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Irradiation of O2 dispersed in solid Ne with ultraviolet light produced infrared absorption lines of O<sub>3</sub> and emission lines from atomic O (^1D\_2  $\rightarrow~^3P_{1,2}),$  molecular O\_2 (A'  $^3\Delta_u$   $\rightarrow~$  X  $^3\Sigma_g)$  and radical OH (A  ${}^{2}\Sigma^{+} \rightarrow X {}^{2}\Pi_{I}$ ) in the visible and near-ultraviolet regions. The threshold wavelength for the formation of O<sub>3</sub> was determined to be 200  $\pm$  4 nm, corresponding to energy 6.20  $\pm$  0.12 eV, which is hence the threshold for dissociation of O2. The thresholds of emission from excited O (<sup>1</sup>D<sub>2</sub>), O<sub>2</sub> (A'  ${}^{3}\Delta_{u}$ ) and OH (A  ${}^{2}\Sigma^{+}$ ) were all observed to be 200  $\pm$  4 nm, the same as for the formation of  $\text{O}_{3}$  in this photochemical system. The results indicate that, once O<sub>3</sub> was generated, it was readily photolyzed to produce the long-lived atom O ( ${}^{1}D_{2}$ ). Further reactions of O ( ${}^{1}D_{2}$ ) with O<sub>3</sub> produced excited O<sub>2</sub> (A'  ${}^{3}\Delta_{u}$ ); reaction with water yielded radical OH (A  ${}^{2}\Sigma^{+}$ ). These results enhance our understanding of the evolution of the transformation of oxygen and open a window for the understanding of complicated processes in the solid phase.

Ozone,  $O_3$ , attracts perpetual scientific attention because it is an important filtering gas in the terrestrial atmosphere to suppress harmful ultraviolet radiation from sunlight. Chapman proposed that photolysis of molecular oxygen generates two oxygen atoms, each of which can combine with  $O_2$  to form ozone in our upper atmosphere.<sup>1</sup> To form ozone in the stratosphere, the initial step thus involves the photochemical dissociation of molecular oxygen by radiation from our sun; the photochemistry of gaseous dioxygen has hence been much investigated.<sup>2–7</sup>

The photodissociation of gaseous molecular oxygen might produce atomic oxygen in states <sup>3</sup>P, <sup>1</sup>D and <sup>1</sup>S *via* separate channels. Assessing the photolysis thresholds for each channel is important for an understanding of the detailed mechanisms

# Thresholds of photolysis of $O_2$ and of formation of $O_3$ from $O_2$ dispersed in solid neon

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involved. According to previous work,<sup>8</sup> the threshold wavelengths greater than 130 nm for the photodissociation of gaseous  $O_2$  are

- $O_2 + h\nu (\lambda > 130 \text{ nm}) \rightarrow O(^3P) + O(^3P) \quad \lambda_{\text{th}} = 242.2 \text{ nm}$  (1a)
  - $\rightarrow$  O (<sup>3</sup>P) + O (<sup>1</sup>D)  $\lambda_{\text{th}} = 175.0 \text{ nm}$  (1b)
  - $\rightarrow$  O (<sup>3</sup>P) + O (<sup>1</sup>S)  $\lambda_{\text{th}} = 133.2 \text{ nm.}$  (1c)

In cold astronomical environments,  $O_2$  exists in the condensed phase.<sup>9,10</sup> The photochemistry of molecular oxygen in the condensed phase might differ appreciably from that of gaseous  $O_2$ ; its photochemistry in the condensed phase thus warrants attention for an understanding of various effects peculiar to that state.<sup>11–16</sup> A comparison of the threshold for photodissociation between gaseous and solid  $O_2$  *via* these channels can increase our insight into the perturbation of absorption and the cage effect in the solid state.

In preceding experiments, we investigated the photochemical reactions of O2 dispersed in solid neon and irradiated at 143 and 173 nm from a synchrotron source.<sup>17</sup> The results indicate that complicated processes occurred for O2 dispersed in solid Ne after far-ultraviolet (FUV) excitation. A report that O<sub>2</sub> dispersed in solid argon at 21 K is not subject to photolytic dissociation if the O2 molecule is efficiently isolated differs radically from our experience of O2 in solid neon, in which ample evidence of dissociation emerged at even smaller concentrations than in solid argon.<sup>18</sup> In contrast, when no inert diluent is present, such as in films of pure O2 at 22 K, there is adequate scope for an O atom, produced by photolysis, to react with a molecule of  $O_2$  in the immediate vicinity of the dissociative event.<sup>19</sup> To acquire further understanding of the photochemical processes in the solid state, in the present work we investigated the thresholds for photolysis of O<sub>2</sub> and for the formation of O<sub>3</sub> from O<sub>2</sub> dispersed in solid neon with excitation at less than 230 nm.

