

Multiphoton photofragmentation of SO₂ at 248 nm

M. W. Wilson, M. Rothschild, D. F. Muller, and C. K. Rhodes

Citation: *The Journal of Chemical Physics* **77**, 1837 (1982); doi: 10.1063/1.444035

View online: <http://dx.doi.org/10.1063/1.444035>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/77/4?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Resonances in multiphoton ionization of helium at 248 nm](#)

AIP Conf. Proc. **525**, 211 (2000); 10.1063/1.1291940

[A laser photofragmentation time-of-flight mass spectrometric study of acetophenone at 193 and 248 nm](#)

J. Chem. Phys. **107**, 7230 (1997); 10.1063/1.474964

[Stateresolved photofragmentation dynamics of Fe\(CO\)₅ at 193, 248, 266, and 351 nm](#)

J. Chem. Phys. **88**, 6658 (1988); 10.1063/1.454406

[Photofragmentation of antimony and bismuth cluster cations at 248 nm](#)

J. Chem. Phys. **88**, 163 (1988); 10.1063/1.454631

[Photofragmentation dynamics of CH₃I at 248 and 266 nm: Vibrational distributions in the CH₃\(v₂\) “umbrella” mode](#)

J. Chem. Phys. **76**, 4766 (1982); 10.1063/1.442795



Multiphoton photofragmentation of SO₂ at 248 nm

M. W. Wilson, M. Rothschild, D. F. Muller, and C. K. Rhodes

Department of Physics, University of Illinois at Chicago Circle, Chicago, Illinois 60680
(Received 22 April 1982; accepted 11 May 1982)

Sequential two-photon photoexcitation of SO₂ at 248 nm is found to lead to a number of primary fragments including S(³P) and SO(*X*³Σ⁻). Further excitation of some of these photoproducts was also observed, occurring by both linear and two-quantum mechanisms. The resulting molecular *X*←*B* (*v*^{''}, 2) ultraviolet fluorescence from SO and the atomic ³P←³S vacuum ultraviolet emission from S atoms were detected and an analysis of the energy flow patterns was made.

I. INTRODUCTION

The emergence in recent years of powerful ultraviolet lasers has made possible the multiphoton excitation of molecules to high-lying states, thus permitting the detailed investigation of the spectroscopic and dynamic properties of those levels.^{1,2} In previous studies, it was frequently observed that the photoexcitation was followed by molecular dissociation, a fact readily enabling the analysis of the behavior of free radicals in their ground or excited states.³⁻⁶ In certain instances, accidental resonances allow the excitation of primary photofragments⁷ or products of chemical reactions involving primary fragments,⁸ and thus, additional species of excited atoms and molecules can be generated.

In the present study, the SO₂ molecule was photodissociated by two-photon stepwise absorption at 248 nm. The pattern of fragmentation was complex involving at least two different channels of dissociation. Furthermore, accidental resonances at 248 nm exist both in the SO (*X*³Σ⁻) and S(³P) photofragments for one and two photon excitation, respectively. In these studies, the ensuing fluorescence in the ultraviolet (UV) and vacuum ultraviolet (VUV) was observed and analyzed.

II. EXPERIMENTAL

The experimental configuration used was similar to that employed in previous experiments.^{8,9} The output from an excimer laser (Lambda Physics model 101, equipped with an unstable resonator), operating at 248 nm, was focused into a stainless steel gas cell containing SO₂. The maximum ultraviolet energy available was typically ~0.2 J in pulses of ~15 ns duration. The repetition rate was 1-2 Hz. The laser energy was readily varied with a set of neutral density filters (Acton Research).

Focusing was achieved with a 10 cm focal length CaF₂ lens, which served also as the entrance window to the cell. The fluorescence from the focal region was collected in a direction perpendicular to the direction of propagation of the 248 nm beam by a LiF lens, and imaged onto the entrance slit of a 1/3 m evacuable monochromator (McPherson model 218). In the performance of these measurements, the monochromator was equipped with various gratings, blazed at wavelengths in the visible, near UV and VUV. The time-integrated fluorescence spectrum at the exit slit of the monochromator was detected with an optical multichannel analyzer (Princeton Applied Research model 1205A), or, alter-

natively, by a photomultiplier whose output was fed into a microprocessor-controlled sample averager. Additionally, the time dependence of the UV fluorescence was observed with a solar blind photomultiplier (EMI model G26H3152), and analyzed with a transient digitizer (Tektronix model 7912AD).

