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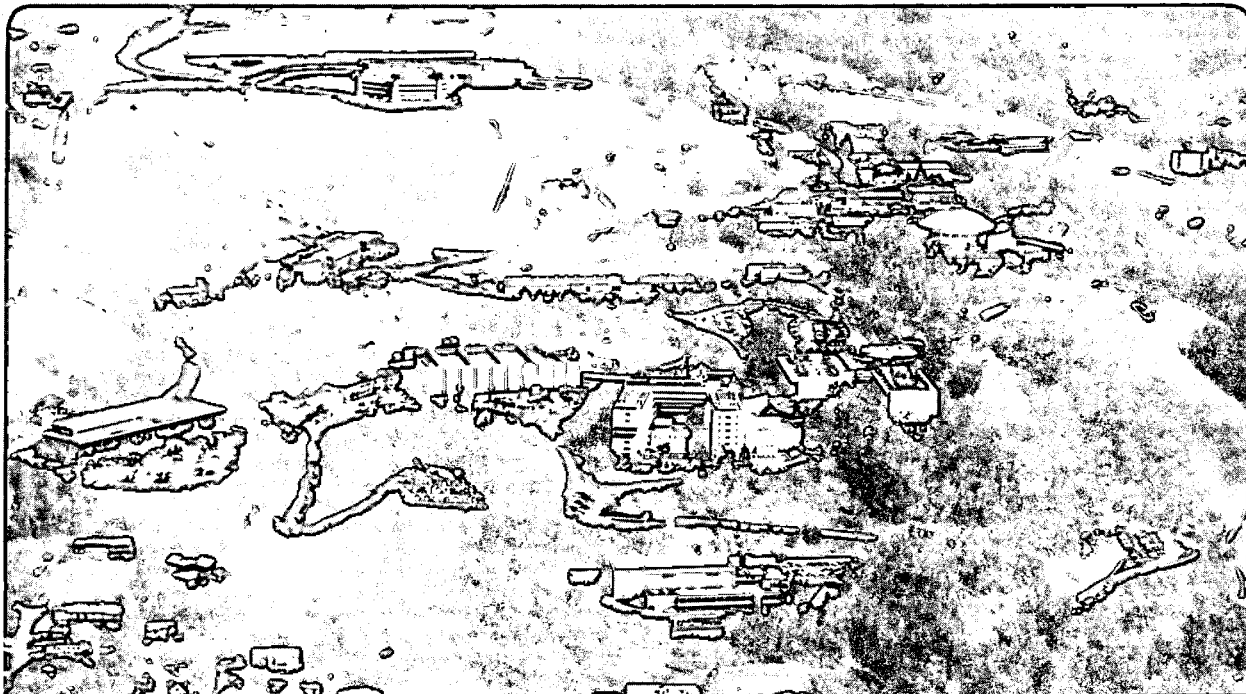
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DISCLAIMER

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USING PULSED LASER PHOTOLYSIS

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ABSTRACT

The application of millimeter-wave microwave spectroscopy to the detection of free radicals and other species generated by pulsed excimer laser photolysis is described. To detect the radical species, a newly developed 140 GHz microwave spectrometer employing a high-Q Fabry-Perot cavity was used. The technique is illustrated by the observation of SO and CS radicals produced by photodissociation at 193 nm of SO_2 and CS_2 respectively. SO absorption signals from the ground vibrational state transition at 138.17 GHz and the first and second excited vibrational state transitions at 137.28 and 136.45 GHz were measured. CS was detected in several excited vibrational states up to $v = 4$. Finally, as an example of the application of the technique to chemical kinetic studies, the reaction rate of SO with NO_2 was determined. The measured rate coefficient at 298K of $(1.46 \pm 0.12) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is in excellent agreement with values reported in other studies. Millimeter-wave spectroscopy is shown to be a sensitive and highly specific probe for the detection of short lived species in gas phase chemical kinetic studies.

