Differential cross section polarization moments: Location of the D-atom transfer in the transition-state region for the reactions \( \text{Cl} + \text{C}_2\text{D}_6 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{C}_2\text{D}_5 \) and \( \text{Cl} + \text{CD}_4 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{CD}_3 \)

T. Peter Rakitzis, S. Alex Kandel, Topaz Lev-On, and Richard N. Zare
Department of Chemistry, Stanford University, Stanford, California 94305

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The photocock technique can permit the measurement of not only the state-to-state differential cross section but also its complete product polarization dependence for all moments of orientation and alignment with \( k \leq 2 \). We have realized this possibility for the reaction \( \text{Cl} + \text{C}_2\text{D}_6 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{C}_2\text{D}_5 \) at a collision energy of 0.25 eV, for which we have measured the differential cross section, \( 1/\sigma (d \sigma_{00}/d \Omega_r) \), and the four polarization-dependent moments of the differential cross section, \( A^{(1)}_{STF} \), \( A^{(2)}_{STF} \), \( A^{(1)}_{STF} \), and \( A^{(2)}_{STF} \), in the stationary target frame (STF), which are defined by

\[
A^{(k)}_{STF} = (d \sigma_{00}/d \Omega_r)/(d \sigma_{00}/d \Omega_r).
\]

For the \( \text{Cl} + \text{CD}_4 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{CD}_3 \) reaction at a collision energy of 0.28 eV we have also determined \( 1/\sigma (d \sigma_{00}/d \Omega_r) \) and \( A^{(2)}_{STF} \). The laboratory speed distributions of the \( \text{DCl}(v' = 0, J' = 1) \) products are measured using 2 + 1 resonance-enhanced multiphoton ionization (REMPI) and the core-extraction technique. The polarization-dependent differential cross sections are determined from the dependence of the core-extracted profiles on the photoysis and probe polarizations. Recent studies have shown that the \( \text{Cl} + \text{CD}_4 \) and \( \text{Cl} + \text{C}_2\text{D}_6 \) both show scattering behavior described by the line-of-centers model and both yield rotationally cold DCl products with little energy in the alkyl fragments. Despite these similarities, we measure \( \text{DCl}(v' = 0, J' = 1) \) product polarizations that differ greatly for these two reactions. For the \( \text{Cl} + \text{CD}_4 \) reaction, we find that \( J_{\text{DCl}} \) is maximally aligned perpendicular to an axis close to the product scattering direction, \( \nu_{\text{DCl}} \). For the \( \text{Cl} + \text{C}_2\text{D}_6 \) reaction, we find that \( J_{\text{DCl}} \) is half-maximally aligned perpendicular to the line-of-centers direction. We interpret these results in terms of the location of the D-atom transfer along the reaction coordinate, positing that the D-atom transfer for the \( \text{Cl} + \text{CD}_4 \) reaction occurs late in the reactive process and the D-atom transfer for the \( \text{Cl} + \text{C}_2\text{D}_6 \) reaction occurs earlier near the distance of closest approach. We interpret the difference in the locations of the D-atom transfer to be the cause of the large differences in the Arrhenius pre-exponential factors of the \( \text{Cl} + \text{CD}_4 \) and \( \text{Cl} + \text{C}_2\text{D}_6 \) reactions. © 1997 American Institute of Physics.

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I. INTRODUCTION

In recent decades, experimental and theoretical efforts to elucidate the dynamics of bimolecular reactions have focused on the state-to-state reactive scattering process. There has been considerable success in connecting the scattering dynamics to a reactive mechanism or to features of the potential-energy surface.¹ Good agreement has been achieved between experiments and fully converged quantum-mechanical calculations for the \( \text{H} + \text{H}_2 \) reaction and the \( \text{F} + \text{H}_2 \) transition state.² The connection between product polarization and the reaction mechanism (and the potential-energy surface), however, is less firmly established. This lack of information is partly caused by the fact that few studies have measured product polarization with scattering-angle resolution, so that direct measures do not exist for the correlation between the product velocity and rotation (\( \nu - J \) correlation).

Recently, the measurement of product polarization as a function of scattering angle has been achieved from photo-initiated reactions with laser detection.⁴⁻⁹ The high product density from this technique allows the state-specific laser detection of the products; such laser-based techniques are readily adaptable to the measurement of polarization parameters. Measurements of polarization-dependent differential cross sections directly provide the three-vector correlation of the reagent velocity, product velocity, and rotational polarization. Hence, the results of such experiments promise to reveal the role of product rotation in the reactive process.

This paper presents product rotational polarization studies of the gas-phase reactions of atomic chlorine with deuterated methane and ethane to give DCl(\( v' = 0, J' = 1 \))

\[
\text{Cl}(2P_{\text{3/2}}) + \text{CD}_4 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{CD}_3, \tag{1}
\]

\[
\text{Cl}(2P_{\text{3/2}}) + \text{C}_2\text{D}_6 \rightarrow \text{DCl}(v' = 0, J' = 1) + \text{C}_2\text{D}_5. \tag{2}
\]

The reaction of chlorine with deuterated methane [reaction (1)] is slightly endothermic, \( \Delta H = +2.7 \text{ kcal/mol} (940 \text{ cm}^{-1}, 0.118 \text{ eV}) \), and the activation energy is estimated to be \( +3.9 \text{ kcal/mol} (1370 \text{ cm}^{-1}, 0.17 \text{ eV}) \). These energies have been calculated by Simpson et al.¹⁰ by correcting the analogous values for the Cl+CH₄ reaction using the harmonic approximation. In contrast, the reaction of chlorine with deuterated ethane [reaction (2)] is nearly thermoneutral, \( \Delta H = -0.25 \text{ kcal/mol} (-90 \text{ cm}^{-1}, -0.01 \text{ eV}) \) and has a smaller activation energy that is estimated to be \( +0.75 \text{ kcal/mol} (260 \text{ cm}^{-1}, 0.033 \text{ eV}) \). These reactions have been studied previously in this laboratory and found to...
give correlated state and scattering measurements.\textsuperscript{10,14} At a collision energy of 0.18 eV, the Cl+CD\textsubscript{4} reaction was found to be back scattered, whereas at 0.25 eV, the DCl product from the Cl+C\textsubscript{2}D\textsubscript{6} reaction was found to scatter nearly isotropically. These results were explained with the line-of-centers model and the hard-sphere scattering model.\textsuperscript{1,10} The line-of-centers model states that the probability of reaction is constant for collisions with kinetic energy along the line of centers in excess of the reactive barrier, and the probability of reaction is zero for other collisions. The line of centers is the axis that connects the two centers of a hard-sphere collision at the point of closest approach. The collision energy used in the experiments for the Cl+CH\textsubscript{4} reaction was about seven times larger than the activation energy; therefore, according to the line-of-centers model, only low impact parameter collisions that lead to back scattering are reactive. In contrast, the collision energy used in the experiments for the Cl+CD\textsubscript{4} reaction was slightly larger than the activation energy; therefore, according to the line-of-centers model, only low impact parameter collisions that lead to back scattering are reactive. In contrast, the collision energy used in the experiments for the Cl+CH\textsubscript{4} reaction was about five times more than the activation energy; in this case, according to the line-of-centers model, reactivity is largely independent of the impact parameter and, according to the hard-sphere scattering model, isotropic scattering results. Additionally, both Cl+CD\textsubscript{4} and Cl+C\textsubscript{2}D\textsubscript{6} reactions produce rotationally cold DCl, which often is taken to indicate that the reactions proceed through linear transition states.

