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Photolysis of O₂ dispersed in solid neon with far-ultraviolet radiation[†]

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Irradiation at 173 or 143 nm of samples of ${}^{16}O_2$ or ${}^{18}O_2$ in solid Ne near 4 K produced many new spectral lines in absorption and emission from the mid-infrared to the near-ultraviolet regions. The major product was ozone, O_3 , that was identified with its mid-infrared and near-ultraviolet absorption lines. Oxygen atoms were formed on photolysis of O_2 and stored in solid neon until the temperature of a sample was increased to 9 K, which enabled their migration and combination to form O_3 and likely also O_2 . O_2 in five excited states and O in two excited states detected through the emission spectra indicate that complicated processes occurred in solid Ne after far-ultraviolet excitation. For the transition ${}^{1}D_2 \rightarrow {}^{3}P_{1,2}$ of O, the lifetime was determined to be 5.87 \pm 0.10 s; the lifetime of the upper state of an unidentified transition associated with an emission feature at 701.7 nm was determined to be 2.34 \pm 0.07 s.

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Introduction

Molecular oxygen, O_2 , captures perennial scientific attention not only because it is the second most abundant chemical element in our terrestrial atmosphere, comprising approximately one fifth of the total content, but also because oxygen is an element essential for life. The importance of the photolysis of O_2 in the terrestrial atmosphere and various other astronomical environments in relation to the ozone cycle and the filtering of ultraviolet radiation cannot be overstated; its photochemical dissociation initiates chemical reactions and acts as a driving force for the evolution of the transformation of oxygen. Molecular oxygen exists also in a condensed phase in cold outer space.^{1–3} Whereas the photochemistry of gaseous O_2 has been much investigated,^{4–7} a corresponding knowledge for solid phases is less extensive, which our present work is designed to remedy.

Several investigations of spectra and reactions of dioxygen molecules and oxygen atoms have been made in solid argon, krypton and xenon,⁸⁻¹⁵ and also dideuterium,^{16,17} but little knowledge is available about these properties of O_2 in solid neon; the use of neon typically yields spectral lines for both

Burnaby, British Columbia V5A186, Canada. E-mail: Ogilvie@cecm.sfu.ca ^c Escuela de Quimica, Universidad de Costa Rica, Ciudad Universitaria Rodrigo vibrational and electronic transitions narrower and with smaller shifts of wavenumber from the gaseous phase than for other noble-gas dispersants,¹⁸ and enables the observations of effects even qualitatively different from those in other matrix materials.

The effective temperature of the surface of our Sun, or its solar sphere, is about 5777 K. In our solar system the photon flux of far-ultraviolet (FUV) radiation from 100 to 200 nm is about one thousandth that from 200 to 900 nm.^{19,20} For other stars with temperatures above 6000 K, the photon flux of far-ultraviolet radiation increases accordingly. The energy of photons within that range, much greater than for visible light, suffices to break any chemical bond in any molecule; far-ultraviolet radiation is likely to be an important driving force that generates chemical compounds in both our solar system and other astrophysical environments. The synchrotron that serves as a photochemical source for our experiments provides access to this radiation.

The photolysis of O_2 with far-ultraviolet light undoubtedly serves as an initial process in the evolution of oxygen species in space. Our present investigation concerns the products of photolysis of O_2 dispersed in solid neon using far-ultraviolet light from a synchrotron. The photochemistry of O_2 in this solid phase differs from that of gaseous and pure solid O_2 . The use of solid neon as an inert dispersant enables one both to trap atomic fragments and other intermediate species that participate in photochemical systems of gaseous and solid O_2 and to detect these species through their absorption and emission spectra, thus enhancing our understanding of complicated processes in these conditions.

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Results

(a) Far-ultraviolet absorption spectra of O₂

Before the photolysis experiments, we recorded the absorption spectrum, in the far-ultraviolet region, of O_2 dispersed in solid neon, ratio 1:500, at 4 K, shown in Fig. 1, with spectra of solid O_2 at 10 K and of gaseous O_2 at 298 K for comparison; the apparatus for these absorption spectra is described elsewhere.²¹ Fig. 1 shows that, of the two wavelengths of radiation from the synchrotron that we applied for photo-chemical purposes, 173 nm is near the onset of intense absorption of O_2 in solid neon and the other, 143 nm, is near the maximum absorption in that particular region. Gaseous or solid neon has no absorption within a region of wavelength >100 nm.

(b) Photolysis of ¹⁶O₂ in Ne – mid-infrared spectra

The recorded infrared absorption spectra are readily amenable to analysis because the wavenumbers of the lines are directly associated with molecular carriers in specific vibrational modes. For samples deposited from a gaseous mixture of ¹⁶O₂ and Ne at a ratio 1:500 onto a KBr window maintained at 4 K, mid-infrared spectra showed the presence of ¹H₂¹⁶O, according to weak lines at 1595.5, 1599.3, 1614.1, 1616.8, 1630.5 and 1635.3 cm⁻¹ in the region of bending mode ν_2 and 3697.0, 3735.4, 3769.7, 3783.5 and 3800.6 cm⁻¹ in the region of stretching modes ν_1 and ν_3 , and of ¹²C¹⁶O₂ at 668 and 2347.7 cm⁻¹ and ¹³C¹⁶O₂ in natural abundance at 2339.3 cm⁻¹, both as adventitious impurities in small proportions; the lines of H₂O were more intense in the experiment with irradiation at 173 nm than at 143 nm. A weak line at 1554.7 cm⁻¹ might be due to ¹⁶O₂ in an asymmetric environment.