The gases used in the present experiment were: SO₂, nominally 99.98% pure (Matheson, anhydrous grade); OCS, 97.5% pure (Air Products, Technical grade); H₂S, 99.5% pure (Matheson, C. P. grade). The liquids SOCl₂ and CS₂ were 97% pure (Aldrich) and 99+% pure (Aldrich, gold label), respectively. They were further purified through a number of freeze-pump-thaw cycles. The SO₂ was also analyzed with the aid of a mass spectrometer. This analysis revealed levels of OCS and CS₂ as high as a few percent.

III. RESULTS AND DISCUSSION

Fluorescence bands in the UV and extending into the visible were observed at all laser intensities in the range 10⁸-10⁹ W/cm², with SO₂ pressures corresponding to 1-20 Torr. The time-integrated intensity of these bands was linear in SO₂ pressure, indicating that no collisional effects played a significant role in the range 1-20 Torr. Also, the temporal behavior of this fluorescence exhibited only slight broadening compared to the laser pulse duration, and this prompt behavior persisted even at the lowest pressures used (~1 Torr).

All the observed fluorescence lines in the 250-450 nm range were identified as belonging to one vibronic series in SO, namely, the *X*³Σ⁻ - *B*³Σ⁻ (*v*^{''}, 2) transitions (for part of the spectrum, see Fig. 1). All but six of the members of this series with *v*^{''} = 0-21 have been observed. Their positions were found to be red shifted by ~30-35 cm⁻¹ as compared to previously determined band origins,¹⁰ and their relative intensities were proportional to their published Franck-Condon factors.^{10,11} The transitions which have not been detected all have Franck-Condon factors smaller than 1 × 10⁻³,^{10,11} except for the (*v*['], *v*^{''}) = (2, 2) line, which is masked by scattered laser light. The observed short decay time, which, due to the laser pulse duration could be determined only to be ≤ 25 ns, also agrees with the measured radiative lifetime of SO (*B*, *v* = 2)¹², namely, *t*_r = 16.2 ns.

No UV emission lines were detected from other excited states of SO, in contrast with previously reported *X*-*A* lines,¹³ although a number of weaker unassigned lines were observed in the 500-700 nm range.

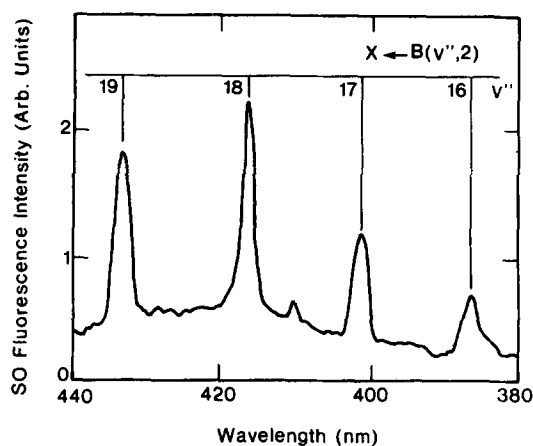


FIG. 1. Part of the molecular SO fluorescence, as recorded on the OMA. The SO₂ pressure was 10 Torr and the laser fluence at the focus was ~ 5 J/cm².

The mechanism whereby the SO ($B^3\Sigma^-$) molecules are generated can be understood from the known spectroscopy and energy levels of SO₂ and SO. The SO₂ molecule has an absorption spectrum in the 230–300 nm region, which is composed of a series of narrow structures superimposed on a broad continuum.¹⁴ The transitions corresponding to the structured and continuous absorption features are¹⁵ $\bar{X}^1A_1-\bar{A}^1A_2$ and $\bar{X}^1A_1-\bar{B}^1B_1$, respectively. At the shorter wavelengths ($\lambda \lesssim 260$ nm), an increasing fraction of the oscillator strength belongs to the $\bar{X}-\bar{B}$ transition.¹³

