

## GAS PHASE GENERATION OF $O_2(^1\Delta_g)$ AT ATMOSPHERIC PRESSURE BY DIRECT LASER EXCITATION<sup>†</sup>

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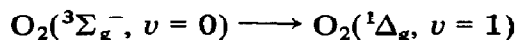
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### Summary

$O_2(^1\Delta_g)$  was generated in the gas phase at atmospheric pressure by direct laser excitation. A Holobeam model 255 Nd-YAG laser with an output at 1065 nm was used to achieve the transition



The mean lifetime  $\tau$  of the resulting excited oxygen species in the gas phase at atmospheric pressure was measured to be  $0.124 \pm 0.012$  s. This corresponds to a bimolecular rate constant  $k_2$  for the overall reaction  $O_2(^1\Delta_g, v = 1) + O_2(^3\Sigma_g^-) \rightarrow 2O_2(^3\Sigma_g^-)$  of  $(3.3 \pm 0.4) \times 10^{-19}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>, a factor of 10 below the currently accepted value for ground state oxygen deactivation of singlet oxygen. Possible reasons for this difference are discussed.

### 1. Introduction

A variety of methods have been developed to generate singlet oxygen in order to study its physical and chemical properties [1]. One method involved the direct optical excitation of oxygen at high pressures, usually in an inert solvent. The advantage of this method is its high selectivity. Evans [2] produced the  $^1\Delta_g$  state of oxygen in a cell containing oxygen at 2000 lbf in<sup>-2</sup> dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane by direct irradiation with an He-Ne laser at 632.2 nm.  $O_2(^1\Delta_g)$  oxidation products with 9,10-diphenylanthracene were observed. Matheson *et al.* [3] observed the singlet oxygen "dimol" emission from neodymium glass laser-pumped oxygen in the gas phase and in 1,1,2-trichloro-1,2,2-trifluoroethane solution. Matheson and

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Lee [4] and Evans and Tucker [5] used an Nd-YAG laser at 1065 nm to generate the  $O_2(^1\Delta_g)$  state in solution at high oxygen pressures up to 140 atm.  $O_2(^1\Delta_g)$  was characterized by its reaction with known chemical acceptors in all these cases. The use of a high intensity dye laser to produce singlet oxygen has also been reported [6], and involved the excitation of a dye sensitizer and energy transfer to ground state oxygen (an indirect method). The reported methods for the direct excitation of ground state oxygen to excited singlet states have all involved high oxygen pressures, in either the gas or the solution phase. We have recently reported the atmospheric gas phase generation of singlet oxygen by chemical photosensitization [7] and direct irradiation using simulated sunlight [8]. We now report the formation of  $O_2(^1\Delta_g)$  in the gas phase at atmospheric pressure using direct laser excitation. Evidence for the formation of  $O_2(^1\Delta_g)$  was obtained in chemical trapping and quenching experiments and in the observation of the characteristic 1.27  $\mu\text{m}$  emission.

## 2. Experimental details

### 2.1. Laser apparatus

The excitation source used was a Holobeam model 255 Nd-YAG laser, which had a nominal output of about 40 W and 80 W in the continuous wave (CW) and the pulsed modes respectively. Chemical trapping experiments were performed in a reactor consisting of a Pyrex tube (30 cm  $\times$  2.5 cm (outside diameter)) with quartz windows 3 mm thick on either end. Teflon glass valves at either end of the reactor allowed the addition and removal of chemical trapping agents. The laser was operated in the CW mode during the chemical trapping experiments, with its beam making a single pass through the center of the Pyrex tube (Fig. 1).

Direct observation of the 1.27  $\mu\text{m}$  emission of  $O_2(^1\Delta_g)$  as it was generated in the gas phase at atmospheric pressure by laser excitation was also studied. The apparatus is shown in Fig. 2. It consisted of an integrating sphere made from a 50 ml glass bulb with two 6 mm glass tubes arranged at right angles to one another. The inner surface of the sphere was aluminized except for a small aperture to permit the entrance of the laser beam. The optical detection system was located at the exit tube of the integrating sphere and was separated from it by a light trap. The detector system con-

