The ionized states of 6,6-dimethylfulvene; the vibrational energy levels studied by photoionization, configuration interaction and density functional calculations

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A R T I C L E   I N F O

A B S T R A C T

A new synchrotron-based photoionization spectrum of 6,6-dimethylfulvene shows significant vibrational fine structure (VFS), in contrast to previous studies; this was successfully analysed by Franck-Condon (FC) methods. The sequence of ionic states in the range 7 to 19 eV has been determined by both symmetry adapted cluster configuration interaction and density functional methods, especially using the long-range corrected version of the Becke three-parameter hybrid functional (B3LYP) using the Coulomb-attenuating method (CAM-B3LYP). Both lead to reliable theoretical values for both the calculated vertical and adiabatic ionization energies. The FC profile for the lowest ionization energy (IE1, X^2A_2) shows extensive VFS which is analysed successfully. The second IE (A^2B_1) shows truncated structure owing to overlap with IE$_1$.

1. Introduction

Recently, we have reported spectral studies, by both vacuum ultraviolet absorption and photoionization, of conjugated and related polyolefinic molecules; these spectra were interpreted by a variety of theoretical methods [1,2]. We now consider another polyolefinic system, cyclopenta-1,3-diene with a methylene group substituent, known as the fulvene system, and shown in Fig. 1(*1,2*). These archetypal cross-conjugated systems are not aromatic, but *1* is isomeric with benzene [3,4]. The single reported photoelectron spectrum of fulvene itself gives vertical ionization energies (VIE) as 8.55 and 9.54 eV, with vibrational structure components at higher and lower energies for each state [5]; these values have been repeated in several publications [6–9]. The overall resolution shown [5] in Fig. 1 of reference 5 is clearly poor by the standards of the time (1971), and it had been our intention to use synchrotron-based experiments to generate a higher quality spectrum.

However, the lack of stability of the parent molecule *1* makes it difficult to store/transport. Successful spectroscopic studies described in the literature are where synthesis and spectroscopy are performed in the same laboratories; our international project makes direct spectroscopic study of *1* impossible for us currently, and we consider 6,6-dimethylfulvene (6,6-DMF, *2*), instead since it is much more stable. The study of *1* is deferred to a more suitable time. The PES for 6,6-DMF (*2*) has not been reported in detail previously, but its 2-lowest VIE were given as 8.08 and 8.75 eV in a general paper on substituted fulvenes [8].

We have obtained the synchrotron-based PES of 6,6-DMF in the energy range up to 50 eV, which encompasses the complete valence shell. Part of this, shown in Fig. 2, exhibits considerable vibrational structure not mentioned in the previous report [8]. We will analyse this structure by Franck-Condon (FC) methods [10]. The principal methods used for our theoretical study were the SAC-CI [11,12] and the FC codes [10] within the Gaussian-16 suite [13]. The 6-311G(d,p) triple zeta basis set [14] was used throughout. The SAC-CI suite was run under default conditions. These include all valence shell molecular orbitals (218 orbitals), with just the 10 core orbitals frozen. The reference configuration was 'RefCISD' the singles and doubles configuration interaction state.