According to eqn (1), gaseous  $O_2$  might dissociate into oxygen atoms when it is subjected to radiation of wavelength less than 242 nm. Each atomic fragment can subsequently

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combine with  $\mathrm{O}_2$  in a reaction that generates ozone, aided by a third body M.

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

In an environment of solid neon at 4 K, dispersed  $O_2$  molecules are surrounded by neon atoms that constitute a cage. Upon irradiation with an energetic photon, a pair of oxygen atoms might be produced and directly recombine to  $O_2$  through the cage effect; the net effect is no dissociation of  $O_2$  in the solid matrix, but emission of radiation by an atom or molecule might be involved. If atomic oxygen as an energetic photolytic fragment can escape from the cage that is the site of its formation, it might migrate and become trapped in the lattice, or react with molecular oxygen at another site to form  $O_3$ . In such a photolytic system,  $O_3$  serves as an indicator of the dissociation of  $O_2$ .

Because the most intense absorption of O2 dispersed in solid neon occurs at 143 nm,<sup>17</sup> corresponding to an energy of 8.67 eV, we first selected 143 nm to excite O2 dispersed in solid neon; after irradiation, we identified O<sub>3</sub> product through its mid-infrared absorption spectrum. The radiation for photolysis was selected from an undulator on beamline 21A2 attached to the 1.5 GeV synchrotron ring of the Taiwan Light Source (TLS) at the National Synchrotron Radiation Research Center (NSRRC).<sup>20,21</sup> Fig. 1(a and b) show infrared absorption spectra of dioxygen dispersed in solid neon at 4 K for  ${}^{16}O_2$ : Ne = 1:5000 and  ${}^{18}O_2$ : Ne = 1:5000, respectively, after irradiation at 143 nm for 5 min; only one vibrational mode,  $\nu_3$ , of ozone was recorded: for  ${}^{16}O_3$  a triplet at 1038.7, 1042.4 and 1045.2 cm<sup>-1</sup>, and for  $^{18}\mathrm{O}_3$  another triplet at 981.6, 985.9 and 987.9  $\mathrm{cm}^{-1.22}$  After irradiation of the sample, other infrared absorption lines of photolysis products were recorded, at 3590.4 cm<sup>-1</sup> due to <sup>16</sup>OH from the minute contaminant H<sub>2</sub><sup>16</sup>O, indicated by depletion lines at 1614.4 and 1630.4 for mode  $\nu_2$  and 3783.2 cm<sup>-1</sup> for mode  $\nu_3$ , and at 2140.9 cm<sup>-1</sup> due to C<sup>16</sup>O from C<sup>16</sup>O<sub>2</sub> with a depletion line at 2347.7 cm<sup>-1</sup> for mode  $\nu_3$  of that precursor. Both contaminants H<sub>2</sub><sup>16</sup>O and C<sup>16</sup>O<sub>2</sub> were present in vestigial proportions after deposition of the samples for 2 h or more; the



**Fig. 1** Infrared absorption spectra of (a)  ${}^{16}O_2: Ne = 1:5000$  and (b)  ${}^{18}O_2: Ne = 1:5000$  at 4 K after irradiation for 5 min at 143 nm.  $\varDelta$  absorbance is the difference of absorbance,  $log_{10}(l_0/l)$ , *i.e.* the absorbance after irradiation minus the absorbance before irradiation.

infrared signals of <sup>16</sup>OH and C<sup>16</sup>O in these experiments, like those of their precursors before photolysis, were thus weak.

