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The ionic and ground states of gamma-pyrone. The photoionization spectrum studied by synchrotron radiation and interpreted by configuration interaction and density functional calculations.

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ABSTRACT

A synchrotron based photoionization spectrum up to 27 eV represents a considerable improvement in resolution over early He(I) and He(II) spectra. Symmetry-adapted coupled cluster calculations of the ionic state sequence, give the sequence of state vertical ionization energies (VIE) as: $1^2B_2 < 1^2B_1 < 1^2A_2 < 2^2B_1 < 1^2A_1$. Generally, these symmetry adapted cluster configuration interaction (SAC-CI) vertical ionic states energies (VIE) match reasonably well with the experimental spectrum over this wide energy range. Density functional calculations of the corresponding adiabatic terms (AIE) were also performed. Higher energy ionic states, were determined by complete active space self-consistent field (CASSCF) methods; these include all π -ionizations and some σ -ionic states. These were analyzed by Franck-Condon (FC) procedures, and compared with experiment. The spectral onset is complex where two states, later shown to be the 1^2B_2 and 1^2B_1 states, are strongly overlapping. Super-

position of the FC vibrational structure for the 1^2B_2 and 1^2B_1 states accounts for most peaks arising in the onset of the PES. However, the small separation of these two ionic states makes vibronic interaction fairly inevitable. In the absence of Herzberg-Teller analyses for ionic states, we have sought and determined a transition state between the 1^2B_2 and 1^2B_1 states, showing that vibronic coupling does occur. The lack of degradation in the vibrational envelope of the higher of the two states contrasts with our previous work on the halogeno-benzenes, where overlapping state envelopes led to considerable widening of the line-width at half-height of the higher energy states.

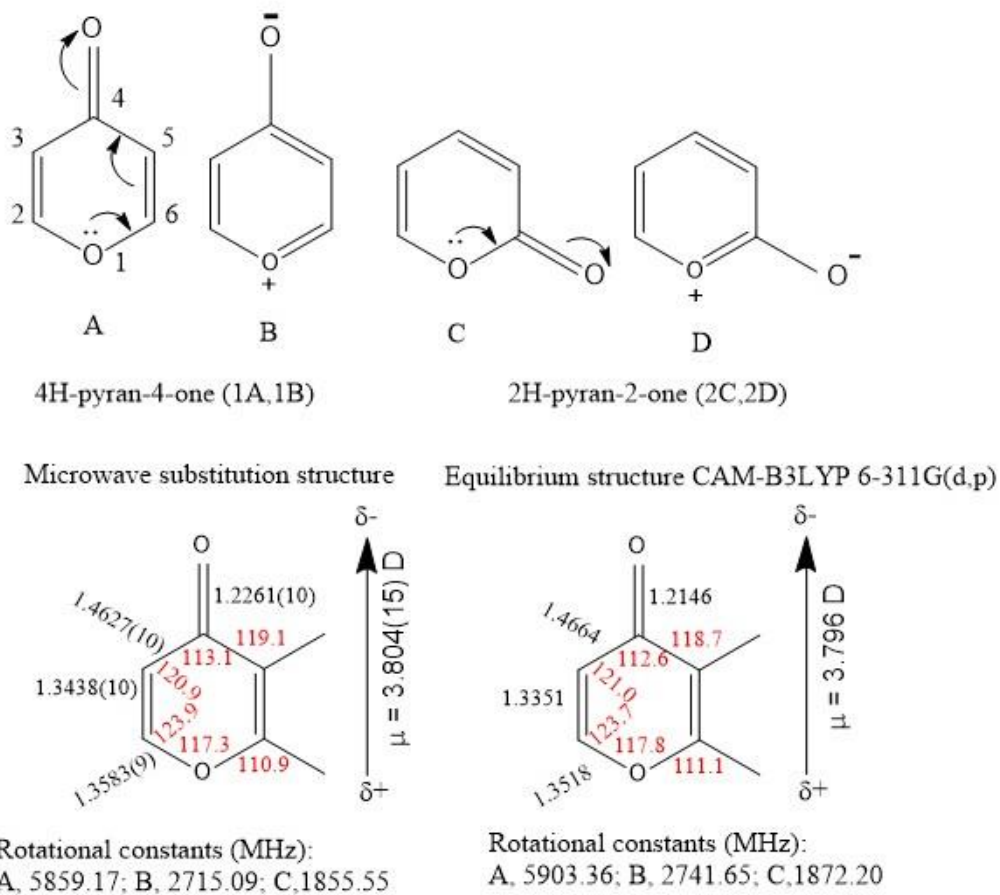
I. INTRODUCTION

Recently we have reported synchrotron based, vacuum ultraviolet (VUV) absorption and high-resolution photoelectron spectra (PES) spectra for several highly conjugated molecules, including cyclooctatetraene (COT),^{1,2} cycloheptatriene (CHT),^{3,4} norbornadiene (NBD),^{5,6} and azulene.^{7,8} A major difference from preceding work for these high profile molecules, is that we have offered Franck-Condon (FC) and Herzberg-Teller (HT) interpretations of the vibrational structure observed in their VUV spectra, and FC for their PES. The use of HT methods for analysis of PES has not been possible in these studies, due to limitations arising from the software available to us, as discussed below. We now report similar studies of the PES of another fully conjugated molecule, γ -pyrone (**I**, shown in Figure 1). This substance is systematically described as 4H-pyran-4-one. A parallel study of the VUV spectrum will be presented in a later paper. The γ -pyrone PES, under He(I) and He(II) conditions was previously reported,⁹ for the valence shell, and for the core C_{1s} and O_{1s} electrons (using $AlK\alpha + MgK\alpha$). The PES were obtained under the low-resolution conditions of that time (1980), so that vibrational analysis was primitive;⁹ indeed, the accompanying theoretical studies,⁹ both semi-empirical and *ab initio* using a minimal basis set, were regarded as sufficiently unreliable that the spectral assignments were based on comparisons of ionization energies (IE) with those of related compounds. Our analysis of the higher resolution PES is accompanied by sophisticated calculations of the electronic structure of the parent molecule and its ionic states.

