

# Microwave Spectrum up to 900 GHz of SO Created in Highly Excited States by Electric Discharge and UV-Laser Photolysis

M. Bogey, S. Civiš,<sup>1</sup> B. Delcroix, C. Demuyne, A. F. Krupnov,<sup>2</sup> J. Quiguer, M.Yu. Tretyakov,<sup>2</sup> and A. Walters

*Laboratoire de Spectroscopie Hertzienne, Centre d'Etudes et de Recherches Lasers et Applications,  
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France*

Received July 12, 1996; in revised form October 14, 1996

SO was created by electric discharge in a mixture of SO<sub>2</sub> and Ar and by UV-laser photolysis of Cl<sub>2</sub>SO. The two methods are compared. The pure rotational spectrum of the  $X^3\Sigma^-$  electronic ground state was measured in highly excited vibrational states up to  $v = 17$ , that of the  $a^1\Delta$  excited state up to  $v = 13$ , and that of the  $b^1\Sigma^+$  excited state up to  $v = 11$ . Measurements up to 900 GHz without harmonic generation were possible thanks to the use of Russian-constructed BWOs. © 1997 Academic Press

## INTRODUCTION

The use of electric discharges in low pressure gas mixtures has become a well developed technique for the production of reactive molecules. The technique of UV-laser photolysis is a complementary technique which offers certain advantages. First, due to the specificity of the bond broken by the laser excitation, reaction products are better defined. Second, it should be possible to form larger reactive molecules which are too easily destroyed in a discharge. Third, the use of pulsed laser radiation provides a possibility of studying the formation and destruction of reactive molecules as a function of time. Our aim has been to couple an excimer laser to an existing submillimeter-wave spectrometer used for the study of rotational transitions in reactive molecules produced by electric discharge. In order to compare the two methods we chose to study SO, which can be formed both by electric discharge and by laser photolysis. Measurements up to 900 GHz without harmonic generation were possible thanks to the use of Russian-constructed BWOs.

SO has a  $\cdots (\pi)^2$  ground state electron configuration which can result in three molecular states,  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$ , with term values 0.0 cm<sup>-1</sup>, 5879.2 cm<sup>-1</sup>, and 10,509.97 cm<sup>-1</sup>, respectively (1). This radical is found in a variety of interstellar environments but has greatly enhanced abundance in selected regions of giant interstellar clouds characterized by high temperatures and gas densities (2). In these so-called star formation regions, temperatures reaching

thousands of K are sporadically generated by shock-waves, so SO may be formed in highly excited states. A further aim of this work was to measure SO in all three electronic states and as highly vibrationally excited as possible.

In choosing SO to study the performance of excimer laser excitation we chose a molecule whose history is intimately connected with that of the microwave spectroscopy of free radicals. It was in 1963 that an article (3) devoted principally to carbon monosulfide mentioned the first millimeter-wave detection of the gaseous SO radical at Duke University in Professor W. Gordy's laboratory. Although CS is not itself a radical, this pioneering article described a technique for producing gaseous short-lived free-radicals by radiofrequency discharge and for measuring their rotational spectra by means of millimeter-wave spectroscopy. A year later, after completion of the measurements and analysis of the results, an article by M. Winnewisser *et al.* (4) reported six transitions of the SO radical in the  $X^3\Sigma^-$  ground state and gave a first series of rotational and magnetic coupling constants. Simultaneously but independently, Powell and Lide (5) published three microwave transitions of this radical produced using a different discharge arrangement. The microwave measurements were expanded by Amano *et al.* (6), who observed transitions in the ground and first vibrationally excited state. Tiemann (7) studied <sup>32</sup>S<sup>16</sup>O, <sup>34</sup>S<sup>16</sup>O, and <sup>32</sup>S<sup>18</sup>O isotopomers and subsequently extended the measurements to the first vibrationally excited state in order to determine both the isotopic and the vibrational dependence of the rotational constants (8).

In 1970 the lowest rotational transition ( $J = 3 \leftarrow 2$ ) of SO in the  $a^1\Delta$  electronic state was measured by Saito (9). This was the first example of microwave absorption in an excited electronic state. Clark and De Lucia (10) subse-

<sup>1</sup> Permanent address: J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic.

<sup>2</sup> Permanent address: Applied Physics Institute of Russian Academy of Sciences, 46 Uljanova Street, 603 600 Nizhnii Novgorod, Russia.

quently reported three more rotational transitions in this excited state and significantly extended measurements of the  $X^3\Sigma^-$  ground state up to  $N = 8$  at the edge of the submillimeter spectral region. The first extensive measurement of highly excited vibrational states of SO in the electronic ground state was carried out by Bogey *et al.* (11), who measured the parent isotopomer in states as high as  $v = 8$  and  $N = 12$ , as well as extending measurements of the other isotopomers. Cazzoli *et al.* (12) extended rotational measurements of the  $X^3\Sigma^-$  and  $a^1\Delta$  states up to 1.8 THz and  $N = 44$ . However, the sideband FIR laser spectrometer employed gave standard deviations of 500 kHz on the measured frequencies, at least five times higher than those usually associated with microwave measurements. It was appropriately in the laboratory of Gisbert Winnewisser that the first microwave terahertz spectrum of SO was measured (2). However, the emphasis of their work was the isotopic dependence, so they measured few vibrationally excited states and published no results for the  $b^1\Sigma^+$  electronic state. Indeed we have found only one previous article, that of Yamamoto (1), which refers to the rotational spectrum of this  $b^1\Sigma^+$  state.

SO can also be created by excimer laser photolysis of  $\text{SO}_2$  (13–17). This method has been used for infrared diode laser spectroscopy (13, 14) and millimeter-wave spectroscopy (15) of the  $X^3\Sigma^-$  state. Two wavelengths are commonly available for photolysis: 193 nm (ArF) and 248 nm (KrF). The former provides the higher energy photons, giving maximum available energy for product excitation. However, photolysis of  $\text{SO}_2$ , even at 193 nm, provides an excess energy of only  $6000\text{ cm}^{-1}$  (18), just superior to that theoretically necessary to create an excited  $a^1\Delta$  electronic state. For the study of SO in highly excited states, the photolysis of  $\text{Cl}_2\text{SO}$  (16–22) at 193 nm is better, owing to the large amount of energy,  $14,000\text{ cm}^{-1}$  or more, which may be distributed to the internal degrees of freedom of the photofragments (18). Photolysis of  $\text{Cl}_2\text{SO}$  at 193 nm has been employed previously for submillimeter-wave (22) and infrared diode laser spectroscopy (18) of SO in the  $a^1\Delta$  state.

It has been debated whether the dissociation mechanism for  $\text{Cl}_2\text{SO}$  by photolysis be stepwise or concerted (23). There is strong evidence (19–21) that at 193 nm the major dissociation channel is concerted three-body dissociation  $\text{Cl}_2\text{SO} \rightarrow \text{SO} + \text{Cl} + \text{Cl}$ .

