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The ionic states of difluoromethane: A reappraisal of the low energy photoelectron spectrum including *ab initio* configuration interaction computations

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The ionic states of difluoromethane: A reappraisal of the low energy photoelectron spectrum including *ab initio* configuration interaction computations

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

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

²*International Centre for Quantum and Molecular Structures, College of Sciences, Shanghai University, 99 Shangda Road, Shanghai 200444, China*

³*Scuola Normale Superiore, Piazza Cavalieri 7, 56126 Pisa, Italy*

⁴*ISM-CNR, Istituto di Struttura della Materia, LD2 Unit, 34149 Trieste, Italy*

⁵*CNR-IOM Laboratorio TASC, Trieste, Italy*

⁶*ISA, Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark*

⁷*Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, USA*

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A new synchrotron-based study of the photoelectron spectrum (PES) of difluoromethane is interpreted by an *ab initio* analysis of the ionic states, which includes Franck-Condon (FC) factors. Double differentiation of the spectrum leads to significant spectral sharpening; the vibrational structure observed is now measured with greater accuracy than in previous studies. Several electronic structure methods are used, including equation of motion coupled cluster calculations with single and double excitations (EOM-CCSD), its ionization potential variant EOM-IP-CCSD, 4th order Møller-Plesset perturbation theory (MP4SDQ) configuration interaction (CI), and complete active space self-consistent-field (CASSCF) methods. The adiabatic ionization energies (AIEs) confirm the assignments as band I, one state 1^2B_1 (12.671 eV); band II, three states, 1^2B_2 (14.259) < 1^2A_1 (15.030) < 1^2A_2 (15.478 eV); and band III, three states, 2^2B_2 (18.055) < 2^2A_1 (18.257) < 2^2B_1 (18.808 eV). The three ionizations in each of the bands II and III lead to selective line broadening of the PES structure, which is attributed to vibronic overlap. The apparent lack of a vibrational structure attributable to both the 1^2A_1 and 2^2A_1 states in the PES arises from line broadening with the preceding states 1^2B_2 and 2^2B_2 , respectively. Although these 2^2A_1 states clearly overlap with their adjacent higher IE, some vibrational structure is observed on the higher IE. The effects of vibronic coupling are evident since the observed structure does not fit closely with the calculated Born-Oppenheimer FC profiles. Correlation of the lowest group of four AIEs in the PES of other members of the CH_2X_2 group, where $X = F, Cl, Br,$ and I , clearly indicate these effects are more general. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4998150>]

I. INTRODUCTION

Owing to the major impact on ozone concentrations in the atmosphere, the use of chlorofluorocarbons (CFCs, also known as *Freons*) in air-conditioning and refrigerating systems has been curtailed.^{1,2} Alternative coolants include the hydrofluorocarbons (HFC) such as difluoromethane (CH_2F_2 alternatively HFC-32). However, these are also being phased out as unsuitable; HFC-32 is not an ozone-depleting substance directly, but its global warming potential is approximately 675 times greater than that of CO_2 itself.^{1,2} In the upper atmosphere, CH_2F_2 is oxidised by the $O(^1D)$ oxygen atom³ that is formed from the photolysis of ozone. The estimated

overall lifetime in the atmosphere of HFC-32 is 5.1 yr, with the primary mechanism for removal via reaction with OH radicals.²

Accurate interpretation of spectral data for CH_2F_2 is important, and this paper concentrates on the ionic states of CH_2F_2 ; since we are primarily concerned with static properties, photochemical studies are only relevant in relation to the excited states involved.

Our ionization energy (IE) range is 12–20 eV. A variety of fragmentation processes^{4–10} compete with direct ionization within that range although these degradations are not expected to be visible in conventional photoelectron spectra. These processes have been summarised in threshold photoelectron-photoion coincidence (TPEPICO) studies⁶ on the dissociation of $CH_2F_2^+$. Such reactions include dissociation to $[CHF_2^+ + H]$ by H loss [13.065(3) eV]⁴ and $[CH_2F^+]$ by F loss [14.30 (6) eV]⁴ and fragmentation to $[CHF + HF]^+$ (13.3 eV).⁴

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

^{b)}Electronic addresses: biczysko@shu.edu.cn; marcello.coreno@elettra.eu; desimone@iom.cnr.it; Cesare.grazioli@elettra.eu; vronning@phys.au.dk; nykj@phys.au.dk; and kpeters@wsu.edu

Complexes between CHF^+ (fluorocarbene cation) and HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), which have the overall stoichiometry CH_2FX^+ , are well known in theoretical studies.¹¹ The complex $[\text{CHF} \cdots \text{HF}]^+$ has C_1 symmetry and is structurally very different from the X^1A_1 ground state of CH_2F_2 . It is claimed¹¹ to be more stable than the corresponding C_{2v} isomer by 929 cm^{-1} . In the light of these complexes, Forsysinski *et al.* considered⁴ the possibility that ionization of CH_2F_2 does not lead to states exhibiting C_{2v} symmetry, but the Franck-Condon factors (FCFs) for these complexes were too low for such species to appear in their Pulsed-Field-Ionization Zero-Kinetic-Energy (PFI-ZEKE) spectrum. However, inconsistent values for appearance potentials determined by electron ionization methods, in principle, might arise from such alternative structures for the species under ionization.⁴

Most early spectral PES results and assignments^{12–14} for CH_2F_2 have been superseded, enabling us to concentrate on recent studies.^{4,8} Electron impact (EI)^{15–18} and theoretical methods^{19,20} are sources where additional information can also be found.

The most accurate experimental determination of the adiabatic IE (AIE) of CH_2F_2 is $12.7252(9)\text{ eV}$, from the PFI-ZEKE spectrum,⁴ which was also subjected to anharmonic analysis.⁵

The threshold photoelectron spectrum (TPES) for CH_2F_2 covers a similar ionization energy range⁶ to our synchrotron-based conventional PES. It differs significantly in the 17–18 eV range, owing to autoionisation effects that are known to be prevalent in TPES.⁶ A comparison is shown in the [supplementary material SM1](#). The TPES study⁶ included a Franck-Condon factor (FCF) analysis for several PES bands. We build upon this study in the current paper.

The PES of CH_2F_2 , shown in Fig. 1, contains just three bands, each having a spectral width of $\sim 2\text{ eV}$. Several previous studies^{4,12–14} have led to the agreement that these bands, in increasing energy order, contain one, three, and three ionic

states, respectively. Thus, in bands II and III, three IEs are compacted into a similar energy range to that of the single IE₁ in band I. Our previous studies of monohalobenzenes ($\text{C}_6\text{H}_6\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}$, and I)^{21,22} clearly indicate that overlapping of IE in photoelectron spectra will lead to major vibronic interactions. Unless these interactions are explicitly considered, even high quality theoretical studies cannot give a satisfactory interpretation.^{21,22}

We believe that previous studies of the CH_2F_2 PES have taken a deceptively simple interpretation of the spectrum. A reason for the current investigation is to analyze the observed PES in unprecedented detail and compare the results with high quality theoretical data, to confirm these views.

