Lifetime determination of the $O(^5S^o)$ metastable state via 1356-Å radiation using a time-of-flight technique

G. Nowak, W. L. Borst,* and J. Fricke
Physikalisches Institut der Universität Würzburg, Röntgenring 8, 8700 Würzburg, Federal Republic of Germany
(Received 5 October 1977)

The lifetime of the $^5S^o$ metastable state of oxygen was measured by monitoring 1356-Å photons from in-flight radiative decay of the metastables in a beam. Metastables were produced by electron-impact dissociation of O_2 and velocity selected using a time-of-flight (TOF) technique. The $^5S^o$ state was identified by passing photons from its radiative decay through a N_2O gas filter, which had a high transmission for 1356-Å radiation and good discrimination against other uv photons of shorter wavelength. The use of O_2 as another filter gas served as a consistency check for the absence of shorter-wavelength radiation. The metastable detector assembly also contained a surface detector that responded to metastable particles in the usual manner by Auger emission of secondary electrons. TOF spectra of the metastable dissociation fragments were measured with both these detectors at various distances from the source. The $O(^5S^o)$ lifetime obtained from a series of photon and particle measurements was found to be 180 ± 5 μsec. This value represents a substantial improvement in accuracy over previous lifetime determinations and the only TOF study in which the $O(^5S^o)$ state was identified through radiative decay.

INTRODUCTION

The present work reports an improved measurement of the lifetime of the $O(^5S^o)$ metastable state and differs in its method from the previous measurements.[1,2] This lifetime is of interest in upper atmospheric and plasma processes. Radiation from the $^5S^o$ state of oxygen is an important emission feature in Earth's upper atmosphere that has been observed by satellite- and rocket-born uv spectrometers. However, detection of this radiation at 1356 Å in a ground-based laboratory is rather difficult, although desirable since it provides a unique identification of the $O(^5S^o)$ state.

By using a gas filter and uv photon counter combined with a time-of-flight (TOF) technique, the faint 1356-Å radiation from decaying $O(^5S^o)$ metastables could be detected and used for a lifetime determination of this state. Additional supporting measurements were also made in the usual way,[1,2] where the metastables were detected by secondary-electron emission from surfaces.

A large range of metastable velocities was covered in the present work. In the previous work, either the slow[1] or fast[2] dissociation fragments had to be used. However, the emphasis in the present study has also been on the slow dissociation products as they cover a larger useful range of flight times at the distances between detector and metastable source that were used.

A comparison of our results obtained with the photon and surface detectors shows good agreement. A combination of these results has yielded a $O(^5S^o)$ lifetime in substantial agreement with the previous results, but with an improved accuracy of at least a factor of 2. Agreement is also good with one theoretical calculation,[3] but poor with another.[4]

EXPERIMENT AND METHOD

Metastable $O(^5S)$ atoms were produced by electron-impact dissociation of O_2.[5] The essential features of the experimental setup are shown in Fig. 1. A general description of the high-intensity metastable source and the entire apparatus has been given before.[6-10] The apparatus is a multipurpose instrument that has been used for studies such as the velocity dependence of the secondary-electron yield from surfaces by metastables,[9,10] excitation transfer collisions between metastables and various gas targets,[7,8] and the present lifetime measurements. The essential features of the apparatus pertaining to the present work shall be described briefly in the following.

Metastables from the source entered a detector chamber where they were monitored both by counting 1356-Å photons from in-flight radiative decay and by secondary-electron emission from the first dynode of an axially mounted nude CuBeO multiplier. Both the photon and particle detectors were rigidly mounted to the detector chamber. The distance between the detector assembly as a whole and the metastable source could be varied by means of an external feedthrough.