## EXPERIMENTAL CONSIDERATIONS

The experimental arrangement consisting of a millimeter-wave source, a cell for producing reactive molecules, a liquid-helium-cooled InSb detector (QMC Instruments, London), and a computer-controlled scanning and data acquisition system has been discussed in previous articles (24, 25). The detection chain has been modified as shown

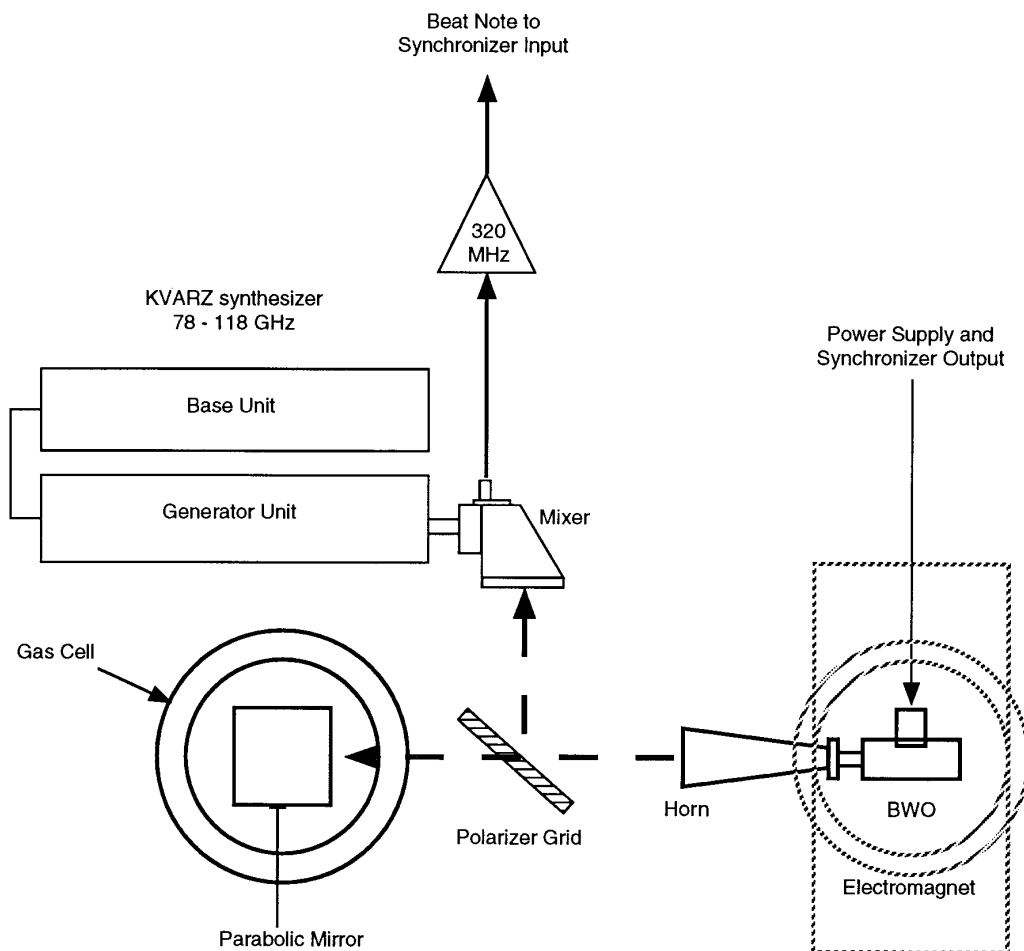
in Fig. 1 in order to obtain time-resolved information. If the transition frequency is known then the frequency of the source can be fixed and the absorption signal measured as a function of time using a digital oscilloscope triggered by laser pulse or discharge extinction. The signal-to-noise ratio can be improved by averaging. A similar technique has already been used with pulsed discharges to discriminate between species of different lifetime and led to the successful identification of the millimeter-wave spectrum of  $\text{H}_2\text{SiO}$  (26).

In addition to two Thomson BWO tubes covering the range from 340 to 470 GHz we have recently acquired Russian constructed BWO tubes, produced by the ISTOK Research and Production company, extending the frequency range of the spectrometer to 1.25 THz. A power supply for these tubes has been supplied by Hydrolab, Nizhnii Novgorod. One tube has already been used in Lille to measure the second rotational transitions of the ammonia molecule around 1.215 THz (27). For this previous work the Russian-constructed BWO was locked against one of the Thomson tubes. However, difficulties in obtaining stable phase-locking led to a poor signal-to-noise ratio. We have subsequently acquired for phase-locking a 78 to 118 GHz frequency synthesizer, supplied by the Institute of Electronic Measurement, KVARZ, Nizhnii Novgorod, so that frequency and phase stabilization can now be carried out as described by Winnewisser *et al.* (28). The frequency synthesizer has a relative accuracy  $\Delta\nu/\nu$  of  $10^{-8}$  corresponding to an absolute accuracy of 9 kHz at 900 GHz. No further external reference is hence necessary for measuring Doppler-broadened line-shapes (as is the case here) since experimental precision is at least several times worse.

The beat signal at 320 MHz, between a harmonic of the synthesizer and the BWO frequency, is obtained by means of a broadband mixer based on a planar Schottky diode and supplied by the Institute for Applied Physics, Nizhnii Novgorod. The diode is placed at the focal point of a semi-parabolic mirror illuminated with the submillimeter radiation. Phase-locking becomes increasingly difficult as frequency increases for several reasons. Output power of the BWO decreases, higher harmonics of the reference oscillator must be used and absorption by moisture in the air increases. Additionally, beam divergence at high frequencies is substantial due to high overmoding of the BWO output waveguide.

In the most recent Cologne setup extreme low-noise amplification of the intermediate frequency from the mixer combined with impedance matching between mixer and amplifier provides stable phase-locking to above 1.2 THz (29). Although we do not possess a similar HEMT amplifier nor correct impedance matching we were able to obtain stable locking up to 900 GHz by employing a somewhat different geometrical arrangement of the phase locking elements





**FIG. 2.** Out of plane mounting of mixer connected directly to Kvarz synthesizer reduces beam-divergence losses before harmonic mixing for phase stabilization. The beam splitter is placed as close to the BWO horn as possible. The remaining radiation is collected and fed into the cell by a parabolic mirror.

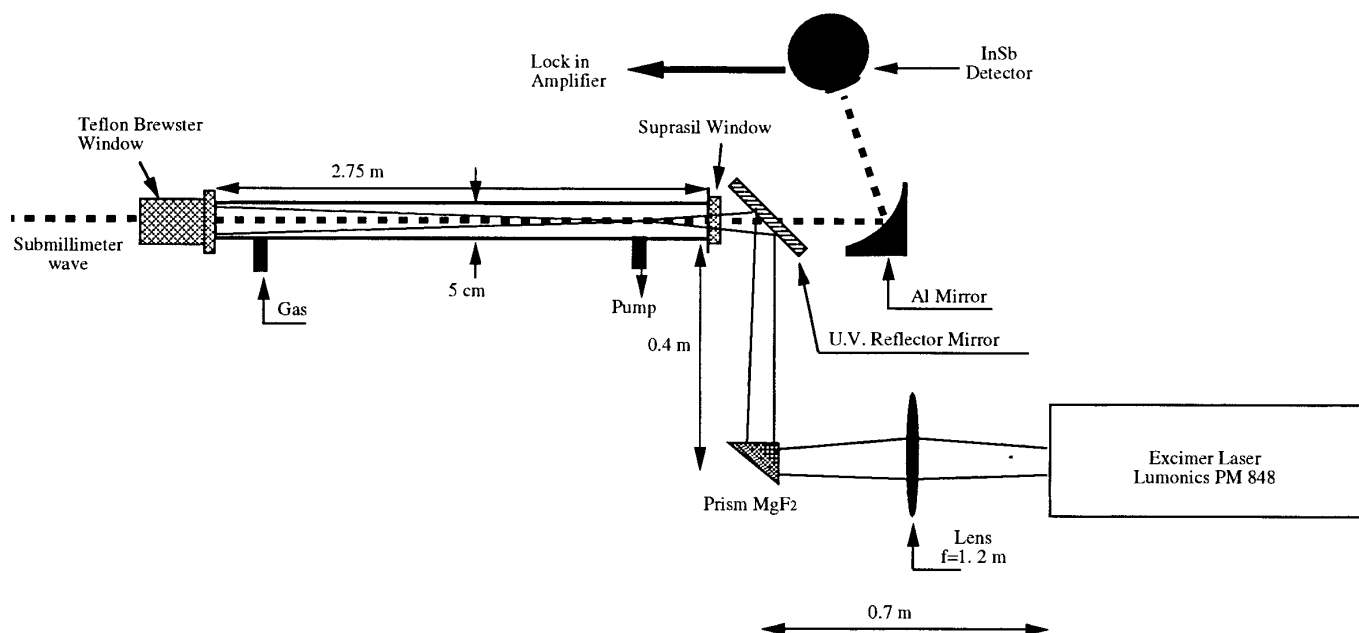
It should be noted that the detector and laser optics are not yet optimised for THz spectroscopy. The performance of the InSb detector, supplied by QMC Instruments, London, starts to fall off above 500 GHz and at 900 GHz its sensitivity is almost one order of magnitude smaller. Furthermore, neither the Suprasil window nor the laser mirror are completely transparent to the millimeter-wave radiation and losses increase dramatically with frequency. At 400 GHz approximately 50% of the millimeter wave power is lost after passage through the two elements. At 800 GHz this loss increases to 90%.