INTRODUCTION

In studies of the kinetics of gas phase chemical reactions, a number of techniques have been used to measure the concentrations of the various species present in the reaction system. These include, among others, UV resonance absorption[1], UV resonance fluorescence[2] using discharge lamps and fixed or tunable laser sources, laser magnetic resonance[3] and gas phase electron paramagnetic resonance (EPR)[4]. Of these various techniques, millimeter-wave spectroscopy[5] is most similar to the EPR method. It is, however, significantly more sensitive than the latter, partly because the degeneracy of the observed transitions is not split by a magnetic field and partly because measurements are typically made at a higher frequency than normally employed in an EPR spectrometer.

While it is presently not as sensitive as some of the methods listed above, the microwave absorption technique has the advantage that it is highly specific. Not only can individual species be identified uniquely, but they can be detected without interference in specific excited vibrational states as well. This specificity is difficult to achieve with the various laser-induced fluorescence methods, especially when applied to the identification of larger polyatomic molecules because the fluorescence spectra of such molecules, if present, tend to be broadband and relatively featureless. Finally, because it is an absorption technique (as opposed to fluorescence), it can be used without extensive calibration procedures to determine the absolute concentration of a particular species.

In the following we present a description of the apparatus used to generate and detect free radicals produced by laser photolysis. We illustrate the method by the detection of SO and CS molecules in various vibrational levels. Finally we apply the method to a measurement of the reaction rate of SO with NO_2.

I. EXPERIMENTAL APPARATUS

Free radical species were generated by UV laser photolysis of suitable precursors using a Lambda Physik model EMG-101 excimer laser. The laser beam was defocused with the aid of a cylindrical calcium fluoride lens in order to illuminate the spectrometer gas sample cell. The laser was operated with an ArF gas mixture and was able to produce up to 80 mJ of energy per pulse at a wavelength of 193 nm. Pulse rates of up to 30/s were used, although most measurements were made at a rate of 10/s.

The molecular species were detected using a superheterodyne microwave spectrometer employing a tunable Fabry–Perot cavity as a sample cell. The construction of the spectrometer is described elsewhere[6,7] in detail and its operation will only be summarized here. Microwave power to operate the spectrometer was provided by a klystron, tunable over a frequency range of 67 to 73 GHz. A portion of the klystron output was converted to 140 GHz by a high efficiency frequency doubler which serves as a source of local oscillator power for a low noise superheterodyne receiver. The remainder of the 70 GHz power was fed to a second frequency doubler which functions as a signal oscillator source. This doubler was additionally modulated at an IF frequency of 30 MHz to produce sidebands on either side of the 140 GHz frequency.

The modulated signal oscillator source was fed to a tunable Fabry-Perot transmission cavity which has a sufficiently high quality factor (Q = 73000) to reject all but one of the sideband frequencies. After passing through the cavity, the microwave signal is detected by the low noise superheterodyne receiver. The actual microwave frequency of the spectrometer was determined by a frequency synthesizer controlled by a PDP-11/34 computer.

In order to detect the transient gas absorption signals produced by the photolysis laser, the spectrometer output is digitized by an 8-bit Transiac model 2008 transient digitizer, a CAMAC based unit with a maximum sampling rate of 20 MHz and a memory size of up to 8K channels. The laser, a monitoring oscilloscope and the digitizer are synchronized using a pulse sequencer also mounted in a CAMAC module and described in Ref. 7. The computer is used to average the digitized data from a number of laser shots and to further process the data.

The Fabry-Perot cavity consists of two mirrors, one flat and the other spherical, enclosed in a vacuum chamber fitted at the top and bottom with UV grade fused silica windows (transmission 90% at 193 nm) to admit the light from the photolysis laser. The horizontal laser beam is directed into the cavity by a UV enhanced aluminized mirror (reflectivity 85%) and makes a single pass through it to a beam dump located below. In some measurements, the laser intensity was reduced by replacing the mirror with an uncoated quartz substrate having a reflectivity of about 5%. The laser beam is expanded to illuminate the entire 4 cm diameter of the windows by positioning it about 2 m away from the cavity and defocussing it in the vertical direction with a cylindrical CaF lens. Since the mirror separation is 7.5 cm and the window diameter is only 4 cm, the effective filling factor for illumination within the cavity is about 50%. This

factor must be taken into account in calculations of the absolute concentration of transient species produced by the photolysis laser. On the other hand, the diameter of the Gaussian microwave beam propagating between the cavity mirrors is only 1.6 cm making it substantially smaller than the laser beam in the transverse direction.

