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A combined theoretical and experimental study of the ionic states of iodopentafluorobenzene

Michael H. Palmer,^{1,a)} Marcello Coreno,^{2,b)} Monica de Simone,^{3,b)}
Søren Vrønning Hoffmann,^{4,b)} Nykola C. Jones,^{4,b)} Cesare Grazioli,^{2,5,b)}
Kirk A. Peterson,^{6,b)} Alberto Baiardi,^{7,b)} Teng Zhang,^{8,b)} and Malgorzata Biczysko^{9,b)}

¹*School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, Scotland, United Kingdom*

²*CNR-IMIP, Montelibretti, c/o Laboratorio Elettra, Trieste, Italy*

³*CNR-IOM Laboratorio TASC, Trieste, Italy*

⁴*ISA, Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark*

⁵*Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy*

⁶*Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, USA*

⁷*Scuola Normale Superiore, Piazza Cavalieri 7, 56126 Pisa, Italy*

⁸*Department of Physics and Astronomy, University of Uppsala, Uppsala, Sweden*

⁹*International Centre for Quantum and Molecular Structures, College of Sciences, Shanghai University, 99 Shangda Road, Shanghai 200444, China*

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A new synchrotron radiation photoelectron spectral (PES) study of iodopentafluorobenzene, together with a theoretical analysis of the spectrum, where Franck-Condon factors are discussed, gives detailed insight into the ionization processes, and this exposes the need for a reinvestigation of the vacuum ultraviolet spectral (VUV) assignments. We have calculated adiabatic ionization energies (AIEs) for several ionic states, using the equation-of-motion coupled cluster method for ionic states combined with multi-configuration self-consistent field calculation study. The AIE sequence is: $X^2B_1 < A^2A_2 < B^2B_2 < C^2B_1 < D^2A_1 < E^3B_1$. This symmetry sequence has a major impact on previous VUV spectral assignments, which now appear to be to optically forbidden states. Changes in the equilibrium structures for these ionic states are relatively small, but a significant decrease and increase in the C–I bond length relative to the X^1A_1 structure occurs for the X^2B_1 and C^2B_1 states, respectively. The PES shows major vibrational overlaps between pairs of ionic states, X with A, and A with B. The result of these overlaps is the loss of vibrational structure and considerable broadening of the higher energy PES state. Although the baseline is nearly re-established between the A and B states, where the two bands are nearly separate, the B state is also broadened by the A state. Only the C ionic state, which shows the most highly developed vibrational structure, can be regarded as free from vibrational coupling to a neighbor state. The Franck-Condon analysis of the PES bands X, A, B, and C is described in detail; the apparent simplicity of some of these bands is illusory, since almost all the observed peaks arise from super-position of several calculated vibrational states. The experimental AIE of the A state, which is submerged under the X state envelope, has been determined by the subtraction of the calculated X state envelope from the observed PES spectrum. The overlap of these PES bands and the apparent closeness of the potential energy curves describing them have been investigated, using the state-averaged, complete active space self-consistent field method. We have identified two structures, one where the potential energy curves for the X and A states cross and another for the A and B states. At these two conical intersections (ConInts), there is zero-energy difference within each pair of states. Although similar in energy, the ConInt for the crossing of the X with A states, and that for the A with B states, shows that the open-shell occupancies correspond to the 4 lowest AIE states, and all four states that are quite different from each other. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4975672>]

I. INTRODUCTION

Recently we reported two new high-resolution, synchrotron-excited photoelectron (PES) and 1-photon vacuum

ultraviolet (VUV) spectra of iodobenzene (PhI, C_6H_5I).^{1,2} When combined with high-level theoretical studies, these gave a more rigorous interpretation of earlier PES and VUV spectra, which included the identification of numerous Rydberg states in the VUV spectrum.² Previous PES and VUV studies of iodopentafluorobenzene (C_6F_5I)^{3,4} showed poorly resolved PES spectra. Comparison with the recently analyzed spectrum of PhI^{1,2} strongly suggested that erroneous

^{a)}Email: m.h.palmer@ed.ac.uk. Tel.: +44 (0) 131 650 4765.

^{b)}Electronic addresses: vronning@phys.au.dk; nykj@phys.au.dk; desimone@iom.cnr.it; marcello.coreno@elettra.eu; teng.zhang@physics.uu.se; kipeters@wsu.edu; alberto.baiardi@sns.it; and biczysko@shu.edu.cn.

Rydberg state assignment³ in the VUV spectrum of C₆F₅I had occurred. The symmetry sequence of the lower ionic states of C₆F₅I was unknown, resulting in several Rydberg states in the VUV spectrum being assigned³ to optically forbidden states.