The Lumonics PM-848 pulsemaster excimer laser operating on ArF at 193 nm produces 20 ns pulses with a maximum repetition rate of 200 Hz and maximum quoted power of 30 W.

In a first series of experiments, SO was produced by photolysis of  $\text{Cl}_2\text{SO}$  flowed through the production cell. A partially throttled diffusion pump was used to evacuate

photolysis end-products and maintain the pressure at 0.01 mbar. An increase in pressure did not result in an increase in signal indicating 100% absorption of the usable laser radiation. Flow rate was optimized by adjusting the throttling of the pump and by means of a needle valve at the gas input.

One major drawback of the photolysis of  $\text{Cl}_2\text{SO}$  is the rich spectra of the stable precursor, which swamps the weaker SO lines. This is a typical problem for other envisaged photolysis precursors. Fortunately, time dependent detection can be used to resolve this problem since the use of a pulsed laser automatically implies concentration modulation of short lived species. The procedure used was as follows. After each frequency step a time-resolved signal was accumulated on a digital oscilloscope for a certain number of laser pulses. Up to 100 laser pulses were used for each frequency point depending on the line intensity. Two gates were then set as illustrated in Fig. 4, one after and one before the laser shot.



**FIG. 3.** Millimeter-wave radiation and excimer laser beam counterpropagate in production cell. UV radiation is focused by a lens and reflected by a prism and mirror before entering cell through a Suprasil window. The window and mirror in the microwave path reduce power reflected by Al mirror onto detector.

The oscilloscope was programmed to output the average signal in each of the two gates to the computer which then calculated the difference between them.

The laser repetition frequency and the position of the gates depend on the lifetime of the state studied. An indication of the lifetime ( $T_{1/2}$ , the time taken for the signal to decay to half of its maximum value), is given in Fig. 4 for the ground and first vibrational states in each electronic configuration. It should be noted that the exact lifetime varies somewhat according to the experimental condition. As can be seen the  $X^3\Sigma^-, v = 0$  state has a significantly longer lifetime and classical rather than time-resolved detection is best adapted to its observation. For all other states the maximum 200 Hz firing rate of the laser is not sufficient to maintain a constant concentration in the cell and time-resolved detection becomes essential. In practice due to problems with the laser this maximum firing rate could not be maintained for long periods and was hence reserved for observation of the weakest transitions.

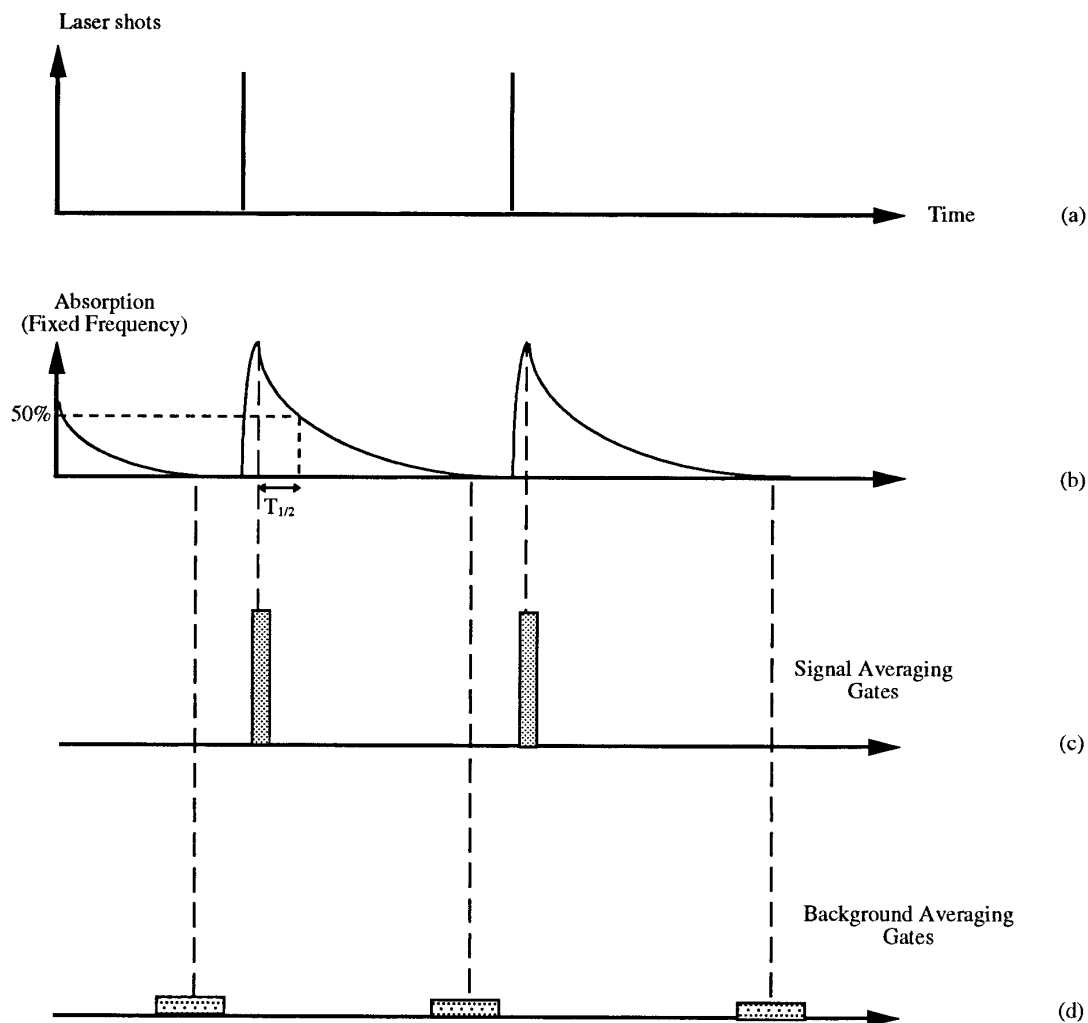
The use of time-resolved or "kinetic" spectroscopy gives spectra free of the effects of standing waves which classically limit sensitivity (24) (see Fig. 5). This concentration modulation technique also discriminates stable or quasi-stable species which are virtually eliminated in the kinetic spectrum. Precursor lines with strong absorption are not completely suppressed but can easily be identified since they appear inverted in the final spectrum. Since the object is not precise temporal information, frequency modulation and

phase-sensitive detection can be used to increase sensitivity as long as a time constant sufficiently short to discriminate between short- and long-lived species can be used. Detection at twice the modulation frequency leads to the second derivative lineshapes seen in the figure.

In a second series of experiments, SO was produced by discharge in a mixture of Ar and SO<sub>2</sub>. As usual in such experiments liquid nitrogen cooling of the discharge cell significantly increased the observed signal. Such extreme cooling could not be used in photolysis of Cl<sub>2</sub>SO due to condensation of the precursor. Unlike the photolysis experiments SO<sub>2</sub> pressures higher than 0.01 mbar gave larger but broader lines. For the weakest lines, pressures up to 0.1 mbar were used to enhance the sensitivity with a small loss in resolution.

