I. Three-center versus four-center HCl-elimination in photolysis of vinyl chloride at 193 nm: Bimodal rotational distribution of HCl (v≤7) detected with time-resolved Fourier-transform spectroscopy

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Following photodissociation of vinyl chloride at 193 nm, fully resolved vibration-rotational emission spectra of HCl in the spectral region 2000–3310 cm⁻¹ are temporally resolved with a step-scan Fourier-transform spectrometer. Under improved resolution and sensitivity, emission from HCl up to v=7 is observed, with J≥32 (limited by overlap at the band head) for v=1–3. All vibrational levels show bimodal rotational distribution with one component corresponding to ~500 K and another corresponding to ~9500 K for v≤4. Vibrational distributions of HCl for both components are determined; the low-J component exhibits inverted vibrational population of HCl. Statistical models are suitable for three-center (α, α) elimination of HCl because of the loose transition state and a small exit barrier for this channel; predicted internal energy distributions of HCl are consistent but slightly less than those observed for the high-J component. Impulse models considering geometries and displacement vectors of transition states during bond breaking predict substantial rotational excitation for three-center elimination of HCl but little rotational excitation for four-center (α, β) elimination; observed internal energy of the low-J component is consistent with that predicted for the four-center elimination channel. Rate coefficients 33.8 and 4.9×10¹¹ s⁻¹ for unimolecular decomposition predicted for three-center and four-center elimination channels, respectively, based on Rice-Ramsberger-Kassel-Marcus theory are consistent with the branching ratio of 0.81:0.19 determined by counting vibrational distribution of HCl to v≤6 for high-J and low-J components. Hence we conclude that observed high-J and low-J components correspond to HCl (v, J) produced from three-center and four-center elimination channels, respectively. © 2001 American Institute of Physics. [DOI: 10.1063/1.1328736]

I. INTRODUCTION

Vinyl chloride (CH₂CHCl) serves as a model unsaturated hydrocarbon for which dissociation might proceed via multiple channels during photolysis. A recent review is given by Blank et al.¹ who employed photofragment translational spectroscopy (PTS) using vacuum ultraviolet (VUV) synchrotron radiation for ionization of products and observed five primary dissociation channels following excitation of CH₂CHCl at 193 nm. Most Cl atoms are translationally hot and originate from dissociation via a hypersurface of an electronically excited state. The remaining channels proceed on the ground electronic surface following internal conversion from the optically prepared state; these include elimination of H, H₂, HCl, and Cl (translationally cold). Two secondary channels eliminating H after elimination of Cl, and Cl after elimination of H from CH₂CHCl, are also identified. In this paper, we focus only on channels that eliminate HCl from CH₂CHCl; these channels might proceed via a transition state involving three or four centers. Berry² employed a chemical laser to determine distributions of vibronic states of HCl (v=4) produced from photolysis of various chloroethylene at λ≥155 nm. He concluded that HCl is produced primarily via a four-center (α, β) elimination channel and rationalized the observed non-statistical vibrational distribution of HCl according to an impulse mechanism in which the “localized” energy is partitioned between internal energy of HCl and relative translational energy of the fragments. Moss et al.³ recorded infrared (IR) emission spectra after photolysis of CH₂CHCl at 193 nm and found substantial vibrational excitation of C₂H₅ and/or CHCl and much rotational excitation in HCl. Donaldson and Leone⁴ used a Fourier-transform infrared (FTIR) spectrometer that synchronously triggers the photolysis laser at 193 nm to record time-resolved IR emission from dissociation of CH₂CHCl. They determined a vibrational distribution of HCl (1≤v≤4) slightly cooler than that reported by Berry,² and proposed that available energy is partitioned statistically into the product modes of a transition state that has a small vibrational wave number (~1500 cm⁻¹) for H–Cl stretching. Blank et al.¹ reported that the photoionization energy threshold of HCl produced from photolysis of vinyl chloride decreases by ~2.2 eV from thermalized HCl, indicating that the HCl fragment has substantial internal energy.
The only report on rotational energy distribution of HCl was by Reilly et al.\textsuperscript{5} who performed pump-probe experiments with a molecular beam containing CH\textsubscript{2}CHCl and detected Cl and HCl after photolysis at 193 nm with (2 + 1)-REMPI (resonantly enhanced multiphoton ionization) followed by time-of-flight (TOF) detection. They found a bimodal rotational distribution with temperatures corresponding to 340 and 22 600 K for HCl in the \( v = 0 \) state. In contrast, they observed a Boltzmann-like distribution corresponding to rotational temperatures of 2100±250 and 1850 ± 140 K for \( v = 1 \) and 2 states of HCl, respectively. Huang et al.\textsuperscript{7} photolysed \( d_1 \)-vinyl chloride (CH\textsubscript{2}CDCl) at 193 nm and found that the rotational state distributions of HCl product are nearly identical for CH\textsubscript{2}CDCl and CH\textsubscript{2}CHCl.

