Boundary Layer Halogens in Coastal Antarctica

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Halogen chemistry in causing rapid surface ozone depletion events (ODEs) in the Arctic springtime (1). Two sources of reactive halogens have been proposed: acidified sea-salt surfaces such as aerosol, frost flowers, or sea salt in surface snow accumulated through horizontal drifting from refrozen lead areas and photodegradable halogenated compounds from anthropogenic and natural origins (2). Halogens are also involved in the oxidation of oceanic dimethyl sulfide (DMS), which may influence formation of cloud condensation nuclei (3), and the oxidation of gaseous elemental Hg in the Arctic troposphere (4). Recently, it was shown that condensable iodine oxide vapors can nucleate very efficiently to form particles, which may have an impact on cloud cover and hence on climate (5, 6).

In the Antarctic, work on bromine species has been mainly concerned with the halogen-catalyzed removal of ozone in the stratosphere (7). Observations over Antarctica of the integrated tropospheric column densities of bromine oxide (BrO) and iodine oxide (IO), have been reported at a coastal site (8, 9) and, in the case of BrO only, from space (10). However, these are integrated measurements: There have been no direct measurements of IO or BrO within the boundary layer above the snowpack. It is also noteworthy that in several Arctic locations, even when elevated BrO was present in the boundary layer during an ODE, IO was not observed (11, 12), although aerosol measurements of filterable iodine have been reported (13).

A field campaign was performed from January 2004 to February 2005 at Halley Station (75°35′S, 26°30′W), which is situated on the Brunt Ice Shelf, Antarctica, about 35 m above sea level (fig. S1). The ice edge is some 12 km north and 30 km west of the station; 20 km southwest is Precious Bay, a semipermanently open patch of water with large areas of fresh sea ice where frost flowers grow in winter and spring. Sea-salt ion concentrations on frost flowers and nearby surface snow are at least three times greater than those in seawater, and this has been linked to the enhanced release of photolabile bromine compounds into the gas phase (14).

The concentrations of IO and BrO were measured with the long-path differential optical absorption spectroscopy technique (LP-DOAS) (15). A folded optical path of 4 km (total path = 8 km) was set up at a height of 4 to 5 m above the snowpack (varying through the year as a result of snow accumulation). The light source was a xenon lamp, whose beam was folded back to a Newtonian telescope receiver by an array of quartz corner-cube reflectors. The path-averaged concentrations of IO and BrO were obtained by fitting laboratory-measured cross sections of the molecules to atmospheric spectra recorded in the visible and near-ultraviolet (UV), respectively (15) (Fig. 1). Between January 2004 and February 2005, IO was measured on 41 days and BrO on 125 days. The two species were not measured simultaneously because they absorb in different spectral regions (Fig. 1).

IO and BrO were detected above the detection limit whenever the solar zenith angle was less than −92° (i.e., twilight and full daylight). The peak concentrations of both species were about 5 × 10^8 molecules cm^{-3} or 20 parts per trillion by volume (pptv), observed during austral spring (October). For BrO, this concentration is similar to the levels observed in the springtime Arctic (16). In contrast, the IO concentration is an order of magnitude larger than the upper limit reported from the Arctic (11, 12) and is actually the highest concentration reported anywhere in the atmosphere. One impact of such high levels of iodine oxides is the formation of ultraviolet aerosol from the polymerization of IO to OIO (6) (OIO forms from the reaction of IO with itself or with BrO), which might explain particle nucleation events observed in summer over sea ice near Antarctica (17).

The concentrations of both IO and BrO exhibited a diurnal cycle, essentially tracking the solar radiation (Figs. 2 and 3). This indicates that both species are produced photochemically and have a boundary layer lifetime of less than 2 hours against nonphotochemical loss processes. The concentrations of IO and BrO were strongly correlated with the local wind direction as well as...
the air mass origin predicted by back trajectory calculations (Fig. 2 and 3). Enhanced concentrations of both radicals were observed when the wind was from the open ice front sector (~200° to 45°), in air masses that had been over sea ice within the previous 24 hours. Although the levels of halogen oxides were lower in continental air that had not been over sea ice for at least 3 days, IO and BrO were often still observed at mixing ratios up to ~6 ppt during sunlight periods, clearly above the instrumental detection limit of 1 to 2 ppt (Figs. 2 and 3). This strongly suggests that halogen activation in sunlight is widespread in the coastal Antarctic boundary layer and not restricted to close proximity to the ice front. This inference is supported by satellite observations of the BrO tropospheric column density over Antarctica (10), which showed that large column abundances are present above all coastal areas of Antarctica between August and November, with smaller amounts between December and April (10).

