Photolysis of pure solid O₃ and O₂ films at 193 nm

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We studied quantitatively the photochemistry of solid O₃ and O₂ films at 193 nm and 22 K with infrared spectroscopy and microgravimetry. Photolysis of pure ozone destroyed O₃, but a small amount of ozone remained in the film at high fluence. Photolysis of pure O₂ produced O₃ in an amount that increased with photon fluence to a stationary level. For both O₂ and O₃ films, the O₃/O₂ ratio at large fluences is ~0.07, about two orders of magnitude larger than those obtained in gas phase photolysis. This enhancement is attributed to the increased photodissociation of O₂ due to photoabsorption by O₂ dimers, a process significant at solid-state densities. We obtain initial quantum yield for ozone synthesis from solid oxygen, Φ(O₃) = 0.24 ± 0.06, and quantum yields for destruction of O₃ and O₂ in their parent solids, Φ(−O₃) = 1.0 ± 0.2 and Φ(−O₂) = 0.36 ± 0.1. Combined with known photoabsorption cross sections, we estimate probabilities for geminate recombination of 0.5 ± 0.1 for O₃ fragments and 0.88 ± 0.03 for oxygen atoms from O₂ dissociation. Using a single parameter kinetic model, we deduce the ratio of reaction cross sections for an O atom with O₂ vs. O₃ to be 0.1–0.2. The general good agreement of the model with the data suggests the validity of the central assumption of efficient energy and spin relaxation of photofragments in the solid prior to their reactions with other species. © 2011 American Institute of Physics. [doi:10.1063/1.3589201]

I. INTRODUCTION

For more than a century, photoabsorption of UV light by ozone has received great attention because of its importance in the protection to life by the ozone layer in the outer atmosphere and in air pollution at ground level. In the last few decades, studies of the photolysis of solid ozone have been made to understand specific solid-state effects1,2 and to explain the observation of condensed ozone on the surfaces of cold satellites3 of the outer planets. The proposal that radiolysis of H₂O and O₂ ices is the source of the condensed ozone in planetary ices has been tested in experiments where thin films were irradiated with energetic particles or photons. Bahrt et al. found4 that radiolysis of pure water ice does not produce any significant amounts of ozone, but Teolis et al.5 discovered that ozone can indeed be produced if water was deposited during irradiation, which enhanced accumulation of radiolytic oxygen. In contrast, ozone is readily produced when O₂ (Ref. 6) and O₂ + H₂O films (Refs. 7 and 8) are irradiated with energetic particles (H⁺, e⁻) and ultraviolet photons.9 In addition to planetary applications, there are predictions by astrochemical models that condensed O₂ and O₃ should be present in the icy grain mantles in dense molecular clouds.10–12 The presence of photosensitive molecules such as O₃ on interstellar grains, which can yield reactive fragments by energetic radiation, could be crucial to chemistry occurring in dark molecular clouds due to a background ultraviolet flux from the decay of hydrogen excited by cosmic rays.

The vast majority of the work on photolysis of oxygen and ozone has been done in the gas phase, motivated by the need to understand the atmospheric ozone problem. Such studies have revealed the existence of multiple photolysis channels with different energy thresholds and involving many excited atomic and molecular states.13 By comparison, the photolysis of ozone and oxygen solids has barely been explored, mostly using photons in the Hartley band, above 200 nm.1, 14, 15 Still unanswered is the question of the photolysis of O₂ in the region of Schumann-Runge bands and continuum, where photoabsorption cross sections differ by orders of magnitude between the gas and the solid. Here we present results of experiments of the photolysis of optically thin (<100 nm) solid films of pure ozone and oxygen at 22 K by 193 nm photons and a simple photochemical model from which we derive initial quantum yields, effective dissociation cross sections and probabilities for geminate recombination and reaction involving O atoms.

