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Dynamical effects of reagent vibrational excitation in the $\text{Cl} + \text{C}_2\text{H}_6(\nu_5 = 1) \rightarrow \text{HCl} + \text{C}_2\text{H}_5$ reaction

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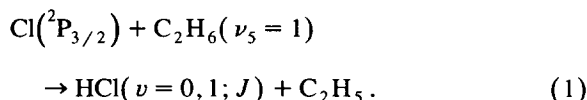
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Abstract

The title reaction is investigated using a photoinitiated technique that allows for the measurement of HCl product vibrational and rotational distributions using resonance enhanced multiphoton ionization (REMPI), the determination of center-of-mass scattering through core extraction, and the deduction of the average internal energy of the C_2H_5 product from HCl spatial anisotropy. Vibrational excitation of the ethane reagent is shown to produce only a 5% to 10% increase in integral reactivity. Production of forward-scattered HCl ($\nu = 1$) is observed, which is similar to the behavior of the chemically related $\text{Cl} + \text{CH}_4(\nu_3 = 1)$ reaction.

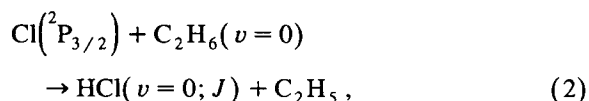
1. Introduction

In this Letter, we present experimental results for the vibrationally excited, state-selected reaction:



The reaction is studied in the gas phase under single-collision conditions at a well defined collision energy of 0.24 eV (1900 cm^{-1}). We report measurements of product rotational and vibrational state distributions and state-resolved differential scattering cross sections, as well as an HCl state-correlated measurement of the C_2H_5 internal energy. The degree of detail in our experimental observations allows significant insight into the mechanism by which this state-selected reaction proceeds. We study the dynamical effect of reagent vibration on chemical

reactivity by comparison with the vibrationally unexcited, ground-state reaction:



for which similar experimental measurements have been performed in this laboratory [1]. Additionally, we report the measurement of the vibrational enhancement for the $\text{Cl} + \text{C}_2\text{H}_6$ reaction; we define this enhancement as the ratio of the integral reactive cross section for reaction (1) to that of reaction (2).

The facility with which these data can be interpreted depends on the previous detailed study of the analogous chlorine + methane reactive system, in which we investigated the reactions of chlorine with ground-state methane and with $\text{CH}_4(\nu_3 = 1)$ [2,3]. The vibrationally excited reactions of methane and ethane show significant similarities, which provides both a basis for interpretation of our measurements

and a means by which to extend the general understanding of the dynamical effects of reagent vibration. In counterpoint, differences in behavior give insight into disparities between the two chemically related reaction systems.

2. Experimental

The experimental apparatus and techniques utilized in this study are similar to those employed for a number of other chemical systems; for a complete description the reader is referred to previous publications [1,4]. Molecular chlorine (99.999%), ethane (99.99%), and helium (99.995%) are premixed and expanded through a pulsed nozzle (General Valve 9-Series, 0.6 mm orifice, 0.5 atm backing pressure). The chemical reaction is initiated in the $\text{Cl}_2/\text{C}_2\text{H}_6$ expansion by the production of atomic chlorine via photolysis of the Cl_2 precursor at 355 nm ($\text{Nd}^{3+}:\text{YAG}$ third harmonic), which produces > 98% ground-state chlorine ($^2\text{P}_{3/2}$) [5]. As this photolytic process proceeds essentially through a single channel, the Cl reagent is produced with a precisely defined velocity of 1680 m/s. Because little thermal motion remains after expansion of the gas mixture, this velocity serves to define the collision energy for the reaction as 0.24 ± 0.03 eV (1900 ± 210 cm^{-1}) [6].

Concurrent with the photoproduction of the chlorine reagent, the ethane reagent is vibrationally excited by direct infrared pumping with the 3.45 μm idler beam of a home-built LiNbO_3 optical parametric oscillator (OPO). The 1.5 cm^{-1} to 2 cm^{-1} bandwidth of the OPO is not sufficient to resolve individual C_2H_6 rotational lines, but the OPO can be tuned to broader spectral features and can be scanned crudely. State distributions and scattering are recorded while exciting C_2H_6 on the Q branch of the ν_5 asymmetric stretch at 2895 cm^{-1} [7].

