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A STUDY OF ALUMINIUM MONOFLUORIDE AND ALUMINIUM TRIFLUORIDE BY HIGH-TEMPERATURE PHOTOELECTRON SPECTROSCOPY

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The HeI photoelectron spectrum of gaseous AlF($X\,^1\Sigma^+$) has been recorded and the first three cationic states have been assigned with the aid of PNO/CEPA calculations. The first band shows vibrational structure and analysis of the component separations and relative intensities leads to values of $\bar{\omega}_e = 1040 \pm 40$ cm^{-1} and $r_e = 1.59 \pm 0.01$ Å in the AlF$^+$($X\,^2\Sigma^+$) state; the corresponding theoretical values are 960 cm^{-1} and 1.60 Å respectively. The first adiabatic ionization potential 9.73 ± 0.01 eV allows a determination of the quantum defect δ in a number of previously observed Rydberg states of AlF. The HeI photoelectron spectrum of gaseous AlF$_3$ has also been obtained. It is assigned on the basis of ab initio molecular orbital calculations and comparison with the corresponding BF$_3$ spectrum.

1. Introduction

As part of our interest in the electronic structure of small molecules produced in the vapour phase by high-temperature pyrolysis [1–5], we have recorded the photoelectron spectra of AlF and AlF$_3$.

Aluminium fluoride has been the subject of a number of previous spectroscopic studies [6–11], probably because it can be produced fairly readily in the vapour phase at only moderately high temperatures (≈ 1000 K) [12,13]. However, although a number of Rydberg states of AlF have been observed [7], no Rydberg series has yet been identified and hence it has not been possible to determine an accurate first ionization potential (IP) of this molecule from optical spectroscopic studies. The only experimental estimates of the first adiabatic IP of AlF come from electron impact mass spectrometry and are consistent with a value of 9.70 ± 0.50 eV [14–16]. In the present work, the photoelectron spectrum of gaseous AlF has been investigated with the aim of providing an improved adiabatic first ionization potential of this molecule. It was also hoped to assign the observed bands with the aid of ab initio quantum mechanical PNO/CEPA calculations, and to determine spectroscopic constants (r_e, $\bar{\omega}_e$, D_e) of the corresponding states of AlF$^+$. As AlF was produced in the vapour phase by heating a stoichiometric mixture of aluminium and aluminium trifluoride, the photoelectron spectrum of AlF$_3$ has also been recorded during the course of this work. It has been assigned by comparison with the well established photoelectron spectrum of BF$_3$ [17–20] and on the basis of ab initio calculations performed for BF$_3$ and AlF$_3$.

2. Experimental

AlF was produced in the vapour phase by heating a stoichiometric mixture of aluminium powder

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and aluminium trifluoride which had previously been intimately mixed and pressed into pellets The pellets were loaded into a graphite furnace which was heated inductively, as has been described earlier [1,21]. The mixture was then slowly warmed to ≈ 500 K to remove any traces of water Once this was achieved, the temperature was slowly raised to 1050 ± 20 K (as measured with a chromel–alumel thermocouple in contact with the furnace) whereupon a photoelectron spectrum was recorded This was attributed to AlF as studies of the vapour composition above Al/AlF_3 mixtures suggest that AlF is the predominant vapour phase species in this temperature range whereas AlF_3 is a minor component [12,13]

The HeI photoelectron spectrum of AlF_3 was recorded by heating solid AlF_3 in a graphite furnace at 1050 ± 20 K. Of the aluminium trihalides, the fluoride appears to be exceptional in that at any given temperature its vapour pressure is several orders of magnitude lower than that of the other halides [22,23] Also, for AlF_3 the dimer concentration is much lower than that of the monomer for all temperatures up to the normal sublimation point In the cases of the other aluminium trihalides, the vapour is predominantly dimeric at the sublimation point [22–24].

The photoelectron spectrometer and inductively heated furnace used in this study have both been described previously [25,26] For the conditions under which AlF and AlF_3 spectra were observed, the usual resolution was 30–35 meV (fwhm), as measured for argon ionized by HeI radiation Spectra were recorded by sweeping the voltage on the hemispheres and calibrated using methyl iodide, carbon monoxide, nitrogen and argon.

3. Computational details

The electronic ground state configuration of AlF($X\,^1\Sigma^+$) may be written as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2$, and at least bands associated with the $(6\sigma)^{-1}$, $(2\pi)^{-1}$ and $(7\sigma)^{-1}$ ionizations are expected in the HeI region.