## RESULTS AND ROTATIONAL SPECTRA

The lines characterized by a low vibrational quantum number  $v$  were rapidly found using predictions based on molecular constants obtained from a fit using previously published transitions for each electronic state:  $X^3\Sigma^-$  (2, 4, 7, 8, 10, 11),  $a^1\Delta$  (2, 10, 22), and  $b^1\Sigma^+$  (1). Owing to the quality of this previous work these lines differed little from predictions. However, as  $v$  increased the difference between calculated and experimental values became significantly higher than the experimental uncertainty. For the highest vibrational states these first predictions gave

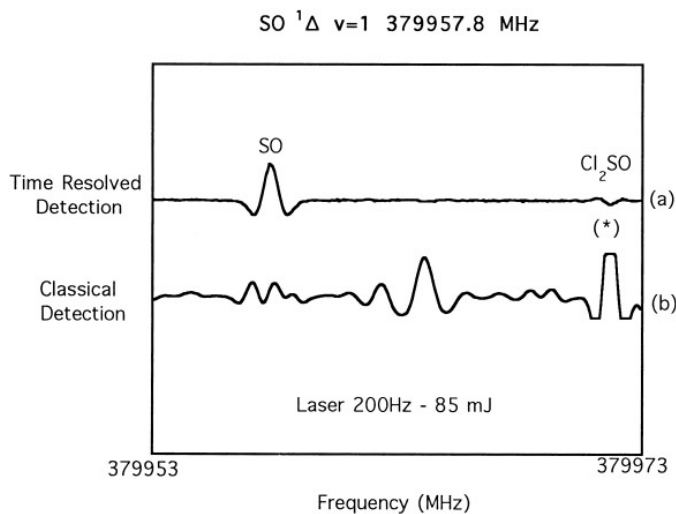


|               | $T_{1/2}$ |             |
|---------------|-----------|-------------|
|               | $v = 0$   | $v = 1$     |
| $X^3\Sigma^-$ | 190 ms    | 270 $\mu$ s |
| $a^1\Delta$   | 3 ms      | 280 $\mu$ s |
| $b^1\Sigma^+$ | 1 ms      | 250 $\mu$ s |

**FIG. 4.** Reactive molecules created after each laser pulse (a) have a short lifetime which leads to a decay (b) in the absorption at a resonant frequency. The maximum absorption is averaged (c) and subtracted from the background determined by placing a gate (d) before the laser pulse. For stable molecules the signal is invariant in time and the subtraction gives zero. For  $v = 1$ , lifetime measurements are maximum values limited by the lock-in-amplifier time constant.

frequencies differing by several tens of MHz from the subsequently measured frequencies. With these predictions alone identification would have been difficult owing

to the forest of lines of different isotopomers of comparable or higher intensity. However, by including systematically new measured lines into the fit, it was possible to



**FIG. 5.** The use of time-resolved detection (a) shows clearly the lines of SO while eliminating baseline and precursor lines. The two traces do not have the same gain; the line of SO cannot be identified by classical detection (b) as it is masked by the stronger precursor spectrum. Very strong precursor lines (\*) appear inverted after time resolved detection.

identify lines up to  $v = 11$  for the  $b^1\Sigma^+$  state (Table 1), up to  $v = 13$  for the  $a^1\Delta$  state (Table 2) and up to  $v = 17$  for the  $X^3\Sigma^-$  state (Table 3).

All lines below 600 GHz were measured following production of SO by laser photolysis. The precision of these results, better than 50 kHz except in the case of lines overlapped by other lines from reactive species, was comparable to previous work. For the  $X^3\Sigma^-$  state laser photolysis allowed transitions up to  $v = 8$  to be observed, as high as previous work using production by electric discharge (11). For the  $a^1\Delta$  state the highest previously published (22) vibrational state  $v = 5$  was measured after production of SO by laser photolysis of  $\text{Cl}_2\text{SO}$ . We were able to measure up to  $v = 10$  using the same method. For the highest electronic state,  $b^1\Sigma^+$ , laser photolysis performed slightly less well than electric discharge by which transitions up to  $v = 8$  have previously been measured. A line at  $v = 7$  was observed but was overlapped. However, the laser was not working at optimum performance due to technical problems.

At frequencies of 800 GHz or more the microwave power losses in the UV coupling elements combined with the poor sensitivity of the detector restricted measurements following laser photolysis to lower vibrationally excited states. Several of the measurements were subsequently repeated following production by electric discharge. As expected the measured frequencies all agreed to better than 50 kHz, with the exception of lines overlapped in one of the two spectra, and were often much closer. Measurements of the highest vibrational states were then completed using electric discharge.

**TABLE 1**  
**Observed Rotational Transitions (in MHz) of SO in the  $b^1\Sigma^+$  State**

| $J'$ | $J''$ | $v$ | OBS. FREQ. |       | OBS. - CALC. | $J'$ | $J''$ | $v$ | OBS. FREQ. |   | OBS. - CALC. |
|------|-------|-----|------------|-------|--------------|------|-------|-----|------------|---|--------------|
| 9    | 8     | 0   | 377343.506 | a,e   | 0.000        |      |       | 3   | 855238.497 | c | -0.006       |
|      |       | 1   | 373902.019 | a,e   | -0.024       |      |       | 4   | 847176.223 | * | -0.465       |
|      |       | 2   | 370457.308 | a,d,* | -0.364       |      |       | 5   | 839100.876 | c | 0.008        |
|      |       | 3   | 367009.494 | a,e   | -0.023       |      |       | 6   | 831008.186 | c | -0.006       |
| 11   | 10    | 0   | 461133.375 | a,e   | -0.014       |      |       | 7   | 822895.523 | c | 0.014        |
|      |       | 1   | 456926.873 | a,e   | -0.040       |      |       | 8   | 814759.331 | c | -0.022       |
|      |       | 2   | 452716.825 | a     | -0.045       |      |       | 9   | 806595.909 | c | -0.013       |
|      |       | 3   | 448502.225 | a     | 0.040        | 22   | 21    | 0   | 921100.768 | c | 0.001        |
|      |       | 4   | 444281.700 | a     | 0.040        |      |       | 1   | 912683.377 | c | -0.038       |
|      |       | 6   | 435817.605 | a     | -0.007       |      |       | 2   | 904258.718 | c | 0.050        |
|      |       | 7   | 431570.700 | d,*   | -0.277       |      |       | 3   | 895824.317 | c | -0.024       |
| 20   | 19    | 0   | 837609.661 | b     | 0.001        |      |       | 4   | 887377.981 | c | -0.022       |
|      |       | 1   | 829958.389 | c     | -0.058       |      |       | 5   | 878917.024 | c | 0.074        |
|      |       | 2   | 822300.576 | c     | 0.009        |      |       | 6   | 870438.146 | c | -0.044       |
|      |       | 3   | 814634.055 | c     | 0.015        |      |       | 7   | 861938.384 | c | -0.036       |
|      |       | 4   | 806956.685 | c     | 0.022        |      |       | 8   | 853414.101 | c | 0.099        |
|      |       | 6   | 791559.319 | c     | 0.021        |      |       | 10  | 836274.859 | c | -0.039       |
| 21   | 20    | 0   | 879364.419 | c     | 0.003        |      |       | 11  | 827651.110 | c | 0.016        |
|      |       | 1   | 871330.230 | c     | 0.062        |      |       |     |            |   |              |

<sup>a</sup> Laser photolysis.

<sup>b</sup> Laser photolysis and electric discharge.

<sup>c</sup> Electric discharge.

<sup>d</sup> Overlapped line.

<sup>e</sup> Also measured by Yamamoto (Ref. 1).

\* Given low weight in fit.

