

# Direct evidence for $\nu_1$ -mode excitation in the infrared multiphoton excitation of $\text{SO}_2$

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We investigated the infrared multiphoton excitation of  $\text{SO}_2$  in bulk samples and in a supersonic jet with the 9R(22), 9R(32), and 9P(32)  $\text{CO}_2$ -laser lines. Coherent anti-Stokes Raman spectra reveal unambiguously that only the  $\nu_1$ -mode at  $1151.3 \text{ cm}^{-1}$  is actually pumped; no  $2\nu_2$  overtone pumping at  $1035.2 \text{ cm}^{-1}$  is observed. From the spectra we directly determine the anharmonic constants  $x_{11} = -3.65 \pm 0.06 \text{ cm}^{-1}$  and  $x_{12} = -3.3 \pm 0.3 \text{ cm}^{-1}$ .

## 1. Introduction

The study of infrared multiphoton excitation of small polyatomic molecules such as  $\text{SO}_2$  has received considerable attention in the literature [1–6]. This molecule is representative of small size systems which, according to the quasicontinuum model [7], can be difficult to excite to high vibrational levels since the density of states at low excitation is relatively small. While observation of inverse electronic excitation in  $\text{SO}_2$  clearly demonstrated that infrared multiphoton excitation to high vibrational levels is possible [1], it is not clear from these studies through which vibrational mode(s) the excitation proceeds. Using time-resolved coherent anti-Stokes Raman spectroscopy (CARS) [8,9], we are able to directly observe the vibrational mode populations of an excited molecular ensemble and hence accurately determine which modes are excited.

The  $\text{SO}_2$  molecule is an asymmetric top ( $C_{2v}$  symmetry) having three vibrational modes (table 1). Since the  $\nu_1$ -mode is Raman active, we can pump any infrared active mode while simultaneously observing the  $\nu_1$  CARS spectrum. For an anharmonic potential the vibrational energy levels are given by [10]

Table 1

Vibrational frequencies for  $\text{SO}_2$  (refs. [14,15]) and  $\text{CO}_2$ -laser lines used in this experiment

$\text{SO}_2$ mode	$\nu$ ( $\text{cm}^{-1}$ )	Activity	$\text{CO}_2$ -line	$\nu$ ( $\text{cm}^{-1}$ )
$\nu_1$	1151.3	R, IR	9R(32)	1085.8
$\nu_2$	517.6	R, IR	9R(22)	1079.8
$2\nu_2$	1035.2	IR	9P(32)	1035.5
$\nu_3$	1361.7	R, IR		

$$E(v_1, v_2, v_3) = \sum_{i=1}^3 \omega_i(v_i + \frac{1}{2}) + \frac{1}{2} \sum_{i,j=1}^3 x_{ij}(v_i + \frac{1}{2})(v_j + \frac{1}{2}), \quad (1)$$

where  $v_i$  is the vibrational quantum number of mode  $i$ ,  $\omega_i$  the mode frequency, and  $x_{ii}$  and  $x_{ij}$  are the self and cross anharmonicities, respectively. For such a potential the CARS signal contains three main features: (1) a ground state peak at the resonant frequency of the Raman probed mode, (2) peaks shifted by multiples of  $2x_{ii} \text{ cm}^{-1}$  from the ground state which correspond to excited levels of the Raman probed mode  $i$ , and (3) peaks shifted by multiples of  $x_{ij} \text{ cm}^{-1}$  from each of the peaks in (1) and (2) corresponding to population in any other vibrational mode  $j \neq i$  (see table 2 below). The intensity of each peak is proportional to the square of the population difference

between the two vibrational levels of the corresponding Raman transition [9].

Ambiguity in previous infrared multiphoton excitation experiments on  $\text{SO}_2$  arose primarily because there is no available  $\text{CO}_2$ -laser line resonant to the  $\nu_1$ -mode. The 9R(32) line is a strong  $\text{CO}_2$ -laser line close to  $\nu_1$ -mode resonance (see table 1); the 9P(32) line is resonant with the first overtone of the  $\nu_2$ -mode; and the 9R(22) line, one of the more intense  $\text{CO}_2$  lines in the 9  $\mu\text{m}$  region, lies between these two bands (71  $\text{cm}^{-1}$  detuned from  $\nu_1$  and 44  $\text{cm}^{-1}$  from  $2\nu_2$ ). Because infrared multiphoton excitation is intensity dependent for a small molecule like  $\text{SO}_2$  [2,11], the strong 9R(22) line is historically the one most often utilized in the literature. It is not immediately clear, however, which of the two aforementioned modes undergoes infrared multiphoton excitation when this line is used.