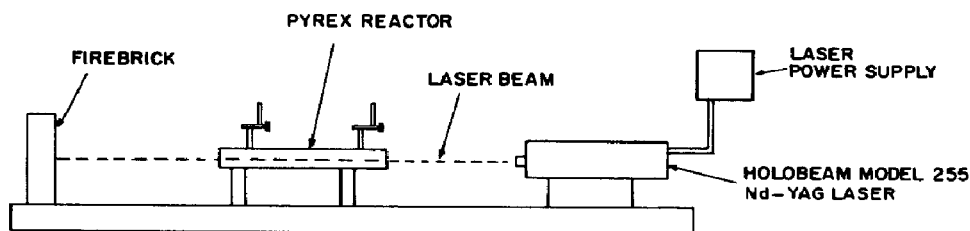


Fig. 1. Apparatus for chemical trapping experiments.

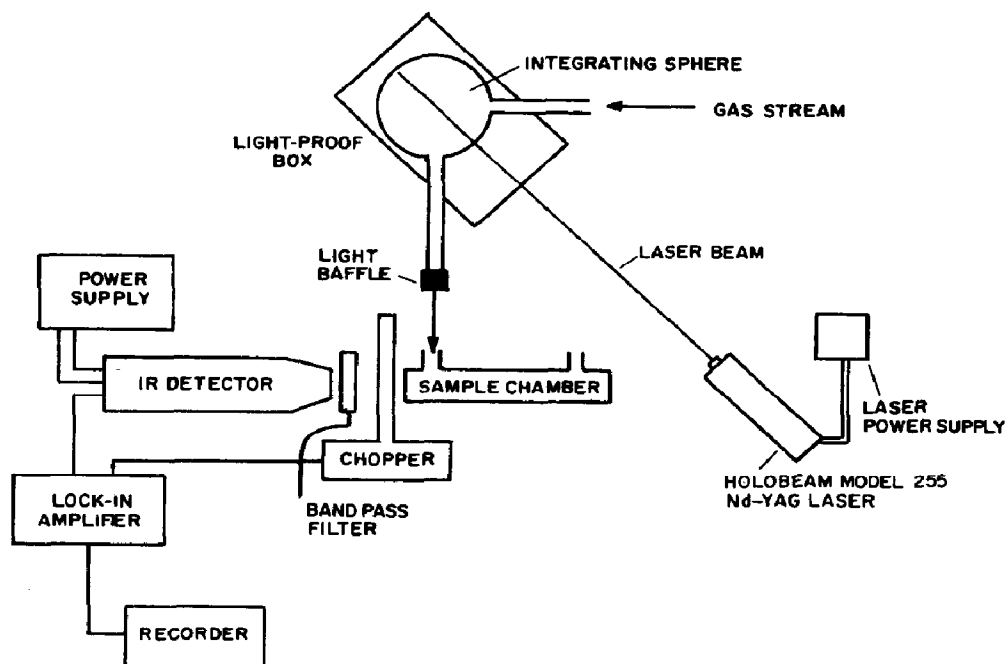


Fig. 2. Apparatus for the observation of the  $1.27 \mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$ .

sisted of an observation chamber into which the gas exiting from the integrating sphere was passed, a light chopper (Princeton Applied Research model 125A), an interference filter ( $\lambda = 1.27 \mu\text{m}$ ; half-bandwidth,  $0.02 \mu\text{m}$ ), a liquid-nitrogen-cooled germanium photodiode detector (Applied Detector Corporation model 403L) and a power supply (Princeton Applied Research Corporation model PS1). The signal was fed into a lock-in amplifier (Applied Detector Corporation model 186A) with the output displayed on a strip chart recorder. During an experiment, air or oxygen (Matheson; zero grade) was passed through the integrating sphere at a flow rate of  $75 \text{ l min}^{-1}$  with the laser operating in the CW mode. The laser beam entered the sphere at right angles to the glass tubes permitting the entrance and exit of the gas.