**TABLE 2**  
**Observed Rotational Transitions (in MHz) of SO in the  $a^1\Delta$  State**

| $J'$ | $J''$ | $v$ | OBS. FREQ. |         | OBS.- CALC. | $J'$ | $J''$ | $v$ | OBS. FREQ. |         | OBS.- CALC. |
|------|-------|-----|------------|---------|-------------|------|-------|-----|------------|---------|-------------|
| 9    | 8     | 0   | 383220.163 | a, f    | 0.027       |      |       |     |            |         |             |
|      |       | 1   | 379957.802 | a, f    | 0.002       |      |       | 3   | 828959.342 | b       | 0.002       |
|      |       | 2   | 376696.988 | a, f    | 0.000       |      |       | 4   | 821712.637 | a       | -0.053      |
|      |       | 3   | 373437.023 | a, f    | 0.016       |      |       | 5   | 814464.134 | a       | 0.061       |
|      |       | 5   | 366916.375 | a, f    | 0.007       | 21   | 20    | 0   | 893120.434 | b, e    | -0.058      |
|      |       | 6   | 363653.899 | a       | 0.002       |      |       | 1   | 885506.074 | b       | 0.063       |
|      |       | 7   | 360388.675 | a       | 0.060       |      |       | 2   | 877894.971 | b       | 0.002       |
|      |       | 8   | 357119.360 | a       | 0.003       |      |       | 3   | 870285.702 | b       | -0.013      |
|      |       | 9   | 353844.833 | a       | -0.005      |      |       | 4   | 862676.386 | b       | -0.026      |
|      |       | 10  | 350563.689 | a       | 0.041       |      |       | 5   | 855065.023 | b       | 0.008       |
| 11   | 10    | 0   | 468318.523 | a       | 0.020       |      |       | 7   | 839826.773 | c, d, * | 0.126       |
|      |       | 1   | 464331.103 | a       | 0.037       |      |       | 8   | 832194.394 | c       | -0.017      |
|      |       | 2   | 460345.488 | a       | 0.004       |      |       | 9   | 824549.474 | c       | -0.045      |
|      |       | 3   | 456360.947 | a       | 0.037       |      |       | 10  | 816888.622 | c       | -0.023      |
|      |       | 4   | 452376.423 | a       | 0.024       |      |       | 11  | 809208.201 | c       | 0.048       |
|      |       | 5   | 448390.906 | a       | 0.007       |      |       | 12  | 801504.079 | c       | -0.003      |
|      |       | 6   | 444403.244 | a       | 0.004       |      |       | 13  | 793772.118 | c       | -0.008      |
|      |       | 8   | 436416.164 | a, d, * | 0.026       | 22   | 21    | 0   | 935517.416 | c       | 0.047       |
|      |       | 9   | 432413.626 | a, d, * | -0.069      |      |       | 2   | 919566.167 | c       | -0.047      |
| 19   | 18    | 0   | 808274.540 | a       | -0.003      |      |       | 3   | 911594.292 | c       | 0.006       |
|      |       | 1   | 801385.743 | a       | 0.017       |      |       | 4   | 903622.123 | c, d, * | -0.158      |
|      |       | 2   | 794500.023 | a       | -0.021      |      |       | 5   | 895648.025 | c       | -0.030      |
|      |       | 3   | 787616.049 | a       | 0.039       |      |       | 6   | 887669.259 | c       | -0.028      |
|      |       | 4   | 780731.964 | a       | -0.006      |      |       | 7   | 879683.228 | c       | -0.047      |
| 20   | 19    | 0   | 850705.895 | a       | -0.041      |      |       | 8   | 871686.989 | c       | -0.020      |
|      |       | 1   | 843454.318 | b       | 0.013       |      |       | 9   | 863677.535 | c       | 0.004       |
|      |       | 2   | 836205.973 | b       | 0.010       |      |       | 10  | 855651.444 | c, d, * | 0.187       |

<sup>a</sup> Laser photolysis.

<sup>b</sup> Laser photolysis and electric discharge.

<sup>c</sup> Electric discharge.

<sup>d</sup> Overlapped line.

<sup>e</sup> Also measured by Klaus *et al.* (Ref. 31).

<sup>f</sup> Also measured by Endo *et al.* (Ref. 22).

\*Given a low weight in the fit.

## THEORY AND ROTATIONAL CONSTANTS

The observed frequencies for the  $b^1\Sigma^+$  state and those measured previously by Yamamoto (*I*) were fitted simultaneously to the following Dunham equation:

$$E(v, J) = \sum_{ij} Y_{ij} \left( v + \frac{1}{2} \right)^i [J(J+1)]^j \quad [1]$$

All lines were given the same weight except those overlapped and one measurement differing by more than  $3\sigma$  from its predicted value. These latter lines were given lower weight. The rotational and centrifugal distortion constants can be calculated as an expansion of the Dunham coefficients (*30*), (see for example *11*)

$$B_v = \sum_n Y_{n1} \left( v + \frac{1}{2} \right)^n \quad [2]$$

$$D_v = -\sum_n Y_{n2} \left( v + \frac{1}{2} \right)^n \quad [3]$$

$$H_v = \sum_n Y_{n3} \left( v + \frac{1}{2} \right)^n \quad [4]$$

11 Dunham coefficients, three more than previous, were determined by a least-squares analysis, as summarized in Table 4. The results are in good agreement with those of Yamamoto but the standard deviation on the constants is significantly lower, particularly for the  $Y_{02}$  and  $Y_{12}$  coefficients. The standard deviation of the fit, 36 kHz, compares favorably with the estimated experimental accuracy which varies from 50 to 150 kHz depending on the intensity of the line and the frequency at which it is measured.

The new rotational frequencies of the  $a^1\Delta$  state and previously published results (*10–17*, *19–22*) were fitted to an expression, similar to that of the  $b^1\Sigma^+$  state, for the energy levels (see for example *22*)



