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Zhimin Qiao, Shutao Sun, Qiao Sun, Jincal Zhao, and Dianxun Wang

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Vacuum synthesis and determination of the ionization energies of different molecular orbitals for BrOBr and HOBr

Zhimin Qiao, Shutao Sun, and Qiao Sun

Center of Molecular Science, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, People's Republic of China and Graduate School of Chinese Academy of Science, Beijing 100080, People's Republic of China

Jincai Zhao and Dianxun Wang^{a)}

Center of Molecular Science, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, People's Republic of China

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Pure BrOBr and HOBr were synthesized in vacuum by heterogeneous reactions of the dried bromine vapor and Br₂/H₂O mixture vapors (5:1) with HgO, respectively, and then characterized by He I photoelectron spectroscopy (PES) and augmented by *ab initio* GAUSSIAN 2 and the outer valence Green's functional calculations. The first PE band at 10.26 eV with vibrational spacing 550 ± 60 cm⁻¹ and the second PE band at 11.23 eV with vibrational spacing 240 ± 60 cm⁻¹ are, respectively, assigned as ionizations of the electrons of the highest occupied molecular orbital (HOMO) (6b₁(39)) and the SHOMO(13b₂(38)) orbitals of BrOBr. The first PE band at 10.73 eV with vibrational spacing 750 ± 60 cm⁻¹ and the second PE band at 11.56 eV with vibrational spacing 650 ± 60 cm⁻¹ are, respectively, assigned as ionizations of the electrons of the HOMO(6a''(22)) and the SHOMO(16a'(21)) orbitals of HOBr. The study does not only provide vacuum synthesis conditions for preparing pure BrOBr and HOBr, but also provide experimental PES results along with theoretical ionization energies of different molecular orbitals for BrOBr and HOBr. © 2003 American Institute of Physics. [DOI: 10.1063/1.1607310]

I. INTRODUCTION

It is universally recognized in the world that halogen-containing compounds lead to ozone depletion in the atmosphere. Many chlorine-containing species are known and have been well characterized. In comparison with the chlorine-containing species, much less is known about bromine-containing species, mainly because of their low thermal stability and the difficulty of obtaining them in a pure state.¹⁻⁴ Bromine-containing species, of either biogenic or anthropogenic origin, released at the earth's surface have been linked to ozone destruction in various altitude regions of the earth's atmosphere.⁵⁻⁷ Recent findings show^{8,9} that the effectively catalytic removal of ozone by bromine on a per atom basis in the polar stratosphere is higher one hundred times than that of chlorine. Consequently, thorough and extensive investigations of bromine-containing species from both experiments and theory are urgently needed.

HOBr, as a reservoir species for bromine, is an important bromine species in the atmosphere,¹⁰ and BrOBr as a precursor of HOBr. But far less is known about their properties in the gas phase, and no gas-phase photoelectron spectroscopy (PES) investigation is available to date. In this paper, we would like to report vacuum synthesis of pure BrOBr and HOBr, and determination of ionization energies of different

molecular orbitals by the PES and both the GAUSSIAN 2 (G2) and the outer valence Green's functional (OVGF) calculations. Studies in the gas phase are more important than those in solution for atmospheric chemistry and the synthesis of pure BrOBr and HOBr could further promote the study of their action in the atmosphere.

II. PES MEASUREMENT

The PES experiments were performed in a double-chamber UPS Machine-II that was built specially to detect transient species as described elsewhere.¹¹ The PE spectra of BrOBr and HOBr were measured at resolutions of about 30 meV as indicated by the Ar⁺(³P_{2/3}) PE peak. The experimental ionization energy (*I_v* in eV) is calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

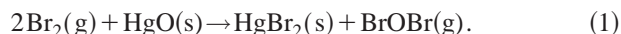
Ab initio (G2) and OVGF calculations. To assign the PES bands of BrOBr and HOBr, both G2 and OVGF calculations have been performed on the ground and ionic states corresponding to ionization of the electron of different molecular orbitals in the C_{2v} symmetry for BrOBr and in the C_s symmetry for HOBr. The G2 procedure has been described in detail by Curtiss *et al.*¹² The OVGF calculations are shown in Ref. 13. The computed ionization energies (*E_v* in eV) are obtained from the difference between the total energy of the resulting cation to the total energy of the ground state of the neutral molecule.