The most notable feature of these experiments is that, when after photolysis we raised the temperature to 9 K to anneal the sample for 10 min and then cooled the sample to 4 K again, the intensities of the IR absorption lines of ozone increased more than 10-50 times, according to the integrated intensities. Fig. 2(upper and lower) display infrared absorption spectra of dioxygen dispersed in solid neon at 4 K for  ${}^{16}O_2$ : Ne = 1:5000 and  ${}^{18}O_2$ : Ne = 1: 5000, respectively, after irradiation at 143 nm for 5 min and annealing at 9 K for 10 min. The much more intense lines measured for 16O3 after annealing had wavenumbers 699.8, 701.5 and 703.4  ${\rm cm}^{-1}$  for mode  $\nu_2$ , 1038.7, 1039.9, 1041.9, 1045.0, 1046.2 and 1048.6 cm<sup>-1</sup> for  $\nu_3$ , 1104.3 cm<sup>-1</sup> for  $\nu_1$ , and 2107.8 and 2110.0 cm<sup>-1</sup> for  $\nu_1 + \nu_3$ . For  ${}^{18}O_3$ , lines at 660.5, 662.0 and 663.9 cm<sup>-1</sup> are associated with mode  $\nu_2$ , lines at 981.6, 982.8, 984.5, 987.6, 993.9, 988.6 and 991.0 cm<sup>-1</sup> with  $\nu_3$ , a line at 1016.8 cm<sup>-1</sup> with  $\nu_1$ , and lines at 1992.1, 1993.3 and 1995.3 cm<sup>-1</sup> with  $\nu_1 + \nu_3$ . Such a remarkably increased intensity of all lines of O3 occurring after the annealing operation indicates that raising the temperature enabled the mobility of trapped atomic oxygen as a photolytic fragment so that it either reformed O2, of which detection with IR absorption is difficult, or produced O<sub>3</sub>, as we observed.

To discover the threshold for the formation of  $O_3$  upon excitation of dioxygen dispersed in solid neon at 4 K, we tuned the wavelength of radiation beyond 140 nm. In separate experiments we selected light at 143, 173, 185, 200, 210, 220 and 230 nm to irradiate the samples of dioxygen dispersed in solid neon (1:500) at 4 K for 5 min; the corresponding infrared absorption spectra are shown as curves (a)–(g), respectively, in Fig. 3. The absorption lines of  $O_3$  clearly appeared after irradiation at wavelengths 143, 173, 185 and 200 nm, but not 210, 220 and 230 nm, even for irradiation prolonged beyond 30 min. In these experiments, the UV radiation was directed from undulator U90 of Taiwan Light Source and regulated by adjusting its gap;<sup>20,21</sup> this mode of operation yields a beam of



**Fig. 2** Infrared absorption spectra of samples of O<sub>2</sub> dispersed in solid neon at 4 K after irradiation for 5 min at 143 nm and annealing at 9 K for 10 min for (upper)  ${}^{16}O_2$ : Ne = 1:5000, (lower)  ${}^{18}O_2$ : Ne = 1:5000.  $\varDelta$  absorbance is the difference of absorbance,  $\log_{10}(I_0/I)$ , *i.e.* the absorbance after irradiation minus the absorbance before irradiation.



Fig. 3 Infrared absorption spectra of  $O_2$  dispersed in neon (1:500) at 4 K after irradiation for 5 min at (a) 143, (b) 173, (c) 185, (d) 200, (e) 210, (f) 220, and (g) 230 nm.

ultraviolet light of relative width 2%, corresponding to a photon energy of width 0.12 eV, or 4 nm, at the selected wavelength.

According to Fig. 3, the threshold for the formation of  $O_3$  is thus about wavelength 200 nm. We hence derive the threshold energy for the generation of  $O_3$  from the photolysis of  $O_2$  dispersed in solid neon at 4 K to be  $6.20 \pm 0.12$  eV ( $200 \pm 4$  nm). As mentioned above, the signals of the infrared lines of ozone increased greatly after annealing the irradiated samples. When this annealing was applied, increased signals for ozone were observed for samples irradiated at 143, 173, 185 and 200 nm, but not at 210, 220 and 230 nm; these phenomena indicate that oxygen atoms were produced and stored upon irradiation at 143, 173, 185 and 200 nm, but not at 210, 220 and 230 nm; but not at 210, 220 and 230 nm. We hence conclude that the threshold energy to produce separate O atoms from photolysis of  $O_2$  dispersed in solid neon at 4 K is also  $6.20 \pm 0.12$  eV ( $200 \pm 4$  nm).

