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I. Three-center versus four-center HCI-elimination in photolysis of vinyl chloride at 193 nm: Bimodal rotational distribution of HCI ($v \le 7$) 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 $2000-3310 \,\mathrm{cm}^{-1}$ 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 $v \le 4$. 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 $4.9 \times 10^{11} \text{ s}^{-1}$ 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 $v \le 6$ 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 distribu-

tions of vibronic states of HCl ($v \leq 4$) produced from photolysis of various chloroethylene at $\lambda \ge 155$ nm. He concluded that HCl is produced primarily via a four-center (α , β) elimination channel and rationalized the observed nonstatistical 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 C₂H₂ and/or CHCCl 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 $(1 \le v \le 4)$ 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 ($\sim 1500 \,\mathrm{cm}^{-1}$) for H–Cl stretching. Blank et al.¹ reported that the photoionization energy threshold of HCl produced from photolysis of vinyl chloride decreases by $\sim 2.2 \text{ eV}$ from thermalized HCl, indicating that the HCl fragment has substantial internal energy.

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The only report on rotational energy distribution of HCl was by Reilly *et al.*⁵ who performed pump-probe experiments with a molecular beam containing CH₂CHCl 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.*⁶ photolyzed d_1 -vinyl chloride (CH₂CDCl) at 193 nm and found that the rotational state distributions of HCl product are nearly identical for CH₂CDCl and CH₂CHCl.

Later, they used velocity-aligned Doppler spectroscopy (VADS) to determine the speed distribution of HCl (v=0-2, J) produced in photolysis of CH₂CHCl at 193 nm and found that released kinetic energy much exceeds that predicted with a statistical model for three-center elimination.⁷ To reconcile this situation they proposed that three-center elimination and isomerization from vinylidene (CCH₂) to acetylene (HCCH) occur in a concerted but nonsynchronous 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=0-2), respectively.⁷ Umemoto *et al.*⁸ photolyzed CH₂CHCl 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°. An average energy of 18 ± 1 kcal mol⁻¹ deduced by Blank *et al.*¹ is consistent with results from VADS if substantial population of HCl with v > 2 is assumed.

Varied branching ratios between channels for threecenter and four-center elimination of HCl during photolysis of vinyl chloride at several wavelengths were reported. Berry² reported a quantum yield of HCl from CH₂CDCl 92% of that from CH₂CHCl for $\lambda \ge 155$ nm, indicating that fourcenter HCl-elimination is the major channel. Ausloos et al.9 observed a nearly equal yield from three-center and fourcenter 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_2H_2 and C_2HD upon IR multiphoton dissociation of deuterated isotopomers of CH₂CHCl reveal a preference for a three-center elimination of HCl; a ratio of 2.3 was reported for three-center to four-center HClelimination channels.^{10,11} REMPI measurements of Huang et al.⁶ produced ratios of 3.9–4.0 for yields of HCl produced from CH₂CHCl to that from CH₂CDCl. These authors originally interpreted the results as signifying a 3:1 preference for three-center over four-center elimination of CH₂CHCl. Following further experiments and a theoretical study by Riehl and Morokuma,¹² Huang *et al.*⁷ proposed a mechanism that includes α , β -migration of H that competes with the threecenter α , α -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.^{13,14} Here we report emission from HCl ($1 \le v \le 7, J \le 32$) during photolysis of CH₂CHCl 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 timeresolved Fourier-transform spectra resembles that described previously.^{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 mm² at the reaction center with a fluence of $40-50 \text{ mJ cm}^{-2}$. We estimated a photolysis yield <50% in the irradiated region based on an absorption cross section of 1.9×10^{-17} cm² for CH₂CHCl.² IR emission was collected with a set of Welsh mirrors and directed into the Fourier-transform spectrometer (Bruker IFS66v) through two CaF₂ lenses. A CaF₂ 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 1×10^5 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 $\sim 0.7 \,\mu$ s. The interval of data acquisition in each time slice is 5 μ s; hence a datum at t μ 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 μ 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 $2000-2900 \text{ cm}^{-1}$, 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.^{13,14}

The partial pressure of CH_2CHCl 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