At first glance, the microscopic behavior of these reactions seems very similar. Thermal rate data show, however, that the Arrhenius pre-exponential factor is about seven times larger for the Cl+C\textsubscript{2}H\textsubscript{6} reaction than for the Cl+CH\textsubscript{4} reaction.\textsuperscript{13} In the absence of similar data, we assume that the Arrhenius pre-exponential factor for Cl+C\textsubscript{2}D\textsubscript{6} is significantly greater than that of Cl+CD\textsubscript{4}. These kinetic measurements show that the Cl+C\textsubscript{2}H\textsubscript{6} reaction is several times more reactive than the Cl+CH\textsubscript{4} reaction, even after differences in activation energies have been taken into account. One interpretation is that the Cl+C\textsubscript{2}H\textsubscript{6} reaction has a larger “cone of acceptance” than the Cl+CH\textsubscript{4} reaction, but this conclusion seems at odds with the observed cold rotational distributions, which, using an impulsive release model, would predict that both reactions should have collinear transition states. Kandel et al.\textsuperscript{14} discussed this discrepancy. They proposed that the rotational distributions are manifestations of different reactive transition states. In particular, the Cl+CH\textsubscript{4} transition state was proposed to be tightly constrained and collinear, in accord with conventional wisdom, whereas the Cl+C\textsubscript{2}H\textsubscript{6} transition state was proposed to be much less constrained. Cold rotational distributions were posited to result from a reactive mechanism in which little torque is applied to the HCl product.

The aim of this paper is to investigate directly the forces experienced by the DCl product at the transition state. This goal is achieved by measuring the alignment of the axis of rotation of the DCl product with respect to the laboratory recoil velocity and the scattering plane as a function of scattering angle. The measurements reported in this paper concern the DCl product polarization from the Cl+CD\textsubscript{4} and Cl+C\textsubscript{2}D\textsubscript{6} reactions in which only a single quantum state, DCl ($\nu'=0, J'=1$), is probed. The reason for this choice is two fold. Both reactions yield products with cold rotational distributions that peak at or close to $J'=1$. Therefore, this product state is representative of the dynamics of these reactions. Additionally, the complete description of the polarization of the $J'=1$ product from a chemical reaction (from unaligned reagents) requires the measurement of only five parameters, the $1/[\sigma (d\sigma_0/d\Omega)]$, $A^{(1)}_{\Omega}$, $A^{(2)}_{\Omega}$, $A^{(3)}_{\Omega}$, and $A^{(2)}_{\Omega}$ [where the $A^{(k)}_{\Omega}$ are given by the $(d\sigma_{\Omega}/d\Omega)/(d\sigma_0/d\Omega)$].\textsuperscript{15} From these measurements, we hope to discern the microscopic differences that account for the differing macroscopic reactivities of the Cl+CD\textsubscript{4} and C\textsubscript{2}D\textsubscript{6} reactions.

II. EXPERIMENT

The experimental apparatus and techniques have been described elsewhere, and a brief overview is detailed here.\textsuperscript{16} Molecular chlorine (Matheson Gases, 99.999%) or C\textsubscript{2}D\textsubscript{6} (Cambridge Isotopes, 98% D-atom purity), and helium carrier gas (Liquid Carbonic, 99.95%) are coexpended through a pulsed nozzle (General Valve 9-Series, 0.6 mm orifice) into the vacuum chamber from a backing pressure of 380 Torr. The translational cooling of the supersonic expansion ensures that the laboratory speeds of the photolytic precursor, Cl\textsubscript{2}, and the target molecule, CD\textsubscript{4} or C\textsubscript{2}D\textsubscript{6}, are nearly the same so that their difference can be neglected. Additionally, the coexpanded molecules are assumed to be vibrationally and rotationally cold (contaminant HCl is measured to have a rotational temperature of 15 K). Monoenergetic Cl$(^{3}P_{3/2})$ atoms are produced by the laser photolysis of Cl\textsubscript{2},\textsuperscript{17} which defines the collision energy of the Cl atoms with the target molecules. The Cl+CD\textsubscript{4} reaction is initiated by the photolysis of Cl\textsubscript{2} with linearly polarized 303.5 nm light (30–40 mJ/pulse), produced from the frequency-doubled output of a Nd$^{3+}$:YAG-pumped tunable dye laser (Continuum PL9020 and ND6000; Exciton, Rhodamine 640 dye); this photolysis wavelength gives a collision energy of 0.28 eV for the Cl+CD\textsubscript{4} reaction. The Cl+C\textsubscript{2}D\textsubscript{6} reaction is initiated by the photolysis of Cl\textsubscript{2} with linearly polarized 355 nm light (90–110 mJ/pulse) from the third harmonic of the Nd$^{3+}$:YAG laser; this photolysis wavelength gives a collision energy of 0.25 eV for the Cl+C\textsubscript{2}D\textsubscript{6} reaction.

Products are allowed to build up for 100 ns before the DCl ($\nu'=0, J'=1$) products are detected via (2+1) REMPI through the $^1\Delta_2-^1\Sigma^+$ (0,0) R(1) transition. The linearly polarized 241.1 nm probe light (1–5 mJ/pulse) is generated from the frequency-doubled output of a Nd$^{3+}$:YAG-pumped tunable dye laser (Spectra-Physics DCR 2A and PDL-3; Exciton, LD489 dye), and it intersects the ionization region at the focus of a 1.1 m lens. The DCl$^{+}$ is detected with a Wiley–McLaren time-of-flight mass spectrometer operated under velocity-sensitive conditions using the core-extraction method.\textsuperscript{16} The polarization-dependent time-of-flight profiles are analyzed with the methods described in the companion paper to give the laboratory speed distribution and the speed-dependent polarization parameters. The values of the $s_k$ in Eq. (16) of the preceding paper associated with the detection of DCl ($\nu'=0, J'=1$) via (2+1) REMPI through the $^1\Delta_2-^1\Sigma^+$ (0,0) R(1) transi-
tion were calculated using the methods described by Kummel et al.\(^{18}\) these values were calculated to be \(s_1(\beta = 45^\circ) = -1\) and \(s_2(\beta = 0^\circ) = 1\).

We define the detection-frame coordinate system as follows: The \(z_d\) axis is parallel to the time-of-flight axis (the detection axis), and the probe laser beam propagation axis is always parallel to the \(y_d\) axis (Fig. 1). The probe polarization is flipped on a shot-to-shot basis between the \(z_d\) axis (parallel to the time-of-flight) and the \(x_d\) axis. The polarization flipping is affected by synchronization to the stress cycle of a photoelastic modulator (Hinds International, PEM-80), and the resulting polarizations have a transmittance ratio of at least 64:1 through a linear polarizer. We frequently performed in situ measurements to confirm that the polarization flipping did not adversely affect the laser beam power or properties in a biased manner. These measurements consisted of detecting unaligned contaminant HCl, which showed that the signal intensities varied by less than 1% between the two polarization states.

For the alignment parameter measurements, the photolysis laser beam polarization is used in three different geometries. For two of these geometries, the photolysis beam counter-propagates with respect to the probe laser and is gently focused with a 35 cm lens to a 1 mm beam at the reaction region. In this configuration, the photolysis polarization is aligned along the \(x_d\) axis or the \(z_d\) axis with a half-wave plate. Ideally, the third photolysis polarization geometry, along the \(y_d\) axis, would be obtained by propagating the photolysis laser beam along the \(x_d\) axis, but the presence of the pulsed nozzle prevents this. Consequently, the photolysis laser beam is directed in the \(x_d-Y_d\) plane at \(25^\circ\) to the \(x_d\) axis, barely missing the pulsed nozzle (Fig. 1). The photolysis beam is focused with a 50 cm cylindrical lens and a 1 m spherical lens to a \(5 \times 0.5\) mm beam; these conditions allow the probe and photolysis laser beams to overlap in the reaction region in an equivalent manner to the counter-propagating geometry. In this configuration, the third photolysis polarization geometry is perpendicular to the time-of-flight axis and parallel to the axis we define as \(y_d’\).