To extract additional fine structures from our photoelectron spectrum, we use two approaches. In the first, we use the second derivative of the spectrum. This approach is related to a signal sharpening technique, originally utilised for deconvolution of electron spin resonance (ESR) spectra.²³ Second, we relatively enhance the weak structure already seen in the PES, on both the rising and trailing edges of the PES bands, by fitting the main structure to analytical functions and analyze the regular residuals (RRs). Together, this leads to the most comprehensive vibrational analysis for CH_2F_2 ionization, as shown in the [supplementary material SM2](#). The influence of hot and cold bands on the vibrational spectral profiles is given in [supplementary material SM3](#), while the interpretation of the wider valence shell PES is given in [supplementary material SM4](#).

To facilitate comparison with other work, we use electron volts (eV) for wide scan energy ranges and ionization energies. Interpretation of the vibrational profiles is facilitated by the use of wavenumber units (cm^{-1}). Some previous studies give alternative ionic state symmetry assignments; these arise from alternative C_{2v} axis choices for σ_v , as either CF_2 or CH_2 group axes. In our C_{2v} study, the CF_2 unit of CH_2F_2 lies in the y,z -plane; where necessary, the alternative choice results have been reassigned to this orientation.

FIG. 1. The PES (black) with the second derivative (2ndD) of the spectral profile superimposed below (red). The definition of the fine structure is much improved in the 2ndD spectrum; this allows more accurate determination of the vibrational frequencies. The extended onset of the first state in band II (A or 1^2B_2) state to low energy is visible in the derivative spectrum, as well as the almost complete lack of structure for the (B) 1^2A_1 state in the center of band II. The vibrational analysis of the fine structure at the tail of band III is preceded by subtraction of a Boltzmann sigmoid function, as is discussed in the text. The sequence of assigned ionic states by symmetry is shown in Fig. 2.

II. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

A. Experimental methods

The photoelectron spectrum was obtained on the Elettra synchrotron using an irradiation energy of 55 eV and an overall energy resolution of 11 meV (89 cm^{-1}) with the same procedure as described previously.²¹ The present range of the spectrum is 12–21 eV, which contains 5000 data points with a spacing of 2 meV (16 cm^{-1}). Similarities and differences in appearance between our photoelectron spectrum and to both the threshold (TPES)⁶ and PFI-ZEKE⁴ spectra are discussed below.

Our new spectrum, shown in Fig. 1, includes the second derivative (2ndD) of the PES signal, which demonstrates the additional signal sharpening obtained. Direct comparison of the PES and 2ndD requires inversion of the latter signal.

B. Computational methods

The use of alternative theoretical strategies became necessary, as shown below. Initially, equilibrium geometries and

harmonic vibrational frequencies for the CH_2F_2 ground state (X^1A_1) and seven cationic states used the EOM-CCSD and the related EOM-IP-CCSD methods, respectively,²⁴ as implemented in the CFOUR program package.²⁵ These states were also obtained with state-averaged (SA) multi-configuration SCF (MCSCF) as implemented in MOLPRO.²⁶ The Møller-Plesset fourth order method,^{27–29} including single, double, and quadruple substitutions (MP4SDQ) as incorporated in the GAUSSIAN-09 suite (G-09),³⁰ was directly capable of performing FC analyses thanks to its ability to localize stationary points, which has proved difficult at the EOM-IP level. The FC analysis and simulation of vibrationally resolved electronic spectra have been performed by means of the Time-Independent Adiabatic Hessian Franck-Condon (TI-AHIFC) model based on the studies of Bloino *et al.*^{31–34} MP4SDQ is known to produce energetic results comparable with CCSD(T),^{27–29} often called the “gold standard” in quantum chemistry.³⁵

Most of the results described here were performed with the augmented, correlation consistent, polarized valence triple (and quadruple) zeta basis sets (aug-cc-pVTZ and aug-cc-pVQZ).^{36,37} The former generates 215 Gaussian basis functions (GBF) with **C** and **F** contracted to 5s4p3d2f functions and **H** contracted to 4s3p2d functions. The latter basis with 425 GBF contains 6s5p4d3f2g functions for **C** and **F** and 5s4p3d2f functions for **H** atoms.

C. Data processing

Given the complex profile of the PES, our pragmatic approach is to simplify the spectrum by the subtraction of mathematical functions across selected ranges of PES energy. These enhance the weak structure by the subtraction of the underlying broad features. The choice of function was based on which function gave the most spectral features in the resulting regular residuals (RRs), where much more detail is visible than on the original PES. The number of data points observed in local RR peaks lies well above the noise level. Where further simplification of the spectra was required, the RRs were subjected to a combination of double differentiation (DD) and fast Fourier transform (FFT) to select the most common frequencies. The nature of some of these sigmoid

Boltzmann or Gaussian functions is shown in the [supplementary material](#).

III. RESULTS

A. General aspects

The most accurate equilibrium spectral structure^{38,39} of CH_2F_2 , using earlier microwave (MW) measurements, is compared in Table I with several ionic states, all constrained to C_{2v} symmetry. Considerable geometric changes occur for the ionic states relative to the X^1A_1 state, both in bond lengths and angles. The experimental MW bond angles show that the **HCH** angle is larger than the **FCF** angle, an example of Bent’s rule.^{40,41} When ionization leads to a considerable structural change, a slow onset occurs in the PES, with a considerable difference between AIE and vertical IE (VIE), as is discussed below. Several of the present PES features in Fig. 1 exemplify this, including those related to the X^2B_1 and A^2B_2 states (IE_1 and IE_2).

Vibrational modes within one symmetry, in a decreasing magnitude sequence, follow the work of Tasinato *et al.*⁴² Modes are numbered as follows: a_1 , 1-4; a_2 , 5; b_1 , 6-7; and b_2 , 8-9. Several high-resolution Fourier transform infrared (FTIR) spectral studies have been reported.^{43–46} However, several of the IR bands analyzed show perturbations through Coriolis and other interactions; our theoretical harmonic values do not include such interactions. The analyses used for comparisons between theory and experiment in the X^1A_1 state are given in Table II.

B. The wide scan PES

Our previous criterion for vibronic interaction is that it must be expected unless the PES baseline is re-established between the contributing states. We have verified the presence of several conical interactions (ConInts), positions²² where crossings occur between the potential energy surfaces for each pair of states. The series of the ConInt results is shown in the [supplementary material](#); these were determined by state-average complete active space SCF studies (CASSCF). At a ConInt, the energies of the two states become equal and share a single structure.

TABLE I. Comparison of the microwave spectral structure^{38,39} of CH_2F_2 with the calculated adiabatic ionization energies (AIEs) for the ground and ionic state structures using the MP4SDQ method (states X, A to C) and EOM-IP-CCSD (states D to F) methods with the aug-cc-pVTZ basis set.

