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Laser-initiated chemical reactions: $Cl+H_2S \rightarrow HCl+HS$: Rate constant, product energy distribution, and direct detection of a chain mechanism

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Laser-initiated, time-resolved infrared chemiluminescence techniques are used to study the detailed kinetics of chlorine/hydrogen sulfide systems. Measurements on the $Cl+H_2S \rightarrow HCl+HS$ reaction are carried out by pulsed laser photolysis of $S_2Cl_2 \rightarrow S_2Cl+Cl$ in a flowing mixture with H_2S, while detecting vibrational chemiluminescence from the HCl product. The measured rate constant for the $Cl+H_2S$ reaction is $6.0 \pm 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} at 296°K. The vibrational product distribution is predominately excitation of HCl to $v=1$ and $v=2$, with the ratio $(v=1):(v=2)=15$. The dynamical interpretation of the $Cl+H_2S$ reaction data is discussed. Photolysis of $Cl_2 \rightarrow 2Cl$ in the presence of H_2S produces a rapid chain reaction, $Cl+H_2S \rightarrow HCl+HS$, $HS+Cl_2 \rightarrow HSCl+Cl$. The chain mechanism and its real time development are observed directly from the product chemiluminescence signal.

I. INTRODUCTION

There has been considerable interest in reactions of the type $A+BC \rightarrow AB+C$, from the standpoint of their dynamics, rates, and vibrational population distributions.[1] Reactions that produce substantial vibrational excitation in the products have been extremely important for chemical lasers.[2] Such reactions may also lead to sources of infrared emission in the upper atmosphere.[3] A wide variety of experimental methods have been used to study $A+BC$ reactions,[4-8] and a wealth of data has been obtained. There are relatively few thorough studies of atom plus triatomic, $A+BCD \rightarrow AB+CD$, reactions. In this case, the vibrational states of either or both product molecules can potentially be excited by the available reaction exothermicity. The partitioning of reaction energy in such $A+BCD$ systems will be a sensitive indicator of the dynamics in the reaction. Most frequently it is observed that the newly formed molecular bond carries away most of the vibrational excitation.[1]

In this paper we report a detailed study of one such $A+BCD$ system, $Cl+H_2S \rightarrow HCl+HS$, $\Delta H=-13$ kcal/mole.[9] The reaction exothermicity is sufficient to excite primarily either the HCl or HS product to $v=1$. The techniques of laser initiation of the reaction and detection of time-resolved infrared chemiluminescence are used to make measurements on the reaction rate constant and the extent of vibrational excitation in the HCl and HS products.

Pulsed laser chemiluminescence methods offer a powerful means to extract novel kinetic data from the time and amplitude information of excited states. In this paper we report one of the few direct observations of the realtime development of a chain reaction mechanism. Photolysis of Cl_2 in Cl_2/H_2S mixtures is observed to undergo a rapid chain sequence, (a) $Cl+H_2S \rightarrow HCl+HS$, (b) $HS+Cl_2 \rightarrow HSCl+Cl$. The chain reaction is detected directly from the time behavior and amplitude of the HCl product vibrational chemiluminescence. Further development of these experiments may provide valuable detailed methods to study and analyze chain reactions for combustion and explosion phenomena.

In the experiments described, Cl atoms are generated by pulsed laser photolysis of either Cl_2 or S_2Cl_2 in a flow of $Cl_2(S_2Cl_2)$, H_2S, and Ar. The Cl_2 source is observed to undergo a chain reaction, whereas the S_2Cl_2 source of Cl atoms does not propagate the chain. Thus, kinetic data on the elementary $Cl+H_2S$ reaction step are readily obtained in the absence of further complicating reactions by using S_2Cl_2 as the source of Cl atoms. Rate constants are measured directly from the time development of the product vibrational chemiluminescence, primarily HCl $(v=1)$. Amplitude measurements using various interference filters and gaseous filters allow estimates of the relative vibrational population distributions to be made for the $Cl+H_2S \rightarrow HCl+HS$ reaction. A discussion of the dynamical interpretation of the $Cl+H_2S$ rate data is given.

II. EXPERIMENTAL

The apparatus consists of a gas handling system and flow reaction cell, a frequency-doubled dye laser for pulsed dissociation of reagents, and an infrared detector and computer signal averaging system to collect the infrared chemiluminescence signals. A schematic of the experimental arrangement is shown in Fig. 1.