We now study the ionization energy sequence in detail, enabling earlier PES and VUV interpretation³ for C₆F₅I to be placed on a more rigorous level. These results will assist a revised study of the VUV spectrum later. Our new PES investigation has similarities to that in our PhI studies,^{1,2} but the current PES spectrum exhibited considerable overlap of the individual ionic state vibrational profiles. Such issues with PES spectra are relatively frequent, but often ignored when measuring ionization energies (IEs). We explore a general theoretical solution and define the criterion for such experimental interactions. For brevity in this study, we use leading references; these describe early work where either the spectra or their interpretation are no longer valid.

We note that “perfluoro effects” can be identified for pairs of compounds, such as C₆H₅I and C₆F₅I, in their molecular property differences.^{5,6} Examples occur in PES spectra. There is very little difference for π -ionization energies (π -IEs) between the two series. In contrast, σ -IE in the F₅ compounds is often several electron volts (eV) higher than those for the H₅ compound.^{5,6} The conventional interpretation is that H₅ shows weak σ -electronic effects, while the π -effect is close to non-existent. There is strong σ -attraction in the F₅ case^{5,6} relative to that for H₅. But the doubly filled (F) electron pairs interact with the 3π -molecular orbitals (MO) each doubly filled (C-ring) interaction, with resultant weak effect.

This paper contains a much-improved PES study for C₆F₅I, with higher resolution and high-count rates, which improve the reliability relative to previous work (and references therein).³ Our high-level theoretical methods, which include vibrational analysis using Franck-Condon (FC) procedures,^{7–10} put the spectral interpretation on a secure footing for the first time.

II. SPECTROSCOPIC AND THEORETICAL METHODS

A. Experimental PES spectroscopy

C₆F₅I (Sigma-Aldrich, CAS Registry Number 827-15-6) was studied on the gas phase photoemission beamline, at the Elettra synchrotron described previously.¹ Our highest resolution PES, shown in Fig. 1, was acquired using a photon energy of 30 eV, over the binding energy range 9.2–12.3 eV with a step size of 1 meV. An expansion, shown in Fig. 2, where the FC envelope is included, is discussed below. The linearity of the PES kinetic energy scale of the electron analyser was confirmed by the use of internally calibrated lines from sample gases such as Ar (3p) and Xe (5p and 4d).¹ The overall experimental energy resolution (including the photon energy and electron analyser) was ~ 8 meV. We estimate our experimental uncertainties in the absolute energies and the energy separations in a particular band system to be approximately ± 2 and ± 0.5 meV, respectively.

FIG. 1. The region of principal interest to the spectral analyses for C₆F₅I recorded at 30 eV irradiation energy. The four lowest ionization energies together with their symmetries are labelled.

The energy of well-defined vibrational structure was determined by fitting sets of Gaussian functions to the observed peaks. However, these band maxima are the resultant of vibronic transitions involving several vibrations, rather than individual vibrational modes, as discussed below. Hence a table of peak maxima for the PES range 9–12 eV is deferred to the [supplementary material](#) as SM1 and shown as Table SM1.

Comparison of our Figs. 1 and 2 with those of Eden *et al.*³ (their Figs. 3 and 4), or Trudel *et al.*⁴ (their Fig. 1), demonstrates our improvement on previous PES spectra.

A wide range scan (8–40 eV) PES spectrum, recorded using 50 eV photons, with an overall experimental energy resolution of 25 meV is also discussed, in relation to symmetry assignments, in more detail in the [supplementary material](#) as SM1.

FIG. 2. The Band I of the experimental PES spectrum (black trace). The stick spectrum (blue) of the X²B₁ Franck-Condon factor (FCF) spectrum is superimposed. A FCF simulation of the PES where the cold band stick spectra for the X²B₁ state are represented by Gaussian functions with half-width at half-maximum (HWHM) of 70 cm^{−1} is shown (in red). The experimental 0–0 band of the X²B₁ state is 75 067 cm^{−1}, preceded by hot bands. The intensity of the theoretical X²B₁ bands X_A–X_F cannot represent the PES. The remainder of this region of the PES spectrum is the A²A₂ state discussed separately below. It is largely represented by the PES bands A_A–A_D.

TABLE I. The experimental adiabatic and vertical ionization energies IE_{1-5} for C_6F_5I , compared with those calculated using the EOMIP and MCSCF methods. Valence shell numbering enables comparison with related molecules.