State		AIE ^a (eV)	AIE ^a (cm ^{−1})	VIE ^a (eV)	VIE−AIE (eV)	C−H (Å)	C−F (Å)	H−C−H (deg)	F−C−F (deg)
1 ² B ₁	X	12.687	103 717 ^b	13.247	0.560	1.170 6	1.271 0	86.6	116.6
1 ² B ₂	A	14.229	114 763	15.155	0.926	1.082 8	1.407 3	122.5	83.5
1 ² A ₁	B	15.218	122 743	15.330	0.112	1.113 0	1.367 9	126.3	118.0
1 ² A ₂	C	15.514	126 321	15.844	0.330	1.084 7	1.423 0	120.2	97.0
2 ² B ₂	D	18.055	145 589	18.826	0.776	1.102 9	1.503 2	138.1	112.5
2 ² A ₁	E	18.257	146 524	18.843	0.677	1.086 4	1.509 1	124.1	93.1
2 ² B ₁	F	18.808	151 696	19.43	0.80	1.151 0	1.439 8	99.5	106.7
X ¹ A ₁	X	0	0	0	0	1.088 3	1.353 7	113.3	108.3
X ¹ A ₁	X	Microwave structure ^c				1.087 03(3)	1.353 23(1)	113.442(9)	108.282(2)

^aRelative to the X^1A_1 ground state energies.

^bForynski *et al.*⁴ gave the X^2B_1 0-0 band as 12.7250 eV (102 636 cm^{-1}).

^cExperimental equilibrium structure; see Ref. 39 for further details.

TABLE II. Calculated harmonic MP4SDQ fundamental vibrational wavenumbers, for the states in bands I, II, and III of the photoelectron spectrum. Imaginary frequencies are denoted by “i.”

Mode	Vibration symmetry	X ¹ A ₁ Expt. ^a	X ¹ A ₁	X ² B ₁	A ² B ₂	B ² A ₁	C ² A ₂	D ² B ₂	E ² A ₁	F ² B ₁
v ₁	a ₁	2947.9(1)	3100	2514 ^b	3162	2751	3141	3141	2923	2959
v ₂	a ₁	1509.60(8)	1570	1292 ^b	1521	1396	1517	1448	1357	1542
v ₃	a ₁	1111.61(7)	1150	1096 ^b	1111	923	1006	841	845	1016
v ₄	a ₁	528.34(3)	540	604	545	453	472	433	361	455
v ₅	a ₂	1256.8(2)	1297	997	1119	1187	1040	781	1199	3617i
v ₆	b ₁	3014.45(4)	3172	2069	3305	3258	3271	3302	3012	1627
v ₇	b ₁	1178.74(6)	1207	618	1182	1358	1165	1057	967	781
v ₈	b ₂	1435.5(1)	1486	1512	2382	1268	1449	1073	1313	1635
v ₉	b ₂	1089.9(1)	1143	1085	1233	1557	651	674	1685i	1188

^aTasinato *et al.*,⁴² gives a detailed analysis of the observed and calculated vibrational spectrum.

^bForysinski *et al.*,⁴ using an aug-cc-pVQZ basis set at the MP2(FC) level, gave theoretical values for the a₁ sequence for both the X¹A₁ and X²B₁ states. The v₄ to v₁ values are as follows: for X¹A₁, 533, 1132, 1562, and 3125 cm⁻¹; similarly, for X²B₁, 605, 1062, 1292, and 2528 cm⁻¹, respectively.

1. Adiabatic ionization energies (AIEs) compared with calculated values

The AIEs results from the EOMIP-CCSD study shown in Table I are superimposed in Fig. 2 (in blue) together with their symmetry assignments. The values are similar to those of Tuckett *et al.*⁸ Because of the slow onset in some PES bands, it is more appropriate to compare the band maxima with calculated vertical IE (VIE). The Tamm-Dancoff approximation (TDA), a single excitation CI method, gives vertical ionization energies (VIEs) closer to experimental maxima; TDA VIEs are shown in red in Fig. 2. These are discussed further in the [supplementary material](#), which includes higher PES bands. The FC analyses are discussed below.

2. Harmonic frequencies for the X¹A₁ and ionic states, compared with experiment

The results for all ionic states thought to be present in bands I and II were obtained using the MP4SDQ procedure and are shown in Table II. No imaginary frequencies occur for these ionic states when using this method; this establishes genuine minima for the state structures. The EOM-IP-CCSD method

led to imaginary frequencies for two of the three states in band III, showing that the apparent equilibrium structures are saddle points; here the full minimum energy structure would distort to lower symmetry. The CASSCF procedure does not lead to imaginary frequencies for any of these three states, showing the importance of a wide range of configurations in these states. However, the C_{2v} structures from all three methods, MP4SDQ, EOM-IP-CCSD, and CASSCF, are very similar, so the distortions for the saddle point structures must be small. For the FC analyses, the a₁ symmetry modes are the most important, and no cases of imaginary frequencies occur for this symmetry. For both our X¹A₁ and X²B₁ ionic state structures, the frequencies are like those calculated by Forysinski *et al.*⁴ who used the MP2 (second order) level of theory, but with a larger basis set.

C. Vibrational analysis of the PES for CH₂F₂

1. The experimental spectrum for CH₂F₂

We measure the principal vibration wavenumbers electronically from the second derivative spectra, by “peak picking” with the Origin 2016 suite. The PES data points are separated in energy by 16.1 cm⁻¹ (0.002 eV) throughout this spectral range (11–20 eV), and approximately 10 data points are included in each peak. Previous studies, reviewed by Tuckett *et al.*,⁸ reported wavenumbers obtained by direct measurement of the PES peaks; since these maxima are not well defined, alternative values arise.^{8,12–14} Further details of our measurements are shown in the [supplementary material](#).

2. Band I of the PES for CH₂F₂

Even band I in the spectrum is deceptively simple, showing an apparent multiplet with 14 maxima having a mean separation of 1069 cm⁻¹ (Fig. 2). However, the peak width increases towards higher energy, indicating the presence of more than one vibration.⁸ Analysis of band I via DD and FFT shows that an apparent set of wavenumbers, 1093, 558, 389, and 288 cm⁻¹, are present. Although the higher pair of values are close to the calculated v₃ and v₄ in Table II, v₃ is also close to 2v₄; furthermore, v₂ ≈ v₃ ≈ ½v₁. These relationships do not hold for CD₂F₂, explaining the PES difference between the

FIG. 2. The EOM-IP-CCSD adiabatic ionization energies and their symmetry assignments (in blue) superimposed on the photoelectron spectrum of CH₂F₂ obtained with 55 eV irradiation. The vertical IEs were obtained with the TDA procedure (red). These methods confirm the assignment of 1, 3, and 3 IEs under bands I, II, and III.⁶

FIG. 3. Band I of the PES with the FC profile superimposed as a stick diagram (blue). The very weak peaks from FC profiles between the main set of vibrations are hot bands. The spectral band origin in the PES occurs at $102\,805\text{ cm}^{-1}$ (12.746 eV). Further details are given in the [supplementary material](#), where a comparison with the corresponding 2nd derivative spectrum is shown; this provides proof that the differentiation procedure is successful elsewhere in the spectrum.

spectra for CH_2F_2 and CD_2F_2 where no distinct vibrations can be identified in the D_2 case. A similar explanation has been used to explain the differing PES appearance of band III for H_2CO and D_2CO .¹⁴

The FC analysis of the vibrational structure arising from the $\text{X}^2\text{B}_1 \leftarrow \text{X}^1\text{A}_1$ transition in band I is demonstrated in Fig. 3; it shows that each of the broad peaks is a complex set of individual vibrational bands. In the range shown, 119 cold vibrational states occur. The leading terms are shown in Table III.

