BNL-62126
INFORMAL REPORT

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**A Preliminary Report on the Photoionization Efficiency Spectrum,
Ionization Energy and Heat of Formation of Br_2O ; and the
Appearance Energy of BrO^+ (Br_2O)**

**R. Peyton Thorn, Jr., P.S. Monks, L.J. Stief, S.-C. Kuo, Z. Zhang and
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August 1995

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Work performed under the auspices of the U.S. Department of Energy by Brookhaven National Laboratory
under Contract No. DE-AC02-76CH00016

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**A Preliminary Report on the Photoionization Efficiency Spectrum,
Ionization Energy and Heat of Formation of Br_2O ;
and the Appearance Energy of BrO^+ (Br_2O)**

by

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INTRODUCTION

In a theoretical study of the molecular and spectroscopic properties of Br_2O , Novak¹ estimated the heat of formation to be $83 \pm 8 \text{ kJ mol}^{-1}$ via a crude "sum of bond enthalpies" procedure. In the same paper, *ab initio* calculations were employed to derive a value of 10.23 eV for the adiabatic ionization energy (IE) of Br_2O . More recently, Orlando and Burkholder² measured the equilibrium constant (K_{eq}) for reaction 1,

From K_{eq} and estimates for $\Delta_f H^\circ_{298}(\text{HOBr})$, they derived a value for $\Delta_f H^\circ_{298}(\text{Br}_2\text{O})$ of 113-159 kJ mol^{-1} . There appear to be no other reports on measurements, calculations or estimates for $\Delta_f H^\circ(\text{Br}_2\text{O})$ and IE (Br_2O).^{3,4}

In the present study, we report experimental results for the photoionization efficiency (PIE) spectrum of Br_2O along with the ionization energy (derived from the ionization threshold) and the appearance energy (AE) of $\text{BrO}^+(\text{Br}_2\text{O})$. A value for the heat of formation of Br_2O is derived from the AE result.

EXPERIMENTAL

Experiments were performed by employing a discharge flow-photoionization mass spectrometer (DF-PIMS) apparatus coupled to beamline U-11 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The apparatus and experimental procedures have been described in detail in previous publications.⁵⁻¹¹

Br₂O was prepared *via* the heterogeneous reaction of bromine vapor on solid mercuric oxide:^{2,12}

Approximately 50 gms of HgO powder were placed in a 5ℓ glass sample bulb, which was evacuated to a pressure of about 10⁻⁵ Torr. Bromine vapor was then expanded into the bulb and, after waiting a few minutes for the reactants and products to come to equilibrium, helium was admitted to achieve a final pressure of about 800 Torr. The resulting mixtures, Br₂/Br₂O/HOBr/He, were analyzed *via* mass spectrometry. The HOBr was presumably generated by reaction of Br₂O with water that was adsorbed on the HgO sample.

The gaseous mixture in the flow reactor was sampled as a molecular beam into the source chamber and subsequently into the photoionization region of the mass spectrometer. Ions were mass selected with an axially aligned quadrupole mass filter, detected with a channeltron/pulse pre-amp and thence counted for preset integration times. Measurements of PIE spectra, the ratio of ion counts/light intensity versus wavelength, were made using tunable vacuum-ultraviolet

(VUV) radiation at the NSLS. A monochromator with a normal incidence grating (1200 lines/mm) was used to disperse the VUV light¹¹ and, where applicable, a LiF filter ($\lambda \geq 103$ nm) was used to eliminate second- and higher-order radiation. For photoionization experiments performed at $\lambda < 105$ nm, it was necessary to correct the PIE data for signal due to second order light.¹⁰ The intensity of the dispersed VUV light was monitored via a sodium salicylate coated window with attached photomultiplier tube.

The helium was of the highest purity obtainable (MG Industries, scientific grade, 99.9999%) and was used directly from a cylinder. Mercuric oxide (HgO, yellow, 99+%, ACS reagent) was obtained from Aldrich Chemical Co. The bromine (Fluka, puriss.p.a. grade, >99.0%) was outgassed by repeated freeze-pump-thaw cycles.