In the present work the potential energy functions of the $X\,^2\Sigma^+$, $A\,^2\Pi$ and $B\,^2\Sigma^+$ states of AlF^- and the $X\,^1\Sigma^+$ state of AlF have been calculated from highly correlated PNO/CEPA electronic wavefunctions In all calculations on AlF a GTO basis set with 12s, 9p, 2d functions for Al and 10s, 6p, 2d functions for F was employed [27] Only the innermost 5s and 4p functions for Al and 4s and 3p functions for F were contracted The electronic wavefunctions have been calculated by the pseudonatural orbital CI (PNO CI) method [28] In this method singly and doubly substituted configurations with respect to the Hartree–Fock determinant are considered The effect of higher order substitutions is approximately taken into account by the coupled electron pair approximation (CEPA) [28]. In these calculations all valence electrons have been correlated Previous experience with atomic orbital basis sets of similar size as used in the present work, suggests that ≈ 75% of the valence correlation energies have been accounted for in the electronic states considered The vertical ionization potentials and spectro-

Table 1
Computed ionization potentials (eV) of AlF($X\,^1\Sigma^+$) [a]

Orbital ionized	Ionic state	ΔSCF value vertical IP	ΔPNO CEPA vertical IP	Experimental vertical IP
7σ	$X\,^2\Sigma^+$	8.53	9.43	9.73 ± 0.01
2π	$A\,^2\Pi$		13.6–15.0 [b]	13.6–15.2 [c]
6σ	$B\,^2\Sigma^+$	14.69	14.67	13.6–15.2 [c]
–	$(C\,^2\Sigma^+)$	–	–	15.33 eV [d]

[a] From the total energies of the particular states at the theoretical neutral R_e (cf table 2)

[b] Obtained for the classical turning points of $v'' = 0$ in $X\,^1\Sigma^+$ AlF as a vertical cut on the repulsive $A\,^2\Pi$ potential energy functions (cf fig 5)

[c] Experimental range of the second PE band of AlF

[d] See text for tentative assignment of this band

Table 2
Theoretical spectroscopic constants [a] of AlF and AlF^+

States	Method	E [b] (au)	R_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
$AlF(X\,^1\Sigma^+)$	RHF	−341.47193	1.641	0.561	0.004	838	5
	PNO/CEPA	−341.72686	1.663	0.546	0.004	804	4.3
	exp. [c]		1.6543	0.5524	0.00498	802.26	4.77
$AlF^+(X\,^2\Sigma^+)$	RHF	−341.15888	1.576	0.609	0.004	1019	4.2
	PNO/CEPA	−341.38047	1.601	0.590	0.004	960	3.7
	exp this work		(1.59±0.01)	–	–	(1040±40)	–
$AlF^+(B\,^2\Sigma^+)$	RHF	−340.93153	1.983	0.385	0.002	440	1
	PNO/CEPA	−341.18709	2.071	0.352	0.005	467	1

[a] Calculated from polynomial fits
[b] Total energies at calculated equilibrium distances
[c] Refs [8–11]

scopic constants obtained from the PNO CI calculations are summarised in tables 1 and 2

For the $AlF^+(X\,^2\Sigma^+) \leftarrow AlF(X\,^1\Sigma^+)$ ionization, Franck–Condon factors have been calculated from vibrational wavefunctions obtained as solutions of the radial Schrodinger equation of nuclear motion using the PNO CEPA potential energy functions as input.

Table 3
Computed and experimental vertical ionization potentials (VIP) (eV) of BF_3 and AlF_3

BF_3 [a]

Orbital	Computed VIP via Koopmans' theorem	Experimental VIP refs [17,18]
$3a_1'$	44.96	–
$2e'$	43.82	–
$4a_1'$	22.88	21.50±0.05
$3e'$	21.76	20.09±0.02
$1a_2''$	20.43	19.13±0.02
$4e'$	18.66	17.14±0.01
$1e''$	18.32	16.67±0.01
$1a_2'$	17.59	15.95±0.02

AlF_3 [a]

Orbital	Computed VIP via Koopmans' theorem	Experimental VIP ±0.02 eV	Band number in fig 2
$4a_1'$	42.00	–	–
$3e'$	41.64	–	–
$5a_1'$	19.55	20.09	D
$4e'$ $2a_2''$	18.38 17.73	17.07	C
$5e'$	17.49	16.10	B
$1e''$ $1a_2'$	17.21 16.72	15.45	A

[a] The experimental geometries used for these calculations are taken from refs. [30–32]

Ab initio SCF calculations have also been performed for AlF_3 and the experimental photoelectron spectrum has been assigned on the basis of Koopmans' theorem applied to the orbital energies obtained for the neutral molecule. The basis set used in these calculations was a double-zeta STO basis set taken from those of Clementi and Roetti [29] with added polarization functions [the exponents used were Al 4s(1.00), 4p(1.00), 3d(1.35) and F 3d(2.01)]. Similar calculations were also performed for BF_3 using the basis set of ref. [1] For both molecules, geometries derived from gas-phase electron diffraction studies were used [30–32] The results of these calculations are summarised in table 3.

