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Direct observation of $O(^3P_J)$ in the photolysis of O_3 at 248 nm

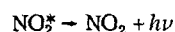
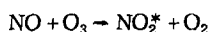
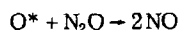
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The photodissociation of O_3 at 248 nm has been studied following photolysis with a KrF excimer laser. The results of the current experiments, which were carried out in absorption using improved high-speed detection electronics, are in good agreement with previous direct observations of significant $O(^3P_J)$ photofragment yield following photolysis at 266 nm. A quantitative estimate of the quantum yield for $O(^1D_2)$ production at 248 nm is 0.85 ± 0.02 . The implications of this observation for earlier studies of $O(^1D_2)$ reactivity are discussed.

I. INTRODUCTION

Photolysis of O_3 in the Hartley continuum below 310 nm is the major source of $O(^1D_2)$ in the atmosphere.¹ In recent years, several attempts have been made to measure the yield of $O(^1D_2)$ ($\equiv O^*$) production following exposure of ozone to ultraviolet radiation²⁻⁸ both at the peak of its absorption band near 250 nm and in the weak tail of the continuum near 300 nm where solar flux still has considerable intensity even at the earth's surface. In general, these studies were carried out either by observation of the chemiluminescence resulting from²⁻⁴



or by chemical analysis of the reaction products of O^* with various added gases.^{5,6} Such experiments permit only relative estimates of O^* yield to be made. Indeed, until 1978 only a single measurement⁷ of the absolute quantum yield had been reported, the value in this case being given as unity for photolysis of O_3 at 253.7 nm in liquid Ar at 87 °K.

Several recent investigations have been carried out in response to the requirement for reliable values of absolute O^* quantum yield in order to refine current models of atmospheric photochemistry. In two chemical studies,^{8,9} involving different schemes, absolute quantum yields for production of O^* ,

$$\Phi = \frac{[O^*]_0}{[O^*]_0 + [O]_0} \quad (1)$$

were reported to be 1.0 within a relatively small range of error (estimated⁹ to be 0.05 in one case) over the range 230–285 nm. In (1), $O \equiv O(^3P_J)$, while the subscript denotes the initial concentration of O^* and O produced by the photolysis.

Direct investigations of O_3 dissociation using photofragment translational spectroscopy (PTS) have, however, revealed that a discernible fraction of the oxygen atoms produced at 266 nm (Ref. 10) and in the region

270–310 nm (Ref. 11) is formed in the ground electronic state. Unfortunately, quantitative estimate of the actual quantum yield for production of O^* was complicated in both instances by the need to obtain calibrations of the relative detection efficiencies for O^* and O as functions of photofragment velocities. Nonetheless, a value $\Phi \sim 0.9$ could be estimated making a minimal number of assumptions involving these parameters.

Another direct study of O_3 photodissociation was carried out in this laboratory.¹² Here, the relative density of O was monitored by following the absorption of atomic resonance radiation at 130 nm after KrF laser photolysis of the source molecule at 248 nm. The resulting value of $\Phi = 0.99 \pm 0.01$ was in good agreement with the chemical studies, but the nominal observation¹³ of significant physical quenching in the collisional deactivation of O^* by CH_4 , H_2O , and N_2O , which had not been reported hitherto, was disquieting and suggested reexamination of the O_3 photolysis problem using a more sophisticated experimental apparatus. The present study involves the use of significantly faster data acquisition equipment thereby improving the system frequency response to better than 10 MHz, over an order of magnitude faster than before. The resulting data demonstrates that Φ for O_3 photolysis is indeed significantly less than unity, and that current models of atmospheric chemistry must be suitably modified to include a lower yield for excited oxygen atoms.

