

High-resolution infrared diode laser spectroscopy of $\text{SO}(^3\Sigma^-)$ in a secondary-slit supersonic expansion \star

Z.S. Huang ¹, J.E. Verdasco ², C. Wittig and R.A. Beaudet

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, USA

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A two-stage pulsed expansion method is reported in which free radicals are generated by laser photolysis just prior to expansion. The technique is applied to the $2\leftarrow 0$ vibrational overtone band of $\text{SO}(X^3\Sigma^-)$. Essentially complete SO_2 photolysis is achieved. Following expansion, SO rotational temperatures are between 16 and 50 K depending on the SO_2 concentration.

1. Introduction

Spectroscopic studies of chemical intermediates further our understanding of the mechanisms and dynamics of elementary reactions. Such studies were pioneered by Smalley and co-workers [1,2], who photolyzed suitable precursors prior to or during supersonic expansion to produce radicals which were subsequently probed by LIF. Advantages such as extensive cooling were immediately apparent. Since the radicals are usually formed in excited states, cooling their internal degrees of freedom results in simplified spectra, facilitating studies of complicated species. These advantages were exploited by Miller and co-workers who obtained high-resolution spectra of free radicals [3]. By using pulsed supersonic expansions in conjunction with a pulse-amplified ring dye laser, they obtained sub-Doppler-resolution, rotationally resolved LIF spectra of a number of aromatic hydrocarbon radicals, e.g., C_5H_5 , C_6F_6^+ , etc. [4–6]. Analyses yielded insight into the structures and properties of these fascinating and important

species, whereas 300 K spectra of these species are so congested that a complete understanding would not have been possible [7]. Recent developments include high-resolution spectroscopy of complexes such as OH-Ar [8,9].

Most spectroscopic studies of radicals using supersonic expansions have involved electronic transitions because of the availability of sensitive probes such as LIF. Since gas densities associated with supersonic expansions are generally low, it is difficult to apply IR methods, due to insufficient detection sensitivity. Thus, most IR spectroscopic studies of radicals have been conducted using long path-length cells [10], where resolution is often limited by Doppler broadening and level distributions are dictated by ambient temperatures. Despite these shortcomings, many important radicals have been studied using this approach, although most of these species have been fairly light [10]. There are good reasons to take advantage of the cooling associated with supersonic expansions in order to extend such studies to heavier and more complex systems.

Following the pioneering experiments of Amirav et al. [11], slit supersonic expansion sources have been used successfully to increase the pathlength, hence optical thickness, across the expansion. This has facilitated IR spectroscopic studies of van der Waals complexes, and in our experiments a 38 mm \times 0.15 mm pulsed slit valve has been used in conjunction with a tunable IR diode laser [12–14].

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¹ Present address: Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA.

² Present address: Departamento de Química-Física, Facultad de Química, Universidad Complutense de Madrid, 28040 Madrid, Spain.

By exploiting a rapid-scan technique, in which typically a 1 cm^{-1} spectral region (4000 resolution elements) is recorded with a single valve opening, a large number of van der Waals complexes have been studied. This approach has the advantage of low temperatures and small Doppler widths (e.g., 20 MHz), due to the flow characteristics of the slit expansion. Consequently, rotationally resolved spectra can be obtained for heavy systems [13,14].

The above developments underscore the feasibility of carrying out IR spectroscopic investigations of free radicals in supersonic expansions, and there are now reports of such spectra. Curl and co-workers report $\text{NH}_2 \nu_1$ transitions following 193 nm NH_3 photolysis [15], with the excimer laser output focused directly into a section used to convert a pin-hole expansion into a slit expansion. Signals were recorded as transient infrared absorptions of a computer-controlled color center laser. Rotational temperatures (T_{RS}) were 25 K and linewidths were ≈ 300 MHz (due presumably to incomplete conversion of the pin-hole expansion into a uniform slit expansion). On the other hand, Cohen et al. employed a cw planar jet in conjunction with a tunable far-infrared (FIR) laser [16]. They produced NH_2 by focusing the excimer laser output directly into the nozzle aperture of an expansion containing NH_3 . The FIR laser probed the transient absorptions of NH_2 rotational transitions: T_{R} was 18 K and linewidths were ≤ 2 MHz. Since the photolysis sources in such experiments are usually pulsed, it is advantageous to develop a pulsed slit expansion to match the excimer laser duty cycle.

