{v}_r\) lies parallel to \(\mathbf{v}_{CM}\), because the ethane reactant is assumed to be stationary relative to the photolysis precursor, \(\text{Cl}_2\). Neglecting any spreads in the reactant velocity distributions, it follows that a simple Jacobian relates the CM angular distribution to the measured LAB frame speed distribution:
\[
P(\cos \theta) = P(v) \frac{w_{CM}}{v}.
\] (5)
where the distribution functions are normalized such that
\[
\int_{-1}^{+1} P(\cos \theta) \cos \theta \, d \cos \theta = \int_{v_{min}}^{v_{max}} P(v) \, dv = 1.
\]

The LAB angular distribution takes the same functional form as that for the molecular photodissociation step employed to generate the translationally excited Cl atoms\(^{3,4}\) (see also the following section). Thus, analogous to molecular photodissociation,\(^{23}\) it follows that we may write the LAB translational anisotropy
\[
\beta(v) = \beta_0 \langle P_2(\cos \theta_v) \rangle = \beta_0 P_2(\cos \theta'_v),
\] (6)
where \(\beta_0\) is the translational anisotropy of the \(\text{Cl} (^2P_{\Sigma})\) atoms generated in the 355 nm photodissociation of molecular \(\text{Cl}_2\), and \(\theta'_v\) is the value of \(\theta_v\) estimated assuming a single CM product speed, \(w\). The right-hand equation in Eq. (6) can therefore be used to estimate \(\theta'_v\) as a function of LAB speed, \(v\). Since all the reactant velocities are known, once \(\theta'_v\) has been determined, the product CM speed, \(w\), and (hence the fractional kinetic energy release, \(f_i\)) can be determined as a function of LAB speed using Eq. (4). Once all the relevant reactant and product speeds are known, the CM scattering angle corresponding to a particular LAB speed can be determined from Eq. (3). It must be emphasized, however, that the simplifying approximation used on the right-hand side of Eq. (6) is that the CM recoil velocity of the products is fixed. Thus, a unique value of \(\theta_v\), i.e., \(\theta'_v\), and hence the product speed \(w\) and center-of-mass scattering angle \(\theta\) can only be obtained from Eq. (6) if the kinetic energy release distribution is a delta function.

2. Method 2

The second analysis method followed that developed to fit the Doppler resolved LIF profiles of the products generated in photon-initiated reactions.\(^3,6,14,15\) Unlike method 1, this procedure allows for the distribution of product CM velocities which arises from population of different internal quantum states in the ethyl coproduct. The method relies on fitting Legendre moments of the image with a set of suitably chosen basis functions. We have recently demonstrated the general approach by applying a similar moment analysis to photofragment ion images.\(^31\) The method has also been illustrated, and tested, using simulated ion images.\(^{15,31}\)

The joint distribution in CM scattering angle \(\theta\) and fractional kinetic energy release \(f_i\) can be written as a Legendre polynomial expansion
\[
P(\theta, w) = P(\theta, f_i) \left| \frac{df_i}{dw} \right| = \sum_{n,m} a_{nm} P_n(\cos \theta) P_m(f_i) \left| \frac{df_i}{dw} \right| ,
\] (7)
where \(w\) is the measured speed of the HCl, and
\[
f_i = \left( 2 f_i - 1 \right),
\]
and \(E'_{r,\text{max}}\), the maximum possible kinetic energy release, is given by
\[
E'_{r,\text{max}} = -\Delta H^\infty_{\text{Cl}} + E_i + E_{\text{C}_2\text{H}_6} - E_{\text{HCl}}.
\]

In these equations \(M\) is the total mass, \(E_i\) is the collision energy, and \(E_{\text{C}_2\text{H}_6}\) and \(E_{\text{HCl}}\), appearing in the final expression, are the average internal energy of the \(\text{C}_2\text{H}_6\) precursor (taken to be zero) and the \textit{fixed} internal energy of the probed HCl quantum state, respectively. The moments of the CM distribution were assumed to be independent of the comparatively narrow spread of reactant relative speeds, \(v_r\).