II. EXPERIMENTAL SETUP

Experiments were performed in an ultrahigh vacuum chamber (base pressure ~10⁻⁹ Torr). Ozone was prepared by applying a Tesla coil discharge to the glass manifold presurized with 100–150 Torr of O₂. Ozone formed from the discharge was condensed to the liquid phase by immersing the manifold in liquid N₂. After 1–2 min of discharge, we removed the remaining O₂ by pumping the manifold and admitted sublimating ozone molecules into the chamber through a Teflon valve.

Ozone molecules from the glass manifold were directed towards a gold-coated quartz crystal microbalance (QCM) (Ref. 16) cooled to 53 K. We chose this temperature to avoid condensation of trace O₂ from the glass manifold or O₂ produced from ozone reacting with any surface inside the chamber.
vacuum chamber. The microbalance measures the areal mass of the condensed film, which is converted into column density (molecules cm$^{-2}$) by dividing by the molecular mass. We deposited films with column densities between $155 \times 10^{15}$ and $160 \times 10^{15}$ O$_3$ cm$^{-2}$ at a rate that varied between 0.15 $\times$ 10$^{15}$ and 0.5 $\times$ 10$^{15}$ O$_3$ cm$^{-2}$ s$^{-1}$. Using the density of 1.65 g cm$^{-3}$ for solid ozone, we obtain film thicknesses of $\sim 75–77$ nm. After deposition at 53 K, the ozone films were heated to 55 K to ensure complete crystallization and cooled to 22 K prior to UV exposure. To study photolysis of solid O$_2$, we deposited films containing $230 \times 10^{15} – 240 \times 10^{15}$ O$_2$ cm$^{-2}$ at 22 K from a microcapillary-array doser at the rate of $0.3 \times 10^{15}$ O$_2$ cm$^{-2}$ s$^{-1}$. These films have a thickness of 80–84 nm, derived using a density of 1.53 g cm$^{-3}$ for solid oxygen.

The films were irradiated with 193 nm pulses produced by ArF excimer laser at normal incidence. The laser beam was defocused using a MgF$_2$ lens ($f = 50$ cm) to cover a rectangular spot $\sim 25$ mm $\times$ 75 mm at the target, larger than the active diameter of the microbalance (6 mm) to avoid multi-photon excitations or heating during each laser pulse. To measure the photon fluence reaching the target, we replaced the QCM with an Ophir power meter, which measured constant beam intensity across the area of the QCM. The laser delivered pulses of 0.72 mJ cm$^{-2}$ uniformly across the films at a rate that was varied from 1 to 3 Hz during the experiment. The energy per pulse was constant within 3% during the experiments. The results did not depend on the value of the fluence per pulse, within errors. The fluence of the laser pulse attenuates as it traverses the film due to absorption from ozone and oxygen molecules. The gold reflects 18% of the light that reaches the substrate, following attenuation at 193 nm. The total fluence is the sum of the incident and reflected values.

The amount of ozone in the film was measured using specular reflectance infrared spectroscopy (35$^\circ$ incidence) at 2 cm$^{-1}$ resolution with a Thermo Nicolet Nexus 670 Fourier transform infrared spectrometer. The O$_3$ column density $\eta_3$ was deduced from the area of the 9.5 and 4.74 $\mu$m ozone absorptions for solid ozone at 22 K, showing a decrease in band area following exposure to 193 nm photons to the indicated fluences in units of 10$^{18}$ photons cm$^{-2}$. The spectra have been displaced vertically for clarity.

For pure ozone, we obtain initial effective band strengths for the $\nu_3$ and $\nu_1 + \nu_3$ bands by dividing the respective band areas by the initial column density measured by the microbalance following deposition. The values are $A^*_{\nu_3} = 3.6 \pm 0.4$ and $0.47 \pm 0.08$ in units of 10$^{-18}$ cm mol$^{-1}$ for the $\nu_3$ and the $\nu_1 + \nu_3$ bands, respectively. As the film is irradiated, the band shape and area change as ozone becomes diluted in O$_2$.