Quite independently of the nature of the absorption at 248 nm, it has been established¹⁶ that the threshold of the lowest channel of dissociation of SO₂, into SO($X^3\Sigma^-$) and O(3P), lies at ~ 219 nm. Therefore, dissociation of SO₂, in the present studies could not take place with the absorption of a single 248 nm quantum. Indeed, it is noted that the energy of two laser photons corresponds to a vibronic transition to the Rydberg \bar{G} state^{17,18} in SO₂. Furthermore, the $\bar{X}-\bar{G}$ transition is two-photon allowed.^{18,13} Thus, upon sequential absorption of two 248 nm quanta, the SO₂ molecule is endowed with sufficient energy to dissociate into a number of possible products¹⁹: SO(X, a, b) + O($^3P, ^1D, ^1S$), O₂(X, a, b) + S($^3P, ^1D, ^1S$). If some of the fragments are SO($X^3\Sigma^-$) molecules in the $v''=2, J'' \approx 15-25$ rovibrational states, these molecules have a resonant transition to the $B^3\Sigma^- (v'=2)$ state,^{10,20} a level which lies within the bandwidth of the free-running excimer laser (248.4 ± 0.2) nm.²¹ The above-mentioned red shift of 30–35 cm⁻¹ is attributed to the resonance condition which applies only to this particular set of rotational levels. Thus, the photoexcitation of SO is a highly selective process, limited only by the spectral width of the laser.

It should be noted that the SO($X^3\Sigma^-$) molecules are primary products of the photodissociation of SO₂. The employment of a narrow bandwidth, tunable laser at 248 nm²² could probe the rotational distribution of the nascent SO, and thereby, provide important clues regarding the energy partitioning in photofragments.^{23–28}

SO($X^3\Sigma^-$) can also be the product of a chemical reac-

tion involving the primary photofragments O₂ ($X^3\Sigma^-$) and S (3P).¹⁹ However, the rate constant of this reaction is sufficiently low²⁷ ($k \sim 2 \times 10^{-12}$ cm³ s⁻¹) that, at $\lesssim 20$ Torr of SO₂, only a negligible fraction of O₂ and S recombine during the laser pulse.

Figure 2 depicts the intensity dependence of the integrated SO fluorescence. As shown by the figure, this dependence is nonlinear at low fluences ($\lesssim 1.0$ J/cm²), represents a linear profile in the intermediate range (1–5 J/cm²), and exhibits saturation above ~ 5 J/cm². The absorption cross section of SO₂ (\bar{X}^1A_1) is¹⁴ $\sigma_{SO_2} \approx 7.5 \times 10^{-20}$ cm² at 248 nm. The effective cross section of the SO ($X-B$) transition was calculated from its oscillator strength¹⁰ ($f \approx 1.1 \times 10^{-4}$), and the ratio of the Doppler width (~ 0.07 cm⁻¹) to the laser linewidth²¹ (~ 70 cm⁻¹): $\sigma_{SO} \approx 1.3 \times 10^{-18}$ cm².

These values of σ_{SO} and σ_{SO_2} were used to calculate the fluences at which these transitions saturate, E_{sat}^{SO} and $E_{sat}^{SO_2}$ and the magnitudes of these saturation fluences are indicated in Fig. 2. Significantly, they correspond to the points at which the order of nonlinearity of the SO fluorescence changes. One more saturation point should have been observed, namely that of the second transition in SO₂: $\bar{B}-\bar{G}$. We attribute the absence of this point to the magnitude of the cross section for the $\bar{B}-\bar{G}$ transition which, being larger than σ_{SO} , lowers the saturation fluence below ~ 0.4 J/cm², the low end of the experimental range.

Other molecules, in addition to SO₂, could be used as "donors" of SO. Such a molecule is SOCl₂, which has a large absorption cross section at 248 nm,²⁸ $\sigma_{SOCl_2} \approx 7 \times 10^{-18}$ cm², and which dissociates into SO + 2Cl.²⁹ Indeed, we have observed identical spectra in the UV, when SO₂ was replaced by SOCl₂. The intensity dependence of the SO fluorescence again exhibited saturation points, but at different fluences. These