For the measurements of orientation moments, a quarter-wave plate is placed after the photoelastic modulator with its optical axis at \(45^\circ\) to either linear probe polarization. This wave plate thus produces right and left circularly polarized light on a shot-to-shot basis. Also, a fourth photolysis polarization geometry is used in which the photolysis polarization is perpendicular to the time-of-flight axis and parallel to the axis we define as \(O’\) (Table I). The \(O’\) axis breaks reflection symmetry with respect to the plane defined by the probe propagation axis and the detection axis and thus allows the detection of orientation parameters. A better position for the photolysis polarization that would improve the sensitivity to the \(A_{sym}^{(1)}\) parameter would have been the \(O\) axis (Table I). This geometry was not realized, however, when the experiments were conducted, though this additional sensitivity did not prove to be crucial. We refer to the time-of-flight profiles from a particular geometry as \(I_{G}^{P}\), where \(P\) refers to the geometry of the photolysis polarization and \(G\) refers to the geometry of the probe polarization. The experimental geometries described above are summarized in Table I. Henceforth, we will refer to them using the \(I_{G}^{P}\) notation.

For differential-cross-section measurements, ion-arrival profiles measured at short photolysis-probe laser delays are subtracted from long delay ion-arrival profiles on a shot-to-shot basis; only signals that grow with time survive this subtraction. This time-dependent subtraction was not used, however, for rotational anisotropy measurements. Instead, we chose to detect \(\text{D}^{37}\text{Cl}^+\) to avoid the subtraction procedures necessary to separate \(\text{D}^{35}\text{Cl}^+\) and nonresonantly produced \(\text{Cl}^+\). The only nonreactive signal in the mass 39 region is \(\text{D}^{37}\text{Cl}\) contaminant present in the beam expansion. Once the differential cross section has been measured, correcting the isotropic profiles for the \(\text{D}^{37}\text{Cl}\) contaminant is simple. Even more important, this contaminant does not disrupt the measurement of rotational anisotropy, as the polarization parameters are proportional to the difference of the profiles with the probe polarization parallel and perpendicular to the time-of-flight axis and the contribution from the DCI contaminant is eliminated in this subtraction because the DCI contaminant is unaligned. As described in the next section, the polariz-

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**Table I.** The relative orientation of the laboratory axes described in the text, with respect to the time-of-flight axis (\(\theta_d\) and \(\varphi_d\) are the spherical polar angles about the TOF axis). For example, in the text, the notations \(Z\), \(x_d\), and \(\perp\) are used to refer to axes that are parallel to the TOF axis, whereas the notations \(X\), \(x_d’\), and \(\perp\) refer to axes that are parallel to an axis that is \(90^\circ\) to the TOF axis with an azimuthal angle of \(0^\circ\).

<table>
<thead>
<tr>
<th>Notation</th>
<th>(\theta_d)</th>
<th>(\varphi_d)</th>
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<tbody>
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<td>(X, x_d), (\perp)</td>
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<td>(0^\circ)</td>
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<td>(-25^\circ)</td>
</tr>
<tr>
<td>(Y, y_d)</td>
<td>(90^\circ)</td>
<td>(90^\circ)</td>
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<td>(Z, z_d), (\parallel)</td>
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<td>(O’)</td>
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tation parameters of DCl products from chemical reactions vary with time in a fashion that makes it convenient to avoid the time-dependent subtraction procedure.

III. POLARIZATION PARAMETERS AND HYPERFINE DEPOLARIZATION

In this paper, we describe product rotational polarization at a particular laboratory velocity with the polarization parameters \( A_q^{(k)} \) (where \( k \leq 2J \) and \( -k \leq q \leq k \)) that are described elsewhere.\(^{19,20}\) Briefly, the symmetry of the scattering plane ensures that the \( A_q^{(k)} \) of \( k \) even are purely real, the \( A_q^{(k)} \) of \( k \) odd are purely imaginary, the \( A_0^{(k)} \) with \( k \) odd vanish, and the \( A_q^{(k)} \) follow the relation\(^{21}\)

\[
A_q^{(k)} = (-1)^{k+q}A_q^{(-k)},
\]

where the \( A_q^{(k)} \) are defined with respect to a coordinate frame whose \( z \) axis is included in the scattering plane. The \( A_q^{(k)} \) as a function of scattering angle are equivalent to the \((d\sigma_{kq}/d\Omega)_{-} \) and \((d\sigma_{00}/d\Omega)_{+} \).\(^{15}\)

The time-dependent effects of hyperfine depolarization on the polarization parameters are well understood,\(^{21-23}\) and we summarize the important results here. The total angular momentum for the \( \chi^11\Sigma^+ \) ground electronic state of DCl, \( F \), is the vector sum of the rotational angular momentum, \( J \), and the nuclear angular momenta of the Cl and D nuclei, \( I_{Cl} \) and \( I_D \), \( I_{Cl} = 3/2 \) for both isotopes of chlorine, whereas \( I_D = 1 \). In this experiment, the bandwidth of our probe laser is much broader than the hyperfine splitting that results from the coupling of \( J \) with the nuclear spins. Therefore, we detect individual values of \( J \) without resolving the hyperfine states. This procedure causes the observed distribution of \( J \) to be affected in a time-dependent manner by the precession of \( J \) about \( F \), resulting in the depolarization of \( J \) with time. The measurement and quantitative description of the depolarization of HCl (\( \nu = 1, J = 1 \)) has been performed in this laboratory.\(^{24}\) The time-dependent factor, \( G_c^{(k)}(t) \), relates the nascent polarization parameters, \( A_q^{(k)}(J, t = 0) \), to the observed polarization parameters at a time \( t' \), \( A_q^{(k)}(J, t = t') \), from a chemical reaction in which products build linearly with time

\[
A_q^{(k)}(J, t = t') = G_c^{(k)}(t')A_q^{(k)}(J, t = 0).
\]

All experiments were conducted detecting D\(^{37}\)Cl (\( \nu = 0, J = 1 \)) at a time delay of 100 ns. Electric resonance measurements by Kaiser\(^{25}\) show that the effect of the deuterium quadrupole moment is negligible on the 100 ns time scale (\( eqQ_B = 187 \) kHz). Therefore, we make hyperfine corrections using the calculations for D\(^{37}\)Cl (\( \nu = 0, J = 1 \)) for which the contributions from the deuterium quadrupole have been ignored. Figure 2 illustrates \( G_c^{(k)}(t) \) for D\(^{37}\)Cl (\( \nu = 0, J = 1 \)) and \( k = 1 \) and 2. This figure shows that at the 100 ns time interval, the nascent values of the polarization parameters with \( k = 1 \) and 2 are reduced to 0.45 and 0.3, respectively. Because all experiments were conducted at 100 ns delays, the measured \( A_q^{(k)} \) of \( k = 1 \) and 2 are corrected by these values.

![Figure 2](image)

**FIG. 2.** The time dependence of the hyperfine depolarization factor \( G_c^{(k)}(t) \) for D\(^{37}\)Cl (\( \nu = 0, J = 1 \)) and \( k = 1 \) and 2. This factor shows the time dependence of the polarization parameters, \( A_q^{(k)} \), of D\(^{37}\)Cl (\( \nu = 0, J = 1 \)) products from a chemical reaction that builds linearly with time.