Photons resulting from the radiative decay of $O(^5S)$ metastables could be "seen" by the photon detector in the viewing region from x_1 to x_2, which had a length of $L = x_2 - x_1 = 3$ cm. Photons were able to reach the detector directly through the

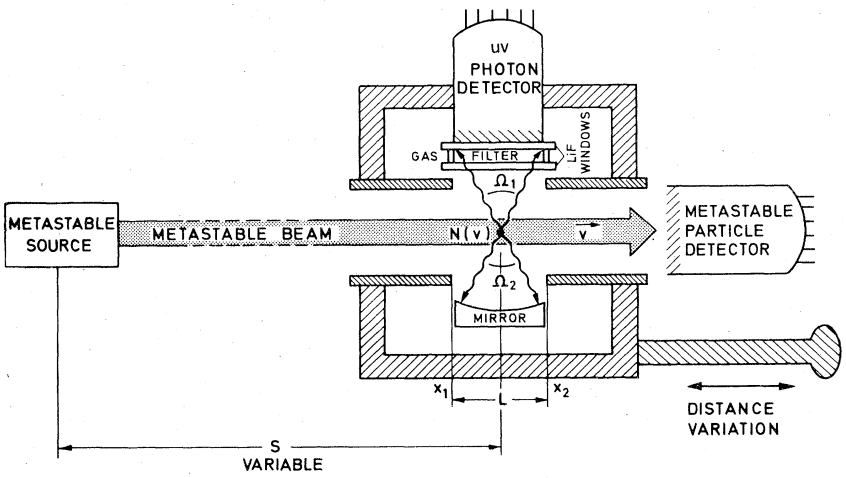

FIG. 1. Schematic of the metastable detection system consisting of a photon counter for 1356-Å radiation from O(^5S) metastable decay and a particle detector using Auger electron emission by the metastables from a CuBeO multiplier surface. Before reaching the photon detector, uv radiation had to pass through a gas filter cell containing N_2O gas with a high transmission for 1356-Å photons and an effective discrimination for shorter wavelengths down to 1260 Å. The distance between metastable source and detector could be varied with an external feedthrough mechanism.

solid angle Ω_1 and also by reflection from a spherical mirror with an effective solid angle Ω_2. The mirror contributed to a signal enhancement of a factor of 5 as compared to the direct mode of detection.

Wavelength selection of the photons was accomplished with a gas filter in front of the detector. The filter cell was of cylindrical shape with two LiF windows as end surfaces. The fill gas in the cell was N_2O with a transmission curve for uv radiation as shown in Fig. 2. N_2O has a high transmission for 1356-Å radiation, while the shorter wavelengths resulting from higher-lying states in oxygen are effectively absorbed down to a wavelength of about 1260 Å. In particular, 1304-Å oxygen resonance radiation was absorbed by the N_2O gas filter. There were two transitions that could have been transmitted by the N_2O filter at shorter wavelengths. These are $2p^3 3s\ ^1D^o \rightarrow 2p^4\ ^1D$ and $2p^3 3s\ ^1P^o \rightarrow 2p^4\ ^1S$ with wavelengths of 1152 and 1218 Å, respectively. Population of the upper states was possible in principle by cascade from long-lived Rydberg states. In order to check for the presence or absence of these wavelengths, O_2 was used as a filter gas with a near 100% transmission for 1218 Å and lower transmission for 1152-Å radiation. No signal whatsoever was observed indicating that certainly no 1218-Å radiation was present. This conclusion is somewhat less certain for 1152-Å radiation due to the very strong variation of the O_2 transmission near this wavelength. It seems, however, that this radiation was not present either, because the transmission of the O_2 gas was probably near 40% and no signal was seen in spite of this fact. Furthermore, any high-lying Rydberg states that could have populated the $2p^3 3s\ ^1D^o$ state were excited with a much smaller cross section than the $^5S^o$ metastable state.[5] For these reasons, it is believed that the present gas-filter technique permitted effective selection of 1356-Å radiation.