4. Results and discussion

The HeI photoelectron spectrum obtained on evaporating a stoichiometric mixture of aluminium and aluminium trifluoride is shown in fig. 1. It shows three bands which were in the same intensity ratio on varying the helium carrier gas pressure and furnace temperature as well as a broad weak feature centred at 16.10 ± 0.05 eV. This spectrum has also been reproduced on heating Al/AlF_3 mixtures containing excess aluminium, except that

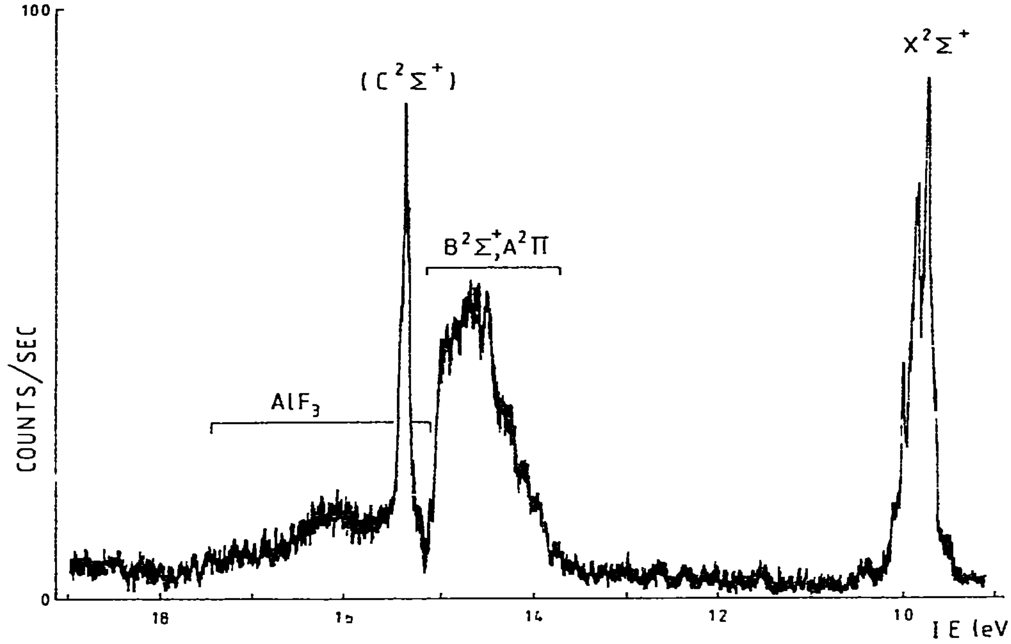

Fig 1 The HeI photoelectron spectrum of AlF($X\,^1\Sigma^+$) obtained on heating a stoichiometric Al/AlF$_3$ mixture Abscissae ionization potential (eV) Ordinate counts s^{-1}

the band positioned at 16.10 eV was much weaker in intensity under these conditions The photoelectron spectrum of AlF$_3$ has also been recorded (see fig. 2). By comparison of the spectra obtained and knowledge of the main species present in each case from vapour pressure measurements, it was con-

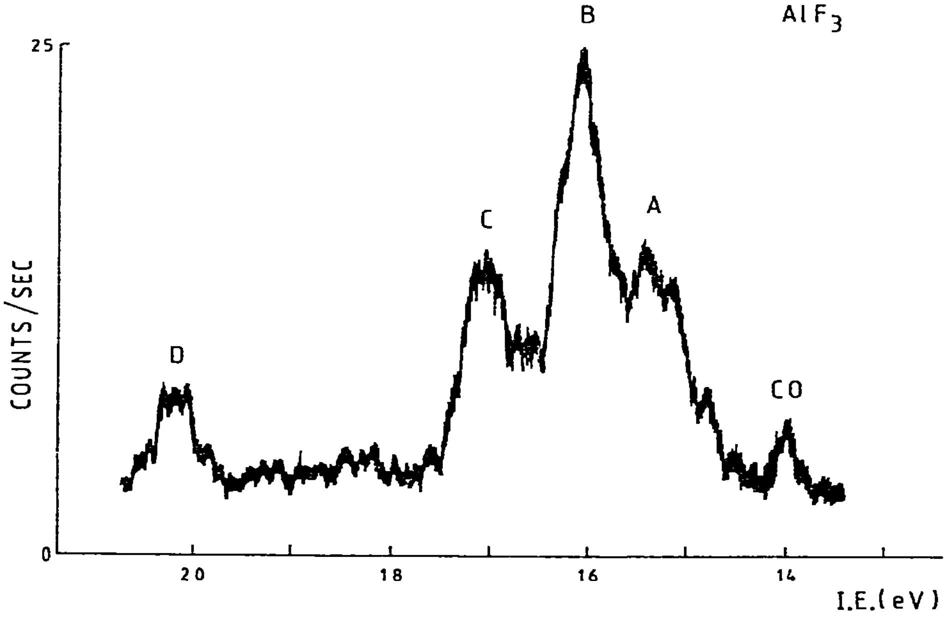

Fig 2 The HeI photoelectron spectrum of AlF$_3$ Abscissae ionization potential (eV) Ordinate counts s^{-1}