IV. RESULTS

A. The Cl+CD\(_4\) reaction

The kinematics of the Cl+CD\(_4\) reaction constrain the laboratory scattering angle (the angle between the velocity vectors of the reagent Cl and product DCl) to be always less than 20°. As discussed in the previous paper, this constraint decreases the sensitivity to the noncylindrically symmetric moments, \( A_0^{(2)\text{stf}} \) and \( A_2^{(2)\text{stf}} \), and thus the \( A_0^{(2)\text{stf}} \) parameter can be measured using two experimental geometries, \( I_{||}^{X} \) and \( I_{\perp}^{X} \) (defined in Table I). For these geometries and for a laboratory scattering angle of 20°, Fig. 3 illustrates that the experimental sensitivity to maximal values of the \( A_0^{(2)\text{stf}} \) and \( A_2^{(2)\text{stf}} \) is several times less than the sensitivity to the \( A_0^{(2)\text{stf}} \) parameter, which has been chosen to be one quarter of its maximal value. Overall, under these conditions, the experimental measurement is at least 20 times more sensitive to the \( A_0^{(2)\text{stf}} \) parameter than to the \( A_0^{(2)\text{stf}} \) and \( A_2^{(2)\text{stf}} \) parameters. Therefore, to excellent approximation, we can attribute the product polarization-dependent signal to the \( A_0^{(2)\text{stf}} \) only. We define the composite profiles of experimental signals as follows:

\[
I_{\text{aniso}}^{X} = 2(I_{||}^{X} - I_{\perp}^{X})
\]

and

\[
I_{\text{iso}}^{X} = I_{||}^{X} + 2I_{\perp}^{X}.
\]

The time-of-flight profiles, \( I_{\text{aniso}}^{X} \) and \( I_{\text{iso}}^{X} \), of the D\(^{37}\)Cl (\( \nu' = 0, J' = 1 \)) product from the \(^{37}\)Cl+CD\(_4\) reaction are shown in Fig. 4. The \( I_{\text{iso}}^{X} \) profile is polarization independent and proportional to the laboratory speed distribution only. The \( I_{\text{aniso}}^{X} \) profile is proportional to the laboratory speed-dependent \( A_0^{(2)\text{stf}} \) parameter only. These profiles are analyzed with the methods described in the previous paper. The speed distribution and differential cross section for the D\(^{37}\)Cl (\( \nu' = 0, J' = 1 \)) product state are shown in Fig. 5, where the scattering is shown to be predominantly in the backward hemisphere. The shape of the \( I_{\text{aniso}}^{X} \) profile is very interesting [Fig. 4(b)]. The core-extraction technique gives a one-to-one...
mapping between time-of-flight and laboratory speed (and hence scattering). Because the $I_{\text{aniso}}$ profile is proportional to the $A_0^{(2)\text{sff}}$ parameter, it is clear upon inspection that this parameter is strongly negative for the back-scattered product (the slower product, in the inner part of the experimental profile) and that it inverts very suddenly to be strongly positive for the side-scattered product (the faster products, on the outer edges of the experimental profile). Because the forward-scattered intensity is very low, the $A_0^{(2)\text{sff}}$ parameter in this region is not well determined, but it seems to be tending toward a negative value again. The results of the fit of $I_{\text{aniso}}$ are shown in Fig. 6, where the quantitative results confirm our expectations from Fig. 4(b). The strong dependence of the $A_0^{(2)\text{sff}}$ parameter on the scattering angle provides the key for the determination of the mechanism of rotational alignment for the Cl+CD$_4$ reaction.

B. The Cl+CD$_3$ reaction

For the Cl+CD$_3$ reaction, the kinematics do not constrain the laboratory scattering angle to be small for all scattering angles. In contrast to the Cl+CD$_4$ reaction, alignment measurements for the Cl+CD$_3$ reaction have significant sensitivity to the $A_1^{(2)\text{sff}}$ and $A_2^{(2)\text{sff}}$ parameters. Additionally, we measure the $A_1^{(1)\text{sff}}$ orientation parameter. Experiments using linearly polarized probe light measure the $A_0^{(2)\text{sff}}$, $A_1^{(2)\text{sff}}$, and $A_2^{(2)\text{sff}}$ parameters, whereas circularly polarized light is used to measure the $A_1^{(1)\text{sff}}$ parameter.

To measure the three $k=2$ alignment parameters, we record probe polarization difference profiles with the photolysis polarization in three different geometries, parallel to the $X$, $Y'$, and $Z$ axes (defined in Table I). Note that the $X$ axis is not quite parallel to the $X'$ axis. As before, we define

$$I_{\text{iso}}^F = I_{\parallel}^F + 2I_{\perp}^F \quad (F = X, Y', Z)$$

and

$$I_{\text{aniso}}^F = 2(I_{\parallel}^F - I_{\perp}^F) \quad (F = X, Y', Z).$$

The profiles $I_{\text{iso}}^F$ are, to a good approximation, independent of product polarization. The summation $I_{\parallel}^F + 2I_{\perp}^F$ rigorously eliminates the $A_0^{(2)\text{sff}}$ parameter, which is responsible for the bulk of the polarization effects; the $A_1^{(2)\text{sff}}$ and $A_2^{(2)\text{sff}}$ parameters are not eliminated, but because their contribution to the total signal is less than 10%, the errors introduced to the speed distribution are small. Measurements by Kandel et al. showed that for the Cl+CD$_3$/CCD$_3$ reactions, the ethyl radical product receives little energy into internal modes. This finding allows us to treat these reactions as atom+diatom reactions, for which we know unambiguously the laboratory scattering angle $\theta_{\text{lab}}$ as a function of laboratory speed, $v_{\text{lab}}$. This approximation is important because the $A_1^{(1)\text{sff}}$, $A_1^{(2)\text{sff}}$, and $A_2^{(2)\text{sff}}$ parameters depend strongly on the
angle $\theta_u$. The basis functions for the analysis of the time-of-flight profiles were generated assuming the ethyl radical is not internally excited.

Figure 7 shows the $I_{iso}^{iso}$ composite profile. As described in the companion paper, the composite profile $I_{iso}^{iso}$ is independent of spatial and rotational anisotropy. The analysis of $I_{iso}^{iso}$ gives the laboratory speed distribution and the differential cross section (Fig. 8). The scattering is nearly isotropic, with a slight preference for forward scattering.

The three $I_{aniso}^{iso}$ profiles are shown in Fig. 9. These signals are proportional to the $A_{0}^{(2)stf}$, $A_{1}^{(2)stf}$, and $A_{2}^{(2)stf}$ parameters only. The $A_{0}^{(2)stf}$ parameter does not depend explicitly on the position of the photolysis polarization, so the contribution of the $A_{0}^{(2)stf}$ is essentially the same for all three profiles. Therefore, the extent to which the three $I_{aniso}$ profiles are different indicates the extent of the contribution from the $A_{1}^{(2)stf}$ and $A_{2}^{(2)stf}$ parameters. Figure 9 shows that the differences are substantial. The profiles are fit using the methods described in the preceding paper, and plots of the $A_{0}^{(2)stf}$, $A_{1}^{(2)stf}$, and $A_{2}^{(2)stf}$ versus scattering angle are shown in Fig. 10. The $A_{q}^{(4)stf}$ versus scattering angle are equivalent to the $(d\sigma_{q}/d\Omega_{q})/(d\sigma_{io}/d\Omega_{io})$. The error bars shown are 2$\sigma$ confidence intervals, derived from the projection of the 15-dimensional 95% confidence ellipsoid (from the nonlinear least squares fit) on the $A_{q}^{(4)stf}$ axes. The sensitivity to the $A_{0}^{(2)stf}$ does not depend explicitly on the laboratory scattering angle, $\theta_u$, whereas the sensitivity to the $A_{1}^{(2)stf}$ is weighted by $\sin 2\theta_u$ and the sensitivity to the $A_{2}^{(2)stf}$ is weighted by $\sin^2 \theta_u$. The consequence of this weighting is that the experimental sensitivity to the $A_{0}^{(2)stf}$ is approximately independent of the scattering angle, and the size of the error bars in Fig. 10 reflects this independence. The sensitivity to the $A_{1}^{(2)stf}$ parameter is poor when $\theta_u \approx 90^\circ$ (in the back-scattered region), and the sensitivity to the $A_{2}^{(2)stf}$ parameter is poor.
when \( \theta_u = 0^\circ \) (in the forward-scattered region); the error bars in Fig. 10 mirror these effects. Additionally, for the most back-scattered product, the laboratory speed, \( v_{\text{lab}} \), is nearly equal to zero. The lack of product time-of-flight resolution for this scattering angle causes the \( A_i^{(2)\text{stf}} \) parameters to vary strongly, resulting in very large confidence intervals.