Excitation of solid O<sub>2</sub> samples with ultraviolet light produced a visible luminescence. With our enhanced end station for photochemistry attached to undulator beamline U90, we recorded the emissions concurrently with the irradiation.<sup>23</sup> Fig. 4 displays nascent emission spectra in the spectral region 570-730 nm from dioxygen dispersed in neon (1:500) at 4 K with excitation at 173, 185, 200, 210, 220 and 230 nm. The most prominent feature in the emission spectra is a narrow line at 701.7 nm, with some additional structure on the side of greater wavelength. Among other emission from excited O2, a strong progression of the transition system A'  ${}^{3}\Delta_{u} \rightarrow X {}^{3}\Sigma_{g}$  of O<sub>2</sub> was also recorded from 335.7 to 751.7 nm for  $\nu' = 0 \rightarrow \nu'' = 3-15$ ,<sup>24,25</sup> as well as a weaker progression of system c  $^1\Sigma_u{}^ \rightarrow$  a  $^1\Delta_{e}\!\!\!\!^{26}$ Another prominent emission line observed at 632.1 nm with shoulders at 630.0 and 636.9 nm is associated with emission of atomic O from transition  ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ .<sup>27</sup> Signals readily assigned to OH in the system A  $^{2}\Sigma^{+}(\nu' = 0) \rightarrow X ^{2}\Pi_{i}$  were observed at 307.8 and 309.0 nm for  $\nu' = 0 \rightarrow \nu'' = 0$  and at 313.6 and 315.0 nm for  $\nu' = 1 \rightarrow \nu'' = 1$ . The same signals observed with the second order of the grating contributed to the emission near 620 nm. In sum, we recorded emission lines of excited O, O2 and OH as they relaxed radiatively to their ground states from dioxygen dispersed in neon (1:500) at 4 K irradiated at 173 nm.



Fig. 4 Nascent visible emission spectra of  $O_2$  dispersed in neon (1:500) at 4 K upon excitation at (a) 173, (b) 185, (c) 200, (d) 210, (e) 220 and (f) 230 nm.

Upon tuning the excitation wavelength, these emission lines appeared clearly also with wavelengths 185 and 200 nm as shown in Fig. 4(b and c), but not 210, 220 and 230 nm as shown in Fig. 4(d-f). The thresholds for the emission of O from transition  ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ , of O<sub>2</sub> from transition A'  ${}^{3}\Delta_{u} \rightarrow X {}^{3}\Sigma_{g}$ , and of OH from transition A  ${}^{2}\Sigma^{+} \rightarrow X {}^{2}\Pi_{i}$  all coincide at 200  $\pm$  4 nm (6.20  $\pm$  0.12 eV); the same threshold as for the formation of O<sub>3</sub> in this photochemical system. We accordingly conclude that the threshold for photolytic dissociation of O<sub>2</sub> to generate O atoms in solid neon at 4 K is thus 200  $\pm$  4 nm (6.20  $\pm$  0.12 eV).

In the gaseous phase, the threshold for photolytic dissociation of  $O_2$  to generate O (<sup>3</sup>P) atoms is 242.2 nm (5.119 eV). Compared to the gaseous phase, our result indicates that extra energy 1.08 eV is required to generate atomic O (<sup>3</sup>P) as the photolysis product to escape the neon cage; this reacts subsequently with  $O_2$  to form  $O_3$  in solid neon, either directly or during the annealing period if trapped initially, as in eqn (2).

In the gaseous phase, ozone is photochemically dissociated as follows:

$$O_3 + h\nu \rightarrow O(^{3}P) + O_2(X^{3}\Sigma_g^{-}) \quad \lambda \le 1180 \text{ nm}$$
 (3a)

$$\rightarrow O(^{1}D) + O_{2}(a^{1}\Delta_{g}) \quad \lambda \leq 310 \text{ nm.}$$
 (3b)

The quantum yields for the production of O (<sup>1</sup>D) from the photolysis of gaseous O<sub>3</sub> have recommended values about 0.85–0.9 in the wavelength region 220–280 nm.<sup>28</sup> We thus assume that the quantum yields for channel (3b) in solid neon are sufficiently great for a wavelength less than 200 nm. Once ozone is irradiated at a wavelength  $\lambda \leq 200$  nm, it can readily dissociate to form atomic O (<sup>1</sup>D) in the photochemical system of O<sub>2</sub> dispersed in solid neon. Fig. 3 indicates that the threshold to form O<sub>3</sub> is at 200 nm; this value is the same as the threshold to form O (<sup>1</sup>D) as displayed in Fig. 4. This result implies that, once ozone is produced, it becomes subject to dissociation to produce atomic O (<sup>1</sup>D) and an excited molecule O<sub>2</sub> as in eqn (3b).