For a reaction initiated by linearly polarized photolysis radiation, the corresponding LAB frame velocity distribution takes a particularly simple form. We define the LAB frame with the \(z\) axis parallel to the photolysis polarization vector \(\mathbf{e}\), and the \(x\) axis along the photolysis propagation vector. (Note that for the pump–probe geometry employed in this work, the photolysis propagation and electric vectors lie in the image plane, i.e., the \(xz\) plane.) In the absence of rotational alignment effects, which tend to be small for HCl due to efficient hyperfine depolarization,\(^{24,32}\) it has been shown\(^3,4,6\) that integration of the joint CM scattering distribution of Eq. (7) over the reagent and precursor velocities leads to the LAB velocity distribution
\[
P(v, \Theta_v) = \sum_L B_L(v) P_L(\cos \Theta_v)
\] (8)
with \(L = 0\) and 2, and where \(\Theta_v\) is the angle between the photolysis \(\mathbf{e}\) vector and the HCl LAB velocity vector, \(\mathbf{v}\). \(P_L(\cdots)\) are the Legendre polynomials. Explicit expressions for the \(B_L(v)\), which are proportional to the bipolar moments \(B_L^e(0, v)\) averaged over all reactant velocities, have been presented previously in the context of Doppler profile analysis.\(^3,6\) \(B_0(v) = P(v)\) is the LAB speed distribution of the products [used in Eq. (5) of method 1], and the LAB frame translational anisotropy is \(\beta(v) = B_2(v)/B_0(v)\) [cf. Eq. (6) of method 1].

The expression for a simulated ion image, \(I(v_r, \phi)\), may be obtained by integrating Eq. (8) over \(v_r\). This yields
\[
I(v_r, \phi) = \sum_L M_L(v_r) P_L(\cos \phi),
\] (9)
where \(v_r\) and \(\phi\) are the radial and angular polar coordinates of the image, and the nonzero moments \(M_L(v_r)\) are given by
Although Eq. (9) could be used to simulate images given known CM distributions, the present approach relies on using Eqs. (10) and (11) to generate sets of basis functions, \( b_L(n,m;v_p) \) which are then fitted to the experimental data. The basis functions were obtained by replacing the full CM frame joint distribution of Eq. (7) used to simulate \( M_L(v_p) \), by the product of two Legendre polynomials, \( P_p(\cos \theta)P_m(\cos \phi) \). The basis functions were generated by Monte Carlo integration of the relevant terms in the CM scattering distribution over all reactant and precursor velocities, in much the same way as previously performed for Doppler-profile analysis. The basis functions used in the present work assumed a translational beam temperature transverse to the beam direction of 50 K, which (as noted in Sec. II A) provides a good description of the images obtained for background HCl. They also allowed for the instrument resolution, which was estimated from Cl-atom photofragmentation distributions, and that both studies were determined by minimizing \( \chi^2 \) for the fit using a genetic algorithm subroutine, in which the fitting coefficients were constrained to lie within their physical limits. The choice of basis function ensures that the coefficients returned by the fit, \( a_{nm} \), correspond to the moments of the joint CM distribution given in Eq. (7). Satisfactory fits to the data could be obtained assuming a joint CM distribution of separable form, for which the \( a_{nm} \) coefficients may be set equal to \( a_p \times d_m \), where \( a_p \) and \( d_m \) are the coefficients for the Legendre expansion of the angular and kinetic energy release distributions, respectively. Converged fits to the data were obtained with three moments in \( \cos \theta \) and five moments in \( f_j \) (also see Sec. III). The error limits on \( P(\cos \theta) \) and \( P(f_j) \) were determined using a Monte Carlo technique, described in detail elsewhere.

### III. RESULTS

Representative, background subtracted ion images are shown in Fig. 2, together with the Legendre moments of order 0, 2, and 4. Note that the fourth order moments are very close to zero within the signal-to-noise ratio of the data. A further qualitative trend, clearly seen in the first Legendre moment, is the shift in intensity towards the center of the image with increasing HCl rotational state. This shift in intensity distribution is qualitatively consistent with the higher HCl rotational states being more backward scattered, as observed previously by Zare and co-workers.