FIG. 1. Infrared emission spectra of HCl recorded at varied intervals after photolysis of CH₂CHCl (130 mTorr) in Ar (1.57 Torr) at 193 nm. (a) 2 μ s, (b) 17 μ s, (c) 47 μ s. Spectral resolution 8 cm⁻¹; averaged over 50 laser pulses at each interferometer scan step.

capacitance manometer (MKS Baratron, model 121, 0-10 Torr) and flow rates were measured with flow meters calibrated according to standard procedures. CH₂CHCl (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 μ s with satisfactory sensitivity, whereas the external PAD1232 board provides an effective temporal resolution $\sim 1 \ \mu$ s 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 CH₂CHCl and Ar (0.13 and 1.57 Torr, respectively) at 193 nm. Emission from highly excited HCl and C₂H₂ 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 $\sim 2 \text{ h}$ 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. 2. High-resolution emission spectra of HCl in two spectral regions, 3200-2850 and 2900-2510 cm⁻¹, recorded $0-5 \ \mu s$ after photolysis of CH₂CHCl (130 mTorr) in Ar (380 mTorr). Spectral resolution 0.3 cm⁻¹; averaged 100 laser pulses at each scan step. The instrument response is corrected. Assignments are shown in stick diagrams.

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FIG. 3. Semilogarithmic plots of relative rotational population of HCl (v = 1-6, symbol \bigcirc) averaged $0-1\mu$ s after photolysis of CH₂CHCl (110 mTorr) in Ar (240 mTorr) at 193 nm. Data reported by Reilly *et al.* (Ref. 5, symbol \triangle) are shifted vertically for clarity. Solid lines represent least-squares fits of low-*J* and high-*J* components.

Figure 2 shows a partial emission spectrum of HCl recorded 0–5 μ s after photolysis of CH₂CHCl (0.130 Torr) and Ar (0.380 Torr) at a resolution of 0.3 cm⁻¹. The spectrum clearly illustrates highly rotational excitation of HCl with obvious R bandheads for v'=1-3. Lines associated with v' up to 7 were observed. Partial assignments are shown in Fig. 2 as stick diagrams, based on spectral parameters reported by Arunan *et al.*¹⁶ and Coxon and Roychowdhury.¹⁷

To study the quenching effect, we recorded emission spectra at 25 ns intervals with an external PAD1232 board. Four separate spectra, recorded under identical conditions, were summed to improve the S/N ratio. Further averaging of spectra recorded in time slices 1–24, 1–40, 41–80, and 80–160 yields spectra corresponding to temporal ranges 0–0.6, 0–1, 1–2, and 2–4 μ s, respectively. Each vibration-rotational line in the *R*-branch was normalized with the instrument response function, integrated, and divided by its respective Einstein coefficient¹⁶ to yield relative population $P_v(J)$. For partially overlapped lines, deconvolution was applied before integration.

We found that quenching is non-negligible for data recorded with 5 μ s resolution; nearly collisionless conditions are attained for $t \leq 1 \mu s$. A more detailed discussion and listing of data may be found in the Electronic Physics Auxiliary Publication Service (EPAPS).¹⁸ The semilogarithmic plots of $P_{\nu}(J)/(2J+1)$ of HCl recorded in the 0–1 μ s range for v =1-6 produced from CH₂CHCl at 0.110 Torr and Ar at 0.240 Torr are shown in Fig. 3, in which v and J indicate vibrational and rotational levels of the emitting state. Bimodal rotational distributions observed for all vibrational levels are fitted with biexponential functions to yield two rotational temperatures. We denote these two components as high-Jand low-J components. Fitted rotational temperatures and population of both high-J and low-J components in each vibrational state observed in a few typical experiments are compared in Table I. Figure 4 illustrates the deconvoluted high-J and low-J components and the fitted overall population distribution for experiment 1b.

