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Reaction dynamics of $CI+H_2S$: Rotational and vibrational distribution of HCI probed with time-resolved Fourier-transform spectroscopy

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Following laser irradiation of a flowing mixture of S₂Cl₂ and H₂S at 308 nm to initiate the reaction of Cl+H₂S, vibration-rotation resolved emission spectra of HCl(v=1,2) in the spectral region 2436-3310 cm⁻¹ are detected with a step-scan time-resolved Fourier-transform spectrometer. The Boltzmann-type rotational distributions of HCl(v=1) and HCl(v=2) yield rotational temperatures that decrease with reaction time; extrapolation to time zero based on data in the range 0.5–4.0 μ s yields nascent rotational temperatures of 1250±70 K and 1270±120 K, respectively; an average rotational energy of 8.3 ± 1.5 kJ mol⁻¹ is determined for HCl(v = 1,2), much greater than a previous report. Observed temporal profiles of the vibrational population of HCl(v=1,2) are fitted with a kinetic model that includes formation and quenching of HCl(v=1,2) to yield a branching ratio of 0.14 ± 0.01 for formation of HCl(v=2)/HCl(v=1) and a thermal rate coefficient of $k_1 = (3.7)$ ± 1.5)×10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Combining an estimate of the vibrational population of HCl(v=0) based on a surprisal analysis of previous investigations on the reaction $Cl+D_2S$, we report a ratio of vibrational distributions of HCl(v=0):(v=1):(v=2)=0.41:0.52:0.07, which gives an average vibrational energy of $23 \pm 4 \text{ kJ mol}^{-1}$ for HCl. Internal energies, especially rotational energy, of HCl derived with this method is more reliable than with previous techniques; the fractions of available energy going into rotation and vibration of HCl are $f_r = 0.12 \pm 0.02$ and $f_v = 0.33 \pm 0.06$, respectively. © 2003 American Institute of Physics. [DOI: 10.1063/1.1592508]

I. INTRODUCTION

The energy disposal of HX (X=F, Cl, Br) from hydrogen abstraction reactions by halogen atoms X has generated continued interest partly because these reactions generate vibrationally inverted HX products that are excellent media for chemical lasers,¹ and partly because the heavy–light–heavy mass relationship in these reactions is a prototype in chemical dynamics.² In these reactions, the newly formed H–X bond carries most vibrational excitation, leaving the counterpart vibrationally cold. The fraction of available energy transforming into vibrational energy of HX, f_v , is typically 0.4–0.5 for various reactions of type X+HY, whereas that into rotational energy of HX, f_r , ranges from 0.1 to 0.2.³

For this type of reactions, infrared (IR) chemiluminescence of HX is generally detected to yield its vibrational and rotational state distributions.⁴ Earlier experiments were carried out either with a fast-flow reactor⁵ or with a cold-wall flow reactor using the arrested-relaxation technique;⁶ a conventional Fourier-transform infrared (FTIR) spectrometer was later coupled to the reactor to provide improved detectivity and spectral resolution. In these experiments for a bimolecular reaction, effects of vibrational quenching on a nascent vibrational distribution are small, but rotational quenching is non-negligible so that direct detection of nascent rotational distribution of products is difficult. A method typically employed to correct for the quenching effects and

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to derive an average rotational energy is to assume a Boltzmann distribution and to transform an observed population distribution, which contains substantial low-*J* components due to quenching, back to the high-*J* envelope.⁷ Because of such a limitation, reported distributions of rotational energies of HX typically have large uncertainties.

Step-scan time-resolved Fourier-transform spectroscopy (TR–FTS) is capable of quantitative measurements of IR chemiluminescence within microsecond range;^{8–12} the temporal evolution of populations of vibrational–rotational levels of each species detected with this technique provides much information on rates of formation and quenching. Our previous applications of this technique to photodissociation of halogen-containing compounds have been successful; observed internal state distributions of HX provide direct evidence of photoelimination of HX via three-center and fourcenter transition states.^{8–11} We report here an application of this technique to dynamics of a bimolecular reaction

$$Cl+H_2S \rightarrow HCl(v,J)+HS(v,J).$$
(1)

Coombe *et al.* reported intense laser emission of HCl(v = 1) that was produced from reaction (1) by irradiating a mixture of H₂S:Cl₂:He (1:10:40 at 40 Torr) with flash lamps.¹³ Dill and Heydtmann employed the arrested relaxation method to observed IR chemiluminescence of HCl from reaction (1) with an FTIR;¹⁴ they reported emission only from HCl(v=1) with a rotational distribution peaked near J'=4 and an average rotational energy of 4.5 kJ mol⁻¹. Braithwaite and Leone detected IR chemiluminescence of HCl to determine rates of formation and the internal state