The properties of γ -pyrone are unusual, especially in terms of reactivity,¹⁰ where it does not behave as a (double) α,β -unsaturated ketone. For example, prolonged treatment with D₂O leads to the 3,5-d₂ isotopomer, while related treatment with ¹⁸O-enriched water incorporates ¹⁸O at both O-atoms. These changes appear to occur to the pyrone system^{11,12} via sequential addition, ring opening, closing and elimination changes. Both ¹H and ¹³C nuclear magnetic resonance spectra (NMR) have been studied in considerable detail, including long range (i.e. across the ring) coupling constants. Interpretation of these values has been controversial, since comparisons with related 5- and 6-membered ring molecules leads to differing conclusions.¹³ The chemical shifts, when compared with those of dihydro-derivatives where the full conjugation is missing, led to the proposition that γ -pyrone supports a ring current.^{10,13-16} The C_{2v} structure clearly shows a fully conjugated π -electron system; the initial conclusion that it is an aromatic molecule emerged by consideration of several contributing canonical forms, such as 1B in Figure 1.

However, microwave (MW) substitution structures for γ -pyrone, and the three related molecules where one or both O-atoms are replaced by S-atoms, gave complete structures which showed classical C=C bond lengths and angles.¹⁷⁻²¹ The MW structure for γ -pyrone is compared with our equilibrium structure using a standard triple-zeta basis, in Figure 1, and discussed below. The vibrationally averaged nematic phase γ -pyrone structures determined from ¹H and ¹³C NMR spectroscopy are in close agreement with the MW results.^{22,23} Magnetic susceptibility anisotropies also analysed by MW, in terms of local and nonlocal contributions, show that both γ -pyrone and the related lactone (α -pyrone), shown as 2C and 2D in Figure 1, have negligibly small non-local contributions; thus both are considered to be non-aromatic by this magnetic criterion.^{17,18,21} Earlier discussions in terms of a ring current, based on NMR chemical shifts, then appear to be improbable.^{24,25}

Figure 1. Top: The structures of the pyran-2- and -4-ones, and the important canonical forms to express the non-classical reactivity. Bottom: A comparison of the microwave substitution structure with the equilibrium structure of γ -pyrone at the CAM-B3LYP level.



II. METHODS

The γ -pyrone sample, CAS registry number 108-97-4, was synthesised by standard methods,^{26,27} and the purity checked by ^1H and ^{13}C nuclear magnetic resonance.^{11,14}

(i) The photoelectron spectrum. This was obtained on the gas-phase line of the Elettra synchrotron (Trieste, Italy), at room temperature, using methods described previously.^{1,3} The sample vapour was irradiated with both 30 eV and 90 eV photon energies. The 30 eV spectrum covers the energy range 8.956 to 11.756 eV with 1463 data points (DPs), separated by 0.002 eV (16 cm^{-1}). A wider scan using 98 eV photons, contains 1972 DPs, with a separation of 0.01 eV up to 16.1 eV, and 0.025 eV for the range 16.1 eV to 45.883 eV. The PES spectrum acquired at $h\nu = 98\text{ eV}$ in the wide range up to 27 eV is shown in Figure 2 and discussed below in the light of our calculated spectral lines.

We adopt a conventional definition of resolution as the minimum separation between two spectral lines where it is possible to distinguish between them; thus the 30 eV spectrum corresponds to an overall resolution close to 8.5 meV. The precision of the measured energies and the resolution were also determined from the half-width of argon PES lines which are known from the literature; Argon was added to the sample as an additional calibrant. Additional peak-fit statistics, using the Multi-peak Fit (Version 2.22) program, including the absolute positions of the principal PES peaks, are listed in the supplementary material SM1 as Table SMI. The complex onset of the PES in the range 9.2 to 10 eV was analysed as shown in Figures 3a and 3b, and is discussed below.

Figure 2. The wide scan photoelectron spectrum from 8 to 27 eV acquired at $h\nu=98$ eV; the energy resolution is circa 40 meV. The principal bands are labelled A to J. The vertical bars are the pole strengths (intensities) from the symmetry-adapted cluster configuration interaction (SAC-CI) calculations of the ionic state energies. The pole strengths have been increased by 0.05 units, to make the numerous very weak states more obvious.