In this Letter, we report a two-stage pulsed slit expansion method in which free radicals are generated by laser photolysis prior to the expansion. The technique is applied to vibrational overtone spectroscopy of $\text{SO}(X^3\Sigma^-)$. Some transitions exhibit absorptions as high as 1% indicating quite high concentrations, and $T_{\text{R}}=16$ K indicates effective cooling. Linewidths are ≈ 60 MHz, limited primarily by diode laser frequency instability. Unique features of the method will be discussed.

2. Experimental

A number of techniques have been used to pro-

duce beams of radicals for spectroscopic studies [3] as well as scattering experiments [17]. These include pyrolysis, discharge, mercury photosensitized reaction, etc. Although they have proven successful for electronic spectroscopy and reactive scattering experiments, there is no report of applications to IR spectroscopy with its requirement of higher concentrations. On the other hand, photolytic radical production offers several advantages. Photodissociation is often selective, producing specific products, and the needed excimer lasers are available. In addition, precursors often have high absorption cross sections, making it feasible to produce high radical concentrations. In the experiments reported below, $\text{SO}(^3\Sigma)$ is produced by



with an absorption cross section of $\approx 10^{-17}\text{ cm}^2$. Thus, laser fluences of $\approx 250\text{ mJ cm}^{-2}$ are adequate to convert nearly all of the precursor molecules in the optical path into products.

A complication associated with producing jet-cooled radicals lies in the fact that these species undergo recombination reactions. Thus, it is critical to introduce them just prior to (or even in) the expansion, to minimize the time available for recombination. On the other hand, since these species are often produced with internal excitation, it is desirable to allow sufficient time for thermalization. The present experiment is designed to accommodate these conflicting requirements.

The pulsed valve has been described in detail elsewhere [13]. It was used without modification except that the slot size was increased to $38\text{ mm} \times 0.5\text{ mm}$ to enhance the throughput. A wedge on the front of the valve serves as a buffer volume for the expansion (see fig. 1). The wedge is 40 mm long, 10 mm high, and 2.5 mm wide at the bottom, and consists of two thin pieces of fused silica. At the tip, the silica pieces are adjusted with a spacer to form a $40\text{ mm} \times 0.2\text{ mm}$ slit. When the valve opens, the buffer volume is pressurized and supersonic expansion proceeds through the second slit. The gas pulse profile is shown in fig. 1. It has a width of 2 ms, a rise time of 0.25 ms, and a fall time (90–10%) of 1.5 ms, which is consistent with the buffer volume. The fact that the expansion is supersonic is verified by observing spectra of van der Waals complexes.