**TABLE 3**  
**Observed Rotational Transitions (in MHz) of SO in the  $X^3\Sigma^-$  State**

| J' | N' | J'' | N'' | v | OBS. FREQ. |         | OBS. - CALC. | J' | N' | J'' | N'' | v  | OBS. FREQ. |       | OBS. - CALC. |
|----|----|-----|-----|---|------------|---------|--------------|----|----|-----|-----|----|------------|-------|--------------|
| 9  | 9  | 8   | 8   | 0 | 387328.795 | a,e     | -0.007       | 13 | 14 | 12  | 13  | 0  | 601258.444 | a,f   | -0.013       |
|    |    |     |     | 1 | 384233.524 | a       | 0.007        | 14 | 14 | 13  | 13  | 0  | 602293.015 | a,f   | -0.017       |
|    |    |     |     | 2 | 381146.014 | a       | 0.009        |    |    |     |     | 1  | 597478.066 | a,f   | 0.012        |
|    |    |     |     | 3 | 378065.986 | a       | -0.023       |    |    |     |     | 2  | 592675.156 | a,f   | 0.001        |
|    |    |     |     | 4 | 374993.240 | a       | 0.009        | 15 | 14 | 14  | 13  | 0  | 603021.646 | a,f   | -0.008       |
|    |    |     |     | 5 | 371927.192 | a,*     | -0.130       |    |    |     |     | 1  | 598227.134 | a,f   | 0.023        |
|    |    |     |     | 6 | 368867.925 | a       | 0.026        |    |    |     |     | 2  | 593445.430 | a,f   | 0.032        |
|    |    |     |     | 7 | 365814.496 | a       | -0.010       |    |    |     |     | 3  | 588676.168 | a     | 0.007        |
| 10 | 9  | 9   | 8   | 0 | 389120.932 | a,e     | -0.048       |    |    |     |     | 4  | 583918.984 | a     | -0.009       |
|    |    |     |     | 1 | 386069.321 | a,e     | -0.014       |    |    |     |     | 7  | 569714.819 | a     | 0.000        |
| 10 | 10 | 9   | 9   | 0 | 430339.544 | a,e     | -0.014       | 18 | 19 | 17  | 18  | 0  | 816495.184 | a     | 0.023        |
|    |    |     |     | 1 | 426900.322 | a       | -0.020       |    |    |     |     | 1  | 809945.972 | b     | 0.008        |
|    |    |     |     | 2 | 423469.739 | a       | -0.021       |    |    |     |     | 2  | 803412.522 | b     | -0.024       |
| 11 | 10 | 10  | 9   | 0 | 431808.196 | a,e     | -0.009       |    |    |     |     | 3  | 796894.330 | b     | -0.001       |
|    |    |     |     | 1 | 428405.894 | a       | 0.054        |    |    |     |     | 4  | 790390.672 | b     | 0.026        |
|    |    |     |     | 2 | 425013.342 | a       | 0.010        |    |    |     |     | 5  | 783900.569 | a,*   | -0.150       |
| 10 | 11 | 9   | 10  | 0 | 471537.818 | a,e     | 0.029        | 19 | 19 | 18  | 18  | 0  | 816972.328 | a     | 0.024        |
|    |    |     |     | 1 | 467710.840 | a       | 0.034        |    |    |     |     | 1  | 810437.559 | b     | 0.043        |
|    |    |     |     | 2 | 463891.903 | a       | 0.002        |    |    |     |     | 2  | 803919.104 | a     | 0.008        |
|    |    |     |     | 3 | 460080.675 | a       | 0.000        |    |    |     |     | 3  | 797416.517 | a     | 0.014        |
|    |    |     |     | 4 | 456276.637 | a       | -0.026       | 20 | 19 | 19  | 18  | 0  | 817307.360 | c     | 0.021        |
|    |    |     |     | 5 | 452479.346 | a       | 0.016        | 20 | 19 | 19  | 18  | 2  | 804277.025 | c     | 0.013        |
|    |    |     |     | 6 | 448688.081 | a       | 0.013        | 20 | 20 | 19  | 19  | 1  | 852986.239 | c     | 0.004        |
| 11 | 11 | 10  | 10  | 0 | 473342.082 | a,d,e,* | -0.091       | 22 | 21 | 21  | 20  | 0  | 902986.622 | c,f   | 0.044        |
|    |    |     |     | 1 | 469559.041 | a       | 0.019        |    |    |     |     | 2  | 888577.631 | c     | -0.028       |
|    |    |     |     | 2 | 465785.389 | a       | 0.021        |    |    |     |     | 3  | 881400.311 | c,f   | -0.001       |
|    |    |     |     | 3 | 462020.899 | a       | 0.001        |    |    |     |     | 4  | 874240.202 | c     | 0.021        |
|    |    |     |     | 4 | 458265.226 | a       | -0.019       |    |    |     |     | 5  | 867096.490 | c     | -0.002       |
|    |    |     |     | 5 | 454517.986 | a       | -0.003       |    |    |     |     | 6  | 859968.391 | c     | 0.028        |
|    |    |     |     | 7 | 447046.790 | a,*     | 0.110        |    |    |     |     | 7  | 852854.917 | c,d,* | 0.120        |
| 12 | 11 | 11  | 10  | 0 | 474559.605 | a,e     | 0.002        |    |    |     |     | 9  | 838666.691 | c     | -0.041       |
|    |    |     |     | 1 | 470807.899 | a       | 0.030        |    |    |     |     | 10 | 831589.614 | c     | 0.020        |
|    |    |     |     | 2 | 467066.721 | a       | 0.015        |    |    |     |     | 11 | 824521.743 | c     | 0.017        |
|    |    |     |     | 3 | 463335.874 | a       | 0.007        |    |    |     |     | 12 | 817461.429 | c     | -0.016       |
|    |    |     |     | 4 | 459615.060 | a       | 0.006        |    |    |     |     | 14 | 803356.135 | c     | 0.007        |
|    |    |     |     | 5 | 455903.948 | a       | -0.021       |    |    |     |     | 15 | 796306.921 | c     | 0.001        |
|    |    |     |     | 6 | 452202.181 | a       | -0.015       |    |    |     |     | 16 | 789256.944 | c     | 0.003        |
|    |    |     |     | 7 | 448509.296 | a       | -0.019       |    |    |     |     | 17 | 782203.658 | c     | -0.004       |
|    |    |     |     | 8 | 444824.858 | a       | 0.019        | 21 | 22 | 20  | 21  | 14 | 840525.687 | c     | -0.017       |
|    |    |     |     |   |            |         |              |    |    |     |     | 15 | 833100.331 | c     | 0.011        |

<sup>a</sup> Laser photolysis.

<sup>b</sup> Laser photolysis and electric discharge.

<sup>c</sup> Electric discharge.

<sup>d</sup> Overlapped line.

<sup>e</sup> Also measured by Bogey *et al.* (Ref. 11).

<sup>f</sup> Also measured by Klaus *et al.* (Ref. 32).

\*Lines given low weight in fit.

$$E(v, J) = \sum_{ij} Y_{ij} \left( v + \frac{1}{2} \right)^i [J(J+1) - 4]^j \quad [5]$$

In their first article on the terahertz spectrum of SO Klaus *et al.* (2) measured two new  $v = 0$  transitions. These measurements have subsequently been repeated with higher accuracy (31) and will be published later. The  $21 \leftarrow 20$  transition recently remeasured in Cologne at 893,120.432 MHz agrees with our measurement to within 2 kHz! The  $24 \leftarrow 23$  transition which they remeasured at 1,020,253.808 MHz did not fit well to our measurements and was subsequently ex-

cluded both in our and their fits. Overlapped lines were given low weight. All other lines were given the same weight. The 11 fitted Dunham coefficients are compared in Table 5 with the results of Endo *et al.* (22) and the earlier results of Klaus *et al.* (2) who fitted respectively 6 and 7 coefficients. The results of Klaus *et al.* were given as isotopically invariant parameters and have been converted. We do not yet possess the constants resulting from a fit to the latest Cologne data which would be expected to give superior results. We determine all coefficients with higher precision than previous work except  $Y_{31}$  which has a higher standard deviation than the value of Ref. 2 due to the determination of two additional

**TABLE 4**  
**Dunham  $Y_{ij}$  Coefficients (MHz) of SO in the  $b^1\Sigma^+$  State**

| Dunham Coefficient | This work                     | Yamamoto <sup>a</sup> |
|--------------------|-------------------------------|-----------------------|
| $Y_{01}$           | 21064.9785(14) <sup>b</sup>   | 21064.9784(46)        |
| $Y_{11}$           | -191.0516(18)                 | -191.0498(57)         |
| $10^2 Y_{21}$      | -4.831(82)                    | -4.96(23)             |
| $10^3 Y_{31}$      | -6.43(17)                     | -5.97(40)             |
| $10^4 Y_{41}$      | -1.87(16)                     | -2.59(23)             |
| $10^6 Y_{51}$      | -3.92(56)                     |                       |
| $10^2 Y_{02}$      | -3.64243(33)                  | -3.6422(23)           |
| $10^4 Y_{12}$      | -1.307(17)                    | -1.33(20)             |
| $10^6 Y_{22}$      | -3.21(45)                     | -4.0(26)              |
| $10^7 Y_{32}$      | -1.88(34)                     |                       |
| $10^8 Y_{03}$      | -1.23(37)                     |                       |
| $\sigma$           | 0.036                         |                       |
| a                  | (Ref. 1)                      |                       |
| b                  | Values in brackets: $1\sigma$ |                       |

higher order constants which were necessary to fit the higher  $v$  lines.