## 2. Experiment and results

The experimental setup has been described previously [12]. Briefly, we use 100 ns pulses from a 10 Hz grating-tuned TEA  $\text{CO}_2$ -laser focused down to a 100  $\mu\text{m}$  spot size by a 0.15 m focal length cylindrical lens to pump  $\text{SO}_2$  (Matheson, anhydrous grade). The experiments were carried out in bulk samples at 13 kPa (100 Torr) and in a pulsed supersonic jet at variable distance  $x$  from a jet nozzle of diameter  $D=0.94$  mm. Varying the distance  $x$  allows fine control of the degree of adiabatic cooling and collision rate. At  $x/D=10$  the vibrational temperature is about 50 K and the collision rate about 0.1 collisions per 100 ns, the width of the excitation pulse. Close to the nozzle, at  $x/D=2$ , the vibrational temperature is closer to room temperature and the collision rate about 10 collisions per 100 ns. The Raman active  $\nu_1$ -mode is probed using a multiplex CARS technique [13]. The probe beams, two narrowband (0.05  $\text{cm}^{-1}$ ) at 532 nm and one broadband (100  $\text{cm}^{-1}$ ) centered at 567 nm, are phase-matched in a BOX-CARS geometry [9] aligned perpendicular to the infrared and molecular beams. The time delay between pump and probe can be adjusted electronically; the results presented here were obtained at a delay of 200 ns. The signal is dispersed by a 1 m grating spectrograph and collected with a Hamamatsu streak cam-

era, which is synchronized with the  $\text{CO}_2$ -laser (40 ns jitter) and which yields a spectrally and temporally resolved spectrum. The spectra are typically averaged over 1000 shots to improve the signal-to-noise ratio. The resulting spectra have a resolution of 0.1  $\text{cm}^{-1}$ .

The multiplex spectrometer is extremely useful since it produces the entire  $\nu_1$ -spectrum in a single shot, revealing all excited modes, self and cross anharmonicities, and relative vibrational populations. We studied the effect of using different  $\text{CO}_2$ -laser lines on the  $\nu_1$ -spectrum in order to determine through which mode(s) the infrared multiphoton excitation proceeds.

Fig. 1 shows spectra obtained in bulk samples. In fig. 1a the large peak at 1151  $\text{cm}^{-1}$  is the ground state peak of the unexcited molecules at the resonant frequency of the probed  $\nu_1$ -mode. Following 2  $\text{J}/\text{cm}^2$  pumping with the 9R(22) line, a number of excited peaks with a distinct, repeating pattern appear, see fig. 1b. The strongest of these new peaks (b) appear at positions shifted by a multiple of  $-7.3$   $\text{cm}^{-1}$  from the ground state peak (a). Furthermore, smaller peaks (c) are visible at a shift of  $-3.3$   $\text{cm}^{-1}$  from each of the peaks a and b.

Spectra obtained in a supersonic jet appear much cleaner and exhibit fewer peaks compared to the bulk data, see figs. 2 and 3. In general, excitation is less efficient in the jet than in bulk samples. Fig. 2 shows a ground state spectrum taken close to the nozzle ( $x/D=2$ ). When the intensity scale is expanded (see fig. 3a), the thermal vibrational population of the excited states becomes visible. These peaks lie at the same spacing as before,  $-7.3$  (b) and  $-3.3$   $\text{cm}^{-1}$  (c), but now only one of each type of peak is visible. Following 9R(22) excitation (fig. 3b), peak b dramatically grows and the ground state peak diminishes, while peak c is unchanged. Spectra taken far from the nozzle ( $x/D=10$ ) show only a ground state peak. We did not observe any depletion of this peak under these circumstances, not even at the maximum available laser fluence of 2.5  $\text{J}/\text{cm}^2$ .

When we tuned to the 9R(32) line, which is closer to resonance with the  $\nu_1$ -mode, a maximum fluence of only 1  $\text{J}/\text{cm}^2$  was attainable. Yet even at this reduced fluence identical excitation to the 9R(22) data was observed in the bulk, indicating a much higher pumping efficiency at this wavelength.