All four a_1 symmetry modes, in a variety of combinations, contribute to our theoretical analysis of band I (Table III). A direct comparison of our analysis in Fig. 3 with Table III, and the corresponding Fig. 2 and Table III shown by Tuckett *et al.*,⁸ shows that the interpretation here is more detailed and gives a better fit between theory and experiment.

Further resolution of the experimental band I profile will need a much wider scan range in a ZEKE-style spectrum. The existing PFI-ZEKE⁴ spectrum lies under the first three maxima shown in Fig. 3 but is limited in range by dissociation. Further details are shown in the [supplementary material](#). Several vibrational frequencies occur in the experimental PFI-ZEKE spectrum;⁴ some of the strongest have wavenumbers 969 , 1137 , 1246 , 1669 , and 2257 cm^{-1} , but the assignment of these is unclear since they do not fit the predicted vibrations of the $[\text{CHF} \cdots \text{HF}]^+$ complex or the X^1A_1 state with C_{2v} symmetry.

3. Band II of the PES

This has widely been recognized as a composite band containing contributions from three ionic states (A, B, and C).⁶ The present AIE study of the symmetry sequence gives $^2\text{B}_2 < ^2\text{A}_1 < ^2\text{A}_2$, in agreement with the studies of Tuckett *et al.*,⁸ Takeshita,¹⁹ and Xi and Huang²⁰ (after allowing for interchange of B_1 and B_2 symmetry axes). The most intense contributions to the theoretical FC profiles are listed in Tables IV–VI. In the present discussion, ionic states of a single symmetry are designated 1, 2, 3 in sequence of low to high energy, rather than using X for the first of each symmetry.

Analysis of band II is most easily accomplished by starting with the two ends since the fine structure is most evident there. The onset of band II shows a set of weak peaks on a rising background; direct measurement of these peak separations gives a wavenumber of 542 cm^{-1} (for the best-defined central region), declining to 505 cm^{-1} at the apparent end of the sequence at $122\,897\text{ cm}^{-1}$ (15.237 eV). Beyond this energy, the structure becomes irregular, and this is attributed to the contributions from the second state (1^2A_1) under the envelope.

Subtraction of a Boltzmann sigmoid background from the rising onset leaves a high RR count rate as shown in Fig. 4. The 1^2B_2 state FC profile is superimposed, and this gives an excellent interpretation of the peak separations.

TABLE III. The 1^2B_1 (X) state for CH_2F_2 . Calculated peak positions (cm^{-1}) for the first ionization energy (IE_1) are based on the harmonic frequencies and assignments. Each observed PES peak is a composite of several fundamental vibrations, as discussed in the text and Fig. 3.

Wavenumber (cm^{-1})	Assignment ^a	Intensity ^b	Wavenumber (cm^{-1})	Assignment ^a	Intensity ^b
0	0-0	4 806	4703	$1^12^13^1$	12 590
1038	3^1	11 240	4760	2^33^1	5 642
1241	2^1	6 350	5537	1^13^3	6 141
2075	3^2	11 050	5594	2^23^3	5 627
2278	2^13^1	14 920	5741	$1^12^13^2$	14 060
2482	2^2	4 572	5798	2^33^2	5 604
3113	3^3	5 703	5944	$1^12^23^1$	9 374
3316	2^13^2	14 760	6778	$1^12^13^3$	8 438
3462	1^13^1	9 265	6982	$1^12^23^2$	10 430
3519	2^23^1	10 770	7185	$1^12^33^1$	4 975
3666	1^12^1	4 822	8019	$1^12^23^3$	6 295
4353	2^13^3	7 681	8165	$1^22^13^2$	5 524
4500	1^13^2	10 290	8223	$1^12^33^2$	5 548
4557	2^23^2	10 730			

^aThe PES energy of the 0-0 transition: $102\,854\text{ cm}^{-1}$.

^bMolar absorption coefficient/ $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$.

TABLE IV. Selected cold band fundamentals and combination bands for the 1^2B_2 state of CH_2F_2 . Intensities in each table are in molar absorption coefficient/dm³ mol⁻¹ cm⁻¹.

1^2B_2 assigned to the A state					
Energy (cm ⁻¹)	Intensity	Assignment	Energy (cm ⁻¹)	Intensity	Assignment
Cold bands					
0		0 ⁰	4827	5 517	2 ¹ 4 ⁷
4292	5270	4 ⁸	5364	8 224	2 ¹ 4 ⁸
4828	6936	4 ⁹	5901	10 900	2 ¹ 4 ⁹
5365	8220	4 ¹⁰	6437	6 242	2 ² 4 ⁸
5901	8872	4 ¹¹	6437	13 010	2 ¹ 4 ¹⁰
6437	8783	4 ¹²	7510	10 060	2 ² 4 ¹⁰
6974	8033	4 ¹³	7510	14 100	2 ¹ 4 ¹²
7510	6829	4 ¹⁴	8046	11 020	2 ² 4 ¹¹
8047	5424	4 ¹⁵	8047	12 990	2 ¹ 4 ¹³

Our alternative signal sharpening double differentiation (DD) technique leads to a sharp drop in residual counts by some 10^3 and is most advantageous when the count rate is extremely high; the additional detail obtained is considerable. After FFT analysis, this yields a mean wavenumber of 533 cm^{-1} , accompanied by a further splitting of 82 cm^{-1} that is also apparent in the second derivative spectrum. The higher value is very close to ν_4 of the 2^2B_2 state in Table II.

The trailing edge of band II shows several very intense maxima. It is appropriate to consider the strong features first; any remainder after assignment might then be attributed to the $1^2A_1 \leftarrow X^1A_1$ transition since the central maximum at $124\,118\text{ cm}^{-1}$ (15.388 eV) shows little discernible structure.

The well-defined maxima on the high-energy side (trailing edge) of band II, sharpened by differentiation, give vibrational separations of 1011 and 501 cm^{-1} , close to those of ν_3 and ν_4 for the 2^2A_2 ionic state in Table II. The alternating intensities suggest that these are not ν_4 and $2\nu_4$.

DD of the trailing edge gave the results displayed in Fig. 5. There is a significant loss in intensity but additional

subsidiary peaks become apparent. The calculated wavenumbers for the 1^2A_2 state fit tightly to the observed spectrum as shown in Table VI. This is less apparent when the vibrational profile of the $1^2A_2 \leftarrow X^1A_1$ transition is directly plotted against the unprocessed photoelectron spectrum in Fig. 6. In these latter circumstances, differences in intensities with the assignment of 1^2A_2 occur; the calculated strong bands appear to be of similar intensity in adjacent pairs; this contrasts with the band II spectrum, where the peaks alternate in intensity.

