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High resolution spectroscopy of the OIO radical: Implications for the ozone-depleting potential of iodine

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[1] The absorption spectrum of iodine dioxide (OIO), obtained at high resolution between 540 and 605 nm by cavity ring-down spectroscopy, exhibits no evidence of coarse rotational structure. Furthermore, a laser induced fluorescence spectrum was not observed when pumping the molecule in this region of the visible spectrum. Ab initio quantum calculations were performed on the ground and first excited states of OIO. The rotational envelopes of the observed absorption bands are very satisfactorily simulated if the lifetime of the excited state is 200 ± 50 fs, indicating prompt predissociation. Quantum calculations indicate photolysis to I + O_2, rather than O + IO. The estimated photodissociation rate of OIO in daylight ranges from 0.36 to 2.2 s^{-1}, depending on the choice of absolute cross-section, which explains why OIO has only been observed in the atmosphere after sunset. Photolysis to yield atomic I will enhance the O_3-depleting potential of iodine in the remote marine boundary layer. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0330 Atmospheric Composition and Structure: Geochemical cycles

1. Introduction

[2] The atmospheric cycle of iodine in the marine boundary layer is potentially significant in the destruction of ozone [*Davis et al.*, 1996], the activation of chlorine and bromine from sea-salt [*Vogt et al.*, 1999], and the removal of nitrogen oxides. The major source of iodine appears to be atomic I produced from the photolysis of biogenic iodocarbons which evade from the ocean. The iodine oxide (IO) radical is then formed by the reaction of I with O_3. Observations of IO in the marine boundary layer [*Allan et al.*, 2000] have been used to constrain a detailed model of iodine which examines these potential impacts [*McFiggans et al.*, 2000].

[3] The iodine dioxide (OIO) radical is formed from the self reaction of IO,

$$\mathrm{IO} + \mathrm{IO} \rightarrow \mathrm{OIO} + \mathrm{I} \tag{1}$$

which has a yield of at least 40% [*Cox et al.*, 1999; *Bloss et al.*, 2001]. We have recently observed OIO in the marine boundary layer at the remote site of Cape Grim (Tasmania), using the technique of differential optical absorption spectroscopy (DOAS) operating in the 540–570 nm spectral region [*Allan et al.*, 2001]. During daytime the OIO concentration was consistently below the detection limit (0.5 parts per trillion (ppt)), from which we determined an upper limit to the OIO lifetime of 20 min, apparently dominated by gas-phase removal and/or photolysis. In contrast, immediately after sunset [OIO] increased to several ppt, before decaying to below the detection limit over several hours. This slow decay would be consistent with uptake of the radical on marine aerosol [*Allan et al.*, 2001].

[4] If the absence of OIO during the day is indeed caused by rapid photolysis, then the O_3 destruction potential of the radical depends critically on the pathway:

$$\mathrm{OIO} + h\nu \rightarrow \mathrm{I} + \mathrm{O}_2 \tag{2a}$$

$$\rightarrow \mathrm{IO} + \mathrm{O}(^3P) \tag{2b}$$

Channel (2a) would enhance O_3 depletion, since the combination of reactions (1) and (2a) removes two O_3, whereas channel (2b) would lead to a null cycle. Several groups [*Himmelmann et al.*, 1996; *Cox et al.*, 1999; *Ingham et al.*, 2000] have shown that OIO has a strong absorption spectrum consisting of sequences of bands grouped in triplets between 480 and 645 nm. However, the bond dissociation energy for OI-O has been calculated from quantum theory to be 288 ± 16 kJ mol^{-1} [*Misra and Marshall*, 1998], corresponding to a photo-dissociation threshold for OIO via channel (2b) of approximately 415 nm. Indeed, *Ingham et al.* [2000] failed to observe O atoms produced from the photolysis of OIO at 532 nm. In contrast, channel 2a is close to thermoneutral [*Misra and Marshall*, 1998], so that absorption in these visible bands could lead to I atom production.

