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# Characterization of Dibromine Monoxide ($Br_2O$) by Bromine K-Edge EXAFS and IR Spectroscopy

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**Abstract:** Dark brown dibromine monoxide ($Br_2O$) has been prepared by controlled decomposition of $BrO_2$ and studied by infrared and UV-vis spectroscopy and bromine K-edge EXAFS. Infrared studies of $Br_2O$ are consistent with $C_{2v}$ symmetry with $\nu_1$ and $\nu_3$ at 508 and 595 cm$^{-1}$, respectively, in the solid and at 528 and 626 cm$^{-1}$ in a nitrogen matrix. The UV-vis spectrum has an intense absorption at 47000 cm$^{-1}$ with successively weaker shoulders at 31 200 and 22 100 cm$^{-1}$. The mass spectrum shows a parent ion (triplet) at 174/176/178 amu. Bromine K-edge EXAFS leads to the first structural characterization of a bromine oxide with $d(\text{Br–O}) = 1.85\ (1)$ Å, $d(\text{Br}\cdots\text{Br}) = 3.07\ (2)$ Å, and Br–O–Br = 112 ± 2°.

Bromine oxides are the least well-characterized binary oxides of any nonradioactive main group element. This is a reflection both of their instability and of their intractable nature, but it is unusual to find an entire group of compounds for which no structural data exists in any phase.

Dark brown dibromine monoxide, $Br_2O$, was first obtained by reaction of bromine with mercury(II) oxide at low temperatures, by using bromine either as a vapor or in $CCl_4$ solution.[1,2] Subsequently it was obtained by careful thermal decomposition of $BrO_2$.[3] Yellow bromine dioxide, $BrO_2$, is formed by ozonization of bromine in a FREON at −78 °C or by passing a high voltage discharge through $Br_2/O_2$ mixtures at low pressures and temperatures.[3,4] Several white or pale cream oxides are reported to be formed by reaction of bromine and ozone at temperatures between ca. −50 and 0 °C and have been formulated as $Br_3O_8$, $BrO_3$, $Br_2O_3$, and $Br_2O_5$,[5a–f] although how many of these are discrete species remains to be established. All the oxides decompose rapidly below room temperature, sometimes explosively.

In the case of $Br_2O$, the IR spectrum of the solid at low temperature has been reported[6] and is consistent with $C_{2v}$ symmetry, and there is evidence that the monomer can be generated in low-temperature matrices by photolysis of a mixture of bromine and ozone.[7,8] A UV-vis spectrum in $CCl_4$ has also been reported.[2] A theoretical study on the effects of thermal vibrations of $Br_2O$ on various EXAFS (X-ray absorption fine structure) parameters has also appeared.[9] As part of a research program on the oxides and oxo-anions of bromine,[10,11] we have prepared $Br_2O$ and characterized it by mass spectrometry, IR, and UV-vis spectroscopy. We have also obtained the first structural data on any bromine oxide, via bromine K-edge EXAFS data, and report these results below.

## Experimental Section

**Preparation of $Br_2O$.** Dibromine monoxide was prepared by passing an electric discharge through a gaseous mixture of bromine and oxygen and condensing the products at 77 K. The initial compound formed is $BrO_2$, and this was subsequently decomposed to yield the desired product. The apparatus was adapted from that of Allen[12] and is shown schematically in Figure 1; an over-riding feature of the design being to minimise the distance traversed by $Br_2O$ molecules in the gas phase and to ensure that any $Br_2$ formed as a result of decomposition could be removed during the $Br_2O$ transfers.

A $Br_2/O_2$ mixture (1:5 by volume) was slowly admitted via a PTFE needle valve at B into the evacuated discharge cell which was surrounded by liquid nitrogen. A dc potential of 1150–1250 V at 40 mA was maintained across the Kanthal-B electrodes. A lilac discharge was observed, and the cream solid products condensed on the cell walls. The discharge was switched off, and the Dewar was removed after every 5 min to allow any ozone formed to disperse (CARE: liquid and solid ozone may explode violently). Typical discharge times were ca. 1 h. The lemon yellow $BrO_2$ formed was warmed to ca. 220 K under dynamic vacuum to remove unreacted bromine and further warmed to room temperature over ca. 2 h. During this final stage dark brown $Br_2O$ and yellow-red $Br_2$ collected in the U-tube (C). The $Br_2$ was pumped away at ca. 220 K, and the tube was sealed off under vacuum at (D). The product could be stored indefinitely at 77 K. Analysis was performed by allowing the $Br_2O$ to decompose to $Br_2$ and $O_2$ in a closed evacuated vessel and measuring the ratio of $Br_2$:$O_2$ produced. Typical results gave a $Br_2$:$O_2$ ratio of 2.04:1.