The gas handling system is comprised of pyrex storage bulbs and tubing. Stopcocks with viton "O" rings coated with a Teflon-based grease are used throughout. The reaction flow tube consists of a quartz vessel, 3 cm in diameter, with infrasil windows sealed directly on the sides to transmit the laser, and a sapphire window for transmission of infrared emission attached to the top

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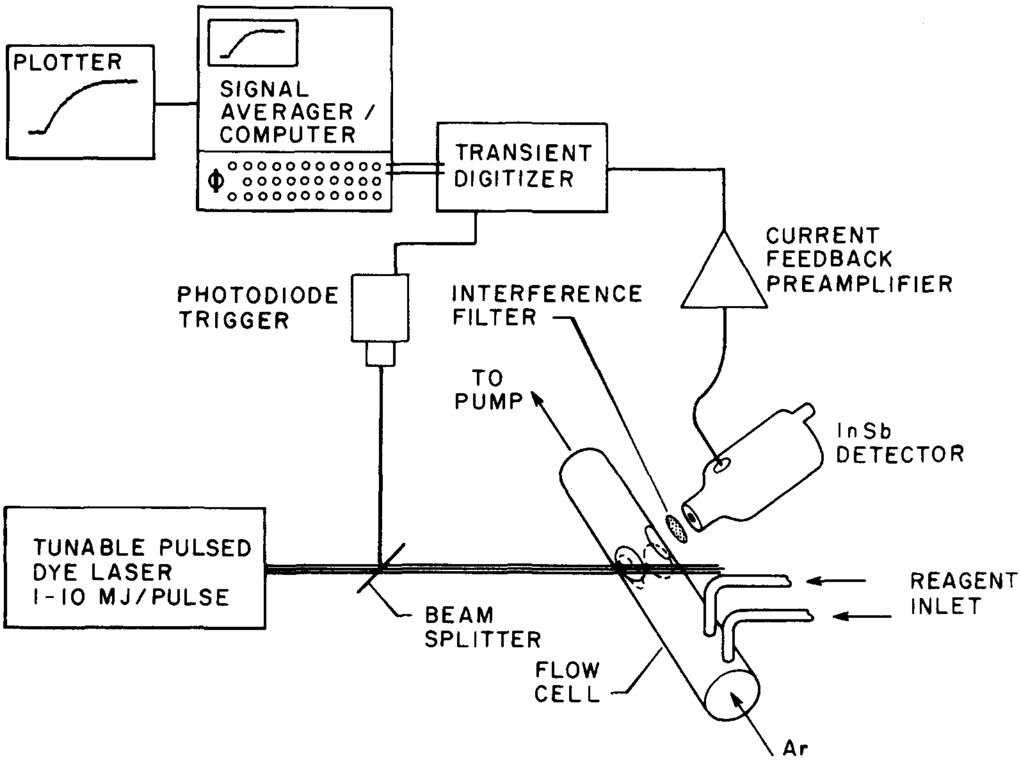

FIG. 1. Experimental apparatus for reaction studies by laser-initiated, infrared chemiluminescence. A flashlamp pumped, frequency-doubled dye laser is used as a photodissociation source of atoms. Infrared chemiluminescence signals from product molecule vibrational states are detected with an InSb detector and signal averaged to enhance the signal to noise.

with black wax. The gases used in these experiments and their purities are: Ar(99.999%), HCl(99%), HBr(99%), H_2S(99.8%), and Cl_2(99.96%). S_2Cl_2(99%) was supplied as a liquid. With the exception of the argon buffer gas, all reagents were degassed at 77 °K several times and then distilled at a few Torr vapor pressure, retaining only the middle fraction of the distillate. The gases are mixed with a series of inlets 10 cm before the fluorescence window. Under the typical flow rates and pressures listed in Table I, prereaction problems[10] of S_2Cl_2 with H_2S are negligible. These flow rates are also sufficient for study of the chain reaction of Cl_2 with H_2S, since the gas mixture is refreshed rapidly enough to keep ahead of the diffusion of the chain burning reagents. Pressures in the reaction vessel are measured with a 0–50 Torr inductance manometer. The gas forepressures are measured with monel Bourdon type gauges. Flows are monitored with ball flow meters or electronic mass flow meters, and are adjusted with monel or stainless steel fine metering valves.

TABLE I. Typical flow conditions for laser initiated chemiluminescence experiments.

