Boron Dibromide and Boron Diiodide Ground State Neutral and Cation. Use of Effective Core Potentials Combined with *ab Initio* and Density Functional Theory

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Received: August 8, 1996; In Final Form: November 15, 1996[⊗]

All-electron and effective core potential (ECP) calculations have been performed on boron dibromide and its cation. These calculations have allowed the determination of a reliable ECP method, which was subsequently used to perform calculations on boron diiodide and its cation. Density functional calculations were then performed using ECPs: this combined approach was found to be an inexpensive way of obtaining reliable results. The results of these methods were then used to calculate ionization energies of these species. The adiabatic ionization energy of each species is calculated to be 6.95 eV (BBr_2) and 6.61 eV (BI_2) using ECP methods. For BBr_2 the adiabatic energy was also calculated using all-electron methods, which showed that the ECP methods were reliable. The expected appearance of the photoelectron spectra of these species is briefly discussed.

I. Introduction

BBr_2 was first identified in argon matrices by Miller and Andrews[1] by radiolysis and ultraviolet photolysis of BBr_3. Two main infrared absorptions were observed for $^{11}BBr_2$: one at 597 cm^{-1} and one at 833 cm^{-1}, the former was assigned to the totally symmetric stretch ν_1 mode and the latter to the antisymmetric stretch ν_3 mode. Isotopic absorptions allowed a lower bound on the bond angle of 116 ± 5° to be derived; consideration of other similar molecules allowed a further estimate of 125 ± 5° to be made. Some time later, Moroz and Sweany[2] observed BBr_2 in argon matrices by photolysis of BBr_3/H_2 mixtures. A band at 833 cm^{-1} was also observed, similar to that seen by Miller and Andrews,[1] and a weak band at 551 cm^{-1}, which was assigned to the symmetric stretch. The band seen at 597 cm^{-1} by Miller and Andrews was also seen by Moroz and Sweany, but assigned to $HBBr_2$. BBr_2 was also observed by Hassanzadeh and Andrews[3] in argon matrices in the reaction of halogens with laser-ablated boron. In the latter work, only the 833 cm^{-1} vibration of $^{11}BBr_2$ was observed. The JANAF tables[4] contain estimated geometric parameters, with a bond angle of 120° (taken as being the same as the tribromide) and a bond length of 1.87 Å (taken to be in between the bond lengths of BBr and BBr_3). Vibrational frequencies were also estimated[4] by taking the force constants of BBr_2 to be the same as those of BBr_3: this gave values of 600, 150, and 830 cm^{-1} for ν_1, ν_2, and ν_3, respectively. Finally, dispersed fluorescence spectra originating from the photoionization of BBr_3 using synchrotron radiation were assigned[5] to transitions to the ground electronic state of BBr_2. In principle, dispersed fluorescence spectra give information on the vibrational frequencies of the lower electronic state; however, the spectra obtained in ref 5 were broad and unresolved and therefore no vibrational information could be obtained. In that work, a broad emission was also attributed to BBr_2^+.

BI_2 was observed by Hassanzadeh and Andrews[3] from the reaction of I_2 with laser-ablated boron atoms. Infrared absorptions were observed in the range 736−745.5 cm^{-1} and assigned to the asymmetric stretch vibration ν_3. Isotopic data allowed a lower limit of the bond angle of 105 ± 6° to be obtained.

The present work follows on from a similar study on BCl_2, where the geometries and vibrational frequencies were calculated using *ab initio* methods.[6] Additionally, in that work, the ionization energy of BCl_2 was calculated at the G2 level of theory, and calculations were performed to obtain a qualitative picture of the excited states of both BCl_2 and BCl_2^+. In the present work, owing to the number of electrons in the title species, especially BI_2 and BI_2^+, effective core potentials (ECPs) are employed; however, these are first checked for reliability by performing all-electron calculations on BBr_2, so that a comparison with the ECP calculations can be made. Additionally, since, even with ECPs, methods such as CCSD(T) become very expensive, the combination of density functional theory and effective core potentials was used. The ionization energies of BBr_2 and BI_2 were also calculated: there appear to be no reported values, measured or estimated, for these two species in the literature.