The central region of band II (with maximum near $124\,100\text{ cm}^{-1}$) does not show sufficient detail to allow further experimental study. However, the unassigned positions, marked X and Y in Fig. 6, can be assigned to the onset of transitions into the B and C states, respectively, since they do not fit the profiles for the B state, which we have identified as 1^2B_2 . The shape of the PES band II between positions X and Y can be interpreted by the three principal FC factors for the $1^2A_1 \leftarrow X^1A_1$ transition. Its calculated profile shows considerable intensity but is overwhelmed by the two adjacent states. Attempts to overlay

TABLE V. Selected cold band fundamentals and combination bands for the 1^2A_1 state of CH_2F_2 . Assignments calculated by the MP4SDQ method.

1^2A_1 assigned to the B state					
Energy (cm ⁻¹)	Intensity	Assignment	Energy (cm ⁻¹)	Intensity	Assignment
Cold bands					
0	19 510	0 ⁰	1367	5 040	3 ¹ 4 ¹
455	386 600	4 ¹	1872	186 400	2 ¹ 4 ¹
909	539 900	4 ²	2326	261 900	2 ¹ 4 ²
1364	451 100	4 ³	2781	219 900	2 ¹ 4 ³
1818	251 000	4 ⁴	3235	122 800	2 ¹ 4 ⁴
2273	97 940	4 ⁵	3289	59 380	2 ² 4 ¹
2727	19 070	4 ⁶	3690	47 940	2 ¹ 4 ⁵
3182	4 494	4 ⁷	3743	50 170	2 ² 4 ²
912	4 734	3 ¹	4198	42 150	2 ² 4 ³
1417	104 700	2 ¹	4652	23 500	2 ² 4 ⁴
2834	22 340	2 ²	4706	6 158	2 ³ 4 ¹
2775	9 852	1 ¹	5160	7 353	2 ³ 4 ²
			5615	3 856	2 ³ 4 ³

TABLE VI. Selected cold band fundamentals and combination bands for the 1^2A_2 state of CH_2F_2 and assignments.

1^2A_2 assigned to the C state					
Energy (cm $^{-1}$)	Intensity	Assignment	Energy (cm $^{-1}$)	Intensity	Assignment
Cold bands					
0	254 500	0 0	1950	152 100	3 1 4 2
472	244 600	4 1	1989	15 990	2 1 4 1
944	102 300	4 2	2308	15 890	3 1 9 2
1006	370 400	3 1	2422	36 260	3 1 4 3
1302	7 478	9 2	2461	6 345	2 1 4 2
1416	24 000	4 3	2523	33 980	2 1 3 1
1478	359 500	3 2 4 1	2894	5 205	3 1 4 4
1517	17 420	2 1	2956	160 000	3 2 4 2
1774	7 129	9 2 4 1	3314	14 940	3 2 9 2
2012	371 800	3 2	3428	39 250	3 2 4 3
2484	368 900	3 2 4 1	3529	29 140	2 1 3 2
3018	218 500	3 3	3901	5 832	3 2 4 4
3490	222 000	3 3 4 1	3962	98 840	3 3 4 2
4024	83 740	3 4	4320	5 432	3 3 9 2
4496	87 260	3 4 4 1	4434	24 980	3 3 4 3
5030	17 160	3 5	4535	10 650	2 1 3 3
5502	18 170	3 5 4 1	4968	39 960	3 4 4 2
6036	3 942	3 6	5441	10 430	3 4 4 3
6508	4 304	3 6 4 1	5541	4 250	2 1 3 4
			5974	8 479	3 5 4 2

the $1^2A_1 \leftarrow X^1A_1$ FC profile on the spectrum only gives a good fit, when the half-width at half-maximum (HWHM) is set to much larger values than the freely standing vibrational structure, where a value near 75 cm $^{-1}$ is suitable. The analysis for band I in Fig. 3 is a standard example.

Lack of structure attributable to the $1^2A_1 \leftarrow X^1A_1$ transition in band II has a parallel for the $2^2A_1 \leftarrow X^1A_1$ transition in band III, which is not visible in the experimental

photoelectron spectrum and is again the middle IE of three closely placed states.

4. Band III of the PES

Vibrational structure is present on both the low and high energy sides of band III but is particularly weak on the trailing side. Previous vibrational analyses agreed over the presence of three ionic states under the envelope (as D, E, and F states), but alternative conclusions^{8,12–14} arose for the symmetry sequence. Tuckett *et al.*⁸ gave the sequence, based on equilibrium structure searches, as $^2B_2 < ^2A_1 < ^2B_1$. Pradeep

FIG. 4. The onset of band II of the PES after subtraction of a Boltzmann sigmoid curve. The 1^2B_2 (A state) FC profile is superimposed in blue. Some 360 data points are contained in the region shown. Almost all the structures are interpreted as 1^2B_2 , with the 0-0 band at 116 051 cm $^{-1}$ (14.388 eV). Several weaker series of vibrational states from the FC profile occur between the main set of vibrations. Structures up to the maximum near 15.4 eV are attributed to a further state (B) here as 1^2A_1 . The peak intensity distribution in the second derivative curve (B) suggests that peaks beyond 122 800 cm $^{-1}$ do not fit the same pattern.

FIG. 5. Trailing edge of band II in the photoelectron spectrum after processing by double differentiation. The 1^2A_1 Franck-Condon profile is superimposed (blue). Alternate peaks correlate with a single FC line, whereas the intervening peaks clearly have a more complex structure.

FIG. 6. The proposed fit of the envelope of the central portion and trailing edge of band II with the two states 1^2A_1 (B state, in green) and 1^2A_2 (C state, in red). Calculated state 0-0 bands are B: $123\,152\text{ cm}^{-1}$ (15.274 eV) and C: $125\,317\text{ cm}^{-1}$ (15.537 eV). The points marked X and Y are where the 0-0 bands of the 1^2A_1 and 1^2A_2 states are thought to lie.

and Shirley¹³ claimed to have analyzed band III in terms of these three states and to have separated vibrational sequences for each state; but this view has been challenged as optimistic,⁶ in the light of the published signal-to-noise.¹³ We agree with this criticism. We will show below that transitions into each of these states have a more complex profile.

Direct measurement of the onset of band III shows the sharp series of peaks that have a mean separation of 681 cm^{-1} . We believe this value correlates with 670 cm^{-1} by Tuckett *et al.*⁸ and 724 cm^{-1} by Pradeep and Shirley.¹³ A weak satellite, initially on the high-energy side, passes through the main sequence. Above $152\,000\text{ cm}^{-1}$ (18.845 eV), there are numerous local maxima on the high-energy side. The peak at $146\,302\text{ cm}^{-1}$ (18.139 eV) appears to be the origin of band III (D state). We amplify this structure in the following description.