cluded that the spectrum shown in fig. 2 arises solely from AlF_3, the first three bands in fig. 1 are due to ionization of AlF and the weak feature centred at 16.10 ± 0.05 eV in fig. 1 arises from AlF_3.

The first band of AlF is the only one which shows resolvable vibrational structure (see fig. 3). The adiabatic and vertical ionization potentials of this band coincide at 9.73 ± 0.01 eV.

This band is assigned on the basis of the calculated ionization energies (see table 1) to the $AlF^+(X\,^2\Sigma^+) \leftarrow AlF(X\,^1\Sigma^+)$ ionization. The difference between the ΔSCF and the experimental vertical IP shown in table 1 gives the correlation correction to the ionization energy. As expected, as the correlation energy in the $X\,^2\Sigma^+$ state is lower than that in the $X\,^1\Sigma^+$ state, the ΔSCF value is lower than the experimental vertical IP and the PNO CEPA value is also lower than this value (by ≈ 0.3 eV) as only ≈ 75% of the valence correlation energy has been accounted for in the PNO CEPA calculations on the $X\,^2\Sigma^+$ and $X\,^1\Sigma^+$ states.

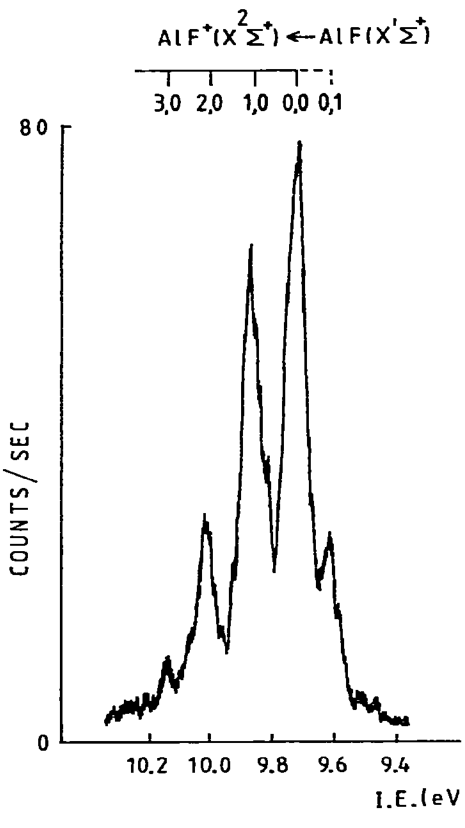

Fig 3. The band assigned to the ionization process $AlF^+(X\,^2\Sigma^+) \leftarrow AlF(X\,^1\Sigma^+)$ Abscissae ionization potential (eV) Ordinate counts s^{-1}

As well as the adiabatic vibrational component at least three other vibrational peaks were observed to higher ionization energy and measurement of their separations gave a value of $\bar{\omega}_e = 1040 \pm 40$ cm^{-1} in the ionic state, a value which compares with 802 cm^{-1} in the ground state of the neutral molecule [8–11]. A similar increase in vibrational frequency on ionization occurs in the BF case [1]. This increase in bond strength has been rationalised previously in terms of an ionic bonding scheme, which has been found more appropriate than a covalent approach in describing the bonding in the group III monohalides and their ions [1,33–36]. Our ab initio SCF calculations indicate that the first ionization process in AlF corresponds essentially to removal of an Al 3s electron with a net strengthening of the ionic bond in the cation. The relative intensities of the three main vibrational components shown in fig. 3, corresponding to the ionizations $v' = 0$, 1 and 2, $AlF^+(X\,^2\Sigma^+) \leftarrow v'' = 0$, $AlF(X\,^1\Sigma^+)$, were measured as 1.00 : 0.82 ± 0.03 : 0 35 ± 0.05. Using the method outlined previously [1] and assuming no vibrational excitation of the neutral molecule, these vibrational relative intensities have been used with a series of Franck–Condon calculations to estimate the equilibrium bond length in the $AlF^+(X\,^2\Sigma^+)$ state as 1.58 ± 0.01 Å. However, in all experimental spectra one vibrational component was observed on the low ionization energy side of the $v' = 0 \leftarrow v'' = 0$ component (see fig 3) and its position was consistent with that expected for the "hot band" due to the ionization process $v' = 0$, $AlF^+(X\,^2\Sigma^+) \leftarrow v'' = 1$, $AlF(X\,^1\Sigma^+)$. The presence of contributions from vibrationally excited AlF in the band makes analysis of the experimental vibrational intensities somewhat difficult because, within the resolution of the experiment, overlap will occur between the following pairs of $v' \leftarrow v''$ transitions; $0 \leftarrow 0$ and $1 \leftarrow 1$, $1 \leftarrow 0$ and $2 \leftarrow 1$, and $2 \leftarrow 0$ and $3 \leftarrow 1$. This obviously means that the intensities of the three main vibrational components in fig. 3 cannot be used directly to estimate the equilibrium bond length in the ion.