Later, they used velocity-aligned Doppler spectroscopy (VADS) to determine the speed distribution of HCl (\( v = 0 \pm 2, J \)) produced in photolysis of CH\textsubscript{2}CHCl at 193 nm and found that released kinetic energy much exceeds that predicted with a statistical model for three-center elimination.\textsuperscript{7} To reconcile this situation they proposed that three-center elimination and isomerization from vinylidene (CCH\textsubscript{2}) to acetylene (HCCCH) occur in a concerted but non-synchronous fashion. The isomerization is expected to be rapid enough to share its exothermicity with nearby HCl fragment so that HCl departs with augmented vibrational and translational energies. The dichotomy between populations of rotational states of HCl with \( v = 0 \) and HCl with \( v > 0 \) is explained according to a vibrationally adiabatic mechanism in which the adiabatic barrier disappears entirely for channels associated with HCl with \( v > 0 \).

The relatively large kinetic energy of HCl derived from VADS is consistent with results from PTS. Average energies determined with VADS are 25±2, 21±2, and 18±1 kcal mol\(^{-1}\) for HCl (\( v = 0 \pm 2 \), \( J \)), respectively.\textsuperscript{7} Umemoto et al.\textsuperscript{8} photolysed CH\textsubscript{2}CHCl at 193 nm and determined the kinetic energy distribution of HCl with an average translational energy of 15±1 kcal mol\(^{-1}\) by means of PTS at a fixed scattering angle of 90\(^\circ\). An average energy of 18±1 kcal mol\(^{-1}\) deduced by Blank et al.\textsuperscript{1} is consistent with results from VADS if substantial population of HCl with \( v > 2 \) is assumed.

Varied branching ratios between channels for three-center and four-center elimination of HCl during photolysis of vinyl chloride at several wavelengths were reported. Berry\textsuperscript{2} reported a quantum yield of HCl from CH\textsubscript{2}CDCl 92% of that from CH\textsubscript{2}CHCl for \( \lambda \geq 155 \) nm, indicating that four-center HCl-elimination is the major channel. Ausloos et al.\textsuperscript{9} observed a nearly equal yield from three-center and four-center elimination in the spectral region 200–220 nm, with the former decreasing in importance at shorter wavelengths. Experiments using GC-MS (gas chromatography—mass spectrometry) detection of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}HD upon IR multiphoton dissociation of deuterated isotopomers of CH\textsubscript{2}CHCl reveal a preference for a three-center elimination of HCl; a ratio of 2.3 was reported for three-center to four-center HCl-elimination channels.\textsuperscript{10,11} REMPI measurements of Huang et al.\textsuperscript{9} produced ratios of 3.9–4.0 for yields of HCl produced from CH\textsubscript{2}CHCl to that from CH\textsubscript{2}CDCl. These authors originally interpreted the results as signifying a 3:1 preference for three-center over four-center elimination of CH\textsubscript{2}CHCl. Following further experiments and a theoretical study by Riehl and Morokuma,\textsuperscript{12} Huang et al.\textsuperscript{7} proposed a mechanism that includes \( \alpha, \beta \)-migration of H that competes with the three-center \( \alpha, \alpha \)-elimination of HCl, with no significant contribution from the four-center elimination.

