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Red-light-induced Photoreaction of DMS–O_3 Complex in a Cryogenic Neon Matrix

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Photoreaction and light absorption of dimethyl sulfide (DMS)–O_3 complex isolated in a cryogenic neon matrix were investigated by FTIR and visible-light absorption spectroscopy. Although visible light does not induce photoreaction for either monomer, a photoreaction to produce dimethyl sulfoxide (DMSO) was observed to occur upon the red light (700–740 nm) irradiation. New electronic absorption bands peaking at 470 and 600 nm due to DMS–O_3 complex appear in a visible spectral region, which are responsible for the photooxidation of DMS to DMSO.

The UV-light photolysis of O_3 is generally considered to be important in atmospheric chemistry, which takes place through the dissociation of the $\tilde{C}^1B_2$ state.[1]

$$O_3 + h\nu(<310\,\text{nm}) \rightarrow O_2(a^1\Delta_g) + O(^1D) \qquad (1)$$

Actually, extremely weak light absorption of O_3 is also known in the visible spectral region, and the photodissociations are energetically possible.

$$O_3 + h\nu(<463\,\text{nm}) \rightarrow O_2(b^1{\Sigma_g}^+) + O(^3P) \qquad (2)$$

$$O_3 + h\nu(<612\,\text{nm}) \rightarrow O_2(a^1\Delta_g) + O(^3P) \qquad (3)$$

$$O_3 + h\nu(<411\,\text{nm}) \rightarrow O_2(X^3{\Sigma_g}^-) + O(^1D) \qquad (4)$$

$$O_3 + h\nu(<1180\,\text{nm}) \rightarrow O_2(X^3{\Sigma_g}^-) + O(^3P) \qquad (5)$$

The light absorption cross section of O_3 $\tilde{B}^1B_1$–$\tilde{X}^1A_1$ is less than an order of $10^{-20}\,\text{cm}^2\,\text{molecule}^{-1}$ at the peak around 600 nm.[2–4] Theoretical calculation estimates the corresponding transition to the $\tilde{B}^1B_1$ state with a small oscillator strength of ca. 10^{-5}.[5] In addition to the $\tilde{B}^1B_1$ state, there are several low-lying electronically excited states for O_3, which can be accessible by visible and near-IR light excitation:[2–4] $\tilde{A}^1A_2$ (ca. 775 nm), $\tilde{a}^3A_2$ (1050 nm), $\tilde{b}^3B_2$ (953 nm), and $\tilde{c}^3B_1$ (855 nm). If the excitations to these electronic states of O_3 are enhanced by interaction with other molecules, photochemistry of O_3 with atmospheric trace gas complex is considered to be important to understand oxidation processes in the atmosphere. However, the absorption bands of O_3 interacting with other molecules in the visible region have not been reported so far to our knowledge. A few IR spectroscopic studies for visible-light-induced reactions of O_3 with halogenated alkanes were reported, which are interpreted to occur through the charge-transfer transitions within the complexes.[6–8] In this study, visible-light-induced photoreaction of dimethyl sulfide (DMS)–O_3 was examined by neon matrix-isolation visible-light absorption and FTIR spectroscopy. DMS is the largest natural source of atmospheric sulfur compounds and a key material in the formation of sulfur aerosols.[9] Although it is well known that the oxidation of DMS mainly occurs by OH radical in the atmosphere, new oxidation pathways are often proposed and the contribution are evaluated constantly. We investigated a photooxidation process of DMS–O_3 and succeeded in finding new visible-light absorption bands of the complex.

Our matrix-isolation IR measurement apparatus was described in previous papers.[10,11] The spectral resolution was $0.5\,\text{cm}^{-1}$ and the accumulation times were 100. UV–visible spectra were measured with a multichannel spectrometer (Stellar Net, EPP-2000C) with 2.5 nm resolution. Ozone produced from O_2 (Taiyo Nissan, 99.999%) by an ozonizer (Kaburagi Kagaku, K6-ST) was stored in a silica gel trap at ca. 200 K and used after mixing with Ne gas. Vaporized DMS and DMSO (Kanto Kagaku) were individually diluted by 50–1000 times with Ne gas. The O_3/Ne and DMS/Ne mixture gases constantly deposited on cooled CsI and CaF_2 plates for IR and UV–visible measurements, respectively. A xenon lamp (Asahi spectra, Max-302) was employed as visible and near-IR irradiation source. Some short-wavelength cutoff filters (Asahi Spectra and Sigma Koki) were used to select irradiating wavelengths.

Figure 1 shows two difference IR spectra of DMS/O_3/Ne associated with photoirradiation and an IR spectrum of DMSO isolated in Ne. We found that photoreaction (6) occurs upon the red-light (700–740 nm) irradiation of the DMS/O_3 matrix as recognized by Figure 1a.

$$\text{DMS} + O_3 + h\nu(\text{visible}) \rightarrow \text{DMSO} + O_2 \qquad (6)$$