Irradiation of these samples at matrix ratio 1:500 and either 173 or 143 nm caused a decrease of intensity of all lines specified above, according to absorbance difference spectra, which indicated that all identified constituents dispersed in solid neon were subject to photochemical decomposition at those wavelengths; the line at 1554.7 cm⁻¹ was too weak in the original spectra for any significance to be attached to the

absorbance difference spectra at that point. After irradiation for various periods, new lines appeared at 2140.4 cm⁻¹, attributed to ¹²C¹⁶O, and 3590.3 cm⁻¹ attributed to ¹⁶O¹H; lines near 699.7 (vibrational mode ν_2), 1038.7 and 1045.2 cm⁻¹ (mode ν_3) are attributed to ¹⁶O₃.²² CO originated from CO₂ that was depleted during irradiation, and OH analogously from H₂O.

The lines of O₃ after annealing had wavenumbers 700.1, 701.5 and 703.4 cm⁻¹ for mode ν_2 , 1038.7, 1042.2, 1045.2 and 1048.2 cm⁻¹ for ν_3 , 1104.0 cm⁻¹ for ν_1 , and 2107.1 and 2109.8 cm⁻¹ for $\nu_1 + \nu_3$. The intensity of all those lines of O₃ increased remarkably after the annealing operation; the ratio of total area under the absorbance curves for all lines of each mode between before and after annealing was at least 20. The simplest interpretation of the formation of O₃ is the combination of atomic O, as a product of photochemical dissociation of O_2 , with a molecule of O_2 . An interpretation of that great increase is that atomic O that was formed during photolysis of O_2 escaped from the site of production to become stored and isolated in the solid neon; raising the temperature enabled the mobility of these atoms and they either reformed O₂, of which absorption is difficultly detectable in the mid-infrared region, or O_3 , as we observed.

The signals of CO and OH were much smaller than the eventual major signals of O_3 , consistent with the precursors of CO and OH being minor impurities. Fig. 2 provides an overview of these spectra after photolysis at 173 and 143 nm.

In experiments with matrix ratio 1:5000 and irradiation at 173 nm, there was no detectible signal of CO after photolysis but a weak signal at 3590 cm⁻¹ indicated the presence of OH after photolysis; in contrast, after irradiation at 143 nm the signal at 3590 cm⁻¹ was smaller than for 173 nm but a weak line at 2141.0 cm⁻¹ indicated the production of CO. These results indicate that oxygen atoms were, as expected, more efficiently trapped and isolated at matrix ratio 1:5000 than at ratio 1:500, but, when mobility was possible in solid neon at 9 K, O₃, and presumably O₂ also, formed readily.



Fig. 1 Absorption spectra in the far-ultraviolet region of (a) gaseous O_2 at 298 K (cross section); (b) O_2 dispersed in solid neon, 1:500, at 4 K (absorbance, offset +0.1), (c) solid O_2 at 10 K (absorbance).



Fig. 2 Infrared absorption spectra of O_2 dispersed in solid neon, 1:500, at 4 K after irradiation for 76 min at (a) 173, (b) 143 nm. Δ abs is the difference of absorbance, $\log_{10}(I_0/I)$, *i.e.* absorbance after irradiation minus absorbance before irradiation. Lines pointing upward from the baseline belong to products of photolysis of the sample; lines pointing downward indicate depletion of species present before photolysis.

(c) Photolysis of ¹⁸O₂ in Ne – mid-infrared spectra

In experiments with ¹⁸O₂ diluted 1:5000 in Ne with irradiation at either 173 or 143 nm, absorption lines in patterns similar to those with ¹⁶O₂ were observed. Spectra before irradiation showed the presence of ¹H₂¹⁸O, according to lines at 1606.8 and 1623.0 cm⁻¹ in the region of vibrational mode ν_2 and 3767.0 cm⁻¹ in the region of mode ν_3 . With irradiation at either wavelength, a line appeared at 3590 cm⁻¹ that is assigned to ${}^{16}O^{1}H$ formed from ${}^{1}H_{2}{}^{16}O$ present as an impurity in a minute proportion after irradiation at both wavelengths; after irradiation at 143 nm and annealing, a triplet of lines at 3523.6, 3525.4 and 3526.4 cm⁻¹ appeared, assigned to ¹⁸O¹H. The spectrum in the region 2300-2350 cm⁻¹ before irradiation showed lines due not only to $^{12}\mathrm{C^{16}O_2}$ at 2347.8 $\mathrm{cm^{-1}}$ but also $^{16}\mathrm{O^{12}C^{18}O}$ at 2330.9 cm⁻¹ and ¹²C¹⁸O₂ at 2312.8 cm⁻¹; the latter two lines, much less intense than the line at 2347.8 cm^{-1} , indicate that isotopically substituted CO₂ might have been an impurity in ¹⁸O₂, which naturally yields ¹²C¹⁸O upon photolysis; CO₂ and O2 are unlikely to exchange O atoms spontaneously at 298 K in a gaseous sample prepared several hours before deposition near 4 K. Weak lines of ${}^{12}C^{16}O$ at 2141.0 cm⁻¹ and of ${}^{12}C^{18}O$ at 2090.0 cm⁻¹ were detected only after irradiation at 143 nm, but the patterns of growth of these two lines differed: the line of ¹²C¹⁸O gained intensity with duration of irradiation later than the line of ${}^{12}C^{16}O$.