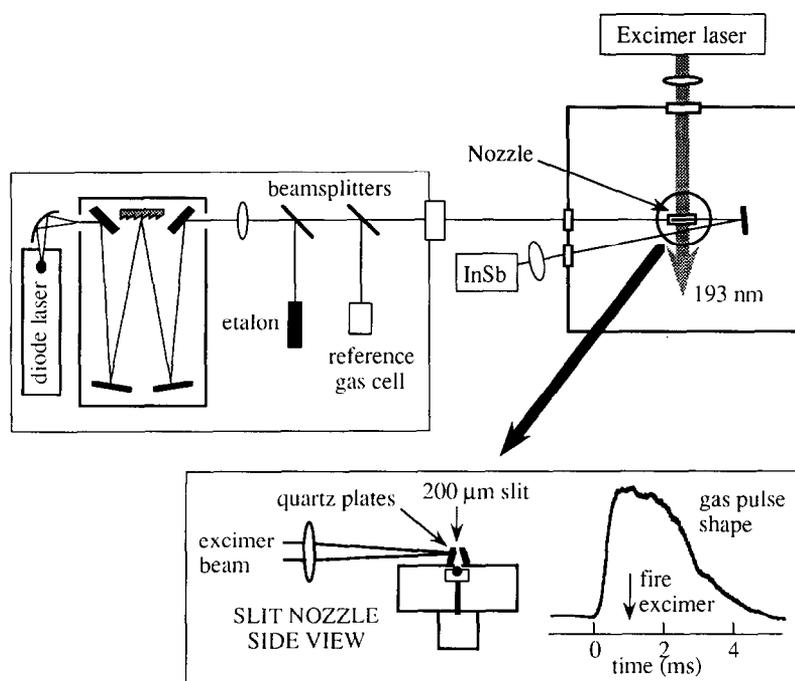


Fig. 1. Schematic of the experiment. The diode laser system is on an optical table and the excimer laser is in a screen room. The gas pulse temporal profile was obtained by monitoring $N_2O P(1)$; the width is similar to that reported previously for the original pulsed valve, indicating that the adaptor does not degrade valve performance.

Photolysis was achieved by focusing the excimer laser radiation to a $40 \text{ mm} \times 1 \text{ mm}$ area inside the buffer volume using a cylindrical lens, with the radiation passing through the two windows forming the wedge. The distance between the focus and the nozzle exit was adjusted in situ, making optimization straightforward. Since the windows remain clear where the radiation passes, it was not necessary to clean the nozzle. With the present two-stage scheme, ablation of nozzle material is also avoided. Initially, radiation was focused directly into the slit, and although signals were as good as with the present configuration, the valve was eventually damaged by ablation.

The overall experiment is illustrated schematically in fig. 1. It is an improvement over our previous apparatus [12–14] and new features are discussed here. The excimer laser is enclosed in a screen room to eliminate rf interference, and the beam enters the expansion chamber through a MgF_2 window after passing through a 50 cm focal length cylindrical lens. The chamber is pumped by a vapor jet booster (Edwards

18B4A, 4000 ℓ/s) backed by a roots blower and a mechanical pump. Typical operating pressures are 1–10 mTorr. The chamber is connected to the pump by a 30 cm diameter inverted U-shaped pipe which serves both to trap pump oil and act as a dump for the pulsed expansion gas.

Tunable IR radiation is obtained from a Laser Analytics diode laser system. After passing through the mode-selecting monochromator, the beam makes a single pass through the expansion and is detected by an InSb detector. A reference gas cell and an air-spaced étalon are used for absolute and relative frequency calibrations. The étalon is an internally coupled confocal étalon (Laser Analytics, SP5945) whose performance has been discussed in detail [18,19]. Compared with Ge étalons, it offers much better thermal and mechanical stability and hence provides more precise frequency markers.

Data acquisition is controlled by a computer and a 12-bit transient digitizer is used to monitor absorptions. Both étalon and reference signals are chopped and detected using lock-in amplifiers whose

outputs are monitored by a 16-channel A/D converter. Triggering is such that the valve opens during a quiet period of the compressor cycle, and the excimer laser is fired after an expansion has formed. A few microseconds later, the digitizer and oscilloscope are triggered. The digitizer samples the waveform prior to and after the trigger, and the computer integrates both waveforms and subtracts the pre-trigger value from the post-trigger one, thus cancelling the baseline. Immediately after the absorption signal is digitized, the A/D convertor is initiated to read both the étalon and reference signals. At the same time, the diode laser is slowly scanned by using the internal sweep generator of the laser control module. The computer is also interfaced to a stepping motor, which adjusts the monochromator setting to allow maximum transmission of the selected laser mode.

All gases were used without further purification. Ar and He carriers are ultra-high purity (99.9995%). Sulfur dioxide (MG Industries) has a stated purity of $\geq 99.985\%$. Stagnation pressures behind the nozzle were typically 3–5 atm.