[5] In this Letter we will describe a high-resolution spectroscopy study of the visible bands of OIO, which provides compelling evidence that absorption in these bands leads to photolysis via channel 2a.

2. Experimental

[6] The experimental arrangement is shown in Figure 1. OIO was prepared in a cavity ring-down (CRD) cell by reaction 1. The IO was formed by reacting CF_3I with O atoms produced by the photolysis of N_2O at 193 nm using an ArF excimer laser (fluence in the cell = $(0.8 - 2.4) \times 10^{16}$ photon cm^{-2}). The reagents were diluted with N_2 gas which flowed into the ends of the 1.45 m long cell and acted as curtains to protect the cavity mirrors (RMI, Boulder: R > 0.999 at 565 nm). The probe beam from a Nd:YAG-pumped dye laser (Sirah Cobra) was steered into the CRD cell, after using a wedged quartz beamsplitter to pick off portions that were directed into an I_2 fluorescence cell and a Coherent Wavemaster for wavelength calibration. In the cell there was a 30 cm overlap between the excimer and dye laser beams. The laser radiation leaking out of the ring-down cavity was passed through a 485 nm cut-on filter and detected with a photomultiplier tube. The data was displayed on a LeCroy 9361C digital oscilloscope and captured on computer by fitting each ring-down signal to an exponential decay. The fluorescence from the I_2 cell and the

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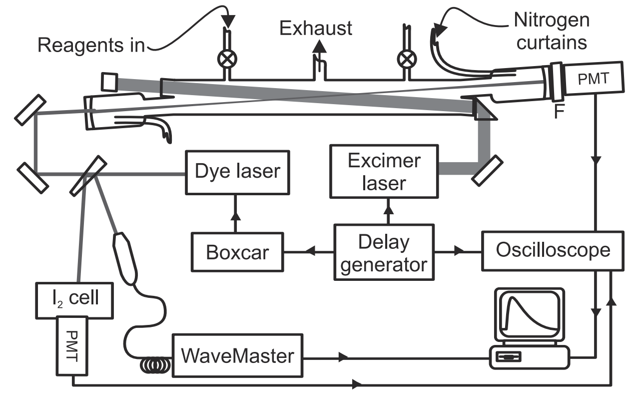

Figure 1. Schematic diagram of the pulsed photolysis/time-resolved cavity ring-down system. PMT = photomultiplier tube, F = filter.

wavelength measured by the Wavemaster were recorded simultaneously.

[7] The spectrum of OIO was recorded by measuring the ring-down time as a function of wavelength, with a constant delay of 100 μs between the excimer and dye laser pulses. All the spectra were contaminated with I_2 absorption to some degree, even though the gas residence time was kept short (0.9 s at 40 torr), and the excimer laser was triggered at only 3 Hz to avoid the build-up of I_2. The ring-down time of the empty cavity was also recorded so that the mirror reflectivities could be used to normalise the raw spectra. Spectra were recorded using coumarin 153 dye pumped with the 355 nm output from the YAG laser, and rhodamine 6G pumped with the 355 nm and then the 532 nm YAG ouput. The laser resolution was better than 0.2 cm^{-1} ($\approx$0.006 nm).

[8] A low resolution absorption spectrum of OIO was also recorded by replacing the CRD mirrors on the cell with optical flats, and using a tungsten-halogen lamp broadband light source at one end of the cell and a spectrometer (0.5 m, f/6.9) and CCD detector (1024 × 256 pixels) at the other. A 600 grooves mm^{-1} grating provided a resolution of 0.6 nm. Spectra were recorded using an electronic liquid crystal shutter (Oriel, Model 50075) to expose the array for a period of 500 μs, starting 75 μs after the excimer pulse. A laser induced fluorescence (LIF) spectrum was then recorded by directing the dye and excimer lasers collinearly down the axis of the cell. LIF was observed with a photomultiplier tube through a viewport situated orthogonal to the axis at the midpoint of the cell, and recorded with a gated integrator. Materials: CF_3I (99% pure, Fluorochem Ltd), N_2 (99.9999%, pure Air products), and N_2O (99.99% pure, Air Products) were used without further purification.

