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Study of the Ionization Process $BF^+(X\ ^2\Sigma^+) \leftarrow BF(X\ ^1\Sigma^+)$ by High-temperature Photoelectron Spectroscopy

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The He I photoelectron spectrum of the BF molecule, produced by passing BF_3 over heated boron, has been recorded. Only one band was observed and it was assigned to the ionization $BF^+(X\ ^2\Sigma^+) \leftarrow BF(X\ ^1\Sigma^+)$. For this band the adiabatic and vertical ionization potentials were coincident at 11.12 ± 0.01 eV and analysis of the observed vibrational structure gave $\bar{w}_e = 1765 \pm 20\ \mathrm{cm}^{-1}$ and $r_e = 1.208 \pm 0.005$ Å for the $BF^+(X\ ^2\Sigma^+)$ state. Estimates of the first and higher vertical ionization potentials of BF are made by *ab initio* ΔSCF and Hartree–Fock–Slater calculations.

Although the vacuum ultraviolet photoelectron spectra of a number of Group III monohalides have been recorded in the vapour phase,[1–8] boron monofluoride, the lightest member of this group, has not previously been investigated with this technique. Nevertheless, photoelectron spectra recorded for some Group III monohalides (TlF, TlX and InX, where X = Cl, Br, I) indicate that an ionic rather than a covalent approach is more appropriate in describing the electronic structure in these molecules. In the case of BF it is therefore expected that an essentially ionic picture would also be more suitable in analysing the photoelectron spectrum. This is in contrast to the isoelectronic molecules CO and N_2 which can be adequately treated in terms of a covalent model.

BF has been studied using a range of spectroscopic techniques.[9–15] Analyses of its emission and absorption electronic spectra gave spectroscopic constants for the electronic ground state as well as many excited states of the neutral molecule. The majority of these excited states could be fitted to Rydberg series, thus allowing an estimate of the first ionization potential (i.p.) of BF to be made.[9,10] The value obtained, 11.115 ± 0.004 eV, compares well with the value, 11.06 ± 0.10 eV, determined by electron impact mass spectrometry.[16] From measurements made on a number of Rydberg states of BF, the 0–1 vibrational separation and the equilibrium bond length, r_e, in $BF^+(X\ ^2\Sigma^+)$ have been estimated as 1680 cm^{-1} and 1.21 Å, respectively.[9] However, despite these estimates no direct spectroscopic measurements have been made on the BF^+ ion. In view of this, it was decided to use photoelectron spectroscopy (p.e.s.) to redetermine the first ionization potential of BF and to characterize the observed ionic states.

EXPERIMENTAL

Previous spectroscopic investigations of BF have usually generated this molecule in the gas phase *via* either a flash discharge or microwave discharge of flowing BF_3. However, both of these methods produce relatively low yields of BF and it was anticipated at the outset of this work that a more efficient way of producing BF in the gas phase would be required in order to study this molecule by photoelectron spectroscopy. Timms, in his pioneering work on the reactions of high-temperature species,[17] has shown that gaseous BF_3 reacts with solid boron at *ca.* 2100 K to produce BF in *ca.* 85% yield and it was this relatively high-yield route which was chosen in the present study.

In this work, solid boron was heated in a graphite furnace of similar design to that used previously.[18,19] Boron trifluoride diluted in helium was passed through the furnace, which was positioned *ca.* 5 cm above the ionization point of the photoelectron spectrometer. Spectra attributable to BF were recorded at furnace temperatures in the range 1900–2200 K, estimated by focussing a calibrated optical pyrometer on the hottest part of the furnace.

The photoelectron spectrometer and inductively heated furnace used in this study have both been described previously.[18,20] For the conditions under which BF was observed, the usual resolution was 30–35 meV (f.w.h.m.), as measured for argon ionized by He I radiation. Spectra were calibrated using methyl iodide, ethyl bromide, argon and carbon monoxide.

COMPUTATIONAL DETAILS

Hartree–Fock and Hartree–Fock–Slater (HFS) calculations were performed in order to predict the vertical ionization potentials of the bands expected in the He I (21.22 eV) photoelectron spectrum of BF.