Subtraction of a Boltzmann function from the onset of band III retains a high counting rate for the RR. The resulting structure is shown in Fig. 7, with the $2^2B_2 \leftarrow X^1A_1$ transition superimposed. The choice of assignment for the onset of band III is difficult. The primary separation mentioned above, 681 cm^{-1} , is not close to the calculated values for a single quantum

FIG. 7. The onset of band III of the PES after subtraction of a Boltzmann sigmoid curve. The 2^2B_2 FC profile is superimposed in blue, with the contributing individual vibrational states shown in red. Some 620 data points are contained in the region shown.

FIG. 8. The onset of band III after double differentiation. The Franck-Condon profile of the D state superimposed as 2^2B_2 shows many similar features. The 2^2A_1 state is also similar, but its lower ν_4 frequency leads to more closely placed strong bands. The 2^2B_1 state does not superimpose satisfactorily. The proximity of the proposed D, E, and F states is expected to lead to some distortion of peak positions and width.

of ν_3 or ν_4 for any of the 2^2B_2 (841 and 433 cm^{-1}), 2^2A_1 (845 and 361 cm^{-1}), or 2^2B_1 (1015 and 455 cm^{-1}) states shown in Table II.

DD leads to a sharper vibrational structure, at the expense of loss of count rate, as shown in Fig. 8. By both methods, each main sequence peak contains numerous data points. Although the peaks in Fig. 8 and some subsidiary ones are relatively close to the PES profile, the fit is far from close. However, the interaction with both the nearby ionic states, 2^2A_1 and 2^2B_1 , make a close fit unlikely, unless vibronic interactions are included.^{22,47}

TABLE VII. The 2^2B_2 state for CH_2F_2 . Calculated peak positions (cm^{-1}) for the ionization energy are based on the harmonic frequencies and assignments. Each observed PES peak is a composite of several fundamental vibrations, as discussed in the text.

2^2B_2 state	Assignment	Intensity
1682	3^2	1 366 000
2115	$3^2 4^1$	986 300
2523	3^3	3 223 000
2956	$3^3 4^1$	2 365 000
3364	3^4	5 445 000
3797	$3^4 4^1$	4 062 000
4206	3^5	7 001 000
4230	$3^4 4^2$	1 098 000
4639	$3^5 4^1$	5 315 000
5047	3^6	7 108 000
5071	$3^5 4^2$	1 470 000
5480	$3^6 4^1$	5 495 000
5654	$2^2 4^1$	1 077 000
5888	3^7	5 832 000
5913	$3^6 4^2$	1 557 000
6321	$3^7 4^2$	4 597 000
6495	$2^1 3^6$	1 069 000
6729	3^8	3 925 000
6754	$3^7 4^2$	1 336 000
7162	$3^8 4^1$	3 158 000
7570	3^9	2 185 000
8003	$3^9 4^1$	1 797 000
8411	3^{10}	1 009 000

TABLE VIII. The 2^2B_1 state for CH_2F_2 . Calculated peak positions (cm^{-1}) for the ionization energy are based on the harmonic frequencies and assignments. Each observed PES peak is a composite of several fundamental vibrations, as discussed in the text.

2^2B_1 state	Assignment	Intensity
0		1 597 000
1016	3^1	5 318 000
1471	$3^1 4^1$	1 648 000
2032	3^2	8 501 000
2487	$3^2 4^1$	2 635 000
2558	$2^1 3^1$	1 094 000
3048	3^3	8 678 000
3503	$3^3 1^1$	2 692 000
3573	$2^1 3^2$	1 667 000
3975	$1^1 3^1$	2 010 000
4063	3^4	6 346 000
4519	$3^4 4^1$	1 969 000
4589	$2^1 3^3$	1 617 000
4991	$1^1 3^2$	3 085 000
5079	3^5	3 533 000
5534	$3^5 4^1$	1 097 000
5605	$2^1 3^4$	1 119 000
6007	$1^1 3^3$	3 015 000
6095	3^6	1 554 000
6533	$1^1 5^1 3^2$	1 159 000
7023	$1^1 3^4$	2 104 000
7549	$1^1 5^1 3^3$	1 105 000
8039	$1^1 3^5$	1 114 000

TABLE IX. The 2^2A_1 state for CH_2F_2 . Calculated vibrational positions (cm^{-1}) for the ionization energy are based on the harmonic frequencies and assignments. Only the most intense vibrational states are shown. Those exciting only fundamentals are all weak, leaving only combination bands as the most intense. Each observed PES peak is a composite of several fundamental vibrations, as discussed in the text.

2^2A_1 state	Assignment	Intensity
2772	$3^2 4^3$	1 480 000
3133	$3^2 4^4$	1 577 000
3256	$3^3 4^2$	1 095 000
3493	$3^2 4^5$	1 205 000
3617	$3^3 4^3$	1 700 000
3769	$2^1 3^2 4^2$	1 004 000
3978	$3^3 4^4$	1 800 000
4129	$2^1 3^2 4^3$	1 551 000
4338	$3^3 4^5$	1 365 000
4462	$3^4 4^3$	1 323 000
4490	$2^1 3^2 4^4$	1 634 000
4614	$2^1 3^3 4^2$	1 130 000
4823	$3^4 4^4$	1 391 000
4851	$2^1 3^2 4^5$	1 232 000
4974	$2^1 3^3 4^3$	1 735 000
5183	$3^4 4^5$	1 046 000
5335	$2^1 3^3 4^4$	1 815 000
5696	$2^1 3^3 4^5$	1 358 000
5819	$2^1 3^4 4^3$	1 312 000
6180	$2^1 3^4 4^4$	1 362 000
6541	$2^1 3^4 4^5$	1 010 000

FIG. 9. The trailing edge of band III after subtraction of a Boltzmann function. The regular residual peaks show an interval near 600 cm^{-1} , which does not correspond to any of the predicted harmonic frequencies for any of the 2^2B_2 , 2^2A_1 , and 2^2B_1 states that lies in this energy range. The FC profile of the 2^2B_1 state is superimposed and shows some similarity.

Many of the most intense FC bands shown for the transitions into these three states in Tables VII–IX occur with two quanta. The onset of band III is dominated by a single wide sequence, and only the $2^2B_2 \leftarrow X^1A_1$ transition appears to fit this. The principal sequence for the $2^2B_1 \leftarrow X^1A_1$ transition is ν_3 (1016 cm^{-1}) rather than ν_4 (455 cm^{-1}). In contrast, the $2^2A_1 \leftarrow X^1A_1$ transition contains many strong lines with small separations, and no single sequence stands out from the considerable number of participating lines.