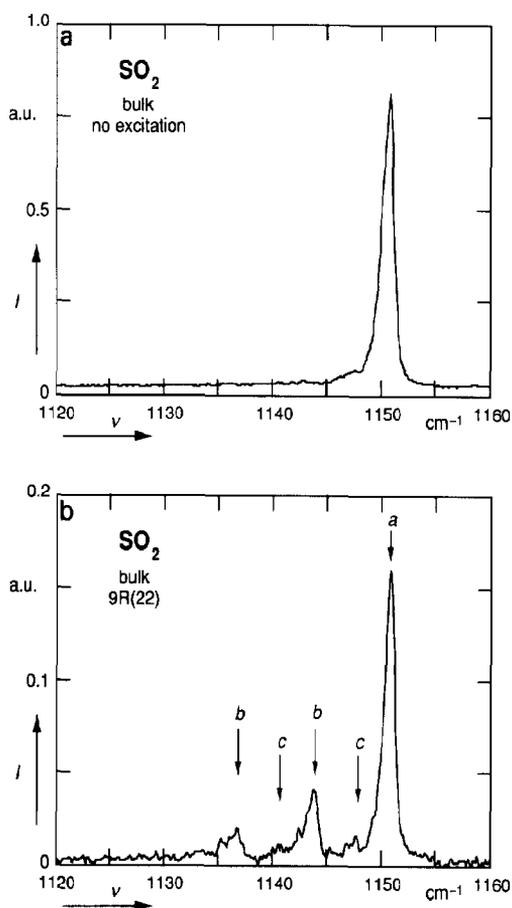


Fig. 1. Vibrational CARS spectrum of  $\text{SO}_2$ . (a) At room temperature and a pressure of 13 kPa (100 Torr). The large peak corresponds to the  $\nu_1$  ground state. (b) At a pressure of 13 kPa (100 Torr) 1.2  $\mu\text{s}$  after 2  $\text{J}/\text{cm}^2$  excitation with the 9R(22)  $\text{CO}_2$ -laser line. A number of excited state peaks b and c appear.

Finally, we attempted to pump the  $\text{SO}_2$   $\nu_2$  first overtone band with the 9P(32) line. However, even with as much as 3  $\text{J}/\text{cm}^2$  of infrared fluence in bulk and beam samples no excitation beyond the thermal excitation shown in fig. 2a was observed.

### 3. Discussion

The above sequence of observations suggests that the  $\text{CO}_2$ -laser excites the  $\nu_1$ -mode. This is substantiated by the higher efficiency of the 9R(32) excitation, since 9R(32) is closer to resonance with  $\nu_1$  than with  $2\nu_2$ , and by the fact that 9P(32), in res-

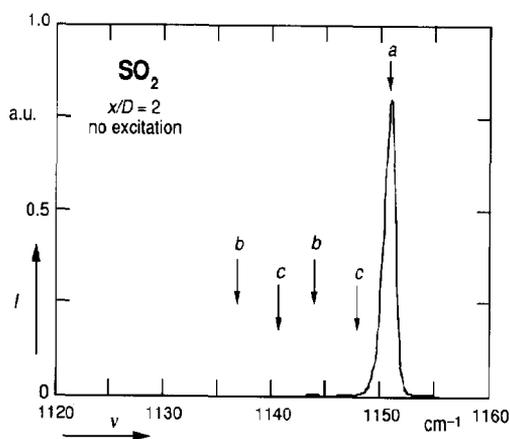


Fig. 2. Vibrational CARS spectrum of  $\text{SO}_2$  obtained in a supersonic beam at  $x/D=2$ . Notice the reduced thermal population of peak c compared to fig. 1a.

onance with the  $2\nu_2$  overtone, produces no observable excitation at all. There are no other overtone or combination bands in this frequency range with significant absorption [14,15]. Hence we are led to the conclusion that figs. 3a and 3b must be a direct observation of infrared multiphoton excitation in the  $\nu_1$ -mode.