Photons from the metastable source were eliminated by the geometry used and would have been detected primarily during the on period of the source. Therefore, only photons from within the detector assembly were able to cause a signal. The lower-lying ^1S and ^1D metastables states in

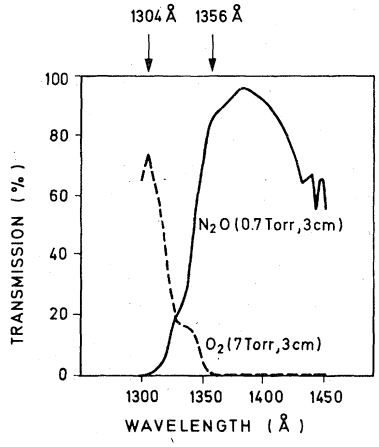

FIG. 2. Transmission curves for uv radiation through N_2O and O_2 filter gases. 1356-Å photons from O(^5S) metastable decay are transmitted efficiently through N_2O gas and nearly perfect discrimination exists between these photons and 1304-Å resonance radiation.

oxygen were not observed in the present experiment because of the long lifetimes and low excitation energies involved, the latter being unable to release photoelectrons from the multiplier.

The probability for the decay of O(^{5}S) metastables within the detection region was of the order of 5% for typical metastable velocities and of course depended inversely upon these. Total signal count rates summed over all TOF intervals during the off period of the source were 1 count/sec or less at the photon detector and several hundred counts per second at the particle detector. The signal accumulation times required for reasonably good statistics in the photon data were 10 to 20 h and for very good statistics in the particle data about $\frac{1}{2}$h. The background in both detectors with the electron gun in the source off was about 10 counts/min.

The distance between the detector and source could be varied between 30 and 50 cm by means of an external feedthrough mechanism that allowed linear movement along a track on which the detector assembly glided. The electronics associated with the apparatus, in particular the TOF electronics, has been described in detail before.[6,7]

The pressure of the O_2 gas in the metastable source was in the millitorr range. It was monitored at a reference point in the gas line to the source and was in the torr range at that point. The background pressure in the differentially pumped detector region was about 10^{-6} torr when taking data. This background was sufficiently small in order to avoid substantial scattering of the metastable beam by the rest gas.

The metastable beam was defined by collimating apertures between the source and the viewing region of the detector assembly. A transverse electric field near the source served to eliminate charged particles and quench high-lying Rydberg states in the beam.

The lifetime determination from the measured photon and particle TOF spectra proceeded as follows: The photon count rate in the velocity interval dv was given by

$$R(v)dv = N(v)dv(\Omega/4\pi)T\gamma Ff2\sinh(L/2v\tau), \quad (1)$$

where $N(v)$ is the number of metastables per source pulse and velocity interval [in units of (velocity)$^{-1}$] at the center of the viewing region a distance s away from the source (see Fig. 1), γ the photoelectric yield of the photon detector, Ω the effective solid angle for photon detection comprised of the angles Ω_1 and Ω_2, T the transmission of the gas filter including the LiF windows, F the pulse counting efficiency, f the beam-pulse repetition rate, and τ the lifetime of the metastable state. The expression $2\sinh(L/2v\tau)$ accounts for metastable decay in the viewing region and results from an integration between the limits $x_1 = -\frac{1}{2}L$ and $x_2 = \frac{1}{2}L$. In the present case, $2\sinh(L/2v\tau) \cong L/v\tau$.

The number of metastables $N(v)$ contains a decay factor $e^{-t/\tau}$ that accounts for beam attenuation due to radiative decay along the distance s between source and center of the detector assembly, where t is the TOF for traversing the distance s. If the number of metastables, that would be in the detector chamber without any decay, is designated by $N_0(v)$, then

$$N(v) = N_0(v)e^{-t/\tau}. \quad (2)$$

Applying Eqs. (1) and (2) to two different distances s_1 and s_2 ($s_2 > s_1$) from the source and taking the ratio of photon count rates at these distances yields for a given velocity

$$R_2(v)/R_1(v) = e^{-(t_2 - t_1)/\tau}. \quad (3)$$

Let $t_1 = s_1/v$ be the TOF for metastables of velocity v to travel the distance s_1, n_1 the TOF channel number corresponding to t_1, and Δt_1 the TOF interval per channel, and similarly for the distance s_2. Then

$$t_1 = s_1/v = \Delta t_1 n_1 \text{ and } t_2 = s_2/v = \Delta t_2 n_2, \quad (4)$$