C ₆ F ₅ I PES results							C ₆ H ₅ I
Expt. IE/eV		EOMIP ^a IE/eV	MCSCF ^b IE/eV	Leading term vacancy	State symmetry	IE sequence	Expt. ² IE/eV
Adiabatic	Vertical	Adiabatic	Adiabatic				
9.307	9.405	9.320	8.872	3b ₁ ⁻¹	X ² B ₁	IE ₁	8.758
(9.613) ^c	9.859	9.591	9.081	1a ₂ ⁻¹	A ² A ₂	IE ₂	9.505
10.479	10.479	10.273	10.228	6b ₂ ⁻¹	B ² B ₂	IE ₃	9.776
11.209	11.209	11.031	10.783	2b ₁ ⁻¹	C ² B ₁	IE ₄	10.543
12.665	12.665	...	12.021	1b ₁ ⁻¹	D ² B ₁	IE ₅	

^aCalculated at the aug-cc-pVTZ X¹A₁ equilibrium structure; Hartree-Fock energy = -7642.408012 a.u.

^bMCSCF method using the Sadlej pVTZ basis set containing 14 active MOs.

^cEstimated value from super-position of the calculated X²B₁ and A²A₂ state FCF profiles.

B. Computational procedures

Equilibrium structures for the neutral ground (X¹A₁) and ionic states (X²B₁, A²A₂, B²B₂, and C(2)²B₁) were obtained by equation-of-motion (EOM) coupled cluster (CC) calculations, including single and double (SD) excitations.^{11–13} The AIE (ionization-potentials, IP) was determined by the EOMIP-CCSD method.^{12,13} The AIE for the 3²B₁ state was obtained using state-averaged (SA) multi-configuration self-consistent field (MCSCF) wave functions,^{14,15} in the presence of the X²B₁ state and 1- and 2-²B₁ states, this enables the relative positions of the 3 states to be determined with confidence.

Modules from each of GAUSSIAN-09 (G-09),¹⁶ CFOUR,¹⁷ and MOLPRO,¹⁸ were utilised. All-electron and effective core potential (ECP) bases were chosen from the EMSL database,^{19,20} depending upon the aspect under study. For example, the EOMIP structural optimization and harmonic frequency study (both using CFOUR), took into account the relative polarities of the C, F, and I atoms, these were represented by correlation consistent double zeta valence + polarization basis sets (cc-pVDZ),²¹ augmented versions (aug-pVDZ), and aug-cc-pVDZ-PP, respectively (analogous TZ sets were also used for the neutral ground state).²² The Sadlej pVTZ²³ (triple zeta valence + polarization basis sets) and 6-311G** bases were also useful.^{24,25}

The 34 core orbitals (18a₁ 5b₁ 9b₂ 2a₂) were frozen in all MCSCF (using MOLPRO) and CI calculations; valence shell numbering (occupancy: 13a₁ 6b₁ 11b₂ 3a₂) is used throughout this paper. All computational results were obtained at the equilibrium geometry for the method used. The Franck-Condon factors (FCFs) vibrational analyses (using the G-09 module) were performed with the consideration of cold bands only, or including temperature effects where required.

The principal calculated AIE results and a comparison with experiment are shown in Table I.

III. RESULTS

A. Overall aspects

Our units for the wide scan PES and for electronic origins are electron volts (eV), which assists comparison with

previous work. A summary of our experimental adiabatic and vertical IEs and a comparison with the calculated theoretical data from the EOMIP and MCSCF methods is shown in Table I. Some higher IEs are shown in the [supplementary material](#) as SM1.

Since vibrational features are important for individual PES bands, we use units of cm⁻¹ for expanded spectra. Infrared (IR) and Raman frequencies from early liquid film results,^{26–28} and previous gas phase IR data^{29,30} have been reported. Not all these data^{26–30} are in close agreement, and we have chosen the largest set available.²⁸ The correlation between our calculated X¹A₁ state fundamental frequency results and these IR experiments²⁸ is close for most vibrations. This gives confidence in the calculated ionic state values, since the PES spectrum does not yield experimental values.

B. The ionic state equilibrium structures of C₆F₅I

No microwave (MW) or electron diffraction (ED) studies of the molecular structure have been reported for C₆F₅I, but an *r_o* structure derived from ¹³C satellites in the ¹⁹F NMR spectrum is known.³¹ The present ground state is comparable; this and a variety of ionic state structures are shown in the [supplementary material](#) as SM2. The X¹A₁ and lowest four cationic states shown are all constrained to C_{2v} symmetry. Although the environment of the I-atom appears to be congested, and might be expected to lead to significant C–I bond length changes on ionization, except for the X and C states, relatively little is observed. Overall C–I changes (Å), where a positive sign is lengthening, are: X²B₁, -0.06; A²A₂, -0.007; B²B₂, +0.008; C²B₁, +0.102Å. All the C–F bonds are shortened in the ionic states, but by relatively small amounts (0.02–0.04 Å), which vary with position. The C–C bonds also shorten in some states, but exceptions occur for C₁C₂ and C₃C₄ in X²B₁, C₂C₃ in A²A₂, C₃C₄ in C²B₁. The deeper the ionic state, the more the C–I bond lengthens, similar to our observations with iodobenzene C₆H₅I. The harmonic frequencies for each state are shown in Table II.