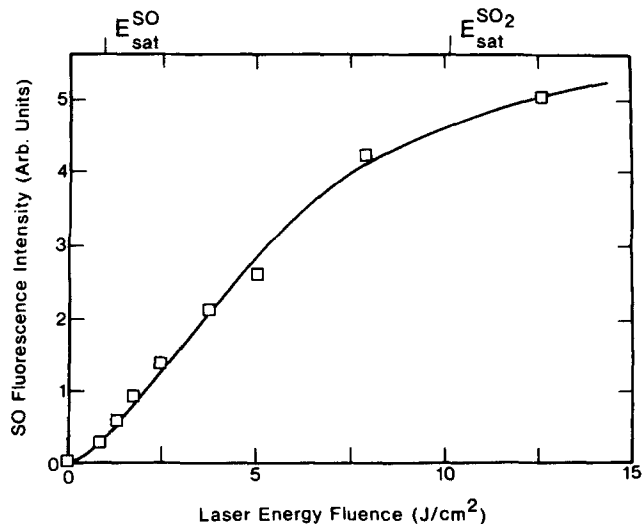


FIG. 2. The dependence of the integrated SO fluorescence on laser fluence at the focus. The fluences at which the $X-B$ transition in SO and the $\bar{X}-\bar{B}$ transition in SO₂ should be saturated are indicated on the upper scale.

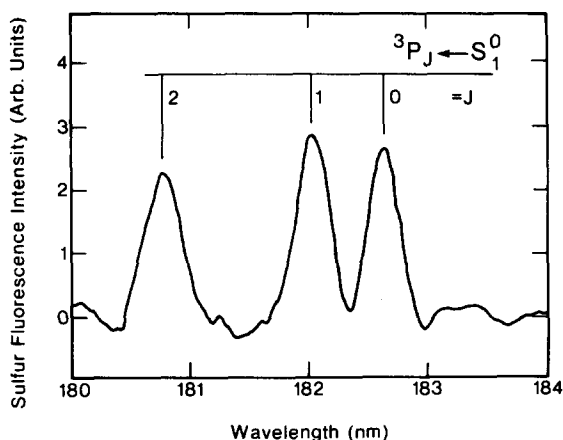
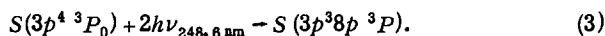
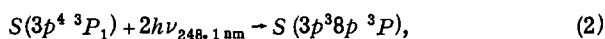
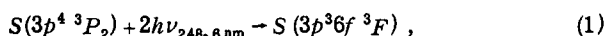


FIG. 3. The atomic fluorescence from the excited ($3p^3 4s$) $^3S_1^0$ state to the three levels of the ($3p^4$) 3P_J ground state in sulfur. The SO₂ pressure was 0.4 Torr, and the laser fluence at the focus was ~ 10 J/cm².

fluences could be correlated to saturation of the transitions in SOCl₂ and SO.

At low pressures of SO₂ (≤ 2 Torr), the 248 nm laser excitation was followed also by vacuum-UV fluorescence of three narrow lines in the vicinity of 182 nm. These lines were identified as belonging to transitions from the first dipole-allowed state in the sulfur atom ($3p^3 4s$) $^3S_1^0$ to its ground state ($3p^4$) $^3P_{0,1,2}$ (see Fig. 3). Naturally, the emission at wavelengths shorter than that of the laser implies the existence of a nonlinear mechanism of optical excitation. Indeed, if sulfur atoms in their ground state are generated during the laser pulse they can be excited in a two-photon process (with no intermediate near resonances) to high-lying states, less than 0.5 eV below the ionization limit³⁰



The excited 3F or 3P state can then relax (probably radiatively) to the $^3S_1^0$ state, from which the 182 nm radiation originates.

The source of most of the ground state sulfur atoms was not the photodissociation of any of the sulfur-containing impurities, which were present in SO₂: OCS, CS₂, and H₂S. To test this assertion, known amounts of the above molecules were introduced into the system and irradiated under identical conditions to those of SO₂. No VUV radiation was detected from CS₂ up to 50 Torr, and only very weak 182 nm sulfur lines were observed from H₂S at 10 Torr and above. The irradiation of OCS did produce significant amounts of 182 nm radiation. However, a comparison of the fluorescence intensities in SO₂ and OCS led to the conclusion that unless the SO₂ samples contained $\sim 50\%$ OCS as impurities, the SO₂ molecules themselves were the origin of sulfur atoms. Clearly, the latter possibility is indicated on the basis of the previously mentioned assay of the impurities in the experimental material. Furthermore, the intensity dependence of the integrated 182 nm radiation exhibited

cubic dependence (I^3) at low intensities and a quadratic dependence (I^2) at intensities higher than approximately E_{sat}^{80} . This behavior strongly supports the conclusion that the excited sulfur atoms were generated from the photodissociation of SO₂.