IV. DISCUSSION

A. Bimodal rotational distribution

It is clear from Figs. 3 and 4 and Table I that photolysis of CH₂CHCl produces highly rotationally excited HCl in vi-

		P _{Ar} /mTorr	t /µs	υ	High-J component			Low-J component		
Expt. no.	P _{CH2CHCI} /mTorr				Temp/K	$\sum_J P_v(J)^{\rm a}$	$E_{\rm rot}/{\rm kJ}~{\rm mol}^{-1}$	Temp/K	$\sum_J P_v(J)^{\rm a}$	$E_{\rm rot}/{\rm kJ}~{\rm mol}^{-1}$
1b	110	240	0-1.0	1	9200±1500	2670 ^b (2320) ^c	60.3 ^b (45.8) ^c	530 ± 200	520	3.7
				2	11000 ± 1800	2410(2105)	60.6(48.8)	500 ± 150	700	3.6
				3	10000 ± 1800	2015(1730)	49.7(38.9)	440 ± 140	670	3.3
				4	10000 ± 3500	1640(1195)	42.3(27.5)	580 ± 200	420	3.6
				5	6000 ± 2100	1200(1080)	28.0(23.8)	520 ± 200	180	2.4
				6	3500 ± 1200	630(630)	15.3(15.3)	360 ± 200	105	3.1
2	115	236	0 - 5.0	1	8500 ± 1600	5385(4755)	57.2(44.0)	520 ± 220	1100	5.1
				2	$11\ 000 \pm 2000$	4070(3600)	58.1 (47.2)	580 ± 160	1820	4.4
				3	6000 ± 1200	2620(2415)	36.4(29.8)	520 ± 140	1470	4.2
				4	4500 ± 800	2560(2240)	29.1(12.9)	400 ± 100	660	3.0
				5	3200 ± 800	1555(1495)	20.5(18.6)	320 ± 100	380	2.0
				6	4200 ± 1200	820(820)	17.6(17.6)	420 ± 120	290	3.0

TABLE I. Experimental conditions, fitted rotational temperature and total rotational population of HCl (v) after photolysis of CH₂CHCl at 193 nm.

 ${}^{a}P_{v}(J) = (\text{integrated emittance}) \times 10\ 000/[(\text{instrumental response factor})(\text{Einstein coefficient})].$

^bFitted values; extrapolated populations up to J=42 are included. See text.

^cSummed values are listed in parentheses; only observed levels are summed. See text.

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FIG. 4. Deconvoluted relative rotational distributions of high-J and low-J components of HCl (v=1-6) recorded 0–1 μ s after photolysis of CH₂CHCl (110 mTorr) in Ar (240 mTorr). Solid lines represent fitted overall population and open circles are experimental data.

brational states $v \le 6$. 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 $\sim 9500 \pm 2000$ K and $\sim 500 \pm 200$ K for HCl ($v \le 4$), respectively. Hence data in experiments nos. 1a (0–0.6 μ s) and 1b (0–1 μ s) are used to determine nascent populations.

Relative rotational populations reported by Reilly *et al.*,⁵ shown in Fig. 3 with symbol Δ 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, $E_{\text{rot}} = \sum_{J} P_{v}(J) E_{r}(J) / \sum_{J} P_{v}(J)$, and is referred to as a "summed value," as listed parenthetically in columns $E_{\rm rot}$ of Table I. Lines associated with large J in a state with large vare 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 $\sim 19300 \,\mathrm{cm}^{-1}$, 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 $E_{\rm rot}$ in Table I by associated population for each vibrational level; energies 47 ± 2 and 37 ± 1 kJ mol⁻¹ are determined from fitted and summed values, respectively. The average rotational energy of the low-J component is 3.8 ± 0.3 kJ mol⁻¹; the error limit only reflects deviations in averaging.

B. Vibrational distribution of HCI(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 popula-

TABLE II. Relative vibrational populations of high-J and low-J components of HCl from photolysis of CH₂CHCl at 193 nm.