TABLE II. Comparison of the infrared and Raman frequencies²⁸ with calculated harmonic (H) and anharmonic (AH) frequencies for the ground and ionic states of C₆F₅I. The vibrational modes for all states are numbered according to the Mulliken convention. Correlation between the ionic states and the X¹A₁ state is via the largest values in the Duschinsky matrix. Further details are given in the [supplementary material](#) as SM2. Imaginary frequency *i*.

State mode	Sym.	Expt. ²⁸ IR + Raman	Calc. X ¹ A ₁		X ² B ₁	A ² A ₂	B ² B ₂	C ² B ₁
			AH	H	H	H	H	H
1	<i>a</i> ₁	1633	1676	1710	1719	1672	1698	1730
2		1507	1533	1567	1528	1589	1570	1570
3		1406	1427	1453	1411	1515	1460	1456
4		1296	1264	1284	1327	1357	1315	1337
5		1083	1074	1091	1132	1130	1098	1112
6		805	803	809	846	812	800	771
7		581	575	580	582	583	581	582
8		489	488	494	490	491	494	483
9		349	352	356	358	371	345	346
10		278	278	280	277	291	269	274
11		204	203	205	212	203	193	185
12	<i>a</i> ₂		655	671	658	712	663	655
13		381	397	405	395	463	399	382
14		110	130	133	124	113	136	127
15	<i>b</i> ₁	600	636	662	676	672	666	679
16			619	635	644	614	621	618
17		349	357	364	410	336	382	363
18		217	212	216	215	206	210	212
19		133	165	167	150	144	162	154
20		114, 90 ³⁰	77	81	70	113	91	76
21	<i>b</i> ₂	1633	1671	1701	1620	1482	1708	1780
22		1517	1521	1553	1438	1403	1580	1590
23		1263	1238	1268	1372	1242	1278	1317
24		1149	1136	1155	1191	1026	1183	1204
25		977	971	987	1010	762	996	1010
26		714	738	747	758	740	754	753
27		438	440	444	390	320	437	454
28		311	308	310	313	284	302	310
29		215	272	274	270	128	270	268
30		129	128	130	138	862i	87	119

C. The electronic structure of C₆F₅I

C₆F₅I has 67 doubly occupied MOs (DOMOs). We assume C_{2v} symmetry for all the present electronic states. The I-atom takes symmetric (S) and antisymmetric (A) combinations with the benzene ring MOs. The group of HOMOs, relevant to the present study, is shown in Fig. 3. This group of MOs is largely unaffected by the presence of F-atoms (a) because the electronegativity effect on the energy is compensated by the π -donor effect of the F atoms, but also (b) because MOs rich in F-atom density occur at higher binding energy. The in-plane σ -orbital 6b₂ is highly localised on the I-atom and is effectively a nonbonding lone-pair. When the electron density contours for C₆F₅I are compared with those for C₆H₅I,¹ the dominance of the C and I-atom density contributions for both molecules is clear. Although the ionization sequence by symmetry is the same for both C₆H₅I and C₆F₅I, the DOMO energy sequence in the X¹A₁ states is dissimilar.

D. Detailed analysis of the C₆F₅I photoelectron spectrum

The region of principal relevance to our analysis (Table I), shown in Fig. 1 (9-12 eV), contains IE1 to IE4. Previous studies of the C₆F₅I PES, summarised in Reference 3, show groups of broad bands, generally lacking vibrational structure.³ The current results show much more developed vibrational structure, especially for both IE₁ and IE₄. Even the apparently simple IE₃ shows bands with a relatively wider structure.³ IE₂, which overlays the tail of the IE₁ band, now contains some vibrational structure. However, each measured peak in all four ionic electronic states is the resultant of several vibrations, as demonstrated in the FCF analyses below. Thus the individual peaks measured become less important, and a summary is deferred to the [supplementary material](#) as Table SMI.

The ionic states X²B₁ and A²A₂ arise from the symmetric and antisymmetric components of the X²E_{1g} state of benzene;

FIG. 3. Constant density (0.02e) MO contour diagrams of $\text{C}_6\text{F}_5\text{I}$. The four highest occupied MOs (HOMOs) using valence shell numbering (see text); when ionized the sequence remains as $3b_1^{-1} < 1a_2^{-1} < 6b_2^{-1} < 2b_1^{-1}$, and we discuss below their assignments to the X, A, B, and C states, respectively. This sequence is the same as that for PhI itself.

the PES separation of the two states is ~ 0.3 eV, to be compared with the EOMIP calculated energy difference of 0.27 eV. The I atom is nodal in the A^2A_2 state, and this is responsible for the similarity of this AIE with the X^2E_{1g} state of C_6H_6 (9.25 eV). Several related compounds, including $\text{C}_6\text{H}_5\text{I}$ (9.505 eV), $\text{C}_6\text{F}_5\text{H}$ (9.90 eV),⁶ and C_6F_6 (10.14 eV), are also relatively close.

