The Photoelectron Spectrum of Boron Trifluoride

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Summary Assignment of the high-resolution photoelectron spectrum of BF_3 shows that the highest occupied orbital is of π (e'') type, rather than σ (a_2' or e') as predicted, and that one of the ionic excited states is probably distorted.

THE photoelectron spectra of the three lighter boron trihalides, measured using low-resolution retarding grid spectrometers, have been reported previously.[1,2] We report here the BF_3 spectrum obtained using a 127° cylindrical electrostatic deflection spectrometer. The complete spectrum is shown in Figure 1, where the last two bands are also shown with higher system gain. Five bands are observed, of which the last two appear to be very weak. This weakness is an instrumental effect; the grid analyser spectrum,[1] which gives true relative intensities, shows that the fourth band is of similar intensity to the second, and that the fifth band is of similar intensity to the first. Vibrational fine structure, which appears on the third, fourth, and fifth bands, indicates that the corresponding molecular orbitals in BF_3 have appreciable bonding character. The measured vertical ionisation potentials are 15·94 $\pm$ 0·02, 16·67 $\pm$ 0·01, 17·14 $\pm$ 0·01, 19·10 $\pm$ 0·03, and 20·03 $\pm$ 0·03 ev.

According to the qualitative arguments of Walsh,[4] some calculations[5] by the CNDO/2 approximate SCF MO method, and some very recent accurate calculations,[6] the orbitals which may possibly be observed using 21·22ev photons are $2a_1'$, $2e'$, $1a_2''$, $3e'$, $1a_2'$, $1e''$, where the numbering system ignores all atomic closed-shell electrons. From symmetry, $1a_2'$ (σ) and $1e''$ (π) have no boron orbital components and so are non-bonding between B and F. Qualitative arguments[4] suggest that $3e'$ is also nonbonding but the CNDO/2 calculations show that although these three orbital sets are the highest in energy, within a range of 1·3 ev of each other, $3e'$ has an appreciable ($2\frac{1}{2}$%) boron character. The other three sets of orbitals are predicted to have strong B–F bonding character and to lie at considerably lower energy (higher I.P.); $2a_1'$ and $2e'$ are σ-bonding, between mainly $2p$-orbitals of fluorine and boron $2s$- or $2p$-orbitals, and $1a_2''$ is the π-bonding orbital.

We assume that the band intensities, as indicated by the retarding grid experiments,[1] are roughly proportional to orbital degeneracy,[7] so since the group of orbitals of lowest I.P. is predicted to be $1e''$, $1a_2'$, $3e'$, we assign the weakest band, the second in Figure 1, to $1a_2'$. The first band, like the second, is structureless and fairly sharp, whereas the third band is broader and shows fine structure. The spacing between the components of the third band corresponds to 690 $\pm$ 90 cm^{-1}, and of the four normal vibrations of the BF_3 molecule[8] ($\nu_1(A_1')$ 888 cm^{-1}, ν_2 (A_2'')691 cm^{-1}, $\nu_3(E')$ 1454 cm^{-1}, ν_4 (E') 480 cm^{-1}) this is closely related to ν_1, which is the only totally symmetric vibration, and to ν_2. Since ν_2 is non-totally symmetric, excitation in double quanta is expected,[9] so that the progression must be assigned to ν_1. The reduction in vibrational frequency in the molecular ion indicates some B–F bonding for the corresponding orbital, so this third band can only be assigned to $3e'$, leaving the first band as the $1e''$ orbital. This conclusion, that the highest occupied orbital is of π-type, is at variance with the approximate calculations,[2,3,5] all of which have $3e'$ as the highest orbital, and with the calculation using a large Gaussian basis set,[6] which indicates an orbital sequence $1a_2' > 1e'' > 3e' > 1a_2'' > 2e' > 2a_1'$. We agree with the accurate calculation that $1e'' > 3e'$, but the first band cannot arise from $1a_2'$, both from the intensity and from the fact that the corresponding orbital in BI_3 shows[10] a spin–orbit splitting which is only consistent with $1e''$.

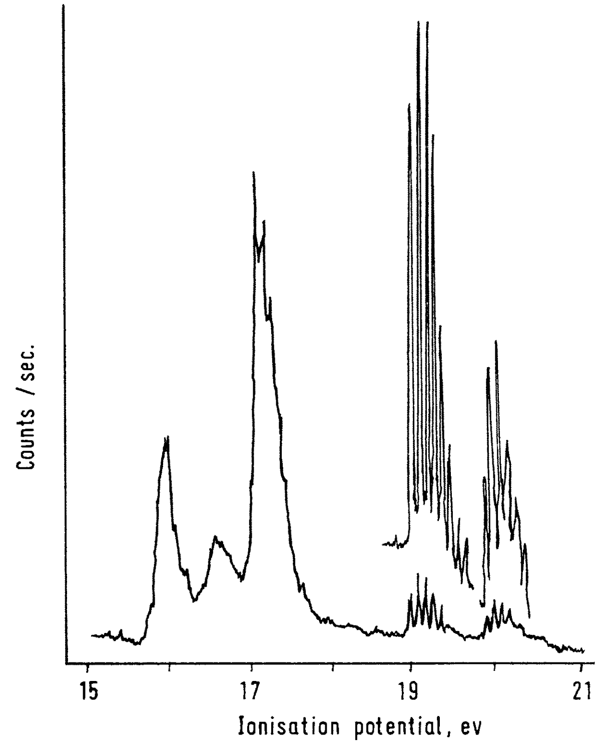

FIGURE 1. *The photoelectron spectrum of boron trifluoride using* HeI(584 Å) *radiation. The last two bands are shown, above the complete spectrum, using a lower count-rate scale on the instrument rate meter.*