The record of IO and BrO concentrations over the entire year is displayed in Fig. 4. The day-to-day concentrations are quite scattered as a result of differences in solar radiation and wind direction. However, the 10-day running average concentrations (solid lines in Fig. 4) show that the seasonal cycles of IO and BrO are remarkably similar, both in timing and absolute concentration. This is quite unexpected, given the different sources of the two halogens (see below). There is a distinct maximum in spring [also seen in the integrated tropospheric column measurements of IO (9), which are consistent with our measurements if all the IO was in the boundary layer]. This is followed by a decrease toward the summer and a possible secondary maximum in autumn. The smaller levels in autumn could be a consequence of lower rates of halogen activation or could result from a less-stable boundary layer allowing faster mixing into the free troposphere. During the polar night, the halogen oxides were never observed above the detection limit of the instrument. However, the first appearance of IO and BrO occurs very early in the Antarctic spring, during twilight: Mixing ratios up to 4 ppt were detected as early as 9 August. This indicates an activation mechanism that is efficient in the absence of direct sunlight or where the activation occurred further north in direct sunlight, with the halogen oxides then persisting for at least 10 hours while being transported to Halley.

We used a photochemical box model (Materials and Methods) to estimate the contributions of halogen chemistry to boundary layer ozone loss in the polar spring. With use of the observed BrO diurnal profile, we estimated the diurnally averaged rate of O3 loss because of bromine chemistry alone to be 0.14 parts per billion (ppb) hour~1. A similar calculation for iodine chemistry alone yields a rate of O3 removal of 0.31 ppb hour~1. However, when iodine and bromine chemistry act together, the modeled loss rate increases to 0.55 ppb hour~1 because the reaction IO + BrO → Br + OIO increases the rate at which BrO is converted back to Br (18) (fig. S2). This fourfold increase in the depletion rate resulting from bromine and iodine chemistry, compared with bromine alone, has not been considered previously in simulations of O3 depletion in the Antarctic troposphere.

The O3 record during the campaign shows three substantial depletion events in September and October 2004. During two of these ODEs, there were no halogen oxide measurements, because of bad visibility in one case and in the other because the DOAS was being used to observe a different species. However, during the third ODE there were IO measurements that appear to be anticorrelated with O3 (fig. S3A). Interestingly, however, plots of the deviation of [O3] from its long-term mean against [IO] or [BrO] do not show a significant correlation (fig. S4). Indeed, the highest IO concentration during the campaign was observed in the presence of 18 ppb of O3 (close to the October average of 19 ppb). Because there is insufficient NOx in the boundary layer to promote photochemical production of O3, there are two possible explanations: Either the halogens were freshly injected into the boundary layer air less than 6 hours before reaching Halley, so that only a small quantity of O3 (less than ~2 ppb) was depleted (which is consistent with trajectories crossing the ice-front sector such as shown in Figs. 2 and 3, top), or O3 was entrained from the free troposphere rapidly enough to offset significant boundary layer depletion (this would require a strong halogen source to offset the simultaneous dilution of IO and BrO). Indeed, the boundary layer at Halley during the sunlit period often

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![Fig. 2. The diurnal variation of the IO mixing ratio (black points with 2σ error bars), the DOAS detection limit for IO (black squares with a dotted line), which varied depending on visibility, and the solar irradiance (black line). The corresponding 8-day air mass back trajectory arriving at Halley (250 m above sea level) is shown adjacent to each diurnal plot. Each circle on the trajectory indicates 24 hours. Trajectories were calculated from the British Atmospheric Data Centre Web service, which uses the European Centre for Medium-Range Weather Forecasts archive. (A) A day in spring (21 October 2004) displaying the highest IO mixing ratio of 20.5 ± 1.2 ppt observed during the campaign; the air mass trajectory indicates a strong oceanic influence. (B) A day in spring (15 October 2004) when the air mass had not been over the ocean for at least 3 days. (C) A day in summer (29 January 2005) with an oceanic air mass. (D) A day in winter (4 May 2004) when IO was below the detection limit of about 2 ppt.](https://www.sciencemag.org/content/sci/317/5838/349/F2.large.jpg)
exhibits extreme variability and is not strongly capped (19). Thus, although elevated halogen oxides are almost certainly a prerequisite for an ODE, the degree of O3 depletion appears to be controlled by the boundary layer meteorology.