After reaction initiation, HCl products are allowed to build for 50 ns before being ionized through 2 + 1 REMPI, via the F–X(0,0), F–X(1,1), and E–X(0,1) bands, using single-photon wavelengths ranging from 240 nm to 247 nm ($\text{Nd}^{3+}:\text{YAG}$ -pumped dye laser; frequency-doubled LD 489) [2,8–11]. The ions are separated in a TOF mass spectrometer and detected on chevroned MCPs. For state distribution measure-

ments, total H^{35}Cl^+ ion signal is monitored as the REMPI probe laser scans over rovibrational transitions. Populations are then determined using previously published empirical correction factors [2,9–11]. To obtain product scattering information, we measure the HCl lab speed distribution through use of the core-extraction technique [4], in which the mass spectrometer is operated in a space-focusing and velocity-sensitive mode. Resulting ion arrival profiles are similar to Doppler-broadened lineshapes and can be analyzed directly to yield the HCl speed distribution [4,12]. This speed distribution can be converted directly to the center-of-mass differential scattering cross section, provided the relative reagent velocity is specified and the state-to-state energetics of the system are known.

The $\text{Cl} + \text{C}_2\text{H}_6$ reaction produces two molecular products, of which only one, HCl, is measured. Therefore, the state-to-state energetics cannot be determined exactly, which complicates the transformation from the measured speed distribution to the differential cross section. Nevertheless, a coincident measurement of the average C_2H_5 internal energy is available through analysis of the product spatial anisotropy. This anisotropy is dependent on the photolysis anisotropy ($\beta = -1$) and the product translational energy release, and it is measured by acquiring ion arrival profiles with the photolysis polarization vector parallel and perpendicular to the time-of-flight axis. This polarization change is effected on an every-other-shot basis through the use of a photoelastic modulator (Hinds International PEM-80).

Several sources of nonreactive background exist in this experiment, including trace quantities of contaminant HCl in the gas mixture and multiphoton dissociative ionization of Cl_2 and C_2H_6 . All such background interferences are removed through a subtraction procedure in which the observed signal with the infrared light absent (and thus without vibrational excitation) is subtracted from the observed signal with the infrared light present. The OPO is operated at half the repetition rate of the other lasers to facilitate this subtraction.

It is important to note that in the current measurement of $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_5 = 1$), our infrared laser bandwidth does not allow rotational state specificity in preparation of the vibrationally excited reagent. Thus, to compare the reactions of Cl with CH_4 and

C_2H_6 , we must assume that reagent rotational state does not influence the dynamics of either reaction to a significant degree. Previous experimental results have shown rotation to produce only small changes in product scattering for $Cl + CH_4$ ($\nu_3 = 1$), which supports this assumption to some extent [2]. Of further concern is the possible influence of vibrational redistribution after preparation of the C_2H_6 reagent and before reaction. This redistribution might occur either in the isolated molecule or as a result of perturbations caused by long-range forces resulting from the approaching chlorine atom. In either case, ethane has a greater density of states than methane and would be expected to suffer from these effects to a larger extent. Because ethane is a relatively small polyatomic molecule at a low level of internal excitation, we make the assumption that vibrational redistribution does not significantly affect the dynamics of this state-selected reaction.

3. Results and analysis

The reaction of atomic chlorine with vibrationally unexcited C_2H_6 proceeds at a large rate under the

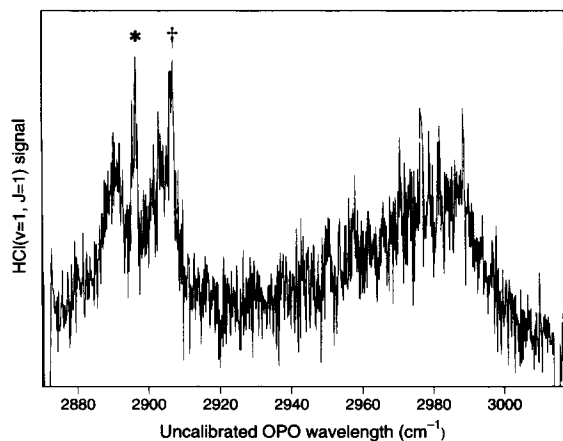


Fig. 1. Infrared action spectrum for the $Cl + C_2H_6$ reaction, in which the probe laser is fixed to detect HCl ($v = 1$, $J = 1$) through the $R(1)$ transition of the $F-X(1,1)$ band. The spectrum measures the increase in reactive signal caused by C_2H_6 infrared absorption, and it shows strong enhancements corresponding to excitation of one vibrational quantum in ν_5 (2895 cm^{-1}) and ν_7 (2985 cm^{-1}). The asterisk (*) indicates the ν_5 Q branch, for which state and scattering measurements are reported in this Letter. The dagger (†) marks an interfering feature resulting from infrared excitation of contaminant HCl ($v = 0$) via the $R(0)$ transition.