^{a)} Author to whom all correspondence should be addressed. Electronic mail: wangdx@infoc3.icas.ac.cn

III. RESULTS AND DISCUSSION

A. Vacuum synthesis of pure BrOBr

Pure BrOBr was synthesized in vacuum by heterogeneous reaction of the bromine vapor with HgO,^{14,15}



As the first step for obtaining pure BrOBr, the moisture in bromine must previously be removed. Bromine was first frozen at -78°C (liquid N_2 /acetone mixture) to degas by a vacuum pumping at 10^{-3} Torr, then dried by passing through P_2O_5 (Aldrich) at 25°C and collected in a tube with two sealed valves. Second, 100 g of HgO (yellow) powder (Aldrich) were previously put in a 500 ml glass flask, which was loosely filled with the glass wool and equipped with inlet and outlet valves. The flask was evacuated to 10^{-3} Torr, and then heated to 100°C for $1\frac{1}{2}$ h to activate HgO. Third, the evacuated flask was filled with dried bromine to about 150 Torr at 0°C in the dark. After approximately 7 min of mixing and reacting between HgO and Br_2 , the reaction gases were transferred into a -196°C liquid nitrogen cooled trap by a rotation pumping system. This procedure was repeated until a sufficient quantity of BrOBr was obtained. The trapped sample was then pumped at -45°C to remove unreacted Br_2 impurity. After a half hour, the brownish-green pure BrOBr was obtained and thence kept at -55°C to avoid BrOBr decomposition prior to its use for PES measurements.

B. Vacuum synthesis of pure HOBr

Pure HOBr was synthesized using similar equipment and procedures as mentioned earlier. First, the HgO sample was prepared exactly as above. Second, the evacuated flask was successively filled with bromine vapor up to 150 Torr and with H_2O vapor up to 30 Torr above that at 25°C in the dark. After approximately 10 min of mixing and reacting between Br_2 , H_2O , and HgO, the reaction gases were transferred to a -196°C liquid nitrogen cooled trap by a rotation pumping system. This procedure was repeated until a sufficient quantity of HOBr was obtained to run a satisfactory PE spectrum. The trapped sample was then pumped at -50°C to remove the Br_2 /BrOBr impurity. After a half hour, the greenish-yellow, pure HOBr was obtained and kept at -65°C to avoid HOBr decomposition prior to its use for PES measurements.

A "pure" PE spectrum of HOBr is obtained under the condition of having strong PE signal due to H_2O . Obviously, this is attributed to the equilibrium reaction (2) for formation of HOBr:¹⁶



If the moisture in bromine was not removed, a mixture PE spectrum of BrOBr, HOBr, and H_2O was obtained [see the (c) of Figs. 1 and 2].

C. Determination of the ionization energies of different molecular orbitals for BrOBr and HOBr

Figure 1(a) is the full PE spectrum of pure BrOBr and a corresponding expanded part in the low ionization energy region (<13.50 eV) is given in Fig. 2(a). Figure 1(b) gives

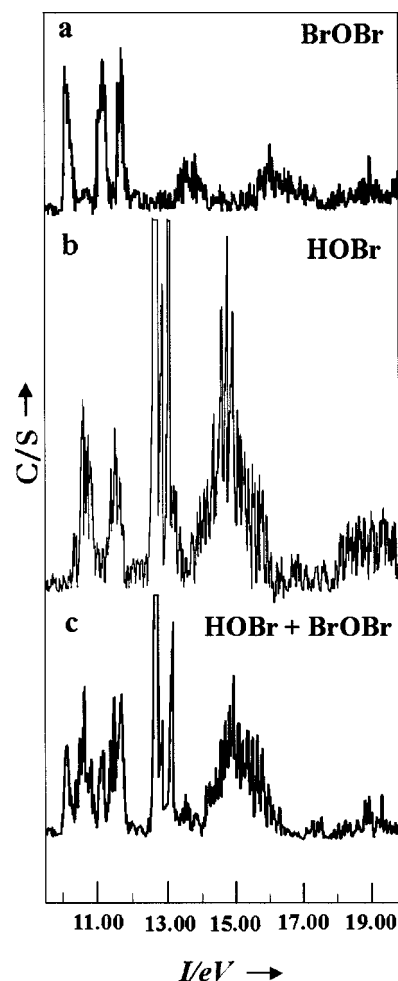


FIG. 1. The complete PE spectra of BrOBr (a), HOBr (b), and a mixture of BrOBr and HOBr (c).

the PE spectrum of HOBr, and its expanded part in the low ionization energy region (<13.50 eV) is shown in Fig. 2(b). Figure 1(c) is the PE spectrum of the products synthesized without removing moisture in bromine and its expanded part in the low ionization energy region (<13.50 eV) is shown in Fig. 2(c). Figures 1(c) and 2(c) are clearly mixture PE spectra of BrOBr and HOBr. The PES bands of H_2O also appear on the (b) and (c) of Figs. 1 and 2.¹⁷

Table I gives the experimental vertical ionization energies (I_v in eV) and computed ionization energies (E_v in eV) by OVGF and G2 methods for BrOBr and HOBr, because theoretical calculations cannot only support PES experimental results, but also predict the character of the species studied/proposed.