None of the 4 lowest AIE have a direct comparison with the second AIE of benzene (A^2E_{2g}) which is entirely CH and CC ring σ -bonding.⁶ Further discussion of the relationship of $\text{C}_6\text{F}_5\text{I}$ to other molecules is deferred to the [supplementary material](#) under SM1.

In PhI, the $A(\pi,^2A_2)$ and $B(\sigma,^2B_2)$ states overlap strongly, leading to mutual collapse of the vibrational structure of these states. The perfluoro effect leads to selective shift to higher binding energy for the σ -ionic state, so that in the $\text{C}_6\text{F}_5\text{I}$ spectrum these two bands are almost separate. Although the B state has a high 0-0 band as expected, the PES lines are broadened: this provides evidence of a weak interaction with the A state, by comparison with the other PES bands. The B state PES profile can be reproduced by a wider FCF bandwidth (HWHM), than is used for the X and C states. In contrast, the C (π -ionic) state in $\text{C}_6\text{F}_5\text{I}$, largely free standing in the PES, shows the most detailed vibrational structure for the present IE. Its AIE (11.249 eV) is slightly larger than that for $\text{C}_6\text{H}_5\text{I}$ (10.543 eV), a reasonable value using the perfluoro effect for π -IE. An earlier proposal⁶ that this C state, the benzene

$1a_{2u}$ analogue for $\text{C}_6\text{F}_5\text{I}$, lies at 12.85 eV cannot be correct, since the necessary perfluoro effect would be too large for a π -ionization.

E. Vibrational analysis of the $\text{C}_6\text{F}_5\text{I}$ PES spectrum

The ionic state harmonic frequency modes (Table II), numbered according to the Mulliken convention, have 1-11 (a_1), 12-14 (a_2), 15-20 (b_1), and 21-30 (b_2), with descending frequency within each symmetry. Almost all of the calculated FC vibrations with significant intensity involve combinations of a_1 modes; a few non- a_1 mode combinations, but with overall a_1 symmetry (e.g., b_1^2), were calculated. We are unable to compute Herzberg-Teller contributions with the current G-09 package.¹⁶ The calculated FC profile based on the harmonic frequencies (Table II) superimposes the PES after scaling by 0.95, as shown in Figs. 4-6. In these FCF profiles of the PES, several hundreds contributing cold band vibrational processes occur for each state. The most intense terms of the Franck-Condon factors (FCFs), for the featured X, A, B, and C state bands, shown in Table III, are limited to the simplest overtones and combinations and other high intensity bands. There are a surprising number of triple combination bands where high intensity is calculated. Almost all of the calculated vibrational states involve a_1 vibrations, but a considerable number of double quanta excitations from modes 15, 16, and 17 (b_1) are found in the FC analyses. Further FC vibrational states for the X, A, B, and C states are given in the [supplementary material](#) as Tables SM3.1 and SM3.2.

The number of calculated vibrational states sharply increases because of hot bands and their sequence bands. Indeed, hot band vibrations occur throughout the observed PES spectral bands; some examples are shown in the [supplementary material](#) as SM4.

1. The X^2B_1 and A^2A_2 state analysis

As stated above, the PES range from 74 000 to 84 000 cm^{-1} (Fig. 2) shows a complex profile, owing to a major

FIG. 4. The 2A_2 state after subtraction of tail of calculated cold bands from the FC analysis of the X^2B_1 state. This subtraction process both removes the calculated X^2B_1 structure below the A^2A_2 state, but allows weak onset for the latter to be exposed. This onset does not contain predicted bands for the X^2B_1 state, and is presumed to arise from the A^2A_2 adiabatic ionization.

FIG. 5. The portion of the experimental PES spectrum attributable to the B^2B_2 state (black trace). The cold band FCF simulation stick spectrum (blue) obtained shows the principal vibrational bands with their assignments. Conversion of the stick spectral intensities into Gaussian peaks with half-width at half-maximum 140 cm^{-1} leads to the continuous red curve; this gives a good representation of the main undulations for the observed PES Band. The proposed 0-0 band is at $84488\text{ (10) cm}^{-1}$. The PES Band showing both the hot and cold band contributions is shown in the [supplementary material](#).