Despite this initial purification, it was found that subsequent studies on $Br_2O$ involving vacuum transfer resulted in the release of some bromine, immediately prior to $Br_2O$ sublimation. The presence of significant amounts of bromine would interfere with the UV-vis and EXAFS studies, but, by employing a tap-Dewar (F) to trap out $Br_2$, it was possible to sublime sufficiently pure $Br_2O$ directly into our cryogenic apparatus. With this attachment a mass spectrum of $Br_2O$ showing a characteristic parent ion triplet at 174/176/178 amu was obtained.

**Spectroscopic Studies.** The details of the cryogenic systems used for UV-vis and IR studies have been described previously,[13] and these present studies were in many respects similar to our previous work on $CrO_2Br_2$, which also evolves bromine on gentle warming. Prior to spray-on, the sample of $Br_2O$ was connected to the glass dome (G) via (E) and slowly warmed in vacuo (tap (H) closed) to condense $Br_2$ in (F). When the darker $Br_2O$ was observed to condense in (F), tap (H) was slowly opened, and the $Br_2O$ deposited directly onto the cold central window either as a molecular solid or in the presence of a large excess of nitrogen from an independent spray-on line. IR and UV-vis spectra were obtained by using Perkin-Elmer PE 983G and PE 554 spectrometers, respectively. Mass spectra were obtained by using a V.G. SXP 400 quadrupole instrument interfaced with a data system, as described elsewhere.[14]

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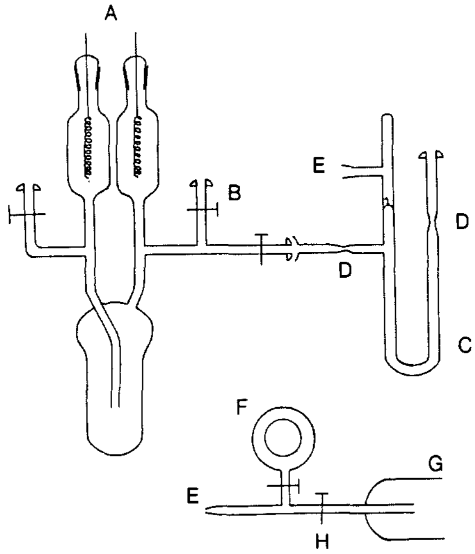

**Figure 1.** A–E: schematic representation of apparatus used for preparation and storage of $Br_2O$. E–G: schematic plan view of apparatus used for deposition.

**Bromine K-Edge EXAFS.** Data were obtained from samples using a closed-cycle cryogenic system incorporating a cooled aluminum central window (0.25 mm) and Mylar outer windows. This equipment could operate over the temperature range 9–300 K, and the details of the apparatus used have been described elsewhere.[15] The EXAFS data were collected at the Synchrotron Radiation Source, Daresbury, on station 9.2 by using a double crystal silicon 220 monochromator at an operating energy of 2 GeV and an average current of 160 mA. Data were collected in transmission mode and calibrated to the Au $L_{II}$ edge[16] at 13.731 keV. Background subtraction was carried out by using the program PAXAS[17] and curve fitting by using the single scattering curved wave theory incorporated in EXCURVE.[18] Phaseshifts and back-scattering factors were calculated by the normal ab initio methods[18] and gave satisfactory results without modification.

## Results and Discussion

Our assessments of the thermal stability of $Br_2O$ have shown that samples are stable for long periods at temperatures below 220 K but that significant decomposition takes place above ca. 250 K. Careful vacuum sublimation at ca. 230 K appeared however to result in only minimal decomposition, and these conditions were therefore employed in our EXAFS and spectroscopic studies.