To obtain the effective band strengths $A^*$ at the end of irradiation, we thermally desorbed the photolyzed ozone and oxygen films and measured the mass change with the microbalance. In Fig. 2 we compare the thermal desorption spectra of ozone and oxygen films, as deposited and photolyzed, while heating at 1 K min$^{-1}$. The desorption rates are obtained

![Image](image-url)
from the time derivative of the mass loss measured with the microbalance. The desorption of the unirradiated ozone film peaks at 64 K while that of photolyzed O₃ has two peaks, one at 32 K and a smaller one at ~58 K. The desorption of unirradiated O₂ peaks at 32 K, while the photolyzed O₂ film also shows an additional smaller peak at 58 K.

We get \( A_\nu^* = (5.1 \pm 1.2) \times 10^{-18} \) and \((0.52 \pm 0.15) \times 10^{-18} \text{ cm mol}^{-1}\) by dividing the area of the \( \nu_3 \) and \( \nu_1 + \nu_2 \) bands at large fluences by the residual O₃ column density obtained from the microbalance measurement of the small desorption between 55 and 60 K in the photolyzed films. The column densities of ozone during irradiation are obtained by dividing the band areas of \( \nu_3 \) and \( \nu_1 + \nu_2 \) bands with the linearly interpolated \( A^* \). Since \( A^* \) for the \( \nu_1 + \nu_3 \) band varies only ~10% with the amount of O₃ in the film, we use this band to quantify the experiments on ozone films. In addition, we observe a small but systematic (~10%) increase in \( \nu_2 \) band area for fluences <5 × 10^{16} \text{ cm}^2. This increase is likely due to variations in the index of refraction caused by effects such as amorphization or compaction. We find that the \( \nu_1 + \nu_3 \) band is free from such interference. For oxygen films, the range of ozone values and therefore the error in \( A^* \) is small. In this case, we use the stronger \( \nu_3 \) band as a measure of ozone column density. Also, the \( \nu_1 + \nu_3 \) band is too weak to be detected at very low fluence. The errors in \( A^* \) are estimated from dispersion in band areas obtained from several experiments, and translate into an error of at most ±15% in the O₃ column densities.

III. RESULTS

All photolysis experiments were performed at 22 K. Figure 1 shows changes in the \( \nu_3 \) and \( \nu_1 + \nu_2 \) bands of a ~75 nm, initially pure, ozone film during photolysis. The band area decreases and its position shifts to lower wavenumber with increasing photon fluence. The shift is more prominent in the \( \nu_3 \) band. Figure 3 shows that \( \eta_3(F) \) decreases nearly exponentially with fluence \( F \) to a stationary level that is 10% of \( \eta_3(0) \).

Figure 4 shows the appearance and growth of the \( \nu_2 \) ozone absorption band during photolysis of solid O₂. For large fluences, the bands measured on initially pure O₂ and O₃ films are essentially the same. In Fig. 5 we show a log-log plot of the fluence dependence of the production of O₃ in irradiated O₂ films.

IV. DISCUSSION

To analyze our experiments we start by summarizing results of gas phase experiments and discuss differences between experiments done in the solid and with free molecules. In the gas phase, photoabsorption of a 193.3 nm (6.41 eV) photon dissociates O₂ into two ground state O(3P) atoms.\(^{22}\)

\[
O_2\left(X^3\Sigma_g^-\right) + h\nu \rightarrow 2O(3P).
\]

The absorption by a free molecule is in the Schumann-Runge region, where the cross section varies over two orders of magnitude across wavelength intervals as small as 0.1 nm, due to closely spaced rovibrational energy levels. Thus, the results of measurements depend on the energy width of the exciting light, which may explain the range of reported cross sections:\(^{23}\) 1.2 × 10^{-22} - 200 × 10^{-22} \text{ cm}^2. Because of the polarization of the medium and the intermolecular interactions, the energy levels in the solid are shifted and broadened compared with the gas phase, as seen in ultraviolet photoabsorption\(^{1,24-26}\) and photoelectron emission\(^{27}\) studies, with cross sections varying smoothly with photon energy. The
photoabsorption cross section of solid O$_2$ at 193 nm is $\sigma_2 = 4.2 \times 10^{-19}$ cm$^2$, orders of magnitude larger than for the free molecule.$^{26}$