The apparatus described above was modified to determine the lifetime of  $\text{O}_2(^1\Delta_g)$ . The modified apparatus is shown in Fig. 3. It consists of a spherical 50 ml glass bulb with two 6 mm glass tubes arranged at right angles to one another. The outer surface of the sphere was blackened except for three small apertures. One permitted the entrance of the laser beam. The sphere was connected to the laser via a light-proof cylinder. The laser beam exited across the sphere and was directed via a light-proof cylinder into a piece of firebrick. The third aperture was located at right angles to the others and permitted the observation of the  $1.27 \mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$  using the optical detector. The detector (germanium photodiode and  $1.27 \mu\text{m}$  band-pass filter) was placed against the sphere and was separated from it by a light shutter. The photodiode was connected directly to a Tektronix oscilloscope (type 556) and camera (type C-12). A switch was arranged such that the

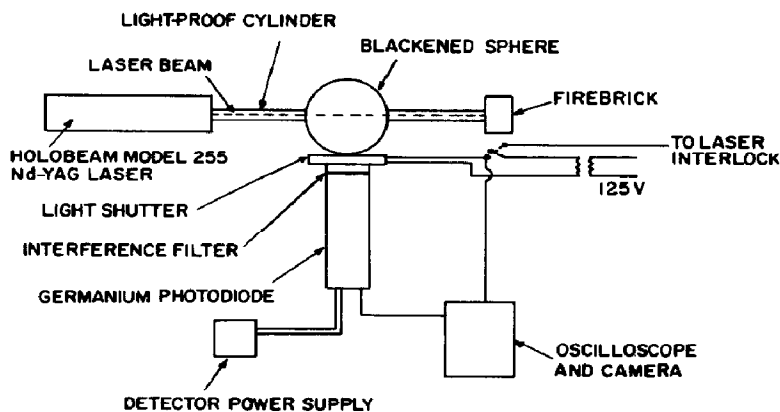


Fig. 3. Apparatus for measuring the  $O_2(^1\Delta_g)$  lifetime.

laser was on for a period of 15 s while the shutter to the detector was closed. The laser was then switched off, using the laser interlock, as the shutter to the detector was opened. The switch also activated a single sweep of the oscilloscope. This produced a tracing of the  $1.27 \mu\text{m}$  emission of  $O_2(^1\Delta_g)$  with respect to time.

## 2.2. Chemicals

Tetramethylethylene (TME) 1 was pretreated by passing it through a column 1 cm  $\times$  10 cm of activated silica gel (24 h at 200 °C). No TME hydroperoxide was detected in the TME that was purified in this series of experiments.

## 2.3. Photo-oxidation

2,3-dimethyl-3-hydroperoxy-1-butene 2 was prepared using the procedure described by Foote *et al.* [9]. The hydroperoxide had a boiling point of 53 - 55 °C at 12 mm pressure (a boiling point of 55 °C at 12 mm is reported in ref. 10). IR and nuclear magnetic resonance (NMR) spectra were consistent with the structure of the hydroperoxide as reported in ref. 10.

2,3-dimethyl-3-hydroxy-1-butene (TME alcohol) was prepared by the reduction of 2 with an excess of sodium borohydride [9]. Gas chromatographic analyses were performed on a Varian model 2700 dual-column chromatograph. The TME alcohol 3 was analyzed on a glass column (10 ft  $\times$  1/8 in (inside diameter)) packed with 10% SP-1000 on 100-120 mesh Chromosorb WAW. The helium flow was 40 ml  $\text{min}^{-1}$ ; the injection and detector temperatures were 200 °C and 225 °C respectively. The initial oven temperature was 50 °C, and the temperature was programmed to 175 °C at 4 °C  $\text{min}^{-1}$  during an analysis. The alcohol 3 had a retention time of 12.5 min using these conditions. The alcohol was also analyzed by gas chromatography-mass spectrometry (GC-MS). The mass spectrum of the alcohol has a parent ion with mass 100 and ions with masses 85, 43, 59, 41 and 57.

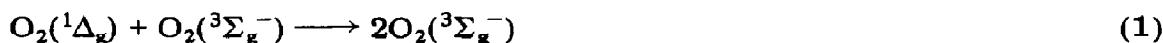
### 2.4. Product analysis

The reactor after irradiation with the laser at 1065 nm was washed with 15 ml of methylene chloride. The washings were added to a 25 ml three-neck flask and 0.025 g  $\text{KBH}_4$  was added slowly to the stirred solution at 0 °C. After 1 h, water (3 ml) was added slowly and this solution was allowed to warm to room temperature. It was stirred for an additional 3 h. The organic layer was separated and analyzed using gas chromatography. One product was observed and it had the same retention time as the authentic TME alcohol 3. Identification of the peak using GC-MS indicated that it was the alcohol 3 (parent ion with mass 100 and ions with masses 85, 43, 59, 41 and 57).