II. Theoretical Details

For the all-electron calculations on BBr_2, the 6-311G* basis set was used as the basic basis set, and further calculations were performed with the 6-311+G* basis set.[7,8] These calculations employed Møller−Plesset perturbation theory[9] to second order (MP2). Density functional theory, in the form of BLYP and B3LYP calculations, were also performed employing the two basis sets mentioned above and also the 6-311+G(3df) basis set. The BLYP method employs the Becke exchange functional[10] together with the Lee, Yang, and Parr (LYP) correlation functional.[11] The B3LYP method[12] uses a hybrid functional, which includes some Hartree−Fock exchange energy.

For the effective core potential (ECP) calculations on BBr_2, the LANL2DZ basis set was used, which, for second-row elements and above, is of double-ζ quality for the valence shells[13]—note that the LANL2DZ acronym implies the used of the Dunning double-ζ (D95) basis set[14] on the first-row elements. To this were added diffuse (sp) (denoted by '+') and d polarization functions. For boron, the first sp function was the standard function from a 6-31+G* basis set, while the second set had an exponent of 0.01; use of a set of two diffuse sp functions on each atom is denoted by '++'. The sets of d, 2d, 3d, and f functions also came from a standard source.[15] For bromine and iodine, the most diffuse sp function had an

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S1089-5639(96)02413-9 CCC: $14.00

TABLE 1: Calculated Geometries and Vibrational Frequencies of BBr_2

level	R/Å	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
MP2/6-311G	1.9186	128.3	527.1	183.8	831.5
MP2/6-311G*	1.8861	126.4	577.7	182.1	879.9
MP2/6-311+G*	1.8861	126.4	575.5	182.3	879.1
BLYP/6-311G*	1.9149	126.5	523.1	169.8	786.4
B3LYP/6-311G*	1.8982	126.6	543.5	175.4	824.4
B3LYP/6-311+G*	1.8974	126.6	541.4	175.3	825.4
B3LYP/6-311+G(3df)	1.8905	126.9	537.7	175.1	827.3
MP2/LANL2DZ	1.9550	127.6	507.1	170.5	794.7
MP2/LANL2DZ+(d)	1.8952	126.6	573.2	180.8	879.7
MP2/LANL2DZ+(2d)	1.8968	127.0	554.7	176.2	858.1
MP2/LANL2DZ++(2d)	1.8965	127.0	553.5	176.2	858.0
B3LYP/LANL2DZ+(2d)	1.9058	126.7	530.6	169.5	823.8
B3LYP/LANL2D++(2d)	1.9055	126.7	529.7	169.6	823.9
CCSD(T)/LANL2DZ+(2d)	1.9068	127.3	538.3	172.5	839.6

TABLE 2: Calculated Geometries and Vibrational Frequencies of BBr_2^+

level	R/Å	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
MP2/6-311G	1.7820	180	323.4	200.6	1231.9
MP2/6-311G*	1.7673	180	345.4	276.1	1293.6
MP2/6-311+G*	1.7682	180	345.0	271.5	1291.4
BLYP/6-311G*	1.7842	180	322.5	261.7	1219.4
B3LYP/6-311G*	1.7717	180	332.7	271.0	1252.3
B3LYP/6-311+G*	1.7717	180	332.7	268.7	1252.3
B3LYP/6-311+G(3df)	1.7682	180	332.0	273.8	1246.9
MP2/LANL2DZ	1.8072	180	314.3	279.0	1212.8
MP2/LANL2DZ+(d)	1.7761	180	344.2	277.1	1285.6
MP2/LANL2DZ+(2d)	1.7823	180	327.5	271.4	1231.4
MP2/LANL2DZ++(2d)	1.7788	180	337.6	285.9	1251.9
B3LYP/LANL2DZ+(2d)	1.7825	180	327.4	271.6	1230.9
B3LYP/LANL2DZ++(2d)	1.7822	180	327.8	272.6	1231.4
CCSD(T)/LANL2DZ+(2d)	1.7872	180	328.2	281.1	1220.6

exponent of 0.027, which was a factor of 5 smaller than the lowest p function exponent in the LANL2DZ basis set—this choice follows that of Chattaray and Schleyer;[16] when two diffuse functions were used, the second had an exponent of 0.0055, one-fifth of the 0.027 diffuse functions. The d and f functions for bromine and iodine are taken from Schwerdtfeger *et al*.[17] and Glukhovtsev *et al*.[18] and the exponents were as follows: for bromine, 1 d (0.389), 2 d (0.8, 0.2), and 3 d (0.13, 0.39, 1.17), 1 f (0.59); for iodine: 1 d (0.266), 2 d (0.2, 0.5), 3 d (0.133, 0.266, 0.532), and 1 f (0.434). In addition to MP2 and B3LYP calculations using ECP basis sets, CCSD(T)[19] calculations were also employed using some of these ECP basis sets.