3. Results and discussion

The IR spectroscopy of $\text{SO}(^3\Sigma^-)$ has been the subject of several investigations [20,21]. Of most relevance to the present report is the work by Kanamori et al. [22], who recorded $\Delta v=1$ absorption spectra ($0 \leq v'' \leq 5$) in the 1100 cm^{-1} region using an IR diode laser. More recently, fundamental and overtone bands were reported by Burkholder et al. using a Fourier transform spectrometer and a multipass absorption cell [23]. These studies make it straightforward to understand and assign SO spectra, thereby facilitating the characterization and optimization of the present machine.

Fig. 2 shows a typical spectrum taken in the 2270 cm^{-1} region. The top panel displays the reference CO_2 absorption spectrum used for absolute frequency calibration; the étalon trace is not included. The bottom trace shows a portion of the $2 \leftarrow 0$ overtone band of jet-cooled SO; each data point is the average of three laser firings at 3 Hz. The diode laser scan rate was 13–15 MHz/point. Spectra contain up to 4000 points and typically cover $1\text{--}2 \text{ cm}^{-1}$, de-

pending on the laser mode. About an hour is required for a scan.

Although the observed transitions are overtones, it is clear that signal to noise ratios are quite satisfactory, and absorptions of $\approx 1\%$ were observed, indicating high radical concentrations. By comparing these absorptions to those of fundamental rovibrational transitions of a strong IR absorber, we deduce that expansion cooled SO is present at concentrations as high as several percent of the initial SO_2 concentration. This is consistent with the above assessment that SO_2 can be almost completely photodissociated in the focal region behind the nozzle.

Approximately 40 transitions were observed, and the frequencies agree with those reported by Burkholder et al. [23]. Uncertainties in absolute frequencies of $\pm 0.0010 \text{ cm}^{-1}$ derive from the infrared standards [24]. Relative uncertainties of $\pm 0.0005 \text{ cm}^{-1}$ derive primarily from the fact that the data were taken in 13–15 MHz increments. Uncertainties can be lessened by slower scan rates.

It is useful to examine the effect of the expansion on SO internal state distributions. SO_2 photodissociation has been studied extensively [25], and 193 nm photolysis produces $\text{SO}(X^3\Sigma^-)$ with 70 and 20% in $v=2$ and 1, and with rotational populations peaked at $N=28$ and 38, respectively [26,27]. Thus, the present case offers a critical test of cooling ability. The three spin components ($F_1: J=N+1$, $F_2: J=N$, $F_3: J=N-1$) have different peak heights ($F_1 > F_2 > F_3$), as seen in fig. 2. This is not due to spin polarization via photodissociation, since the nascent distribution has $F_3 > F_1 > F_2$ [27]. On the other hand, the energy levels of the three components differ by as much as 6 cm^{-1} . Although intensity differences among these transitions are difficult to discern at 300 K [27], they are significant at low temperatures. The lower energy F_1 components are more intense, indicating that the spin rotation components are cooled efficiently in the expansion, i.e. the spin components are in equilibrium with the rotational degrees of freedom.

Fig. 3 shows a Boltzmann rotational distribution with $T_R=50 \text{ K}$. This high temperature is attributed to the high SO_2 concentration used in the expansion (5% in Ar). Under such conditions, it is likely that extensive SO_2 clustering inhibits cooling of SO. To verify this, we investigated cooling of CO_2 under