Given the different experimental procedures employed, it is important to establish that the present raw experimental data agree with those obtained previously by Zare and co-workers, using core extraction, and that both studies probe the nascent HCl products. The most direct comparison between the two studies that can be made is with the derived
LAB frame velocity distributions. In Fig. 3 the HCl($v' = 0, j' = 1$) LAB speed distribution and LAB translational anisotropy, $\beta(v)$, obtained from the two experiments are compared. The distributions from the present experiments were obtained by direct Abel inversion, followed by appropriate integration of the resulting slice through the 3D velocity distribution. The good agreement between the two studies strongly supports the view that both experiments probe the HCl under single collision conditions. It also suggests that the ion-imaging data are not significantly perturbed by fly-out of Cl reactants or HCl products from the probe region during the delay between pump and probe laser pulses. In the present study such fly-out would occur preferentially orthogonal to the photolysis laser propagation direction, leading to a distortion of the LAB angular distribution inferred from the image. A further indication that the ion-imaging data are not significantly altered by fly-out comes from the fact that the fourth order and higher Legendre moments of the images are zero within experimental precision (see Fig. 2), as consistent with Eqs. (8) and (9). These considerations, together with the Cl ion image shown in Fig 1(a), and the direct comparison with previous work from the Stanford group, confirm that the data from the ion-imaging experiments truly reflects the nascent LAB frame velocity distribution, and that secondary collisions involving either Cl or HCl are of minor importance.

We now turn to the image analysis using method 1, assuming, in the first instance, that the ethyl radical takes zero internal energy. In this limit, the CM angular distribution is obtained by direct transformation of the LAB speed distributions obtained by Abel inversion (illustrated in Fig. 3), using Eq. (5). In Fig. 4 we compare the transformed image data with analogous results from the HCl core extraction experiments of Zare and co-workers. The agreement between the two studies is excellent, again reinforcing the view that they yield nearly identical LAB velocity distributions. Also shown are the CM angular distributions obtained from a fit to the data with basis functions generated assuming that $j' = 1$. The basis functions used in this latter case also take no account of the finite velocity resolution of the experiment, and the finite beam temperature. Data are shown for $j' = 1$, $j' = 3$, and $j' = 6$. 

FIG. 3. (a) The LAB speed distribution and (b) the velocity dependent translational anisotropy parameter $\beta(v)$ obtained in the present study by direct Abel inversion of the ion-images [solid line in (a) and solid points in (b)], and in the REMPI core extraction data of Zare and co-workers (open points with error bars) (Ref. 20). Both data sets are for HCl($v' = 0, j' = 1$). 

FIG. 4. Comparison between the angular distributions obtained assuming the ethyl coproducts are born internally cold. Fine noisy line, the present results of direct inversion of the ion image. Dashed line with open points and error bars: the results of Zare and co-workers (Ref. 20). Dark smooth line, the result of fits to the data with basis functions generated assuming that $j' = 1$. The basis functions used in this latter case also take no account of the finite velocity resolution of the experiment, and the finite beam temperature. Data are shown for (a) $j' = 1$, (b) $j' = 3$, and (c) $j' = 6$. 


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method I, the basis functions also neglect the instrument resolution function and employ a reduced beam temperature of 10 K. The results of fits with these basis functions are again very similar to previous work,\textsuperscript{20} and to the results obtained using method 1. These comparisons therefore serve to validate the raw ion-imaging data, and to preclude errors in the basis function generation and fitting procedures.