Gas	Flow (μmoles/sec)
Argon	235
S_2Cl_2/Argon (10%)	3
H_2S/Argon (10%)	0–12
Gas	**Typical pressure (Torr)**
Argon	40
S_2Cl_2	0.05
H_2S	0–0.2

A commercial flashlamp pumped dye laser is used for a photodissociation light source to generate halogen atoms. The frequency doubled output at 300 nm produces 1 mJ pulses with 2 μsec duration. The laser beam is collimated by a 50 cm focal length quartz lens. A multiple reflection mirror arrangement is used to enhance the absorption of the laser beam by the S_2Cl_2 and Cl_2 in the reaction cell. A 1.3 cm × 1.3 cm, 77 °K, InSb detector is used to obtain time-resolved signals of the product vibrational chemiluminescence. The signals are captured by a transient digitizer, with the sweep initiated by a photodiode detecting the laser pulse. The digital data of amplitude versus time are subsequently stored and added in a signal averager to enhance the signal to noise. For a typical reaction, $X + HY \rightarrow HX^{\dagger} + Y$, where † denotes vibrational excitation, the progress of the reaction is monitored by the time-resolved infrared emission of the vibrationally excited product molecules. Different states of the product molecules may be monitored independently by proper selection of gaseous and interference filters to isolate specific bands on the detector. A typical set of signals from the HCl product of the $Cl + H_2S \rightarrow HCl + HS$ reaction is shown in Fig. 2. Shown on two different time scales are the rapidly rising portion, corresponding to the formation of the vibrationally excited species, and the subsequent slow decay due to vibrational deactivation of the excited product molecules. Linear semilogarithmic plots of amplitudes versus time are obtained from the risetime portion of the signal after correcting for the slower vibrational deactivation time.[10] From these plots, the rate of the $Cl + H_2S$ reaction is determined. For a few very short time experiments, the

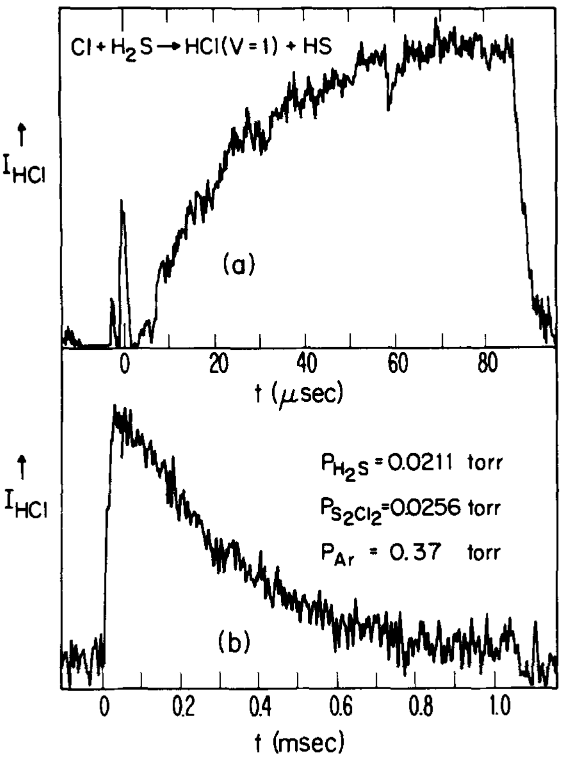

FIG. 2. Typical infrared chemiluminescence signals from the reaction $Cl + H_2S \rightarrow HCl(v) + HS$ using S_2Cl_2 as the photodissociation source of Cl atoms. (a) Risetime indicative of $Cl + H_2S \rightarrow HCl + HS$ reaction rate constant. (b) Decay due to eventual vibrational deactivation of the $HCl(v)$. The spike is due to electronic noise.

observed risetime, τ_{obs}, was corrected for the finite response time of the detection system, $\tau_{apparatus} = 1.75$ μsec, according to the equation $\tau_{real} = (\tau^2_{observed} - \tau^2_{apparatus})^{1/2}$.

III. RESULTS

A. The $Cl + H_2S \rightarrow HCl + HS$ reaction

In the typical laser-initiated study of chlorine atom reactions, e.g. $Cl + HI$ and $Cl + HBr$,[10] molecular Cl_2 is used as the photolysis source of Cl atoms. When mixtures of $Cl_2 + H_2S$ in argon are photolyzed by 300 nm laser pulses, product $HCl(v)$ chemiluminescence signals are observed. However, both the time behavior and amplitude of the signals indicate that a more complex set of reactions is taking place, and not simply the elementary reaction $Cl + H_2S \rightarrow HCl + HS$. In a comparison with the signals from $Cl + HBr \rightarrow HCl^\dagger + Br$, which is known to be a simple, single step reaction, the $Cl + H_2S$ signals are 10–100 times greater in amplitude. One such comparison run is shown in Fig. 3, where the Cl_2 pressure was held constant, and H_2S merely substituted for HBr in the reaction. Since H_2S is not photolyzed by the 300 nm light, it is apparent that the signal behavior is due to a chain mechanism, which is discussed below.