Lines at 660.3, 661.9 and 663.6 cm⁻¹, all associated with product ¹⁸O₃, for mode ν_2 were recorded after irradiation at both wavelengths and only after annealing, but the patterns differed somewhat: the line at 663.6 cm⁻¹ was more intense than the line at 660.3 cm⁻¹ after irradiation at 143 nm but less intense after irradiation at 173 nm. For mode ν_3 before annealing three weak lines appeared at 981.8, 982.6 and 987.8 cm^{-1} , attributed to ¹⁸O₃, whereas after annealing another 13 lines were recorded, at 988.7, 990.9, 991.8, 992.9, 993.9, 994.9, 998.0, 998.9, 1016.0, 1017.0,1024.9, 1025.7 and 1042.7 cm⁻¹. Assignments are complicated because each isotopic variant of O₃ shows apparently three major lines; comparisons with shifts of wavenumbers calculated for varied isotopic composition indicate that lines at 981.8, 982.6 and 984.7 cm⁻¹ are likely assignable to ${}^{18}O_3$, lines at 987.8, 990.9 and 991.8 cm $^{-1}$ might be assignable to ¹⁸O¹⁸O¹⁶O, and a line at 1042.7 cm⁻¹ to a vestige of ¹⁸O¹⁶O¹⁸O;²² the isotopic characters of other lines seem undecipherable. Three features after annealing at 1992.1, 1993.2 and 1995.0 cm⁻¹ are all assigned to $\nu_1 + \nu_3$ of ¹⁸O₃, whereas there was no discernible absorption in this region before annealing. Fig. 3 displays mid-infrared absorption spectra of ¹⁸O₂ dispersed in solid neon, 1:5000, at 4 K before photolysis, after photolysis at 173 nm for various durations, and after annealing the samples to 9 K.

(d) Photolysis of O₂ in Ne – ultraviolet, visible and near-infrared absorption spectra

We recorded absorption spectra in the range 200–1100 nm of samples at matrix ratio 1:5000 and at intervals between varied periods of irradiation with light at 173 and 143 nm before



Fig. 3 Infrared absorption spectra of ¹⁸O₂ dispersed in solid neon, 1:5000, at 4 K; (a) absorbance before irradiation, (b) Δ abs after irradiation at 173 nm, (c) Δ abs after annealing at 9 K. Δ abs is the difference of absorbance, $\log_{10}(l_0/l)$, *i.e.* absorbance after irradiation minus absorbance before irradiation.

annealing, and after annealing. Before annealing, there were two weak and broad lines with maxima near 258 and 270 nm and width (full width at half maximum stature) ~ 2200 cm⁻¹ in both cases. In experiments with irradiation of ¹⁶O₂ at 143 nm, before annealing two narrow lines appeared at 315.0 and 317.3 nm, whereas with irradiation of both ¹⁶O₂ and ¹⁸O₂ at 173 nm and of ¹⁸O₂ at 143 nm three other lines appeared at 307.3, 308.0 and 308.3 nm. The latter three features are assigned to lines (0, 0) of electronic transition A ²Σ⁺–X ²Π_r of OH; their absence from the experiment with ¹⁶O₂ irradiated at 143 nm is consistent with an only faint hint of a line at 3590 cm⁻¹ in the mid-infrared absorption spectrum and the small intensities of mid-infrared lines of impurity precursor H₂O on that occasion.

After annealing, the specified lines after irradiation at 143 nm retained some intensity, but two lines produced on irradiation of ¹⁶O₂ at 173 nm at 315.0 and 317.3 nm pointed downward from the baseline of the absorbance spectrum as if in emission whereas no positive absorption was perceptible at those wavelengths before annealing. After annealing, the absorption in the region less than 300 nm increased greatly, with a single maximum near 253 nm and width 6200 cm^{-1} . These results apply equally to experiments with irradiation at both 173 and 143 nm and with ¹⁶O₂ and ¹⁸O₂. Consistent with the infrared absorption of ozone that exhibited such a great increase after annealing, this absorption continuum is assigned to O_3 in the so-called Hartley band that in the gaseous phase shows a similar profile; in our experiments there was no indication of absorption corresponding to either the Huggins bands from 300 to 350 nm or the Chappuis bands from 450–700 nm.^{23,24}

In the visible and near-infrared region there was only one feature in absorption before annealing. Its centre was about 595 nm after irradiation of ${}^{16}O_2$ and 596 nm after irradiation of ${}^{18}O_3$ with widths approximately 1500 and 1450 cm⁻¹. The differences between these values for these isotopic species are small but might be significant. This line persisted after annealing.

(e) Photolysis of ${}^{16}O_2$ in Ne – near-ultraviolet, visible and near-infrared emission spectra

In contrast with the absorption spectra in all regions, the emission spectra have many and complicated discrete features. A distinction between emission of reactant, *i.e.* O₂, and products of photolysis is readily practicable because the intensity of emission lines from O2, in various electronic states, decreased with the duration of irradiation because of depletion of that reactant, whereas the intensity of emission lines of products increased with that duration. Major spectral features, listed in Table 1, hence due to O_2 were the long series of lines that are readily assigned to progressions in system A' $^3\Delta_{\rm u}$ \rightarrow X $^3\Sigma_{\rm g}^{-,25}$ listed in Table 2, and system c ${}^{1}\Sigma_{u}^{-} \rightarrow a {}^{1}\Delta_{g}$,²⁴ listed in Table 3; for the latter system on excitation at both 173 and 143 nm and at matrix ratios 1:500 and 1:5000, two distinct progressions of which corresponding members are separated by about 100 cm^{-1} . Emission lines at 761.6 and 864.8 nm, observed during irradiation at both 173 and 143 nm, are assigned to transitions from state b ${}^{1}\Sigma_{g}^{+}\nu' = 0$ to the electronic ground state X ${}^{3}\Sigma_{g}^{-}\nu'' = 0, 1$ in a short progression,²⁴ listed in Table 1.

Emission of atomic O was observed in the transition ${}^{1}S \rightarrow {}^{1}D_{2}$ at 556.2 nm for excitation at 143 nm and the transitions ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ at 629.7 and 636.9 nm for excitation at both 173 and 143 nm,²⁶ listed in Table 1, but line (0, 13) of system A' ${}^{3}\Delta_{u} \rightarrow X {}^{3}\Sigma_{g}^{-}$ interfered with the latter atomic lines. Fig. 4 shows the more intense emission features.