The electronic ground-state configuration of $BF(X\ ^1\Sigma^+)$ may be written as $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2$, and from the known photoelectron spectra of CO and N_2, only three bands are expected for BF in the He I region, corresponding to the $(5\sigma)^{-1}$, $(1\pi)^{-1}$ and $(4\sigma)^{-1}$ ionizations. For the BF^+ states produced by these one-electron ionizations, ΔSCF vertical ionization potentials have been predicted by performing Hartree–Fock SCF calculations using the ATMOL 3 suite of programs[21] for both the neutral molecule and the three ionic states under consideration. All calculations were performed at the experimental equilibrium bond length of $BF(X\ ^1\Sigma^+)$ of 1.2626 Å.[9,12] The basis set used in these *ab initio* calculations was an STO double-zeta basis taken from those of Clementi[22] with added polarization functions [the exponents used were B 3*d* (2.30) and F 3*d* (2.01)]. Also, the semi-empirical method of Liu and Verhaegen[23] was used to estimate the correlation energy differences between the neutral molecule and the ionic states under consideration and these values allowed corrected ΔSCF vertical ionization potentials of BF to be obtained.

Calculations have also been performed using the Hartree–Fock–Slater LCAO method.[24,25] In this approach the non-local exchange potential occurring in the Hartree–Fock equations is replaced by the local $X\alpha$ exchange potential proposed by Slater containing a single adjustable parameter α.[26] In this present study α was always kept constant at a value of 0.7.[25] Basis sets used were of triple-zeta quality with the atomic cores kept frozen. For boron and fluorine the outermost 2*s* and 2*p* orbitals were treated as valence with the 1*s* orbitals treated as core. Vertical ionization potentials were estimated by Slater's transition-state method,[27] which to a large extent includes relaxation effects by removing half an electron from the orbital out of which ionization takes place. The results obtained from these HFS calculations and the *ab initio* ΔSCF calculations are summarised in table 1.

In order to estimate the vibrational band envelope in the first band of the photoelectron spectrum of BF, use was made of the computed *ab initio* potential energy curves for $BF(X\ ^1\Sigma^+)$ and $BF^+(X\ ^2\Sigma^+)$. The procedure involved computing wavefunctions and SCF total energies for each state at five points within ±0.2 Å of the potential-energy minimum and fitting the energy points obtained to a fourth-order polynomial in $(r - r_e)$. This led to the predicted values shown in table 2 for r_e and $\bar{w}_e$ in $BF(X\ ^1\Sigma^+)$ and $BF^+(X\ ^2\Sigma^+)$. As expected for a calculation of this type,[29] comparison of the computed $BF(X\ ^1\Sigma^+)$ values with those known experimentally[9,12] shows that the computed $\bar{w}_e$ values are somewhat high, whereas the computed r_e values are slightly low.

TABLE 1.—COMPUTED VERTICAL IONIZATION POTENTIALS (eV) OF BF($X\ ^1\Sigma^+$)[a]

			ref. (28)		this work			
orbital ionized	ionic state	HFS transition state	Koopmans' theorem v.i.p.	ΔSCF v.i.p.	Koopmans' theorem v.i.p.	ΔSCF v.i.p.	ΔSCF plus correlation correction	experimental value
5σ	$X\ ^2\Sigma^+$	10.99	11.00	10.09	10.99	10.08	11.82	11.12
1π	$^2\Pi$	18.94	20.25	16.76	20.28	17.23	19.09	—
4σ	$^2\Sigma^+$	21.75	23.23	—	23.23	20.49	22.43	—

[a] All calculations were performed at the equilibrium bond length of BF($X\ ^1\Sigma^+$) of 1.2626 Å.[9,12]