Other photolysis sources of Cl atoms were sought which would suppress the chain reaction, in order to study the initial $Cl + H_2S \rightarrow HCl + HS$ reaction step directly. The molecule S_2Cl_2 was found to produce Cl atoms on dissociation with 300 nm light, with no apparent additional chain or side reactions. The photochemistry of S_2Cl_2 in the near ultraviolet is not well understood. In the flash photolysis of S_2Cl_2 at $\lambda > 185$ nm, $\lambda > 200$ nm and $\lambda > 300$ nm, Donovan *et al.*[11] suggest that the primary product is SCl. In our work, however, reactions characteristic of direct production of Cl atoms are observed both with HBr and H_2S when S_2Cl_2 is photolyzed at 300 nm. If SCl is also a primary product of the S_2Cl_2 photolysis, it does not appear to play any further role in the reaction kinetics. In addition, the results of Donovan *et al.*[11] are obtained with kJ flash energies, which may introduce some biradical reactions which are not present in our mJ laser pulse system. There is no information at this time on the relative contributions of $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ atoms in the photolysis of S_2Cl_2, although this distribution may affect the observed rates.

A straightforward set of kinetic equations may be used to describe the short time behavior of the $Cl + H_2S$ experiments performed with the S_2Cl_2 source:

$$S_2Cl_2 \xrightarrow{300\text{ nm}} S_2Cl + Cl$$

$$Cl + H_2S \xrightarrow{k_1} HCl + HS \quad \Delta H = -13\text{ kcal/mole} \qquad (1)$$

$$HCl^\dagger + m \xrightarrow{k_m^{HCl}} HCl + m\ ,$$

where k_1 is the rate constant of the $Cl + H_2S$ reaction, and k_m^{HCl} is the vibrational deactivation rate constant for HCl with various gases in the system. The possibility exists in reaction (1) that either HCl or HS could be excited vibrationally. A similar vibrational deactivation pathway exists for HS,

$$HS^\dagger + m \xrightarrow{k_m^{HS}} HS + m\ .$$

Since $HCl(v=1)$ requires 8.3 kcal/mole excitation energy and $HS(v=1)$ is 7.4 kcal/mole, and given only 13 kcal/mole available exothermicity, the predominant vi-

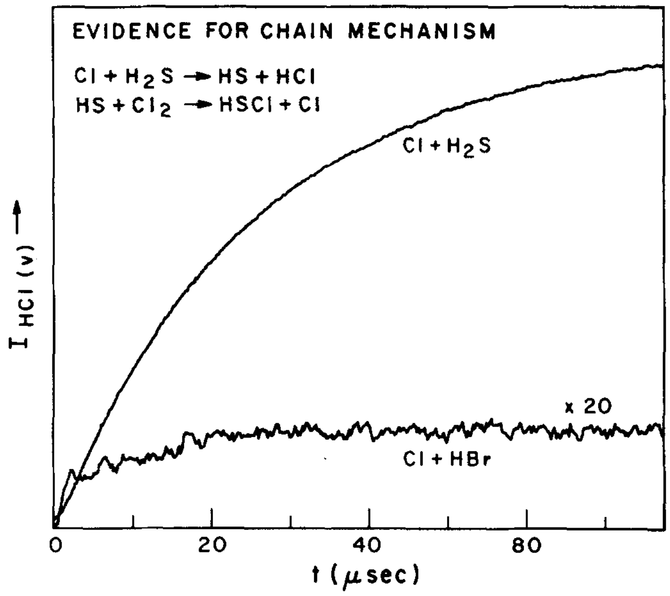

FIG. 3. $HCl(v)$ product signals showing evidence for the chain reaction behavior of Cl_2/H_2S mixtures. In the plot labelled $Cl + H_2S$, a mixture of a few Torr each of Cl_2 and H_2S is photolyzed to produce Cl atoms. In the plot labelled $Cl + HBr$, HBr gas is substituted for H_2S at the same flow rate. The $Cl + HBr$ signal has been plotted on a 20 times more sensitive scale.