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distribution of HCl produced from reaction (1) that was initiated with laser irradiation.¹⁵ By comparison of the signal filtered with a gas cell filled with HCl with that through an interference filter passing emissions of HCl(v=1,2), they estimated [HCl(v=2)]/[HCl(v=1)]=0.067. They also determined a rate coefficient of $(6.0\pm1.2)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹ for reaction (1). Later, Nesbitt and Leone used a similar method and reported a revised branching ratio of $[HCl(v=2)]/[HCl(v=1)] \le 0.02$ and a rate coefficient $(7.3\pm0.9)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹.¹⁶ More recent measurements on the rate coefficient of reaction (1) range from 4.0 to 10.5×10^{-11} cm³ molecule⁻¹ s⁻¹.¹⁷⁻²¹ HS was found to be vibrationally cold.¹⁵

Agrawalla and Setser³ detected infrared chemiluminescence of DCl and laser-induced fluorescence of DS to study the reaction of Cl with D_2S in a fast-flow reactor,

$$Cl+D_2S \rightarrow DCl(v,J)+DS(v,J).$$
 (2)

They determined $[DCl(v=2)]/[DCl(v=1)] \cong 3/7$ and $[DS(v=1)]/[DS(v=0)] = 0.08 \pm 0.04$. Hossenlopp *et al.* used time-resolved infrared diode laser absorption spectroscopy to probe DCl that was produced from reaction (2) and determined a vibrational distribution of [DCl(v=0)]: $[DCl(v=1)]:[DCl(v=2)] = 33 \pm 7:56 \pm 7:11 \pm 3$; they also determined a rate coefficient of $(3.2 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for reaction (2).²²

Using TR–FTS, we determined the nascent rotational and vibrational distribution of HCl produced from reaction (1). Our results show a rotational energy of HCl much greater than that reported previously, but consistent with other similar reactions.

II. EXPERIMENTS

The apparatus employed to obtain step-scan timeresolved Fourier-transform spectra has been described previously;^{8,10} only a brief summary is given here. A telescope mildly focused the photolysis beam from a XeCl laser (308 nm) to \sim 20 mm² at the reaction center with a fluence $\sim 100 \text{ mJ cm}^{-2}$. A filter passing 2436–3310 cm⁻¹ was employed for detection of HCl. The transient signal of an InSb detector with a rise time of 0.22 μ s was amplified with an effective bandwidth of 1 MHz before being digitized with either an internal digitizer (16-bit, 5- μ s resolution) or an external data-acquisition board (PAD1232, 12-bit ADC, 25 ns resolution). Data were typically averaged over 60 laser pulses at each scan step; 4188 scan steps were performed to yield an interferogram resulting in a spectrum of resolution 0.5 cm^{-1} . For analysis of nascent rotational distributions, typically 20 consecutive time-resolved spectra at 25 ns intervals were summed to yield a satisfactory spectrum representing emission averaged over a period of 0.5 μ s. For analysis of the vibrational distribution and quenching, 150 spectra were typically recorded at 5 μ s intervals with the internal ADC.

Flow rates of H_2S and Ar were measured with mass flow meters, and that of S_2Cl_2 was determined with a dP/dt method that measures the pressure increase in a calibrated volume over a specific period of time. Typical flow rates and partial pressures are 0.04–0.10 STP cm³ s⁻¹ and 0.017–

0.043 Torr for H_2S , 0.11–0.22 STP cm³ s⁻¹ and 0.045–0.090 Torr for S_2Cl_2 , and 0.94–2.60 STP cm³ s⁻¹ and 0.40–1.11 Torr for Ar; STP indicates standard temperature at 273 K and pressure at 1 atm. Ar (Scott Specialty Gases, 99.999%) and H_2S (AGA Specialty Gases, 99.95%) were used without purification. S_2Cl_2 (Hayashi Co., 99%) was degassed at 180 K before use.