For ${}^{16}O_2$: Ne at ratio 1:500 and with excitation at 173 nm, the most prominent feature in the emission spectrum during irradiation at 173 nm was a narrow line at 701.7 nm, with some

Table 1	Lines	of	¹⁶ O ₂	in	three	systems	and	of	¹⁶ O	in	two	transition	าร
emitted	during	irra	diatio	n c	of ¹⁶ O ₂	in Ne at	4 K						

λ^a/nm	ν^b/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	ν', ν''^{d}	ν^{e}/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	$\Delta \nu^{f}/cm^{-}$
$O_2 b^{-1}\Sigma$	$\Sigma_{g}^{+} \rightarrow X^{3}\Sigma_{g}^{-}$	-				
761.6	13 127	, ,	0, 0	13120.8		6
864.8	11561	1566	0, 1	11564.4	1556.4	-3
O_2 ?						
403.3	24857					
$O^{1}S \rightarrow$	\cdot ¹ D ₂					
556.2	17974			17924.7		49
$O^{1}D_{2}$	$\rightarrow {}^{3}P_{1,2}$					
629.7	15871			15867.9		3
636.9	15697	174		15683.6	184.3	13
Unider	tified prod	luct, no O-is	sotopic sl	nift		
361.9	27 626		-			
379.4	26346	1280				

 373.4
 20340
 1280

 398.9
 25062
 1284

O₂, unidentified transition 701.7 14 249

^{*a*} Wavelength λ/nm is measured in air. ^{*b*} Wavenumber ν/cm^{-1} pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ is the progressive difference from the preceding row. ^{*d*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*e*} ν/cm^{-1} are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*f*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

Table 2 Prominent emission lines recorded during irradiation of $^{16}O_2$ in Ne at 4 K, with lines calculated for system A' $^3\Delta_u \rightarrow X \, ^3\Sigma_g^-$, gaseous O_2 for comparison

O ₂ in M	le		Gaseou	is O ₂	Matrix – gas	
λ^a/nm	ν^b/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	ν', ν''^{d}	ν^{e}/cm^{-1}	$\Delta \nu^b/{ m cm}^{-1}$	$\Delta \nu^{f}/\mathrm{cm}^{-1}$
			0, 0	32816.8		
			0,1	31284.1	1556.4	
			0, 2	29774.8	1532.7	
335.7	29780		0,3	28288.6	1509.3	5
353.4	28288	1492	0,4	26825.3	1486.2	-1
372.7	26823	1465	0, 5	25384.7	1463.3	-2
394.1	25368	1456	0,6	23966.8	1440.6	-17
417.6	23 940	1428	0,7	22571.7	1417.9	-27
443.8	22627	1413	0, 8	21199.1	1395.1	-45
472.7	21149	1377	0, 9	19849.2	1372.6	-50
505.4	19781	1368	0, 10	18521.9	1349.9	-68
542.1	18442	1339	0, 11	17217.6	1327.3	-80
583.7	17128	1314	0, 12	15936.2	1304.3	-90
631.3	15836	1292	0, 13	14677.8	1281.4	-100
686.6	14565	1271	0, 14	32816.8	1258.5	-113
751.7	13 303	1262	0, 15	13442.2	1235.6	-139

^{*a*} Wavelength λ/nm is measured in air. ^{*b*} Wavenumber ν/cm^{-1} pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ is the progressive difference from the preceding row. ^{*d*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*e*} ν/cm^{-1} are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*f*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

Table 3 Weak lines in two progressions of O_2 in solid Ne, emitted during photolysis of ${}^{16}O_2$, at 173 nm compared with transitions in system c ${}^{1}\Sigma_{u}^{-} \rightarrow a {}^{1}\Delta_{\alpha}$ of gaseous O_2

O ₂ in Ne				Gaseou			
λ^a/nm	ν^b/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	$\Delta \nu^d$	ν', ν''^{e}	ν^{f}/cm^{-1}	$\Delta \nu^{c}/cm^{-1}$	$\Delta \nu^{g}/\mathrm{cm}^{-1}$
				0, 0	24794.5		
				0, 1	23336.7	1457.8	
				0, 2	21904.9	1431.8	
483.8	20664			0, 3	20498.7	1406.2	165
518.8	19270	1394		0, 4	19118.5	1380.2	151
558.3	17 907	1363		0, 5	17763.9	1354.6	143
603.6	16 563	1344		0,6	16435.3	1328.6	128
655.5	15251	1312		0, 7	15132.4	1302.9	119
715.7	13 969	1282		0, 8	13855.2	1277.2	114
786.5	12711	1258		0, 9	12604.0	1251.2	107
Second	l progress	ion					
486.4	20 555		109	0, 3	20498.7		56
521.8	19159	1396	111	0, 4	19118.5	1380.2	40
561.7	17 798	1361	109	0, 5	17763.9	1354.6	34
607.3	16462	1336	101	0,6	16435.3	1328.6	27
659.6	15 157	1305	94	0, 7	15132.4	1302.9	25
719.0	13 905	1252	64	0, 8	13855.2	1277.2	50

^{*a*} Wavelength λ/nm is measured in air. ^{*b*} Wavenumber ν/cm^{-1} pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ is the progressive difference from the preceding row. ^{*d*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ between the nearest values in the two progressions. ^{*e*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*f*} ν/cm^{-1} are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*g*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

additional structure on the side of greater wavelength; during irradiation at 143 nm, this line was prominent but not the



Fig. 4 Emission spectra recorded during irradiation of O_2 dispersed in solid neon excited at (a) 143, (b) 173 nm with assignments of some lines.

most intense. At ratio 1:5000, this line had moderate intensity during irradiation at 173 nm but was weak during irradiation at 143 nm. For this line, not previously reported,²⁷ the present experiments provide no basis of an assignment.