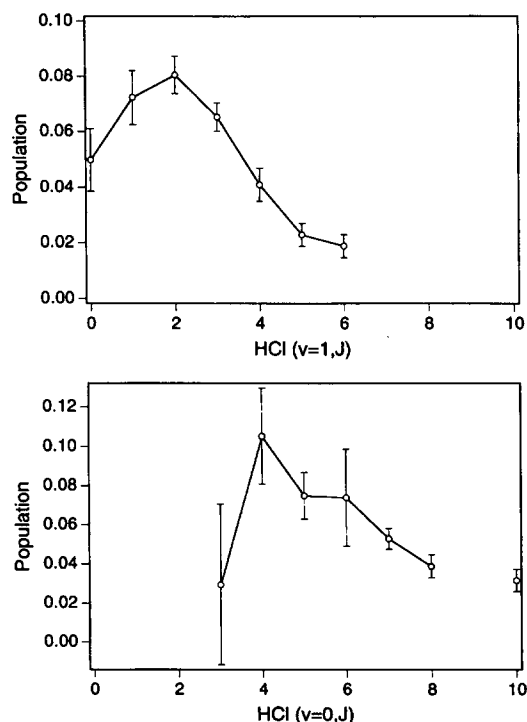


Fig. 2. Vibrationally enhanced HCl ($v = 0$) and HCl ($v = 1$) rotational state distributions for $Cl + C_2H_6$ ($\nu_5 = 1$). These distributions show the difference between C_2H_6 ($\nu_5 = 1$) and C_2H_6 ($v = 0$) reactivity. Populations are scaled so that the total integrated product is unity. The scales for the $v = 0$ and $v = 1$ products are absolutely related and reflect a 2:3 vibrational branching ratio. Error bars are 1σ , based on statistical analysis of replicate measurements. Note that negative populations are physically possible and would indicate vibrational deactivation of the reaction.

experimental conditions employed and compounds the difficulty of our measurements and analysis. The OPO pumps 40% to 50% of the ethane from the ground state to the first vibrationally excited state, and these excited molecules no longer react as C_2H_6 ($v = 0$). Thus, all direct measurements we make reflect the *change* in reactivity resulting from C_2H_6 vibrational excitation. This change is a constant of nature and does not depend on the way in which the experiment is carried out. We therefore refer to this change as the vibrationally *enhanced* reaction, as distinguished from the vibrationally *excited* reaction; these two can be connected using knowledge of the reactivity of ground-state ethane.

Fig. 1 shows the infrared action spectrum for the $\text{Cl} + \text{C}_2\text{H}_6$ reaction, in which the probe laser is fixed to detect HCl ($v = 1$, $J = 1$) through the $\text{R}(1)$ transition of the $\text{F-X}(1,1)$ band and the OPO crudely scanned across the vibrational spectrum of C_2H_6 . The spanned frequency range encompasses the ν_5 (asymmetric stretch), ν_7 (symmetric stretch), and $\nu_8 + \nu_{11}$ (bending + scissoring) vibrational bands. Our home-built OPO is not constructed for such scans, and neither frequency nor intensity of the spectrum can be relied upon quantitatively; however, our qualitative result is that infrared absorption that results in C_2H_6 stretching clearly acts to increase reactivity. All state distribution and scattering measurements are recorded while pumping the Q branch of the ν_5 mode at 2895 cm^{-1} , as this affords the greatest concentration of states and, consequently, the greatest population transferred to $v = 1$ and the most resulting reactive signal. Preliminary measurements on $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_7 = 1$) show no marked differences from the ν_5 results.