III. RESULTS AND DISCUSSION

Following previous reports,¹⁵ we employed S₂Cl₂ rather than Cl₂ as a source of Cl atoms because HS reacts with Cl₂ readily and propagates chain reactions; reaction of HS with Cl₂ produces HSCl that further reacts with Cl or Cl₂ to form HCl in its highly vibrationally excited states, consequently interfering with measurements.¹⁵ Photodissociation of S₂Cl₂ in a molecular beam at 308 nm has been extensively investigated with fragmentation translational spectroscopy.²³ At this wavelength, S₂Cl₂ undergoes a simple S-Cl bond scission with fragments carrying translational energy averaged at 88 kJ mol⁻¹. The average translational energy of Cl atoms immediately after photolysis is thus 64 kJ mol⁻¹, yielding an average collisional energy of 33.6 kJ mol⁻¹ between Cl and H₂S. At a pressure of 0.6 Torr, there are more than ten collisions within 1 μ s; hence most Cl atoms are thermalized within 1 μ s. At 0 K, reaction (1) has an enthalpy of reaction of $\Delta H^{\circ} = -57.7 \text{ kJ mol}^{-1}$, derived from enthalpies of formation (in unit of kJ mol⁻¹) of Cl (119.62), H_2S (-17.58), HS (136.49), and HCl (-92.13).²⁴ Hence the available energy for reaction (1) at 298 K is \sim 69 kJ mol⁻¹, after taking into account of translational and rotational energies of Cl and H_2S , but without adding a calculated barrier height of ~ 5 $kJ mol^{-1}$ (Ref. 25) that is smaller than thermal energy. Available energy used for reaction (1) in previous work was 64 $kJ \text{ mol}^{-1}$,³ or 50 $kJ \text{ mol}^{-1}$.¹⁴

Although the branching between spin–orbit states of Cl produced from photolysis of S₂Cl₂ at 235 nm has been determined to be $[Cl({}^{2}P_{1/2})]:[Cl({}^{2}P_{3/2})]=35:65$ by the threedimensional (3D) imaging technique,²⁶ there is no such information for photolysis of S₂Cl₂ at 308 nm. We assume that most $Cl({}^{2}P_{1/2})$, if produced, is quenched under out experimental conditions.

To observe directly a nascent rotational distribution of products from a bimolecular reaction in a flow system is difficult because one is unlikely to find a condition for the reaction to proceed to produce products in detectable amount while maintaining a nearly collisionless condition to avoid rotational quenching. By decreasing the pressure of the reagent as much as possible while maintaining a satisfactory signal to noise ratio, we recorded emission of HCl with a fast external digitizer at 25 ns resolution, followed by averaging every 20 consecutive time-resolved spectra to yield spectra with resolution of 0.5 μ s; a nascent rotational population of HCl was subsequently derived by short extrapolation to t=0 based on observed population. To determine the vibrational distribution of HCl, we added about 1.1 Torr of Ar to thermalize the rotational excitation and used an internal 16bit digitizer at 5 μ s resolution to obtain temporal profiles of HCl(v) up to 750 μ s after initiation of reaction. We looked carefully but found no evidence of emission of HS (v).

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FIG. 1. Infrared emission spectra of HCl in spectral region 2500–3100 cm⁻¹ recorded after irradiation of a flowing mixture of S₂Cl₂ (0.090 Torr), H₂S (0.087 Torr), and Ar (0.403 Torr) with a XeCl excimer laser at 308 nm. Spectral resolution is 0.5 cm⁻¹; 60 laser pulses were averaged at each scan step. (A) 1.0–1.5 μ s, (B) 1.5–2.0 μ s, and (C) 2.0–2.5 μ s after laser irradiation. Assignments are shown as stick diagrams; J" values are listed in parentheses.

A. Nascent rotational distribution of HCI(v)

Figure 1 shows partial emission spectra of HCl recorded 1.0–1.5, 1.5–2.0, and 2.0–2.5 μ s after photolysis of a flowing mixture containing S₂Cl₂ (0.090 Torr), H₂S (0.087 Torr), and Ar (0.403 Torr) at a spectral resolution of 0.5 cm^{-1} . Assignments based on spectral parameters reported by Arunan et al.²⁷ and Coxon and Roychowdhury²⁸ are shown as stick diagrams; notations P(J'') and R(J'') are used. The spectrum shows emission of HCl(v=1) with rotational levels J' up to 12 and weak emission of HCl(v=2) with J' up to 9. Each vibration-rotation line in the P branch was normalized with the instrument response function, integrated, and divided by its respective Einstein coefficient²⁷ to yield a relative population $P_{n}(J')$. Semilogarithmic plots of $P_v(J')/(2J'+1)$ vs J'(J'+1) for HCl(v=1) at a few representative intervals after reaction are shown in Fig. 2. Data of overlapped lines, J'=2 and 9 of v'=1, are not shown. Fitted Boltzmann-type rotational distributions yield rotational temperatures of 1090 ± 140 K (1.0–1.5 µs), 1030 ± 100 K (1.5–2.0 μ s), and 920 ± 40 K (2.0–2.5 μ s) for HCl(v=1); the uncertainties represent one standard deviation in fitting. Also shown in Fig. 2 are the rotational distribution of HCl(v=1) reported by Dill and Heydtmann;¹⁴ their results correspond to a temperature smaller than ours, as expected. Emission lines associated with HCl(v=2) are treated similarly to derive associated rotational temperature; results are summarized in Table I.