Nevertheless, as the contribution from the $v''=1$ and $v''=2$ AlF(X$^1\Sigma^+$) levels in fig. 3 was small, the following approximate procedure was adopted. Use of the computed Franck–Condon factors for the $v'=0 \leftarrow v''=0$ and $v'=0 \leftarrow v''=1$ transitions (calculated with $\bar{\omega}_e = 1040$ cm^{-1} and $r_e = 1.58$ Å in the ion) with the corresponding experimental component intensities (1 : 0.25 ± 0.05) leads to an estimated AlF(X$^1\Sigma^+$) vibrational temperature of 950 ± 50 K, a value which is slightly lower than the furnace temperature of 1050 ± 20 K probably because of collisional deactivation of the AlF molecules before ionization. This effective vibrational temperature together with the computed Franck–Condon factors for the ionizations $v''=0$ and $v''=1$ to $v'=0$, 1, 2 and 3 allows a small correction to be made to the experimental band intensities to yield a more accurate estimate of the experimental intensity ratio of the processes $v'=0$, 1, 2 $\leftarrow v''=0$. These modified intensities then led, via a series of Franck–Condon calculations [1], to a new estimate of the equilibrium bond length in the AlF$^+$(X$^2\Sigma^+$) state which was slightly increased from the original value to 1.59 ± 0.01 Å. The vibrational temperature of AlF(X$^1\Sigma^+$) was also redetermined using Franck–Condon factors recalculated at this ionic bond length together with the experimental vibrational intensity ratios and found to be essentially unchanged from the initial value of 950 ± 50 K.

In order to check the values of $\bar{\omega}_e$ and r_e derived for AlF$^+$(X$^2\Sigma^+$) from the experimental spectra, theoretical vibrational envelopes of the first photoelectron band have been calculated from the PNO CEPA potential energy curves for the $v' \leftarrow v''=0$ and $v' \leftarrow v''=1$ progressions and both envelopes are shown schematically in fig 4 In constructing these envelopes the calculated Franck–Condon