The reaction gases were pumped through the cavity by a liquid nitrogen trapped diffusion pump and were introduced by means of adjustable needle valves. The gas mixtures employed were obtained through the use of calibrated flowmeters and, in some cases, by partial pressure measurements as described below. The pressure in the chamber was measured with an MKS Baratron pressure gauge (1 Torr full scale). At a cell pressure of 200 mTorr the gas residence time was about 100 ms. This could be increased by operating the cell at higher pressure and throttling the exit flow with a valve provided for that purpose.

II. MEASUREMENTS OF UNSTABLE SPECIES

A. Detection of SO Free Radicals

As described in Ref. 8, SO free radicals can be produced efficiently by photolysis of SO_2 at 193 nm where the absorption cross section[8] is 1.1×10^{-17} cm^2. In order to illustrate the production and detection of SO, a mixture of SO_2 diluted in Ar was pumped through the sample cell at a total pressure of 200 mTorr. The concentration of SO_2 was maintained at 4.5% (9 mTorr, 2.9×10^{14} $molec/cm^3$) by means of the calibrated flowmeters. The spectrometer was tuned to the (4,3)-(3,2) rotational transition of SO, $\nu = 0$ at 138.17 GHz. The laser was then pulsed at a rate of 10 Hz and the spectrometer output signal was averaged

for a total of 4000 shots. The result is shown in Fig. 1 in the trace labeled (a). In order to display the baseline, the transient digitizer was triggered a short time before the firing of the laser (at $t = 0$). The large pulse at time, $t = 0$ is due to an electrical disturbance caused by the firing of the laser. As can be seen, the SO signal begins abruptly at a value about 40% of its maximum and then grows exponentially to a final value of about 1.6 mV.

Figure 1, trace (b) shows the same measurement repeated with the spectrometer tuned to the (4,3)-(3,2) rotational transition of SO, $\nu = 1$ which occurs at a frequency of 137.28 GHz. The absorption signal begins abruptly at 0.6 mV and decays exponentially to zero. Similar data was obtained for the $\nu = 2$ transition of SO at 136.45 GHz.

The measured decay rate of 1.5 ms for the excited vibrational states of SO is very nearly equal to the growth rate of the SO, $\nu = 0$ state. Evidently the latter can be attributed to the increased concentration of SO, $\nu = 0$ resulting from the decay of the vibrationally excited SO molecules. While we did not look for vibrational states with $\nu > 2$, it is evident that a significant amount of vibrationally excited SO is produced by the photolysis. The translational energy distribution of the photofragments of SO_2 at 193 nm was investigated by Freedman et al[10] who concluded that a large amount of vibrationally excited SO should be produced. On the other hand, similar measurements by Kawasaki et al[11] led them to conclude that relatively little vibrational excitation of the SO product should result from the photolysis. The available energy for product excitation is given by $E_{AVL} = h\omega + E_I - D_o$, where E_I is the internal energy and D_o is the bond dissociation energy of SO_2 and is about 19.5 kcal/mol at $\lambda = 193$ nm using numerical values from Ref. 11. Thus the production of vibrationally excited SO up to $\nu = 6$ is energetically possible.

Since the absorption coefficients, γ_0 are well known for most rotational transitions, the measured absorption signal can be used to determine the actual concentration of a given species. For small concentrations, the voltage change, ΔV at the output of the spectrometer[6] is given by

$$\Delta V = \frac{V_0 c \, Q_L \eta \gamma_0 C_0}{2\pi\nu_0} \tag{1}$$

where V_0 is the total voltage at the spectrometer output, ν_0 is the microwave frequency, Q_L is the Q of the loaded cavity, c is the velocity of light, η is the filling factor and C_0 is the fractional concentration of the absorbing species. The molecular concentration, [X] is then given by

$$[X] = 3.24\times10^{13} \, pC_0 \quad (molec/cm^3) \tag{2}$$

where p is the cell pressure in mTorr and a temperature of 298K is assumed.