		-	-				
Expt. no.	v = 1	v = 2	v=3	v=4	v=5	v=6	
High-J component							
$0-1 \ \mu s^a$	$0.264 \pm 0.011^{\circ}$	0.213 ± 0.016	0.184 ± 0.006	0.156 ± 0.001	0.118 ± 0.005	0.066 ± 0.006	
	$(0.265 \pm 0.012)^{d}$	(0.218 ± 0.021)	(0.182 ± 0.013)	(0.140 ± 0.011)	(0.121 ± 0.002)	(0.076 ± 0.006)	
$0-5 \ \mu s^b$	$0.310 \pm 0.007^{\circ}$	0.239 ± 0.001	0.165 ± 0.011	0.154 ± 0.004	0.084 ± 0.008	0.049 ± 0.001	
	$(0.308 \pm 0.002)^{d}$	(0.240 ± 0.005)	(0.169 ± 0.011)	(0.148 ± 0.002)	(0.087 ± 0.011)	(0.053 ± 0.000)	
PST(3-center) ^e	0.393	0.254	0.160	0.099	0.059	0.034	
SSE(3-center) ^e	0.354	0.246	0.168	0.112	0.073	0.047	
Low-J component							
$0-1 \ \mu s^a$	0.194 ± 0.005	0.272 ± 0.002	0.255 ± 0.005	0.151 ± 0.013	0.078 ± 0.010	0.051 ± 0.011	
$0-5 \ \mu s^b$	0.190 ± 0.002	0.325 ± 0.006	0.260 ± 0.003	0.120 ± 0.005	0.066 ± 0.001	0.047 ± 0.004	

^aAverage of experiments 1a and 1b.

^bAverage of experiments 2 and 3.

^cDerived from fitted values; see text.

^dDerived from summed values; see text.

^eFor three-center elimination with $\nu_{\rm HCl} = 1500 \text{ cm}^{-1}$ and $E_{\rm ava} = 341 \text{ kJ mol}^{-1}$.

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FIG. 5. Comparison of relative vibrational distributions of HCl for both high-*J* and low-*J* components after photolysis of CH₂CHCl (110 mTorr) in Ar (240 mTorr) at 193 nm. \blacktriangle : this work (from "fitted population"); \diamondsuit : Donaldson and Leone (Ref. 4); \bigcirc : Berry (Ref. 2); solid lines: SSE calculation; dotted lines: PST calculations; see text and Table II.

tion''). 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. Distributions 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 26000 ± 3000 K for HCl with v = 1-5. 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 Leone⁴ appears to correspond to a slightly smaller temperature, presumably due to vibrational quenching in a period 15–30 μ s before their data acquisition.

Based on observed vibrational distribution for v = 1-5 of the high-*J* component, we estimate by linear extrapolation the relative population of v = 0 of HCl to be 0.32 ± 0.03 in Fig. 5. Because the population in Fig. 5 was normalized for HCl (v = 1-6), 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 = 0-4). Our values of 74 ± 3 (fitted value) and 72

TABLE III. Comparison of average internal energy of high-J and low-J components of HCl with statistical and impulse model calculations.

	High-1	Low-I	Three-center elimination ^a			Four-center elimination ^b	
	component	component	PST	SSE	Impulse ^c	Impulse ^c	
$E_{\rm rot}/{\rm kJ}$	47 ± 2 $(37\pm 1)^{d}$	3.8±0.3	37	36	52	2.8	
$E_{\rm vib}/{\rm kJ}$	74 ± 3^{e}	$81\!\pm\!2^{\rm f}$	55	66			

^aAvailable energy 341 kJ mol⁻¹.

^bAvailable energy 515 kJ mol⁻¹.

^cAssuming that the impulse force is along the displacement vector corresponding to the imaginary mode of the transition state predicted with the B3LYP method; see text.

^dFrom summed values; see text.

^eIncluding only v = 0-6; $E = 80 \text{ kJ mol}^{-1}$ if extrapolated population of v = 7-8 are included.

^fIncluding only v = 0-6; $E = 88 \text{ kJ mol}^{-1}$ if extrapolated population of v = 7-8 are included.

 $\pm 1 \text{ kJ mol}^{-1}$ (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 ± 0.05 have little effect on calculations of average vibrational energy. The relative distribution for $v \ge 3$ corresponds to a temperature slightly smaller than that observed for the high-*J* component. Consequently, the averaged vibrational energy 81 ± 2 kJ mol⁻¹ for the low-*J* component (v= 1-6) 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 threecenter and four-center elimination channels in Table III.