To measure the \( A_i^{(1)\text{stf}} \) orientation parameter, we record time-of-flight profiles with right and left circularly polarized probe light and with the photolysis polarization parallel to the \( O' \) axis (defined in Table I), which breaks the reflection symmetry of the plane defined by the probe propagation direction and the detection axis (this condition is necessary to have nonzero sensitivity to the orientation parameters). We define the composite experimental profiles as follows:

\[
I_{\text{iso}}^{O'} = I_{+Y}^{O'} + I_{-Y}^{O'}
\]

and

\[
I_{\text{aniso}}^{O'} = I_{+Y}^{O'} - I_{-Y}^{O'}.
\]

The profile \( I_{\text{iso}}^{O'} \) is, to a good approximation, independent of product polarization, whereas the \( I_{\text{aniso}}^{O'} \) profile is proportional to the \( A_i^{(1)\text{stf}} \) parameter only. Figure 11(a) shows the \( I_{\text{iso}}^{O'} \) profile and \( I_{\text{aniso}}^{O'} \) profile (magnified by 10) with fits; it is clear that the \( A_i^{(1)\text{stf}} \) parameter is zero at all speeds within the precision of the measurement. The \((d\sigma_{11}^{\text{stf}}/d\Omega_r)/(d\sigma_{00}^{\text{stf}}/d\Omega_r)\)
cross section is shown in Fig. 11(b). Figures 10 and 11 may be regarded as key results for the Cl+C_2D_6 reaction.

V. DISCUSSION

A. Cl+CD_4 product alignment

The STF is unlikely to be the best reference frame for understanding reaction dynamics because the STF is defined with respect to the laboratory velocity of a particular experimental configuration. Knowledge of all three of the \( A_q^{(2)} \) parameters is necessary to calculate any \( A_q^{(2)} \) parameter in another reference frame. Hence, as we have measured only the \( A_0^{(2)} \) parameter for Cl+CD_4, we cannot determine directly the product alignment in an arbitrary reference frame. Instead, we elucidate the product alignment mechanism by comparing the STF parameter predictions of simple physical models to the \( A_0^{(2)} \) parameter measurements. Fortunately, the \( A_0^{(2)} \) parameter measurement versus scattering angle varies in a fashion that strongly suggests the alignment mechanism: The \( A_0^{(2)} \) parameter inverts sharply from strongly negative in the back-scattered region to strongly positive in the side-scattered region (see Fig. 6). The \( A_0^{(2)} \) parameter seems to be tending again toward negative values in the forward-scattered region, though this measurement is less certain, as there is very little forward-scattered product. One interpretation of these results would be that the alignment mechanism changes drastically with scattering angle, but we prefer another interpretation because of its simplicity. Our interpretation assumes that the alignment mechanism does not change with scattering angle, but instead, the angle between the dynamically important reference frame and the STF changes with scattering angle. In this model, the sharp STF-parameter variations are the manifestation of frame transformations. The obvious candidate for a vector that changes its angle with respect to \( \nu_{\text{DCI}}^{\text{lab}} \) versus scattering angle is the product center-of-mass velocity, \( \nu_{\text{DCI}} \). Figure 12 shows that \( \nu_{\text{DCI}} \) is approximately antiparallel to \( \nu_{\text{DCI}}^{\text{lab}} \) for back-scattered products, parallel to \( \nu_{\text{DCI}}^{\text{lab}} \) for forward-scattered products, and approximately perpendicular to \( \nu_{\text{DCI}}^{\text{lab}} \) for side-scattered products. The transformation of the polarization parameters in the product scattering frame, \( A_q^{(2)} \nu_{\text{psf}}^{\text{lab}} \), to the \( A_0^{(2)} \) as a function of the angle between \( \nu_{\text{DCI}}^{\text{lab}} \) and \( \nu_{\text{DCI}} \), \( \theta_s \), is given by Eqs. (11) and (12)

\[
A_0^{(2)} = \sum_{q=-1}^2 D_q^2 \phi = 0, \theta = \theta_s, \chi = 0 \right) A_q^{(2)} \nu_{\text{psf}}^{\text{lab}}.
\]

\[
A_0^{(2)} = \frac{1}{2} (3 \cos^2 \theta_s - 1) A_0^{(2)} \nu_{\text{psf}}^{\text{lab}} - \sqrt{\frac{3}{2}} \sin 2 \theta_s A_1^{(2)} \nu_{\text{psf}}^{\text{lab}}
\]

\[+ \sqrt{\frac{3}{2}} \sin^2 \theta_s A_2^{(2)} \nu_{\text{psf}}^{\text{lab}},
\]

where the relationship between \( \theta_s \) and the scattering angle, \( \theta \), is given by

\[
\tan \theta_s = \frac{\sin \theta}{\nu_{\text{DCI}}^{\text{lab}} / \nu_{\text{CM}}}.
\]
Figure 13 shows how constant values of the $A_q^{(2)}$ in the product scattering frame transform to the $A_{0q}^{(2)stf}$. Clearly, the $A_0^{(2)psf}$, with a constant and maximal value of $-1.0$, captures the general trend of the scattering dependence of the $A_0^{(2)stf}$, in contrast, the $A_1^{(2)psf}$ and $A_2^{(2)psf}$ do not. Therefore, we reach the conclusion that the data can be approximated by $A_0^{(2)psf} = -1.0$, $A_1^{(2)psf} = \frac{\sqrt{3}}{8}$, and $A_2^{(2)psf} = -\frac{\sqrt{3}}{8}$. The spatial distribution of $J_{DCI}$ for DCl ($v' = 0$, $J' = 1$) from the Cl+CD$_4$ reaction constructed from the measurement, $A_2^{(2)psf} = 0.2$, $A_1^{(2)psf} = 0.0$, and $A_2^{(2)psf} = -0.3$. Notice that the distribution of $J_{DCI}$ is approximately cylindrically symmetric with respect to an axis that is in the scattering plane but perpendicular to $v_{lab}^{DCI}$. If we rotate the alignment parameters to this new frame described by the Euler angles ($\varphi = 0$, $\theta = \pi/2$, $\chi = 0$) using Eq. (14)

$$A_q^{(k)new} = \sum_{q' = -k}^{k} D_{q'q}^k(\varphi = 0, \theta = \pi/2, \chi = 0) A_q^{(k)stf},$$

we find that the distribution of $J_{DCI}$ is approximately cylindrically symmetric with respect to this new frame ($A_0^{(2)new} = -0.5$, $A_1^{(2)new} = 0.0$, $A_2^{(2)new} = 0.0$). At first sight, we reach the peculiar conclusion that (except for the forward-scattered region) $J_{DCI}$ is cylindrically symmetric to a vector in the scattering plane that is always perpendicular to the seemingly arbitrary $v_{lab}^{DCI}$. However, upon closer examination of a Newton diagram in which $u_{CM} = u_{AB}$, which the Newton diagram of Cl+CD$_4$ very closely resembles (Fig. 15), we notice that the bisector of the angle between $u_{CM}$ and $u_{AB}$ is rigorously perpendicular to $v_{lab}^{DCI}$. For hard-sphere scattering, this bisector is known as the line of centers. For the Cl+CD$_4$ reaction, $v_{lab}^{DCI}$ is almost exactly perpendicular to the line of centers. Hence, the data determine that $u_{CM}$ and $u_{AB}$ is $u_{CM}$