The assignment of the fifth band in Figure 1 as arising from $2e'$ follows from its intensity and also from the fine structure which is shown in detail in Figure 2. A long intense vibrational progression is observed, with a spacing of 720 $\pm$ 20 cm^{-1}, showing the strongly bonding character of the orbital. An additional weak progression is also evident, and this corresponds to a frequency of only 660 $\pm$ 30 cm^{-1}. This weaker progression cannot be related to any of the BF_3 frequencies, so we conclude that the corresponding state of BF_3^+ does not have D_{3h} symmetry but is distorted, probably to C_{2v}, so that additional totally symmetric frequencies appear. Such a distortion is likely only as a result of orbital degeneracy in the D_{3h} molecular ion *via* the Jahn–Teller effect, and so the corresponding BF_3

orbital must be $2e'$. Excitation of more than one vibration has been observed in the visible–u.v. spectra of the NO_3 radical and has been assigned[11] to the operation of such a static Jahn–Teller effect, *i.e.* a distortion in which there is a large energy barrier between the equivalent distorted configurations.[12] So far as we are aware this effect has not previously been observed in photoelectron spectra, though the double intensity maxima predicted[13] in the dynamic Jahn–Teller effect (very low energy barrier between equivalent distorted configurations) have been observed in the photoelectron spectra of a number of hydrogen-containing compounds with 3-fold or higher symmetry axes.[7,14,15]

The fourth band must be either $1a_2''$ or $2a_1'$, with the remaining orbital being of higher I.P. than 21 ev. $2a_1'$ is very unlikely to lie above $2e'$, from the smaller number of node planes in $2a_1'$, or alternatively from the lower energy of the boron $2s$-orbital compared to the $2p$-orbital, so we assign the fourth band as the orbital $1a_2''$. This assignment is confirmed by our BCl_3 spectrum, [10] where the $1a_1'$ orbital may be positively identified, because of its sharpness resulting from s–p mixing, and lies 2·2 ev below $2e'$.

The experimental orbital energy sequence, $1e'' > 3a_2' > 3e' > 1a_2'' > 2e' > 2a_1'$, is in agreement with that predicted by the most recent accurate calculations[6] except for the position of $1a_2'$. Though these calculations overestimate the absolute I.P., the addition of 2·3 ev (the difference of calculated and experimental first I.P.) to the eigenvalues brings them very close to coincidence with the experimental I.P.

The energy separation ΔE_π of the π-type orbitals $1e''$, $1a_2''$ provides a measure of the π-stabilisation energy of the molecule; our CNDO/2 calculations indicate that ΔE_π is approximately two-thirds of the "vertical π-reorganisation energy"[15] for BF_3 for a range of values of the π-interaction constant. The ratio of ΔE_π to the vertical π-energy is likely to be rather higher in the heavier halides because the more diffuse orbitals will have smaller Coulomb repulsion integrals. Our values[10] of ΔE_π for the four trihalides are: BF_3 3·1 ev, BCl_3 2·6 ev, BBr_3 2·6 ev, and BI_3 2·0 ev; this sequence follows the predicted sequence of vertical π-reorganisation energies[16] and is the sequence required by the usual explanation[17] of the Lewis-acidity sequence of these molecules; in particular BF_3 has the greatest π-energy stabilisation although the amount of π-back-donation is believed[3] to be smallest for this molecule.

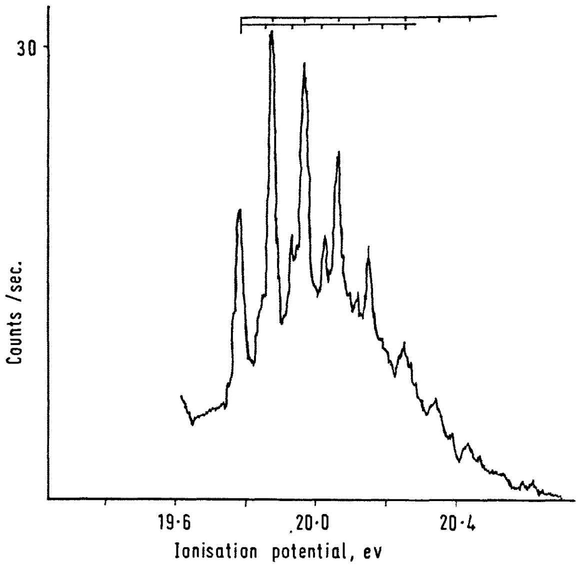

FIGURE 2. *The fifth band in the* BF_3 *spectrum, recorded with a time constant of* 30 *sec., scan speed* 0·010 ev/*min.*

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