and from this

$$t_2/t_1 = s_2/s_1 = \Delta t_2 n_2/\Delta t_1 n_1. \quad (5)$$

We now require that for the data taken at the distances s_1 and s_2, the TOF's corresponding to the same velocity fall into the same channel, i.e., we must have $n_1 = n_2 = n$. This fixes the ratio of TOF intervals per channel and results in

$$\Delta t_2/\Delta t_1 = s_2/s_1. \quad (6)$$

We then have $t_2 = \Delta t_2 n$ and $t_1 = \Delta t_1 n$. Substituting this into Eq. (3), we obtain

$$R_2(v)/R_1(v) = R_2(t_2)/R_1(t_1) = e^{-(\Delta t_2 - \Delta t_1)n/\tau} \quad (7)$$

or

$$\ln(R_1/R_2) = (\Delta t_2 - \Delta t_1)n/\tau. \quad (8)$$

A plot of the logarithm of the ratio of photon count rates versus TOF channel number n should then yield a straight line with a slope of $(\Delta t_2 - \Delta t_1)/\tau$, from which the lifetime τ can be determined.

Equation (8) also holds for TOF measurements with the particle detector. For the particle count rate, Eq. (1) needs to be modified yielding

$$R(v)dv = N(v)dv\gamma Ff, \quad (9)$$

where now $N(v)$ is the number of metastables per source pulse and velocity interval at the position of the first dynode of the particle multiplier, γ the secondary-electron yield for metastables on

the CuBeO dynode surface, and F and f are defined as in Eq. (1). The distance s is now to be understood as that between metastable source and first dynode of the particle detector. Using Eq. (9) and following the same outline as given above for the photon count rates, one obtains the result given by Eq. (8) also for the particle count rates. Hence the lifetime determinations using the photon and particle data are completely analogous. The TOF spectra measured with the photon and particle detectors and the resulting lifetimes are described in the following section.

RESULTS AND DISCUSSION

Time-of-flight spectra measured with the photon detector are shown in Fig. 3. Having chosen the TOF interval per channel according to Eq. (6), metastables with the same velocity fell into the same channels and the spectra could be directly compared. For a given electron energy in the source, the spectra taken at the two distances $s_1 = 31$ cm and $s_2 = 46.5$ cm differ from each other. This obviously is a direct consequence of the greater metastable decay at the longer distance, where the TOF spectra have smaller values, in particular at the higher TOF channels corresponding to the slower metastables, and the peaks are shifted slightly towards shorter TOF's.

The ratio of photon count rates was taken from these spectra according to Eq. (8) and is plotted in Fig. 4. It is seen that the data points follow a straight line within the existing statistical scatter. The straight line is a least-squares fit to the points between the vertical lines shown. Beyond these lines, the statistics were too poor at the longer TOF's and the structure in the "fast" peak at short TOF's too sharp to yield reliable data. However, a portion of the fast metastables is included in the straight-line fits. The straight lines do not go through the origin as they should according to Eq. (8), because no distinction was made between the counts accumulated in the TOF channels and the actual count rates. Not normaliz-

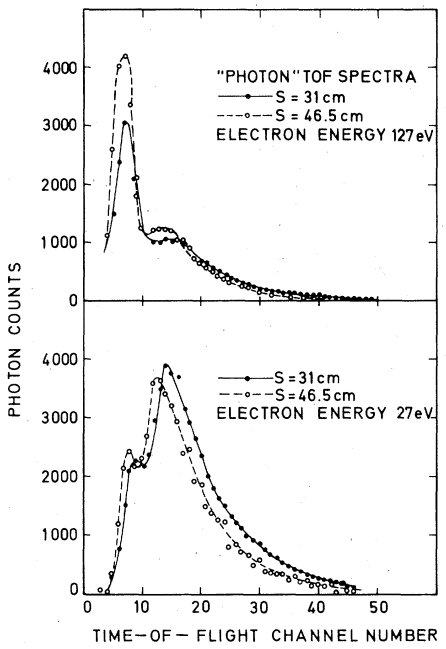

FIG. 3. Time-of-flight spectra measured with the uv photon detector at electron energies of 127 eV (upper part) and 27 eV (lower part), and distances of 31 and 46.5 cm between metastable detector and source. Plotted is the total number of photon counts accumulated in each TOF channel as a function of TOF channel number. The time scale was 8 and 12 μsec/channel for $s = 31$ and 46.5 cm, respectively. The measurement times ranged between 4 and 24 h. The ordinate scale for the 27-eV data at 46.5 cm is expanded by a factor of 2.5.