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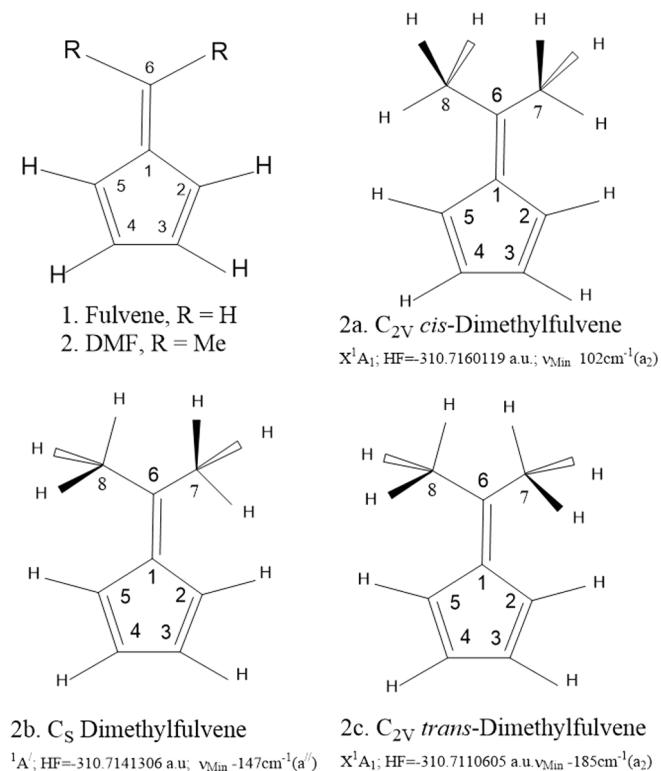
Fig. 1. The structures of fulvene (1) and 6,6-dimethylfulvene (2, DMF) including two conformers with less favourable structures. The numbering used in this study is shown.
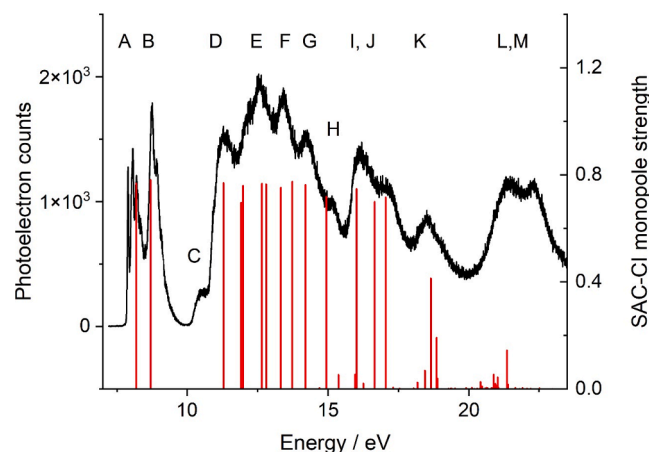

Fig. 2. The UV-photoelectron spectrum of 6,6-dimethylfulvene recorded at hv = 50 eV with the scaled symmetry-adapted cluster configuration interaction (SAC-CI) ionic states (in red). We have no explanation for the small peak labelled C in the figure; it does not appear to be part of the main spectrum.The collapse of pole strength for the ionic states with energies higher than 17.5 eV, shows that 1-electron processes are being replaced by 2-electron processes including ionization and simultaneous electronic excitation. Thus the region L + M is only sampled at this onset. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Equilibrium structures for the FC study use the CAM-B3LYP functional, and hence lead to the adiabatic ionization energies (AIE) [15]. The SAC-CI study was performed at the equilibrium structure for the X^1A_1 ground state and generate VIE.

2. Materials and methods

The photoelectron spectrum 6,6-dimethylfulvene was obtained at room temperature on the gas-phase line of the Elettra synchrotron (Trieste, Italy) [16] using the SES200 [17]. Binding energy scale was calibrated against the Ar 3p lines. The total resolution of the measured PES spectra is a function of the photon excitation energy and is 10 meV for the spectrum measured at hv = 30 eV (bands A and B with vibrational resolution) and 30 meV for the spectrum measured at hv = 50 eV. The sample of 6,6-Dimethylfulvene used for the measurements was prepared by a standard method [18].

3. Results

Internal rotation of the two CH_3 groups in 6,6-DMF lead to the conformers shown in Fig. 1; all were tested under standard conditions. The lowest energy conformer (Figure 1,**2A**) has only positive vibrational frequencies (ν_{min} 102 cm^{-1}(a$_2$)), and is the conformer studied here. Conformers 2**B** and 2**C** lie 0.0019 eV (15.2 cm^{-1}) and 0.0050 eV (39.9 cm^{-1}) higher in energy, each with one imaginary frequency (ν_{min} −147 cm^{-1}(a$^{//}$) and ν_{min} −185 cm^{-1}(a$_2$) respectively). Thus structures 2b and 2c are saddle points, have no role in the photoelectron study below, and are not discussed further. The X^1A_1 molecular structure and comparisons with microwave spectral and electron diffraction results are presented in the supplementary material as SM1.

A. The wide scan photoelectron spectrum for the 6,6-dimethylfulvene system. The region up to 23 eV is shown in Fig. 2; a wider range is shown in the supplementary material as SM2. For convenience in the analysis below, the spectrum has been dissected into bands A to M; the SAC-CI calculated energy levels are superimposed on this figure. Only bands A and B show vibrational structure, and this is discussed in detail below.