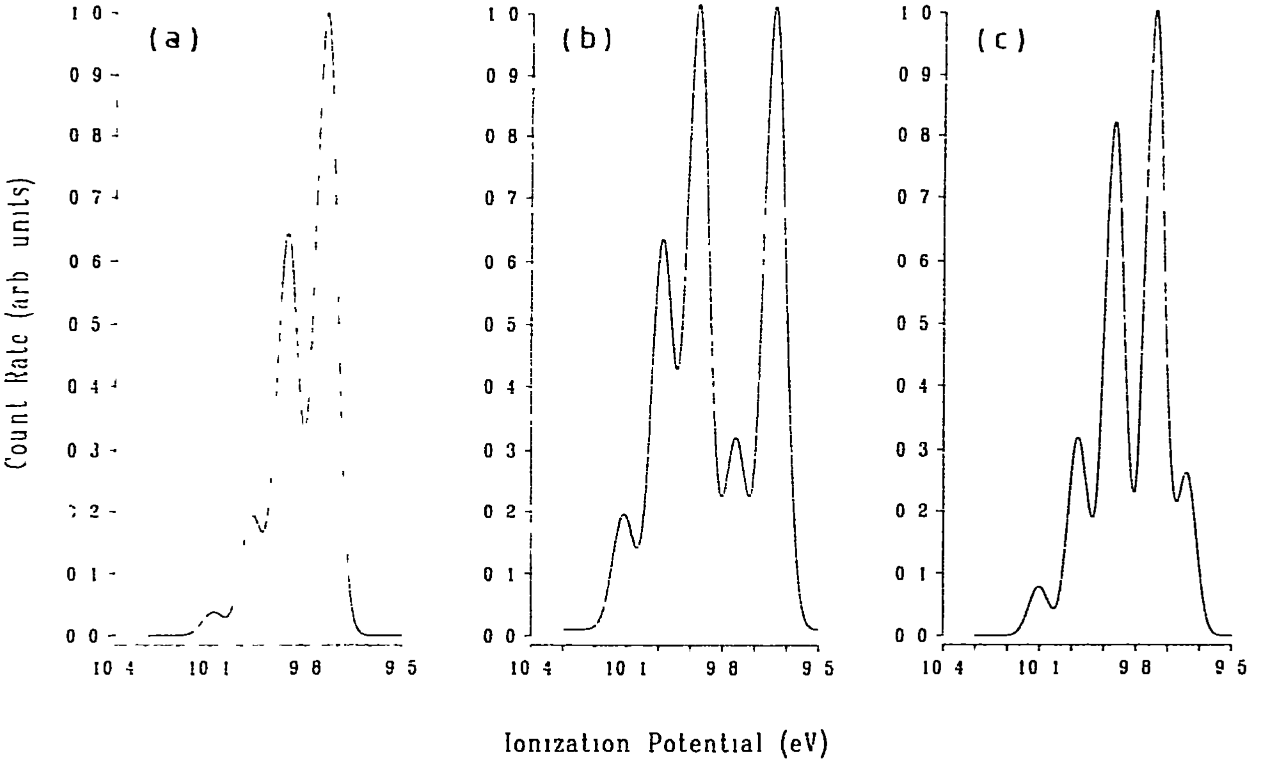

Fig 4 (a) Vibrational envelope for the X $^2\Sigma^+$ ($v'=0, 1, 2$ 3)AlF$^+$ ← X $^1\Sigma^+$ ($v''=0$)AlF ionization calculated from the PNO CEPA potentials The adiabatic IP was taken from experiment (b) PNO CEPA computed vibrational envelope for the AlF$^+$ (X $^2\Sigma^+$)($v'=$ 0 1, 2, 3) ← AlF(X $^1\Sigma^+$)($v''=1$) ionization The $v'=0 \leftarrow v''=1$ position was taken from experiment (c) Simulated first band of AlF obtained by adding (a) and (b) in the ratio of 1 0 25 (a) and (b) have not been plotted with the same scaling factors, i e the intensities in (a) and (b) are not directly comparable factors have been used with gaussian line shapes with a width at half height of 80 meV determined by the experimental resolution. It is immediately seen from the figure that the $v' \leftarrow v'' = 1$ progression exhibits a rather irregular envelope largely because of the small overlap between the $v'' = 1$ and $v' = 1$ vibrational wavefunctions. However, if both envelopes are added together with a weighting factor of 1 : 0.25 the resulting theoretical spectrum (fig. 4) is in very good agreement with the experimental envelope (fig. 3).

The quality of the PNO CEPA potential energy functions for both states can also be judged from the computed spectroscopic constants (r_e and $\bar{\omega}_e$) for the AlF($X\,^1\Sigma^+$) state for which very accurate experimental values are available [8–11] (see table 2). The theoretical equilibrium bond length, r_e, is too large by 0.009 Å and the corresponding vibrational frequency, $\bar{\omega}_e$, is overestimated by 2 cm^{-1}. For the $AlF^+(X\,^2\Sigma^+)$ state, the computed r_e is expected to be accurate to within ±0.01 Å and $\bar{\omega}_e$ is expected to be within 50 cm^{-1} of the experimental value. Comparison with the corresponding experimentally derived parameters shows that values of r_e obtained by both methods are in good agreement. However, the computed value of $\bar{\omega}_e$ of 960 ± 50 cm^{-1} compares with 1040 ± 40 cm^{-1} determined from the experimental vibrational separations This difference may arise from uncertainties in measurement of vibrational separations in an envelope which contains contributions from ionization of vibrationally excited AlF. As a result, we consider that an average of theoretical and experimental values is the most reliable estimate for $\bar{\omega}_e$ of $AlF^+(X\,^2\Sigma^+)$ i.e. $\bar{\omega}_e = 1000 \pm 40$ cm^{-1}.

Another parameter which can be determined from the first band of AlF is the dissociation energy in the ground state of the ion. Assuming, as seems likely, that AlF($X\,^1\Sigma^+$) dissociates to Al(^2P) and F(^2P) and $AlF^+(X\,^2\Sigma^+)$ dissociates to $Al^+(^1S)$ and F(^2P) then the first adiabatic ionization energy of AlF, 9.73 ± 0.01 eV, can be used with the known dissociation energy, D_0, of AlF($X\,^1\Sigma^+$), 6.89 ± 0.13 eV [15], and the first ionization potential of aluminium, 5.98 eV [37], to estimate the dissociation energy, D_0, in $AlF^+(X\,^2\Sigma^+)$ as 3.14 ± 0.14 eV.