For the free ozone molecule, photoabsorption at 193 nm leads to O ($^3P$) and electronically excited O ($^1D$) (1.97 eV) in roughly equal proportions,$^{28,29}$ with a cross section $\sigma_3 = 4.3 \times 10^{-19}$ cm$^2$.

$$O_3(X^1A_1) + h\nu \rightarrow O(^1D) + O_2(a^1\Delta_g, b^1\Sigma_g^+) , \quad (2)$$

$$O_3(X^1A_1) + h\nu \rightarrow O(^3P) + O_2(X^3\Sigma_g^-), \quad (3)$$

where the O$_2$ in (3) may be vibrationally hot. Dissociation into three O atoms$^{29}$ or production of O ($^1S$) (Ref. 30) has yields two orders of magnitude smaller than those for O ($^1D$) or O ($^3P$) production. In the solid, $\sigma_3 = (2.50 \pm 0.05) \times 10^{-18}$ cm$^2$, obtained by extrapolating measurements of Sedlacek and Wight$^1$ from 200 to 193 nm. This value is 5.8 times larger than for gas phase ozone.

In the gas phase, the main reactions of the oxygen radicals are $^2,^22$

$$O(^1D) + O_2(X^3\Sigma_g^-) + M \rightarrow O_3(X^1A_1) + M, \quad (4)$$

$$O(^3P) + O_2(X^3\Sigma_g^-) + M \rightarrow O_3(X^1A_1) + M, \quad (5)$$

$$O(^1D) + O_3(X^1A_1) \rightarrow 2O_2(X^3\Sigma_g^-), \quad (6)$$

$$O(^3P) + O_3(X^1A_1) \rightarrow 2O_2(X^3\Sigma_g^-), \quad (7)$$

$$O_2(X^3\Sigma_g^-, v^*) + O_2 \rightarrow O_3(X^1A_1) + O(^3P). \quad (8)$$

In (8) $v^*$ denotes high vibrational excitation (>4.2 eV) and M is a third body needed to conserve energy and momentum in the association reactions.

In the solid state, the picture is modified not only because of possibly different branching ratios, but also because of inter-molecular interactions that produce many ways to dissipate kinetic, vibrational and electronic energy. Prominent is the cage effect, where dissociation products can bounce back from neighboring molecules (the cage) and recombine (geminate recombination), thereby lowering the effective dissociation cross section.

The high molecular density in the solid state has multiple implications. For instance, a photon may actually interact with a pair of O$_2$ molecules or dimer, a process that causes absorption in the visible region in the Earth’s atmosphere and on planetary ices$^{31}$ and also causes ultraviolet absorption at photon energies between 4.5 and 7 eV in O$_2$ at high pressures.$^{32}$ Photoabsorption by the (O$_2$)$_2$ dimer is much more efficient than the dipole-forbidden transitions of the isolated molecule, and is likely the reason for the larger photoabsorption cross section of the solid at 193 nm, mentioned above.

The transformation of electronic energy into kinetic energy during dissociation is different from the gas phase since the recoiling products in the solid interact with surrounding molecules, setting them in motion as well. This sharing of kinetic energy implies that the energy of a given dissociation product, say, an O atom, is lower than in the gas phase and cannot be derived simply from the photon energy and the bond energy of the molecule. In the following, we will assume that reaction products dissipate their energy (vibrational, electronic and kinetic) before they react, because of many-body interactions in the solid, including multi-phonon relaxation processes and multiple crossing of potential energy surfaces. We also assume that spin, which is important in the transformation cross section.