Table 2 lists the anharmonic shifts of all possible peaks that might appear in the  $\text{SO}_2$  CARS spectrum. To establish the identity of the b and c peaks we first note the absence of both peaks far from the nozzle without  $\text{CO}_2$ -laser excitation. This proves that these peaks must be hot bands with detectable room temperature population that disappear when the ensemble is vibrationally cooled by adiabatic expansion in the jet. From the dramatic growth of the b peak in fig 3b it then follows that the b peaks correspond to the  $\nu_1$ -mode; the two b peaks in fig. 1b are the  $\nu_1$ -mode  $\nu=1$  and  $\nu=2$  levels. The satellite peaks c then correspond to thermal (unpumped) population in the  $\nu=1$  level or another mode.

The location of the b peaks yields a value for the  $\nu_1$  self anharmonicity of  $x_{11} = -3.65 \text{ cm}^{-1}$ , in close agreement with published values of around  $-3.7 \text{ cm}^{-1}$  (table 3). The c peaks can be assigned to the  $010 \rightarrow 110$  and  $110 \rightarrow 210$  Raman transitions based on their positions relative to the a and b peaks and the observation that their intensities are unaffected by IR pumping. Thus the c peaks represent thermal  $\nu_2$

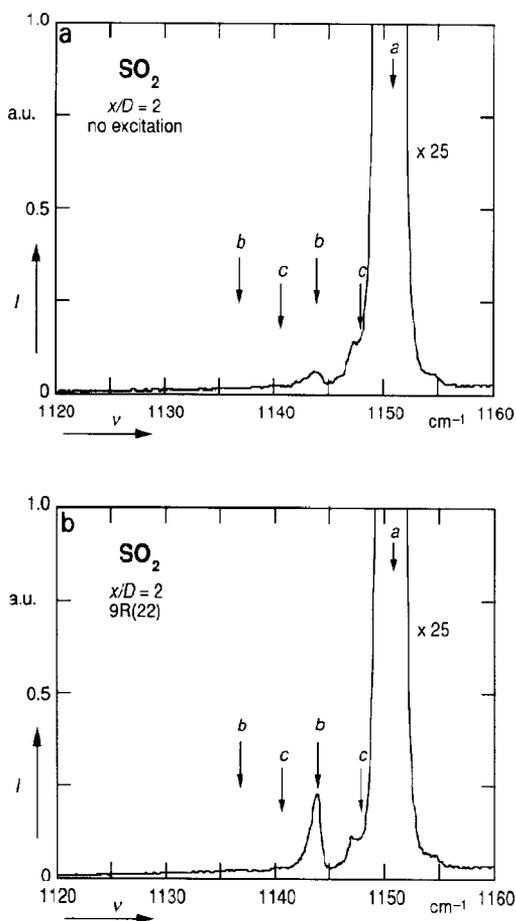


Fig. 3. (a) Same as fig. 2 with scale expanded by a factor of 25 to reveal the thermal population of the excited state peaks. (b) Vibrational CARS spectrum of  $\text{SO}_2$  in a supersonic beam at  $x/D=2$ , 200 ns after  $1 \text{ J/cm}^2$  excitation with the 9R(22)  $\text{CO}_2$ -laser line. As a result of the excitation, peak b grows (cf. (a)).

population, and yield a value for  $x_{12}$  of  $-3.3 \pm 0.3 \text{ cm}^{-1}$ .

A comparison of the peak intensities in figs. 1b and 3b, after correction for the spectral profile of the broadband dye-laser, shows that the vibrational temperatures following excitation in the bulk and in the beam are roughly 1200 and 700 K, respectively. There are two possible reasons for the much less efficient excitation of the  $\nu_1$ -mode in the molecular beam. First, since the collision rate in the beam is much lower, collisionally assisted excitation may be reduced. Second, rotational cooling due to adiabatic expansion limits the spectral overlap with the  $\text{CO}_2$ -laser line. To estimate the importance of this effect,

we first assume that  $\text{SO}_2$  can be approximated as a prolate symmetric top molecule [10]. For such a molecule,  $\nu_1$  and  $2\nu_2$  are categorized as type-B bands [10], whose infrared absorption spectra are characterized by a number of overlapping Q-branches. From the expression for the rotational energy of a symmetric top [18],

$$E_{J,K} = BJ(J+1) + (A-B)K^2, \quad (2)$$

where  $A$  and  $B$  are rotational constants related to the molecular moments of inertia, we see that the Q-branch lines ( $\Delta J=0$ ,  $\Delta K = \pm 1$ ) occur at frequencies given by