Vibrationally enhanced state distributions for $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_5 = 1$) \rightarrow HCl ($v = 0$, J) and HCl ($v = 1$, J) are presented in Fig. 2. The HCl ($v = 0$) measure-

ment is complicated by the large amount of $v = 0$, low- J product formed by the $\text{Cl} + \text{C}_2\text{H}_6$ ($v = 0$) reaction; for example, for HCl ($v = 0$, $J = 3$), there are 50 to 100 times more signal resulting from the ground-state reaction, which increases the difficulty of measuring small vibrationally induced differences. Formation of $v = 0$ product is still the major reactive channel for the vibrationally enhanced reaction and accounts for 60% of products formed; 40% of products are produced vibrationally excited, in $v = 1$. No HCl ($v = 2$) was observed, though the energetics of the reaction allow for its formation. Although the sensitivity of the $\text{F-X}(1,2)$ band is not known, we can reasonably assume detection sensitivity comparable with that of the $\text{F-X}(0,1)$ band, and therefore we estimate that HCl ($v = 2$) comprises less than 5% of the total product yield [13]. The HCl ($v = 0$) and HCl ($v = 1$) rotational state distributions are markedly like those previously measured for $\text{Cl} + \text{CH}_4$ ($\nu_3 = 1$) [2]. Both reactions show similar vibrational branching ratios and relatively hot rotational state distributions for HCl ($v = 0$); the HCl ($v = 1$) product shows a tendency to populate higher rotational states for the $\text{Cl} + \text{ethane}$ reaction.

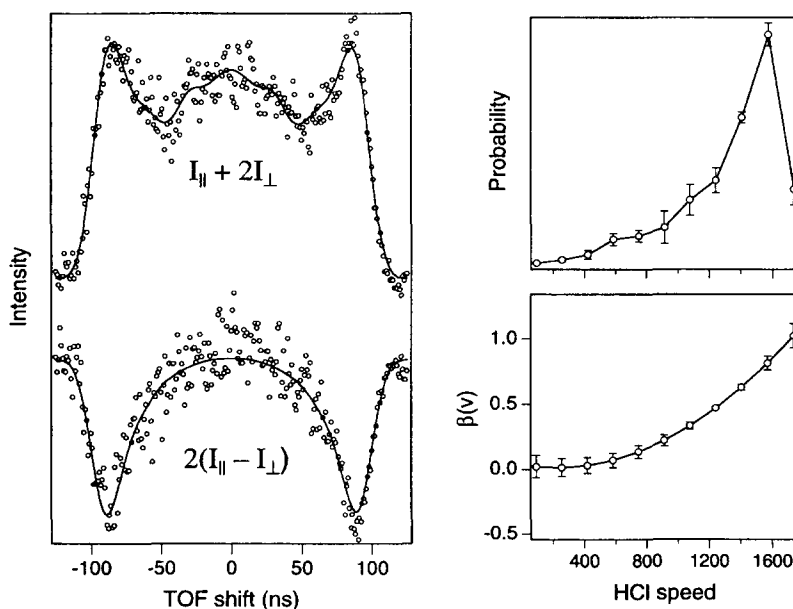


Fig. 3. Isotropic ($I_{\parallel} + 2I_{\perp}$) and anisotropic ($2(I_{\parallel} - I_{\perp})$) core-extracted ion arrival profiles for $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_5 = 1$) \rightarrow HCl ($v = 1$, $J = 1$), detected on the $\text{R}(1)$ transition of the $\text{F-X}(1,1)$ band. The two profiles are offset for clarity and otherwise use the same intensity scale. The speed distribution and speed-dependent product anisotropy are presented alongside the data, with statistical 1σ error bars.

Core-extracted ion arrival profiles for $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_5 = 1$) \rightarrow $\text{HCl}(\nu = 1, J = 1)$ are recorded on the R(1) transition of the F–X(1,1) band at an extraction field of 62 V/cm. Nascency of the speed distribution is assured by a very short initiation to probe delay of 50 ns. Profiles are recorded concurrently with the photolysis polarization parallel (I_{\parallel}) and perpendicular (I_{\perp}) to the time-of-flight axis. These data are then analyzed through the formation of composite profiles, which are presented in Fig. 3. The isotropic profile, $I_{\parallel} + 2I_{\perp}$, removes all dependence on the photolysis spatial anisotropy and thus provides a direct measurement of the speed distribution, which is shown alongside. The speed distribution is sharply peaked at the fastest speeds energetically allowable, which indicates a predominance of forward scattering in the differential cross section. This behavior is in accordance with published differential cross sections for $\text{Cl} + \text{CH}_4$ ($\nu_3 = 1$), which show complete forward scattering for the $\nu = 1$ product. Inversion of the speed distribution to the differential cross section requires knowledge of the exact state-to-state energetics for the reaction and is discussed later in this section.