TABLE 2.—EXPERIMENTAL AND CALCULATED SPECTROSCOPIC CONSTANTS FOR $BF(X\ ^1\Sigma^+)$ AND $BF^+(X\ ^2\Sigma^+)$

	$BF(X\ ^1\Sigma^+)$		$BF^+(X\ ^2\Sigma^+)$	
	experimental[a]	calculated[b]	experimental,[c] this work	calculated[b]
equilibrium bond length, r_e/Å	1.2626	1.2452	1.208±0.005	1.1987
vibrational frequency, $\bar{w}_e$/cm^{-1}	1402.1	1538	1765±20	1802
anharmonicity, $\bar{w}_e x_e$/cm^{-1}	11.84	12.4	—	10.7

[a] See ref. (9) and (12). [b] This work; see text for details. [c] Obtained from analysis of the first band observed in the photoelectron spectrum of BF; see text for details.

The computed parameters shown in table 2 were used to calculate the corresponding photoelectron band envelope. The procedure for each state involved using the parameters r_e, $\bar{w}_e$ and $\bar{w}_e x_e$ to construct a Morse potential and then determining the vibrational wavefunctions by solving the radial Schrödinger equation. The Franck–Condon factors obtained in this way for ionization from the $v'' = 0$ vibrational level of $BF(X\ ^1\Sigma^+)$ to the $v' = 0$, 1 and 2 vibrational levels of $BF^+(X\ ^2\Sigma^+)$ were 1.00, 0.39 and 0.07. Although this procedure neglects the effects of electron correlation, it was anticipated that these values would be useful in identifying the first band arising from ionization of $BF(X\ ^1\Sigma^+)$ in the experimental photoelectron spectrum.

Ab initio calculations over a wide range of bond lengths have also been performed for the $BF^+(A\ ^2\Pi)$ state obtained formally by the $(1\pi)^{-1}$ ionization from $BF(X\ ^1\Sigma^+)$. The potential-energy curve obtained was dissociative, in agreement with a similar study performed by Nesbet,[20,31] who also failed to obtain an energy minimum in the calculated potential-energy curve. The second band in the photoelectron spectrum of BF is therefore expected to be broad and structureless. This is supported by some calculations on the vibrational structure in the photoelectron spectrum of BF using a Green's function method, where it is expected that the equilibrium geometry changes due to ionization from the 1π and 4σ orbitals in BF will be considerable, and may lead to dissociative behaviour in these ions.[32] Broad bands corresponding to the $(1\pi)^{-1}$ and $(4\sigma)^{-1}$ ionizations have also been predicted by a more approximate method based on calculating observed spectra from vertical ionization potentials derived by perturbation corrections to Koopmans' theorem.[33]

RESULTS AND DISCUSSION

The He I photoelectron spectrum recorded for BF_3 passed over heated boron is shown in fig. 1. Bands attributable to BF_3[34,35] were observed in this spectrum as well as a weak band arising from carbon monoxide which is produced from a reaction between the alumina insulating ceramic and graphite. However, one extra band was observed in the 11.0–12.0 eV ionization energy region and an expanded

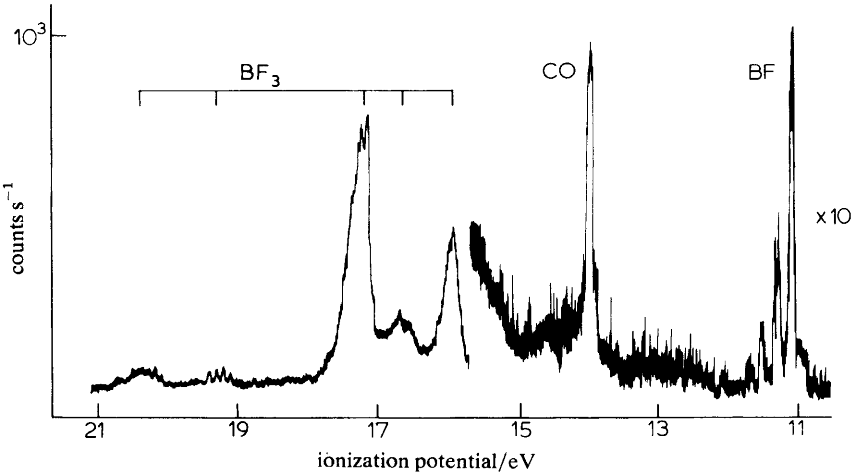

FIG. 1.—He I photoelectron spectrum recorded for BF_3 passed over heated boron at 2100 K.