Although O (<sup>1</sup>D) is transient, we derived its lifetime to be 5.87  $\pm$  0.10 s in solid neon.<sup>17</sup> Some possible reactions of O (<sup>1</sup>D) follow.

$$O(^{1}D) + O(^{3}P) \rightarrow O_{2}(X ^{3}\Sigma_{g}^{-})$$
 (4)

$$O(^{1}D) + O(^{1}D) \rightarrow O_{2}(A'^{3}\Delta_{u})$$
 (5a)

$$\rightarrow O_2 \left( B^{3} \Sigma_{u}^{-} \right)$$
 (5b)

$$O(^{1}D) + O_{3} \rightarrow O_{2}(A' ^{3}\Delta_{u}) + O_{2}(X ^{3}\Sigma_{g}^{-})$$
(6a)

$$\rightarrow O_2 \left( B^{3} \Sigma_{u}^{-} \right) + O_2 \left( X^{3} \Sigma_{g}^{-} \right)$$
(6b)

In this photochemical system, reactions of atomic O (<sup>1</sup>D) might hence produce excited O<sub>2</sub> in states A'  ${}^{3}\Delta_{u}$  and B  ${}^{3}\Sigma_{u}^{-}$ ; these excited oxygen molecules relax radiatively with emission as shown in Fig. 4, and consequently share the same threshold, 200 nm, as ozone.

Our photolysis experiments with quantitative detection of infrared absorption and visible emission spectra provide accurately determined threshold wavelengths, both for the dissociation of O<sub>2</sub> and for the formation of O<sub>3</sub> in the solid state. This investigation opens a new window for an understanding of the detailed mechanism of the photochemical processes of oxygen species in the solid state. For example, we detected the OH radical from impurity H<sub>2</sub>O in this photochemical process. In previous work,<sup>29</sup> the threshold wavelength for the formation of the OH radical from H<sub>2</sub>O dispersed in solid neon was determined at 6.87  $\pm$  0.02 eV, which is greater than the threshold 6.20  $\pm$  0.12 eV for the formation of OH (A  $^{2}\Sigma^{+}$ ) radical in this work. The observed OH (A  ${}^{2}\Sigma^{+}$ ) radical was hence not directly generated from the photodissociation of H<sub>2</sub>O in this photochemical system. To explain the formation of the OH (A  ${}^{2}\Sigma^{+}$ ) radical in this system, the most likely route involves a reaction with oxygen species. Atomic O  $(^{1}D)$  can react with, apart from other oxygen species, water to generate the excited OH radical.

$$O(^{1}D) + H_{2}O \rightarrow OH(A^{2}\Sigma^{+}) + OH(X^{2}\Pi_{i})$$
 (7)

Accordingly, this reaction hence produces excited OH ( $A^{2}\Sigma^{+}$ ), which emits radiation, and shares the same threshold, 200 nm, as O (<sup>1</sup>D). Our study of the thresholds for the dissociation and formation of various species thus provides information for an understanding of the photolytic mechanism in the solid state.

In summary, irradiation of dioxygen, O<sub>2</sub>, dispersed in solid Ne near 4 K with ultraviolet light from a synchrotron, produced infrared absorption lines of ozone, O3, and visible emission lines from atomic O ( ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ ), molecular O<sub>2</sub> (A'  ${}^{3}\Delta_{u} \rightarrow X {}^{3}\Sigma_{g}$ ) and radical OH (A  ${}^{2}\Sigma^{+} \rightarrow X {}^{2}\Pi_{I}$ ). The threshold to form ozone was determined to be 200  $\pm$  4 nm, corresponding to an energy of 6.20  $\pm$  0.12 eV; the threshold for the photodissociation of  $O_2$ dispersed in solid neon is thus newly derived to be 200  $\pm$  4 nm (6.20  $\pm$  0.12 eV). The thresholds for emission from atomic O  $^{1}D_{2}$ ,  $O_2$  A'  $^3\Delta_u$  and radical OH A  $^2\Sigma^{\scriptscriptstyle +}$  all coincide at 200  $\pm$  4 nm, the same as for the formation of O<sub>3</sub> in this photochemical system. These results indicate that, once  $O_3$  was generated, it could be readily photolyzed to produce long-lived atomic O <sup>1</sup>D<sub>2</sub>. Further reactions of O  ${}^{1}D_{2}$  with O<sub>3</sub> generated excited O<sub>2</sub>, A'  ${}^{3}\Delta_{u}$ , and with water produced radical OH (A  ${}^{2}\Sigma^{+}$ ). This investigation improves our understanding of the transformations of oxygen species and

opens a window for an understanding of the mechanism of photolysis in the solid phase.

### Conflicts of interest

There is no conflict to declare.

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