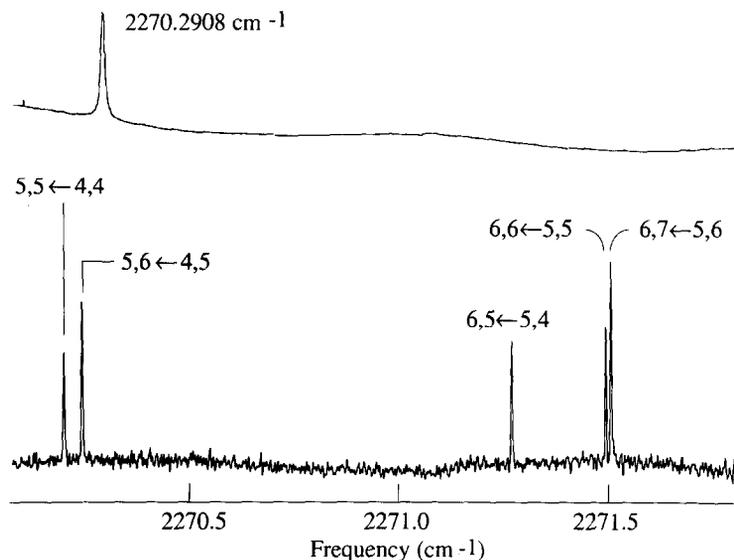


Fig. 2. Portion of the SO $2 \leftarrow 0$ overtone spectrum (4000 data points); assignments are of the form $N', J' \leftarrow N'', J''$.

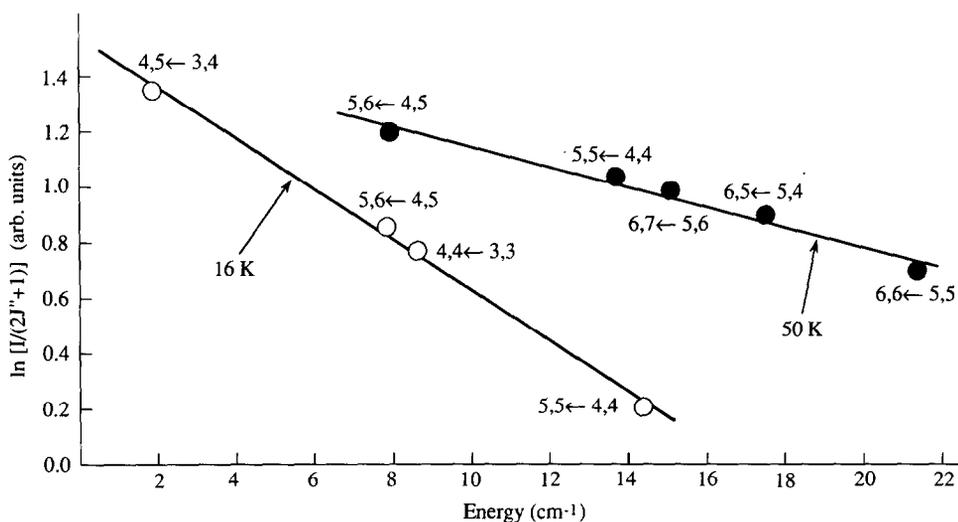


Fig. 3. Boltzmann plots showing rotational temperatures: dark circles are for 5% SO_2 in Ar; open circles are for 1% SO_2 in Ar. The horizontal axis is the energy of the lower level in the transition; assignments are included. Solid lines are least-squares fits.

identical conditions, i.e. seeding a small amount of CO_2 ($< 0.1\%$) into the mixture and measuring T_R for CO_2 . The same T_R was obtained as for SO, indicating that T_R is limited by the expansion itself. Better cooling was observed with more dilute mixtures. Fig. 3 shows an SO rotational distribution obtained using 1% SO_2 in Ar, for which $T_R = 16$ K.

Cooling is improved by less clustering. These results indicate that the present approach is effective in producing cold radicals for spectroscopic studies. As discussed earlier, although short-term ($< 1 \mu\text{s}$) laser frequency stability (< 20 MHz) is comparable to Doppler broadening in the expansion [12,13], performance can be degraded by averaging longer term

frequency drift. The linewidths observed in this study are typically 60 MHz, which is dominated by frequency instability of the diode laser. Better resolution can be achieved by stabilization or a higher resolution laser.

4. Conclusion

A method has been developed to generate high concentrations of cold radicals to facilitate IR spectroscopic studies, and it has been applied successfully to the SO overtone spectrum. It will be possible to study more complicated intermediates by taking advantage of the low temperatures and narrow linewidths provided by the supersonic slit expansion. Several improvements can also be made to further increase S/N. The buffer volume can be decreased to enhance the intensity of the free jet, and multipassing will increase the optical thickness and hence sensitivity. Thus, this approach may well become a powerful tool for studying properties and structures of transient radicals.

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