For the SO (4,3)-(3,2) transition, the pressure broadened peak absorption coefficient[9] is $\gamma_0 = 2.97\times10^{-2}$ cm^{-1} for the linewidth parameter, $(\Delta\nu)_1 = 4.4$ MHz/Torr determined by measuring the line profile. With this absorption coefficient and the quantities $V_0 = 230$ mV, $\Delta V = 1.6$ mV, $Q_L = 73000$, and a filling factor of 0.5 as described above we find for the SO concentration, [SO] $= 1.2\times10^{12}$ molec/cm^3.

Since the cross section ($\sigma = 1.1\times10^{-17}$ cm^2) for SO_2 photolysis at 193 nm is known[8], it is possible to estimate the concentration of SO produced in the spectrometer cavity by measuring the laser intensity, I_0. The latter was determined by measuring the laser energy with a Scientech power meter, the cross-

sectional area of the beam at the cavity position and estimating the window, mirror and lens losses. I_o was found to be 4.3×10^{14} photons/cm^2 per shot. Since the absorbing medium is optically thin, $[SO] = \sigma I_o [SO_2]$ yielding the value $[SO] = 1.38 \times 10^{12}$ molec/cm^3. This result is in very good agreement with the value measured above with the spectrometer considering all of the approximations involved in obtaining it.
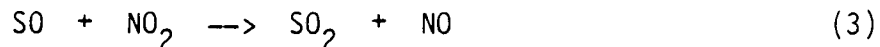
B. Detection of CS

As a further example of the detection of transient species, a mixture of CS_2 diluted in Ar was photolyzed at 193 nm. The photodissociation cross section of CS_2 at this wavelength is quite large ($\sigma \sim 2 \times 10^{-16}$ cm^2) making it a convenient source of CS molecules for chemical reaction studies[12]. In addition, the photolysis of CS_2 is known[13] to produce CS in a number of excited vibrational states with excitation up to at least $\nu = 7$ previously observed[13]. The microwave spectrum of CS has been extensively studied and the transition frequencies in the 140 GHz region for vibrational levels up to $\nu = 20$ have been determined[14].

The CS_2 mixture in Ar was generated by introducing the liquid reagent into a flowing Ar stream using a calibrated syringe pump. Since the vapor pressure of CS_2 is 350 Torr at room temperature[12], all of the liquid is evaporated in the Ar stream. The flow rates were adjusted to produce a 10% concentration of CS_2 and the mixture was introduced to the cavity at a cell pressure of 100 mTorr. The microwave spectrometer was tuned to a frequency of 142.71 GHz corresponding[14] to the $\nu = 4$ vibrational level. The resulting absorption signal is shown in Fig. 2. The CS signal decays exponentially with a time constant of 1.15 ms.

The rapid vibrational relaxation is attributed[12] to interaction with atomic sulfur also produced in the photolysis. This and similar results obtained for the $\nu = 3$ level show that good microwave absorption signals for this species can readily be obtained with the present apparatus.

C. Reaction Rate of SO with NO_2

The rate coefficient at 298 K for the relatively fast reaction

$$SO + NO_2 \longrightarrow SO_2 + NO \qquad\qquad (3)$$

has been reported in two recent studies[8,15]. Since these measurements have been made using two quite different methods (laser photolysis plus chemiluminescence SO detection[8] and discharge-flow with mass spectrometric detection of SO[15]) with results in good agreement ($(1.48 \pm 0.20) \times 10^{-11}$ and $(1.36 \pm 0.10) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} respectively), the reaction is a good candidate for evaluating the present technique.

SO was produced as described above by photodissociation of SO_2 diluted in Ar at a total cell pressure of 550 mTorr. NO_2 was added to the cell through a second needle valve. The concentration of the added NO_2 was determined by measuring the change in the cell pressure. At the pressures used, the concentration of the dimer, N_2O_4 is entirely negligible. The frequency of the microwave spectrometer was tuned to the SO, $\nu = 0$ rotational transition and the SO decay rate was fitted to an exponential time constant for a number of different NO_2 concentrations.

In order to maintain psuedo-first-order conditions for the reaction kinetics, the inequality [SO] << [NO_2] was maintained in all cases. This was done by reducing the concentration of SO_2 in the Ar mixture as required and by replacing the high reflectivity laser mirror with an uncoated quartz plate to reduce the laser intensity.