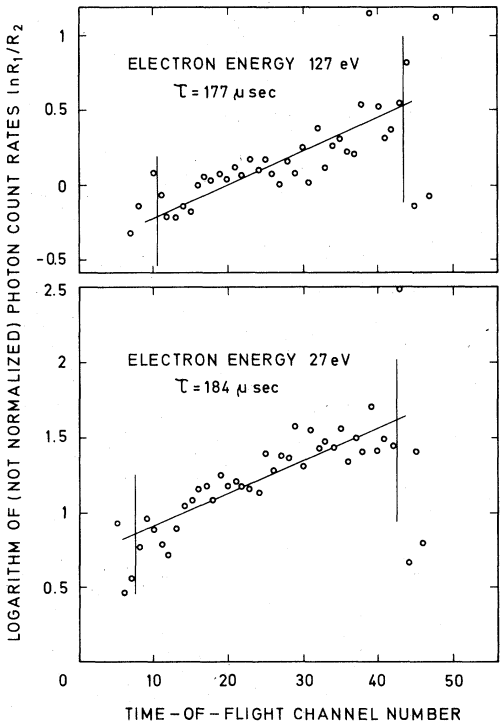

FIG. 4. Logarithm of the ratio of photon count rates R_1/R_2 measured at distances of 31 and 46.5 cm, respectively. The data shown were obtained by pointwise division of the curves in Fig. 3. The straight lines are least-squares fits to the data points between the vertical bars. The lifetimes listed were determined from the straight-line slopes (see text).

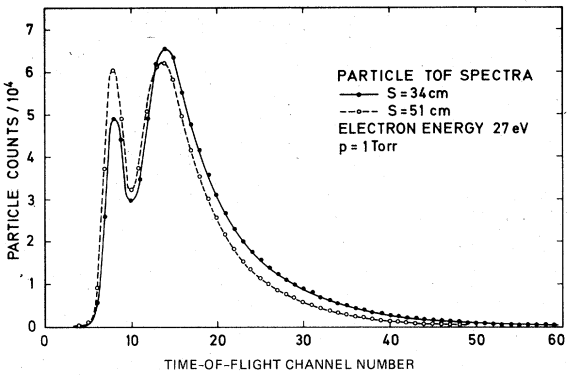

FIG. 5. Time-of-flight spectra measured with the metastable particle detector at an electron energy of 27 eV and O_2 reference pressure of 1 torr in the gas line to the metastable source. The time scale was 8 and 12 μsec/channel for source distances of 34 and 51 cm, respectively. Counting times were about 30 min. Similar to Fig. 3, the effect of increased metastable decay at the larger distance can be clearly seen from the reduction in the relative height of the second peak and also from the smaller signal at the higher TOF channels. The pronounced difference between the particle and photon spectra (Fig. 3) taken at the same electron energy of 27 eV is due to the increased probability for photon detection for lower metastable velocities, i.e., higher TOF channels.

ing the spectra in Fig. 3 to actual count rates adds a constant to Eq. (8). This is of no consequence for the lifetime determinations. The division of the two data sets into each other results in greater statistical fluctuations than the individual ones in each TOF curve.

The lifetimes obtained from the straight-line slopes are also listed in Fig. 4. Despite the fact that the TOF spectra for the two electron energies in Fig. 3 are very different in shape and count rates, the same lifetime of about 180 μsec resulted within the statistical accuracy of the measurement.

In order to corroborate the lifetime determination from the photon data and further check the consistency of the method, TOF spectra were also taken with the particle detector. These are shown in Fig. 5. The statistics were much better in the particle data since the count rates were several hundred times larger. Again, the differences in the shape of the TOF spectra at the two detector distances are clearly seen. In particular, the pronounced difference in the relative peak heights is to be noted.