A major distinction between irradiation at 173 and 143 nm was that, under the latter condition, lines of ¹²C¹⁶O in a progression known as Cameron bands, implying electronic transition $a' {}^{3}\Pi_{r} \rightarrow X {}^{1}\Sigma^{+}$, were recorded in emission (in first, second and third orders of the grating) but not in absorption; the wavenumbers of these lines in the vibrational progression are compared with the corresponding data for gaseous ¹²C¹⁶O²⁴ in Table S1 (in ESI[†]). In contrast, during excitation at 173 nm a short sequence of lines of OH²⁴ included (0,0) members at 307.7 and 309.0 nm and (1,1) members, of smaller intensities, at 313.5 and 314.9 nm, listed in Table S2 (in ESI⁺). Another product of photolysis, because its emission became more intense with increasing duration of irradiation, is associated with lines at 361.9 and 379.4 nm, observed at dispersion ratio 1:5000 and for excitation at both 173 and 143 nm; no assignment is suggested.

Besides the generally narrow, but with barely resolvable fine structure, lines described above, appearing after irradiation at 143 nm but not 173 nm, several broad lines (widths $\sim 100 \text{ cm}^{-1}$ at half maximum stature) are tentatively assigned to O₃, listed in Table 4; the intensities of these lines increased with increasing duration of irradiation, befitting attribution to a product of photolysis.

(f) Photolysis of ${}^{18}O_2$ in Ne – near-ultraviolet, visible and near-infrared emission spectra

In the near-infrared, visible and near-ultraviolet regions, no distinct absorption feature was discernible before irradiation of the samples, but emission spectra recorded during irradiation and absorption spectra recorded after irradiation showed many lines. At either wavelength of irradiation, a prominent sequence of lines, with some apparent structure on the sides of smaller wavenumber, appeared; these data are listed in Table 5, which we assign to electronic transition A' ${}^{3}\Delta_{u} \rightarrow X {}^{1}\Sigma^{+}$ with

Table 4 Broad lines in emission present during irradiation of $\rm ^{16}O_2$ at 143 nm but not at 173 nm; some wavenumber differences are indicated

λ/nm	ν/cm^{-1}	$\Delta \nu/\mathrm{cm}^{-1}$	$\Delta \nu/cm^{-1}$	
539.3	18 537			
542.2	18 4 39	98		
594.8	16797		1742	
598.2	16712	85		
646.0	15 475		1322	
679.3	14717	758		
713.0	14 021	696		
720.3	13 880	141	1595	
726.2	13767	113		
736.5	13 575	92	305	
742.1	13 471	103		
782.6	12773		801	
789.0	12670	103		
822.1	12 159		614	
827.7	12 077	82		
841.0	11 886		273	
847.5	11 795	91		

Table 5 Prominent emission lines recorded during irradiation of $^{18}O_2$ in Ne at 4 K, with lines calculated for system A' $^3\Delta_u \rightarrow X \, ^3\Sigma_g^-$, gaseous $^{18}O_2$ for comparison

¹⁸ O ₂ in	Ne		Gaseou	18 ¹⁸ O ₂	Matrix – gas	
λ^a/nm	ν^{b}/cm^{-1}	$\Delta \nu^{c}/cm^{-1}$	ν', ν''^d	ν^{e}/cm^{-1}	$\Delta \nu^{c}/cm^{-1}$	$\Delta \nu^{f}/\mathrm{cm}^{-1}$
			0, 0	34394.7		
			0, 1	32926.3	1468.4	
			0, 2	31478.9	1447.4	
			0, 3	30052.4	1426.5	
			0, 4	28646.4	1406.0	
367.5	27203		0,5	27260.7	1385.7	-58
386.3	25879	1324	0,6	25895.4	1365.3	-16
408.4	24479	1400	0,7	24550.2	1345.2	-71
431.9	23147	1332	0, 8	23225.1	1325.1	-78
457.9	21 833	1314	0,9	21920.1	1305.0	-87
486.7	20541	1292	0, 10	20635.3	1284.8	-94
518.7	19274	1267	0, 11	19370.8	1264.5	-97
553.8	18052	1222	0, 12	18126.4	1244.4	-74
596.6	16757	1295	0, 13	16902.4	1224.0	-145
645.3	15492	1265	0, 14	15698.6	1203.8	-207
702.3	14238	1254	0, 15	14515.6	1183.0	-277

^{*a*} Wavelength λ/nm is measured in air. ^{*b*} Wavenumber ν/cm^{-1} pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ is the progressive difference from the preceding row. ^{*d*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*e*} ν/cm^{-1} are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*f*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

vibrational structure $(0, \nu'')$ and $\nu'' = 5,..., 15$ according to wavelengths calculated on the basis of known spectral parameters of ${}^{16}O_2$.²⁴ Fig. 5 displays the emission features from farultraviolet photolysis of ${}^{18}O_2$ in Ne. Another and much less intense system of ${}^{18}O_2$ is identified as c ${}^{1}\Sigma_{u}^{-} \rightarrow a {}^{1}\Delta_{g}$ with vibrational structure $(0, \nu'')$ and $\nu'' = 2,..., 9$ are listed in Table 6. Lines at 761.7, 857.9 and 975.9 nm are due to transitions from state b ${}^{1}\Sigma_{g}^{+} \nu' = 0$ of ${}^{18}O_2$ to the electronic ground state X ${}^{3}\Sigma_{g}^{-} \nu'' = 0-2$, listed in Table 7.

On excitation of samples of ¹⁸O₂ in neon at both 173 and 143 nm, the emission spectra exhibited transitions $A' {}^{3}\Delta_{u} \nu' = 0 \rightarrow X {}^{1}\Sigma^{+}\nu'' = 15$ at 702.3 nm and c ${}^{1}\Sigma_{u}^{-}\nu' = 0 \rightarrow a {}^{1}\Delta_{g}\nu'' = 8$ at 698.7 nm;



Fig. 5 Emission spectra recorded during irradiation of $^{18}\text{O}_2$ dispersed in solid neon excited at (a) 143, (b) 173 nm with assignments of some lines.