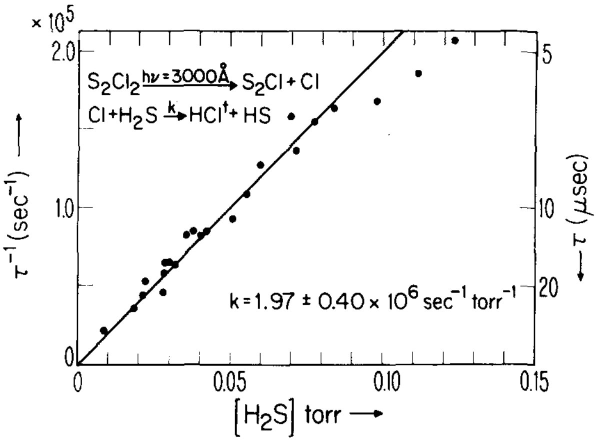

FIG. 4. Plot of the HCl vibrational emission rate, $1/\tau_{HCl}{}^{\dagger}$ vs P_{H_2S}, for the reaction $Cl + H_2S \rightarrow HCl(v) + HS$. The points for $P \geq 0.1$ Torr overlap with the time of the tail of the laser pulse.

brational excitation is expected to be in either HCl($v = 1$) or HS($v = 1$). More exactly, a fraction of the translational energy is always available to the reaction, as well as the energy of any activation barrier. This can amount typically to 2 or 3 kcal. In addition, the heat of formation of the HS radical is still relatively uncertain. Thus, the 13 kcal/mole exothermicity could be in error by several kcal/mole. In light of these facts, we find no discrepancy in observing a small amount of vibrational excitation to HCl($v = 2$) in the $Cl + H_2S$ reaction product.

Since the H_2S concentration is always in great excess compared to the Cl atom density generated by the photolysis laser ($> 10^{14}$/cc compared to 10^{13}/cc), the Cl atoms react with the H_2S in a pseudo-first-order manner. If either product molecule is excited vibrationally a signal will be seen. The kinetics of the formation and deactivation of excited product molecules in such a system has been worked out numerous times before. The result is

$$[HCl(v=1)]_t = A\left\{\exp\left(-\sum_m k_m^{HCl}[m]t\right) - \exp(k_1[H_2S]t)\right\}.$$

Thus a time-dependent signal is observed which has a double exponential form. The first term is indicative of the slow vibrational deactivation, and the second term, the rise time, is characteristic of the rate of reaction (1). From the measured risetimes and pressures of H_2S, the rate constant k_1 is extracted directly. Identical expressions may be written for the excited species HCl ($v = 2$), HS($v = 1$), and HS($v = 2$), where only the constant A takes on different values depending on the exact partitioning of the reaction exothermicity among the different vibrational states. Thus we are able to extract information concerning the relative extent of vibrational excitation in the HCl and HS products from relative amplitude measurements.

After properly fitting the deactivation part of the fluorescence curves, e.g. as in Fig. 2b, the correct risetime of the reaction is obtained. Figure 4 shows the set of data taken for the rate constant determination of reaction (1), plotted as $1/\tau$ vs [H_2S]. The H_2S pressure was varied from 0–0.13 Torr. A least-squares fit of the data in Fig. 4 gives $k_1 = 6.0 \pm 1.2 \times 10^{-11}$ cm^3 molec^{-1} sec^{-1} at 296 °K, where the error quoted is two standard deviations from the mean. This rapid reaction rate constant is similar in magnitude to others measured, such as the exothermic Cl + HBr (8.4×10^{-12} cm^3 molec^{-1} sec^{-1}) and Cl + HI (1.55×10^{-10} cm^3 molec^{-1} sec^{-1}) systems.[10]

In a separate set of experiments, the relative production of the vibrational states HCl($v = 2$), HCl($v = 1$), and HS($v = 1, 2$) were measured. This was accomplished in the following manner. First the entire signal from all excited state products is observed using a germanium flat on the detector, which transmits uniformly the emission from the HCl and HS, but blocks scattered laser light. An evacuated, 1 cm path, gas filter cell was permanently mounted between the detector and the reaction cell. This cell was filled with 300 Torr of HCl to block the entire HCl($v = 1 \rightarrow 0$) emission, which is a substantial fraction of the entire signal. The remaining signal from an average of six runs comprised 12 ± 6% of the total signal amplitude. The rather large error associated with this measurement is a result of the poor signal to noise. The time behavior of this remaining signal rises with the same rate as the total signal, but decays somewhat more rapidly. The laser power was varied over a factor of two, and no change in the risetime of this signal was found. Thus, the signal could not be the result of secondary energy transfer processes such as $2HCl(v=1) \rightleftharpoons HCl(v=2) + HCl(v=0)$, which would depend on the concentration of excited species in the laser beam volume. Thus it is most likely that the signal is from a direct reaction product of the $Cl + H_2S$ and probably either HCl ($v = 2$) or HS($v = 1, 2$).