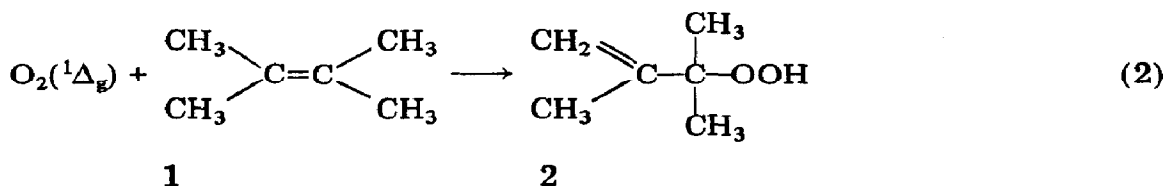
The oxidation product was also analyzed on an SE-30 WCOT 50 m  $\times$  0.5 mm glass capillary column. The helium flow was 2 ml  $\text{min}^{-1}$ ; the injector and detector temperatures were 200 °C and 225 °C respectively. The column temperature was held isothermal at 50 °C for 5 min. The oven was then programmed at a rate of 4 °C  $\text{min}^{-1}$  to 150 °C and held at this temperature for 20 min. The alcohol 3 had a retention time of 9.5 min, which was identical with the retention time of an authentic sample of the alcohol.

### 3. Results

The output of the Nd-YAG laser at 1065 nm lies within the  $\text{O}_2(^3\Sigma_g^-, \nu = 0) \rightarrow \text{O}_2(^1\Delta_g, \nu = 1)$  absorption manifold of the oxygen molecule centered at 1064 nm. The absorption coefficient for the above transition is given by  $c = 3.3 \times 10^{-7} P^2 \text{ cm}^{-1} \text{ atm}^2$  with  $P$  in atmospheres [11]. For the 25 cm reactor the fraction of photons entering the cell that is absorbed in the transition at 1 atm oxygen pressure is about  $8.3 \times 10^{-6}$ . Assuming that the Nd-YAG laser (CW mode) provides a minimum power of 10 W, the number of photons absorbed by  $\text{O}_2$  in the  $\text{O}_2(^3\Sigma_g^-, \nu = 0) \rightarrow \text{O}_2(^1\Delta_g, \nu = 1)$  transition is  $1.1 \times 10^{14}$  photons  $\text{s}^{-1}$ . An irradiation lasting 1 h is estimated to produce  $4 \times 10^{17}$  molecules of  $\text{O}_2(^1\Delta_g)$ . If 1% TME is added to the gas cell, the only significant  $\text{O}_2(^1\Delta_g)$  processes to be considered are



for which  $k = 1.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  [12] and



for which  $k = 1 \times 10^{-15} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$  [13]. Using these assumptions it was estimated that a detectable quantity of 2 (about  $10^{-6}$  mol) will be formed in 1 h.

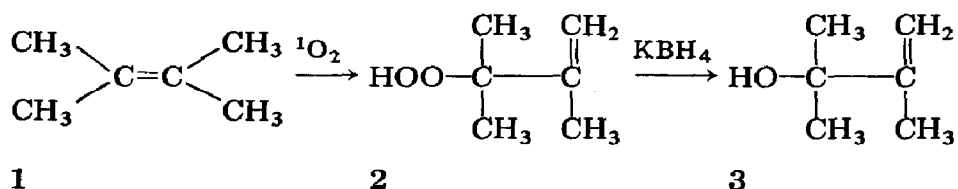
TABLE 1

Atmospheric gas phase oxidation of tetramethylethylene by  $O_2(^1\Delta_g)$  generated by direct laser excitation<sup>a</sup>

Experiment	Conditions	Irradiation time (h)	$O_2(^1\Delta_g)$ captured (mol h <sup>-1</sup> )
1	1% TME in O <sub>2</sub>	1.5	$1.85 \times 10^{-6}$
2	1% TME in O <sub>2</sub>	0	0
3	1% TME in O <sub>2</sub>	1.5	$1.23 \times 10^{-6}$
4	1% TME in O <sub>2</sub>	0	0
5	1% TME in air	2.5	$1.02 \times 10^{-7}$
6	1% TME in air	0	0
7	1% TME in air	2.5	$1.67 \times 10^{-7}$
8	1% TME in air	0	0

<sup>a</sup> Ambient temperature and pressure.