The anisotropic profile, $2(I_{\parallel} - I_{\perp})$, provides a measurement of the HCl product speed-dependent spatial anisotropy, also shown in Fig. 3. This anisot-

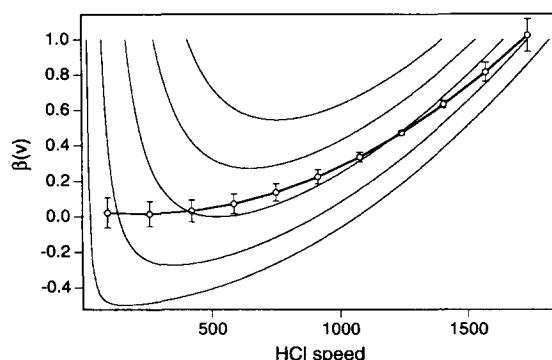


Fig. 4. Spatial anisotropy and scattering analysis for $\text{HCl}(\nu = 1, J = 1)$ product. The speed-dependent anisotropy measurement pictured in Fig. 3 is presented, along with contours showing predicted speed-dependent anisotropy for varying levels of C_2H_5 product internal excitation. The outermost contour is calculated assuming that the ethyl product takes no energy from the reaction into internal modes; successive inner contours are shown for increments of 500 cm^{-1} ethyl internal energy.

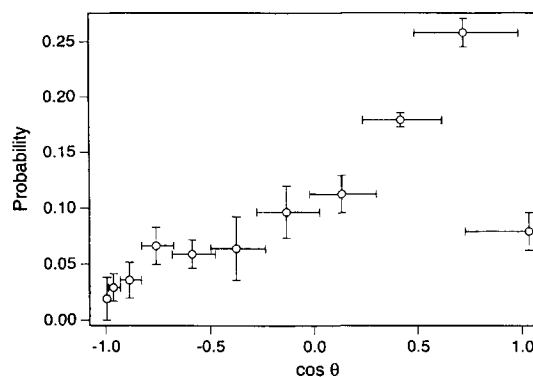


Fig. 5. Estimated differential cross section for the $\text{Cl} + \text{C}_2\text{H}_6$ ($\nu_5 = 1$) \rightarrow $\text{HCl}(\nu = 1, J = 1)$ reaction. The average energy calculated from speed-dependent anisotropy data shown in Fig. 4 was used to convert the measured HCl speed distribution to a differential cross section. Vertical error bars result from 1σ statistical variation in the speed distribution measurement. Horizontal bars result primarily from the speed resolution of the instrument and secondarily from statistical distribution in the measurement of spatial anisotropy. Overlap of horizontal bars (especially noticeable in the forward three points) may indicate HCl products that scatter into the same angles but with varying degrees of coincident C_2H_5 internal excitation.

ropy allows the determination of the C_2H_5 internal energy state, as discussed in previous publications [1,2,12]. Fig. 4 shows the measured speed-dependent anisotropy distribution plotted along with calculated contours showing possible anisotropy distributions for varying amounts of ethyl excitation; the outermost contour would result if the ethyl radical contained no energy in its internal modes, and inner contours would result from increasing ethyl internal energy. The ethyl radical becomes significantly excited in the reaction; its average internal energy is $858 \pm 71 \text{ cm}^{-1}$. An important point is that the measurement of C_2H_5 energy is an inherently averaged quantity, and the *distribution* of internal states cannot be determined. With the assumption that this distribution is peaked about the average, however, we can extract the $\text{HCl}(\nu = 1, J = 1)$ state-to-state differential cross section, which is presented in Fig. 5. The combined speed and anisotropy measurements contain more information than a differential cross section. A rigorous presentation of this information would require a three-dimensional plot which detailed HCl scattering as a function of ethyl internal energy. Consequently, in collapsing this information

into a two-dimensional graph, it is possible for the resulting differential cross section to be multiple valued. This effect is seen in the overlap of horizontal resolution bars in the forward region and indicates our experimental sensitivity to HCl product that is formed in the same state, scatters into the same center-of-mass angle, but is formed coincidentally with C_2H_5 containing varying amounts of internal energy.