II. EXPERIMENTAL

The apparatus has previously been described in detail^{12,13} and will only be briefly described here. Dilute mixtures ($\sim 1:10^4$) of ozone in helium were photolyzed in a mirrored $1 \times 1 \times 10$ cm cell using a KrF excimer laser. The use of a rare gas clean-up and recycling system¹⁴ both increased the energy of the KrF excimer laser (to ~ 100 mJ) and permitted its use at higher repetition rates (~ 2 Hz). The density of oxygen atoms in the ground 3P_J state was monitored using time-resolved atomic absorption spectroscopy at 130–131 nm. The resonance radiation, $3^3S_1^0 \rightarrow 2^3P_J$, was excited in an electrodeless discharge lamp. After passing through the photolysis cell, the output of the lamp was dispersed using a 0.2 m monochromator and detected with a solar blind photomultiplier. Fresh O_3/He solutions were constantly flowed through the cell.

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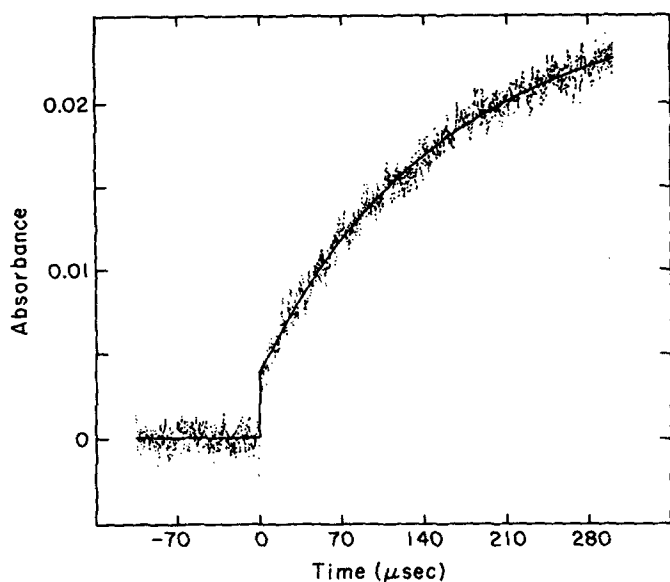
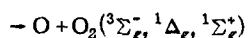
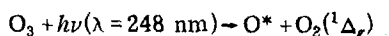


FIG. 1. Temporal profile of absorption by O(³P_J) following photolysis of O₃ (0.5 mTorr) in He (10 Torr). The least squares fit of Eq. (5) to this data yields $k^* = (6.4 \pm 0.07) \times 10^3 \text{ s}^{-1}$ and $\Phi = 0.85 \pm 0.01$.

The major change in the apparatus involved the use of high-speed data acquisition equipment. The photocurrent of the solar blind photomultiplier (EMR S41G-08-18) was fed into the input of a Tektronix oscilloscope. This device provided a factor of 6.5 amplification at its output connector when on the 10 mV/div input scale. In addition, the electrical impedance was dropped to 50 Ω from that selected by placing a precision resistor in parallel with the 1 M Ω input impedance of the oscilloscope amplifier. A further gain of 10 \times was obtained with a C-Cor amplifier after the oscilloscope. The measurement time constant, fixed with a specific length of low-capacitance coaxial cable between the photomultiplier and oscilloscope input, was selected to approximate that required by the Nyquist criterion, i.e., twice the sampling interval of the Biomation 8100 Transient Recorder used to capture the temporal profile of the absorption by oxygen atoms. Enhancement of the signal-to-noise ratio of the absorption transient was accomplished using a Nicolet 1074 Signal Averager interfaced to the Transient Recorder. Typically 1000 separate kinetic runs were averaged to achieve the signal quality illustrated in Fig. 1.

III. RESULTS

The photochemical and kinetic processes of interest in the current system are given by



Both (3) and (4) are so slow under the present experimental conditions that only the growth of ground state

oxygen atom density could be observed on the time scale of interest. It has been previously demonstrated^{12,15} that removal of a single oxygen atom in the ¹D₂ state upon collision with O₃ results, on the average, in the production of 1.0 ground state atom, although the mechanism of this deactivation may involve contributions from several elementary steps,



so long as $k_{2b} = k_{2c}$. Representation of this deactivation by (2) simply gives the overall stoichiometry of the process which is the parameter of importance here.