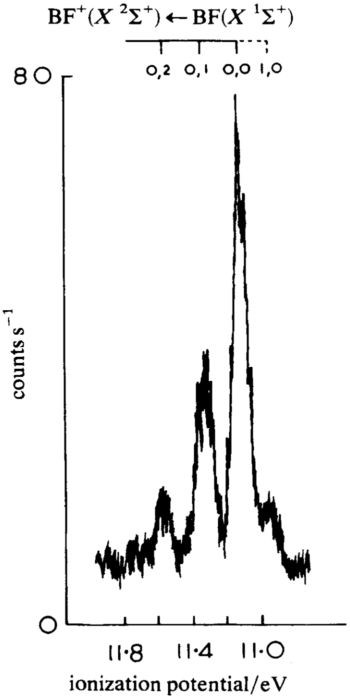

FIG. 2.—Band assigned to the $BF^+(X\ ^2\Sigma^+) \leftarrow BF(X\ ^1\Sigma^+)$ ionization.

scan of this part of the spectrum is shown in fig. 2. Three vibrational components were clearly visible in this band, with the adiabatic component being the most intense at 11.12 ± 0.01 eV. This value is in good agreement with the first adiabatic ionization potential (i.p.) of BF expected from Rydberg-series measurements[9] and from electron impact mass spectrometry.[16] The measured relative intensities of the three vibrational components were 1.0:(0.49 ± 0.07):(0.14 ± 0.04), in good agreement with the band envelope computed in this work of 1.0:0.39:0.07. On the basis of this evidence, as well as the computed vertical ionization potentials shown in table 1, the band at 11.12 eV ionization energy was assigned to the $BF^+(X\ ^2\Sigma^+) \leftarrow BF(X\ ^1\Sigma^+)$ ionization.

Measurement of the observed vibrational separations over a large number of spectra led to an estimate of $\bar{w}_e = 1765 \pm 20\ \text{cm}^{-1}$ in the $BF^+(X\ ^2\Sigma^+)$ state, a value which is significantly larger than the vibrational frequency of $1402\ \text{cm}^{-1}$ in $BF(X\ ^1\Sigma^+)$.[9]

This indicates that removal of a 5σ electron from $BF(X\ ^1\Sigma^+)$ strengthens the bond in the ion. At first sight this is surprising since, in terms of a simple covalent picture, the 5σ molecular orbital is formally bonding and ionization of an electron from this level would lead to a reduction of vibrational frequency in the ion, as observed in nitrogen. However, as indicated earlier, an ionic model is more appropriate in interpreting the photoelectron spectra of the Group III monohalides. Inspection of the results of our *ab initio* calculations shows that the first ionization potential of BF corresponds to an essentially B $2s$ ionization with a charge density change on ionization of

$$\overset{+0.46}{\mathrm{B}} - \overset{-0.46}{\mathrm{F}} \rightarrow \overset{+1.38}{\mathrm{B}} - \overset{-0.38}{\mathrm{F}}\ .$$

Clearly such a charge density change will lead to a strengthening of the ionic bond and a corresponding increase in vibrational frequency in the ion over that in the ground state of the neutral molecule. This increase in vibrational frequency on ionization has been reasonably well predicted by the *ab initio* calculations described earlier (table 2).