Table 6 Weak lines in one consequence of $^{18}O_2$ in solid Ne compared with transitions in system c $^{1}\Sigma_{u}^{-} \rightarrow a \, ^{1}\Delta_q$ of gaseous $^{18}O_2$

¹⁸ O ₂ in	Ne		Gaseou	Matrix – gas		
λ^a/nm	ν^b/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	ν', ν''^d	ν^{e}/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	$\Delta \nu^{f}/cm^{-1}$
			0, 0	24814.2		
			0, 1	23438.7	1375.5	
452.9	22074		0, 2	22086.0	1352.7	-12
480.8	20793	1281	0, 3	20756.4	1329.6	37
514.2	19442	1351	0, 4	19449.6	1306.8	-8
551.6	18124	1318	0, 5	18165.8	1283.8	-42
594.1	16828	1296	0,6	16904.8	1261.0	-77
642.9	15550	1278	0, 7	15666.9	1237.9	-119
698.7	14 308	1242	0, 8	14451.8	1215.1	-144
763.8	13 089	1219	0, 9	13259.7	1192.1	-171

^{*a*} Wavelength λ/nm is measured in air. ^{*b*} Wavenumber ν/cm^{-1} pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu/\text{cm}^{-1}$ is the progressive difference from the preceding row. ^{*d*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*e*} ν/cm^{-1} are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*f*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

Table 7 Emission lines recorded during irradiation of $^{18}O_2$ in Ne at 4 K, with lines calculated for system O_2 b $^1\Sigma^+_g \to X \ ^3\Sigma^-_g$ of gaseous $^{18}O_2$ for comparison

λ^a/nm	ν^b/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	ν', ν''^d	ν^{e}/cm^{-1}	$\Delta \nu^{c}/\mathrm{cm}^{-1}$	$\Delta \nu^{f}/\mathrm{cm}^{-1}$
761.5	13 128		0, 0	13125.0		3
857.9	11653	1475	0, 1	11656.8	1468	-4
975.9	10244	1409	0, 2	10209.2	1447	35

^{*a*} Wavelength λ /nm is measured in air. ^{*b*} Wavenumber ν /cm⁻¹ pertains to vacuum. ^{*c*} Wavenumber difference $\Delta\nu$ /cm⁻¹ is the progressive difference from the preceding row. ^{*d*} ν' , ν'' denotes the vibrational numbering for transitions between the vibrational ground state $\nu' = 0$ of O₂ of an excited electronic state and vibrational state $\nu'' \geq 0$ in a lower electronic state. ^{*e*} ν /cm⁻¹ are wavenumbers calculated for gaseous O₂ for the transitions in the preceding column. ^{*f*} $\Delta\nu$ is the difference/cm⁻¹ between value for dispersion in Ne and calculated for gaseous phase.

there was no indication of a separate line as a counterpart of the line of ${}^{16}O_2$ at 701.7 nm in neon.

The emission lines of OH in the experiments with ${}^{18}O_2$ and irradiation at 143 nm have essentially the same wavelengths as

presented in Table S2 (in ESI[†]). A major distinction between irradiation at 173 and 143 nm was that, under the latter condition, lines of both ¹²C¹⁶O and ¹²C¹⁸O in the electronic transition a' ${}^{3}\Pi_{r} \rightarrow X {}^{1}\Sigma^{+}$, were recorded in emission but not in absorption; the wavenumbers of the new lines are compared with the corresponding data for gaseous ¹²C¹⁸O in Table S3 (in ESI^{\dagger}). Fig. S1 (in ESI^{\dagger}) shows the emission spectra of ¹²C¹⁶O and ¹²C¹⁸O as a function of duration of irradiation of a sample of ¹⁸O₂ in Ne at 143 nm. A notable aspect of these spectra, as Fig. S1 (ESI^{\dagger}) shows, is that the intensities of lines of ¹²C¹⁶O increase earlier than those of ¹²C¹⁸O during irradiation, indicating that the latter product is formed indirectly, likely from an $^{18}\!O$ atom produced on photolysis of $^{18}\!O_2$ that reacts with ${}^{12}C^{16}O_2$ or ${}^{12}C^{16}O_2$, itself formed from photolysis of ${}^{12}C^{16}O_2$, to form ¹⁸O¹²C¹⁶O, which becomes subject to photolysis. The broad lines that appear after irradiation at 143 nm but not 173 nm are more numerous in experiments with ¹⁸O₂ than with $^{16}O_2$; the wavelengths are listed in Table S4 (in ESI⁺). Apart from those extra lines, the other lines for both isotopic variants have the same wavelengths within uncertainty of measurement. Narrow emission lines of a product of photolysis, because their intensity increases with duration of excitation, at 398.8, 379.5 and 361.9 nm appear likewise to be unaffected on isotopic substitution.

(g) Temporal variation of visible emission spectra

In these experiments we measured the temporal variation of emission, after excitation was terminated, that persisted beyond 0.5 s, by means of sequential spectra separated consecutively by 1.167 s (integrating time of the signal 1 s, readout time of the detector 0.05 s, and transfer to the computer 0.117 s). Two separate spectral features exhibited a measurable decay. Fig. 6 shows the temporal emission of the feature with maximum near 701.7 nm for O_2 dispersed in neon (1:500) at 4 K after discontinuation of irradiation at 143 nm; in the inset of Fig. 6, a semi-logarithmic plot of the integrated intensity of this feature indicates a single exponential decay with a lifetime 2.34 \pm 0.07 s.



Fig. 6 Temporal variation of emission persisting from O₂ dispersed in Ne (1:500) at 4 K after termination of irradiation at 143 nm; the inset indicates a single exponential decay with lifetime 2.34 ± 0.07 s.



Fig. 7 Temporal variation of emission persisting for O transitions ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ at 632 nm from O₂ dispersed in Ne (1:500) at 4 K after termination of irradiation at 143 nm; the inset indicates a single exponential decay of this feature with lifetime 5.87 \pm 0.10 s.