The decrease in rotational temperature of HCl(v=1) after initiation of reaction is shown in Fig. 3 for two total pressures (0.580 and 0.830 Torr); rotational temperature is smaller at a greater pressure or a greater reaction period because quenching is more effective. We fitted all data to an exponential decay

$$T = 298 + (T_0 - 298)\exp(-kt) \tag{3}$$

in which T_0 is the nascent rotational temperature and k is a decay coefficient that varies linearly with pressure. Values of $T_0=1270\pm40$ and 1230 ± 50 K were derived for experi-

ments with pressures 0.580 and 0.830 Torr, respectively; an average value of $T_0 = 1250 \pm 70$ K is thus derived. Similarly, values of $T_0 = 1290 \pm 120$ and 1250 ± 80 K were derived for HCl(v = 2) in experiments with pressures 0.580 and 0.830 Torr; an average value of $T_0 = 1270 \pm 120$ K is thus derived.

Average rotational energies $E_r(v)$ for HCl(v=1) and HCl(v=2) were derived by summing a product of level energy and normalized population $P_v(J)$ for all rotational level in each vibrational state; for overlapped lines, the populations were estimated with interpolation based on Fig. 2. Only



FIG. 2. Semilogarithmic plots of relative rotational populations of HCl(v = 1) after irradiation of a flowing mixture of S₂Cl₂ (0.090 Torr), H₂S (0.087 Torr), and Ar (0.403 Torr) at 308 nm. (A) 1.0–1.5 μ s, (B) 1.5–2.0 μ s, and (C) 2.0–2.5 μ s after laser irradiation; (D) data reported by Dill and Heydtman (Ref. 14; symbol ∇). Solid lines represent least-squares fits. For (B)–(D) the *y* axes are displaced vertically for clarity.

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TABLE I. Rotational temperature (T_r) , rotational energy (E_r) , and nascent rotational energy (E_r^0) of HCl(v = 1, 2) produced from Cl+H₂S in various reaction periods.

	HCl(v=1)				HCl(v=2)					
Time /µs	<i>T</i> _{<i>r</i>} /K	$\Sigma_J P_v(J)^{\mathrm{a}}$	$E_r(v)$ /kJ mol ⁻¹	$\frac{E_r^0(v)^{\rm b}}{/\rm kJ\ mol^{-1}}$	<i>T_r</i> /K	$\Sigma_J P_v(J)^a$	$E_r(v)$ /kJ mol ⁻¹	$\frac{E_r^0(v)^{\rm b}}{\rm /kJ\ mol^{-1}}$		
0.580 Torr	$(T_r^0 = 1270 \pm 40 \text{ K})$				$(T_r^0 = 1290 \pm 120 \text{ K})$					
1.0 - 1.5	1090 ± 140	2435	7.00 ± 0.39	8.1	1190 ± 540	560	4.83 ± 0.61	5.2		
1.5 - 2.0	1030 ± 100	2991	6.76 ± 0.29	8.3	1070 ± 260	530	4.62 ± 0.34	5.6		
2.0 - 2.5	920 ± 40	3353	6.56 ± 0.15	9.1	1020 ± 350	500	4.30 ± 0.55	5.4		
2.5 - 3.0	890 ± 60	4091	6.34 ± 0.42	9.1	890 ± 240	684	4.42 ± 0.49	6.4		
3.0-3.5	870 ± 50	4216	5.97 ± 0.20	8.7	1040 ± 90	616	4.50 ± 0.15	5.6		
3.5 - 4.0	820 ± 40	4672	5.74 ± 0.15	8.9	920 ± 160	686	3.98 ± 0.32	5.6		
0.830 Torr	$(T_r^0 = 1230 \pm 50 \text{ K})$				$(T_r^0 = 1250 \pm 80 \text{ K})$					
0.5 - 1.0	1010 ± 70	3470	6.53 ± 0.22	7.9	1190 ± 370	544	4.40 ± 0.45	4.6		
1.0 - 1.5	850 ± 30	4498	5.91 ± 0.12	8.5	990 ± 300	558	4.46 ± 0.51	5.6		
1.5 - 2.0	840 ± 40	5816	5.85 ± 0.18	8.5	870 ± 150	679	4.11 ± 0.34	5.9		
2.0 - 2.5	820 ± 20	6829	$5.78 {\pm} 0.10$	8.6	910 ± 120	865	4.26 ± 0.25	5.8		
2.5 - 3.0	780 ± 20	7761	5.58 ± 0.09	8.7	830 ± 140	896	3.95 ± 0.34	5.9		
3.0-3.5	780 ± 40	8512	5.63 ± 0.17	8.8	760 ± 80	897	4.16 ± 0.23	6.8		
3.5 - 4.0	720 ± 30	9543	5.44 ± 0.15	9.2	800 ± 100	1083	4.04 ± 0.26	5.7		
	Ave. $E_r^0(v=1) = 8.6 \pm 0.7$						Ave. $E_r^0(v=2) = 5.7 \pm 1.4$			