All calculations employed the *Gaussian 94* suite of programs.[20] Note that, in the MP2 and CCSD(T) calculations, the frozen core approximation was used. For the open-shell, neutral species, unrestricted wave functions were used; however, in all cases $\langle S^2 \rangle$ was ≤ 0.76, showing that spin contamination was small.

III. Results and Discussion

(a) Geometries and Vibrational Frequencies. *Boron Dibromide Neutral and Cation*. The results from the various levels of calculation for BBr_2 are given in Table 1. In all cases the calculated equilibrium bond angle is greater than 120° as would be expected, owing to the lessened repulsive interactions between the halide atoms in BX_2 molecules *vs* BX_3 molecules; the angle is similarly greater than 120° for BCl_2.[6] The all-electron calculations at the MP2 level indicate that the diffuse function is not very important in the determination of the molecular geometry nor the vibrational frequencies. On the other hand, going from 6-311G to 6-311G* shows that the addition of polarization functions makes significant differences to all calculated properties, except perhaps to the bond angle, which seems to be reliably calculated at all levels of theory. It is unfortunate that there is so little experimental data available for comparison with the calculated geometries; however, there are experimental values for the symmetric and asymmetric stretch vibrational frequencies. Miller and Andrews[1] obtain a value of 833 cm^{-1} for the asymmetric stretch, which was confirmed by Moroz and Sweany[2] and Hassanzadeh and Andrews.[3] The all-electron calculated values at the MP2 level are in rather poor agreement with this value, as is the BLYP/6-311G* value. The B3LYP method can be seen to be performing very well, however, with the largest basis set 6-311+G(3df) being in excellent agreement with experiment, especially considering that the experimental value is a fundamental and that the calculated value is a harmonic frequency. Similar behavior is obtained for the symmetric stretch, which has an experimental fundamental frequency of 551 cm^{-1} (ref 2); the agreement is not quite so good, although reasonable. The good behavior of the B3LYP method, with relatively large basis sets, has been noted previously by Bauschlicher and Partridge[21] and Martin *et al*.[22]

Turning now to the ECP results, it can be seen that these all predict slightly longer bond lengths than the all-electron methods, with the bond angle being very slightly larger (although, with the different basis sets used, it is difficult to compare these directly). As with the all-electron methods, the diffuse sp functions seem to be having very little effect, but the d polarization functions are very important for obtaining reliable results. It appears that the addition of one diffuse sp set and two d functions allows reliable results to be obtained, with the sp set being of minor importance. MP2 and B3LYP calculations with this LANL2DZ+(2d) basis set showed reasonable agreement with experiment, with the MP2 method giving very good agreement for ν_1, but not ν_3, and *vice versa* for the B3LYP method. A calculation using this basis set at the CCSD(T) level gave slightly better agreement with experiment when both vibrational modes were considered. Comparison with the approximate values from the JANAF tables[4] (*vide supra*) shows that these were fairly accurate estimates.

The results for the cation are shown in Table 2, and in all cases the equilibrium geometry is linear (which was assumed in most cases, but is confirmed by the three real frequencies). Again the addition of d polarization functions to the basis set is important, with the addition of sp diffuse function being very much less so. The MP2 frequencies are again significantly different from the B3LYP values, and if the neutral results are indicative, the B3LYP results will be the most reliable. The B3LYP/6-311+G(3df) results are in excellent agreement with the CCSD(T) calculation with the LANL2DZ+(2d) basis set.