Figure 3 shows the SO absorption signal for an NO_2 concentration of zero in (a) and for a concentration of 5.2×10^{12} molec/cm^3 (added pressure 1.6 mTorr) in (b). The data in both curves represent an average of 4000 laser shots at a rate of 10 Hz (6.7 minutes per run). The initial SO concentration can be estimated from the peak signal amplitude in curve (a) and the cell pressure, the other conditions being the same as in Fig. 1. We find the value [SO] = 2.1×10^{11} molec/cm^3 which satisfies the above inequality. The solid line in (b) is the result of an exponential fit of the measured data with a time constant of 12.9 ms.

In Fig. 4 is shown a plot of the SO decay rate as a function of the NO_2 concentration. From a linear least squares fit of the data we obtain for reaction (3), the value $k_3 = (1.46 \pm 0.12) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1}, where the quoted uncertainty is 2σ as obtained from the fitting procedure. The intercept of the fitted line with the y-axis is zero to within the uncertainty of the fit. The resulting value for k_3 is in excellent agreement with the results obtained previously[8,15] and provides good supporting evidence for the validity of the methods used.

III. DISCUSSION

A microwave spectrometer system for detecting gaseous molecular species produced by excimer laser photolysis has been described. We have demonstrated its

operation by detecting the transient species SO and CS in various vibrational states and have shown that quantitative measurements of the concentration of these species can be made with a minimum of difficulty. This capability and the ability to detect stable product species of larger molecular weight should be useful in kinetic studies of reactions in which psuedo-first-order rate conditions are difficult to achieve. Finally we have applied the system to a measurement of the reaction rate of SO with NO_2 with results in good agreement with values obtained previously by other methods.

In order that the amplitude of the spectrometer output signal accurately reflect the actual concentration of the species being measured, it is important that the system be in thermal equilibrium. This is, of course, a necessary condition in any measurement in which specific transitions are being probed. On the other hand, the product state distributions immediately following photolysis are definitely not in thermal equilibrium as shown, for example, in studies[13,16] of CS_2 and NO_2 photolysis. Therefore, it is necessary to wait until equilibrium is established before making a measurement.

In the case of rotational transitions, the significant relaxation rates include[17] the rotational-rotational rate, τ_{RR} and the rotational-translational rate, τ_{RT} . The rate τ_{RR} can be inferred directly from a measurement of the linewidth (assuming $T_1 = T_2$) of the rotational transitions. For the case of SO reported here, at a pressure of 500 mTorr, the observed linewidth (see Section II,A) is $\Delta\nu = 2.1 \times 10^6$ Hz and the corresponding relaxation rate[17] is given by $\tau_{RR} = 1/(2\pi\Delta\nu)$ or 7.6×10^{-8} s, much shorter than the time scale of our observations. τ_{RT} is expected[17] to be somewhat longer than τ_{RR}. However, even if τ_{RT} is 1000 times longer than τ_{RR}, we would expect the rotational system to be in equi-

librium with the room temperature Ar bath over our measurement time scale. The vibrational relaxation rate, τ_{VT} is of course, much longer than the above rates as evidenced by measurements such as those already presented above.

In summary, the results obtained above have shown that the millimeter-wave spectroscopic technique in combination with laser photolysis merits further investigation as a highly sensitive species probe in kinetics research. Its principal virtues in this respect include its high specificity, non-invasive character, and ability to detect stable reaction products.