To determine further which additional species is actually excited, an available interference filter which isolates only the HCl($v = 2 \rightarrow 1, 1 \rightarrow 0$) lines were used. Figure 5 shows the vibration-rotation spectral lines of both

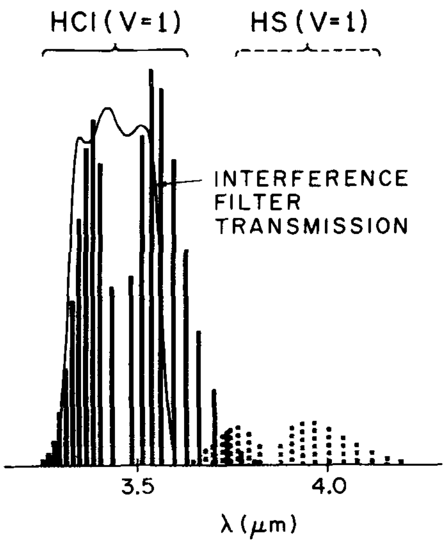

FIG. 5. The spectral lines of HCl($v = 1$) and HS($v = 1$) and the overlap of the interference filter used to look only at HCl(v). The relative amplitudes have been chosen to reflect the calculated transitions strengths of HCl($v = 1$–0) vs HS($v = 1$–0).

$HCl(v=1)$ and $HS(v=1)$, with the transmission curve of this interference filter superimposed. The filter blocks the HS lines completely, and transmits a large fraction of the $HCl(v=1\rightarrow 0)$ lines. Since the anharmonicity shift of $HCl(v=2\rightarrow 1)$ is only 103 cm^{-1}, this filter also passes nearly the same fraction of the $HCl(v=2\rightarrow 1)$ lines. The same experiment was carried out, first measuring the total signal, and then the fraction transmitted when 300 Torr of HCl was added to block the HCl(1–0) emission. The ratio of signals was essentially the same using this interference filter. Thus it appears that the species primarily responsible for the signal which is not blocked by the HCl gas is most likely $HCl(v=2)$. On the basis of these measurements and taking into account the radiative lifetimes of $HCl(v=1)$ and $HCl(v=2)$, we estimate that the ratio $HCl(v=1/HCl)(v=2)$ is approximately 15. A qualitative comparison of the HCl signal amplitude from the $Cl+H_2S$ reaction versus the $Cl+HBr$ reaction indicates that a substantial (~95) fraction of the total HCl product molecules are excited to $HCl(v=1)$, however prereaction in the case of the $Cl+HBr$ prevented *very* accurate measurements.

Whether the HS fragment is excited to any extent at all is difficult to answer. From the experimental observations, no component of the signal can be attributed to $HS(v=1,2)$ at this time. However, our ability to detect $HS(v=1)$ in emission depends entirely on the finite signal to noise of the experiment and the radiative lifetime of the $HS(v=1)$ for spontaneous emission. Detection of $HS(v=1)$ has not been reported in emission, so the strength of its vibrational transition is uncertain. To determine our experimental limit in detecting $HS(v=1)$, a calculation was made by Wendoloski to determine the relative transition dipole moments of HCl and HS.[12] The dipole moments and their derivatives were obtained at a selfconsistent field level using Pople's 4–31 G type basis sets,[13] augmented by an energy optimized $2sp$ bond function. The dipole derivatives were calculated numerically using displacements of ± 0.02 and ± 0.04 Å from R_e. For HCl, $\partial\mu/\partial r$ was calculated to be 0.910 D $Å^{-1}$, compared to an experimental value of 0.928 D $Å^{-1}$.[14] For HS, $\partial\mu/\partial r$ is 0.290 D $Å^{-1}$, which gives a calculated radiative lifetime for $HS(v=1)$ which is nearly ten times longer than for $HCl(v=1)$. Since the signal amplitude is proportional to $1/\tau_{\rm rad}$, our capability to detect $HS(v=1)$ is a factor of ten worse than for $HCl(v=1)$. Because of the low signal to noise even in our best runs, we can only estimate that any excitation into $HS(v=1,2)$ is probably less than 30% of the $HCl(v=1)$ concentration.