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

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 theoreticalculations of Riehl and Morokuma¹² using cal QCISD(T)/6-311+G(d,p) at MP2/6-31G(d,p) optimized geometries, with zero-point energy corrected. The threecenter elimination channel has a small ($\sim 11 \text{ kJ mol}^{-1}$) exit (reverse) barrier. Given the large amount (\sim 341 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



FIG. 6. Energies (in kJ mol⁻¹) of transition states (TS3 and TS4) and dissociation products relative to CH₂CHCl. Values using QCISD(T)/6311+G(d,p) at MP2/6-31G(d,p) optimized geometries are taken from Riehl and Morokuma (Ref. 12) with zero-point energy corrected.

 $CH_2CFCl.^{22}$ Hence, the total angular momentum was not constrained in our model calculations. We employed vibrational wave number of vinylidene predicted by Chang *et al.*²³ and the energies (corrected for zero-point energy) of precursor and products predicted by Riehl and Morokuma.¹² Vibrational wave numbers 1500 cm⁻¹ were used for HCl, as suggested by Donaldson and Leone.⁴

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.^{1,7} 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 fourcenter 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



FIG. 7. Geometries of transition states for three-center elimination (TS3) and four-center elimination (TS4) of HCl from vinyl chloride predicted with the B3LYP/aug-cc-pVTZ method. Results by Riehl and Morokuma (Ref. 12) using MP2/6-31G(d,p) are also shown in parentheses for comparison. Bond lengths are in Å. Displacement vectors corresponding to imaginary wave numbers are shown in the lower part.

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 Morokuma¹² 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 threecenter and four-center HCl-elimination channels with B3LYP/aug-cc-pVTZ density functional theory^{24,25} using GAUSSIAN 98 programs.²⁶ Predicted geometry of TS3 and TS4 is shown in Fig. 7 with structural parameters indicated. Parameters predicted by Riehl and Morokuma with a frozencore Moller-Plesset second-order perturbation method,²⁷ 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

TABLE IV. Vibrational wave numbers (cm^{-1}) of transition states TS3 and TS4 predicted with the B3LYP/aug-cc-pVTZ method.

	TS3		TS4			
3192	3115	1734	3414	3298	1842	
1463	1239	831	1548	861	836	
805	684	477	801	695	624	
266	151		344	280		
219i			1559i			

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 C_2H_2 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 $3.8 \pm 0.3 \text{ kJ mol}^{-1}$. 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.

E. Branching ratio and RRKM rates of dissociation

We estimate the rate of dissociation of vinyl chloride irradiated at 193 nm with a microcannonical 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 $330 \text{ kJ} \text{ mol}^{-1}$ on the transition state and four-center elimination with an energy $295 \text{ kJ} \text{ mol}^{-1}$ are calculated to be $33.8 \text{ and } 4.9 \times 10^{11} \text{ s}^{-1}$, 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 $\Sigma_{v,J}P_v(J)$ 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 CH₂CDCl 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).^{5,7} Our data show no obvious variation in bimodal rotational distributions for all observed vibrational levels.

Assuming that previously reported^{1,7} average translational energy \sim 75 kJ mol⁻¹ is mainly due to the major threecenter elimination channel, our observation of an internal energy $\sim 120 \text{ kJ mol}^{-1}$ for HCl implies an internal energy \sim 146 kJ mol⁻¹ for vinylidene after photolysis at 193 nm. This value is much smaller than one typically expects, considering the complexity of vinylidene as compared with HCl. However, if the exothermicity of isomerization of vinylidene to acetylene is included in the available energy, the internal energy of acetylene product becomes $\sim 320 \text{ kJ mol}^{-1}$. For the four-center elimination channel, if an average translational energy $\sim 75 \text{ kJ mol}^{-1}$ is used, our results imply an internal energy of $\sim 355 \text{ kJ mol}^{-1}$ for acetylene. Unfortunately, because of its complexity, we are unable to assign or simulate observed emission spectrum of acetylene in the 3 μ m region at this stage.

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 K and the other corresponding to \sim 9500 K. The two components with low and high rotational temperatures correspond to HCl (v,J) produced from fourcenter 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 threecenter:four-center elimination predicted with the RRKM theory.

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