The near-UV molecular fluorescence discussed above has established that at least one of the dissociation channels of SO₂ (\tilde{G}) yields SO and O, and that some of the SO($X^3\Sigma^-$), with rotational quantum number $J \leq 25$ are further excited to SO($B^3\Sigma^-, v' = 2$). It is known that the SO($B, v' = 2$) state is rotationally predissociated³¹ for $J \geq 39$. Nevertheless, the molecules excited in the present experiment have $J \leq 25$, states which are ~ 400 cm⁻¹ below $J = 39$, a factor preventing any direct predissociation. Collisional predissociation is likewise excluded, since the S atomic lines were observed at pressures below 1 Torr, a pressure sufficiently low that collisional effects occurring during the 15 ns laser pulse would be negligible. Moreover, the SO molecular fluorescence did not exhibit any quenching effects at pressures as high as 10 Torr.

Another possibility for the production of sulfur atoms from SO is the subsequent excitation of $B^3\Sigma^-$ states to high lying Rydberg states of SO which could predissociate in S(3P) and O($^3P, ^1D, ^1S$). We note that the ionization potential of SO is²⁰ 10.3 eV, only ~ 0.3 eV above the energy of two 248 nm quanta. However, the intensity dependence of the 182 nm emission indicates that, at fluences above ~ 5 J/cm², the process through which S(3P) is generated is saturated. Furthermore, if this process involved depopulation of the fluorescing SO($B^3\Sigma^-$) state, the ultraviolet molecular fluorescence arising from this level should decrease at those fluences. This expected behavior is contrary to the experimental evidence (see Fig. 2), and it is concluded that SO is not a significant precursor of S.

Since neither impurities nor SO are indicated as the principal source of S(3P), it remains that the sulfur

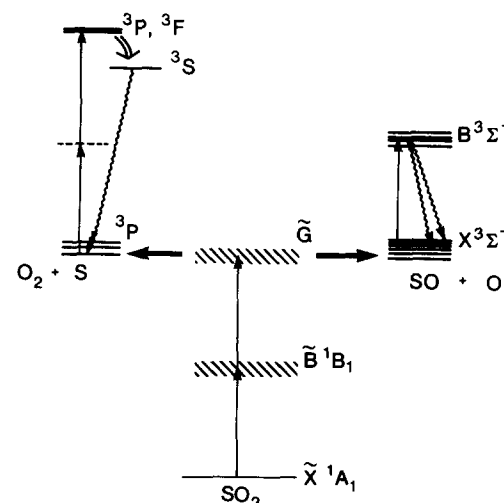


FIG. 4. A schematic diagram of the various excitation and dissociation processes reported in this study. The energy levels are not drawn to scale. Vertical arrows denote photoexcitation, horizontal arrows denote dissociation, and the wiggly arrows represent the observed fluorescence.

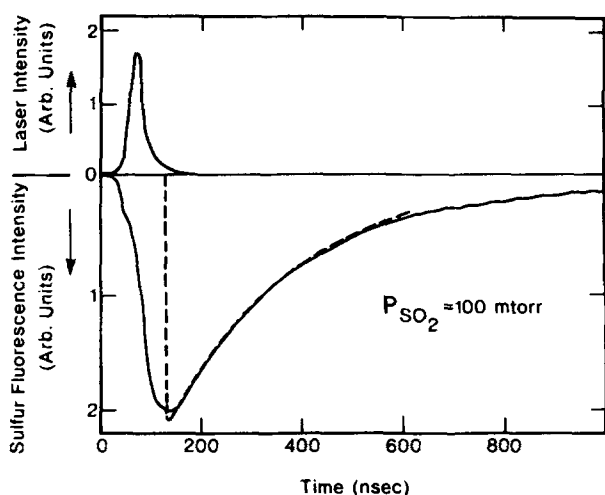


FIG. 5. The temporal behavior of the atomic sulfur fluorescence (solid line, lower trace), the laser pulse (upper trace), and the theoretical best fitting curve (broken line). The theoretical model applies only after the laser pulse is over, and therefore, the theoretical and experimental risetimes are different.

atoms observed must be a primary photoproduct of SO₂. This implies that the excited SO₂ (\bar{G}) state dissociates through at least two different channels, SO($X^3\Sigma^-$) + O and O₂ + S(3P), as indicated in Fig. 4. In this connection, it should be noted that the vibrational band at 124 nm corresponds to the $v=4$ excitation of the ν_2 bending mode¹⁸ of SO₂. The geometry of the excited state is, therefore, conducive to the formation of molecular oxygen and the simultaneous breaking of the two S-O bonds. Indeed, it has been reported¹⁹ that S(3P) and S(1D) were among the primary photofragments of SO₂ at 124 nm and at 117 nm.