ACKNOWLEDGEMENTS

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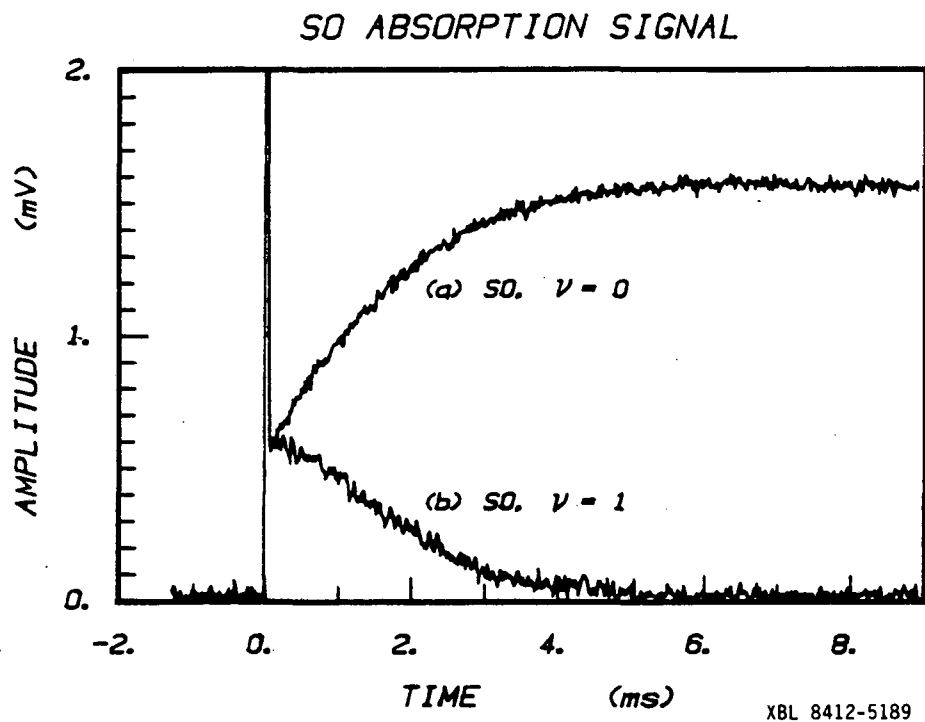
SO ABSORPTION SIGNAL

Fig. 1   SO absorption signal for (a) ground vibrational level at 138.17 GHz
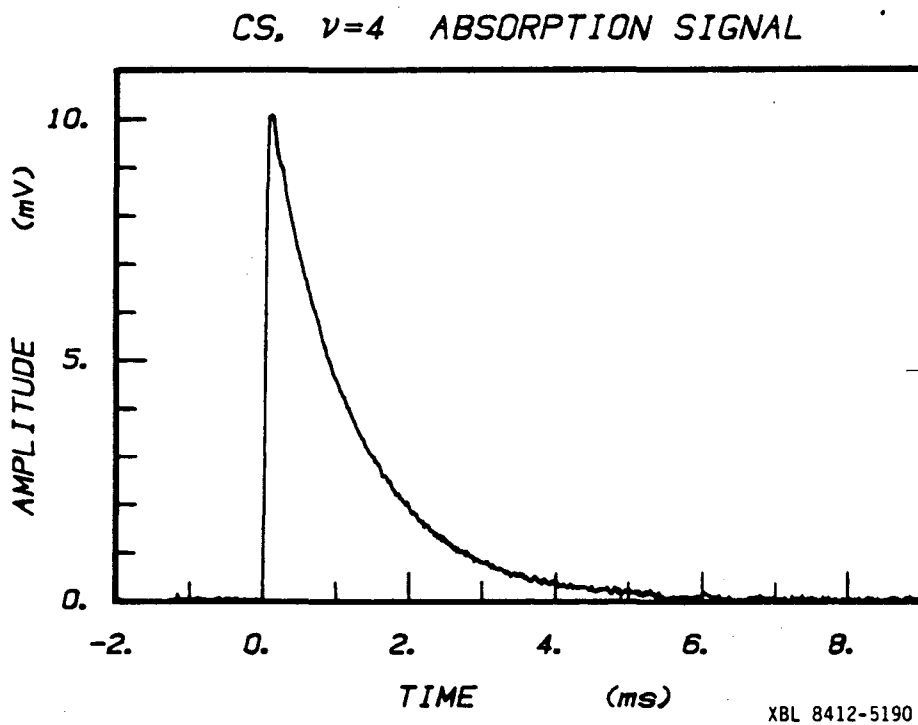and (b) first excited vibrational level at 137.28 GHz.