The temporal dependence (Fig. 1) of the oxygen atom concentration is given by

$$[\text{O}]_t = [\text{O}]_0 + [\text{O}^*]_0 [1 - \exp(k^* t)], \quad (5)$$

where $k^* = k_{\text{O}_3}[\text{O}_3] + k_{\text{He}}[\text{He}] + K$. The absorbance actually measured in these experiments is related to the O-atom concentrations by the modified Beer-Lambert law

$$A_t = (\epsilon l [\text{O}]_t)^\gamma, \quad (6)$$

where the symbols have been previously defined.¹⁶ The parameter γ which accounts for resonance lamp self-reversal and emitter-absorber line shape mismatches will approach unity at low absorbances. The present experiments were carried out in such a low-absorbance regime, as was confirmed from the dependence of long-time absorbance at 130 nm on laser power,¹⁷

$$\ln A_\infty = \text{const.} + \gamma \ln P_{\text{laser}}.$$

A value of $\gamma = 1.00 \pm 0.05$ was obtained over the concentration range used here (Fig. 2). As this value suggests that Beer's Law behavior is indeed adhered to in these studies, two different techniques were used for analysis. In the first, γ was assumed to be unity and Eq. (5) was fit to the data using the analysis techniques described hitherto.¹³ From the parameters, $[\text{O}]_0$ and $[\text{O}^*]_0$, obtained from the least squares fits to the oxygen atom absorbance at $P_{\text{He}} = 10$ Torr, a value of $\Phi = 0.84 \pm 0.02$ was derived. Alternatively, the value of $\gamma = 1.0$ was used as an initial guess for this parameter in the nonlinear least squares fit of

$$A_t = (\epsilon l)^\gamma ([\text{O}]_0 + [\text{O}^*]_0 [1 - \exp(k^* t)])^\gamma \quad (7)$$

to the data. Here, a value of $\Phi = 0.85 \pm 0.01$ was obtained. We therefore believe that $\Phi = 0.85 \pm 0.02$ is a reasonable estimate of the quantum yield for O* in the photolysis of O₃ at 248 nm. As a check of the experimental technique, k_{O_3} was determined from the values of k^* observed over the range of O₃ pressures used here (1.0–3.0 $\times 10^{-3}$ Torr). The derived value of $k_{\text{O}_3} = 2.5 \pm 0.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ is in good agreement with $2.4 \pm 0.1 \times 10^{-10}$ reported in earlier studies.^{12,18–20}

The major result reported here, namely, that $\Phi = 0.85 \pm 0.02$, is in qualitative agreement with the observation of PTS studies that ~10% of the photolysis of O₃ in the Hartley continuum results in the production of ground state oxygen atoms.^{10,11} The present experiment permitted a quantitative determination of this parameter

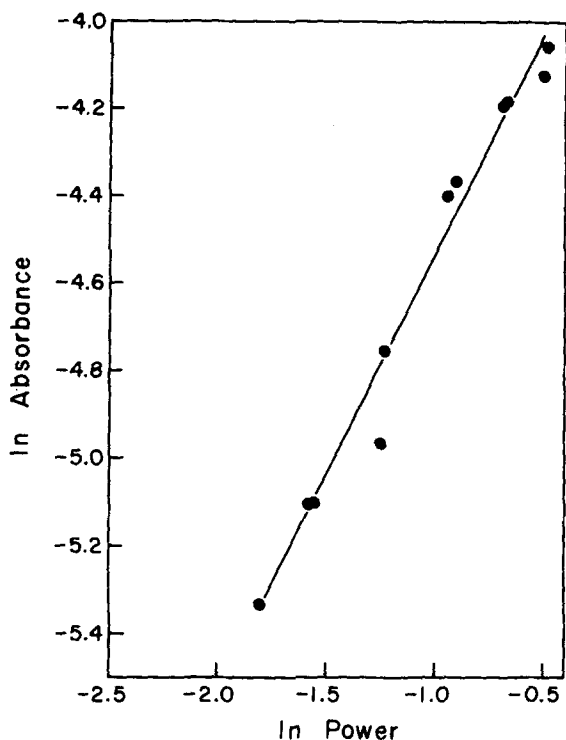


FIG. 2. Curve-of-growth plot of $\ln A$ vs \ln power which demonstrates the validity of Eq. (6) over the range of absorbances used in this study. Conditions were $P_{O_3} = 0.75$ mTorr, $P_{He} = 10$ Torr. Laser power was varied over the range 15–55 mJ.