 ${}^{a}P_{v}(J) =$ (relative intergrated emittance)/[(instrumental response factor)(Einstein coefficient)]; arbitrary unit.

observed levels HCl($v=1, J \le 12$) and HCl($v=2, J \le 9$) are summed, hence averaged rotational energies of HCl(v=1) and HCl(v=2) are different, even though their rotational temperatures are nearly identical. Nascent rotational energies $E_r^0(v)$ were derived on multiplying experimental rotational energies $E_r(v)$ at each intervals by a correction factor T_0/T , as listed in Table I. As Table I shows, such correction yields consistent nascent average rotational energies, even when the rotational distribution is substantially quenched near 4 μ s after initiation of the reaction. We averaged values listed in Table I and obtained $E_r^0(v)=8.6\pm0.7$ and 5.7 ± 1.4 kJ mol⁻¹ for v=1 and v=2, respectively; the error



FIG. 3. Variation of rotational temperatures as a function of period after irradiation; solid lines represent least-squares fits of Eq. (3); see text.

limits represent one standard deviation in fitting. An averaged nascent rotational energy $E_r^0 = 8.3 \pm 1.5 \text{ kJ mol}^{-1}$ for HCl(v = 1,2) was derived on multiplying $E_r^0(v)$ by its corresponding vibrational population. The only previously reported value¹⁴ of $E_r = 4.5 \text{ kJ mol}^{-1}$ is about 54% of our value.

The largest rotational level (J'=9) observed for HCl(v=2) lies at 6549 cm⁻¹ above the ground state. With the same energy, J' = 18 level of HCl(v=1) should be populated. We observed rotational levels of HCl(v=1) only up to J' = 12; the absence of higher levels might be due to limited detectivity. We assume a Boltzman distribution and associate an extrapolated population with unobserved lines for J' = 13-18 of v=1. Average nascent rotational energies for HCl(v=1), $E_r^0(v=1)=10.6\pm0.8$ and 10.1 ± 0.6 kJ mol⁻¹ in experiments under pressures of 0.580 and 0.830 Torr, respectively, are determined by including these fitted populations; the average value of $E_r^0(v=1)=10.3\pm1.0$ kJ mol⁻¹ and the average rotational energy of HCl(v=1,2), $E_r^0=9.7 \pm 1.7$ kJ mol⁻¹, should be taken as upper limits.

B. Vibrational distribution and rate coefficient

Experiments were carried out with flowing gaseous mixtures containing S_2Cl_2 (~0.045 Torr), H_2S (0.017–0.043 Torr), and Ar (~1.09 Torr); HCl emission was recorded at 5 μ s intervals. Figure 4 shows partial emission spectra of HCl recorded at 41.5 and 161.5 μ s after photolysis of a flowing mixture containing S_2Cl_2 (0.045 Torr), H_2S (0.043 Torr), and Ar (1.09 Torr) at a spectral resolution of 1.0 cm⁻¹. The ratios of signal to noise for these spectra are better than those recorded for rotational studies because a 16-bit ADC was used and because more HCl was produced at a later reaction period. The rotational temperature is determined as previously described; it reaches ~350±50 K at 5 μ s, indicating a nearly thermal distribution for rotation under these experi-

 $^{{}^{}b}E_{r}^{0} = E_{r} \times (T_{r}^{0}/T_{r}).$



FIG. 4. Infrared emission spectra of HCl in spectral region 2500–3100 cm⁻¹ recorded at 41.5 (A) and 161.5 μ s (B) after photolysis of a flowing mixture of S₂Cl₂ (0.045 Torr), H₂S (0.043 Torr), and Ar (1.09 Torr) with a XeCl excimer laser at 308 nm. Spectral resolution is 1.0 cm⁻¹; 60 laser pulses were averaged at each scan step. Assignments are shown as stick diagrams.

mental conditions. We averaged values of $\Sigma_J P_v(J')$ associated with each vibrational state to yield relative vibrational populations.