**IR Studies.** The IR spectrum of solid $Br_2O$ was first obtained by Campbell et al.[6] who assigned features at 504, 197, and 587 $cm^{-1}$ to modes $\nu_1$, $\nu_2$, and $\nu_3$ of a triatomic species. They also report $^{18}O$ enrichment studies, in which absorption bands due to $Br_2{}^{18}O$ were identified at ca. 476 and 553 $cm^{-1}$. These $^{18}O$ results serve to demonstrate that solid $Br_2O$ is essentially molecular. Subsequent experiments by Pascal[19] reported values of $\nu_1$ and $\nu_3$, for solid $Br_2O$ at 506 and 592 $cm^{-1}$, respectively.

Our IR spectra of solid $Br_2O$ (ca. 12 K) are in excellent agreement with these previous studies. Two prominent absorptions were obtained at 508 and 595 $cm^{-1}$ immediately after deposition, and these shifted slightly on annealing to 504 and 582 $cm^{-1}$, respectively, revealing a shoulder at ca. 595 $cm^{-1}$. Typical spectra are shown in Figure 2.

Our nitrogen matrix spectra of $Br_2O$ showed corresponding features at 528 and 626 $cm^{-1}$, and a typical spectrum is shown in Figure 2C. As expected the bands are significantly sharper than in the solid phase, and there is a small frequency shift. However, in view of the similarity between the solid and matrix spectra, there would seem to be no difficulties in assigning the bands at 528 and 626 $cm^{-1}$ as $\nu_1$ and $\nu_3$, respectively, for the isolated monomer. Attempts to resolve bromine isotope structure on these bands were not successful; the splittings involved (estimated to be ca. 1 $cm^{-1}$) being comparable with the resolution of our spectrometer.

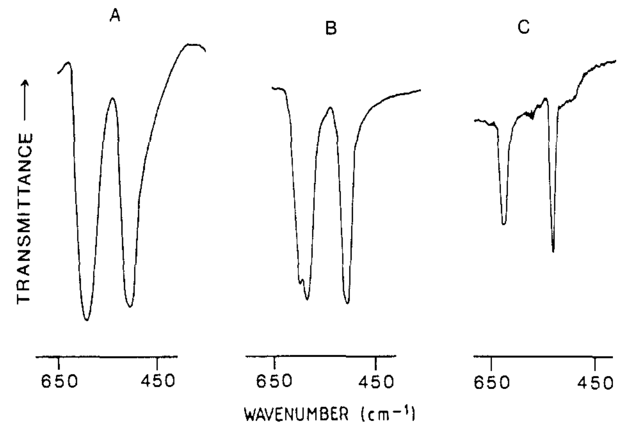

**Figure 2.** The infrared spectrum of $Br_2O$: (A) solid as deposited at ca. 12 K, (B) solid after annealing to ca. 160 K, (C) in a $N_2$ matrix at ca. 12 K.