The analysis according to method I can be refined along the lines described in Sec. II B so that the HCl CM recoil velocity, $w_i$, is estimated using the velocity dependence of the translational anisotropy, $\beta(v)$.\textsuperscript{20,21} The angular distribution obtained using this method is shown in Fig. 5(a), in which it is compared with the HCl($v' = 0, j' = 1$) data from Ref. 21. As seen from the figure, this analysis yields very similar CM angular distributions to those obtained assuming that the ethyl radical is internally cold, even though on average the method predicts a significant internal excitation in the ethyl coproducts of $\sim 500 \text{ cm}^{-1}$ [see Fig. 5(b)]. We believe that there are inherent problems with this inversion method. The highest LAB speed, $v_{\text{max}}$, must correspond to forward scattered products with the highest possible CM kinetic energy releases—these products are necessarily accompanied by coproducts with low internal excitation, and possess a $\beta(v)$ parameter close to the limiting value of $-1.0$ (see Fig. 3). Within this analysis procedure, these products, and only these products, are assigned to the forward scattering region. If there is a distribution of CM kinetic energy releases, lower LAB speeds will tend to be assigned to scattering angles away from the forward direction, even though they might contain contributions from forward scattered products. Similar difficulties arise for the HCl products generated with the very lowest LAB speeds. These slow products necessarily correspond to backward scattered HCl, with ethyl coproducts born in low internal states. HCl products born with slightly higher LAB speeds will once more be exclusively assigned to scattering angles away from the extreme backward direction, even though those LAB velocities might correspond to backward scattered products accompanied by internally excited ethyl radicals. Therefore, this inversion method inherently biases the angular distribution away from the extreme backward and forward direction, and towards the sideways direction. Furthermore, in cases where the coproducts are internally excited, the inversion procedure yields an artificial dependence of the internal excitation on scattering angle (or LAB speed). This is evident from the inverted internal energy data shown in Fig. 5(b), which is plotted as a function of CM scattering angle. Very similar behavior was observed previously using this analysis method by Zare and co-workers,\textsuperscript{20,21} as also shown in Fig. 5(b).

In summary, although the inversion analysis provides an exact fit to the data, we believe it is inappropriate for several reasons: (i) the assumption of a delta function in kinetic energy release used on the right-hand side of Eq. (6) is generally unrealistic, (ii) the returned CM angular distribution is artificially biased away from the extreme forward and backward scattered directions, and (iii) the inversion method yields an artificial dependence of coproduct internal energy on scattering angle, which show more internal excitation in the sideways direction than in the extreme forward and backward directions.

Some of the difficulties associated with the direct inversion procedure described above can be overcome by fitting the data according to method 2, but using basis functions obtained assuming a delta function in fractional kinetic energy release $f_i$. In these fits we assume the fixed $f_i$ value to be independent of scattering angle. In Fig. 6 both the fits to the data and the returned CM angular distributions are shown for fixed values of $f_i$ between 1.0 and 0.6. These data are compared with the results of the full analysis using method 2, which are shown in the bottom panel of the figure. Unlike in Fig. 4, the basis functions used in all these fits allow for a finite instrument resolution and beam temperature, and the fits are performed simultaneously to both moments of the image. The only difference between the fits is the assumptions made about the kinetic energy release distribution. Note that the returned angular distribution obtained with fixed $f_i = 1.0$ is very similar to that obtained in Fig. 4, suggesting that inclusion of a beam temperature and an instrumental resolution function are not critical parameters to the correct analysis.

The fits using the full analysis yield significantly better $\chi^2$ values than those obtained by fixing $f_i$ (see Fig. 6). $\chi^2$ values for each of the fits are given in the figure caption. In the case of fixed $f_i$, the fits to the data may be significantly improved by reducing $f_i$ from 1.0 to $\sim 0.7$, which is close to the mean kinetic energy release $\langle f_i \rangle = 0.69$ obtained for this
sis functions in both and energetics, but the general approach to addressing this question, because each reaction has different kinematics and energetics, can be returned reliably in this case by optimizing the energy release distribution. However, the returned distribution obtained by fixing \( f_t \) to 0.7, which provides the best fixed energy release fit to the data, is almost indistinguishable from the fully optimized result obtained using basis functions in both \( \theta \) and \( f_j \). Figure 6 demonstrates that although the best fits to the data are obtained using a distribution of kinetic energy releases, the CM angular distribution can be returned reliably in this case by optimizing the fixed value of \( f_j \) employed in generating the basis functions.

An important issue is the energy and angular resolution of the PHOTOLOC experiment, and related to this, the extent to which the CM scattering and fractional kinetic energy release distributions returned by method 2 depend on the number of moments employed. There is no single answer to this question, because each reaction has different kinematics and energetics, but the general approach to addressing this issue is illustrated below. In Fig. 7 we compare returned \( P(\cos \theta) \) and \( P(f_j) \) distributions obtained from the analysis using method 2 as the number of moments is varied. The error bars shown on the data are the result of the Monte Carlo analysis, and reflect (generous) uncertainties in the fitting procedure. As noted in Sec. II B, the truncation point for the number of basis functions employed is determined by observing the dependence of \( \chi^2 \) on the number of fitting coefficients. In the present case, \( \chi^2 \) dropped by an insignificant amount when the number of moments was increased above three in the CM angular distribution and five in the energy release distribution. However, the returned distributions are remarkably self-consistent as the number of moments is varied, as demonstrated in the figure. The fact that the fits to the data cease to improve in quality as the number of moments is increased above these values merely confirms that the experiment is insensitive to features with more structure than can be generated with three or five moments. The resolution of the experiment is thus defined by the number of moments that can be extracted reliably from the data. Note that the assumption of a delta function in kinetic energy release, used in method 1, is not only unrealistic physically, but also implies an infinite energy resolution.