B. Cl+C$_2$D$_6$ product polarization

In contrast to the Cl+CD$_4$ reaction, we have a complete measurement of the $A_q^{(2)}$ in the STF for the DCl ($v' = 0$, $J' = 1$) product of the Cl+C$_2$D$_6$ reaction at a collision energy of 0.25 eV. Instead of making assumptions about the product alignment in other reference frames, we can transform the $A_q^{(2)stf}$ directly to any other frame. As revealed in Fig. 10, with the exception of the forward-scattered region ($\cos \theta > 0.5$), all three $A_q^{(2)stf}$ parameters are approximately constant versus scattering angle ($A_0^{(2)stf} = 0.2$, $A_1^{(2)stf} = 0.0$, $A_2^{(2)stf} = -0.3$). A plot of the spatial distribution of $J_{DCI}$ described by this measurement is shown in Fig. 14, where $J_{DCI}$ appears to be preferentially perpendicular to an axis that is in the scattering plane but at 90° to $v_{lab}^{DCI}$. If we rotate the alignment parameters to this new frame described by the Euler angles ($\varphi = 0$, $\theta = \pi/2$, $\chi = 0$) using Eq. (14)

$$A_q^{(k)new} = \sum_{q' = -k}^{k} D_{q'q}^k(\varphi = 0, \theta = \pi/2, \chi = 0) A_q^{(k)stf},$$

we find that the distribution of $J_{DCI}$ is approximately cylindrically symmetric with respect to this new frame ($A_0^{(2)new} = -0.5$, $A_1^{(2)new} = 0.0$, $A_2^{(2)new} = 0.0$). At first sight, we reach the peculiar conclusion that (except for the forward-scattered region) $J_{DCI}$ is cylindrically symmetric to a vector in the scattering plane that is always perpendicular to the seemingly arbitrary $v_{lab}^{DCI}$. However, upon closer examination of a Newton diagram in which $u_{CM} = u_{AB}$, which the Newton diagram of Cl+CD$_4$ very closely resembles (Fig. 15), we notice that the bisector of the angle between $u_{CM}$ and $u_{AB}$ is rigorously perpendicular to $v_{lab}^{DCI}$. For hard-sphere scattering, this bisector is known as the line of centers. For the Cl+CD$_4$ reaction, $v_{lab}^{DCI}$ is almost exactly perpendicular to the line of centers. Hence, the data determine that (except for the forward-scattered region) $J_{DCI}$ is aligned in the plane perpendicular to the line of centers. The STF parameters arising from such an alignment ($A_0^{(2)loc} = -0.5$, $A_1^{(2)loc} = 0.0$, $A_2^{(2)loc} = 0.0$) are shown in Fig. 10, and, of course, agree well with the data.
As noted earlier, the product alignment changes suddenly in the forward-scattered region. In this region, the experimental sensitivity to the \( A_2^{(2)\text{stf}} \) parameter is very poor and does not allow accurate determination of the parameter. If we assume that the alignment is cylindrically symmetric about an axis \( F' \), the values of the \( A_0^{(2)\text{stf}} \) and the \( A_1^{(2)\text{stf}} \) indicate that \( J_{\text{DCI}} \) is aligned perpendicularly to an axis that makes an angle of \( \sim 125^\circ \) to \( v_{\text{DCI}}^\text{lab} \) (the counter-clockwise angle from \( v_{\text{DCI}}^\text{lab} \) to \( F' \) is about \( 125^\circ \), as discussed in the next section). In particular, an alignment of \( A_0^{(2)\text{stf}} \approx -1.0 \), \( A_1^{(2)\text{stf}} \approx 0.0 \), and \( A_2^{(2)\text{stf}} \approx 0.0 \) gives \( A_0^{(2)\text{stf}} \approx 0.0 \) and \( A_1^{(2)\text{stf}} \approx +0.5 \), which is consistent with the data. This measurement, however, does not allow us to determine unambiguously the azimuthal angle of \( F' \) about \( v_{\text{DCI}}^\text{lab} \), which we are assuming to be 0 (placing \( F' \) in the scattering plane). Finally, the measurement of zero for the noncylindrically symmetric \( A_1^{(1)\text{stf}} \) parameter is consistent with the observation from the \( k=2 \) parameters that \( J_{\text{DCI}} \) is distributed with cylindrical symmetry.

### C. M-state populations

The discussion of product polarization in Sec. V A and V B used the experimentally convenient alignment parameter formalism. Using this formalism, we showed that the product polarizations for both the \( \text{Cl}+\text{CD}_4 \) and \( \text{Cl}+\text{C}_2D_6 \) reactions exhibit cylindrical symmetry about dynamically important axes and can be described with the cylindrically symmetric alignment parameters, \( A_j^{(k)} \). Orr-Ewing et al. have reported an expression that relates the cylindrically symmetric alignment parameters to \( m \)-state populations, \( p(J,m) \).

### D. Rotational alignment mechanisms

Our conclusions from the previous section show that the product polarizations from the two reactions are very different yet very simple. For the \( \text{Cl}+\text{CD}_4 \) reaction, \( J_{\text{DCI}} \) is aligned in the plane perpendicular to the product separation direction, \( u_{\text{DCI}} \). For the \( \text{Cl}+\text{C}_2D_6 \) reaction, \( J_{\text{DCI}} \) is aligned in the
plane perpendicular to the line of centers; in the forward-scattered region, the alignment of $J_{\text{DCl}}$ is consistent with being aligned in the plane perpendicular to $F'$, which is an axis that is intermediate between the line of centers and $u_{\text{Cl}}$. In this section, we present a model that can explain the observed product polarization effects.

In general, the product alignment does not allow the unambiguous elucidation of the alignment mechanism; undoubtedly, markedly different potential surfaces might give products with similar rotational polarizations. In the present case, however, we are comparing the DCl product rotational polarizations from two very similar reactions, that of chlorine atoms with deuterated methane and with deuterated ethane. Both reactions are of the kinematic type $\text{H}+\text{LH} \rightarrow \text{HL}+\text{H}$, both involve the breaking of a $\text{C}$–$\text{D}$ bond and the formation of a $\text{D}$–$\text{Cl}$ bond, both reactions yield rotationally and vibrationally cold products, and the scattering from both reactions can be described with the line-of-centers model. Despite these similarities, we observe that the rotational polarization from these two reactions differ significantly from each other; in addition, it is well known that $\text{Cl}+\text{C}_2\text{D}_6$ is significantly more reactive than $\text{Cl}+\text{CD}_4$.

Therefore, we present a mechanism for the product alignment that aims to connect the two major dissimilarities for these two reactions.

The most obvious difference between the product alignment from the two reactions is that the alignment from the $\text{Cl}+\text{C}_2\text{D}_6$ reaction is correlated to the scattering angle, whereas the alignment from the $\text{Cl}+\text{CD}_4$ reaction is scattering-angle independent. This behavior indicates that, for the $\text{Cl}+\text{C}_2\text{D}_6$ reaction, the alignment is determined sufficiently early in the reactive process such that the reagent approach direction is dynamically significant. In contrast, for the $\text{Cl}+\text{CD}_4$ reaction, the alignment is determined late in the reactive process, at which point memory of the scattering angle has been lost.