Fig. 7 shows an analogous emission of the transitions of atomic O, ${}^{1}D_{2} \rightarrow {}^{3}P_{1,2}$ at 633 nm, which indicates a single exponential decay with lifetime 5.87 \pm 0.10 s (vs. 147 s for gaseous O).^{28,29} The shape of the spectral feature in Fig. 6 and 7 is common to many other emission features throughout the near-ultraviolet, visible and near-infrared regions, but not for the emission lines of CO between 200 and 260 nm; specifically, a separate line appears at smaller wavelength beside the main feature and then a gradual decrease of intensity at larger wavelength ensues that might imply several unresolved components, all within a span of order 200 cm⁻¹. This span seems independent of the dispersion ratio, whether 1:500 or 1:5000. The fact that the intrinsic widths of isolated lines of constituents of samples dispersed in Ne are smaller than the widths observed for other noble gases⁸⁻¹⁵ facilitated our analysis of these experiments.

Discussion

Regarding the photochemical reactions within our samples as characterised by their infrared absorption spectra before irradiation at a selected wavelength, the results are interpreted simply as follows. The photolysis of O2 produced directly O atoms, which we detected directly by their emission spectra; the photolysis of minor impurity H₂O produced OH radicals and the photolysis of minor impurity CO2 produced CO. The O atoms reacted with O_2 to produce O_3 , which was the major product detected in the infrared spectra before annealing, but O3 was likely generated also in other manners, such as the combination of three O atoms. The most notable feature of these experiments is that O atoms were undoubtedly isolated effectively and stored within the Ne lattice near 4 K, at both matrix ratios O_2 : Ne, 1:500 and 1:5000, but became, to some extent, mobile so as to migrate and hence to recombine, to form O₃, which we detected directly, and likely also O₂, as a result of our annealing operation.

This effective isolation of O atoms contrasts strongly with our observation of the production of carbon chains of length up to C_{20} during photolysis of methane in neon, which seemed to involve the migration of C atoms in solid neon under experimental conditions similar to those of the present experiments but with excitation at wavelengths to 121.6 nm;³⁰ in the latter experiments, an increased dilution, to matrix ratio 1:10000, seemed even to favour the extended chains. Our mid-infrared spectra after photolysis of O₂ provide no evidence for the production of chains of oxygen atoms. Our observation of emission of atomic O in transition ${}^{1}S \rightarrow {}^{1}D_{2}$ on excitation at 143 nm but not 173 nm is consistent with a threshold for excitation of the latter transition for a sample of O₂ in Ar at 1:500 and 15 K that was found to be 147 nm.¹¹

The variation of the relative intensities of emission of ¹²C¹⁶O and ¹²C¹⁸O in Fig. S1 (in ESI[†]) with duration of irradiation of our sample indicates that complicated processes occur in the solid neon even when the sample is maintained at 4 K. The significance of that variation is that the directly detected products, such as O_3 , OH and CO, of the photochemical reactions of O_2 , H₂O and CO₂, respectively, are just as liable to be subject to photochemical degradation as the nominal initial reactant, O₂. Under the action of the far-ultraviolet light that all constituents of our samples, except neon, absorb to a greater or lesser extent at either 173 or 143 nm, molecules were clearly being formed and dissociated into atoms in continuous dynamic processes, of which the spectra recorded at various intervals provided only glimpses of the consequences. Such a lack of specificity is an inevitable characteristic of the application of excitation in this far-ultraviolet region, even with essentially monochromatic light, in which many small stable molecules absorb light and undergo either direct dissociation or transitions into electronically excited states from which dissociation might proceed.

The electronic states that pertain to our experiments are X $^3\Sigma_g^-,~a~^1\Delta_g,~b~^1\Sigma_g^+,~c~^1\Sigma_u^-,~A'~^3\Delta_u,~A~^3\Sigma_u^+$ and B $^3\Sigma_u^-$ of $O_2,$ and states ³P_{1,2}, ¹D₂, ¹S of atomic O. In experiments with O₂ in crystals of Kr or Xe, states X ${}^{3}\Sigma_{g}^{-}$, A' ${}^{3}\Delta_{u}$, a ${}^{1}\Delta_{g}$, b ${}^{1}\Sigma_{g}^{+}$ and c ${}^{1}\Sigma_{u}^{-}$ were involved in those emission spectra;¹⁴ comparison of the published spectra from those experiments indicates that the widths of typical lines in the near-ultraviolet, visible and nearinfrared regions are much smaller for our Ne host than the widths of lines with Kr and Xe hosts.¹⁴ The progressive increase, with increased vibrational excitation, of a difference of wavenumber between gaseous O2 and O2 in Ne for a particular member of a progression, observable in Tables 2 and 3 for instance, has been attributed to the effect of the environment on the potential-energy curve for a molecule in a condensed phase.³¹ The combination of two oxygen atoms each in its ground state ³P generates molecular oxygen in six electronic states – X ${}^{3}\Sigma_{g}^{-}$, a ${}^{1}\Delta_{g}$, b ${}^{1}\Sigma_{g}^{+}$, c ${}^{1}\Sigma_{u}^{-}$, A' ${}^{3}\Delta_{u}$ and A ${}^{3}\Sigma_{u}^{+}$ in order of increasing energy at their minima - and each such electronic state supports vibrational states of varied number. The larger differences between wavenumbers of lines in the progression $c~^1\!\Sigma_u^ \rightarrow~a~^1\!\Delta_g$ might reflect the fact that the vibrational states for gaseous O₂ in electronic state a are poorly characterised because of lack of data.