The trailing edge of band III shows a very weak structure. Direct measurement of the lowest separation suggests a value of 632 cm^{-1} , increasing with energy. This value is smaller than that determined by direct measurement of the PES band III by both Tuckett *et al.*⁸ and Brundle *et al.*¹² (670 and 645 cm^{-1} , respectively). As mentioned above, the claim¹³ to have partially resolved three progressions in band III with frequencies 724 , 673 , and 727 cm^{-1} , for the D, E, and F states, respectively, seems improbable given the figure shown.⁸ After subtraction of a Boltzmann function in the present study, the regular residuals shown in Fig. 9 were then processed to yield mean wavenumbers over several separations of 876 , 612 , and 318 cm^{-1} by FFT. The resulting structure shows a main sequence of relatively broad bands, with a set of weaker but sharper bands, which become subsumed in the main sequence as the energy increases. A series of fits using the harmonic frequencies (Table II) in the FC analysis were attempted; only the calculated FC profile for the $2^2B_1 \leftarrow X^1A_1$ transition (Table VIII) showed similar features, but the fit is relatively poor.

IV. DISCUSSION

A. The overall PES envelopes

The additional weak structure observed here, when compared with previous studies, is attributed to the very high count rate and large number of data points in the current PES study. This has enabled a more detailed numerical analysis.

We have given strong support for earlier proposals that the three valence shell PES bands (I, II, and III) do contain one, three, and three ionizations. However, the situation is much more complex than previously recognized and we have rejected some unrealistic analyses. The overlay of the ionic state vibrational profiles calculated by FC analysis shows that only the $X^2B_1 \leftarrow X^1A_1$ transition in band I is isolated and can be subjected to straightforward analysis. Even there, a rigorous simulation of the PES structure for band I must include hot bands in the FCF calculations.

The FC profiles for all transitions, shown in Tables III–IX, show that the observed spectral peaks are the resultant of numerous vibrational states. Correlations of the spacing of these complex bands with single vibrations of the electronic ground state are too simplistic and hence unreliable. Each of the transitions into A, C, D, and F states show vibrational structures, but much of this is overlaid by the structure of adjacent ionizations, and all are subject to perturbation. However, for these transitions, a significant vibrational structure can be recognized by comparison with the FC profiles even though a clear overlap with other ones occurs. Even among the transitions showing strong FC intensity, this makes the identification of the experimental AIE difficult (as in the 1^2A_1 state) and almost impossible in others, such as the 2^2A_1 state. The most highly developed structure on the high-energy end of band II is easily attributed to the $1^2A_2 \leftarrow X^1A_1$ transition since it has a relatively intense 0-0 band in the FC profile. The fit of this as the C state is tentative as demonstrated in Fig. 6, owing to the absence of a detailed structure in the center of band II.

The very slow rise in intensity for the A state band is only compatible with the theoretical profile of the $1^2B_2 \leftarrow X^1A_1$ transition (Fig. 4), in agreement with Tuckett *et al.*⁸ who attempted a FC fit. The poorly resolved central region (B state) of band II is assigned to the $2^2A_1 \leftarrow X^1A_1$ transition (Fig. 3); its FC profile shows a considerable number of closely placed vibrational states. For reasonable line widths with a HWHM of 75 cm^{-1} , this transition becomes a broad nearly featureless band. Similar considerations apply to the $2^2A_1 \leftarrow X^1A_1$ transition in band III. Both these states are discussed further below.

The present analysis of the onset and trailing edge of band III leads to similar conclusions in relation to the two states involved, 2^2B_2 and 2^2B_1 , respectively. However, the measured vibration frequencies are significantly different from previous measurements of 2^2B_2 .

B. Vibronic effects from the overlay of vibrational state profiles

In recent papers of this series, we have drawn attention to the inevitability of vibronic interactions when the PES baseline is not re-established between each pair of two or more transitions into ionic states.²² In the present bands II and III, it is agreed that each band contains transitions into three states. Using band I as an indicator, this single-state transition has a width greater than 2 eV or $16\,000\text{ cm}^{-1}$. Overall both bands II and III show similar width but each contain three states. Hence, we can be certain that vibronic interactions will occur within each of the trios of states. In band II, the difference in calculated AIE between A and C states is calculated to be 1.3 eV ;

for band III states, the corresponding AIE separation is 0.8 eV . In both these cases, the calculated state order is different from the assigned sequence of AIE, but this is unimportant to the situation here, where the energy range is critical.

The principal transitions, where the photoelectron spectrum has collapsed to a broad relatively featureless one, are in the centers of two trios of states. In both bands, a vibrational structure is observed for the transitions into higher energy states, $1^2A_2 \leftarrow X^1A_1$ and $2^2B_1 \leftarrow X^1A_1$, respectively. In band II, it is probable that the high intensity of the vibrations is too large to be completely dampened by vibronic coupling. In band III, the $2^2B_1 \leftarrow X^1A_1$ transition vibrational progression intensities are greatly weakened but visible in the present PES.

The central states, 1^2A_1 and 2^2A_1 , have less effect on their adjacent lower AIE, so the effect is largely limited to the (higher AIE) trailing edge states. The largest presumed vibronic interactions are 1^2B_2 on 1^2A_1 , while interactions of 1^2A_1 on 1^2A_2 and 2^2A_1 on 2^2B_1 are much weaker. All the MOs involved have leading term vacancies in the ionic states as shown in Fig. 10. The principal C–H density occurs in $6a_1$ (symmetric) and $2b_1$ (antisymmetric); in contrast, $4b_2$ and $1a_2$ are nodal at the CH₂ group and can be described as F-atom “lone pair (LP)” MOs. This continues into band III, where further LP examples occur. The innermost state of the current states of interest, 1^2B_1 , is virtually a CF₂ group π -MO across the two F-atoms.

FIG. 10. The 4 highest occupied molecular orbitals (HOMOs), their symmetries, and adiabatic ionization energy sequence. The $6a_1$ and $4b_2$ MOs switch order in the AIEs. The orientation of the MOs is such that for $2b_1$, $6a_1$, and $1a_2$, the CH₂ group is forward. The HOMO and HOMO-1 show significant CH₂ bonding density, while HOMO-2 and HOMO-3 are largely “lone pair” MOs on the F-atoms. The next three MOs are shown in the [supplementary material](#).

C. Comparison of the calculated energy levels

The EOM-IP-CCSD calculations show many similarities to the MP4SDQ calculations shown in Tables IV–VI. MP4SDQ calculations are numerically close to CCSD(T) calculations, a method often known as the “gold-standard” in quantum chemistry,⁴³ and hence MP4SDQ are not just an arbitrary point on the MPn series of levels. Currently neither the CCSD(T) or EOM-IP-CCSD calculations, as computed by the CFOUR suite, can be directly processed in the FC package available in G-09. Thus, MP4SD calculations, which can take advantage of fully internal procedures in G-09 and related higher numerical accuracy, can be safely used as a substitute.

An additional conclusion concerns CASSCF calculations; its use in the present study does not lead to imaginary frequencies and contrast with EOM-IP-CCSD as found here. Imaginary vibration frequencies imply a saddle point rather than a full minimum; distortion to a lower symmetry state is to be expected. Fortunately, in the current study, the differences in structures at the saddle points and minima obtained in the MP4SDQ and CASSCF methods are very small. These imaginary frequencies can distort the vibrational frequency manifold. It appears that the non-dynamical correlation contained in CASSCF and higher excitations of the MP4SD calculations have a significant effect on the curvature of some portions of the relevant potential energy surfaces for these states.