We explain the observed product polarization effects in terms of a simple dynamical model in conjunction with the location of the D-atom transfer along the reaction coordinate. We assume that the transfer of the D atom occurs on a time scale that is fast compared to the motion of the Cl atoms and alkyl radicals, that the transfer motion (for the ensemble average) is cylindrically symmetric with respect to the C–Cl axis at the transfer point, and that the transfer motion is responsible for the asymptotic rotational motion of the DCl. Therefore, this model predicts that the rotational axis of the DCl product will be aligned in the plane perpendicular to the C–Cl axis at the transfer point. To predict the product polarization with this model, we must know how the positions of the C and Cl nuclei vary with the reaction coordinate, and at what point the D-atom transfer occurs. As discussed at the beginning of Sec. I, we qualitatively describe the scattering behavior of the $\text{Cl}+\text{CD}_4$ and $\text{Cl}+\text{C}_2\text{D}_6$ reaction using the hard-sphere scattering model, in which the angle of incidence is equal to the angle of reflection (Fig. 17). Using this scattering model, if the D-atom transfer occurs at the point of closest approach of the C and Cl atoms, the C–Cl axis is parallel to the line of centers and thus the transfer motion is cylindrically symmetric with respect to the line-of-centers direction (Fig. 17); if the D-atom transfer occurs after the closest approach, the C–Cl axis is approximately parallel to $u_{\text{DCl}}$.

Using this model, we explain the product polarization measurements by proposing that for the $\text{Cl}+\text{CD}_4$ reaction, the D-atom transfer occurs late in the reactive process, which leads to an alignment of $J_{\text{DCl}}$ in the plane perpendicular to an axis close to $u_{\text{DCl}}$. For the $\text{Cl}+\text{C}_2\text{D}_6$ reaction, we propose that the D-atom transfer occurs approximately at the point of closest approach, which leads to an alignment of $J_{\text{DCl}}$ in the plane perpendicular to the line of centers; the sudden change in product alignment observed in the forward-scattered region is discussed later. In terms of ideas introduced by Polanyi,26,27 the $\text{Cl}+\text{CD}_4$ reaction proceeds through a late transition state, where the transfer point is past the closest approach of the C and Cl atoms, whereas the $\text{Cl}+\text{C}_2\text{D}_6$ reaction proceeds through an earlier transition state, where the transfer point is approximately at the closest approach of the C and Cl atoms.

It is clear from Fig. 17 that the C–Cl axis becomes closely parallel to $u_{\text{DCl}}$ only for product separations that are large compared to the hard-sphere radii of the reactants. Therefore, according to this model, we might expect that the DCl polarization from the $\text{Cl}+\text{CD}_4$ reaction will be aligned perpendicular to an axis that is shifted from $u_{\text{DCl}}$ toward the line of centers. In Fig. 18, we show the measured $(d\sigma^{\text{eff}}/d\Omega_{\text{rr}})/(d\sigma^{\text{tot}}/d\Omega_{\text{rr}})$ for the $\text{Cl}+\text{CD}_4$ reaction along with the $(d\sigma^{\text{eff}}/d\Omega_{\text{rr}})/(d\sigma^{\text{tot}}/d\Omega_{\text{rr}})$ predictions for the DCl polarization aligned in the plane perpendicular to $u_{\text{DCl}}$, the line of centers, and an axis that bisects $u_{\text{DCl}}$ and the line of centers. This plot shows that the $\text{Cl}+\text{CD}_4$ rotational anisotropy data are consistent with $J_{\text{DCl}}$ being aligned in the plane perpendicular to an axis close to $u_{\text{DCl}}$, whereas an alignment of $J_{\text{DCl}}$ in the plane perpendicular to the line of centers gives

![FIG. 17. Center-of-mass scattering diagram that shows that at the point of closest approach (open circles) the C–Cl axis is parallel to the line of centers, while as the products separate (black circles), the C–Cl axis is approximately parallel to $u_{\text{DCl}}$.](image)
laboratory has shown that C–H stretch excitation enhances translation in enhancing reactivity. Previous work in this laboratory showed the Cl\(^+\)CH\(_4\) reaction is explained well using the concepts of Polanyi, whereas for reactions with early barriers the Cl\(^+\)D\(_4\) reaction is found to be maximally aligned (\(A_{0}^{(2)\text{stf}} \approx 0.5\)), albeit in different reference frames. The reduction of the degree of alignment for the DCl from the Cl\(^+\)CH\(_4\) reaction proceeds through a late transition state.

Polanyi has made predictions about the location of the reactive barrier and the effectiveness of vibrational excitation on the enhancement of reactivity.\(^{26,27}\) In particular, for reactions with late barriers (in which the transition state resembles the products) reactant vibration is more efficient than translation in enhancing reactivity, whereas for reactions with early barriers (in which the transition state resembles the reactants) reactant vibration is less efficient than translation in enhancing reactivity. Previous work in this laboratory has shown that C–H stretch excitation enhances the Cl\(^+\)CH\(_4\) reaction by a factor of 30 at 0.16 eV collision energy, whereas the Cl\(^+\)C\(_2\)H\(_6\) reaction is enhanced by 5\% to 10\% at a collision energy of 0.23 eV.\(^{28}\) This dramatic difference in the effect of vibrational excitation on these two reactions is explained well using the concepts of Polanyi, where the Cl\(^+\)CH\(_4\) reaction is predicted to have a late barrier and the Cl\(^+\)C\(_2\)H\(_6\) reaction is predicted to have an earlier barrier. The qualitative conclusions about the rotational alignment are consistent with this picture. The late transition state of the Cl\(^+\)CD\(_4\) reaction ensures that the product rotational alignment is determined late in the reactive process, with no memory of the reagent approach direction; the earlier transition state of the Cl\(^+\)C\(_2\)D\(_6\) reaction allows the product rotational alignment to be determined early enough in the reactive process to show effects of the reagent approach direction.

\textit{Ab initio} calculations by Truong et al.\(^{29}\) and Duncan et al.\(^{30}\) have shown that the Cl\(^+\)CH\(_4\) reaction proceeds through a late transition state. In addition, Duncan et al.\(^{30}\) have predicted that the thermal rate of the Cl\(^+\)CH\(_4\) reaction is markedly enhanced by C–H stretch excitation. In contrast, the Cl\(^+\)C\(_2\)H\(_6\) reaction is nearly barrierless; for this reason, we expect that the atom transfer occurs approximately at the closest approach of the Cl and C atoms. We believe that the difference in the location of the atom transfer for the Cl\(^+\)CD\(_4\) and Cl\(^+\)C\(_2\)D\(_6\) reactions is responsible for the large difference in reactivity observed for these reactions (as noted in Sec. I, we expect the Arrhenius pre-exponential factor for the Cl\(^+\)C\(_2\)D\(_6\) reaction to be significantly larger than that of the Cl\(^+\)CD\(_4\) reaction). In particular, we believe that the late transition state of the Cl\(^+\)CD\(_4\) reaction (with a late D-atom transfer) is associated with a low probability of D-atom transfer. This behavior leads to a small Arrhenius pre-exponential factor. In contrast, the earlier transition state of the Cl\(^+\)C\(_2\)D\(_6\) reaction (with an earlier D-atom transfer) is associated with a high probability of D-atom transfer. This behavior leads to a larger Arrhenius pre-exponential factor.