3. Results and Discussion

[9] The OIO absorption cross section measured at high resolution by CRD is compared with the low resolution broadband spectrum in Figure 2 (the experimental conditions are listed in the figure caption). The CRD spectrum is made up of three separate scans as indicated. First the I_2 contamination was removed. This was done simply by subtracting the scaled I_2 fluorescence spectrum which was recorded simultaneously. This does not account for the continuum absorption by I_2 in this region but, as the inset to Figure 2 shows, the highly structured I_2 absorption is a minor part of the overall absorption that was observed. The scans were then corrected for mirror reflectivity and normalised to each other using the broadband spectrum.

[10] In order to interpret the absence of structure in the high resolution CRD spectrum, we also carried out ab initio quantum calculations on the ground and excited states of OIO. The Gaussian 98 suite of programs [*Frisch et al.*, 1998] was used with a recently published basis set for I [*Glukhovtsev et al.*, 1995], and the standard 6–311 + g(2d, p) basis set for O. As expected, the results for the $^2B_1$ ground state are similar to those obtained by *Misra and Marshall* [1998]: r(I-O) = 1.82 Å, ∠(O-I-O) = 110.5°. Calculations on the excited electronic states were performed using the CI-singles method [*Frisch et al.*, 1998]. This reveals a strongly-allowed transition (oscillator strength f = 0.0351) to the first excited $^2B_2$ state, which is 2.23 eV vertically above the ground state. This corresponds to a wavelength of 557 nm, in good agreement with the observed absorption bands. The optimised geometry of this excited state is quite different from the ground state: r(I-O) =1.94 Å, ∠(O-I-O) = 94.8°.

[11] The band contours in the CRD spectrum in Figure 2 were simulated by taking the ab initio rotational constants and using them to simulate the spectrum of an asymmetric top molecule. The convolution of the laser linewidth and Doppler width was determined by fitting a Gaussian line profile to the LIF spectrum of IF (see below), yielding a linewidth $\approx$0.14 cm^{-1}. The resulting band contour of OIO is shown in Figure 3 (marked Laser), and exhibits both coarse and fine structure expected from an asymmetric top that undergoes a large geometry change on excitation. This