CS, ν=4   ABSORPTION SIGNAL

Fig. 2   Absorption signal for CS, ν = 4 vibrational level at 142.71 GHz.
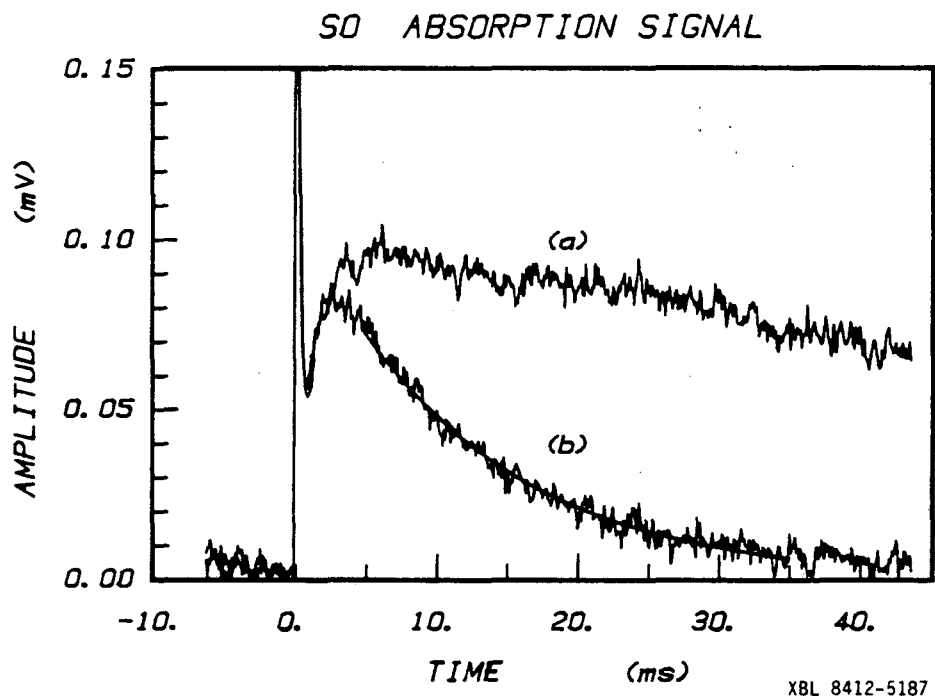
SO ABSORPTION SIGNAL

Fig. 3 Decay of SO absorption signal for (a) $[NO_2] = 0$ and (b) $[NO_2] = 5.2 \times 10^{12}$ molec/cm^3. Initial SO concentration approximately 2.1×10^{11} molec/cm^3.
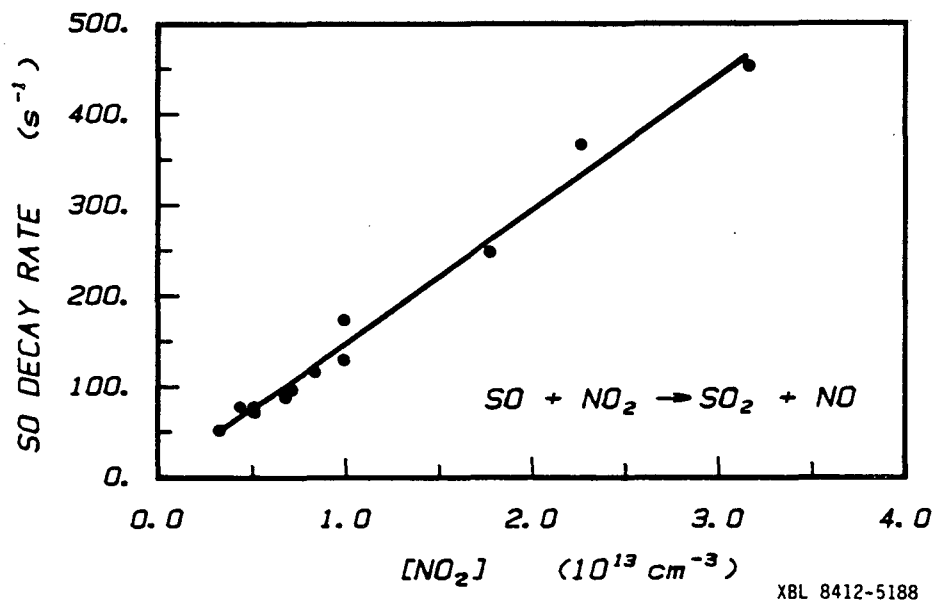

Fig. 4 SO decay rate versus NO_2 concentration. $[Ar] = 540$ mTorr; $[SO_2] \sim 12$ mTorr.