Comparison of the profile of the PES with the calculated electronic state energies showed that a linear correlation could be established, leading to the equation: VIE$_{Scaled}$ = 0.909(15)*SAC-CI$_{Calc}$ + 1.073 (199), where standard errors are in parentheses, and the correlation coefficient (adjacent R^2) is 0.9990. We note in passing, that in the absence of an improved photoelectron spectrum for fulvene itself, if we adopt the Heilbronner et al spectrum [5], we can perform a more rigorous analysis of it, also based on the SAC-CI method. A group of the Heilbronner peaks measured on their PES, was compared with SAC-CI calculated values; this led to a very similar linear correlation with the equation: VIE$_{Scaled}$ = 0.903 (11)*SAC-CI$_{Calc}$ + 1.221 (137) eV, with standard errors in parentheses and a correlation coefficient of 0.9997. Further details of the SAC-CI results for fulvene are shown in SM3. The slopes and intercepts in these two equations show very similar correlations.

B. The theoretical ionic states of 6,6-dimethylfulvene.

(i) **The effect of the methyl groups.** The principal differences between the fulvene and 6,6-DMF PES spectra occur in the 11–13 eV regions, with bands D, E, F and G. Each CH_3 group introduces (2σ + 1π) MOs to the system, where 1σ-MO is largely of 2s nature and with a binding energy higher than 20 eV. The remaining = 4σ + 2π MOs form symmetric and antisymmetric combinations. The new π-states present in 6,6-DMF but absent in fulvene itself are: 13.84 eV(A$_2$), 15.28 (B$_1$), as seen in Table 1. This situation is similar to isobutene (H$_2$C = CMe$_2$) [19], where these MOs occur in PES bands near 13.8 (1a$_2$$^{-1}$) and 15.03 eV (1b$_1$$^{-1}$) which were calculated at 13.47 and 14.89 eV [19]; the splitting is similar, and we believe that 6,6-dimethylfulvene can be viewed as a merged version of cyclopentadiene and isobutene.

(ii) **The ionic state structures.** Our analysis of the neutral ground state for 6,6-DMF conforms to C$_{2V}$ symmetry with the 2-Me groups eclipsed. However, we could not assume the same would be true for the cationic states. Thus, we used a completely

Table 1

The theoretical ionization energies by the symmetry-adapted cluster method (SAC-CI) for 6,6-dimethylfulvene, together with the experimental VIEs. The SAC-CI results have not been obtained for the full range of VIE. The scaled ionization energies are used in Fig. 2. The collapse of pole strength is discussed in the caption to Fig. 2. The SAC-CI monopole strength is equivalent to the oscillator strength in several other codes. The experimental peak maxima are as shown, but multipeak fitting shows that some maxima must be treated as two or more peaks, as implied by the SACCI results; these additional peaks move the apparent VIE by small amounts.

Peak label	PES Peak maxima / eV	PES Peak fit maxima / eV	Ionic state symmetry	SAC-CI energy / eV	SAC-CI monopole strength	Scaled Ionization energies / eV
A	8.050	8.06	A_2 (π)	7.713	0.927	8.185
B	8.738	8.74	$B_1(\pi)$	8.310	0.952	8.724
C		10.4				
D	11.311	11.1	B_2	11.186	0.936	11.320
E			$B_1(\pi)$	11.911	0.850	11.975
E		12.1	A_1	11.933	0.922	11.995
E	12.575	12.6	A_1	12.628	0.931	12.622
E			B_2	12.885	0.933	12.854
F	13.403	13.4	B_2	13.447	0.916	13.362
F			$A_2(\pi)$	13.842	0.936	13.718
G	14.231	14.2	A_1	14.363	0.926	14.189
G			B_2	14.410	0.926	14.231
H	15.103	15.2	$B_1(\pi)$	15.280	0.891	15.017
I	16.160	16.0	A_1	16.348	0.907	15.981
I			A_1	17.052	0.841	16.616
J	17.033	17.2	B_2	17.485	0.858	17.007
K	18.504	18.5	A_1	19.443	0.301	18.775
L	21.397	21.3				
M	22.247	23.3				