overlap of IE_1 (X^2B_1) with the IE_2 (A^2A_2) ionic state. The calculated X^2B_1 vibrations reproduce the main peak positions of these regions at $\sim 76\,000$ and $\sim 77\,250\text{ cm}^{-1}$, although they do not reproduce the internal intensities accurately; although this points to slight inadequacy of the present theoretical description, definition of the fundamental structure is sufficient. The 0-0 band of the X^2B_1 state lies at $75\,067\text{ cm}^{-1}$ (9.307 eV); this energy is chosen from the calculated correlation of the major calculated cold bands under X_A and X_B (Fig. 2) with experiment. An important feature is that the calculations show that IE_1 clearly has additional higher vibrational components (X_C-X_F) underlying the higher PES structure. Since the X^2B_1 state cannot account for much of the observed PES above $78\,240\text{ cm}^{-1}$ (9.700 eV), this structure must be attributed to IE_2 identified here as the A^2A_2 state.

FIG. 6. The portion of the experimental PES spectrum attributable to the $(C)^2\tilde{2}B_1$ state (black trace) is shown together with the hot (red) and cold band (blue) FCF simulation obtained by plotting the stick spectrum, including sequence bands. The proposed 0-0 band is close to 90408 cm^{-1} , preceded by hot bands.

The calculated and observed gap in the FCF for the X state near $78\,000\text{ cm}^{-1}$ is followed by a new onset in the PES profile; the X state structure X_C-X_F is lost below this higher state. Subtraction of the whole of the calculated X^2B_1 state FC spectrum from the observed PES leads to almost total removal of the principal (X_A and X_B) portions of the X^2B_1 state. A HWHM of 70 cm^{-1} was used, a value consistent with the experimental X^2B_1 PES line width. Removal of the calculated components X_C-X_F from the PES envelope exposes sharp maxima for the A state (Fig. 4). Critically, two sharp peaks occur at this onset, which have no correlation with the X^2B_1 FCF profile; these can be fitted to the A^2A_2 state FCF cold band profile and identify the AIE 0-0 band. Thus we believe that the AIE of the A^2A_2 state actually lies below the tail of the X^2B_1 state and close to $77\,500\text{ cm}^{-1}$ (9.613 eV). This enables the FCF profile to be best superimposed on the PES (Fig. 4). Our FCF simulates the “subtracted” A^2A_2 state as a set of four groups (A_A to A_D) of FCF bands.

2. The vibrational profile of the X^2B_1 state

The X^2B_1 PES band (Fig. 2) is deceptively simple; however, what appears as simple vibrational structure, under detailed theoretical study, shows instead that all of the observed peaks are the super-position of several vibrations. The most prominent a_1 modes in the PES of X^2B_1 are 11^1 , 10^1 , 8^1 , 4^1 , and 2^1 and more than one quantum of each are predicted to have significant intensities. Several double, triple, and quadruple combination bands, largely involving these modes, also give high intensity vibrations. Modes 7, 6, and 5 do not appear to contribute strongly to the PES profile (Table III). Further vibrational states having high intensities are listed in the [supplementary material](#) under SM3.

3. The vibrational profile of the A^2A_2 state

Two series 11^1 , 11^2 , 11^3 , and 11^4 and 2^1 , 2^2 , and 2^3 are prominent here. Several combination bands involving modes 2, 11 or both have high intensity, with 2^111^1 , 2^111^2 , 8^111^1 , 8^111^2 , 10^111^1 and the three simultaneously excited modes $2^18^111^1$ and $2^13^111^1$ are also particularly evident. Modes 7 and 4 do not appear to be prominent in the A state. Hence several of the same a_1 fundamentals occur in the X and A state (Fig. 5) profiles (Table III).

4. The vibrational profile of the B^2B_2 state

Although IE_3 (Fig. 5) has a very dominant 0-0 band, the PES baseline shows a significant non-zero count rate near $83\,500\text{ cm}^{-1}$, which arises from significant overlap with IE_2 . Weak vibronic interaction between these two states seems inevitable. The observation that the PES peaks of the 2B_2 state are considerably broadened, supports this proposal. The most intense cold band theoretical contributions arise from the a_1 modes, 11, 10, 9, and 8, as shown in Figure 5. The vibrational sequence 11^1-11^4 is notable. The most intense calculated combinations of two simultaneously excited modes are 9^111^1 , 10^111^1 , 9^110^1 ; several FCF with three simultaneously excited modes, including $6^19^111^1$, also have high intensity. Finally, some non- a_1 modes with significant intensity are excited, and these include 15^2 , 16^2 , and 17^2 (all b_1^2). A selection of the

TABLE III. Selected Franck-Condon calculated ionic state frequencies, intensities, and vibrational assignments which appear to be significant contributors to the PES. Examples of PES simulations are shown in Figures 4–6, but in all cases the simulation demonstrates that groups of these individual vibrational states occur together.