The experiments were performed in the Pyrex reactor described earlier (Fig. 1). During the experiments the reactor was placed in the beam of the Nd-YAG laser operating in the CW mode. A control experiment, *i.e.* without irradiation, was also performed. The production of detectable quantities of  $O_2(^1\Delta_g)$  was demonstrated in all experiments using this procedure except the control experiments. The results are shown in Table 1. TME 1 consistently converted to its known singlet oxygen product, 2,3-dimethyl-3-hydroperoxy-1-butene 2 [14]. IR and NMR spectra of this product were identical with the corresponding spectra of 2,3-dimethyl-3-hydroperoxy-1-butene obtained via the solution photo-oxidation of TME:



The hydroperoxide was reduced to the corresponding alcohol 3 with  $\text{KBH}_4$  for the purpose of a gas-liquid chromatography (GLC) analysis. The product alcohol 3 has the same mass spectrum and GLC retention times (two columns) as an authentic sample. Coinjection of 3 and the authentic alcohol led to GLC peak enhancement. Yields were determined by GLC on the basis of calibration with authentic alcohol. No TME hydroperoxide was detected in the control experiments, *i.e.* identical experiments with the laser off.

Further evidence for the formation of  $O_2(^1\Delta_g)$  in the gas phase at atmospheric pressure was obtained by the observation of the 1.27  $\mu\text{m}$  emission of  $O_2(^1\Delta_g)$ . The apparatus that was used in these experiments is shown in Fig. 2. The Nd-YAG laser was operated in the CW mode. The laser beam was directed into the center of an integrating sphere, as dry oxygen passed

through it and then into the observation chamber of a germanium photodiode detector. A record of the 1.27  $\mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$  during these experiments is presented in Table 2.

TABLE 2

Observation of the 1.27  $\mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$  generated by direct laser excitation

<i>Experiment</i>	<i>Conditions</i>	<i>Laser</i>	<i>Intensity of 1.27 <math>\mu\text{m}</math> emission (optional units)</i>
1	$\text{O}_2$ , 75 l $\text{min}^{-1}$ at 25 °C	Off	0.00
2	$\text{O}_2$ , 75 l $\text{min}^{-1}$ at 25 °C	On	0.52
3	$\text{N}_2$ , 75 l $\text{min}^{-1}$ at 25 °C	Off	0.00
4	$\text{N}_2$ , 75 l $\text{min}^{-1}$ at 25 °C	On	0.00
5	$\text{O}_2$ , 75 l $\text{min}^{-1}$ at 25 °C <sup>a</sup>	On	0.04
6	$\text{O}_2$ , 75 l $\text{min}^{-1}$ at 25 °C <sup>b</sup>	On	0.00

<sup>a</sup> About 5 mM TME added to the oxygen gas.

<sup>b</sup> About 3 mM triethylamine added to the oxygen gas.

Detectable quantities of  $\text{O}_2(^1\Delta_g)$  were generated whenever oxygen was passed through the integrating sphere with the laser operating. When a chemical acceptor such as TME (about 5 mM) was introduced into the flowing oxygen stream following the integrating sphere, the 1.27  $\mu\text{m}$  emission and thus the  $\text{O}_2(^1\Delta_g)$  concentration dropped to near zero. Chemical trapping experiments have shown that a detector response of about 0.52 corresponds to a  $^1\text{O}_2$  concentration of about 2 ppb. Similarly the introduction of a known singlet oxygen quencher, triethylamine [15], (about 3 mM) into the oxygen stream resulted in about 90% reduction in the 1.27  $\mu\text{m}$  emission.

The 1.27  $\mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$  decreased as the concentration of oxygen decreased and was undetectable at an oxygen concentration of less than 40 vol.%. Nitrogen was used as the diluting gas. The 1.27  $\mu\text{m}$  emission was not observed when dry nitrogen was passed through the integrating sphere with the laser operating.