general z-matrix formulation, where all bond lengths, angles and dihedral angles were different, and a C_1 symmetry equilibrium structure was sought. When this was done for the neutral state, it regenerated the eclipsed X^1A_1 structure above. The lowest cationic state was close to the $^2A_2$ state, but strictly C_1 symmetry; small differences in angles (<2°) occur from the C_{2V} version. The proximity of the methyl group hydrogen atoms in the Me-C-Me group automatically leads to non-bonded interactions, and we do not consider Jahn-Teller distortion to be an issue. The equilibrium structure of the second ionization (IE$_2$) for 6,6-DMF, shows a C_2 symmetry structure, where all vibration frequencies are positive; alternative CH_3 group conformations such as C_{2V} or C_S gave negative frequencies. These C_1 and C_2 structures were used in the successful interpretation of the PES bands A and B in Figs. 3 and 4 respectively, as discussed below.
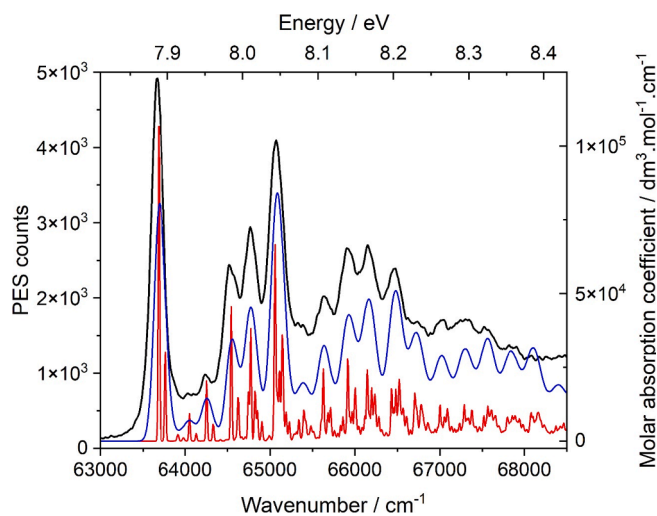

Fig. 3. The expanded band A of 6,6-dimethylfulvene recorded at $h\nu = 30$ eV with the calculated Franck-Condon profiles where the half-width at half-maxima (HWHM) are 10 cm^{-1} (in red) and 75 cm^{-1} (blue). The energy scale has been converted to wavenumbers since these are the units for the FC calculation, and the spectrum shows vibrational frequencies. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
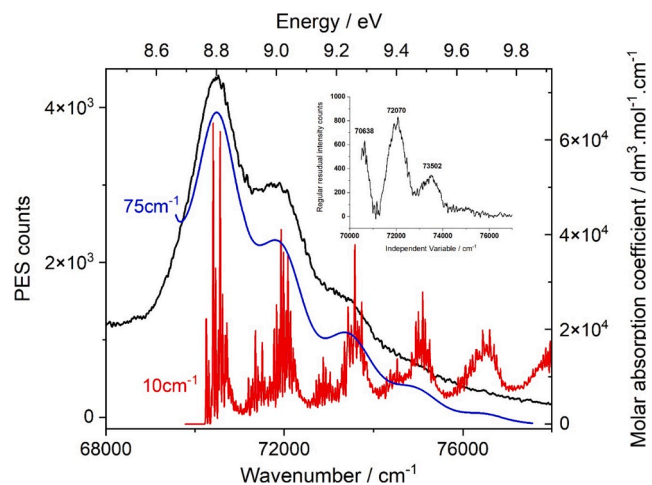

Fig. 4. The expanded band B of 6,6-dimethylfulvene recorded at $h\nu = 30$ eV with the calculated Franck-Condon profiles. The red peaks are the unperturbed FC profile with HWHM 10 cm^{-1}. The blue line (with HWHM 75 cm^{-1}) is based on an exponential function fitted to the high energy side of the figure. This discloses the shoulders of the slope as distinct maxima. The same function is then used as a multiplier for the red FC profiles, to enforce the same exponential decay; that was performed using the 75 cm^{-1} peaks, which represent normal unperturbed PES peaks. The IE$_A$ 0–0 band is seen close to 8.7 eV with IE$_V$ close to 8.80 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

C. The vibrational structure in 6,6-DMF ionic states. The CAM-B3LYP density functional together with the 6-311G (d, p) basis set was used throughout this and following sections. Up to 8 simultaneous vibrational excitations are included in the FC analyses. All intensities are in units of molar absorption coefficient (dm^3.mol^{-1}.cm^{-1}). FC analyses which are superimposed on Figs. 3 and 4, use peaks with half-width at half-maxima (HWHM) of 10 cm^{-1} (in red) and 75 cm^{-1} (in blue). Previous experience has shown that an isolated single peak ionization is generally well fitted by a 75 cm^{-1} peak. We discuss these bandwidths [20] below.