A. Initial cross sections and quantum yields in solid ozone

For low fluences, the variation of the ozone column density $\eta_3$ with $F$ is given by

$$\frac{d\eta_3}{dF} = -m_3(1 - \alpha_3)\sigma_3\eta_3, \quad (14)$$

where $\eta_3$ is the ozone column density, $F$ is the fluence, $m_3$ is the mass of ozone, $\alpha_3$ is the optical thickness, and $\sigma_3$ is the cross section for ozone production.
B. Initial cross sections and quantum yields in solid O$_2$

The O atoms resulting from photoabsorption and subsequent dissociation can either recombine to reform O$_2$ or react with additional O$_2$ to form two ozone molecules: $-3$ O$_2$ $\rightarrow$ 2 O$_3$. The initial photodissociation of O$_2$ is described by

$$\frac{d\eta_2}{dF} = -m_2(1 - \alpha_2)\sigma_2\eta_2,$$

where $m_2$ is the number of O$_2$ molecules that are destroyed per net dissociation event. Since the number of oxygen atoms in the matrix is conserved, Eq. (16) is integrated to

$$\ln \left[ 1 - \frac{3\eta_3}{2\eta_3(0)} \right] = -m_2(1 - \alpha_2)\sigma_2 F.$$

The bottom panel in Fig. 6 shows a fit of Eq. (17) to experimental results at low fluences, which gives an average slope of $m_2(1 - \alpha_2)\sigma_2 = (1.5 \pm 0.3) \times 10^{-19}$ cm$^2$. Since $\sigma_2 = 4.2 \times 10^{-19}$ cm$^2$ (Ref. 25–27), with an estimated uncertainty of 25%, the quantum yield for O$_2$ destruction is $\Phi(-O_2) = 0.36 \pm 0.10$. Furthermore, $m_2 = 3$, because 2 O escaping recombination after O$_2$ dissociation react with 2 additional O$_2$, producing 2 O$_3$. Thus, the probability of geminate recombination is $\alpha_2 = 0.88 \pm 0.03$, nearly twice the value for ozone. Since each dissociation produces two ozone molecules, $\Phi(O_3) = (2/3)\Phi(-O_2) = 0.24 \pm 0.06$ for ozone synthesis.

C. Ozone/oxygen ratios at high fluences

The saturation $\eta_3/\eta_2$ for O$_3$ photolysis at high fluence is 0.070 ± 0.030, with little variation among experiments. For experiments with O$_2$ films, the ratio ranged from 0.05 to 0.08 in different O$_2$ experiments. It is possible that photolysis of O$_2$ films is affected by trace impurities present in the ultra-high vacuum environment. The saturation $\eta_3/\eta_2$ in the solid phase is nearly two orders of magnitude larger than gas phase values, due mostly to the much larger O$_2$ photodissociation cross section in the solid and, to a lesser extent, to larger probability for geminate recombination (absent in the gas phase) of dissociation fragments from O$_2$ vs. O$_3$. The enhancement in photoabsorption cross section due to O$_2$–O$_2$ dimer interaction, possible at high densities, is responsible for higher $\eta_3/\eta_2$.

D. Rate equations and fluence dependence

Modeling ozone production and destruction on the basis of the Chapman equations is difficult because of the existence of two widely different time scales, those for reactions of atomic O atoms and for the buildup of radiation products in the film. We circumvent this problem by assuming that O atoms are consumed by reactions as soon as they are formed. This means that they do not accumulate in the film to a significant level, which should be a good assumption based on previous discussions. Thus, the evolution of the O$_3$ and O$_2$, determined by a competition between creation and destruction rates, is given by

$$\frac{d\eta_3}{dF} = -\sigma_3\eta_3 - \sigma_3\eta_3 \frac{\eta_3}{\eta} + \sigma_3\eta_3 R_{23} \frac{\eta_2}{\eta*} - 2\sigma_2\eta_2 \frac{\eta_3}{\eta*} + 2\sigma_2\eta_2 R_{23} \frac{\eta_2}{\eta*},$$

where $\eta_3/\eta_2$ gives the initial O$_3$ destruction in a 156 $\times$ 10$^{15}$ O$_2$ cm$^{-2}$ film irradiated with 0.72 mJ cm$^{-2}$ laser pulses. Bottom: initial O$_3$ synthesis in several O$_2$ films (230 $\times$ 10$^{15}$ – 240 $\times$ 10$^{15}$ O$_2$ cm$^{-2}$) when irradiated with 0.72 mJ cm$^{-2}$ laser pulses. The significance of the slope of the solid lines of both panels is discussed in the text.