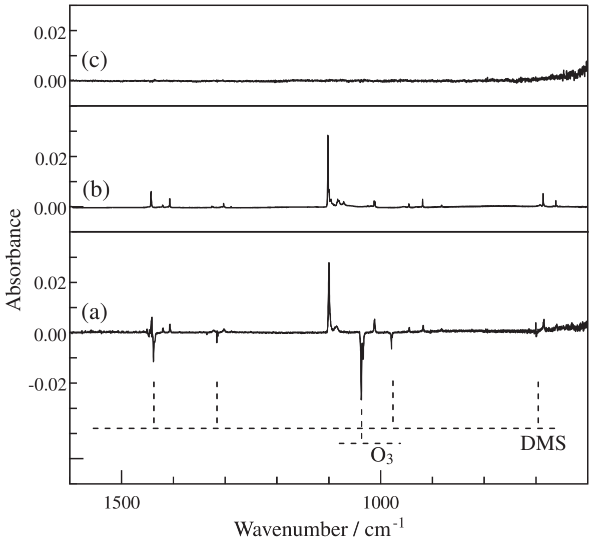

Figure 1. (a) A difference IR spectrum of DMS/O_3/Ne (=ca. 1/1/1000) associated with red-light (700–740 nm) irradiation for 90 min. (b) An IR spectrum of DMSO/Ne (=1/1000). (c) A difference IR spectrum of DMS/O_3/Ne associated with NIR (900–1050 nm) irradiation for 60 min. Broken bars at the bottom indicate the band positions due to DMS and O_3 vibrations within DMS–O_3 complex.

The positive product bands in Figure 1a correspond to the IR bands of DMSO shown in Figure 1b, while the negative reactant bands in Figure 1a are identified as the DMS and O_3 vibrations of the DMS–O_3 complex as indicated by the broken bars at the bottom of Figure 1. The negative reactant bands are slightly shifted from the corresponding monomer bands, meaning that the irradiation of DMS–O_3 complex at 700–740 nm induces the photoreaction (6) to yield DMSO. Further oxidation to dimethyl sulfone ($DMSO_2$) was not recognized in our system, though $DMSO_2$ was reported to be produced in the photolysis of DMS/O_3/Ar, where oxygen atoms are produced from O_3 monomers by intense 514.5-nm laser irradiation and then react with DMS to yield $DMSO_2$ in addition to DMSO.[12] The IR intensity of the O_3 monomer band did not change, and atomic oxygen was not generated in our low intensity red-light irradiation. We observed the red-light-induced oxygen-atom transfer within DMS–O_3 complex to yield DMSO selectively. Other photoproducts including $DMSO_2$ were not detected in even higher sample concentration, DMS/O_3/Ne = ca. 1/1/100. It should be of note that no photoreaction took place by the NIR-light (900–1050 nm) irradiation as shown in Figure 1c, though O_3 has some forbidden transitions in the NIR region.[1–5]

The red-light-induced photoreaction of DMS–O_3 complex was also confirmed by UV–visible spectroscopy. Figure 2 shows the absorption spectra of O_3/Ne and DMS/O_3/Ne in the visible spectral region. DMS and DMSO do not have any visible absorption. The Chappuis band (410–660 nm) of O_3 monomer is not recognized as shown in Figure 2b because of the small absorption coefficient.[3] By contrast, Figure 2a shows that two intense bands appear around 470 and 600 nm in the DMS/O_3 matrix. It might be suggested that the visible-light absorption due to O_3 is drastically enhanced by molecular interaction with DMS. As seen in Figure 2a, both the 470 and 600 nm bands turn out to be bleached with the red-light irradiation and finally disappear after 120 min. Both bands due to the DMS–O_3 complex also similarly decrease in intensity with other visible-light irradiation between 400 and 700 nm.

The 600 nm band of the complex is close to the extremely weak $\tilde{B}^1B_1$–$\tilde{X}^1A_1$ transition (Chappuis band) of gaseous O_3, but there exists no definite monomer band corresponding to the intense 470 nm band of the complex.[5] We unfortunately could not assign these complex bands at the present moment. It is well known that the electronic transitions of O_3 are complicated, and several optically forbidden bands exist in a visible-NIR region.[5,13] In addition, the vertical electron transition energies of O_3 are theoretically expected[14] and experimentally confirmed[10,15] to be lowered by the molecular complex formation with water.

We are still performing experiments and have succeeded in measuring a similar visible-light absorption spectra due to O_3 complexes with other molecules. The visible-light-induced photoreactions of O_3 complexes with other molecules might be important to understand O_3 chemistry in the atmosphere.

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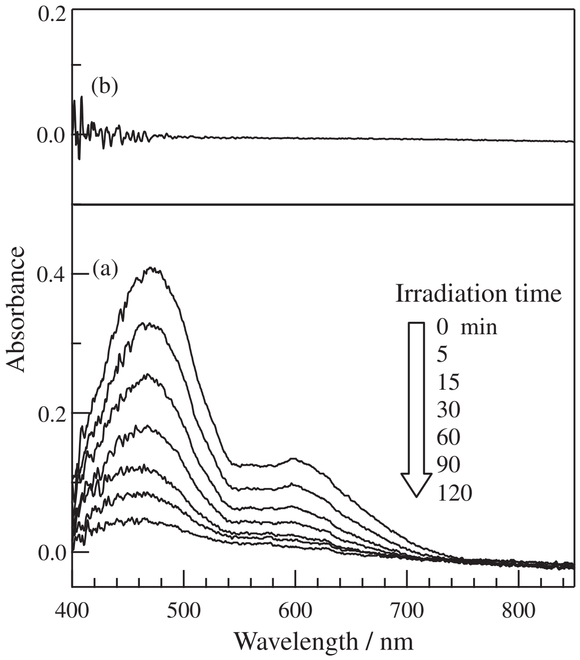

Figure 2. (a) Red-light (700–740 nm) irradiation time dependence of the absorption due to DMS–O_3 complex. The complex was prepared in a DMS/O_3/Ne (=ca. 1/1/200) matrix. (b) A visible spectrum recorded for the O_3/Ne (=1/100).

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