(i) **The first ionization band A.** An expanded version of Fig. 2, with the FC analyses superimposed, is shown in Fig. 3; it gives the

measured lowest ionization (IE$_1$) of 7.8932 eV (63664 cm^{-1}). Scaling the relationship between the theoretical (red and blue) results to the experimental vibrational energies has been performed in this Figure. The fit equation is: PES$_{Obs.}$ = 0.953(7) * PES$_{Calc}$ + 3031 cm^{-1}, with correlation coefficient 0.9997, and standard error in parentheses. This correlation is particularly good for the spectrum up to ~ 66500 cm^{-1}. At higher wavenumbers, the differences between calculated and observed peaks, are still small, since all the principal observed peaks in the PES are still evident, and most of these are composites of several vibrational bands rather than individual vibrations. Even at the band onset, some of the very weak bands observed in the PES near 64000 cm^{-1} are present in the calculated results. The most intense vibrational states appearing in the Franck-Condon interpretation of the spectrum are in Table 2. Many fundamental modes (M) are present, but overtones and combination bands are included. The 0–0 band is the most intense by far, followed by one of the ring breathing modes (M31).

(ii) **The second ionization band B for 6,6-DMF**. Poorly resolved PES structure for band B of 6,6-DMF is seen in Fig. 4. The C$_2$ conformer FC profile is superimposed in red; this theoretical profile, as shown in Table 3, is generated without reference to the band A spectral data and so is unperturbed by band A. In comparison, the experimental spectrum is strongly perturbed, since almost all the vibrational structure is absent. Comparison between theory and experiment requires additional treatment. Further detail can be extracted from the experimental PES by fitting the data points from the peak maximum at higher energy, to an exponential decay function, and plotting the regular residuals (RR). The function used is a standard one, namely: y - y$_0$ = A$_1$*exp(-x/t$_1$); it is described further in the supplementary material as SM4. We use this same fitting function in order to build an exponential decay into the un-perturbed FC profile. The resulting RR for the PES fit, shown in the inset to Fig. 4, give the maxima for the satellite peaks more accurately; these are separated from the spectral maximum of band B at 70638 cm^{-1} (8.7578 eV) by 1432 cm^{-1}.

The PES count rate between bands A and B, shown in both Figs. 2 and 4, never approaches zero at the baseline; this accounts for the near absence of vibrational structure in band B; we have met this phenomenon on several occasions previously [20,21]. Suffice it to say at this point, that interference occurs between the vibrational sequence of band

Table 2
The most intense calculated Franck-Condon frequencies for IE$_1$.

Frequencies / cm^{-1}	Modes in ascending sequence by frequency	Intensities[a]
0	0–0	106,600
82	1^1	25,280
589	11^1	20,380
892	15^1	29,270
974	15^1;1^1	10,670
1101	23^1	16,150
1131	24^1	27,970
1184	26^1	10,870
1428	31^1	42,230
1455	33^1	14,680
1480	35^1	14,280
1510	31^1;1^1	15,210
1522	37^1	21,300
2023	24^1;15^1	13,640
2320	31^1;15^1	22,260
2414	37^1;15^1	10,310
2559	31^1;24^1	20,740
2653	37^1;24^1	10,800
2856	31^2	14,830
2950	37^1;31^1	15,000

[a] Molar absorption coefficient (dm^3.mol^{-1}.cm^{-1}).

Table 3
The most intense calculated Franck-Condon frequencies for IE$_2$.

Frequencies / cm^{-1}	Modes in ascending sequence by frequency	Intensities[a]
0	0–0	3175
59	1^1	1306
161	4^1	7978
322	4^2	6796
343	4^1;2^2;1^1	1267
379	6^1	54
407	4^1;2^4	1157
579	10^1	29
832	14^1	85
894	16^1	152
930	17^1	338
992	21^1	685
1182	25^1	100
1368	28^1	147
1427	31^1	156
1492	34^1	376
1542	36^1	439
1594	37^1	1345
1814	34^1;4^2	2130
1814	37^1;4^1;1^1	2303
1916	37^1;4^2	2510
1975	37^1;4^2;1^1	1693
2077	37^1;4^3	1075
3327	39^1;4^2	2375
3592	41^1;4^3	1417
4980	39^1;34^1;4^3	1139
5082	39^1;37^1;4^3	1251
6493	39^2;4^3	1314
6654	39^2;4^4	1121

A with that of band B. Thus the X^{2}A$_2$ and A^{2}B$_1$ states are strongly coupled to each other and a conical intersection occurs between them; we continue this topic in the discussion below.

The exponential decay function above gives a scaling factor for the unperturbed FC profile, where all peak intensities become a product of the theoretical molar absorption coefficient with the exponential function. When this is done, the resulting profile becomes the blue line in Fig. 4. For simplicity the blue line uses a 75 cm^{-1} value for the HWHM, since there is insufficient space to insert the 10 cm^{-1} set of values.