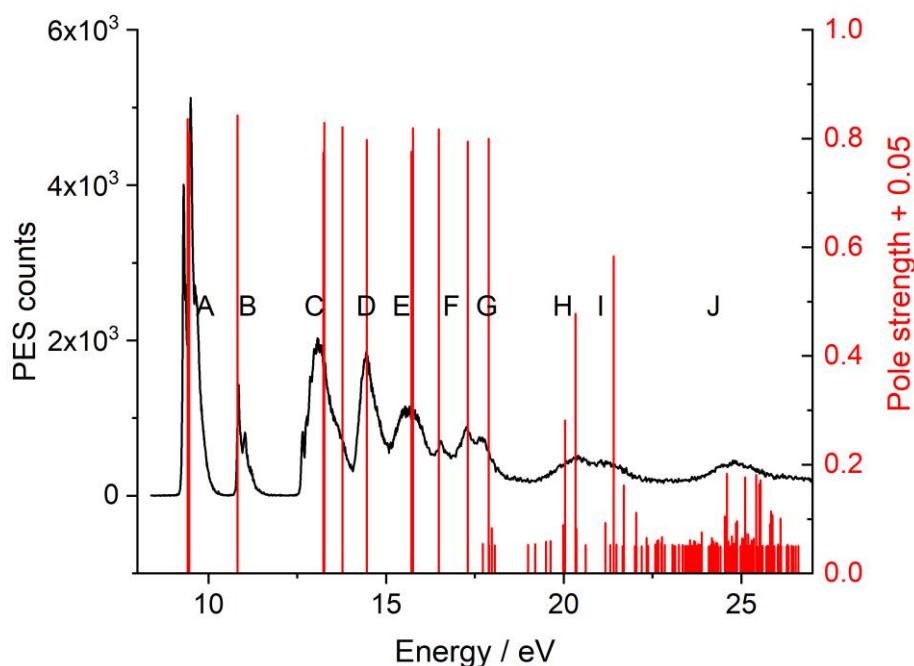
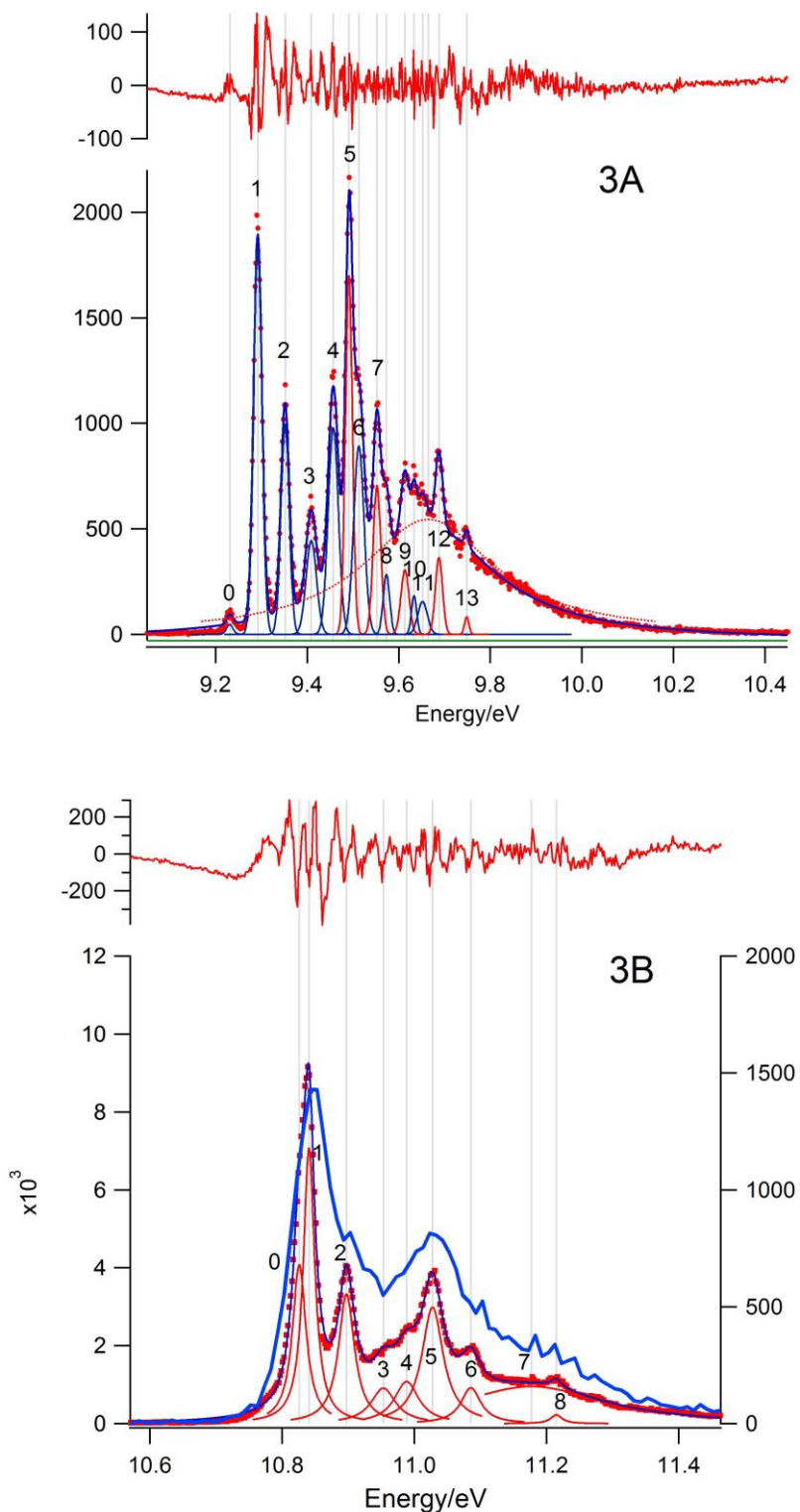


Figure 3. The onset (3A) and second band (3B) of the γ -pyrone PES measured at $h\nu=30$ eV, energy resolution circa 9 meV. Both are discussed in detail below. The higher resolution spectrum of the second band is compared with the lower resolution measurements performed at $h\nu=98$ eV (blue line in the figure). The measured peak positions are shown in the supplementary material as Table SMI.