The total angular momentum  $\mathbf{J}$ , for a diatomic molecule in the  $X^3\Sigma^-$  state is given by the coupling between the molecular angular momentum  $\mathbf{N}$  and the electronic spin momentum  $\mathbf{S}$  which leads to the well-known effective Hamiltonian (see for example 8, 11, 12, 30)

$$\begin{aligned} \mathbf{H} = & B_v \mathbf{N}^2 + \frac{2}{3} \lambda_v (3\mathbf{S}_z^2 - \mathbf{S}^2) + \gamma_v \mathbf{N}\mathbf{S} - D_v \mathbf{N}^4 \\ & + \frac{1}{3} D_\lambda [(3\mathbf{S}_z^2 - \mathbf{S}^2), \mathbf{N}^2]_+ + D_\gamma \mathbf{N}^2 \mathbf{N}\mathbf{S} + H_v \mathbf{N}^6. \end{aligned} \quad [6]$$

The additional constants  $\lambda_v$  and  $\gamma_v$  represent respectively the spin-spin and spin-rotation coupling and  $D_\lambda$  and  $D_\gamma$  the centrifugal contribution to these constants. They can be expanded analogously to the rotational constants (see for example 8, 11):

$$\begin{aligned} X_v = & X_e + \alpha_x \left( v + \frac{1}{2} \right) + \gamma_x \left( v + \frac{1}{2} \right)^2 \\ & + \delta_x \left( v + \frac{1}{2} \right)^3 + \epsilon_x \left( v + \frac{1}{2} \right)^4 \quad [7] \\ X_v = & (\lambda_v, \gamma_v, D_\lambda, D_\gamma). \end{aligned}$$

The 23 fitted molecular constants given in Table 6 are based on a global fit of our new results and most previously published frequencies (4, 7, 8, 10, 11). The latest measurements of Klaus *et al.* (32) carried out at Cologne and Nobeyama, Japan, which were sent to us prior to publication, have also been included in the fit. These results agree much better than those reported by Klaus *et al.* in 1994 (2). Since the different measured frequencies had differing precision it was found best to weight all the results as the inverse square of the supposed uncertainty. Most of our measured frequencies were allotted a precision of 50 kHz. Overlapped lines and measurements differing by more than  $3\sigma$  were allotted a precision of 1 MHz as in previous fits. Transitions measured both by us and by Klaus *et al.* agreed to better than the supposed experimental precision. Transitions measured by Cazzoli *et al.* (12), using sideband laser spectroscopy, up to 1.88 THz were also included in the fit with an estimated standard deviation of 500 kHz.

Table 6 compares our latest fit with the previous results of Bogey *et al.*, and the latest constants of Klaus *et al.* converted from mass independent units. The results of Klaus *et al.* are also based on a global fit but excluding the sideband laser measurements. The inclusion of these latter measurements in our fit gave only a minor improvement and varied little the values of the fitted constants, except for the coefficient  $Y_{03}$  which took a value of  $-1.6 \times 10^{-8}$  when they were excluded, more than twice as large as the value given in Table 6. This coefficient was necessary for a good fit of the high frequency data but in view of its changeability should be taken as a fitting constant and not a realistic molecular parameter. Since our results are based on higher vibrational states we determine four additional higher order constants for the main isotopomer. The inclusion of the results of Klaus *et al.* in our fit had little effect on these higher order constants but improved the standard deviation on the others.

## DISCUSSION

One purpose of this article has been to compare the use of laser photolysis as a method of production of reactive molecules for subsequent study by submillimeter-wave spectroscopy with that of the more widely used method of electric discharge. The results have shown that laser photolysis of  $\text{Cl}_2\text{SO}$  at 193 nm compares favorably with electric discharge of  $\text{SO}_2$  for the production and study of excited states of SO. However, the successful use of an ultra-violet laser combined with the BWOs for THz spectroscopy will require a modification in the way in which the laser beam is introduced into the cell in order to cut down microwave power losses in the coupling elements. At highest frequencies it was the discharge which gave highest experimental sensitivity and led to the measurement

**TABLE 5**  
**Dunham  $Y_{ij}$  Coefficients (MHz) of SO in the  $a^1\Delta$  State**

| Dunham Coefficient | This work                   | Endo <i>et al.</i> <sup>a</sup> | Klaus <i>et al.</i> <sup>b</sup> |
|--------------------|-----------------------------|---------------------------------|----------------------------------|
| $Y_{01}$           | 21386.0582(19) <sup>c</sup> | 21386.074(11)                   | 21386.0603(41)                   |
| $Y_{11}$           | -181.3450(19)               | -181.366(14)                    | -181.368(49)                     |
| $10^2 Y_{21}$      | 6.704(73)                   | 7.72(53)                        | 7.78(20)                         |
| $10^3 Y_{31}$      | -4.98(14)                   | -7.26(58)                       | -7.313(20)                       |
| $10^4 Y_{41}$      | -1.51(12)                   |                                 |                                  |
| $10^6 Y_{51}$      | -3.21(39)                   |                                 |                                  |
| $10^2 Y_{02}$      | -3.49910(40)                | -3.5057(83)                     | -3.4935(21)                      |
| $10^5 Y_{12}$      | -7.65(18)                   | 5.4(42)                         | -7.81(14)                        |
| $10^7 Y_{22}$      | -8.5(41)                    |                                 |                                  |
| $10^7 Y_{32}$      | -2.12(26)                   |                                 |                                  |
| $10^8 Y_{03}$      | -2.15(40)                   |                                 | -10.9(21)                        |
| $\sigma$           | 0.030                       |                                 |                                  |

<sup>a</sup> (Ref. 22)

<sup>b</sup> (Ref. 2) Values converted from mass independent parameters

<sup>c</sup> Values in brackets:  $1\sigma$

of the highest vibrationally excited states. It should however be noted that the comparison of the two methods for the study of SO is not entirely equitable. This radical was chosen as a small simple reactive molecule which is known to be created by discharge in mixtures of gaseous precursors such as SO<sub>2</sub> and since its spectra can easily be identified using predictions based on previous measurements. Planned future work on larger reactive molecules and on the study of reactive products of atmospheric pollutants (see for example 33) is based on theoretical and experimental work which characterizes the breakup of photosensitive precursors following UV irradiation at a given wavelength. It is not at all sure, however, if these new reactive molecules could be formed by discharge, or even, if they could be produced, whether it would be possible to identify their spectra amongst the other unknown products created simultaneously. On the other hand product concentration modulation following a laser pulse combined with time resolved detection has been shown to successfully discriminate not only against the precursor but also against all other molecules formed, provided their lifetime is significantly different from that of the molecule under study. It should also be remarked that the measurements of SO using SO<sub>2</sub> were taken with 10 times higher pressure in the cell than was

the case for the photolysis of Cl<sub>2</sub>SO. Early technical problems with the laser which limited the output power to well below its specified value have now been resolved. Since sample pressure was limited by total laser absorption it should now be possible to increase this pressure with a consequent increase in sensitivity. Finally, we would like to point out that the sensitivity following production of SO by discharge in SO<sub>2</sub> *without liquid nitrogen cooling* of the cell was significantly less than that obtained by photolysis. Cl<sub>2</sub>SO could not be cooled in this way owing to condensation at the exit of the axial glass rod (34) used to uniformly distribute the sample in the cell. This cooling has been found to significantly increase the signal due to molecules formed by discharge in gaseous precursors but cannot be used with the solid or liquid precursors envisaged for future work on larger reactive molecules.

We have shown that laser photolysis can be used as an alternative production method for radicals studied by millimeter- and submillimeter-wave spectroscopy even for the study of high lying electronic and vibrational states. This is to our knowledge the first time that laser photolysis has been used to determine the rotational spectrum of SO in the  $b^1\Sigma^+$  state at 10,509.97 cm<sup>-1</sup> above the ground electronic configuration.