The relative intensities of the vibrational components in the first band of BF can also be used to estimate the equilibrium bond length, r_e, in $BF^+(X\ ^2\Sigma^+)$. The method adopted has been outlined elsewhere.[20] In brief, a Morse potential (as determined by the parameters r_e, $\bar{w}_e$ and $\bar{w}_e x_e$) was assumed for both the molecule and the ion and a series of Franck–Condon calculations was made for a range of equilibrium bond lengths in the ion until the experimental and computed vibrational component intensities showed the best fit, as determined by a least-squares procedure. Using this approach, the equilibrium bond length for $BF^+(X\ ^2\Sigma^+)$ was computed as 1.208 ± 0.005 Å, in good agreement with a value of 1.21 Å derived from measurements on a number of Rydberg states of BF. Also, from the observed first adiabatic i.p. of BF, the known dissociation energy, D_e, of $BF(X\ ^1\Sigma^+)$ of 7.90 ± 0.13 eV,[36,37] and the first ionization potential of atomic boron of 8.296 eV,[38] the dissociation energy, D_e, in the $BF^+(X\ ^2\Sigma^+)$ state can be estimated as 5.09 ± 0.14 eV. This value was derived by making the reasonable assumption that $BF^+(X\ ^2\Sigma^+)$ dissociates to $B^+(^1S)$ and $F(^2P)$.

In all the observed spectra, the first band of BF exhibited a weak component on the low ionization energy side of the $v' = 0 \leftarrow v'' = 0$ component and separated from it by $1340 \pm 60\ \text{cm}^{-1}$. As this value is close to the $(v'' = 0)$–$(v'' = 1)$ separation in $BF(X\ ^1\Sigma^+)$ and as the intensity of this component relative to the intensity of the components arising from ionization of $v'' = 0$ increased with increasing furnace temperature and was dependent on carrier-gas pressure, it was assigned to the $BF^+(X\ ^2\Sigma^+, v' = 0) \leftarrow BF(X\ ^1\Sigma^+, v'' = 1)$ ionization. However, for a furnace temperature of 2100 ± 30 K the intensity of this band relative to the other observed components could be maximised and for these conditions the computed Franck–Condon factors obtained with experimental spectroscopic constants for both the molecule and ion could be used to yield an effective vibrational temperature of 1800 ± 100 K. Alternatively, by recording spectra at relatively low furnace temperatures and by changing the inert-gas pressure, the 'hot' band contribution to the first band of BF could be reduced and only spectra in which these contributions were very low, as estimated from the $v'=0 \leftarrow v''=1$ component intensity, were used to estimate the equilibrium bond length in the ion using the Franck–Condon procedure outlined earlier.

A careful search has been made of the ionization energy region above 15.0 eV. However, no bands were observed which were proportional in intensity to the first band of BF. This is not surprising because this region contains several bands arising from BF_3 and, as discussed earlier, the band associated with the $(1\pi)^{-1}$ ionization of BF is expected to be broad and structureless. Also, the band associated with the $(4\sigma)^{-1}$ BF ionization probably lies outside the He I photon-energy range (see table 1).

As only the first band corresponding to the $(5\sigma)^{-1}$ ionization has been observed in the photoelectron spectrum of BF, it is clearly not possible to test the accuracy of the predicted vertical ionization pontentials quoted in table 1 for the bands corresponding to the $(1\pi)^{-1}$ and $(4\sigma)^{-1}$ ionizations. However, table 1 shows that the Koopmans' theorem first vertical i.p., obtained from an *ab initio* calculation near the Hartree–Fock limit,[28] is very close to the experimental value. This implies that for this ionization there is an accidental balance between reorganisation and correlation corrections to the Koopmans' theorem value. The first vertical i.p. of BF obtained by HFS calculations is also in good agreement with the experimental value. As noted previously for CO and N_2,[19,25] this arises because the transition-state approach allows for most of the reorganisation energy between the molecule and the ion and the correlation energy changes on ionization are allowed for, at least partially, within the formulation of the HFS method.

In summary, this work has involved the measurement of the first adiabatic ionization potential of BF and the determination of the parameters r_e, $\bar{w}_e$ and D_e for the $BF^+(X\ ^2\Sigma^+)$ state. The values obtained are in each case in good agreement with the corresponding estimates derived from Rydberg-series measurements. Unfortunately only one band was observed in the photoelectron spectrum of BF but, as indicated by known spectra of thallium and indium monohalides, the heavier Group III monohalides should show at least three bands in their He I photoelectron spectra.

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