- (ii) **Theoretical methods.** Several computational chemistry suites were used since none offers us a complete analysis. The equilibrium structures for the X^1A_1 ground state and several of the lowest ionic states of each symmetry were determined using the GAUSSIAN suite (G-16).²⁸ Several density functional theory (DFT) functionals²⁹⁻³¹ were tested. Overall, the long-

range corrected, Coulomb-attenuating version of the Becke method with the Lee–Yang–Parr hybrid functional (CAM-B3LYP),^{31,32} gave the best results. This conclusion is based on energy separations between ionic states, and also balance between the 0-0 band and vibrational satellite intensities determined by the Pisa software, as discussed below.

The 2^2B_1 and 3^2B_1 states are not accessible by that procedure, since collapse to the 1^2B_1 state occurs during structure determination; these and other higher states were successfully accessed by complete active space SCF (CASSCF). The number of roots of the required symmetry are selected, and the structure optimized for that root (here 1, 2 or 3). Initially, the Hartree-Fock wave-function is reordered to make the active CASSCF MOs the highest occupied orbitals; for example: $1b_1^2$, $2b_1^2$ and 3^2b_1 ; the active virtual orbitals were similarly re-ordered to be of the required symmetry. In this way, the CASSCF method is forced to generate the required states of appropriate symmetry. Using the 6-311G(d, p) basis set, a 3- (or 5-) electrons within the 8-orbital CASSCF, conventionally termed CAS[3,8]SCF, gave two roots of 2B_1 symmetry, as linear combinations; the higher energy one was optimized. The same procedure was applied to the CAS[5,8]SCF case leading to the third state. Perusal of the leading configurations showed that the state required was present, and that no higher intruder state had been obtained. Similar CASSCF procedures were performed for both the 2- and 3^2B_2 states; but we were unable to obtain an equilibrium structure for the 2^2A_1 state.

Input wave-functions for the Franck-Condon (FC) analyses³³⁻³⁵ were determined by the CAM-B3LYP or CASSCF methods. AIE determined by these methods in G-16, are based upon energy differences between ground and excited state *both at the excited state equilibrium geometry*; standard AIE in spectroscopy use the difference in energy between the excited state and the ground state, *each at their equilibrium structures*. Potentially, these differences could alter the state symmetry sequence of ionic states when closely spaced states occur. Direct calculation of the vertical ionization energies (VIE) was also performed by the symmetry-adapted cluster configuration interaction (SAC-CI)³⁶⁻⁴⁰ method within G-16. These were determined at the equilibrium structure of the X^1A_1 ground state.

The reference configurations were from the singles and doubles configuration interaction level (RefCISD). The active space for the SAC-CI included orbital energies from -1.1 to 0.86 a.u.

We also used the Tamm-Dancoff approximation (TDA) method⁴¹⁻⁴³ over a wider energy range; this single excitation CI method, a simpler method, is a component of the GAMESS-UK suite.⁴⁴ The 6-311G(d, p) basis set, a valence triple zeta (VTZ) basis,⁴⁵⁻⁴⁷ was used throughout this study; the core orbitals (1a₁ to 5a₁, 1b₂ and 2b₂), representing the 1s_O and 1s_C orbitals are frozen. Valence shell labelling of orbitals is used, and these are: 1a₁ to 8a₁, 1b₁ to 3b₁, 1b₂ to 6b₂, and 1a₂; all these are doubly occupied in the X¹A₁ ground state.

It is important to note that G-16, including the Pisa software for FC studies, labels the harmonic frequencies in ascending frequency order irrespective of symmetry, which contrasts with the normal spectroscopic convention: a₁ < a₂ < b₁ < b₂. In γ -pyrone, where FC processes are occurring, the vibrationally active modes are all of a₁ symmetry, with labels 1 to 11.

III. RESULTS and DISCUSSION

(i) The ground state of γ -pyrone.

(a). The experimental and calculated structures for γ -pyrone.

Comparison of the microwave substitution C-C and C-O bond lengths^{17,18} with the CAM-B3LYP equilibrium structure, as in Figure 1, shows median differences (MD) of 0.0065 Å overall; the C=O bond length is larger by 0.0115 Å with the C=C bond lengths being slightly smaller. The absolute MD in the angles (internal CCC and external CCH) is 0.2°. Similarly, comparison between the MW rotational constants (RC, A,B,C) with the calculated ones gives differences of -44, -27 and -17 MHz for A, B and C respectively. Substitution and equilibrium structures are expected to be very similar, but not identical; these very small differences demonstrate the high quality of these calculations. The calculated dipole moment is close to that determined by the Stark effect.¹⁹ The structure shown in Figure 1 is adopted for the X¹A₁ ground state throughout the FC analyses below. The calculated structures for the ionic states, which are not central to the present paper, are shown in the supplementary material as SM2.

(b). The γ -pyrone X^1A_1 vibrational spectrum.