D. Comparison with related chemical species

It is important to place the current study in a wider context such that more general lessons can be learnt. We have taken the opportunity to reconsider the lowest four electronic states for the CH_2X_2 series, where $\text{X} = \text{F}, \text{Cl}, \text{Br},$ and I . Several earlier PES studies have reported on one or more of this series.¹⁴ We have correlated our results for these as shown in Fig. 11 and re-evaluated the AIE for the highest four states for each

FIG. 11. A comparison of the photoelectron spectra for the first four dihalogenomethane ionization energies. A progressive separation of the first ionization potential from the next three higher ionizations occurs. The onset of the spectra shifts to higher energy as the electronegativity of the halogen increases. A further shift occurs for the next group of IE for the iodo-, bromo-, and chloro-compounds with the fluoro-compound values lying even higher. The assignments proposed for the first four ionic states, shown in Table X, revise earlier studies.

TABLE X. The adiabatic ionization energies for the CH_2X_2 series of compounds, where $\text{X} = \text{F}, \text{Cl}, \text{Br},$ and I , together with their equilibrium structures ($\text{\AA}$ and degrees).

CH_2I_2	AIE (eV)	C–H	HCH	C–X	XCX
X^1A_1	0.0	1.0794	110.6	2.1804	122.3
2B_1	9.3647	1.0898	107.8	2.1617	120.0
2A_2	9.4982	1.0801	112.2	2.2070	125.3
2B_2	9.9314	1.0794	114.3	2.1487	131.0
2A_1	9.9413	1.0851	114.7	2.1628	117.6
CH_2Br_2					
X^1A_1	0.0	1.0795	110.8	1.9440	123.0
2B_2	9.7644	1.0803	115.5	1.9475	133.1
2B_1	10.2983	1.0966	106.1	1.9101	119.8
2A_2	10.6501	1.0808	112.6	1.9713	125.5
2A_1	10.6760	1.0849	116.5	1.9665	119.0
CH_2Cl_2					
X^1A_1	0.0	1.0987	111.2	1.7922	123.9
2B_2	10.6961	1.0974	116.8	1.7964	133.5
2B_1	10.9647	1.1279	102.3	1.7343	120.0
2A_1	11.4471	1.1074	117.4	1.7911	118.9
2A_2	11.6026	1.0975	114.3	1.8281	126.3
CH_2F_2					
X^1A_1	0.0	1.0837	113.0	1.3711	125.7
2B_1	12.4303	1.1725	82.0	1.2785	121.5
2B_2	13.9503	1.0803	121.6	1.4256	137.7
2A_1	15.0567	1.0935	125.3	1.4107	122.8
$2A_2$	15.1155	1.0813	119.8	1.4486	131.0

molecule. The results, including the equilibrium structures, are shown in Table X.

V. CONCLUSIONS

This new study of the outer-valence shell photoelectron spectrum of CH_2F_2 explores the spectrum in significantly more detail than previously; this arises from the very high synchrotron counting rate and closely spaced data points. Numerical analysis is performed to extract the vibrational structure in unprecedented detail by the removal of broad features. Removing Boltzmann sigmoid curves from slowly increasing or decreasing PES bands is particularly useful. Alternatively, double differentiation is very successful since it extracts a wider set of turning points than direct processing of the spectra. These DD spectra show that numerous vibrations are present. To separate these from noise, the repeating nature of the vibrations across a spectral band is utilized. Fast-Fourier-transform of the resultants does this automatically. Overall, these processes lead to more vibrational structure than is usually obtained by manual means.

The Franck-Condon profiles have been obtained using a series of MP4SDQ and CASSCF calculations. These two methods could be used interchangeably in this study. Although some saddle points occur when the symmetry is constrained to C_{2v} in the EOM-IP-CCSD results, the adiabatic ionization energies and harmonic vibration frequencies are very much like the other theoretical methods used here.

This work confirms the most probable sequence of ionic states in the three observed PES bands is 1^2B_1 (band I) $< 1^2B_2 < 1^2A_1 < 1^2A_2$ (band II) $< 2^2B_2 < 2^2A_1 < 2^2B_1$ (band III).

We propose that the apparently missing 1^2A_1 and 2^2A_1 states are accounted for by the vibrational overlay of lower ionic states, leading to a major vibronic overlap, and these higher IE states collapse as a result. The narrow energy ranges of about 2 eV for three ionic states make major levels of vibronic coupling inevitable. Our formal proposal is that unless the vibrational profiles of two or more transitions into electronic ionic states are not separate in the PES, then vibronic coupling should be assumed.^{48–50} Measured vibrational separations will at best be perturbed values and are not directly comparable with the harmonic wavenumbers derived from theoretical equilibrium structures. As an indicator, a gap in the PES should occur, where the baseline is re-established, before a succeeding state is regarded as unperturbed. Application of this principle would have major implications for the analysis of many published photoelectron spectra.¹⁴

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for **SM1**. A comparison of the present synchrotron-based conventional photoelectron spectrum obtained at 55 eV with the threshold photoelectron spectrum (TPES) for CH_2F_2 over a similar ionization energy range. **Figure SM1.1** Comparison of the PES (black) and TPES (red) for CH_2F_2 . **SM2**. Relationship to the PFI-ZEKE spectrum. **Figure SM2.1** Comparison of the vibrational structure for the PES with the PFI-ZEKE spectrum. **SM3**. Differentiation and subtraction of mathematical functions in the spectral analysis. **SM3.1** Spectral analysis. **SM3.1.1** Results for band I. **Table SM3.1** Band I of the PES for CH_2F_2 peak maxima (cm^{-1}) measured by direct and 2nd derivative procedures. **Figure SM3.2.1**. The 2nd derivative of band I of the PES compared with the Franck-Condon profile. **SM3.2.2** Results for band II. **Table SM3.2**. Direct and 2nd derivative peak maxima in the onset of band II in the PES for CH_2F_2 . **SM3.3** Results for band III. **Figure SM3.1.3**. Band II of the PES. **Table SM3.3**. Onset of band III in the PES for CH_2F_2 measurements by direct measurement and 2nd derivative peak maxima. **Figure SM3.3**. The onset of band III of the PES. **SM4.1** Incorporation of hot and cold bands into the theoretical interpretation. **Table SM4**. Comparison of the PES harmonic vibronic structure for the lowest 4 ionic states of CH_2F_2 at the MP4SDQ levels. **SM5**. Further occupied MOs of CH_2F_2 . **SM6**. Fitting of the observed profile to the 1^2B_1 state (x) of CH_2F_2 , by a series of Gaussian peaks. **Table SM6.1**. Gaussian fit analysis of the band I of the PES. **Figure SM6**. A fit of the experimental envelope of band I of the PES. **SM7**. The outer valence shell PES for CH_2F_2 . **Table SM7**. Tamm-Dancoff approximation (TDA) and Green's Function (GF) methods. **SM8**. Conical intersections for CH_2F_2 . **Table SM8**. The conical interaction structures and energies.

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