We have demonstrated that step-scan time-resolved Fourier-transform spectroscopy (TR-FTS) provides much improved resolution and sensitivity over previous IR emission techniques.\textsuperscript{13,14} Here we report emission from HCl (1 \( \leq v \leq 7 \), \( J \leq 32 \)) during photolysis of CH\textsubscript{2}CHCl at 193 nm by means of TR-FTS. A bimodal rotational distribution of HCl is observed for all vibrational states, yielding enhanced understanding of HCl-elimination channels.

II. EXPERIMENT

The apparatus employed to obtain step-scan time-resolved Fourier-transform spectra resembles that described previously.\textsuperscript{13,14} An ArF excimer laser (Lambda Physik LPX120i), operated at 30–60 Hz with pulse energy 8–10 mJ was employed as a photolysis source. A telescope served to focus the laser beam to about 20 mm\(^2\) at the reaction center with a fluence of 40–50 mJ cm\(^{-2}\). We estimated a photolysis yield <50% in the irradiated region based on an absorption cross section of 1.9×10\(^{-17}\) cm\(^2\) for CH\textsubscript{2}CHCl.\textsuperscript{2} IR emission was collected with a set of Welsh mirrors and directed into the Fourier-transform spectrometer (Bruker IFS66v) through two CaF\(_2\) lenses. A CaF\(_2\) beam splitter and an InSb detector cooled to 77 K were used. Filters passing either 2850–3310 cm\(^{-1}\) (OCLI, W03024-6 and W03999-4) or 2000–2900 cm\(^{-1}\) (OCLI, W04212-4) and an iris were placed in the sample compartment of the spectrometer. The detected transient signal, amplified with a gain of 1×10\(^{6}\) V/A (bandwidth 1.5 MHz), was further amplified with a low-noise voltage amplifier (bandwidth 1 MHz, gain typically set at 50), and sent to the internal A/D converter (16 bit, 200 kHz) of the spectrometer. The response time of the IR detector is ~0.7 \( \mu s \). The interval of data acquisition in each time slice is 5 \( \mu s \); hence a datum at \( t \mu s \) represents an average of signal in a range \( t \pm 2.5 \mu s \). The first datum was acquired \( \sim 2.5 \mu s \) (designated as 0–5 \( \mu s \)) after laser irradiation. Typically 300–350 time slices were acquired at 5 \( \mu s \) intervals and the signal was averaged for 50–60 laser pulses at each scan step; 3416 and 5979 scan steps were performed to yield a spectrum with resolution 0.3 cm\(^{-1}\) in the spectral range 2850–3310 and 2000–2900 cm\(^{-1}\), respectively.

In some experiments we employed the same InSb detector and amplifiers as described previously but digitized the signal with an external board (PAD1232, 40 MHz, 12 bit ADC) at 25 ns resolution. The first 40 spectra thus obtained were subsequently averaged to yield a satisfactory spectrum representing emission in the period 0–1 \( \mu s \) after photolysis. A blackbody source (Graseby, model 564, maintained at 1273 K) was employed to determine the response function of the instrument, as described previously.\textsuperscript{13,14}

The partial pressure of CH\textsubscript{2}CHCl was kept in the range 110–180 mTorr. Ar (240–420 mTorr) was added near the entrance photolysis port to avoid brown deposit on the quartz window. The pressure of the system was measured with a
capacitance manometer (MKS Baratron, model 121, 0–10 Torr) and flow rates were measured with flow meters calibrated according to standard procedures. CH$_2$CHCl (Merck, 99.95%) was used without purification except for degassing; no impurity was detected in IR spectra.