Theoretical determination of the vibrational envelopes of the ionic states is important in this study; consideration of the ground state data will give an indication of the reliability of the theoretical results for the ionic states. In addition to gas-phase and theoretical investigations,^{48,49} this has previously been investigated by matrix-isolation Fourier-transform infrared spectroscopy (FTIR), where the absorption bands were assigned by Hartree-Fock calculations at the 6-31G* level.⁵⁰ Our theoretical CAM-B3LYP study was performed with the larger 6-311G(d,p) basis set, at both the harmonic and anharmonic frequency levels. The anharmonic procedure includes 2-order perturbation theory (PT2).⁵¹ The results, shown in Table I, lead to a correlation between the calculated anharmonic frequencies with the experimental Raman or IR data as: $\nu_{\text{Anhar}} = 0.993(4) \cdot \nu_{\text{R}} - 1.1(66) \text{ cm}^{-1}$ and $\nu_{\text{Anhar}} = 0.976(5) \cdot \nu_{\text{IR}} + 15(10) \text{ cm}^{-1}$ respectively, where the standard errors (SE) are in parentheses. The intercept for the Raman correlation is significantly lower than its SE, which suggests a zero intercept, while the slope is close to unity; similarly, the IR intercept is close to its SE. The correlation coefficients (adjacent R^2) are 0.9996 and 0.9995 respectively. This near identity between the theoretical and experimental ground state frequencies supports Fausto et al⁵⁰ and ourselves in assigning the experimental spectra on the basis of correlating two sequences of ascending numbers. We note in passing, that Fausto et al⁵⁰ suggest that Fermi resonances (FR) occur close to 1412 and 1685 cm^{-1} . The present study identifies several FR, including ones at 1412 and 1422 cm^{-1} , but none near 1685 cm^{-1} . The 1412 cm^{-1} one involves modes 22 with modes 11+17.

Table I. Calculated frequencies and assignments for the X^1A_1 state of γ -pyrone compared with experimental values.

Anharmonic frequency / cm^{-1}	Harmonic frequency / cm^{-1}	Normal mode	Ascending sequence	Symmetry	Infrared / cm^{-1} [50]	Raman / cm^{-1} [50]	Fausto et al HF /6-31G* [50]
3111	3246	1	27	A_1	3092	3130	3067
3128	3225	2	25	A_1	3045	3076	3038
1766	1794	3	23	A_1	1677,1659	1700,1672	1757
1685	1716	4	22	A_1	1637	1658	1656
1403	1434	5	19	A_1	1399	1398	1390
1206	1224	6	16	A_1	1203,1197	1198	1178

1014	1031	7	14	A ₁	1010,1004	1008	988
938	953	8	11	A ₁	922	924	907
799	820	9	8	A ₁		790	769
503	509	10	5	A ₁	503	504	479
982	1003	11	13	A ₂			987
823	837	12	9	A ₂	(824)	822	808
404	410	13	2	A ₂			393
976	997	14	12	B ₁	969	960	981
870	882	15	10	B ₁	852	850	850
738	749	16	7	B ₁	734	730	721
441	449	17	3	B ₁		395	418
155	158	18	1	B ₁		175	152
3111	3243	19	26	B ₂	3068	3095	3064
3126	3225	20	24	B ₂	3021	3076	3037
1617	1650	21	21	B ₂	1610	1610	1589
1404	1446	22	20	B ₂	1469,1462	1415	1399
1327	1355	23	18	B ₂	1319	1318	1304
1211	1238	24	17	B ₂	1216	1220	1193
1032	1052	25	15	B ₂	1029,1026	1029	1013
646	653	26	6	B ₂	644	641	621
461	463	27	4	B ₂	456	453	442

(c). The nature of the bonding in γ -pyrone.

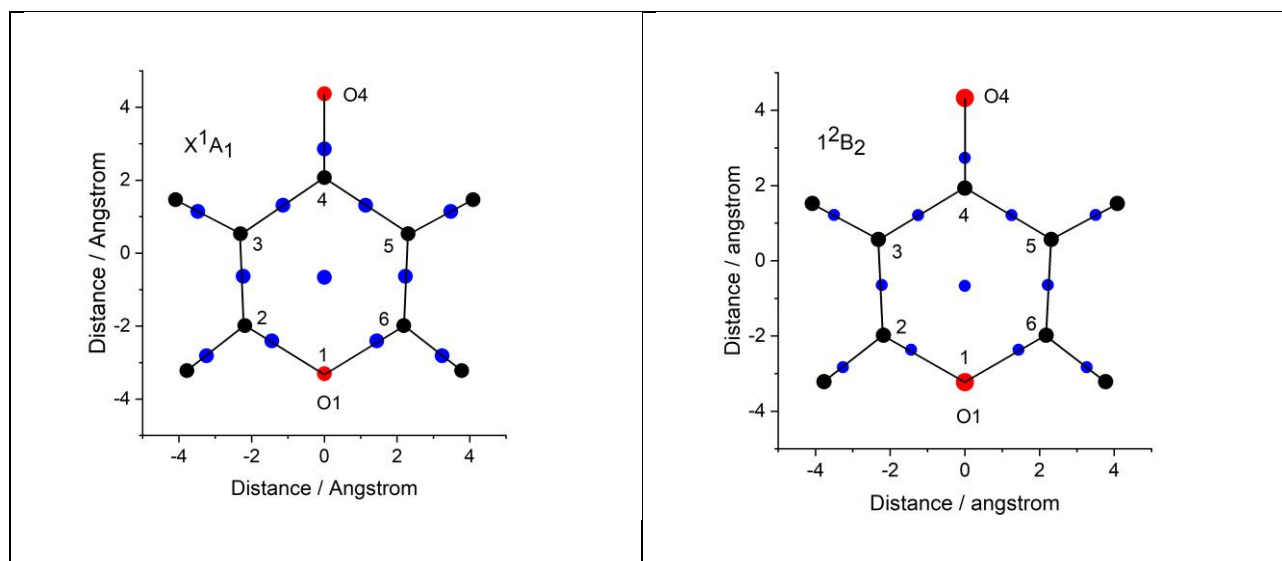
The atoms in molecules (AIM) approach, devised by Bader,⁵²⁻⁵⁴ was used to evaluate the variation in electron density along the inter-nuclear distances for the constituent atoms. This is determined directly, for any electronic state, by integration of the *ab initio* wave-functions. If the electron density along the axis between each pair of atoms, directly bonded or not, reaches a minimum value, then a critical point (CP) is defined between that pair of atomic neighbours. The positions of these CP minima define the range of each atomic basin. In the absence of a second nucleus, non-bonded electrons, as for the O-atom lone pairs in γ -pyrone, do not generate a CP in AIM. Similarly, as a result of the planar molecule where the π -electron density is identical above and below the internuclear axes, no CP arises. Thus the CP are effectively determined by polarization of the σ -electron density. The role of lone pairs and π -bonds has been considered in AIM terms⁵⁵ for dissociation processes, but this is irrelevant here, since we are discussing the AIM issue at equilibrium.