The integral effect of vibration on reactivity is investigated through the measurement of the vibrational enhancement, the ratio of reactivity between reactions (1) and (2). This is achieved through the determination of the ratio of signals for the vibrationally excited and ground-state reactions (distinguished by the presence or absence of infrared light), which are measured on a single product state populated by both reactions: $v = 1$, $J = 1$. The ratio of total products is then computed using knowledge of both reactions' product state distributions. Integrating over all product states observed, we calculate a 0.025 ($\sigma = 0.007$) increase in reactivity with vibrational excitation. Because the measurement of the $v = 0$ rotational state distribution for reaction (1) is incomplete, a Boltzmann fit to the measured distribution is used to estimate the populations of unobserved states. Using this estimation, we determine the total increase in signal to be 0.03. Signal from the vibrationally excited reaction was found to show little dependence on infrared power, indicating saturation of the ethane vibrational transition and therefore 40% to 50% population transfer to ν_5 through Q-branch transitions. We conclude that vibrationally excited ethane is 1.05 to 1.1 times more reactive than ground-state ethane. This small vibrational enhancement is in stark contrast to the 30-fold increase in reactivity observed for Cl + methane [3].

Because the population of vibrationally excited reagents necessarily depletes ground-state reagents, our experiment directly measures the changes in differential and integral reactivity effected by reagent vibrational excitation. For Cl + C_2H_6 ($\nu_5 = 1$), this enhancement of reactivity produces rotationally hot HCl ($v = 0$) products and significant amounts of forward-scattered HCl ($v = 1$). Moreover, the small integral vibrational enhancement demonstrates that C_2H_6 ($\nu_5 = 1$) reacts much like C_2H_6 ($v = 0$). Thus, an investigation that could prepare C_2H_6 ($\nu_5 = 1$)

alone would observe a cold rotational distribution of HCl ($v = 0$), as was seen for ground-state ethane, and very little ($< 3\%$) population of HCl ($v = 1$). These results are in sharp contrast to Cl + methane, for which ground-state reactivity is negligible. Examination of the total vibrationally excited reactivity highlights the differences between ethane and methane. However, analysis of the state and scattering properties of only those products enhanced by vibrational excitation of ethane reveals significant similarities between the two systems.

4. Discussion

We have employed a photoinitiated technique to study the reaction of atomic chlorine with state-selected ethane, C_2H_6 ($\nu_5 = 1$). Rotational state distributions for HCl ($v = 0$) and HCl ($v = 1$) products have been measured. They show rotationally hot ground-state HCl and colder vibrationally excited products. A state-resolved center-of-mass scattering cross section has been recorded for HCl ($v = 1$, $J = 1$) and demonstrates a propensity for forward scattering. Additionally, measurement of the speed-dependent HCl product spatial anisotropy allows for the determination of the average coincident C_2H_5 internal energy, which is nearly 1000 cm^{-1} . Measurement of the effect of reagent vibrational excitation on integral reactivity shows that vibration enhances the reactivity of ethane by only 5% to 10%. Results of measurements of both integral and differential properties of the reaction are best understood by comparison with other reactive systems; we consider in particular Cl + CH_4 ($\nu_3 = 1$) and Cl + HD ($v = 1$).

The Cl + CH_4 ($\nu_3 = 1$) reaction has been shown to produce nearly completely forward-scattered HCl ($v = 1$) product [2]. This scattering was attributed to a nonimpulsive stripping mechanism in which atomic chlorine abstracts hydrogen at large impact parameters. The lack of velocity-changing reactive forces was posited to result from the near-thermoneutral energetics of the system, which allow the hydrogen to transfer from the methane to the chlorine without significant change in energy. The HCl ($v = 0$) is produced from a state-to-state exothermic process and thus results in significant release of forces during the reaction; this vibrationally unexcited product

was observed to be primarily back- and side-scattered. The propensity for forward scattered products to be formed in state-to-state thermoneutral channels has been observed in experimental measurements and theoretical studies of $F + H_2 \rightarrow HF$ ($v = 3$) [14,15] and in theoretical predictions for $Cl + HD$ ($v = 1$) \rightarrow HCl ($v = 1$) [16].