Boron Diiodide Neutral and Cation. Consideration of the values in Tables 1 and 2 shows that the LANL2DZ basis set, when augmented by one sp diffuse set and two sets of polarization functions, performs as well as the 6-311+G(3df) basis set at the B3LYP level for boron dibromide, as indicated by their good agreement with experimental values. Thus, calculations were performed on BI_2 and BI_2^+ using the LANL2DZ basis set, augmented with a set of diffuse sp functions, and one or two sets of d functions. The results of these calculations are shown in Tables 3 and 4. The geometry of the neutral (Table 3) may be seen to have a bond angle of about 129°, which follows a trend of increasing bond angle on going from BCl_2 to BI_2. The bond length is also longer than that in BBr_2, as expected. The only experimental vibrational frequency available for comparison is the value of the asymmetric stretch, measured by Hassanzadeh and Andrews[3] of 736–745.5 cm^{-1}. The results show that the MP2 level is not

TABLE 3: Calculated Geometries and Vibrational Frequencies of BI_2

level	R/Å	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
MP2/LANL2DZ+(d)	2.0974	128.7	461.5	125.8	771.4
MP2/LANL2DZ+(2d)	2.0967	129.1	454.3	125.4	769.2
B3LYP/LANL2DZ+(d)	2.1093	129.3	429.3	119.8	736.1
B3LYP/LANL2DZ+(2d)	2.1086	128.8	431.0	118.8	734.1
CCSD(T)/LANL2DZ+(2d)	2.1098	129.5	436.6	122.1	751.0

TABLE 4: Calculated Geometries and Vibrational Frequencies of BI_2^+

level	R/Å	θ/deg	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
MP2/LANL2DZ+(d)	1.9707	180	239.3	237.4	1110.7
MP2/LANL2DZ+(2d)	1.9736	180	235.0	225.9	1089.4
B3LYP/LANL2DZ+(d)	1.9780	180	228.4	226.9	1076.5
B3LYP/LANL2DZ+(2d)	1.9796	180	225.7	224.3	1069.6
CCSD(T)/LANL2DZ+(2d)	1.9867	180	225.3	218.8	1051.0

TABLE 5: Calculated Adiabatic Ionization Energies (eV) of BBr_2 and BI_2. Values in Parentheses have been Corrected for ZPVE

level	BBr_2	BI_2
MP2/LANL2DZ+(2d)	6.874 (6.906)	6.539 (6.565)
B3LYP/LANL2DZ+(2d)	7.217 (7.253)	6.884 (6.913)
CCSD(T)/LANL2DZ+(2d)	6.924 (6.959)	6.577 (6.602)
CCSD(T)/LANL2DZ+(3df)[a]	6.929 (6.964)	6.596 (6.621)

[a] Single-point energy calculation at CCSD(T)/LANL2DZ+(2d)-optimized geometry. See text for details. The correction for the ZPVE was calculated using the CCSD(T)/LANL2DZ+(2d) vibrational frequencies (remembering that the linear cations have a doubly degenerate bending vibration).

performing very well, but the B3LYP method and the CCSD(T) method both give good agreement with the experimental value. Any further comparisons, especially with respect to the cations, will have to await more experimental data.

In passing, it is worth noting that the linearity of the cations of these complexes is to be expected, as they are isoelectronic with Group 2 halides. These have the trend[23] that the light Group 2 metals form linear molecules with all of the halides; however, the structures become bent as the metal atom becomes heavier. Thus, since boron dihalide cations are isoelectronic with the beryllium dihalide molecules, a linear equilibrium structure is to be expected.

(b) Ionization Energies. The difference between the calculated energies of the neutral and cation at their respective equilibrium geometries, corrected for the zero-point vibrational energy (ZPVE), gives the adiabatic ionization energy (AIE). The VIE was also calculated; however, it is not obvious how to correct the VIE for zero-point energy, and therefore no correction has been made.

Boron Dibromide. The adiabatic ionization energies for BBr_2 have been calculated at the MP2/LANL2DZ+(2d), B3LYP/LANL2DZ+(2d), and CCSD(T)/LANL2DZ+(2d) levels of theory, and the results are given in Table 5. Inclusion of ZPVE increases the values slightly. Additionally, a further single-point energy calculation was performed at the CCSD(T) level for both the cation and the neutral, employing a LANL2DZ+(3df) basis set. This calculation was performed at the CCSD(T)/LANL2DZ+(2d)-optimized geometry; correction for ZPVE was achieved by taking the frequencies from the CCSD(T)/LANL2DZ+(2d) calculation. A further calculation on the cation at the geometry of the neutral with the larger basis set gave a vertical ionization energy of 8.295 eV (no correction for ZPVE has been made to this value).