$$\begin{aligned} \nu &= \nu_0 + (A' - B') \pm 2(A' - B')K \\ &+ [(A' - B') - (A'' - B'')]K^2 \\ &\approx \nu_0 + (A' - B') \pm 2(A' - B')K, \end{aligned} \quad (3)$$

where the single and double primes refer to the final and initial states, respectively. Thus, the Q-branch lines are separated approximately by  $2(A-B) \text{ cm}^{-1}$ . For the  $\text{SO}_2$   $\nu_1$ -band one has  $2(A-B) = 3.4 \text{ cm}^{-1}$  [15], so the  $71 \text{ cm}^{-1}$  detuning from band center for the 9R(22)  $\text{CO}_2$ -laser line overlaps with the rotational band around  $K=21$ . At room temperature the rotational distribution for  $\text{SO}_2$  peaks at  $J=17$ , so pumping by 9R(22) at a nominal detuning of  $71 \text{ cm}^{-1}$  is not surprising.

Far from the nozzle in a supersonic jet, after the adiabatic expansion, the rotational distribution is greatly cooled to low  $J$ -value, as evidenced by narrowing of the ground state peak in the spectrum. As a result of this, the overlap between the  $\text{CO}_2$ -line and the rotational bands is reduced and the pumping becomes less efficient to the point where it is not observed at all.

The absence of  $\nu_2$  first overtone excitation is probably due to an extremely small cross section for this excitation [4]. While it is an allowed transition, it is not observed in absorption spectra [4], nor in collisional energy transfer experiments [19].

Finally we note that no peaks attributable to the isotopic species  $^{34}\text{SO}_2$  or  $\text{S}^{18}\text{O}_2$  and reported in the literature [5,14,15,20] were observed in our experiment. Since the intensity of the peaks in CARS spectra is proportional to the square of the density [9], the intensities of the peaks for these isotopes are reduced by the square of the corresponding abun-

Table 2

Coherent anti-Stokes Raman peaks and their anharmonic shifts for SO<sub>2</sub>. The first three columns show the two  $\nu_1$ -mode levels involved in the CARS probe, the corresponding anharmonic shift and the literature value for this shift. The next column indicates how intensity of peak changes after IR-pumping, and the last two columns give the assignment and observed shift

CARS transition	Anharmonicity	Shift (cm <sup>-1</sup> ) [16]	Observed behavior	Assignment	Observed shift (cm <sup>-1</sup> )
$lmn \rightarrow (l+1)mn$	$2lx_{11} + nx_{12} + mx_{13}$				
000→100	none	0.0	↓	a	0.0
100→200	$2x_{11}$	-7.3	↑	b	-7.3
200→300	$4x_{11}$	-14.6	↑	b	-14.6
010→110	$x_{12}$	-3.1	-	c	-3.3
110→210	$2x_{11} + x_{12}$	-10.4	-	c	-10.6
$l20 \rightarrow (l+1)20$	$2lx_{11} + 2x_{12}$	$-7.3l - 6.2$			

Table 3

Values of the anharmonic constants  $x_{11}$  and  $x_{12}$  in cm<sup>-1</sup> as reported in this Letter and in the literature

	This work	Ref. [10]	Ref. [17]	Ref. [15]	Ref. [16]
$x_{11}$	$-3.65 \pm 0.06$	-3.99	-3.71	-3.711	-3.655
$x_{12}$	$-3.3 \pm 0.3$	-2.05	-3.03	-4.236	-3.129

dance. For <sup>34</sup>SO<sub>2</sub>, with a 4.2% abundance, for example, the ground state peak intensity will be reduced by a factor of  $1.8 \times 10^{-3}$  with respect to the naturally abundant isotope, <sup>32</sup>SO<sub>2</sub>. Consequently these peaks are too weak to be detected using CARS.

#### 4. Conclusion

Our results unambiguously show that 9R(22) and 9R(32) pumping of SO<sub>2</sub> lead to excitation of the  $\nu_1$ -mode at 1151.3 cm<sup>-1</sup>. While these lines are significantly detuned from the band head, they fall near the peak of the rotational Q-branch of the  $\nu_1$ -mode at room temperature. The data presented here also illustrate the utility of the multiplex BOXCARS technique for direct observation of mode-selective excitation.

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