III. RESULTS

Data acquisition in two modes was performed with identical detector and amplifiers. The internal 16 bit A/D converter of the spectrometer provides temporal resolution of 5 μs with satisfactory sensitivity, whereas the external PAD1232 board provides an effective temporal resolution ~1 μs with decreased signal-to-noise (S/N) ratio. In this paper, we focus on only the first available acquisition window that corresponds to a near collisionless condition to obtain information on nascent vibration-rotational distributions of HCl after photolysis. Modeling of temporal profiles to provide kinetic information and branching ratios of other channels will be presented in a forthcoming paper.15

Figure 1 shows representative emission spectra recorded at a resolution of 8 cm$^{-1}$ after photolysis of a flowing mixture of CH$_2$CHCl and Ar (0.13 and 1.57 Torr, respectively) at 193 nm. Emission from highly excited HCl and C$_2$H$_2$ were observed immediately after laser photolysis (trace A); at a later stage (traces B and C) these molecules were quenched to lower vibrational states. Overtone ($\Delta v = -2$) emission of HCl in the range 4500–6000 cm$^{-1}$ was also observed.

To limit the period of data acquisition to ~2 h so as to assure stability of experimental conditions, high-resolution spectra were recorded in two sections (2000–2900 and 2850–3310 cm$^{-1}$) with proper filters placed in the optical path. The variations in relative distribution of duplicated lines in overlapped sections are typically within 5%. For improved accuracy, we normalized these two spectra according to overlapped lines.

![FIG. 1. Infrared emission spectra of HCl recorded at varied intervals after photolysis of CH$_2$CHCl (130 mTorr) in Ar (1.57 Torr) at 193 nm. (a) 2 μs, (b) 17 μs, (c) 47 μs. Spectral resolution 8 cm$^{-1}$; averaged over 50 laser pulses at each interferometer scan step.](image-url)
TABLE I. Experimental conditions, fitted rotational temperature and total rotational population of HCl (v = 1–6) after photolysis of CH2CHCl at 193 nm.

<table>
<thead>
<tr>
<th>Expt no.</th>
<th>PCH2CHCl/mTorr</th>
<th>PAr/mTorr</th>
<th>t/μs</th>
<th>v</th>
<th>Temp/K</th>
<th>( \sum_{J} P_{J}(v) \times E_{rot}/kJ ) mol (^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>110</td>
<td>240</td>
<td>0–1.0</td>
<td>1</td>
<td>9200±1500</td>
<td>2670(92)×10⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11000±1800</td>
<td>2410(2105)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>10000±1800</td>
<td>2015(1730)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>10000±3500</td>
<td>1640(1195)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>6000±2100</td>
<td>1200(1080)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>3500±1200</td>
<td>630(630)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>3400±1200</td>
<td>600(600)</td>
</tr>
<tr>
<td>2</td>
<td>115</td>
<td>236</td>
<td>0–5.0</td>
<td>1</td>
<td>8500±1600</td>
<td>5385(4755)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11000±2000</td>
<td>4070(3600)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>6000±1200</td>
<td>2620(2415)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>4500±800</td>
<td>2560(2240)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>3200±800</td>
<td>1555(1495)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>4200±1200</td>
<td>820(820)</td>
</tr>
</tbody>
</table>

\( P_{J}(v) = \text{(integrated emittance)×10⁰[(instrumental response factor)/Einstein coefficient]} \).

\( ^{a} \) Fitted values; extrapolated populations up to J = 42 are included. See text.

\( ^{b} \) Summed values are listed in parentheses; only observed levels are summed. See text.
brational states $v \leq 6$. As pressure and the time of the detection window are decreased to attain nearly collisionless conditions as in experiment 1b, the rotational temperature of high-$J$ and low-$J$ components converge to $\sim 9500 \pm 200$ K and $\sim 500\pm 200$ K for HCl ($v \leq 4$), respectively. Hence data in experiments nos. 1a (0–6 $\mu$s) and 1b (0–1 $\mu$s) are used to determine nascent populations.

Relative rotational populations reported by Reilly et al.\(^5\) shown in Fig. 3 with symbol $\Delta$ but shifted downward for clarity, are consistent with our data except for the absence of high-$J$ parts. The absence of high-$J$ lines of HCl in the $v > 0$ states in their work might be due to lack of sensitivity for these transitions in the REMPI scheme. Observation of low-$J$ components of HCl in their experiments under collisionless conditions in a supersonic jet also supports our conclusion that observed low-$J$ components are nascent, rather than from rotational quenching.