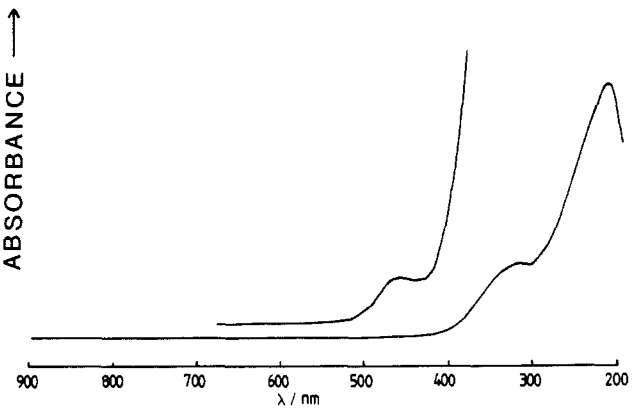

**Figure 3.** The UV–vis spectrum of $Br_2O$ in an $N_2$ matrix at ca. 12 K.

These nitrogen matrix frequencies for $Br_2O$ are very similar to features previously observed during the course of photochemical studies in the $Br_2/O_3$ system in argon matrices.[7,8] Here, the authors noted a prominent band at 526.1 $cm^{-1}$ and an associated weak feature at 623.4 $cm^{-1}$. Both these absorptions show $^{18}O$ isotope effects consistent with their assignment as $\nu_1$ and $\nu_3$ fundamentals of monomeric $Br_2O$. However, the unexpectedly low intensity of $\nu_3$ could not readily be explained. The suggestion put forward by the authors[8] is that the $Br_2O$ generated photochemically is perturbed by the presence of other species (e.g., $O_2$) and that this interaction has a strongly differential effect upon the intensities of $\nu_1$ and $\nu_3$. However, if this were the case, one might anticipate that there would be a corresponding differential frequency perturbation (compared with our $N_2$ matrix values), and one might also expect one of the modes to show an anomalous $^{16}O/^{18}O$ isotope shift. Neither of these consequences would seem to be apparent.

An alternative explanation which could account for anomalous band intensities in the photochemical experiment would be to postulate that the $Br_2O$ molecules formed in situ are orientated in such a way that the dipole change associated with $\nu_3$ lies along the direction of the incident IR beam. This could occur by two possible mechanisms. Firstly, there may be a preferred orientation of reactants relative to the incident photolysis beam, and secondly there is the possibility that the majority of the $Br_2O$ molecules formed photolytically are simultaneously decomposed unless they

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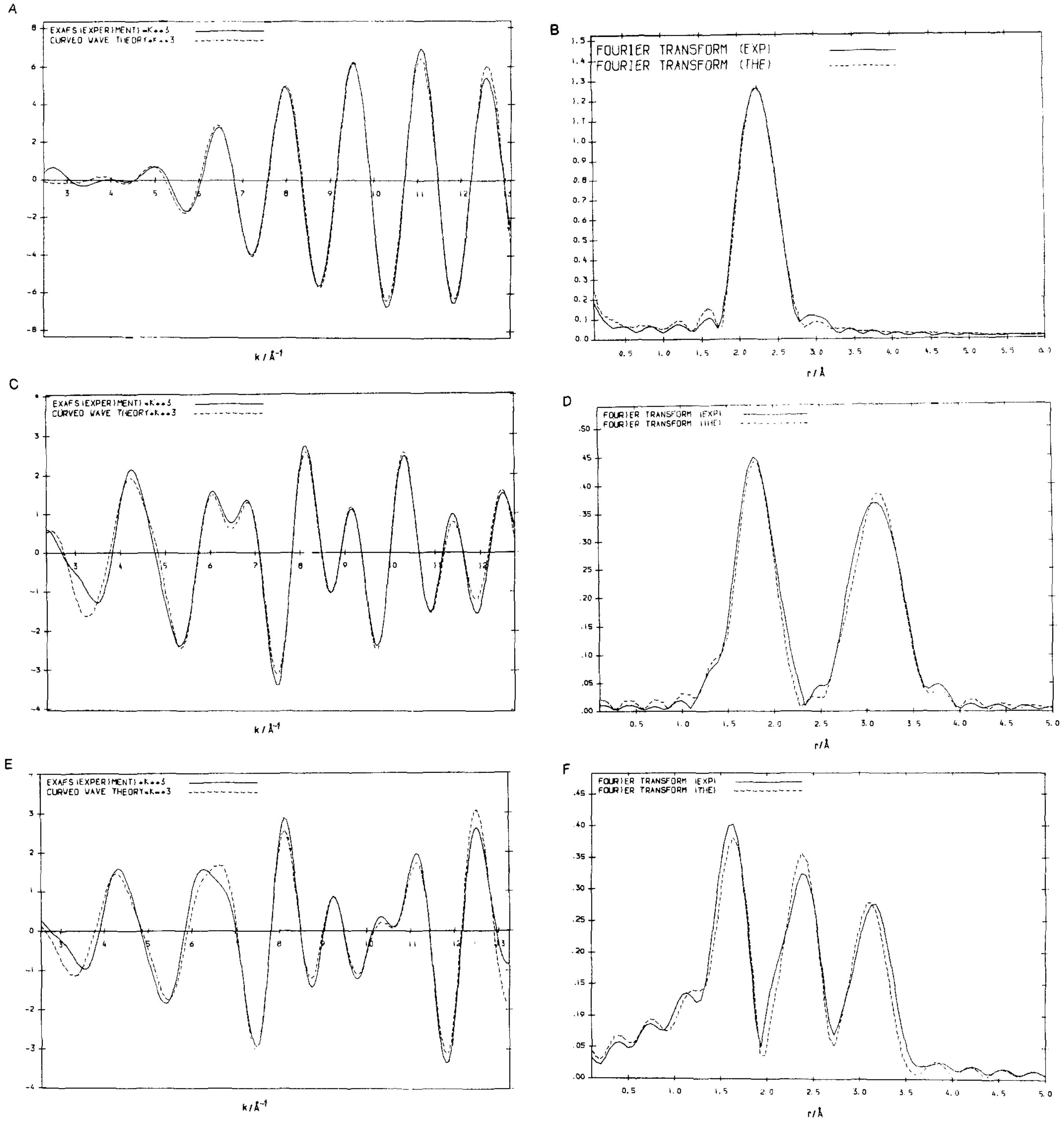