The second band of AlF, shown in fig. 1, is broad and no vibrational structure was resolved. The band onset and maxima were measured as 13.65 ± 0.02 eV and 14.75 ± 0.02 eV respectively. As can be seen from fig. 5 two more cationic states, the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states are expected in the HeI region. In nine-valence electron cations such as N_2^+, CO^+, SiO^+, and CS^+, the $A\,^2\Pi$ states exhibit well resolved vibrational fine structure whereas for BF^+ [38] or $AlCl^+$ [33] it is known that the $A\,^2\Pi$ states are repulsive, the potential energy functions exhibiting only shallow polarization minima at large internuclear distances.

The second band of AlF can, however, be unambiguously assigned on the basis of the PNO CEPA calculations performed in this work. In fig. 5 the parts of the potential energy functions needed for this assignment are shown. The $B\,^2\Sigma^+$ state of

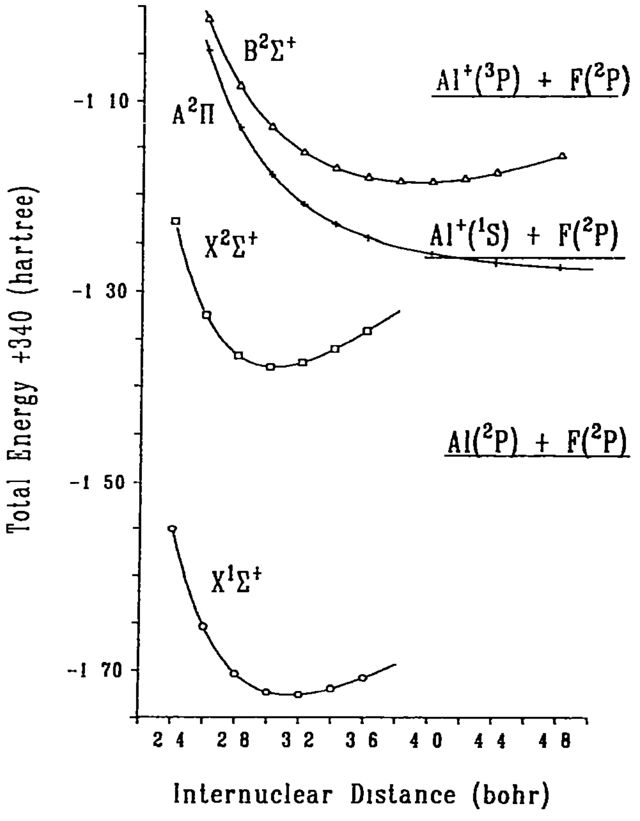

Fig 5 The PNO CEPA calculated potential energy functions for the $X\,^1\Sigma^+$ state of AlF and the $X\,^2\Sigma^+$, $A\,^2\Pi$ and $B\,^2\Sigma^+$ states of AlF^+ in the internuclear distance range 2.4–3 8 au

AlF^+ dissociates to $Al^+(^3P) + F(^2P)$ and the $X\,^2\Sigma^+$ state dissociates to $Al^+(^1S) + F(^2P)$. Close to the equilibrium internuclear distance of the $X\,^2\Sigma^+$ state, the 7σ orbital exhibits the approximate occupancy (Al) $3s3p\sigma$ whereas at longer distances it becomes (Al) $3s^2$. The reverse occupancy change occurs for the 6σ molecular orbital. Therefore, there is an avoided crossing of the X and B states of AlF^+ at larger internuclear distances due to the changes of the 7σ and 6σ molecular orbital characters. For this reason the $B\,^2\Sigma^+$ potential curve is rather shallow and its equilibrium internuclear distance is larger than that of the $X\,^2\Sigma^+$ state by 0.47 Å (see table 2). The $A\,^2\Pi$ state is calculated to be repulsive and to lie below the $B\,^2\Sigma^+$ state (see fig. 5). From internuclear distances defined by the classical turning points of the $v' = 0$ level in $AlF(X\,^1\Sigma^+)$ it is possible to calculate an energy range for the $AlF^+(A\,^2\Pi) \leftarrow AlF(X\,^1\Sigma^+)$ band as 13.6–15.0 eV. The Franck–Condon factors for ionization to the polarization minimum of the $A\,^2\Pi$ state are very small as are the Franck–Condon factors for ionization to the $B\,^2\Sigma^+$ state. The adiabatic ionization energy to the $B\,^2\Sigma^+$ state is calculated to be 14.67 eV (see table 1). According to these theoretical results, the second broad band in the photoelectron spectrum of AlF corresponds to ionization to both the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states of AlF^+. It should also be noted that in view of this assignment the sharp band observed at 15.33 eV vertical ionization energy must be due to ionization to a higher state of AlF^+. As no further formally allowed bands are expected in the HeI region, this sharp band must be due to a shake-up state of AlF^+. These states have not been explicitly treated in the present calculations but by analogy with the known photoelectron spectrum of CS [39–41] this band is tentatively assigned to a $^2\Sigma^+$ state arising from the configuration $(2\pi)^{-1}(7\sigma)^{-1}(3\pi)^{+1}$.