The average rotational energy of each vibrational state of HCl is calculated on summing a product of rotational energy and normalized population for each observed rotational level, $E_{\text{rot}} = \sum J P_v(J) E_v(J)/\sum J P_v(J)$, and is referred to as a ‘‘summed value,’’ as listed parenthetically in columns $E_{\text{rot}}$ of Table I. Lines associated with large $J$ in a state with large $v$ are more difficult to detect because sensitivity is limited. We assume a Boltzmann distribution for high-$J$ components and associate an extrapolated population with unobserved lines up to $J_{\text{max}}(v)$=42, 38, 35, 31, 26, 20 for $v = 1–6$, respectively; they correspond to a vibration-rotational energy of $\sim 19300$ cm$^{-1}$, the highest observed value in $v = 6$. Rotational energies thus obtained are referred to as ‘‘fitted values’’ in Table I. Fitted and summed values for the low-$J$ component are nearly identical; hence only fitted values are listed in Table I. The average rotational energy of the high-$J$ component (averaged for experiments 1a and 1b) is obtained by multiplying $E_{\text{rot}}$ in Table I by associated population for each vibrational level; energies $47 \pm 2$ and $37 \pm 1$ kJ mol$^{-1}$ are determined from fitted and summed values, respectively. The average rotational energy of the low-$J$ component is $3.8 \pm 0.3$ kJ mol$^{-1}$; the error limit only reflects deviations in averaging.

### B. Vibrational distribution of HCl($v$)

We summed and normalized relative populations $P_v(J)$ of observed rotational lines associated with each vibrational state to obtain a relative vibrational population (referred to as ‘‘summed population’’). Summation of observed and extrapolated populations for $J$ up to $J_{\text{max}}(v)$ yields an expected vibrational population (referred to as ‘‘fitted population’’).

#### Table II. Relative vibrational populations of high-$J$ and low-$J$ components of HCl from photolysis of CH$_2$CHCl at 193 nm.

<table>
<thead>
<tr>
<th>Expt. no.</th>
<th>$v = 1$</th>
<th>$v = 2$</th>
<th>$v = 3$</th>
<th>$v = 4$</th>
<th>$v = 5$</th>
<th>$v = 6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-$J$ component</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–1 $\mu$s$^a$</td>
<td>$0.264 \pm 0.011$</td>
<td>$0.213 \pm 0.016$</td>
<td>$0.184 \pm 0.006$</td>
<td>$0.156 \pm 0.001$</td>
<td>$0.118 \pm 0.005$</td>
<td>$0.066 \pm 0.006$</td>
</tr>
<tr>
<td>0–5 $\mu$s$^b$</td>
<td>$0.310 \pm 0.007$</td>
<td>$0.239 \pm 0.001$</td>
<td>$0.165 \pm 0.011$</td>
<td>$0.154 \pm 0.004$</td>
<td>$0.084 \pm 0.008$</td>
<td>$0.049 \pm 0.001$</td>
</tr>
<tr>
<td>PST(3-center)$^c$</td>
<td>0.393</td>
<td>0.254</td>
<td>0.160</td>
<td>0.099</td>
<td>0.059</td>
<td>0.034</td>
</tr>
<tr>
<td>SSE(3-center)$^c$</td>
<td>0.354</td>
<td>0.246</td>
<td>0.168</td>
<td>0.112</td>
<td>0.073</td>
<td>0.047</td>
</tr>
<tr>
<td>Low-$J$ component</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–1 $\mu$s$^a$</td>
<td>$0.194 \pm 0.005$</td>
<td>$0.272 \pm 0.002$</td>
<td>$0.255 \pm 0.005$</td>
<td>$0.151 \pm 0.013$</td>
<td>$0.078 \pm 0.010$</td>
<td>$0.051 \pm 0.011$</td>
</tr>
<tr>
<td>0–5 $\mu$s$^b$</td>
<td>$0.190 \pm 0.002$</td>
<td>$0.325 \pm 0.006$</td>
<td>$0.260 \pm 0.003$</td>
<td>$0.120 \pm 0.005$</td>
<td>$0.066 \pm 0.001$</td>
<td>$0.047 \pm 0.004$</td>
</tr>
</tbody>
</table>