**Figure 4.** Calculated and experimental $k^3$-weighted EXAFS and their Fourier transforms for the systems: $Br_2$ at ca. 10 K (A and B), $Br_2O$ at ca. 160 K (C and D), and $Br_2/Br_2O$ at ca. 10 K (E and F).

have a specific orientation with respect to the incident radiation.

Whichever mechanism is responsible for the anomalously low intensity of $\nu_3$ in the photochemical studies, the IR matrix spectrum of $Br_2O$ obtained by direct vapor deposition poses no such problems and supports the view that solid $Br_2O$ contains essentially molecular $Br_2O$ units with $C_{2v}$ symmetry.

**UV-vis Studies.** The UV-visible spectrum of $Br_2O$ in a nitrogen matrix at 12 K is shown in Figure 3. As can be seen it consists of a strong absorption at ca. 47 000 $cm^{-1}$ with a weaker shoulder at ca. 31 200 $cm^{-1}$ and a much weaker but well-defined shoulder at ca. 22 100 $cm^{-1}$. It is not possible to measure extinction coefficients for samples deposited in this way, but the relative intensities of the peaks are evident in the spectrum shown. The spectrum is in rather poor agreement with the published one[2] which was obtained for $Br_2O$ in $CCl_4$ solution. In the absence of a detailed molecular orbital treatment of $Br_2O$, no assignment of this spectrum has been attempted, but it serves as a further characterization of the molecule and demonstrates the absence

**Table I.** EXAFS Parameters

| compd | shell | bond length[a]/Å | $2\sigma^2$/Å$^2$ | $E_0$/eV | VPI | FI[b] | $R$[c] |
|---|---|---|---|---|---|---|---|
| $Br_2$ | Br–Br | 2.29 (2) | 0.003 | 8.73 | −2.94 | 0.22 | 10.0 |
| $Br_2O$ | Br–O | 1.85 (1) | 0.008 | 7.41 | −2.09 | 0.11 | 13.8 |
| | Br···Br | 3.07 (2) | 0.012 | | | | |
| $Br_2O/Br_2$ | Br–O | 1.86 (2) | 0.003 | | | | |
| | Br–Br | 2.30 (2) | 0.004 | 8.35 | −2.72 | 0.19 | 20.6 |
| | Br···Br | 3.09 (3) | 0.008 | | | | |

[a] Errors arising from data collection and analysis are estimated at 0.01–0.02 Å in first shell distances and 0.02–0.04 Å for subsequent shells. [b] $FI = \sum_i((\chi_i^T - \chi_i^E)(k_i)^3)^2$. [c] $R = (\int|\chi^T - \chi^E|k^3dk/\int|\chi^E|k^3dk) \times 100\%$.

**Table II.** Structural Data for $X_2O$ (X = F, Cl, Br)

| compd | $r_X{}^a$/Å | $d$(X–O)/Å | $d$(X···X)/Å | X–O–X/deg | technique | ref |
|---|---|---|---|---|---|---|
| $F_2O$ | 0.71 | 1.4053 (4) | 2.201 (1)[b] | 103.1 (1) | microwave | 21 |
| $Cl_2O$ | 0.99 | 1.693 (3) | 2.795 (4) | 111.2 (3) | electron diffraction | 22 |
| | | 1.700 (1) | 2.800 (1)[b] | 110.86 (4) | microwave | 23 |
| $Br_2O$ | 1.14 | 1.85 (1) | 3.07 (2) | 112 (2)[b] | EXAFS | this work |

[a] Covalent radii taken from the following: Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th ed.; John Wiley: 1988. [b] Calculated by triangulation.

of significant amounts of $Br_2$ from the sample.