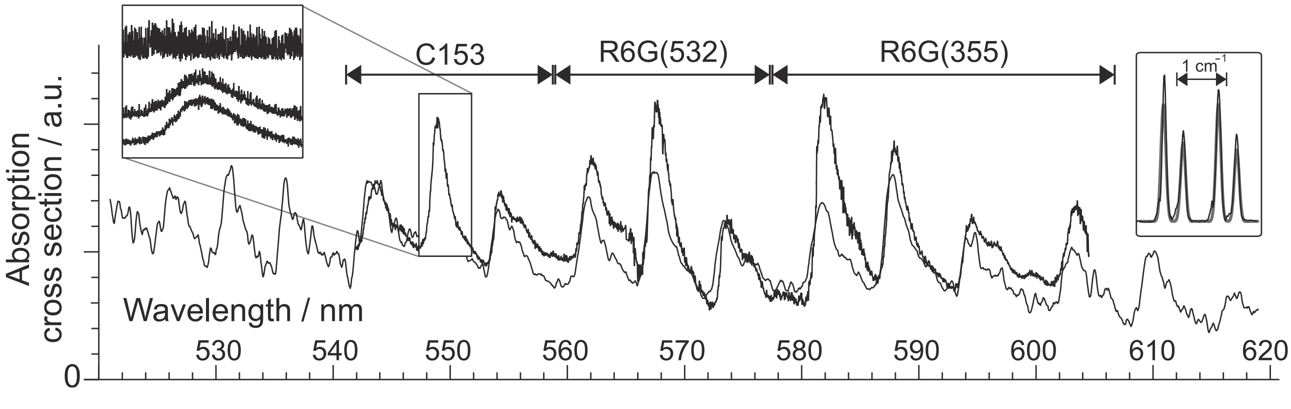

Figure 2. The absorption cross section of OIO at 300 K measured at better than 0.006 nm resolution by CRD spectroscopy (thick line), and at 0.6 nm resolution by a grating spectrometer (thin line). See the text for a discussion of the absolute cross section. The scanning ranges of the CRD dye laser are indicated at the top of the figure. The inset left shows the I_2 fluorescence spectrum in the region of one of the OIO bands and effect of subtracting I_2 contamination. The inset right shows lines of the IF LIF spectrum (black) and a simulation of the spectrum with a laser linewidth of 0.12 cm^{-1} (grey). Experimental conditions: [CF_3I] = (2.2 – 2.8) × 10^{16} cm^{-3}, [N_2O] = (0.8 –1.7) × 10^{17} cm^{-3}, [M] = 1.3 × 10^{18} cm^{-3}.

structure is clearly absent in the CRD spectrum. The remaining band contours shown in Figure 3 correspond to upper state lifetimes marked in the figure. These are obtained by convoluting the laser limited band contour with a further Lorentzian line profile whose full width at half maximum corresponds to the lifetime indicated. Taking an upper state lifetime of 200 ± 50 fs produces a very satisfactory fit of the simulated rotational band contour to that observed (Figure 3).

[12] Additional evidence for this short lifetime is that no laser induced fluorescence (LIF) from OIO was observed between 535 nm and 570 nm. The only LIF observed was from I_2 and IF. The latter, produced by the reaction sequence $O + CF_3 \rightarrow F + CF_2O$ followed by $F + CF_3I \rightarrow IF + CF_3$ [*Breheny et al.*, 2000], is a trace species in this experimental system. The spectrum was recorded with no contamination from I_2 by a suitable choice of the boxcar gate. The signal to noise on the lines shown in the inset to Figure 2 shows the sensitivity of this technique to a trace species and allows us to measure the convolution of the laser linewidth and the residual Doppler width. IF was identified from an excellent simulation of the rotational structure in one of the IF bands.

[13] There is therefore compelling experimental evidence that transition to the $^2B_2$ upper state of OIO leads to prompt predissociation. As stated above, photolysis to IO + O can be excluded on thermodynamic grounds [*Misra and Marshall*, 1998]. Therefore, we conclude that OIO must largely predissociate to $I + O_2$ following absorption in the 500–620 nm region. Figure 4 illustrates the relevant potential energy curves, calculated at the same level of theory as above except with the smaller 6-311G basis set for O. This was used for computational efficiency, with only a modest sacrifice in accuracy. These curves were calculated under C_{2v} symmetry: the reaction coordinate is the distance r(I-X) between I and X, where X is a dummy atom located midway between the O atoms. For each value of r(I-X) on a particular surface, r(O-X) was optimised to minimise the potential energy. The exception to this is the $^2B_2$ surface vertically above the $^2B_1$ ground state.

[14] Vertical excitation of OIO($^2B_2$–$^2B_1$) is indicated by the grey lines which correspond to the wavelength limits (520–620 nm) in the present study. This shows that the CI-Singles method yields sensible excitation energies for this molecule. Relaxation of the $^2B_2$ state then leads to a closing of the O-I-O bond angle, followed by predissociation via an avoided crossing between this surface and the $^2B_2$ surface correlating with $I + O_2(^1\Delta_g)$. If C_{2v} symmetry is broken, then predissociation can also occur to the $^2A_1$ surface yielding $I + O_2(^3\Sigma_g^-)$, since both $^2B_2$ and $^2A_1$ resolve to $^2A'$ under C_s symmetry.