RESULTS AND DISCUSSION

As an example of the PIMS experiment, the PIE spectrum of Br_2 ($m/z=160$) was measured over the wavelength range of $\lambda=110$ to 120 nm. As shown in Fig. 1, the onset for ionization at $\lambda=117.9_3$ nm corresponds to an adiabatic ionization energy of $10.51_6 \pm 0.01_1$ eV. This result is in good agreement with the recommended value (10.515eV)⁴ and it demonstrates once again that the wavelength calibration, established by location of zero order, is excellent.^{9,10} In addition to the onset, the PIE spectrum of Br_2 displays the vibrational steps ($v'=0-8$) in the cation. Even though the superimposed structure (presumably due to vibrational autoionization) perturbs these transitions, there is generally good agreement with results from a recent photoelectron spectroscopy study.¹³

In Fig. 2, we show a mass scan of the BrO^+ (from dissociative ionization of Br_2O) and HOBr^+ over the range $m/z=93-99$ at an excitation energy of 11.92 eV(104nm). These data demonstrate the excellent mass resolution attained in the DFPIMS experiments.

The PIE spectrum for Br_2O , at $m/z=176$, is shown in Figure 3 over the wavelength range of 100 to 125 nm at 0.13nm resolution and at 0.2nm intervals. The adiabatic ionization energy for Br_2O , derived from the onset of ionization indicated in Fig. 3 at 120.8 nm, is $10.26_4 \pm 0.01_1$ eV. Also shown in Fig. 3 is the PIE spectrum of BrO^+ that is formed via dissociative ionization of Br_2O . The threshold for the appearance of BrO^+ was examined in more detail, as shown in Fig. 4, over the wavelength range 104 to 110 nm at a resolution of 0.13 nm (fwhm) and 0.1 nm

intervals. The onset for BrO^+ occurs at 105.84, nm which corresponds to an appearance energy of $11.71_4 \pm 0.01_1$ eV.

The appearance energy determined here may be used to derive the heat of formation of Br_2O as discussed in the following derivation. First, the AE must be corrected for the internal energy in Br_2O by methods discussed by Traeger and McLoughlin:^{14,15}

$$\text{AE}_0(\text{BrO}^+, \text{Br}_2\text{O}) = \text{AE}_{298} + E_i \quad (3)$$

$$= \text{AE}_{298} + (H_{298} - H_0)_{\text{Br}_2\text{O}} - 5/2 RT \quad (4)$$

$$= 1136.4 \text{ kJ mol}^{-1}$$

From this value for AE_0 , we may compute $\Delta_f H^\circ_0(\text{Br}_2\text{O})$ using the heat of formation of $\Delta_f H^\circ_0(\text{BrO}^+)$ that, in turn, has been derived from the ionization energy⁶ for BrO and the heat of formation¹⁶ of BrO . For the dissociative ionization of Br_2O to form BrO^+ ,

the heats of formation are related to AE_0 by equation (6),

$$\text{AE}_0 = \Delta_f H^\circ_0(\text{BrO}^+) + \Delta_f H^\circ_0(\text{Br}) - \Delta_f H^\circ_0(\text{Br}_2\text{O}). \quad (6)$$

Rearranging and using values from the latest NIST-JANAF evaluation:¹⁷

$$\Delta_f H^\circ_0(\text{Br}_2\text{O}) = \Delta_f H^\circ_0(\text{BrO}^+) + \Delta_f H^\circ_0(\text{Br}) - \text{AE}_0 \quad (7)$$

$$= 1142.6 + 117.9 - 1136.4$$

$$\Delta_f H^\circ_0(\text{Br}_2\text{O}) = 124.1 \text{ kJ mol}^{-1}$$

and thus $\Delta_f H^\circ_{298}(\text{Br}_2\text{O}) = 107.1 \text{ kJ mol}^{-1}$, by applying the correction of 17 kJ mol^{-1} given in ref. 17. The uncertainty associated with this derivation of $\Delta_f H^\circ_{298}(\text{Br}_2\text{O})$ is conservatively estimated to be $\pm 7 \text{ kJ mol}^{-1}$. This value for $\Delta_f H^\circ_{298}(\text{Br}_2\text{O})$ may then be related to