It is reassuring that the general features of the AlF spectrum observed in this work are in good agreement with that known for the HeI photoelectron spectra of the thallium and indium monohalides [33–36]. For these molecules, as in the AlF case, three bands were observed with the first and third bands being sharp and the second band being very broad. In view of the assignment of the second band in AlF, it seems likely that the second band in the spectra of the thallium and indium monohalides also arises from ionization to both the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states.

The assignment of the photoelectron spectrum of AlF_3 (summarised in table 3) has been achieved with the aid of SCF calculations performed for both BF_3 and AlF_3 and by comparison with the known photoelectron spectrum of BF_3. In neutral BF_3, the three outermost filled molecular orbitals are of $1a_2'$, $1e''$ and $4e'$ symmetry. The $1a_2'$ and $1e''$ orbitals are composed of linear combinations of F(2p) orbitals whereas the $4e'$ molecular orbital is composed mainly of F(2p) symmetry combinations with small contributions from B(2p) atomic orbitals. The next two molecular orbitals, the $1a_2''$ and $3d'$ levels, are also mainly F(2p) in character. A similar situation also arises in AlF_3 where the outermost five occupied molecular orbitals are also mainly F(2p) in character. In the HeI photoelectron spectrum of BF_3, the first three bands arise from ionization of the $1a_2'$, $1e''$ and $4e'$ levels (at experimental vertical ionization potentials of 15.95, 16.67 and 17.14 eV respectively [17,18]) with the $(4e')^{-1}$ band being the most intense and the $(1e'')^{-1}$ band being the weakest. On this basis and from the computed ionization energies in table 3, the photoelectron spectrum of AlF_3 is assigned in the following way. Band B in fig. 2 is attributed to the $(5e')^{-1}$ ionization whereas band A is attributed to two unresolved bands arising from the $(1e'')^{-1}$ and $(1a_2)^{-1}$ ionizations. The other observed bands in the AlF_3 spectrum, bands C and D, are assigned as shown in table 3.

Perhaps one of the more significant measurements to be forthcoming from this present study is an improved estimate of the first adiabatic IP of AlF. The value obtained, 9.73 ± 0.01 eV, is in agreement with the value expected from electron impact mass spectrometry, 9.70 ± 0.50 eV [14–16], but the error limits have been considerably reduced. Although a number of Rydberg states of AlF have previously been observed by Barrow and co-workers [7], detailed analysis of these states was not possible because an accurate value of the first ionization potential of AlF was not available. A preliminary analysis was nevertheless presented [7] based on a value of the AlF IP (9.92 eV) estimated

Table 4
Redetermination of the quantum defects of a number of singlet Rydberg states of AlF [a]

State	Character of the excited electron from ref [7]	T_0 from ref [7] (eV)	$n-\delta$ [b]	n	δ [b]
$H\,^1\Sigma^+$	4pσ	8.405	3.204(2.998)	4	0.79(1.00)
$F\,^1\Pi$	4pπ	8.216	2.997(2.827)	4	1.00(1.17)
$G\,^1\Sigma^+$	3dσ	8.282	3.065(2.884)	3	−0.06(0.12)
$E\,^1\Pi$	3dπ	7.953	2.767(2.631)	3	0.23(0.37)
$D\,^1\Delta$	3dδ	7.647	2.555(2.447)	3	0.45(0.55)
$C\,^1\Sigma^+$	4sσ	7.210	2.323(2.241)	4	1.67(1.76)

[a] The T_0 values listed in this table are taken from table 6 of ref [7] The parameters $(n-\delta)$ and δ are derived assuming IP(AlF) = 9.73 eV, as determined in this work

[b] The $(n-\delta)$ and δ values shown in parentheses are derived on the assumption that IP(AlF) = 9.92 eV (see ref [7])

by analogy with known Rydberg series in BF However, the more reliable ionization potential of AlF determined in this work allows a redetermination of the quantum defects of the Rydberg states observed by Barrow and co-workers [7] assuming that the atomic character of the observed excited states ($C\,^1\Sigma^+$, $D\,^1\Delta$, $E\,^1\Pi$, $G\,^1\Sigma^+$, $F\,^1\Pi$ and $H\,^1\Sigma^+$) is unchanged from that given in ref. [7]. This latter assumption is supported for the $D\,^1\Delta$ state by recent ab initio molecular orbital calculations [42]. The results of the reanalysis are presented in table 4 with the original values of Barrow et al. [7] given in parentheses. Clearly identification of other Rydberg states of AlF would be extremely useful and would lead to a further improvement in the first IP of AlF. It is therefore hoped that this present work will stimulate further interest in this problem and lead to further spectroscopic studies on AlF.

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