The CP for the X^1A_1 and lowest ionic (1^2B_2) states, are shown in Figure 4. Those between the $C_\beta C_\gamma$ bonds, involving atoms $C_3 + C_4$, and $C_4 + C_5$, lie close to the mid-point of these bonds, implying nearly

equivalent atomic basins. That is not the case for the $C_\alpha C_\beta$ bonds, $C_2 C_3$ and $C_6 C_5$, where the CP are shifted towards the β -positions. This shows the bonds are polarized in the sense $C_\alpha^{\delta+} C_\beta^{\delta-}$. All the C-O and C=O bonds are strongly polarized $C^{\delta+} O^{\delta-}$ with the (notionally single) C-O σ -bonds more polar than the C = O π -bond. All C-H bonds are polarized $C^{\delta-} H^{\delta+}$. There are no CP between non-adjacent atoms, but the ring centre shows a CP. There is considerable similarity in the positions of the CP between the neutral and ionic states, implying very similar σ -polarization; only the 1^2B_2 state is exemplified as a result of these similarities.

The integrated intensities for the atomic basins at the unique centres are shown in the supplementary material as Table SM3. These show that the O_4 and O_1 oxygen atoms have very similar total electron densities, while their attached C-atoms, C_4 and C_2+C_6 all have similar electron densities. These conclusions are distinct from Mulliken analyses, where the atomic populations of basis functions are summed; in such analyses the total density associated with a basis function (BF) is attributed to the atom where the BF is based.

Figure 4. The critical points (CP, marked in blue) along the bonded pairs of atoms are as determined by the Atoms in Molecules (AIM) approach. These are the positions where the electron density along the axis between a pair of atoms, determined from the integrated electron density, reaches a minimal value. The regions between a CP and an individual atom represent the intersection of the two atomic basins. A local minimum occurs at the ring centre with respect to all of the ring structure both in the ground state and all of the ionic states at the CAM-B3LYP level. The ionic states are represented by the 1^2B_2 ionic state; the other ionic states give very similar sets of CP.



(ii) The ionic states.