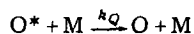
and suggests that earlier chemical studies^{8,9} were prone to systematic error not accounted for in the reaction schemes proposed for O₃ and N₂O photochemistry. These results also demonstrate that earlier direct measurements carried out in this laboratory¹² were too slow to permit observation of the photolytic production of O(³P_J) in the photodissociation of O₃.

DISCUSSION

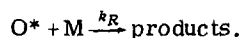
It is now clear from direct measurements utilizing several different techniques that a substantial fraction of the oxygen atoms resulting from the photolysis of O₃ in the Hartley continuum are formed initially in the ground electronic state, 2³P_J. It appears that model calculations of atmospheric photochemistry should, therefore, be corrected to account for the concomitant lowering of the O* concentration arising from the photodissociation of O₃. Additionally, studies of the relative yield of O* near the thermochemical threshold for production of O* and O₂(¹Δ_g) at 310 nm,²⁻⁶ must similarly be recalibrated as these have, in general, assumed an absolute O* yield of unity near the peak of the Hartley band. Unfortunately, it is not so clear how this calibration should be accomplished as the wavelength range covered by these chemical studies do not, in general, include that of the current measurement, 248 nm. The most recent of the relative determinations⁸ does include measurements at 250 and 255 nm, but the experimental precision does not give a clear indication of any trends in relative O* yield near or to the low wavelength side of the Hartley band peak. A direct examination of the wavelength dependence of ϕ is currently under way in

this laboratory using the experimental techniques described above, the goal being the resolution of the continuum spectrum of O₃ in a manner similar to that demonstrated¹⁷ for Br₂. It would, in our opinion, be quite surprising if ϕ did not demonstrate some wavelength dependence over the region 250–300 nm, as this would imply that potential surfaces arising from O* + O₂(¹Δ_g) and O + O₂(³Σ_g⁻, ¹Δ_g, ¹Σ_g⁺) are closely coincident over the vertical transition energy range from ~33 000–40 000 cm⁻¹. This seems unlikely as the photofragment products lie at significantly different energies, e.g., $\Delta E(2^1D_2 - 2^3P_J) \sim 15\,500$ cm⁻¹.

The current results also require that a previous study in this laboratory¹³ of O* deactivation by atmospheric gases be re-examined. In particular, it was reported¹³ that deactivating collisions between O* and N₂O, CH₄, and H₂O resulted in some quenching



in addition to reaction



The values of $k_Q/(k_Q + k_R)$ reported for O* deactivation by N₂O, CH₄, and H₂O were 0.12 ± 0.03 , 0.12 ± 0.04 , and 0.14 ± 0.04 , respectively, and were derived under the assumption that $\phi = 1.0$. As the quantum yield is clearly significantly less than unity, it is now apparent that quenching of O* to O upon collision with these molecules does not occur to any measurable extent. Indeed, it is quite straightforward to demonstrate that, for the special case of $k_Q \ll k_R$, the value of $k_Q/(k_Q + k_R)$ reported in the previous work represents the fractional yield of ground state oxygen atoms in the initial photolysis of O₃. The estimate obtained by averaging these results, 0.13 ± 0.02 , is in quite satisfactory agreement with the value 0.15 ± 0.02 derived from the value of ϕ reported above. It should be noted that the conclusions concerning deactivation by CO₂, which is accompanied by quenching only, as well as the overall yield of one O atom formed per O* deactivated by O₃, remain unaffected by the revised value of ϕ reported here, as these may be directly compared to the O atom yield in the O* quenching by N₂ where no reactive removal is thermochemically possible.

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