Table II gives the vibrational frequencies (cm^{-1}) obtained in the PES experiments, theoretical calculations along with literature values for BrOBr and HOBr. These results further support the present assignments for the PES bands of BrOBr and HOBr.

In Fig. 1(a), four bands are evident at 10.26, 11.23, 11.73, and 13.34 eV as well as a broad band centered near 16.25 eV in the PE spectrum of BrOBr. The band at the lowest energy 10.26 eV is the first PES band of BrOBr because its value is in excellent agreement with the reported

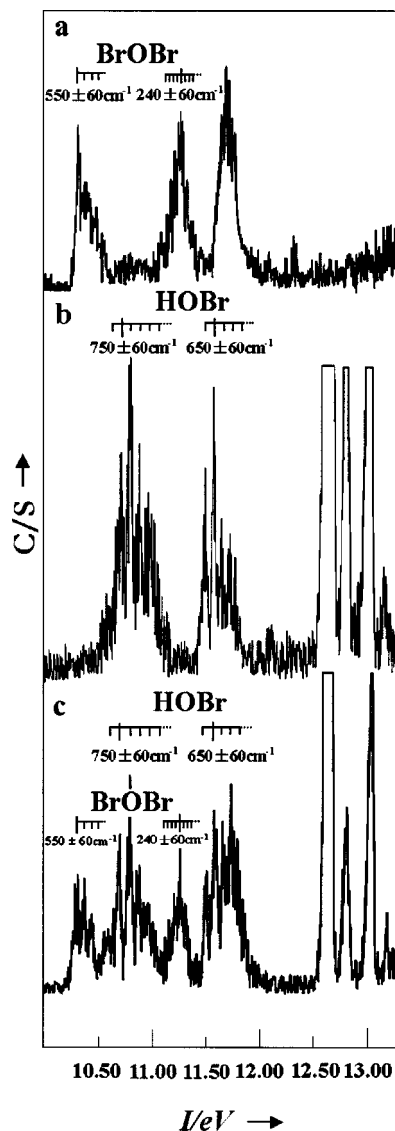


FIG. 2. The expanded PE spectra of BrOBr (a), HOBr (b), and a mixture of BrOBr and HOBr (c) in the low ionization energy region (<13.50 eV).

experimental value $10.264 \text{ eV}^{18(a)}$ and calculated values $10.23 \text{ eV}^{18(b)}$. The present PES value, 10.26 eV , agrees reasonably well with our computed values 10.369 (G2) and 10.404 (OVGF) (see Table I). The vibrational spacing ($550 \pm 60 \text{ cm}^{-1}$) of the first band is somewhat larger than that of the reported Br–O stretch model (533 cm^{-1} (Ref. 15)) and the calculated values (see Table II) for the neutral BrOBr. This shows that ionization corresponding to the first band results from removal of the electron of an antibonding orbital. The highest occupied molecular orbital (HOMO) $6b_1$ of BrOBr (see Table I) is just an antibonding π orbital. The adiabatic ionization energy (I_a) is equivalent to the vertical ionization energy (I_v) on the first band, because the $6b_1$ embodies mainly the contribution of the two Br atoms, which is similar to the lone-pair of bromine.

The band at 11.23 eV with a vibrational spacing of $240 \pm 60 \text{ cm}^{-1}$ is the second PE band of BrOBr because this value agrees with the computed value of 11.113 (OVGF) and because a long vibrational progression (at least 8) should relate to ionization of the electron of a strong bonding $13b_2$

TABLE I. He I experimental vertical ionization energies (I_v in eV), computed ionization energies (in eV) by OVGF and G2 methods for the PES bands of BrOBr(C_{2v}) and HOBr(C_s). [The geometries of BrOBr and HOBr were optimized at the B3LYP/6-311++g** level. The calculation by the OVGF method is at the 6-311++G** basis set level. The molecular orbitals associated with each ionization band are designated according to their atomic and bonding character. Experimental vertical ionization energies (I_v in eV) are given in the form of overlapping band maxima since the observed bands are associated with varying orbital ionization numbers.]

Species	I_v (eV)		OVGF (eV)	G2 (eV)	MO	Character
BrOBr	10.26	10.26	10.404	10.369	$6b_1(39)$	n_{Br}
		10.33				
		10.40				
		10.47				
		11.11				
		11.14				
		11.17				
		11.20				
	11.23	11.23	11.113		$13b_2(38)$	$\sigma_{\text{Br-O}}$
		11.26				
HOBr	11.73		11.332		$15a_1(37)$	$\sigma_{\text{Br-O}}$
			11.480		$5a_2(36)$	n_{Br}
	13.34		14.820		$14a_1(35)$	$\sigma_{\text{Br-O}}$
		10.64		10.645		
	10.73	10.73	10.689		$6a''(22)$	$\pi_{\text{Br-O}}$
		10.82				
		10.91				
		11.48				
	11.56	11.56	11.254		$16a'(21)$	n_{Br}
		11.64				
	11.72					
	14.20		13.748		$15a'(20)$	$\sigma_{\text{Br-O}}$
	14.74		14.717		$5a''(19)$	$\pi_{\text{Br-O}}$
			17.293		$14a'(18)$	$\sigma_{\text{Br-O}}$