X^2B_1					
Energy/cm ⁻¹	Intensity	Assignment	Energy/cm ⁻¹	Intensity	Assignment
0	110 900	0 ⁰	980	4 454	8 ²
212	700 80	11 ¹	1327	40 400	4 ¹
424	313 00	11 ²	2654	10 860	4 ²
636	83 59	11 ³	1411	91 84	3 ¹
277	24 710	10 ¹	1528	85 200	2 ¹
554	3 287	10 ²	3056	40 620	2 ²
358	11 430	9 ¹	1719	2 227	1 ¹
490	35 200	8 ¹			
A^2A_2					
0	30 240	0 ⁰	291	11 850	10 ¹
203	30 810	11 ¹	582	3 141	10 ²
406	23 990	11 ²	371	4 262	9 ¹
609	12 210	11 ³	491	16 970	8 ¹
812	4 563	11 ⁴	982	3 740	8 ²
B^2B_2					
0	65 040	0 ⁰	579	374	11 ³
193	30 570	11 ¹	558	508	10 ²
269	8 544	10 ¹	614	1980	9 ¹ 10 ¹
345	16 310	9 ¹	687	1642	8 ¹ 11 ¹
386	4 432	11 ²	764	517	17 ² (b ₁ ²)
462	3 791	10 ¹ 11 ¹	839	674	8 ¹ ;9 ¹
494	2 022	8 ¹	880	279	8 ¹ ;11 ²
538	12 280	9 ¹ 11 ¹	883	1596	9 ² ;11 ¹
C^2B_1					
0	463 700	0 ⁰	1337	9 197	4 ¹
185	18 450	11 ¹	1358	9 730	15 ² (b ₁ ²)
274	35 480	10 ¹	1542	11 390	6 ²
346	47 020	9 ¹	1570	189 100	2 ¹
483	145 000	8 ¹	1595	16 070	5 ¹ 8 ¹
757	9 501	8 ¹ 10 ¹	1730	119 400	1 ¹
771	93 550	6 ¹	1844	18 380	2 ¹ 10 ¹
829	20 590	8 ¹ 9 ¹	1883	10 850	5 ¹ 6 ¹
966	25 670	8 ²	1916	26 320	2 ¹ 9 ¹
1112	39 070	5 ¹	2053	74 920	2 ¹ 8 ¹
1117	13 740	6 ¹ 9 ¹	2076	14 880	1 ¹ 9 ¹
1254	35 170	6 ¹ 8 ¹	2213	32 830	1 ¹ 8 ¹
1297	21 840	15 ¹ 16 ¹ (b ₁ ²)	2341	54 170	2 ¹ 6 ¹

lower frequency vibrations is shown in Table III, with further examples shown in the [supplementary material](#) under SM3.

5. The vibrational profile of the C^2B_1 state

Both the B and C state PES profiles are markedly improved from those of Figs. 3 and 4 in Eden *et al.*³ The larger separation (5906 cm⁻¹) of the C state from the B²B₂ state reduces the possibility for vibronic interaction, and C shows significant vibrational structure (Fig. 6). Although this state has a strong 0-0 band, a rich variety of a₁ modes are stimulated. The most intense single combination modes include 2¹10¹, 6¹8¹, 6¹9¹, 2¹10¹, and 8¹9¹. Only modes 7, 5, 4, and 3 make little

contribution. However, unlike the lower ionic states, a considerable number of other symmetry modes occur, including 15¹16¹(b₁²) and 15²(b₁²).

6. PES spectra for C₆H₅I and C₆F₅I

Only the four lowest IE, 1²B₁, 1²A₂, 1²B₂, and 2²B₁ are considered here. For both C₆H₅I and C₆F₅I, the assignment of these is to the X, A, B, and C states, respectively. Significant differences between the spectra occur, owing to the internal spacing leading to different levels of vibronic coupling between nearest neighbours. Our criterion in determining whether there is an interaction between adjacent IE or not is

TABLE IV. Comparison of the adiabatic ionization energies (eV) for $\text{C}_6\text{F}_5\text{I}$ and $\text{C}_6\text{H}_5\text{I}$. Pairs of states where overlap of the vibrational states occurs are indicated in italics.

	X^2B_1	A^2A_2	B^2B_2	C^2B_1
$\text{C}_6\text{F}_5\text{I}$	9.307	9.613	10.479	11.209
$\text{C}_6\text{H}_5\text{I}$	8.758	9.505	9.776	10.543

purely pragmatic. It depends on whether the general baseline of the PES is established between the bands in question in the PES. For example, the PES count between the X^2B_1 and A^2A_2 states never returns to the general baseline in the region near $78\,000\text{ cm}^{-1}$.