The $Cl + C_2H_6$ ($\nu_5 = 1$) \rightarrow HCl ($v = 1$, $J = 1$) reaction is 937 cm^{-1} exothermic [17]. The unobserved C_2H_5 product is polyatomic and possesses internal degrees of freedom, however, and the extent of C_2H_5 excitation determines the exact state-to-state energetics of the system. We propose that the reaction mechanism for HCl ($v = 1$) formation favors a state-to-state thermoneutral process. This proposal is borne out by the ethyl product internal energy, which ranges from 700 cm^{-1} to 1200 cm^{-1} over nearly the entire HCl speed distribution, which closely matches the reaction exothermicity. Furthermore, the fastest HCl product formed (1730 m/s), which requires complete conversion of the exothermicity into kinetic energy, shows a precipitous drop from the next fastest product (1570 m/s) in its probability of formation, as shown in Fig. 3. Of the HCl products that can be formed via a thermoneutral process, forward scattering is sharply favored, in a similar fashion to the $Cl + CH_4$ ($\nu_3 = 1$) reaction.

Neither forward scattering nor a preference for thermoneutral atom transfer is seen in the isoenergetic $Cl + C_2H_6$ ($\nu = 0$) \rightarrow HCl ($v = 0$) reaction, for which the HCl product scatters near-isotropically and the reaction exothermicity contributes to product translational energy. It is interesting to speculate on the fate of the vibrationally excited HCl product in the hypothetical instance of a vibrationally excited atom + diatom system with similar energetics to $Cl + C_2H_6$ ($\nu_5 = 1$). In this case, it would be difficult for the internal energy of the products to be such that the reaction proceeded via a thermoneutral process, and it seems reasonable to predict that the vibrationally adiabatic channel would not show sharp forward scattering. This prediction may be verified for theoretical calculations of the $Cl + HD$ ($v = 1$) \rightarrow $DCI + H$ reaction, which has no thermoneutral channel and scatters near-isotropically in all product states [16]. Forward scattering is thus distinctive of the dynamics of vibrationally excited reactions that undergo thermoneutral hydrogen abstraction to form

vibrationally excited products, and it has been observed or calculated for the $Cl + CH_4$ ($\nu_3 = 1$), $Cl + HD$ ($v = 1$), and $Cl + C_2H_6$ ($\nu_5 = 1$) reactions.

We consider in yet more detail the comparison of the reactions of chlorine atoms with vibrationally excited CH_4 and C_2H_6 . Both systems form forward-scattered HCl ($v = 1$) product, as discussed above. Additionally, the reactions yield both similar product rotational distributions and HCl ($v = 1$): HCl ($v = 0$) vibrational branching ratios. However, a disparity exists between the two systems in the effect of vibration on integral reactivity; measured vibrational enhancements are 30 and 1.05 to 1.1 for CH_4 and C_2H_6 , respectively. Previous results for $Cl + CH_4$ demonstrated that the effect of vibrational excitation on reactivity was to allow reaction to occur at all impact parameters and to decrease or remove geometric restrictions at the reactive transition state. The similarity of state distributions and scattering behavior for the methane and ethane reactions indicates that vibration has an analogous impact on the $Cl + C_2H_6$ system. Differences in vibrational enhancement are explained by differences in reactivity of the ground-state hydrocarbons; to wit, although vibration opens the 'cone of acceptance' for reactivity, $Cl + C_2H_6$ ($\nu = 0$) is already nearly completely reactive. Thus, reactivity is enhanced little by vibrational excitation of C_2H_6 , in contrast to CH_4 , which is largely unreactive in its ground vibrational level. Our previous measurements of ground-state ethane showed broad, near-isotropic scattering, as opposed to backward scattering observed for $Cl + CD_4$ ($\nu = 0$). Furthermore, $Cl +$ ethane proceeds at a far greater thermal rate, on which we based the suggestion that the $Cl + C_2H_6$ transition state places few geometric constraints on reaction, allowing most reagent configurations to proceed toward products. We propose that the small measured vibrational enhancement for $Cl + C_2H_6$ ($\nu_5 = 1$) is further evidence that the 'cone of acceptance' is already open for the reaction of atomic chlorine with C_2H_6 .

Acknowledgements

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