The great increase of mid-infrared and near-ultraviolet absorption due to O_3 as a result of our annealing operation indicates,

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as described above, that O atoms are effectively stored in our Ne dispersions at 4 K. The temporal variation of the emission from O atoms in state ¹D, as shown in Fig. 7, indicates that relaxation, by an either radiative or non-radiative process, of the oxygen atoms to their ground states after formation through photochemical dissociation of O₂ occurs on a measurable time scale, with a lifetime about 6 s, which implies that O ¹D atoms persist for such a duration within the Ne environment after their formation through the dissociation of O₂.

Although the photochemical production of O₃ from O₂ with radiation absorbed by O_2 in the far-ultraviolet region at 173 or 143 nm might seem to constitute a simple process, the absorption and emission spectra that we have recorded from the mid-infrared to the near-ultraviolet region, and the temporal variation of the emission of molecular and atomic lines in Fig. 6 and 7, indicate that many states of O atoms and O₂ molecules are involved. In contrast with the absorption lines of product O₃ in the mid-infrared region that are readily assignable to particular isotopic variants and their specific vibrational modes, the absorption and emission spectra in the visible and nearultraviolet regions have many unassigned features, many of them likely, but at present unprovably, associated with O₃, as listed in the several tables herein. As ozone is an important constituent of our terrestrial atmosphere and other astronomical environments, further experimental and computational effort is strongly warranted to increase our knowledge of the spectral properties of this important chemical substance in varied conditions.

In the investigation of the photochemistry of O_2 dispersed in neon, our application of not only absorption spectra in the far-ultraviolet, near-ultraviolet, visible, near-infrared and midinfrared regions and emission spectra in the near-ultraviolet, visible and near-infrared regions but also the temporal variation of emission in the visible region demonstrates the powerful resources that contemporary instruments enable one to apply concurrently in an intensive investigation of a significant chemical system. A conventional use of only mid-infrared absorption spectra in the traditional conduct of matrix-isolation experiments would fail to generate many data crucial for a profound understanding of a chosen photochemical system.

Conclusion

Our photochemical experiments with concurrent detection of infrared absorption and electronic absorption and emission spectra provide evidence for the formation of O₃, O atoms, and O₂ in five electronically excited states – a ${}^{1}\Delta_{g}$, b ${}^{1}\Sigma_{g}^{+}$, c ${}^{1}\Sigma_{u}^{-}$, A' ${}^{3}\Delta_{u}$, and A ${}^{3}\Sigma_{u}^{+}$ – upon irradiation of O₂ dispersed in solid neon near 4 K with far-ultraviolet light from a synchrotron source. The five excited states of O₂ and two excited states of O detected indicate that complicated processes occurred in solid Ne after far-ultraviolet excitation. This investigation of the spectra and formation of oxygen species from far-ultraviolet photolysis of dioxygen in solid neon has provided information that can enhance our understanding of aurora, airglow, nightglow and

the evolution of the oxygen transformation and prebiotic molecules containing oxygen atoms.

Experiments

The apparatus for photochemical experiments on solid samples using far-ultraviolet light from a synchrotron is described elsewhere.^{32,33} The radiation for photolysis was selected from an undulator on beamline 21A2 attached to the 1.5 GeV synchrotron ring in Taiwan Light Source (TLS) at National Synchrotron Radiation Research Center (NSRRC). This beamline provides tunable and pseudo-continuous far-ultraviolet light with photon flux $\sim 10^{16}$ photons s⁻¹ (bandwidth 2%); after absorption by a gaseous and a crystalline filter to suppress harmonics from the undulator, the selected far-ultraviolet light delivers about $\sim 10^{15}$ photons s⁻¹ to the samples. Gaseous mixtures of O₂ and neon in designed proportions were deposited on a cold KBr disc over a period 1-6 h, before irradiation of a sample at a selected wavelength and for designed durations; a closed-cycle refrigerator (Janis RDK-415) cooled the KBr substrate to ~ 4 K within an enclosure evacuated to $<4 \mu$ Pa.

During irradiation with far-ultraviolet light, we recorded simultaneously the near-ultraviolet, visible and near-infrared emission in spectral range 200-1100 nm from our solid sample. This emission was dispersed with a monochromator (iHR320) and detected with a charge-coupled detector (1024 \times 256 pixels, Horiba Symphony II, image mode). After irradiation for selected periods, we recorded near-ultraviolet, visible and near-infrared absorption spectra, 200-1100 nm, in transmission during the same experiment (monochromator iHR320 and CCD detector); the uncertainties of measured wavelengths are likely to be 5 cm⁻¹ near 800 nm or \sim 30 cm⁻¹ near 300 nm. The nominal resolution in the near-infrared, visible and near-ultraviolet regions is respectively 0.24, 0.24 and 0.12 nm. Before and after irradiation for each period, we likewise recorded infrared absorption spectra in transmission with an interferometric spectrometer (Bomem, DA8, KBr beamsplitter, HgCdTe detector cooled to 77 K, resolution 0.5 cm⁻¹, wavenumber accuracy 0.1 cm⁻¹, range 500–4000 cm⁻¹). The spectrum of a sample before irradiation served as a basis to evaluate photochemical effects, as indicated in difference absorbance spectra of the sample after irradiation for various intervals relative to that spectrum before irradiation.

After cycles of sufficient number comprising irradiation for a specific duration with concurrent recording of emission spectra and recording of absorption spectra before and after irradiation, before the conclusion of each experiment we undertook an operation called annealing; the temperature of the sample in darkness was raised from 4 K to 9 K for 10 min, after which a sample was again cooled to 4 K and absorption spectra were recorded. During that period at 9 K, the solid neon was not volatile, but the lattice expanded; spectral evidence indicated that limited diffusion of species within the solid occurred, facilitating further formation of products identified through their spectra.

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The chemical substances in these experiments were ${}^{16}O_2$ (99.999%, Matheson), ${}^{18}O_2$ (>95%, Cambridge Isotope Laboratories, Inc.), and Ne (99.999%, Scott Specialty Gases), all used without purification.

Conflicts of interest

There is no conflict to declare.

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