The complete set of results from the method 2 analysis, plotted as a function of HCl(\( v' = 0 \)) rotational quantum state \( j' \), is presented in Fig. 8. The left-hand column shows the angular distributions, while that on the right shows the distributions in fractional kinetic energy release. Figure 8 demonstrates that with increasing HCl rotational state, the CM angular distribution shifts towards the backward direction. This trend is the same as that observed by Zare and co-workers, although with the present analysis, all of the
angular distributions are more forward scattered than those derived from previous studies\textsuperscript{20} (compare Fig. 8 with Fig. 4). The right-hand panels of Fig. 8 show the kinetic energy release distributions. Although there is a general trend towards higher kinetic energy releases for higher HCl angular momentum states, the returned kinetic energy release distributions are remarkably self-consistent. Note that the \( f_t \) values shown on the \( x \) axes of these figures refers to the fractional energy release for the specific HCl channel in question. The mean values obtained from these data, \( \langle f_t \rangle \), corrected for the HCl(\( v' = 0, j' = 0 \)) rotational energy, are shown in Table I. The average internal excitation in the ethyl cofragment is seen to decrease slightly with increasing HCl rotational state. The mean ethyl radical internal excitation, averaged over all populated HCl quantum states, is \( \langle f_{\text{int}} \rangle = 0.22 \). The weights for each rotational state in the averaging procedure were taken from the HCl(\( v = 5, j = 0 \)) rotational populations previously determined by Zare and co-workers.\textsuperscript{20}

The data shown in Fig. 8 may be used to generate a contour plot of the total product flux as a function of CM scattering angle and HCl speed, as shown in Fig. 9. In generating this plot the angular and kinetic energy release distributions for the individual HCl rotational states have been averaged using the same weighting factors as above. The contour plot therefore mimics the data that would be obtained from a crossed-molecular beam experiment without product quantum state resolution. Note that the angular distribution averaged over HCl quantum state is very broad, but peaks in the forward direction, since the dominant contribution is from HCl(\( v' = 0, j' = 1 \)).\textsuperscript{20}

![Fig. 8](image_url)  
FIG. 8. Returned angular (a) and kinetic energy release (b) distributions for HCl(\( v' = 0, j' = 0 \)) (top panels) through to HCl(\( v' = 0, j' = 6 \)) (bottom panels). As noted in the text, optimum fits to the data were obtained with three moments in \( \cos \theta \) and five moments in \( f_t \). Error bars represent 2\( \sigma \) errors resulting from statistical errors in the fits. Note that in (b) the \( f_t \) scale refers to the state-specific fractional kinetic energy release, which does not include the rotational energy in the HCl product (see Table I).

![Fig. 9](image_url)  
FIG. 9. Contour plot of the total product velocity-angle flux averaged over HCl rotational state using the rotational populations reported by Zare and co-workers.\textsuperscript{20} The plots were obtained using the results shown in Fig. 8.

### Table I

<table>
<thead>
<tr>
<th>HCl(( v' = 0, j' ))</th>
<th>( f_{\text{rot}}(\text{HCl}) )</th>
<th>( f_t )</th>
<th>( f_{\text{int}}(\text{C}_2\text{H}_5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.72</td>
<td>0.28</td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.80</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.69</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>0.70</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>0.07</td>
<td>0.75</td>
<td>0.18</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>0.79</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>0.70</td>
<td>0.15</td>
</tr>
<tr>
<td>Average</td>
<td>0.02</td>
<td>0.76</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The data have been obtained assuming a mean available energy of 2860 cm\(^{-1}\). The errors on the state-resolved \( f_t \) values are typically \( \pm 0.05 \). The averaging over rotational state was accomplished using the HCl(\( v' = 0 \)) rotational distribution determined by Zare and co-workers (Ref. 20). This distribution peaks quite sharply at HCl(\( v' = 0, j' = 1 \)). HCl(\( v' = 1 \)), which is only just energetically accessible, has been shown previously to be produced in negligible quantities (Ref. 20).
IV. DISCUSSION AND CONCLUSIONS