The apparatus was modified and a second series of experiments was performed to determine the lifetime of  $\text{O}_2(^1\Delta_g)$  in the gas phase at atmospheric pressure. The apparatus is outlined in Fig. 3. During an experiment the blackened sphere is filled with dry oxygen at 1 atm pressure and sealed. The laser beam was allowed to pass through the sphere via two small apertures. After 15 s irradiation, the laser was switched off and the light shutter separating the sphere from the optical detector is opened allowing a measurement of the 1.27  $\mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$ . A typical oscilloscope tracing is shown in Fig. 4. The decay of  $\text{O}_2(^1\Delta_g)$  followed a pseudo-first-order relationship. The kinetic data are presented in Table 3. The rate constant observed for the decay of  $\text{O}_2(^1\Delta_g)$  was  $8.10 \text{ s}^{-1}$  which yielded a value of the lifetime  $\tau$  of 0.124 s.

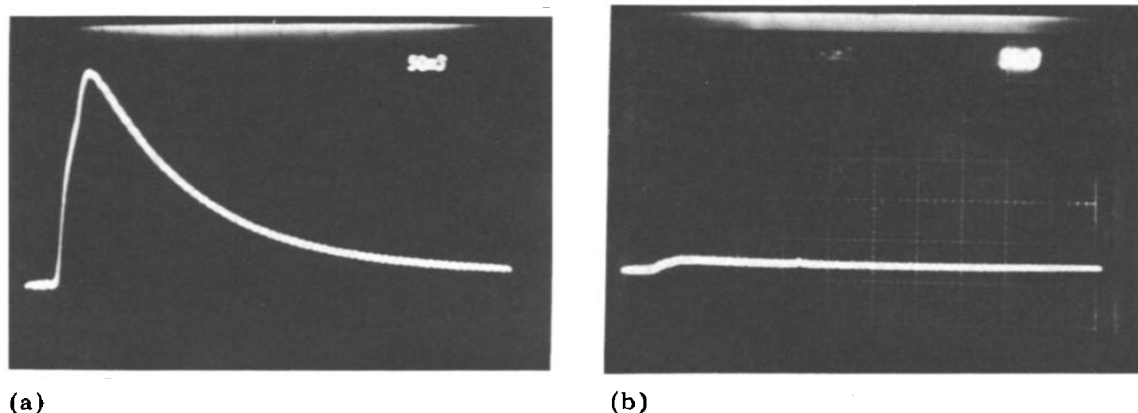


Fig. 4. Tracings of the 1.27  $\mu\text{m}$  emission of  $\text{O}_2(^1\Delta_g)$  for laser excitation of (a) molecular oxygen and (b) the control.

TABLE 3

Observed rate constants and lifetimes  $\tau$  for  $\text{O}_2(^1\Delta_g)$  decay

Experiment	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )	Lifetime $\tau$ (s)
1	8.22	0.122
2	7.73	0.129
3	7.21	0.139
4	9.31	0.107
5	8.01	0.124
Mean	$8.10 \pm 0.78$	$0.124 \pm 0.012$

In this determination, the only obvious important singlet oxygen deactivation process is the reaction  $\text{O}_2(^1\Delta_g) + \text{O}_2(^3\Sigma_g^-) \rightarrow 2\text{O}_2(^3\Sigma_g^-)$ . Wall deactivation, with the assumption of 100% efficiency, could at most account for removal of 4% of the  $\text{O}_2(^1\Delta_g)$ . The bimolecular rate constant  $k_2$  for the collisional deactivation of  $\text{O}_2(^1\Delta_g, v=1)$  by  $\text{O}_2(^3\Sigma_g^-)$  is calculated at  $(3.3 \pm 0.4) \times 10^{-19} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ . This value appears to be about a factor of 10 smaller than most of the currently accepted values listed in Table 4. All these latter determinations were made at system pressures of a few torrs, except one [19], in which oxygen pressures up to 100 Torr were investigated. In all cases, competing  $\text{O}_2(^1\Delta_g)$  deactivating processes were taking place, which, if incorrectly accounted for, could result in high  $\text{O}_2(^1\Delta_g) + \text{O}_2(^3\Sigma_g^-)$  deactivation rates being reported. Alternatively, the lower value reported here may indicate that the  $\text{O}_2(^1\Delta_g, v=1) \rightarrow \text{O}_2(^1\Delta_g, v=0)$  transition is sufficiently slow to affect the overall deactivation process  $\text{O}_2(^1\Delta_g, v=0) \rightarrow \text{O}_2(^3\Sigma_g^-)$ .