The theoretical FC frequencies calculated for IE$_2$ show some particularly low values, with 4 below 162 cm^{-1}; this also leads to the very compact appearance of band B. The lowest, 59.5 cm^{-1}, mode (M1) in the ascending frequency list, is relatively intense; other active fundamental modes are: 379 (M6), 579 (M10), 832 (M14), 894 (M16), 930 (M17), 1182 (M25), 1368 (M28), 1427 (M31), 1492 (M34), and 1542 cm^{-1} (M36). The principal carrier of the repeating unit is M37 (1593 cm^{-1}) with relatively high intensity (1345 units). The FC profile for band B shows a set of multiplets with increasing complexity and anharmonicity as the frequency increases; the mean separation is 1795 cm^{-1} over the first 6 peaks from the maximum, while the first separation is 1505 cm^{-1}, close to the 1432 cm^{-1} value determined from the spectrum. Several binary combinations contain 161 (M4) and 322 (2xM4) cm^{-1}.

4. Discussion

We have obtained a synchrotron based wide scan PES for the 6,6-dimethyl-derivative of fulvene over the range 7 to 23 eV. This has been successfully interpreted by the SAC-CI method, thus putting the assignment on a rigorous level. The two lowest IE are confirmed as X^{2}A$_2$ and A^{2}B$_1$, in agreement with the early studies; the nature of these two ionizations are very different. The significant vibrational structure on IE$_1$, has been interpreted in detail. IE$_2$ shows a very different profile which is attributed to overlap of the IE$_1$ vibrations with those of IE$_2$. The PES count rate fails to descend to the spectral baseline between the two IE. This is a classic 2-mode vibronic interaction case of the type investigated by Bâldea et al. [22,23] for fluorobenzene. In that example, the energy separation between the X^{2}B$_1$ and A^{2}A$_2$ states is 0.40 eV; it was

shown that conical intersections occur between these two states, as well as others between higher states. Although the spectrum between the two states in the PES spectrum of PhF nearly reaches the baseline, significant interactions were observed. This led to the necessity to broaden the vibrational profile to FWHM = 132 meV (1065 cm^{-1}) to reproduce the broadened PES bands [22]. In a related interpretation, the same authors suggest that interpretation of the MATI spectrum [24] of PhF requires the super-position of the separate X^2B_1 and A^2A_2 states.

Two examples from our previous studies on iodobenzene and fluorobenzene were analysed similarly later [19,20], using similar procedures. In these cases, the best estimates for the two leading VIE are 8.758 and 9.505 eV [19], and 9.206 and 9.802 eV [20], leading to VIE separations of ~ 0.75 and ~ 0.6 eV. The present difference in VIE for bands A and B of 6,6-DMF is 6859 cm^{-1} (0.850 eV). In the current study, we have used the observed near collapse of the intensity of the A^2B_1 state to a single line, to provide a template for the peak relaxation via an exponential decline on the high energy side. That same fitted function gave residuals which defined the undulations accurately, enabling the principal groupings of vibrational states to be established. Finally, in a new approach, we have used this same exponential function as a multiplier of the FC profile; this leads to a direct measure of the attenuation of the FC structure following interference from the X^2A_2 state. The sheer number of peaks shown in the 10 cm^{-1} FC analysis of Fig. 4, is too large, but the use of a 75 cm^{-1} FC profile where the increased line width consolidates the 10 cm^{-1} lines into broad groups, gives a good match to the experimental PES.

5. Conclusions

We have generated a synchrotron based photoelectron spectrum for 6,6-dimethylfulvene. The fine structure found on the two lowest ionization energies has been interpreted by Franck-Condon methods. In the second IE, the A^2B_1 state, we have used numerical methods to determine the effects of the shortened lifetime arising from vibronic coupling with the first IE, the X^2A_2 state. The exponential decay of the A^2B_1 band, when used to simulate the attenuation of the FC profile arising from the vibronic coupling leads to a realistic simulation of the observed spectrum. This procedure is markedly different from previous work of ours, where we increased the width of the FC peaks by major amounts, in order to merge the individual contributions to the overall spectrum.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Dedication

This paper is dedicated to Professor Kozo Kuchitsu, as an outstanding scientist, who was widely respected for his work, and dedication to international collaboration and dissemination of science.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2022.139558.

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