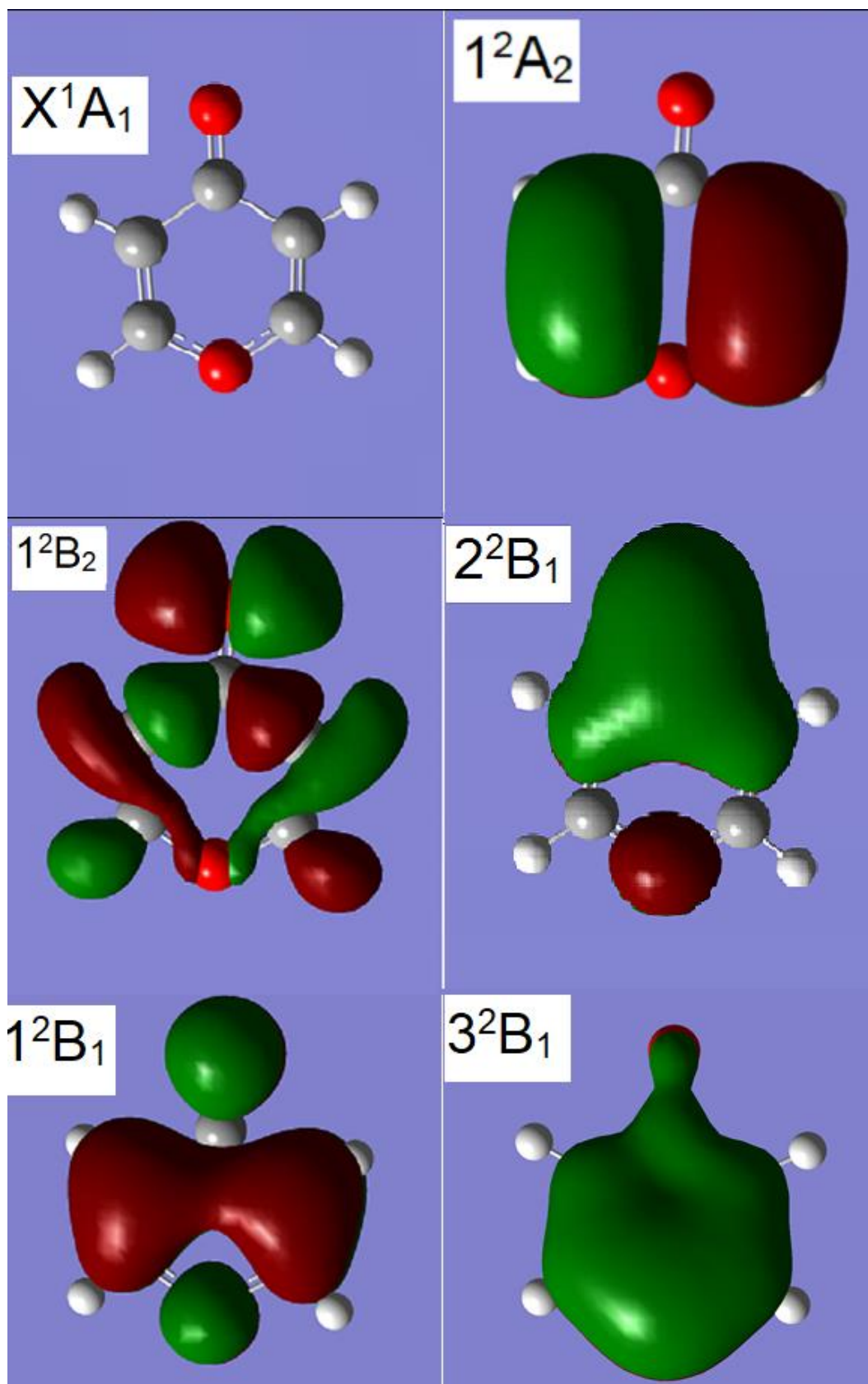
General points. The principal orbitals of interest for the γ -pyrone skeleton are the π - and lone pair-molecular orbitals (MOs), shown in Figure 5, together with the X^1A_1 ground state. The two highest occupied molecular orbitals (HOMOs, $6b_2$ and $3b_1$), have nearly degenerate orbital energies at the Hartree-Fock single configuration level; the corresponding ionic states, 1^2B_2 and 1^2B_1 , are dominated by the vacancies $6b_2^{-1}$ and $3b_1^{-1}$, at the symmetry-adapted cluster configuration interaction (SAC-CI) level (Table II). The symmetric π -MOs, 1^2B_1 to 3^2B_1 , show an unusual electron distribution, especially in 2^2B_1 , where the C_2+C_6 atoms are nodal. The upper part of the MO has a similar grouping to the trimethylene methane ($C(CH_2)_3$) system;^{56,57} this molecule has the highest sum of bond orders in any hydrocarbon, and was extensively studied by MO methods, prior to its detection as a triplet state, where it was identified by electron spin resonance and other methods.⁵⁸⁻⁶³ The lowest γ -pyrone IE, 1^2B_2 , shows a much more complex set of density nodal planes than expected for what is historically a lone pair orbital on the O_4 atom. The next IE, 1^2B_1 shows the direct interaction between the two oxygen atoms with the $C=C$ π -bonds.

(a) The wide scan photoelectron spectrum.

The wide-scan PES, depicted in Figure 2 above, also shows the SAC-CI calculated VIE and their intensities (pole strengths) superimposed; the numerical results are shown in Table II. Generally, the SAC-CI main groupings match reasonably well with the experimental spectrum over a wide energy

range. In Figure 2, the SAC-CI energies have been slightly scaled to bring the calculated ionizations in the 20 to 27 eV range closer to the broad peaks observed in that range of the PES; the linear correlation derived is: $IE_{\text{Observed}} = 0.9198 * IE_{\text{Calc}} + 0.987 \text{ eV}$; the slope close to unity and small intercept is typical of our recent studies.^{1,3,5,7} Pole strengths range from zero to one; those shown in Figure 2 have been increased by 0.05 units to make the contributions of numerous higher energy ionic states more obvious; most of these have very low intensity. The 2^2B_1 and 1^2A_1 states are effectively degenerate in the SAC-CI study, but separated by 1471 cm^{-1} (0.182 eV) in the CASSCF determination. Under similar CASSCF conditions, the 3^2B_1 and 3^2B_2 states are separated by 2383 cm^{-1} (0.296 eV). The 1^2B_2 and 3^2B_2 states are separated by 3.567 eV.

Figure 5. The lowest π - and σ -orbital electron density contours, together with the structure of the X^1A_1 ground state, where the hatching between O_1 and C_2+C_6 is a feature of the graphical drawing package, is merely diagrammatic, and shows the fully conjugated system.



A related single excitation configuration interaction method, the Tamm-Dancoff approximation (TDA),⁴¹⁻⁴³ also generates a very similar correlation up to 23 eV, and hence is not shown. These

theoretical energies enable correlation with the experimental PES; many more high energy states are potentially exhibited by this method, and at significantly lower computational cost.

(b) Assignment of the ionic state vibrational structure.