Once the S(3P) is generated, a nonresonant two-photon excitation to a 3P or 3F state takes place according to the processes specified in Reactions (1)–(3). The detailed energy relaxation pathways from the excited state to the 3S state, which is the upper state of the 182 nm radiation, are not clearly evident from the observations made in this study. However, the temporal behavior of the fluorescence can be analyzed to determine an average rate of energy flow into the 3S state. The 182 nm radiation exhibited a rise time which did not change with pressure (up to ~2 Torr), and which coincided with the full duration of the laser pulse (~50 ns). The decay time was longer, approximately 100–500 ns, and decreased with increasing pressure (Fig. 5). The temporal behavior of the fluorescence $I_f(t)$ observed after the laser pulse, can be fitted by a double-exponential curve, which is derived from the standard set of rate equations

$$I_f(t) = C[\exp(-K_r t) - \exp(-Wt)], \quad (4)$$

in which C is an experimental constant, K_r is the radiative decay rate³² of the 3S state ($K_r = 7.1 \times 10^8 \text{ s}^{-1}$), and W represents the decay rate of the excited 3P or 3F state. Collisional deactivation rates of the 3S state were assumed to be negligible compared to K_r ($p \leq 2$ Torr), but W denotes the sum of both radiative and

collisional rates, and can be written in the form

$$W(p) = (\tau_r)^{-1} + kp, \quad (5)$$

in which k represents the collisional rate constant and p the pressure.

The experimental decay curves were fitted to Eq. (4), with $W(p)$ as an adjustable parameter. A typical fit, at $p = 0.1$ Torr, is shown in Fig. 5. It should be pointed out, however, that the simple model which leads to Eq. (4) is applicable only after the termination of the laser pulse. Therefore, the rising portion of the theoretical curve was not adjusted to the experimental curve. A linear best fit of the values of W as a function of SO₂ pressure ($0.1 \text{ Torr} \leq p \leq 1.0 \text{ Torr}$) yielded the following values: $\tau_r = (250 \pm 50) \text{ ns}$, $k = (1.6 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

IV. CONCLUSIONS

Both molecular fluorescence (250–450 nm) of SO($X^3\Sigma^-$) and the atomic emission lines of S(3S – 3P) at 182 nm were observed upon irradiation of SO₂ with intense radiation at 248 nm. Analysis of these emissions indicated that the SO₂ molecule absorbed two quanta and was excited to a strongly vibrating bending mode of a high lying electronic state. Furthermore, in this excited configuration, dissociation into both SO + O and S + O₂ channels became possible. The primary photoproducts SO($X^3\Sigma^-$, $v'' = 2$, $15 \leq J'' \leq 25$) and S($^3P_{0,1,2}$), were further excited in linear and nonresonant two-photon processes, respectively. In the case of SO, prompt reradiation was observed, whereas in S the upper state first relaxed to the lowest 3S level from which 182 nm radiation was generated in a transition to the S(3P) ground state. It is observed that appreciable densities of atomic and molecular excited states can be generated by nonlinear processes of this nature, since the molecular transitions in SO₂ and in SO were readily saturated at the available laser intensities. In related studies, it was also demonstrated that irradiation of other molecules which contain SO, such as SOCl₂, also produce SO molecular fluorescence. Similarly, the atomic sulfur lines were seen in the excitation of the sulfur containing molecules OCS and H₂S.

A final comment concerning the suitability of the use of high brightness²² tunable excimer systems in molecular studies of this type is indicated. Since linewidths less than the rotational spacing are easily generated,²² the rotational distribution of the nascent SO molecule could be simply determined. Also, the relative population of the three fine structure levels of the ground state nascent sulfur atom could likewise be measured. Furthermore, the two-photon excitation of S(3P) could be saturated, thus making possible an optically excited vacuum ultraviolet three-level laser at 182 nm.