$^a$Average of experiments 1a and 1b.
$^b$Average of experiments 2 and 3.
$^c$Derived from fitted values; see text.
$^d$Derived from summed values; see text.
$^e$For three-center elimination with $v_{HCl} = 1500$ cm$^{-1}$ and $E_{\text{ex}} = 341$ kJ mol$^{-1}$. 
Averaged vibrational distribution for high-\(J\) and low-\(J\) components recorded in a short period (experiments 1a and 1b) and a long period (experiments 2 and 3) are listed in Table II for comparison. The vibrational distributions thus derived from summed population and fitted population of the high-\(J\) component are similar. Distinctions derived from fitted values are used for discussion, unless noted.

Vibrational distributions of high-\(J\) and low-\(J\) components are compared with previous reports and statistical predictions in Fig. 5. The vibrational distribution of the high-\(J\) component is nearly Boltzmann, corresponding to a vibrational temperature of 26 000 \(\pm\) 3000 K for HCl with \(v = 1 \rightarrow 5\). Observed population of \(v = 6\) is slightly lower than that expected for a Boltzmann distribution; presumably quenching of this state is still not negligible. Observed distribution agrees well with those reported by Berry.\(^2\) Vibrational distribution reported by Donaldson and Leone\(^4\) appears to correspond to a slightly smaller temperature, presumably due to vibrational quenching in a period 15–30 \(\mu\)s before their data acquisition.

Based on observed vibrational distribution for \(v = 1 \rightarrow 5\) of the high-\(J\) component, we estimate by linear extrapolation the relative population of \(v = 0\) of HCl to be 0.32 \(\pm\) 0.03 in Fig. 5. Because the population in Fig. 5 was normalized for HCl \((v = 1 \rightarrow 6)\), this value indicates that about 24.2% (0.32/1.32) of the total population of HCl is in its \(v = 0\) state.

The average vibrational energy may be determined from observed and extrapolated vibrational population. Berry reported a vibrational energy of 58 kJ mol\(^{-1}\) for HCl \((v = 0 \rightarrow 4)\). Our values of 74 \(\pm\) 3 (fitted value) and 72 ± 1 kJ mol\(^{-1}\) (summed value) for the high-\(J\) component include \(v = 0\) to 6 levels of HCl. If vibrational distributions are extrapolated to \(v = 8\), average vibrational energies 80 (high-\(J\)) and 88 kJ mol\(^{-1}\) (low-\(J\)) are derived.

The vibrational population of the low-\(J\) component is inverted, with \(v = 2\) having the greatest population. The population of \(v = 0\) is estimated by fitting Fig. 5 with a smooth curve; relatively large uncertainties of the small value 0.13 \(\pm\) 0.05 have little effect on calculations of average vibrational energy. The relative distribution for \(v \geq 3\) corresponds to a temperature slightly smaller than that observed for the high-\(J\) component. Consequently, the averaged vibrational energy 81 \(\pm\) 2 kJ mol\(^{-1}\) for the low-\(J\) component \((v = 1 \rightarrow 6)\) is only slightly greater than that of the high-\(J\) component. Observed averaged rotational and vibrational energies of both high-\(J\) and low-\(J\) components are compared with those according to various model calculations for three-center and four-center elimination channels in Table III.