B. The chain reaction of Cl_2+H_2S

In the earlier work of Coombe *et al.*[15] on an HCl chemical laser using Cl_2/H_2S, it was postulated that a chain reaction mechanism was unlikely and that the only pertinent reaction leading to the $HCl(v=1\rightarrow 0)$ laser was the fast $Cl+H_2S\rightarrow HCl+HS$ step. As we have already mentioned above, when Cl_2 is photolyzed in a flowing mixture with H_2S, a chain reaction is observed directly from the product HCl chemiluminescence, which is one to two orders of magnitude greater than signals without the chain (Fig. 3). The experimental results conclusively indicate that a second reaction is important,

$$HS+Cl_2\xrightarrow{k_2}HSCl+Cl \qquad (2)$$

which generates another Cl atom for each one used up by Reaction (1). It is likely that the advantage of the additional chain mechanism in the Cl_2/H_2S chemical laser is balanced by the deleterious effect of the strong deactivation[15] of $HCl(v=1)$ by H_2S. Thus the Cl_2/H_2S chemical laser does not show the true potential of a chain reaction laser.

The product vibrational distribution in the chain reaction was analyzed with the same techniques described in Sec. IIIA. In this case, once again, no vibrational emission from HS was observed. This is not a surprising result, since in addition to the expected weakness of the $HS(v=1)$ emission, now the HS is also consumed by reaction (2). As the $HCl(v)$ product builds up over many cycles of the chain, the concentration of HS and Cl remain at relatively constant and small concentrations. The vibrational emission from HCl was found to have a much greater fraction of states in $(v>1)$, as determined again by the attenuation of the signal with the HCl gas filter cell. The relative amounts of $HCl(v>1):HCl(v=1)$ varied with the Cl_2/H_2S composition and pressures. The raw data signals were typically composed of 50% in HCl $(v>1)$. There are three possible reactions which are exothermic enough to contribute significantly to the HCl $(v>1)$ population

$$Cl+HS\rightarrow HCl(v)+S \quad \Delta H=-31\ \text{kcal/mole (Ref. 9)} \qquad (3)$$

$$HSCl+Cl_2\rightarrow SCl_2+HCl(v) \quad \Delta H=-30\ \text{kcal/mole} \qquad (4)$$

$$Cl+HSCl\rightarrow HCl(v)+SCl \quad \Delta H=-39\ \text{kcal/mole}\ . \qquad (5)$$

In Reactions (4) and (5) the heats of formation of HSCl, SCl_2, and SCl have been taken to be +2, −5, and +14 kcal/mole respectively.[15,16] Reaction (3) is certain to be a rapid, contributing reaction. Reaction (4) may have some geometric barriers to reaction, and thus it is uncertain whether this reaction would contribute at all. Reaction (5) again is likely to be rapid and may represent the most significant contribution to the additional product HCl. This is especially true since the concentration of HSCl accumulates in time and will serve to efficiently remove Cl as its pressure becomes large. The chain reaction signal behavior, and the extent of excitation in $HCl(v>1)$ could be adequately accounted for by reactions (1), (2), and (5), however, we cannot rule out the possibility of reactions (3) and (4) being important also.

At this time we have not undertaken a detailed experimental study of the chain reaction mechanism. However, from a brief analysis of the kinetics and some typical chain data behavior, we can make some qualitative comments concerning the mechanisms and magnitudes of rates. The chain reaction was examined for a number of runs with Cl_2 pressures in the range of 0.6–3 Torr and H_2S pressures of 0.01–0.1 Torr. If we ignore for the moment the effects of reactions (3), (4), and (5), and only solve the kinetics of the chain steps (1) and (2), we get a simple result. The form of the $HCl(v)$ emission as a function of time after the laser pulse is given by

$$[\mathrm{HCl}(v)]_t = At + B[1 - \exp(-Ct)] \ .$$

We see that there is a brief exponential induction time, which depends on $C = k_1[\mathrm{H_2S}] + k_2[\mathrm{Cl_2}]$, followed by a signal linear in t, whose slope is governed by $A = k_1[\mathrm{H_2S}] \times k_2[\mathrm{Cl_2}][\mathrm{Cl}]_0/(k_1[\mathrm{H_2S}] + k_2[\mathrm{Cl_2}])$. Typically, the initial concentration of chlorine atoms $[\mathrm{Cl}]_0$ is small compared to the concentrations of H_2S and Cl_2. Thus, the chain steps (1) and (2) can make many cycles before depleting the original reagent concentration. The initial rate of rise of the linear portion of the signal approaches $k_1[\mathrm{H_2S}][\mathrm{Cl}]_0$ if $k_2[\mathrm{Cl_2}] \gg k_1[\mathrm{H_2S}]$, and approaches $k_2[\mathrm{Cl_2}][\mathrm{Cl}]_0$ if $k_1[\mathrm{H_2S}] \gg k_2[\mathrm{Cl_2}]$. Experimentally we find that the rising signal has a definite linear regime and that the the limit of $k_1[\mathrm{H_2S}][\mathrm{Cl}]_0$ is reached when $[\mathrm{Cl_2}] \approx 10-20[\mathrm{H_2S}]$. Thus it would appear likely that the rate constants k_1 and k_2 are of similar orders of magnitude. The reduction of signal to noise with decreasing Cl_2 pressure precluded using Cl_2 pressures low enough to extract the rate constant k_2 exactly from the experiments. An experiment is being prepared to use S_2Cl_2 as a constant, well-defined source of initial $[\mathrm{Cl}]_0$ atoms, and then to add varying amounts of Cl_2 through an additional reagent inlet, to obtain k_2.