A difference also exists in the photon and particle TOF spectra for the same electron energy of 27 eV. This is not surprising in view of the fact that the particle detector monitors the velocity spectrum of the metastables according to Eq. (9), whereas the photon detector measures this spectrum multiplied by a velocity-dependent function according to Eq. (1), the latter being proportional to $1/v$ in our case. This is directly related to the fact that the slower metastables remain in the viewing region of the detector for a longer period of time and thus have a greater probability for radiative decay in that region than the faster metastables.

Taking the ratio of particle count rates and proceeding according to Eq. (8) in the same fashion as in the photon case, the data in Fig. 6 were obtained. The top part of Fig. 6 was determined from the spectra shown in Fig. 5, which were taken at a reference pressure of 1 torr of O_2 in the gas line to the metastable source. (As mentioned above, the source pressure itself was in the millitorr range.) It is seen that the statistical accuracy is better than in the photon measurement, but that the lifetime is again the same. The other two

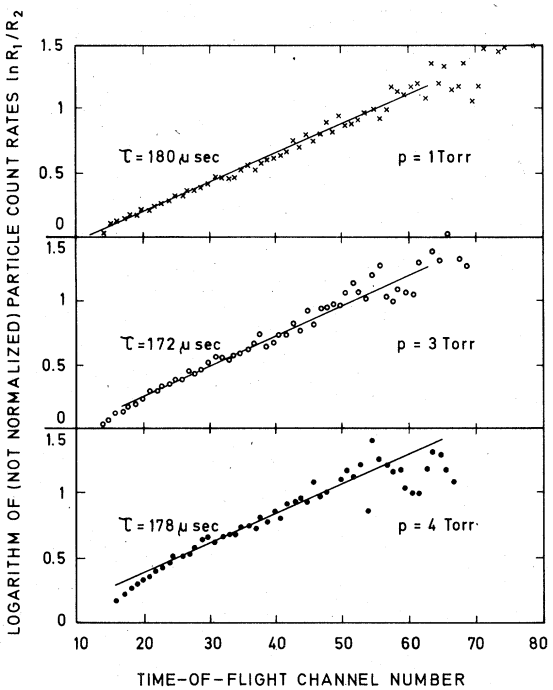

FIG. 6. Logarithm of the ratio of particle count rates measured at source distances of 34 and 51 cm, respectively, an electron energy of 27 eV, and O_2 reference pressures of 1, 3, and 4 torr in the gas line to the metastable source. (The source pressure was in the millitorr range.) Within the statistical uncertainties of the experiment, the lifetime did not depend on source pressure. The points in the uppermost part of the figure were obtained by dividing the curves in Fig. 5. The lifetimes deduced from the straight-line slopes are consistent with those from the photon data (Fig. 4).

data sets in Fig. 6 were obtained at gas line pressures of 3 and 4 torr. As is to be expected, they resulted in the same lifetime within the uncertainties of the experiment. All measurements in Fig. 6 were taken at an electron energy of 27 eV, where the metastable beam was relatively pure consisting primarily of $O(^5S^o)$ metastables.[5] At higher electron energies in the source, indications existed for the presence of other long-lived species in the beam. This was no hindrance in the photon measurement, since the $O(^5S^o)$ state was specifically identified there. However, the particle measurements were limited to low electron energies in the source if one wished to obtain clean results that were indicative of the $^5S^o$ metastable state alone.

The results shown in Figs. 4 and 6 yielded a lifetime of 180 μsec for the $O(^5S^o)$ state with a possible uncertainty of ± 5 μsec. In taking the average of the various lifetime determinations, some emphasis was put on the photon data and the lowest value of 172 μsec in the particle data was left off. The remaining four values of 177 and 184 μsec from the photon data and 180 and 178 μsec from the particle data yielded an average of 180 μsec with a statistical error of 2 μsec as calculated from the formula

$$\Delta\tau = \left(\frac{\sum_{i=1}^{n} (\tau_i - \langle\tau\rangle)^2}{n(n-1)} \right)^{1/2}, \tag{10}$$

where $\langle\tau\rangle$ is the average of the various independent measurements τ_i and n is the number of measurements (in our case $n = 4$). Additional measurements (not shown) corroborate the present value of 180 μsec.