### C. Statistical model calculations for the three-center elimination of HCl

For a dissociation channel without exit barrier, statistical theories such as phase space theory (PST)\(^19,20\) and separate statistical ensemble (SSE)\(^21\) are expected to predict satisfactorily distribution of rotational and vibrational states of products. Energies of three- and four-center HCl-elimination channels are shown in Fig. 6 according to theoretical calculations of Riehl and Morokuma\(^12\) using QCISD(T)/6-311G(d,p) at MP2/6-31G(d,p) optimized geometries, with zero-point energy corrected. The three-center elimination channel has a small \((\sim 11\text{ kJ mol}^{-1})\) exit (reverse) barrier. Given the large amount \((\sim 341\text{ kJ mol}^{-1})\) of excess energy for this channel, one expects statistical theories to describe adequately the distribution of product states. Because experiments were performed under bulk conditions in which parent molecules were prepared with medium rotational angular momentum, constraints on angular momentum affect negligibly the observed population in this work, as suggested in the case of HF-elimination from...
CH₂CFCI. Hence, the total angular momentum was not constrained in our model calculations. We employed vibrational wave number of vinylidene predicted by Chang et al. and the energies (corrected for zero-point energy) of precursor and products predicted by Riehl and Morokuma. Vibrational wave numbers 1500 cm⁻¹ were used for HCl, as suggested by Donaldson and Leone.

The vibrational distribution of HCl was calculated with both PST and SSE models. The SSE (PST) model predicts an average vibrational energy of 66 (55) kJ mol⁻¹, slightly smaller than the experimental value of 74±3 kJ mol⁻¹ for the high-J component. Statistical models predict an average rotational energy of ~37 kJ mol⁻¹ for HCl, smaller than the fitted experimental value of 47±2 kJ mol⁻¹ but similar to the summed value of 37±1 kJ mol⁻¹ for the high-J component.

Observed internal energies of the high-J component agree satisfactorily with those predicted for the three-center elimination. That observed experimental values are slightly larger than statistical predictions is consistent with a model proposed previously to explain why observed translational energy of HCl is greater than statistical prediction. The model indicates that the exothermicity of isomerization of vinylidene to acetylene may be utilized to excite HCl in the three-center channel.

Statistical calculations were also performed for the four-center channel for comparison, even though one expects unsatisfactory results in view of the tight transition state and a large exit barrier for this channel. Rotational energy of 50 (51) kJ mol⁻¹ and vibrational energy of 97 (82) kJ mol⁻¹ were derived with the SSE (PST) model.

The inverted vibrational distribution of the low-J component cannot be reproduced with statistical models. Observed average vibrational energy of 81±2 kJ mol⁻¹ is much greater than that predicted for three-center HCl-elimination, but similar to that predicted with the PST model for the four-center elimination. The rotational energy of the low-J component is much smaller than that predicted statistically for either elimination channel. This suggests that the low-J component may be associated with a dynamically controlled dissociation process that typically occurs with a tight transition state.

D. Transition states and the impulse model

Although Riehl and Morokuma reported geometry and energy of transition states for various unimolecular elimination channels of vinyl chloride, vibrational wave numbers of transition states were not listed. We performed calculations on transition states TS3 and TS4, respectively, of three-center and four-center HCl-elimination channels with B3LYP/aug-cc-pVTZ density functional theory using GAUSSIAN 98 programs. Predicted geometry of TS3 and TS4 is shown in Fig. 7 with structural parameters indicated. Parameters predicted by Riehl and Morokuma with a frozen-core Møller-Plesset second-order perturbation method, MP2/6-31G(d,p), are also listed parenthetically for comparison. Vibrational wave numbers of TS3 and TS4 are listed in Table IV. The imaginary vibrational wave numbers are 219i and 1559i for TS3 and TS4, respectively; displacement vectors of corresponding motion of these modes are shown in the lower part of Fig. 7.

The rotational energy may be predicted with a model considering motions of the reaction coordinates derived from displacement vectors corresponding to the imaginary modes of both transition states. If a molecule dissociates instantaneously once it reaches the transition state, no energy flows beyond the saddle point. The direction of the repulsive force...
is assumed to follow the displacement vectors. Hence displacement vectors shown in Fig. 7 imply substantial rotational excitation of HCl in the three-center elimination because the H atom moves nearly parallel to the C–Cl bond with a large impact parameter toward the Cl atom. If we distribute the available energy between H and C₂H₅ according to classical mechanics and calculate the dynamics after the energized H atom moves toward the Cl atom along the displacement vector, a rotational energy of 52 kJ mol⁻¹ is predicted for three-center elimination with an available energy of 341 kJ mol⁻¹. This value is close to the experimental value of 47 ± 2 kJ mol⁻¹.