As a test of the reliability of the ECP basis sets for calculating accurate ionization energies, all-electron calculations were performed. These were CCSD(T)/6311+G(3df) single-point energy calculations at the respective MP2/6-311+G* optimized geometries of the neutral and the cation. An AIE of 7.047 eV and a VIE of 8.331 eV, where no account of ZPVE has been taken, were obtained. It may be seen that this result is only *ca.* 0.1 eV away from the best ECP result (Table 5), showing that the ECP methodology is valid.

Boron Diiodide. The adiabatic ionization energy for this species has also been obtained at the MP2/LANL2DZ+(2d), B3LYP/LANL2DZ+(2d), and CCSD(T)/LANL2DZ+(2d) levels of theory; the results are given in Table 5. These values increase slightly, as for BBr_2, when ZPVE is included. As for BBr_2, the extra single-point energy calculations were performed using the LANL2DZ+(3df) basis set (again, ZPVE was calculated using CCSD(T)/LANL2DZ+(2d) vibrational frequencies). The VIE was calculated to be 7.710 eV, where no account of ZPVE has been taken.

Discussion of Ionization Energies. It may be seen that the ionization energies of BBr_2 and BI_2 are quite low and that there is a very large difference between the AIE and the VIE. Looking at Tables 1−4, it may be seen that the major geometry change upon ionization for these two species is in the bond angle, which changes from 125−130° to 180°; the change in the bond length is not insignificant either, with a shortening of just over 0.1 Å upon ionization. Thus, it is to be expected that a photoelectron spectrum of these species would consist of a long progression in the ν_2 mode, with contributions from the ν_1 mode. The photoelectron spectra would be extremely complicated, however, as the ν_1 and ν_2 modes of BBr_2^+ have very similar vibrational frequencies; these are almost identical in the case of BI_2^+. With the limited resolution of conventional photoelectron spectroscopy, the spectrum would probably appear only partially resolved—higher resolution, laser-based methods would be required in order to be able to pick out the separate components of each progression.

(c) Relativistic and Spin−Orbit Effects. An extension of the G2 method has been formulated by Glukhovtsev *et al.* in order to study bromine- and iodine-containing molecules.[18] In that work, they compared results using relativistic and nonrelativistic ECPs and nonrelativistic all-electron calculations. Their conclusion was that relativistic effects were not affecting the calculated properties, and of particular relevance to the present paper is that ionization energies were not sensitive to relativistic effects. Thus, it is unlikely that relativistic effects are very important here for the calculation of the ionization energies. As it happens, the 6-311G basis set and the ECP potential for bromine are both nonrelativistic, whereas the iodine ECP has relativistic effects included.

With regard to the geometry, Pyykkö[24] has summarized the effects of relativity on molecular geometries and the trend is for bond lengths to get shorter when relativistic effects are included. Thus, the calculated boron dibromide bond lengths may be slightly too long, although relativistic effects should not be of too much importance. The effect of relativity on bond angles is not yet known.[24] Spin−orbit coupling has been shown to be important for bromine- and iodine-containing compounds,[18] but for the compounds considered here, the neutral state is bent, and the linear cationic state is not electronically degenerate, and so this effect is not present.

IV. Conclusions

Effective core potentials have been used to investigate the ground state neutrals and cations of boron dibromide and boron diiodide. The results of all-electron calculations were compared to those from ECP calculations for boron dibromide, and it was found that the LANL2DZ+(2d) basis set appeared to give reliable results. Calculations were then performed on boron diiodide using only ECP methods. For both species, ECPs were used with the B3LYP density functional methods, and this combined approach was found to be an inexpensive way of obtaining accurate results. The agreement with experiment was similar for the CCSD(T) and B3LYP calculations using the LANL2DZ+(2d) basis set. The ionization energies of BBr_2 and BI_2 were calculated; these are quite low, and follow a trend of decreasing ionization energy as the halide gets heavier. The photoelectron spectrum was expected to be very rich in structure, owing to the large geometry changes that accompany ionization; however, it was doubted whether conventional photoelectron spectroscopy would be clearly able to resolve this structure.

Acknowledgments. We thank the EPSRC (U.K.) for the provision of computer time. T.G.W. is grateful to the Lloyd's of London Tercentenary Foundation for the Award of a Fellowship.

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