**Bromine K-Edge EXAFS.** Bromine K-edge EXAFS data were collected from solid samples sublimed onto a thin aluminum window held initially at 10 K. Such deposits were frequently contaminated by appreciable quantities of bromine as a result of decomposition during deposition. An initial data set was acquired at 10 K, and the sample was then warmed to 160 K at which temperature the bromine impurity was pumped away. Further data sets were then collected at this temperature and analyzed in detail. EXAFS data were also obtained independently on solid $Br_2$ at 10 K to act as a model compound. The pre-edge background was removed by fitting the pre-edge region to a cubic polynomial and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated by using polynomials or spline functions, and the optimum function was judged by minimizing the intensity of chemically insignificant shells at low $r$ in the Fourier transform. Fourier filtered (1–3.5 Å) $k^3$-weighted data were used for curve fitting and calculated, and experimental data for $Br_2$, $Br_2O$, and for $Br_2O$ contaminated with $Br_2$ are shown in Figure 4. Refined EXAFS parameters are presented in Table I.

Fourier-filtered data for $Br_2$ were refined to $R$ = 10.0 and a Debye–Waller factor of 0.003 Å$^2$, with $d$(Br–Br) = 2.29 (2) Å in good agreement with the literature value of 2.27 (1) Å.[20] The refined value of AFAC was 0.82, and this value was used in all further calculations since it is dependent largely on the central atom type and not its chemical environment.

The bromine EXAFS data for $Br_2O$ at 160 K was refined to $R$ = 13.8, with $d$(Br–O) = 1.85 (1) Å and $d$(Br···Br) = 3.07 (2) Å with respective Debye–Waller factors of 0.008 and 0.012 Å$^2$. This leads by triangulation to a bond angle Br–O–Br of 112 ± 2°.

Fourier transforms of data from samples of $Br_2O$ contaminated with $Br_2$ clearly show Br–O, Br···Br, and Br–Br distances (Figure 4). Whilst attempts to model such data were frustrated by imperfect background subtractions, best fit ($R$ = 20.6) bond distances $d$(Br–Br) = 2.30 (2) Å, $d$(Br–O) = 1.86 (2) Å, and $d$(Br···Br) = 3.09 (3) Å are in satisfactory agreement with those from the pure systems. Discrepancies in the Debye–Waller parameters may arise from either amplitude problems introduced by background subtractions or from differing thermal motions at the two temperatures.

The Br–O bond length at 1.85 Å in $Br_2O$ compares well with the 1.81 Å recently obtained by us[11] for $BrO^-$ which contains bromine in the same formal oxidation state, whilst comparison with the other $X_2O$ (X = F, Cl; Table II) shows an increase of 0.15 Å in $d$(X–O) from $Cl_2O$ to $Br_2O$ which parallels the difference in the halogen covalent radii. The intramolecular Br···Br distance of 3.07 Å is somewhat shorter than other known examples. In $CH_2Br_2$ values of 3.209 Å (microwave[24]) and 3.19 Å (EXAFS[25]) have been reported, whilst the value[26] in $COBr_2$ of 3.35 Å results from a surprisingly long C–Br distance. Glidewell[27] has estimated a minimum nonbonded Br···Br contact in a Br–Y–Br unit (Y = C, N, O, or F) of 3.12 Å. It is also interesting to note that the bond angle in $Br_2O$ derived from our EXAFS data is in remarkably good agreement with that derived from the earlier matrix IR studies[8] where a value of 113° was estimated from isotope shifts.

## Conclusions

Samples of solid and matrix-isolated $Br_2O$ have been successfully characterized by a variety of techniques and in particular have yielded the first structural data on any bromine oxide. However, the more general conclusion which emerges from this work is that the combination of low-temperature spectroscopic and EXAFS techniques may constitute an important strategy in the characterization of highly reactive chemical species.

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