In order to gain additional insight into the overlap region of these two states, we sought a simultaneous two-state equilibrium structure, where the energies of the two states are identical and share a common structure. This conical interaction (ConInt) between the two states is performed under complete active space self-consistent field (CASSCF) conditions. A crossover of the theoretical potential energy curves of the X^2B_1 and A^2A_2 states for this region was found at 10.380 eV ($83\,722\text{ cm}^{-1}$), very close to the observed overlap of the two PES states. In contrast to our previous study of a ConInt for PhF ,³² no single parameter in the structure is necessary, since we are determining the complete structure where the two states have the same total energy, in a 2-state CASSCF. The two potential energy surfaces must be close in that region of the PES spectrum, and this confirms that vibronic interaction between the two states must occur.

In a similar study, a further conical interaction, this time between the A^2A_2 and B^2B_2 states, was found at 10.215 eV ($82\,393\text{ cm}^{-1}$). This ConInt shows that even when the PES peaks are nearly completely separated, vibronic interaction between the A and B states of $\text{C}_6\text{F}_5\text{I}$ can still be demonstrated, in the energy region relevant to the PES spectrum. The individuality of the 4 states in this ConInt is unambiguous from the CASSCF leading terms in the wave-functions and the contributing singly occupied MOs.

The inversion of the expected ConInt energy sequence, that for X and A lies above that for A and B, is purely a result of curvature in the potential energy curves. We conclude that vibronic interaction within each of the two pairs of states is inevitable. These interacting cases with potential energy curve crossing, associated conical interaction, are closely related to the ConInt that was found for X^2B_1 and A^2A_2 in PhF ,³² and this demonstration may be applicable to many other PES situations where bands are incompletely separated. The situations where vibronic interactions occur for the two molecules PhI and $\text{C}_6\text{F}_5\text{I}$ are shown in Table IV.

IV. CONCLUSIONS

This new PES study for $\text{C}_6\text{F}_5\text{I}$ makes substantial vibrational structure observable for the first time and allows us to determine and analyze the first four AIEs. When combined with the calculated ionic state results, the symmetry of several lower ionic states now seems to be unambiguous, namely, $\text{X}^2\text{B}_1 < \text{A}^2\text{A}_2 < \text{B}^2\text{B}_2 < \text{C}^2\text{B}_1 < \text{D}^2\text{A}_1 < \text{E}^3\text{B}_1$. Several of these conclusions arise from the ability to fit the PES

profile with Franck-Condon profiles of the appropriate symmetry. However, as with previous papers of this series, we recognize the importance of vibronic interactions, resulting from the overlap of the state vibrational sequences of the ionic states. Given that these vibronic interactions lie outside the current scope of our theoretical packages, we can only account for these effects by means of the FC profiles broadening with varying bandwidth. We applied this widely with the PhX series, where $\text{X} = \text{I},^{1,2} \text{Br},^{33} \text{Cl},^{34} \text{ and F}.$ ³²

Close proximity or overlapping between IE is relatively common in PES. As a consequence, the true IE, vertical as well as adiabatic, may not be at the places identified in early PES work. We believe that conical interactions, determined by theoretical means, are likely to occur frequently when interpreting the PES for polyatomic molecules. Many older PES spectra,³⁵ determined long before interacting states were computable via ConInt, have been used for ionization energy estimation and spectral assignments. ConInts could well have occurred in some of these situations, and hence our studies suggest that reinvestigation may be necessary to clarify these situations. Our pragmatic criterion for the presence of a ConInt is that the PES baseline is not completely re-established between groups of ionic state peaks.

There is a frequent need for additional knowledge in cases where PES spectra show complex vibrational profiles. One method is by careful consideration of the Franck-Condon profiles, as performed here. Our re-interpretation of the $\text{C}_6\text{F}_5\text{I}$ higher resolution PES is now on a rigorous footing. In a following paper, we will offer a re-assignment of the Rydberg and valence states in the VUV spectrum, with increased confidence as a result of the present PES study results. This is important, since new methods of analyzing VUV spectra combined with the development of computational methodologies allow for the simulation of vibrationally resolved electronic spectra, which can be directly compared with experiment. This leads to an improvement in understanding and analysis of the latter, and on occasion will include revision of previous findings.³⁶

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for SM1—the PES of $\text{C}_6\text{F}_5\text{I}$, SM2—structures of the neutral ground and some ionic states of $\text{C}_6\text{F}_5\text{I}$, SM3—Franck-Condon ionic state calculated frequencies, intensities, and vibrational assignments, SM4—the contributions of separate cold and hot band vibrations in the PES, SM5—the equilibrium structures of the two conical intersections involving the X^2B_1 and A^2A_2 states ($6b_1^{-1}$ with $3a_2^{-1}$) and A^2A_2 ($3a_2^{-1}$) with B^2B_2 ($11b_2^{-1}$).

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