which integrates to

$$\ln \left[ \frac{\eta_3}{\eta_3(0)} \right] = -m_3(1 - \alpha_3)\sigma_3 F.$$  

Here $\sigma_3$ is the photoabsorption cross section and $\alpha_3$ is the probability of geminate recombination of O + O$_2$ back to O$_3$. The factor $m_3$ takes into account the additional ozone molecule destroyed in a subsequent reaction by the O photoabsorption dissociation fragment. The product $m_3(1 - \alpha_3)$ gives the initial quantum yield $\Phi(-O_3)$, or number of ozone molecules destroyed per absorbed photon and $\sigma_3 = (1 - \alpha_3)\sigma_3$ is the net dissociation cross section in the solid.

The top panel in Fig. 6 shows a fit of Eq. (15) to the experimental $\eta_3(F)$ for two values of fluence per laser pulse. The fit gives a slope $m_3(1 - \alpha_3)\sigma_3 = \Phi(-O_3) \sigma_3 = (2.4 \pm 0.4) \times 10^{-18}$ cm$^2$, which is nearly equal to the photoabsorption cross section, $\sigma_3 = (2.50 \pm 0.05) \times 10^{-18}$ cm$^2$. Thus, the initial quantum yield for O$_2$ photodestruction is $\Phi(-O_2) = 1.0 \pm 0.2$, not too different from the value of 1.5 ± 0.2 reported for 308 nm photons on solid ozone, on the higher wavelength edge of the Hartley band. Since, according to (13), another ozone molecule is destroyed after each dissociation event, $m_3 = 2$, the value of $\Phi(-O_3)$ for the gas phase, where there is no cage effect. Therefore, the probability for geminate recombination of O$_2$ and O is $\alpha_3 = 0.5 \pm 0.1$. 

![Figure 6](image-url)
TABLE I. Comparison of different parameters obtained from 193 nm photolysis of solid O$_2$ and O$_3$ film with gas phase values.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Gas (from literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_2^*(10^{20}$ cm$^2$)</td>
<td>5 $\pm$ 1$^a$</td>
</tr>
<tr>
<td>$\sigma_3^*(10^{-18}$ cm$^2$)</td>
<td>1.2 $\pm$ 0.2$^c$</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>0.5 $\pm$ 0.1</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.88 $\pm$ 0.03</td>
</tr>
<tr>
<td>$\Phi(-O_2)$</td>
<td>1.0 $\pm$ 0.2</td>
</tr>
<tr>
<td>$\Phi(-O_3)$</td>
<td>0.36 $\pm$ 0.10</td>
</tr>
<tr>
<td>$\Phi(O_3)$</td>
<td>0.24 $\pm$ 0.06</td>
</tr>
<tr>
<td>$\eta_1:\eta_2$ (large $F$)</td>
<td>0.05 $\pm$ 0.08 (O$_2$)</td>
</tr>
<tr>
<td>$\eta_1:2\eta_2$ (0)</td>
<td>0.070 $\pm$ 0.03 (O$_3$)</td>
</tr>
<tr>
<td>$R_{23}$</td>
<td>0.2 $\pm$ 0.22 (O$_3$)</td>
</tr>
<tr>
<td></td>
<td>0.1 $\pm$ 0.18 (O$_2$)</td>
</tr>
</tbody>
</table>

$^a$ $\sigma_2^*$ required to get $\sigma_2^*$ is obtained from Refs. 25 and 26.
$^b$ Reference 23.
$^c$ $\sigma_3^*$ required to get $\sigma_3^*$ is obtained from Ref. 1.
$^d$ Reference 38.

where $\sigma_2^* = \sigma_1 (1-\alpha_i)$ are the net dissociation cross sections. The first term accounts for reduction in O$_3$ column density due to photoabsorption followed by dissociation, which produces O and O$_3$ fragments; the other terms describe reactions of O atoms with additional O$_2$ or O$_3$ molecules that occur according to their relative abundances in the films and their respective reaction cross sections. The second and the third terms are for O formed from photodissociation of O$_3$; the last two are for the two O atoms from photodissociation of O$_2$. $R_{23}$ is the ratio of reaction cross sections of O with O$_2$ and O$_3$, and $\eta = R_{23} \eta_2 + \eta_3$.