It should be emphasized that the TOF spectra shown in Fig. 3 serve primarily as illustrations. In order to determine the lifetime with a good degree of accuracy, one has to resort to the original digital TOF data. This avoids possible drafting errors, especially at the higher TOF channels, where the signals are small. The present lifetimes were obtained from least-squares fits to the quantity $\ln(R_1/R_2)$ [see Eq. (8)], where the signal ratios were directly calculated from the digital data. Figures 4 and 6 again serve only as illustrations.

The systematic errors in the present measurement were probably small since the spatial extent of the metastable source was only a few millimeters as compared to a source-detector distance that ranged between 30 and 50 cm. The timing error in the TOF electronics was completely negligible. The time resolution of the photon detector was about 5% to 10% and was determined by the finite length of the viewing region in the detector. This may have led to some broadening in the sharp first peak in the photon TOF spectra and consequently to an uncertainty in the ratio of count rates in the first few TOF channels. As already mentioned, some of the fast metastables were included in the present lifetime determination, but the emphasis was on the slow metastable dissociation fragments. It may be worth noting that the particle detector was not limited in its time resolution because the detection surface has zero spatial extent in the direction of the beam. The total systematic error was estimated to be about 3 μsec. This combines with the statistical error to an uncertainty of 5 μsec in the value for the lifetime.

A comparison of the existing lifetime values for the $O(^5S^o)$ state is given in Table I. The three experimental values are in good agreement within the limits of error. The theoretical value calculated by Nicolaides[3] also agrees well with the mea-

TABLE I. Comparison of $O(^5S)$ lifetime determinations.

Lifetime (μ sec)	Author	Technique
180 ± 5	This work	TOF technique $O(^5S^o)$ identification via 1356-Å photons Metastable detection also via Auger electron emission from surfaces Slow and fast dissociation fragments
170 ± 25	Wells and Zipf	TOF technique Metastable detection via Auger electrons Slow dissociation fragments
185 ± 10	Johnson	TOF technique Metastable detection via Auger electrons Fast dissociation fragments
192	Nicolaides	Theoretical calculation
595	Garstang	Theoretical calculation

surements, while Garstang's value[4] seems to be too high.

It is believed that the present lifetime determination for the O($^5S^o$) state offers the greatest accuracy so far. The experiment described here also is the only one in which the O($^5S^o$) state was identified through its 1356-Å radiation from natural decay. In the other two experiments,[1,2] the presence of the $^5S^o$ state was inferred, albeit with sound arguments.

ACKNOWLEDGMENTS

We wish to thank Professor V. Dose for making available to us his data acquisition system. One of us (W.L.B.) wishes to acknowledge with thanks support by Deutsche Forschungsgemeinschaft.

---

*Presently on leave from Southern Illinois University, Carbondale, Ill. 62901.

[1]W. C. Wells and E. C. Zipf, Phys. Rev. A 9, 568 (1974).
[2]Charles E. Johnson, Phys. Rev. A 5, 2688 (1972).
[3]Cleanthis A. Nicolaides, Chem. Phys. Lett. 17, 436 (1972).
[4]R. H. Garstang, Proc. Camb. Philos. Soc. 57, 115 (1961).
[5]W. L. Borst and E. C. Zipf, Phys. Rev. A 4, 153 (1971).
[6]H. D. Wolf, diplomarbiet (Physikalisches Institut der Universität Würzburg, 1976) (unpublished).
[7]J. Windrich, H.D. Wolf, and J. Fricke, J. Phys. B 11, 1 (1978).
[8]G. Nowak, W. L. Borst, and J. Fricke, in *Tenth International Conference on the Physics of Atomic and Electronic Collisions, Abstracts of Papers*, edited by M. Barat and J. Reinhardt (Commissariat á l'Energie Atomique, Paris, 1977), p. 554.
[9]W. L. Borst, G. Nowak, and J. Fricke, in Ref. 8, p. 1292.
[10]W. L. Borst, G. Nowack, and J. Fricke, Phys. Rev. A 17, 838 (1978).