These high levels of halogen oxides will change the oxidizing capacity of the Antarctic boundary layer by increasing the NO2/NO ratio (e.g., via IO + NO → NO2 + I) and by decreasing the HO2/OH ratio (e.g., via HO2 + IO → HOI + O2; HOI subsequently undergoes loss in aerosol or photolysis to OH). The formation of gas-phase BrONO2 and IONO2, followed by fast deposition to the snowpack or aerosol, will remove NO2 and accelerate the activation of bromide and chloride from sea-salt surfaces (20). The rate of DMS oxidation by BrO will be an order of magnitude faster than that by OH at average mixing ratios of 4 ppt and 0.01 ppt, respectively, making BrO the most important oxidant of DMS around coastal Antarctica. Atomic Br is also highly reactive toward certain organic compounds (21) and elemental Hg at low temperatures (22). The removal of Hg should be further enhanced by the atomic iodine that must exist in steady state with the observed IO (23).

A final point to consider is the source of iodine. High concentrations of phytoplankton, which colonize the underside of sea ice, extend over large areas of the Weddell Sea (24, 25). Phytoplankton produce iodocarbons such as CH2I2 and CH2IBr and probably I2. These photolabile species (compared with the much less photolabile biogenic bromocarbons) then provide a source of inorganic iodine in the boundary layer. The high levels of IO in the boundary layer must then be sustained either through the photolysis of the higher iodine oxides (e.g., OIO, I2O3, I2O4, and I2O5), which likely form from IO (26), or the recycling of these species through aerosols or the snowpack. The uptake of species such as HOI on halide-rich surfaces will also trigger the release of bromine in the form of IBr. Such a coupling may explain the strikingly sim-
Intra- and Intermolecular Band Dispersion in an Organic Crystal

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The high crystallinity of many inorganic materials allows their band structures to be determined through angle-resolved photoemission spectroscopy (ARPES). Similar studies of conjugated organic molecules of interest in optoelectronics are often hampered by difficulties in growing well-ordered and well-oriented crystals or films. We have grown crystalline films of uniaxially oriented sexiphenyl molecules and obtained ARPES data. Supported by density-functional calculations, we show that, in the direction parallel to the principal molecular axis, a quasi-one-dimensional band structure of a system of well-defined finite size develops out of individual molecular orbitals. In contrast, perpendicular to the molecules, the band structure reflects the periodicity of the molecular crystal, and continuous bands with a large dispersion were observed.

The bulk band structures of many crystalline inorganic materials have been determined experimentally with methods such as angle-resolved valence band photoemission spectroscopy (ARPES), in part because single crystals with almost any desired orientation are available and well-defined surface terminations can be prepared in situ. For their organic counterparts, this situation is not the case because single crystals of organics generally face three basic problems: Their small size limits signal, these materials are not highly conductive and thus charging, and the orientations available are limited to their cleavage planes. Numerous attempts to measure band structures on in situ grown organic films have had limited success because of inherent disorder in these films. The propensity of the molecules to crystallize leads to a multiplicity of crystallite orientations and morphologies unless great care is taken. The challenge lies in growing thin films on conducting substrates with a single unique crystallite orientation (1–7).

Although thin films of conjugated organic molecules are entering the marketplace as the active elements in various optoelectronic devices, the basic understanding of their electronic structure, crucial to their function, is lacking. The electronic band structure, electron energy versus momentum $E(k)$, of the conjugated $\pi$ system defines both the electronic properties and the optical properties of the so-called organic semiconductors.

Here we report the electronic $\pi$ band structure of sexiphenyl (6P), a rodlike molecule with six phenyl rings linked together in the para-position, obtained with ARPES from a (20-3) oriented crystalline film and compare the results with ab initio calculations (8). This orientation can be grown on weakly interacting anisotropic substrates, such as Cu(110)-(p(2x1))O or TiO$_2$(110), which uniaxially align the molecules parallel to the atomic corrugation of the substrate (9–13). The band dispersions were measured parallel to the long molecular axis and in two directions perpendicular to the molecule. In the direction parallel to the molecules, the observed dispersion, that is, the energy spread of related orbitals constituting a band, is determined by the molecule itself. This so-called intramolecular dispersion provides a textbook example of the formation of the band structure from discrete orbitals of a quasi–one-dimensional system of well-defined finite size. Perpendicular to the molecule’s long axis, continuous bands reflecting the crystal lattice periodicity were observed. This anisotropy, together with the contribution from the various $\pi$ orbitals with different intermolecular overlap, is discussed in light of band structure calculations (14, 15).

The 200 Å-thick films investigated consisted of rectangular 6P(20-3) crystallites (~200 nm by 500 nm), which completely tilted the p(2x1) oxygen-reconstructed Cu(110) sub-

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