Figure 5 shows representative temporal profiles of HCl(v=1) and HCl(v=2) obtained upon photolysis of a flowing mixture containing S_2Cl_2 (0.045 Torr), H_2S (0.043 Torr), and Ar (1.09 Torr). We fit both temporal profiles collectively with a commercial kinetic modeling program FACSIMILE²⁹ according to a model containing the following reactions:

$$Cl+H_2S \rightarrow HCl(v=1)+HS$$
, rate= $k_1^I[Cl]$, branching γ_1 ,
(1a)

 $Cl+H_2S \rightarrow HCl(v=2)+HS$, rate= $k_1^I[Cl]$, branching γ_2 , (1b)

$$\operatorname{HCl}(v=2) \to \operatorname{HCl}(v=1), \quad \operatorname{rate} = k_{q2}[\operatorname{HCl}(v=2)], \quad (4)$$



FIG. 5. Temporal profiles of HCl (v) recorded after photolysis of a flowing mixture of S₂Cl₂ (0.045 Torr), H₂S (0.043 Torr), and Ar (1.09 Torr) with a XeCl excimer laser at 308 nm. (A) HCl(v=1), (B) HCl(v=2).

$$\operatorname{HCl}(v=1) \to \operatorname{HCl}(v=0), \quad \operatorname{rate} = k_{ql}[\operatorname{HCl}(v=1)], \quad (5)$$

in which $k_1^I = k_1 \times [H_2S]$ is the pseudo-first-order rate coefficient and k_{q1} and k_{q2} are rate coefficients of vibrational quenching. Typically we fit the later portion of temporal profiles with a single exponential decay to derive estimates of k_{a1} and k_{a2} , followed by fitting both temporal profiles collectively with the above model by keeping both k_{a1} and k_{a2} invariant to derive estimates of $[Cl]_0$ (relative value), k_1^I and γ_2/γ_1 . Finally these five parameters were further optimized to provide the best fit. Values of k_1^I , γ_2/γ_1 , k_{q1} , and k_{q2} thus derived under various experimental conditions are listed in Table II; we report an average value of $\gamma_2/\gamma_1 = 0.143$ ± 0.009 , corresponding to a product ratio [HCl(v=2)]/ [HCl(v=1)]. Our observed value is greater than a value $\gamma_2/\gamma_1 = 0.07$ reported by Braithwaite and Leone who used filters to distinguish populations of separate vibrational states.15

Previous work^{3,14} used a ratio [HCl(v=0)]/[HCl(v=1)]=0.6, estimated by a surprisal analysis based on an experimentally observed value of [HCl(v=2)]/[HCl(v=1)]=0.40 for the reaction^{30,31}

$$Cl+HBr \rightarrow HCl(v=1,2)+Br,$$
 (6)

because reaction (6) has an exothermicity and a ratio of atomic masses involved similar to those of reaction (1). If this value is used, the vibrational distribution of HCl in reaction (1) becomes 34:58:8; consequently the average vibrational energy is 25.4 kJ mol⁻¹. Because the ratio [HCl(v = 2)]/[HCl(v = 1)]=0.14 observed for reaction (1) is much smaller than the value of 0.40 observed for reaction (6), we are uncertain about such an estimate of [HCl(v = 0)].

The population of v = 0 is typically estimated with surprisal analysis based on an observed vibrational distribution for $v \ge 1$. However, in this work, such an analysis has large errors because only two data points are available. Hossenlopp *et al.*²² used time-resolved infrared diode laser absorption spectroscopy to probe DCl product from reaction (2) and determined a vibrational distribution of $[DCl(v=0)]:[DCl(v=1)]:[DCl(v=2)]=33\pm7:56\pm7:11\pm3$. They carried out a

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TABLE II. Experimental conditions and fitted rate coefficients and branching ratios for the reaction $Cl+H_2S \rightarrow HCl(v, J) + HS$.

Expt. No.	1	2	3	4	Average
P _{H₂S} /mTorr	17	25	33	43	
$P_{S_2Cl_2}/mTorr$	46	45	44	45	
P _{Ar} /mTorr	1110	1090	1070	1090	
laser fluence /mJ cm^{-2}	88	88	79	88	
% S ₂ Cl ₂ photolyzed	3.4	3.4	3.1	3.4	
$k_{a1}/10^3 \text{ s}^{-1}$	9.8 ± 0.7	10.5 ± 0.6	10.7 ± 0.6	10.3 ± 0.5	
$k_{q2}/10^3 \text{ s}^{-1}$	7.5 ± 0.8	9.5 ± 0.7	10.9 ± 1.0	10.5 ± 1.0	
$k_1^{I}/10^3 \text{ s}^{-1}$	23.0 ± 1.9	28.6 ± 2.0	36.1 ± 2.8	49.1 ± 3.5	
$k_1/10^{-11} \text{ cm}^3$	4.2 ± 0.4	3.5 ± 0.3	3.4 ± 0.3	3.5 ± 0.3	3.7 ± 0.4
$molecule^{-1} s^{-1}$					
γ_2 / γ_1	0.148	0.152	0.135	0.135	0.143
	±0.013	± 0.010	±0.011	± 0.010	±0.009