In Sec. III we have presented the results of new ion imaging, PHOTOLOC experiments on the title reaction. Analysis of the data using a basis function fitting method suggests that over 20% of the available energy is channeled into the internal modes of the ethyl product. Ideally, it would be helpful to be able to compare with the results from crossed-molecular beam experiments, but to our knowledge no such experiments have been performed on the Cl plus ethane system. However, there have been crossed-beam studies of the reaction of Cl with propane, and some higher alkanes. Although direct comparison with the present data is not possible, it is noteworthy that these studies reveal significant internal excitation in the products. In the case of Cl + C₃H₈, it is known from the REMPI experiments of Dagdigian and co-workers that the HCl products of this reaction carry away little internal excitation (as in the present Cl + C₂H₆ reaction). Thus, the interpretation of the beam experiments must be that the propyl products are internally excited. This conclusion is in broad agreement with the present findings. Note that, as with the previous experiments on the title reaction, the PHOTOLOC studies by Dagdigian and co-workers of the Cl reactions with partially deuterated propane assumed that the propyl radical coproducts were born internally cold. For this reason, the CM angular distributions derived from those studies were probably artificially biased in the backwards direction. A final piece of evidence in support of the present results comes from a very recent study of the title reaction, and the Cl + butane reaction, by Toomes and Kitsopoulos using a parallel molecular beam method. Like the present work, that study also indicates significant internal excitation of the alkyl radical coproduct.

Given that the ethyl radical is produced with significant internal excitation, one must conclude that the C₂H₅ moiety does not behave as a spectator. Kinetic studies suggest that the reaction has only a small barrier, although it is slightly exothermic. The kinematics of the reaction are those of a light atom abstraction, which favors the transfer of reactant kinetic energy to the products, and the release of the reaction exothermicity into the HCl internal degrees of freedom. The absence of internal excitation in the HCl product has been ascribed to the rather modest energy release from a transition state that is collinear in Cl–H–C, as is consistent with recent ab initio calculations.

Two possible sources of ethyl product internal excitation spring to mind. If all the observed ethyl product internal excitation were rotational in origin, this would correspond to rotational excitation of ethyl to Jₜ₁ = 30 about the b or c axes. This degree of rotational excitation might well be associated with impulsive release of the barrier energy in the exit channel of the reaction, which would act along the breaking H–C bond. Such an impulse would lead to a torque on the ethyl moiety, since the axis of the breaking bond does not pass through the CM of the ethyl fragment. In fact, if we assume a CH₃–C₂H₅ transition state (TS) geometry similar to that obtained in the most recent ab initio calculations, ethyl angular momenta of ~20ℏ can be generated by an impulsive release of only ~930 cm⁻¹, which corresponds to the reaction exothermicity.

An alternative possibility is that the ethyl radical internal excitation is associated with energy release into vibrational modes, perhaps associated with relaxation of the out-of-plane CH₂ rocking mode from its bent geometry in the transition state to the (average) planar geometry in the free ethyl products. The maximum excitation generated by this mechanism can be estimated from the Franck–Condon overlap between the bending wave functions of the transition state and the ethyl products. If we assume similar bending force constants for the wagging mode in the TS and the free ethyl radical, this model predicts very significant vibrational excitation of the wagging mode of the CH₂ unit, with a broad vibrational population peaking at ν ~ 5. This level of excitation is unrealistic, but smaller levels of excitation would be generated if the geometry of the CH₂ moiety relaxed more gradually to that of the products.

Although these considerations are qualitative, they serve to illustrate that internal excitation of the ethyl radical products could be generated by either (or both) of the above mechanisms. They also suggest that the ethyl fragment will need to be treated carefully in any reduced dimensionality dynamical calculations on this or related reactions.

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