In our experiments, the linear portion of the signal for the chain reaction lasts for only 5-10 cycles of the chain. Then the slope of the signal starts to decrease. There are several reasons for this behavior. First, the limiting reagent can be depleted substantially causing the chain reaction to end. This depends on the density $[\mathrm{Cl}]_0$, and thus on the focussing and energy of the laser. Typically our $[\mathrm{Cl}]_0$ is less than 1% of the $[\mathrm{Cl_2}]$, but this can be a substantial fraction of the $[\mathrm{H_2S}]$, if the H_2S is the limiting reagent. Second, $\mathrm{HCl}(v)$ is efficiently deactivated by several species in the gas mixtuare, such as H_2S. Third, depletion of Cl atoms can occur by reactions of Cl with HS and HSCl. In our estimation, this third reason is an important intrinsic chemical effect which terminates the chain reaction. Since we do observe a substantial fraction of the total vibrational chemiluminescence from HCl in $v > 1$, these reactions are viewed to be very important in causing the eventual slow down of the chain steps (1) and (2). Finally, of course, there are termination effects due to radical and atom recombinations in the gas phase and on the walls, and the eventual passage of the excited species in the flow out of the view of the detector. In all of the experimental conditions looked at here, the signals are actually over before the excited species would pass from the detector view.

All of these effects can be readily built into a more detailed kinetic model, in order to extract precise rate data for chain reactions using the pulsed laser, infrared chemiluminescence techniques. The potential of such methods for learning more about combustion and explosion phenomena is readily apparent, and virtually unexplored.

IV. DISCUSSION AND CONCLUSION

The dynamical picture of the $Cl + H_2S$ reaction (1) appears to have many similarities to other $A + BCD$ type reactions.[1] Trajectory studies for this class of reactions predict a high degree of vibrational excitation will be retained in the newly formed AB bond if the energy release occurs on an attractive energy surface.[1] The bond order of the CD fragment rarely changes significantly, thus the CD molecule is almost completely unperturbed by the reactive event. Our experimental results indicate excitation predominantly in the newly formed HCl product of the $Cl + H_2S$ reaction. No excitation was observed in the HS product. Although the experiment was unable to detect less than about 30% excitation in the HS fragment, the large extent of $\mathrm{HCl}(v = 1, 2)$ production observed would appear to preclude a similarly large fraction of excitation in the HS. The rapid, 6×10^{-11} $\mathrm{cm^3}$ $\mathrm{molec^{-1}}$ $\mathrm{sec^{-1}}$ rate constant for the $Cl + H_2S$ reaction also indicates a close similarity to the reactions Cl + HBr and Cl + HI. As in these reactions,[10,17] we expect the $Cl + H_2S$ reactions to have little or no activation barrier and an initially attractive energy surface. In the model of Mei and Moore,[17] the Cl atom would attack the S atom in H_2S first because of a strongly attractive potential. Within the time scale of the collision, one of the H atoms rotates around to then react with the Cl and depart along the exit channel with the Cl. Secondary encounters between the HCl and HS fragments would appear unlikely, since these might favor redistribution of the vibrational excitation to the lower frequency HS fragment.

The experimental chain reaction results indicate that the reaction (2) of HS with Cl_2 is also rapid, even though nearly thermoneutral. This reaction provides the necessary step in propagating the chain reaction between Cl_2 and H_2S. A further series of atom-radical reactions, (3)-(5), appear to be excellent possibilities for important chain termination steps. Two of these reactions, (3) and (5), are expected to be rapid and may produce HCl in higher vibrational states as well. The chain reaction mechanism has not been explored in detail. However, it is evident that the laser-initiated techniques described here can be used as a powerful means of sorting out the pertinent kinetic data in chain reaction events. Thus we expect the further development of these chain reaction experiments to provide valuable new methods to study combustion and explosion phenomena.

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