**TABLE 6**  
**Molecular Constants (MHz) of SO in the  $X^3\Sigma^-$  State**

|                          | This work                    | Bogey <i>et al.</i> <sup>a</sup> | Klaus <i>et al.</i> <sup>b</sup> |
|--------------------------|------------------------------|----------------------------------|----------------------------------|
| $Y_{01}$                 | 21609.70280(53) <sup>c</sup> | 21609.7067(24)                   | 21609.70081(49)                  |
| $Y_{11}$                 | -172.40456(49)               | -172.4094(40)                    | -172.4008(10)                    |
| $Y_{21}$                 | 0.22460(17)                  | 0.2282(16)                       | 0.22401(66)                      |
| $10^3 Y_{31}$            | -1.664(28)                   | -2.57(17)                        | -1.59(15)                        |
| $10^5 Y_{41}$            | -8.12(18)                    |                                  |                                  |
| $10^6 Y_{51}$            | -1.411(42)                   |                                  |                                  |
| $10^2 Y_{02}$            | -3.390957(85)                | -3.3894(10)                      | -3.39048(11)                     |
| $10^5 Y_{12}$            | -1.205(47)                   | 0.14 <sup>d</sup>                | -2.31(11)                        |
| $10^7 Y_{22}$            | -9.67(62)                    |                                  |                                  |
| $10^9 Y_{03}$            | -7.39(27)                    | -2 <sup>d</sup>                  | -10.4(12)                        |
| $10^9 Y_{13}$            |                              |                                  | 7.6(12)                          |
| $\lambda_e$              | 157795.93(11)                | 157795.671(74)                   | 157795.534(68)                   |
| $\alpha_\lambda$         | 911.16(26)                   | 911.92(19)                       | 912.26(20)                       |
| $\gamma_\lambda$         | 11.39(11)                    | 10.85(11)                        | 10.74(15)                        |
| $\delta_\lambda$         | 0.214(16)                    | 0.386(13)                        | 0.345(37)                        |
| $10^2 \epsilon_\lambda$  | 1.516(68)                    |                                  | 0.69(27)                         |
| $10^1 D_{e\lambda}$      | 0.30431(21)                  | 0.3053(12)                       | 0.30431(19)                      |
| $10^3 \alpha_{D\lambda}$ | 4.17(26)                     | 4.3(12)                          | 4.28(34)                         |
| $10^4 \gamma_{D\lambda}$ | 2.97(44)                     |                                  | 2.76(69)                         |
| $\gamma_e$               | -167.6434(45)                | -167.680(20)                     | 167.6552(35)                     |
| $\alpha_\gamma$          | -1.3274(40)                  | -1.266(22)                       | -1.3119(60)                      |
| $10^2 \gamma_\gamma$     | 2.101(64)                    |                                  | 1.94(13)                         |
| $10^4 D_{e\gamma}$       | -5.331(76)                   |                                  | -5.186(35)                       |
| $10^5 \alpha_{D\gamma}$  | 1.29(36)                     |                                  |                                  |
| $\sigma$                 | 0.020                        |                                  |                                  |

<sup>a</sup> (Ref. 11)

<sup>b</sup> (Ref. 32) Values converted from mass independent parameters

<sup>c</sup> Values in brackets:  $1\sigma$

<sup>d</sup> Derived value

## ACKNOWLEDGMENTS

The Laboratoire de Spectroscopie Hertzienne is a research unit associated with the CNRS. The Centre d'Études et de Recherches Lasers et Applications (CERLA) is supported by the French Research Ministry, the Nord-Pas de Calais Region, and the European Regional Economic Development Fund. The acquisition of new BWOs and an excimer laser was funded in part by the CNRS. M.Yu.T. thanks the European Union (PECO Contract CIPDCT 94-0614), A.F.K. thanks the Nord-Pas de Calais Region and S.C.

thanks the CNRS for supporting their stay in Lille. The authors wish to thank Th. Klaus and G. Winnemisser for sending their latest measurements before publication.

## REFERENCES

1. S. Yamamoto, *Chem. Phys. Lett.* **212**, 113 (1993).
2. Th. Klaus, S. P. Belov, A. H. Saleck, G. Winnemisser, and E. Herbst, *J. Mol. Spectrosc.* **168**, 235 (1994).

3. R. Kewley, K. V. L. N. Sastry, M. Winnewisser, and W. Gordy, *J. Chem. Phys.* **39**, 2856 (1963).
4. M. Winnewisser, K. V. L. N. Sastry, R. L. Cook, and W. Gordy, *J. Chem. Phys.* **41**, 1687 (1964).
5. F. X. Powell and D. R. Lide, *J. Chem. Phys.* **41**, 1413 (1964).
6. T. Amano, E. Hirota, and Y. Morino, *J. Phys. Soc. Jpn.* **22**, 399 (1967).
7. E. Tiemann, *J. Mol. Spectrosc.* **51**, 316 (1974).
8. E. Tiemann, *J. Mol. Spectrosc.* **91**, 60 (1982).
9. S. Saito, *J. Chem. Phys.* **53**, 2544 (1970).
10. W. W. Clark and F. C. De Lucia, *J. Mol. Spectrosc.* **60**, 332 (1976).
11. M. Bogey, C. Demuynck, and J. L. Destombes, *Chem. Phys.* **66**, 99 (1982).
12. G. Cazzoli, L. Cludi, G. Gotti, C. Degli Esposti, and L. Dore, *J. Mol. Spectrosc.* **167**, 468 (1994).
13. H. Kanamori, J. E. Butler, K. Kawaguchi, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.* **113**, 262 (1985).
14. H. Kanamori, J. E. Butler, K. Kawaguchi, C. Yamada, and E. Hirota, *J. Chem. Phys.* **83**, 611 (1985).
15. W. F. Kolbe and B. Leskovar, *Rev. Sci. Instrum.* **56**, 1577 (1985).
16. J. Wildt, E. H. Fink, and F. Zabel, *Chem. Phys.* **80**, 167 (1983).
17. X. Chen, F. Asmar, H. Wang, and B. R. Weiner, *J. Phys. Chem.* **95**, 6415 (1991).
18. H. Kanamori, E. Tiemann, and E. Hirota, *J. Chem. Phys.* **89**, 621 (1988).
19. H. Wang, X. Chen, and B. R. Weiner, *J. Phys. Chem.* **97**, 12,260 (1993).
20. M. Kawasaki, K. Kasatani, H. Sato, H. Shinohara, N. Nishi, H. Ohtoshi, and I. Tanaka, *Chem. Phys.* **91**, 285 (1984).
21. G. Baum, C. S. Effenhauser, P. Felder, and J. R. Huber, *J. Phys. Chem.* **96**, 756 (1992).
22. Y. Endo, H. Kanamori, and E. Hirota, *Chem. Phys. Lett.* **141**, 129 (1987).
23. C. E. M. Strauss and P. L. Houston, *J. Phys. Chem.* **94**, 8751 (1990).
24. M. Bogey, H. Bolvin, M. Cordonnier, C. Demuynck, J. L. Destombes, and A. G. Császár, *J. Chem. Phys.* **100**, 8614 (1994).
25. J. L. Destombes, M. Bogey, M. Cordonnier, C. Demuynck, and A. Walters, in "Molecules and Grains in Space" (I. Nenner Ed.), Conference Proceedings No. 312, p. 268, American Institute of Physics, 1994.
26. S. Bailleux, M. Bogey, C. Demuynck, J. L. Destombes, and A. Walters, *J. Chem. Phys.* **101**, 2729 (1994).
27. A. F. Krupnov, M. Yu. Tretyakov, M. Bogey, S. Bailleux, A. Walters, B. Delcroix, and S. Civis, *J. Mol. Spectrosc.* **176**, 442 (1996).
28. G. Winnewisser, A. F. Krupnov, M. Yu. Tretyakov, M. Liedke, F. Lewen, A. H. Saleck, R. Schieder, A. P. Shkaev, and S. V. Volokhov, *J. Mol. Spectrosc.* **165**, 294 (1994).
29. S. P. Belov, F. Lewen, Th. Klaus, and G. Winnewisser, *J. Mol. Spectrosc.* **174**, 606 (1995).
30. D. De Santis, A. Lurio, T. A. Miller, and R. S. Freund, *J. Chem. Phys.* **58**, 4625 (1973).
31. Th. Klaus and G. Winnewisser, personal communication.
32. Th. Klaus, A. H. Saleck, S. P. Belov, G. Winnewisser, Y. Hirahara, M. Hayashi, E. Kagi, and K. Kawaguchi, *J. Mol. Spectrosc.* **180**, 606 (1996).
33. J. S. Levine (Ed.), "The Photochemistry of Atmospheres, Earth, the Other Planets, and Comets," Academic Press, Orlando, FL, 1985.
34. M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, *Phys. Rev. Lett.* **66**, 413 (1991).