ACKNOWLEDGMENTS

The authors thank S. Vendetta and M. Klawitter for building the microcomputer-controlled sample averager, and Dr. R. P. Burns for help in the mass-spectrometric analysis of SO₂. This work was supported by the National Science Foundation under grant number NSF PHY81-16626, the Department of Energy under

contract number DE-AC02-80ET33065, the Office of Naval Research, and the Air Force Office of Scientific Research under grant number AFOSR-79-0130.

- ¹D. J. Kligler and C. K. Rhodes, *Phys. Rev. Lett.* **40**, 309 (1978).
- ²J. Bokor, J. Zavelovich, and C. K. Rhodes, *J. Chem. Phys.* **72**, 965 (1980).
- ³L. Pasternack and J. R. McDonald, *Chem. Phys.* **43**, 173 (1979).
- ⁴V. M. Donnelly, A. P. Baronavski, and J. R. McDonald, *Chem. Phys.* **43**, 283 (1979).
- ⁵C. Fotakis, M. Martin, K. Lawley, and R. J. Donovan, *Chem. Phys. Lett.* **80**, 598 (1981).
- ⁶R. J. Donovan, in *Gas Kinetics and Energy Transfer* (The Royal Society of Chemistry, London, 1981), Vol. 4.
- ⁷M. W. Wilson, M. Rothschild, D. F. Muller, and C. K. Rhodes, *J. Chem. Phys.* **76**, 4452 (1982).
- ⁸J. Zavelovich, M. Rothschild, W. Gornik, and C. K. Rhodes, *J. Chem. Phys.* **74**, 6787 (1981).
- ⁹M. Rothschild, W. Gornik, J. Zavelovich, and C. K. Rhodes, *J. Chem. Phys.* **75**, 3794 (1981).
- ¹⁰G. R. Hébert and R. V. Hodder, *J. Phys.* B **7**, 2244 (1974).
- ¹¹W. H. Smith and H. S. Liszt, *J. Quant. Spectrosc. Radiat. Transfer* **11**, 45 (1971).
- ¹²W. H. Smith, *J. Quant. Spectrosc. Radiat. Transfer* **9**, 1191 (1969).
- ¹³C. Fotakis, *Chem. Phys. Lett.* **82**, 68 (1981).
- ¹⁴P. Warneck, F. F. Marmo, and J. O. Sullivan, *J. Chem. Phys.* **40**, 1132 (1964).
- ¹⁵J. C. Brand, J. L. Hardwick, D. R. Humphrey, Y. Hamada, and A. J. Merer, *Can. J. Phys.* **54**, 186 (1976).
- ¹⁶H. Okabe, *J. Am. Chem. Soc.* **93**, 7095 (1971).
- ¹⁷G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
- ¹⁸I. W. Watkins, *J. Mol. Spectrosc.* **29**, 402 (1969).
- ¹⁹C. Lalo and C. Vermeil, *J. Photochem.* **3**, 441 (1974/75).
- ²⁰K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
- ²¹T. R. Loree, K. B. Butterfield, and D. L. Barker, *Appl. Phys. Lett.* **32**, 171 (1978).
- ²²R. T. Hawkins, H. Egger, J. Bokor, and C. K. Rhodes, *Appl. Phys. Lett.* **36**, 391 (1980).
- ²³O. Atabek, J. A. Beswick, R. Le Febvre, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **65**, 4035 (1976).
- ²⁴A. Freedman, S.-C. Yang, and R. Bersohn, *J. Chem. Phys.* **70**, 5313 (1979).
- ²⁵M. D. Morse and K. F. Freed, *Chem. Phys. Lett.* **74**, 49 (1980).
- ²⁶W. G. Hawkins and P. L. Houston, *J. Chem. Phys.* **76**, 729 (1982).
- ²⁷D. D. Davis, R. B. Klemm, and M. Pilling, *Int. J. Chem. Kinet.* **IV**, 367 (1972).
- ²⁸A. P. Uthman, P. J. Demlein, T. D. Allston, M. C. Withiam, M. J. McClements, and G. A. Takacs, *J. Phys. Chem.* **82**, 2252 (1978).
- ²⁹R. J. Donovan, D. Husain, and P. T. Jackson, *Trans. Faraday Soc.* **65**, 2930 (1969).
- ³⁰C. E. Moore, *Atomic Energy Levels*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. **35** (1971), Vol. I.
- ³¹E. V. Martin, *Phys. Rev.* **41**, 167 (1932).
- ³²W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. **22** (1969), Vol. II.