orbital. The third band at 11.73 eV may be ascribed to ionization of the electrons of both $15a_1$ and $5a_2$ orbitals because the computed ionization energies 11.332 eV (OVGF) for $15a_1$ and 11.480 eV (OVGF) for $5a_2$ are very close to this PES value and because such a high intensity band could be the result of ionization of the electrons of multiple orbitals.¹⁷ The bands of BrOBr in the high ionization energy region have lower intensity because photoionization cross sections of heavy elements are low for He I radiation,¹⁷ and the broad band usually relates to ionization of the electrons of several orbitals (see Table I).

From the (b) of both Figs. 1 and 2, it is clearly seen that the highest intensity peak at 12.61 eV is the first band of H_2O .¹⁷ The band at 14.74 eV with vibrational spacing

TABLE II. The vibrational frequencies (cm^{-1}) of experiments, calculations, and literature for BrOBr and HOBr. (The three DFT methods are all at the 6-311++G** basis set level.)

Species	This expt	The calculated values			Literature	Assign
		B3P86	B3LYP	B3PW91		
BrOBr	550 ± 60 240 ± 60	526.78	509.73	523.69	533 ^a	Br–O stretch
HOBr	750 ± 60 650 ± 60	626.38	606.03	623.20	620 ^b	Br–O stretch

^aReference 15.

^bReference 20.

$970 \pm 60 \text{ cm}^{-1}$ and a long vibrational progression is the second band of H_2O . The abnormally high intensity of the sixth, seventh, and eighth vibrational peaks of the second band of H_2O is attributed to overlapping with the bands of other species. The remaining four bands at 10.73, 11.56, 14.20, 14.74 are attributed to the PE spectrum of HOBr. The band at the lowest energy 10.73 eV is the first PE band of HOBr because the adiabatic ionization energy at 10.64 eV is in excellent agreement with and thus confirms the reported experimental values 10.617 eV,^{19(a)} 10.638 eV,^{19(b)} and a calculated value 10.65 eV.^{19(c)} The present PES value is equivalent to our G2 calculated value of 10.645 eV and matches well the OVGf value 10.689 (see Table I). The third vibrational peak at 10.82 eV on the first band has the highest intensity because the β peak of HeI radiation for the first band at 12.61 eV of H_2O overlaps on the third vibrational peak of the first band of HOBr. The vibrational spacing $750 \pm 60 \text{ cm}^{-1}$ is larger than the reported value of 620 cm^{-1} (Ref. 20) for the Br–O stretch model of the neutral HOBr molecule (see Table II). This shows that ionization corresponding to the first band is the result of removal of the electron of an antibonding orbital. This is not only consistent with the character of the HOMO $6a''$ in which there has been the contribution of dominant Br and O atoms (see Table I), but also this assignment is further supported by the calculated vibrational frequency 626.38 cm^{-1} (B3P86), 606.03 cm^{-1} (B3LYP), and 623.20 cm^{-1} (B3PW91) for the Br–O stretch model of the HOBr (see Table II).

The band at 11.56 eV with a vibrational spacing of $650 \pm 60 \text{ cm}^{-1}$ is the second PE band of HOBr. It results from ionization of the electron of the $16a'$, because its value matches the computed values of 11.254 eV (OVGF) and 11.804 eV (HF/6-311++G**) (see Table I). The band at 12.61 eV is the first band of H_2O , because the PE spectrum of HOBr is obtained under condition of H_2O existence for reaction (2). In fact, the bands of H_2O are also used as a calibration for the PE spectrum of the new species.

The bands in the high ionization energy region ($>13.50 \text{ eV}$) are the overlapping bands of HOBr and H_2O . A clear shoulder at 14.20 eV is designated as the third band of HOBr, because there is no band of H_2O in this region.¹⁷ This band corresponds to ionization of the electron of the $15a'$ (20) orbital. An obvious high intensity band at 14.74 eV is the result of overlapping of the bands of both HOBr and H_2O because the band centered near 14.74 eV of H_2O should have a symmetrical shape, the same as with its low ioniza-

tion energy side.¹⁷ That is, the PE spectrum of HOBr consists of at least four bands at 10.73, 11.56, 14.20, and 14.74 eV.

The (c) of both Figs. 1 and 2 are PE spectra of a mixture of BrOBr and HOBr which were synthesized without removing moisture from bromine. It further demonstrates that the (a) of Figs. 1 and 2 are the PE spectra of pure BrOBr and the (b) of Figs. 1 and 2 are the PE spectra of pure HOBr.

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