Equation (18) has only one unknown, $R_{23}$, and can be used to fit the numerical derivatives of the fluence dependences of O$_3$ column density. The fit is subjected to the following constraints: $d\eta_3/dF = 2\sigma_2^* \eta_2$ (0) or $-2\sigma_3^* \eta_3$ (0) or for O$_2$ and O$_3$, respectively, at low $F$, within errors, $d\eta_2/dF = 0$ at saturation fluences and $\int_0^F \frac{d\eta_2}{dF} dF = \eta_3(F) - \eta_3(0)$, known accurately from the microbalance data. The fit to the O$_3$ photolysis data shown in Fig. 3 gives $R_{23} = 0.21$. This implies that O atoms are five times less likely to react when they encounter an O$_2$ vs. an O$_3$ molecule. The fit applied to different O$_2$ photolysis experiments give $R_{23}$ in the range of 0.1–0.18, a variation that we mentioned above for the $\eta_3:2\eta_2$ values at high fluence. The results of some fits are shown in Fig. 5. The range of $R_{23}$ values may indicate limitations in the model, such as the assumption of energy and spin relaxation, but it is also possibly connected with effects of trace amounts of impurities from deposition of background gas even at ultrahigh vacuum pressures, which could also account for the variations in the saturation $\eta_3:2\eta_2$ values. Among the results reported here, the saturation $\eta_3:2\eta_2$ are the most reliable since they come directly from the measurements. The coefficients $\alpha_2$ and $\alpha_3$ are obtained from initial slopes and rely on photoabsorption cross sections measured elsewhere, but they are less dependent on the model than $R_{23}$.

Table I summarizes the results of these experiments and compares them with gas phase values. The remarkably higher photoabsorption cross section of solid O$_2$ at 193 nm is due to the contribution of O$_2$ dimer absorption, absent in the gas phase. The enhanced photoabsorption increases the number of O that can react with O$_2$ to form O$_3$, leading to the higher $\eta_3:2\eta_2$ ratio in the solid, at the end of irradiation. This is likely also the reason for the observed 50-fold increase in the final $\eta_3:2\eta_2$ ratio observed in photolysis of solid O$_2$ at 210 nm compared to 250 nm.

V. ASTROPHYSICAL IMPLICATIONS

The prospect of the presence of reactive species such as ozone in low temperature environments such as the molecular clouds is interesting because radiolytic O atoms can start multiple routes of molecular synthesis in the interstellar medium. An estimate of the solid O$_2$ abundance in molecular clouds, based on observations of the weak O$_2$ transition at 6.45 $\mu$m and the profile of the 4.67 $\mu$m CO absorption feature, gave upper limits of 6 $\times$ 10$^{17}$–12 $\times$ 10$^{17}$ O$_2$ cm$^{-2}$, which only accounts for $\sim$6% of total oxygen budget in the interstellar medium (ISM). These O$_2$ condensed on the grains can be partially converted into ozone by energetic cosmic rays or the UV radiation they generate by exciting the background hydrogen gas. Though, so far, results of the observations have been negative on the presence of O$_3$ on the grains, it is possible that the 9.6 $\mu$m ozone absorption is masked by a broad absorption feature at $\sim$10 $\mu$m due to silicates or other materials. Photodissociation of ozone produces O atoms that could react with other molecules, such as CO to produce CO$_2$, possibly assisted by the localized energy deposition. If this process is relevant, it could help to resolve the problem of accounting for the observed abundance of solid CO$_2$ in interstellar clouds.

ACKNOWLEDGMENTS

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