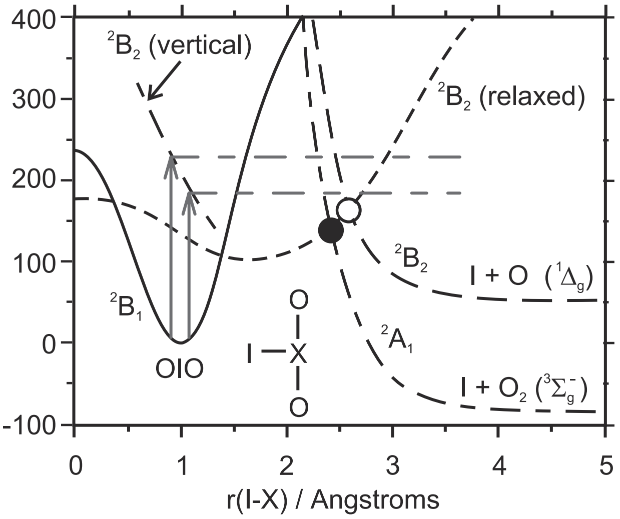

Figure 4. Potential energy curves for OIO dissociating to $I + O_2$, calculated using the CI-singles method (see text). The dummy atom X is defined in the text. The avoided crossing under both C_2v and C_s symmetry is indicated with an open circle, and that under just C_s symmetry with a shaded circle. The horizontal grey lines indicate the range of excitation energies available between 520 and 620 nm.

[15] It should be noted that although *Ingham et al.* [2000] detected I atom production from pulsed irradiation at 532 nm of a reaction mixture containing OIO, they concluded that the I atoms were produced by sequential 2-photon absorption by OIO, and the linear dependence of the I atom yield on laser fluence was explained by saturation of the first step. However, this interpretation of their experiment is probably not correct. Firstly, the absolute OIO absorption cross section estimated by *Ingham et al.* [2000] may be considerably overestimated (see below). Secondly, the first OIO transition would not have been saturated in their experiment, since the $^2B_2$ lifetime is only about 200 fs. Hence, the I atom production observed by *Ingham et al.* [2000] was probably due to a unit quantum yield for channel 2a.

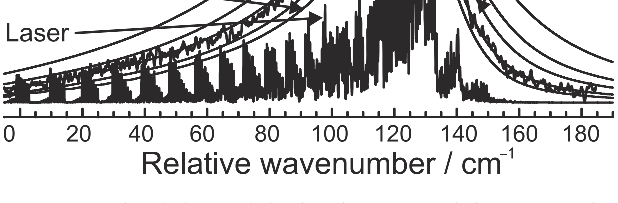

Figure 3. Simulations of the band contour of the OIO peak at 549 nm using rotational constants for an asymmetric top from the ab initio calculations. See the text for further details.

[16] At present there is considerable uncertainty regarding the absolute absorption cross section of OIO. For the substantial absorption peak at 549 nm, *Cox et al.* [1999] have reported a value of 1.1×10^{-17} cm^2, compared with 6.8×10^{-17} cm^2 from *Ingham et al.* [2000] when their cross section is adjusted to the same 40% yield of OIO in reaction 1 [*Allan et al.*, 2001]. If we take our broadband spectrum between 520 and 620 nm (Figure 2) and scale it to either of these cross sections at 549 nm, then the photolysis rates are $J = 0.36$ s^{-1} or 2.2 s^{-1}, respectively, for mid-summer, 40°N at midday.

4. Conclusions

[17] An absorption spectrum of OIO taken at high resolution between 540 and 605 nm reveals no evidence for coarse rotational structure, implying prompt predissociation. Quantum calculations show this almost certainly leads to $I + O_2$. This has two consequences. First, the photolysis lifetime is about 1 s, which explains why the radical has only been observed after sunset [*Allan et al.*, 2001]. Second, this photolysis channel enhances the ozone-depleting cycle of OIO, since each time OIO is formed from the IO self-reaction up to two O_3 molecules are destroyed. Although we have recently measured the reaction of OIO with NO to be quite rapid [k(300 K) = (6.34 ± 1.08) × 10^{-12} cm^3 molecule^{-1} s^{-1}], this will not compete with photolysis in the remote marine boundary layer except immediately after sunset.

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