surprisal analysis for two models. For a model assuming that available energy does not distribute into vibration of DS (cold-DS model) with a prior function

$$P^{0}(f_{v}) = (1 - f_{v})^{3} / \Sigma (1 - f_{v})^{3},$$
(7)

in which f_v is the ratio of the DCl vibrational energy to the total available energy,

$$\ln[P(f_v)/P^0(f_v)] = -0.83 + 4.6f_v \tag{8}$$

was derived. The surprisal plot for a model with an assumption that vibrational energies of both DCl and DS are statistically distributed (warm-DS model) with a prior function

$$P^{0}(f'_{v}) = (1 - f'_{v})^{5/2} / \Sigma (1 - f'_{v})^{5/2},$$
(9)

in which f'_v is defined as the sum of vibrational energies of DCl and DS divided by the total available energy, does not fit as well as the cold-DS model; this is consistent with experimental observation of little vibrational excitation of DS.²²

We assume that the surprisal plot is the same for reactions (1) and (2) and estimated the vibrational distribution of HCl(v) for v=0-2 from corresponding values of f_v . The normalized vibrational distribution of HCl for v=0-2 is approximately 40:50:10 based on the cold-HS model. Using the estimated ratio of [HCl(v=0)]/[HCl(v=1)]=0.8, we derive a vibrational distribution of 41:52:7, which yields an average vibrational energy of 22.7 kJ mol⁻¹ for HCl. Considering possible errors associated with experimental measurements and estimate of the population of HCl(v=0), we report an average vibrational energy of $23 \pm 4 \text{ kJ mol}^{-1}$ for HCl. This value is within experimental uncertainties of a previously reported value of 22 kJ mol⁻¹ that used [HCl(v $=0)]/[HCl(v=1)]=0.6;^3$ an average vibrational energy of 19 kJ mol⁻¹ is derived if [HCl(v=0)]/[HCl(v=1)]=0.8 is used.

C. Reaction dynamics and the transition state of CI+H₂S

With an available energy of 69 kJ mol⁻¹, the fraction of energy that leads to vibrational excitation of HCl is $\langle f_v \rangle$ = 0.33±0.06 and the fraction of energy that leads to rotational energy, $\langle f_r \rangle$, is 0.12±0.02. The value of f_v is similar to that (0.32, using an available energy of 69 kJ mol⁻¹ instead of 64 kJ mol⁻¹ that they used) reported by Agrawalla and Setser,³ but slightly greater than the value of 0.28 when the same ratio, [HCl(v=0)]/[HCl(v=1)]=0.8, is employed. Our value of $\langle f_r \rangle = 0.12$ is much greater than the value 0.065 reported previously (using a revised available energy),¹⁴ but is consistent with other similar reactions involving Cl or F atoms, with $\langle f_r \rangle$ in the range 0.13–0.19.³

We performed calculations to locate structures of transition state for the reaction $Cl+H_2S$ with the B3LYP/aug-ccpVTZ density functional theory^{32,33} using the Gaussian 98 program.³⁴ Geometries of transition state and displacement vectors corresponding to imaginary vibrational wave numbers predicted with the B3LYP method are shown in Fig. 6. This transition structure has a H–Cl bond length of 1.619 Å, smaller than a value of 1.65 Å previously report by Wilson and Hirst,²⁵ who employed the MP2(full)/6-311G** method to predict the transition structure; molecular parameters reported by them are listed parenthetically in Fig. 6 for comparison. Predicted vibrational wave numbers for the transition state are 98, 214, 407, 1206, 2679, and 953.7*i* cm⁻¹.

The dynamics for H abstraction by Cl atoms are expected to be dominated by consequences of the heavy–light–heavy mass combination.² The kinematic effect of the Cl–H-S mass combination is more important than details of the potential surface in determining the internal energies of HCl. The small internal energy of the radical fragment HS is consistent with rapid motion of the reacting H atom, which leaves without interacting with the remainder of the radical fragment.