Ab initio calculations by Truong et al.\(^{29}\) and Duncan et al.\(^{30}\) have shown that the Cl\(^+\)CH\(_4\) reaction proceeds through a late transition state. In addition, Duncan et al.\(^{30}\) have predicted that the thermal rate of the Cl\(^+\)CH\(_4\) reaction is markedly enhanced by C–H stretch excitation. In contrast, the Cl\(^+\)C\(_2\)H\(_6\) reaction is nearly barrierless; for this reason, we expect that the atom transfer occurs approximately at the closest approach of the Cl and C atoms. We believe that the difference in the location of the atom transfer for the Cl\(^+\)CD\(_4\) and Cl\(^+\)C\(_2\)D\(_6\) reactions is responsible for the large difference in reactivity observed for these reactions (as noted in Sec. I, we expect the Arrhenius pre-exponential factor for the Cl\(^+\)C\(_2\)D\(_6\) reaction to be significantly larger than that of the Cl\(^+\)CD\(_4\) reaction). In particular, we believe that the late transition state of the Cl\(^+\)CD\(_4\) reaction (with a late D-atom transfer) is associated with a low probability of D-atom transfer. This behavior leads to a small Arrhenius pre-exponential factor. In contrast, the earlier transition state of the Cl\(^+\)C\(_2\)D\(_6\) reaction (with an earlier D-atom transfer) is associated with a high probability of D-atom transfer. This behavior leads to a larger Arrhenius pre-exponential factor.

The marked enhancement in reactivity for the Cl\(^+\)CH\(_4\) reaction caused by C–H stretch excitation is postulated to occur as a result of the shift of the H-atom transfer to earlier in the reactive encounter, which gives C–H stretch-excited Cl\(^+\)CH\(_4\) an earlier transition state, as for Cl\(^+\)C\(_2\)D\(_6\). Therefore, we expect that the HCl product alignment from this reaction also should change to resemble that from the Cl\(^+\)C\(_2\)D\(_6\) reaction. In agreement with this expectation, previous work in this laboratory showed the HCl (\(v' = 1\), \(J' = 1\)) product polarization from this reaction to be aligned in the plane perpendicular to the line of centers.\(^{9}\)

We note that the DCl (\(v' = 0\), \(J' = 1\)) polarization from the Cl\(^+\)CD\(_4\) reaction is found to be maximally aligned (\(A_{0}^{(2)\text{stf}} \approx -1.0\)), whereas that from the Cl\(^+\)C\(_2\)D\(_6\) reaction is found to be half-maximally aligned (\(A_{0}^{(2)\text{loc}} \approx -0.5\)), albeit in different reference frames. The reduction of the degree of alignment for the DCl from the Cl\(^+\)C\(_2\)D\(_6\) reaction can be explained by positing that the location of the transfer of the D atoms occurs with some symmetric spread about the closest approach of the C and Cl atoms, instead of exactly at the closest approach. The averaging over the spread of transfer locations causes the reduction in the measured alignment. The symmetric spread ensures that \(A_{0}^{(2)\text{stf}} = 0\), as observed. The width and functional form of the spread reduce the values of the \(A_{0}^{(2)\text{stf}}\) and \(A_{2}^{(2)\text{stf}}\); a uniform spread of \(\pm 40^\circ\) about the line of centers results in an alignment reduction that is consistent with the data. For the Cl\(^+\)CD\(_4\) reaction, however, the D-atom transfer occurs late in the reactive process such that small changes in the transfer location make negligible changes in the direction of the C–Cl axis, and hence there is little reduction in the product alignment in this case.
Sec. V B, we found that in the forward-scattered region, $J_{\text{DCI}}$ is consistent with being aligned in the plane perpendicular to the axis $F^\prime$ (see Fig. 19), which deviates about 30° from the line of centers. Therefore, one possible explanation for the polarization of the forward-scattered product is that it results from large-impact-parameter super-specular trajectories that have been deviated by about 30°. For a super-specular trajectory, the C–Cl axis at the point of closest approach (given here by $F^\prime$) is rotated counterclockwise with respect to the expected position of the line of centers if the trajectory were specular (see Fig. 19). As shown in Fig. 19, the angle between $u_{\text{CM}}$ and $F^\prime$ (the angle of incidence) is smaller than the angle between $F^\prime$ and $u_{\text{DCI}}$ (the angle of reflection), as is the case for super-specular trajectories.

The model for the product polarization presented here assumes that the effects of other transition-state or exit-channel forces are negligible (such as the effect of the DCI/alkyl complex on the DCl polarization). The DCl/CD$_3$ van der Waals complex has been shown to possess $C_{3v}$ symmetry,\textsuperscript{31} however, the well depth is not well known; Duncan et al.\textsuperscript{30} calculated a value of 2.32 kcal/mol at the BH&HLYP level, whereas Chen et al.\textsuperscript{31} calculated a value of 0.63 kcal/mol using G1 theory.\textsuperscript{31} The effect of the DCl/CD$_3$ complex on DCI product rotation is not known. If the dynamical effect of the complex is to align product rotation in the plane perpendicular to the product velocity, $u_{\text{DCI}}$, we note that this is not the case for the effect of the DCI/CD$_4$ complex on the DCI ($\nu' = 0, J' = 1$) product from the Cl+CD$_4$ reaction, nor the effect of the HCl/CH$_3$ complex on the HCl ($\nu' = 1, J' = 1$) product from the Cl+CH$_4$ ($\nu_3 = 1$) reaction.\textsuperscript{3} (For both of these channels $J_{\text{DCI}}$ is aligned in the plane perpendicular to the line of centers.) Without further information on the effect of the DCI/CD$_4$ complex on product rotation, we assume that the major forces responsible for the product alignment are transition-state forces, and not late exit-channel interactions.

VI. SUMMARY AND CONCLUSIONS

This work represents the complete description of the product polarization from the Cl+CD$_4$ reactant ($\nu' = 0, J' = 1$) + CD$_2$D reaction. We report the differential cross section, $1/\sigma(d\sigma_{00}/d\Omega_\nu)$, and all four of the stationary target frame scattering-angle-dependent polarization parameters ($A_{11}^{(1)\text{stf}}$, $A_{00}^{(2)\text{stf}}$, $A_{11}^{(2)\text{stf}}$, and $A_{22}^{(2)\text{stf}}$); additionally, we report the $1/\sigma(d\sigma_{00}/d\Omega_\nu)$ and the $A_{22}^{(2)\text{stf}}$ parameter for the Cl+CD$_4$→DCI($\nu' = 0, J' = 1$) + CD$_3$ reaction. Measurements show that the product polarization from both reactions can be described in a simple fashion. For the Cl+CD$_3$ reaction, $J_{\text{DCI}}$ is aligned in the plane perpendicular to an axis close to the product separation direction, $u_{\text{DCI}}$. For the Cl+CD$_2$D reaction (with the exception of the forward-scattered region), $J_{\text{DCI}}$ is aligned in the plane perpendicular to the line of centers, while in the forward-scattered region, the data are consistent with an alignment of $J_{\text{DCI}}$ in the plane perpendicular to an axis between the line of centers and $u_{\text{DCI}}$. We explain these results in terms of a simple model in which the rotational alignment of the DCI product is caused by the transfer motion of the D-atom, such that the DCI polarization is cylindrically symmetric with respect to the C–Cl axis at the point of transfer. We propose that the transfer point is late in the reactive process for the Cl+CD$_4$ reaction, such that the C–Cl axis is approximately parallel to $u_{\text{DCI}}$. For the Cl+CD$_2$D reaction, we propose that the transfer point is near the point of closest approach, such that the C–Cl axis is approximately parallel to the line of centers. In the context of this model, the product polarization reveals that the Cl+CD$_4$ reaction proceeds through a late transition state and the Cl+CD$_2$D reaction proceeds through an earlier transition state. Finally, we propose that the difference in the location of the D-atom transfer for these reactions is responsible for the differences observed in their macroscopic reactivities.

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