In contrast, substantial vibrational excitation but little rotational excitation is predicted according to displacement vectors of four-center HCl-elimination in Fig. 7 because the H atom is moving toward Cl with a small impact parameter. With an available energy of 515 kJ mol⁻¹ a rotational energy of 2.8 kJ mol⁻¹ is predicted for this channel, consistent with the experimental value of 3.8 ± 0.3 kJ mol⁻¹. Hence, the impulse model using displacement vectors of imaginary frequencies describes satisfactorily rotational and vibrational distributions observed for the low-J components of HCl as resulting from four-center elimination.

### V. CONCLUSION

Rotationally resolved emission from HCl up to \( v = 7 \) is observed in the spectral range 2000–3310 cm⁻¹ after photolysis of vinyl chloride at 193 nm. All vibrational levels show a bimodal rotational distribution with one component corresponding to \( \sim 500 \text{ K} \) and the other corresponding to \( \sim 9500 \text{ K} \). The two components with low and high rotational temperatures correspond to HCl \( (v,J) \) produced from four-center and three-center HCl-elimination channels, respectively. The four-center channel produces HCl with little rotation and inverted vibrational population. Statistical models predict satisfactorily internal energy distribution of HCl from three-center elimination. Impulse models considering geometries and displacement vectors of transition states during bond breaking predict the rotational distribution of both channels satisfactorily. The branching ratio of 0.81:0.19 determined for high-J and low-J components is consistent with rate coefficients for unimolecular decomposition via three-center:four-center elimination predicted with the RRKM theory.

### E. Branching ratio and RRKM rates of dissociation

We estimate the rate of dissociation of vinyl chloride irradiated at 193 nm with a microcanonical transition state theory. The Whitten–Robinovitch equations²⁸ were used to calculate the density of states and number of transition states. Because elimination of HCl occurs on the ground electronic surface, we use vibrational wave number of the ground state of vinyl chloride. The rate of dissociation for three-center elimination with an energy 330 kJ mol⁻¹ on the transition state and four-center elimination with an energy 295 kJ mol⁻¹ are calculated to be 33.8 and \( 4.9 \times 10^{11} \text{ s}^{-1} \), respectively. Accordingly, the branching ratio for formation of HCl according to three- and four-center processes is estimated to be 0.87:0.13.

Estimates of populations of HCl \( (v = 0) \) for low-J and high-J components are described in Sec. IV B. The branching ratio is determined by comparing \( \Sigma_{\nu,J} P_{\nu,J} \) for \( v = 0 \)–6 (Table I) of high-J and low-J components of HCl. The estimated ratio 0.81:0.19 is consistent with that predicted for three-center and four-center elimination channels with RRKM theory. If population of higher vibrational states is linearly extrapolated to \( v = 8 \), the branching ratio becomes 0.84:0.16. Previous reports on photolysis of CH₂CDSL at 193 nm: 0.75:0.25 (Ref. 6) and 0.70:0.30 (Ref. 11) show a slightly more proportionate amount of four-center elimination, but the discrepancies are probably within experimental uncertainties.

Based on discussions of Secs. IV C–IV E, we conclude that observed high-J and low-J components correspond well with HCl produced via three-center and four-center elimination, respectively. A model with vibrational adiabaticity was proposed to explain reported dichotomy between the rotational state distribution of HCl \( (v = 0) \) and HCl \( (v > 0) \).

Our data show no obvious variation in bimodal rotational distributions for all observed vibrational levels.

Firstly, because of its complexity, we are unable to assign or simulate observed emission spectrum of acetylene in the 3 \( \mu \text{m} \) region at this stage.

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