$\Delta_f H^\circ_{298}(\text{HOBr})$ through the equilibrium constant, reported by Orlando and Burkholder. For reaction (1), $K_{eq}(298\text{K}) = 0.02 \pm 0.002$,² and thence,

$$\Delta_f H^\circ_{298}(\text{Br}_2\text{O}) - 2 \Delta_f H^\circ_{298}(\text{HOBr}) = 232.2 \text{ kJ mol}^{-1}. \quad (8)$$

$$\begin{aligned} \text{Thus, } \Delta_f H^\circ_{298}(\text{HOBr}) &= [\Delta_f H^\circ_{298}(\text{Br}_2\text{O}) - 232.2] / 2 \\ &= -62.6 (\pm 23) \text{ kJ mol}^{-1} \end{aligned}$$

This result for $\Delta_f H^\circ_{298}(\text{HOBr})$ is in good agreement with the average (51.0 kJ mol^{-1}) of three independently derived values (reported by Monks et al.⁸ and McGrath and Rowland¹⁸, and later by Ruscic and Berkowitz¹⁹) and therefore it demonstrates an internal consistency in the system under investigation.

ACKNOWLEDGEMENT

RPT, Jr. and PSM would like to thank the NAS/NRC for awards of Research Associateships. The work at GSFC was supported by the NASA Upper Atmosphere Research Program. ZZ was supported under the Laboratory Directed Research and Development Program at Brookhaven National Laboratory. The work at BNL was supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC02-76CH00016.

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FIGURE CAPTIONS

- Figure 1 Photoionization efficiency spectrum of Br_2 ($m/z = 160$) between $\lambda = 110$ and 120nm at a nominal resolution of 0.12nm and with 0.05nm steps. Photoionization efficiency is ion counts divided by light intensity in arbitrary units. The arrow indicates the onset of ionization at $\lambda = 117.90\text{nm}$ ($\text{IE} = 10.516 \pm 0.01\text{eV}$). The superposed lines (at $117.90, 117.32, 116.78, 116.32, 115.95, 115.50, 115.02, 114.58$ and 114.15nm) indicate the vibrational steps ($v'=0-8$) in the Br_2 cation.
- Figure 2 Mass scan of the products BrO (formed via dissociative ionization of Br_2O) and HOBr from the sample mixture at an excitation wavelength of 104nm (11.92eV), m/z range = $93-99$ at $0.1 m/z$ steps.
- Figure 3 Photoionization efficiency spectrum (filled circles) of Br_2O ($m/z = 176$) between $\lambda = 100.0$ and 125.0 nm at a nominal resolution of 0.13 nm and 0.2 nm steps. The arrow indicates the onset of ionization at $\lambda = 120.8 \text{ nm}$ ($\text{IE} = 10.264 \pm 0.011 \text{ eV}$). Also shown in this figure (open circles) is the photoionization efficiency spectrum of $\text{BrO}^+(\text{Br}_2\text{O})$ ($m/z=95$) between $\lambda=90.0$ and 110.0nm at a nominal resolution of 0.14nm and 0.2nm steps.
- Figure 4 Photoionization threshold region for the appearance of $\text{BrO}^+(\text{Br}_2\text{O})$ ($m/z=95$) between $\lambda=104.0$ and 110.0nm at a nominal resolution of 0.13nm and 0.1nm steps. The linear extrapolation of the spectrum to the baseline yields an onset at 105.84_3nm ($\text{AE}_{298}=11.714\text{eV}$).