TABLE 4

Literature rate constants for the collisional deactivation of  $O_2(^1\Delta_g)$  by  $O_2(^3\Sigma_g^-)$ 

$k_1$ (molecule <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup> )	Reference	Year
$(1.47 \pm 0.05) \times 10^{-18}$	Leiss <i>et al.</i> [16]	1978
$(1.7 \pm 0.1) \times 10^{-18}$	Becker <i>et al.</i> [17]	1971
$(2.4 \pm 0.2) \times 10^{-18}$	Wayne [18]	1970
$(2.0 \pm 0.2) \times 10^{-18}$	Steer <i>et al.</i> [19]	1969
$(2.2 \pm 0.1) \times 10^{-18}$	Findlay <i>et al.</i> [20]	1969
$\leq 2.8 \times 10^{-19}$	Winer and Bayes [21]	1966

#### 4. Conclusions

$O_2(^1\Delta_g)$  was generated in the gas phase at 1 atm total pressure using direct laser excitation. Although the concentration of  $O_2(^1\Delta_g)$  generated in the gas phase is low, about 0.01 ppm, its lifetime is sufficiently long to study gas phase reactions of chemical substrates. This apparatus may be especially useful in studying environmental oxidations in which long exposure times are typical.

#### Acknowledgment

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#### References

- 1 R. W. Murray and H. H. Wasserman, *Singlet Oxygen*, Academic Press, New York, 1979.
- 2 D. F. Evans, *J. Chem. Soc., Chem. Commun.*, (1969) 367.
- 3 I. B. C. Matheson, J. Lee, B. S. Yamenaski and M. L. Wolbarsht, *Chem. Phys. Lett.*, 27 (1974) 355.
- 4 I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, 7 (1970) 475.
- 5 D. F. Evans and J. N. Tucker, *J. Chem. Soc., Faraday Trans. II*, 72 (1979) 1961.
- 6 G. W. Koroll and A. Singh, *Photochem. Photobiol.*, 28 (1978) 611.
- 7 W. C. Eisenberg, A. Snelson, R. Butler, J. Veltman and R. W. Murray, *Tetrahedron Lett.*, 22 (1981) 377.
- 8 W. C. Eisenberg, K. Taylor, J. Veltman and R. W. Murray, *J. Am. Chem. Soc.*, 109 (1982) 1104.
- 9 C. S. Foote, S. Wexler, W. Ando and R. Higgins, *J. Am. Chem. Soc.*, 90 (1968) 975.
- 10 G. O. Schenck and K. H. Schultz-Elte, *Justus Liebigs Ann. Chem.*, 618 (1958) 185.
- 11 D. I. Dianov-Klokov, *Opt. Spectrosc.*, 16 (1964) 224.

- 12 P. Borrell and M. D. Pedley, *Chem. Phys. Lett.*, 51 (1977) 300.
- 13 R. D. Ashford and E. A. Ogryzlo, *J. Am. Chem. Soc.*, 97 (1975) 3604.
- 14 C. S. Foote, *Acc. Chem. Res.*, 1 (1968) 104.
- 15 J. N. Pitts and J. W. Coomber, *Environ. Sci. Technol.*, 4 (1970) 506.
- 16 A. Leiss, U. Schurath, K. H. Becker and E. H. Fink, *J. Photochem.*, 8 (1978) 211.
- 17 K. H. Becker, W. Groth and M. Schurath, *Chem. Phys. Lett.*, 8 (1971) 259.
- 18 R. P. Wayne, *Ann. N.Y. Acad. Sci.*, 171 (1970) 199.
- 19 R. P. Steer, R. A. Ackerman and J. N. Pitts, Jr., *J. Chem. Phys.*, 51 (1969) 843.
- 20 F. D. Findlay, C. J. Fortin and D. R. Snelling, *Chem. Phys. Lett.*, 3 (1969) 284.
- 21 A. M. Winer and K. D. Bayes, *J. Chem. Phys.*, 70 (1966) 302.