If the modified impulse model is valid, rotational energies can be predicted according to the equation

$$E_r = [m_{\rm Cl}m_{\rm S}/(m_{\rm H} + m_{\rm Cl})(m_{\rm H} + m_{\rm S})]E_{\rm avail}\sin^2\alpha \qquad (10)$$

in which E_{avail} is the available energy and α is the torque angle between the direction of motion of H and that of the H–Cl bond in the reaction coordinate of the transition structure.^{9,10} If we use the small value of $\alpha = 1.5^{\circ}$ calculated for the vector of reaction coordinate based on the vibrational motion corresponding to the imaginary frequency, little rotational energy is expected for HCl from reaction (1), in contrast to the experimental observation. The impulse model using displacement vectors of imaginary frequencies is hence unfit for prediction of rotational distributions of HCl produced from reaction of Cl+H₂S. In contrast, if we consider



FIG. 6. Geometry (A) and vector displacements (B) of transition state for the reaction $Cl+H_2S$ predicted with the B3LYP/aug-cc-pVTZ method. Displacement vectors corresponding to imaginary wave numbers are shown in solid arrows in the lower part. Bond lengths have unit of Å. Results from Wilson and Hirst (Ref. 25) are shown in parentheses.

the geometry of the transition state and assume that breaking the H–S bond provides the impulse, the torque angle of α =42.1° for HCl production yields a rotational energy ~30 kJ mol⁻¹ according to Eq. (10); this value is much greater than our experimental value. The impulse model is sensitive to the torque angle which is subject to large errors associated with calculations using various methods.

Wilson and Hirst²⁵ performed calculations on the abstraction path of reaction (1) and predicted a rate coefficient of 2.8×10^{-12} cm³ molecule⁻¹ s⁻¹, much smaller than reported experimental values in the range (4.0-10.5) $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.¹⁵⁻²¹ They also located an adduct $H_2S \cdot Cl$, with Cl attaching to the S-end of H_2S , for the reaction of Cl and H₂S; the bond distance of S-Cl is predicted to be 2.71 Å and there is no barrier for this path. They proposed that the adduct $H_2S \cdot Cl$ might play a critical role in the reaction, and the small negative temperature dependence is consistent with such a model. If the $H_2S \cdot Cl$ adduct is formed rapidly, rearrangement of the adduct to form HS and HCl might serve as the rate-determining step. The involvement of the adduct $H_2S \cdot Cl$ would lead to greater rotational excitation of HCl. Further theoretical studies on the potential energy surfaces and associated reaction dynamics are needed in order to provide more detailed information on this reaction and to compare with experimental results.

D. Comparison of rate coefficients

Pseudo-first-order rate coefficients k_1^I derived with model fitting of temporal profiles of both vibrational populations of HCl(v = 1,2) are listed in Table II. Bimolecular rate coefficients k_1 were derived by dividing k_1^I by [H₂S]; an average value of $(3.7 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ is derived. We have verified that, in the model fitting with the FACSIMILE program, although data for formation of HCl(v = 0) are unavailable, fitted rate coefficient represents a total rate coefficient for the decay of Cl atoms. Considering that these experiments were not specifically designed for accurate kinetic measurements and that only a small range of $[H_2S]$ was employed, we report a rate coefficient $k_1 = (3.7 \pm 1.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for reaction (1), with listed uncertainties representing estimated errors. This value is close to the small value, $(4.0\pm0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, reported previously by Clyne and Ono,¹⁷ but slightly smaller than more recent values of $(7.4\pm1.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, reported by Nicovich *et al.*²¹

IV. CONCLUSION

Rotationally resolved infrared emission of HCl (v = 1and 2) is observed with a step-scan Fourier-transform spectrometer after irradiation of a flowing mixture of S₂Cl₂, H₂S, and Ar with an excimer laser at 308 nm to initiate the reaction Cl+H₂S. Average rotational energy and its fraction of partition derived with this technique, $E_r = 8.3$ ± 1.5 kJ mol⁻¹ and $\langle f_r \rangle = 0.12 \pm 0.02$, are much greater than previous reports, but consistent with those determined for similar reactions involving Cl or F atoms. Observed vibrational excitation of $[HCl(v=2)]/[HCl(v=1)]=0.14\pm0.01$ indicates slightly more excitation of HCl(v=2) than previously reported, with estimated fraction of energy partition into vibration, $\langle f_v \rangle = 0.33 \pm 0.06$ within experimental uncertainties of that reported previously. Improved temporal resolution and detection sensitivity of time-resolved Fouriertransform spectroscopy proves useful in determining internal-state distributions of products from bimolecular reactions, especially in measuring nascent rotational distributions which could not be determined directly previously. We hope that such information obtained with this technique will stimulate more theoretical calculations and provide further understanding on reaction dynamics of more complex systems.

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