Determination of the adiabatic ionization energies using the CAM-B3LYP functional, shows that the AIE for the two lowest ionic states are reversed from the Hartree-Fock single-configuration order of 1^2B_2 and 1^2B_1 ; the AIE are 1^2B_2 9.065 and 1^2B_1 9.328 eV. The experimental PES separation of the two IE is 0.20 eV, as discussed below. The only other low-lying AIE are 1^2A_2 and 1^2A_1 where we calculate their AIE close to 11 and 13 eV respectively.

Table II. The low energy region of the photoelectron spectrum of γ -pyrone determined with the scaled symmetry-adapted cluster CI (SAC-CI) theoretical pole strength intensities. Entries are limited to pole strengths greater than 0.1; a further selection is in the supplementary material as part of SM4. In Figure 3, the SAC-CI results have been scaled to fit the experimental energy range, using the linear correlation $IE_{\text{Observed}} = 0.9198 * IE_{\text{Calc}} + 0.987$ eV.

SAC-CI calc. IE / eV	SAC-CI scaled IE / eV	Intensity	Symmetry	Band assignment in Figure 2
9.193	9.325	0.755	1^2B_2	A
9.282	9.407	0.789	1^2B_1	
10.780	10.787	0.795	1^2A_2	B
13.234	13.047	0.722	2^2B_1	C
13.373	13.175	0.778	1^2A_1	
13.848	13.612	0.773	2^2B_2	D
14.563	14.271	0.744	2^2A_1	
16.015	15.608	0.727	3^2B_1	E
16.058	15.648	0.770	3^2B_2	
16.901	16.424	0.768	3^2A_1	F
17.702	17.162	0.746	4^2B_2	G
18.343	17.752	0.737	4^2A_1	
20.764	19.982	0.279	5^2A_1	H
21.064	20.258	0.382	6^2A_1	
22.222	21.324	0.463	5^2B_2	I
22.473	21.555	0.216	6^2B_2	

(iii) Vibrational structure

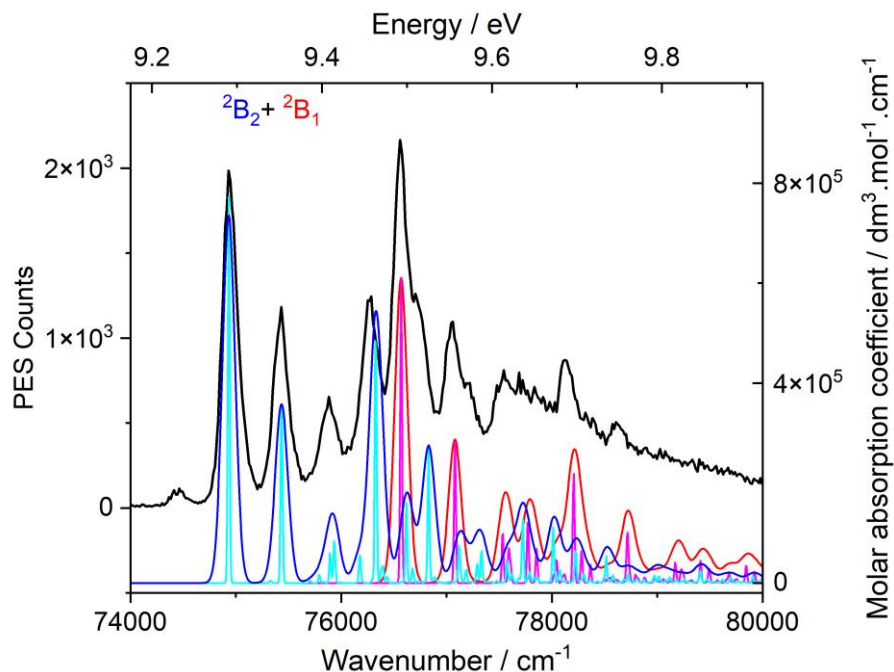
(a) The ionic states (1^2B_2 and 1^2B_1) in the energy range 9.2 to 9.9 eV (Band A).

This onset band, shown in Figure 6, is complex and cannot be rationalized solely in terms of the predicted vibrational structure for the lowest ionic state, 1^2B_2 , at the Franck-Condon level (FC).

However, if the observed band is accepted as the resultant profile from both 1^2B_2 and 1^2B_1 , then we arrive at the combined profile shown, and as listed in Tables III and IV. All the observed principal peaks are accounted for, with the exception of those in the region between 77500 (9.609 eV) and 78000 cm^{-1} (9.671 eV). The calculated separation of the two states given above is 2121 cm^{-1} (0.263 eV), relatively close to the calculated separation of the 0-0 bands for the two states. These 0-0 bands are by far the most intense for either state. This analysis is limited to FC assignments, and ignores Hertzberg-Teller (HT) effects where non-symmetric vibrations are allowed. Currently, we are unable to perform HT on ionic states, since the Pisa version of the software has not yet been extended to ionic states. This is discussed further below.

Clearly, the vibrational profiles (VP) for these two states overlap considerably. In the case of iodobenzene, where similar overlapping VP occur for the A^2A_2 and B^2B_2 states, in order to simulate the observed spectra different bandwidths (line widths) were required for each state⁶⁴. The increase in the required bandwidths was attributed to internal conversion between these two states, and also with the lowest state X^2B_1 , which shows a highly resolved spectrum. Study of the band separations between the four lowest IE of the 4-mono-halogenobenzenes gave a good demonstration of the effect; bands vary in energy for change in the halogen; the reader is referred to Figure 2 in the iodobenzene study.⁶⁴ The fluorobenzene results extend several earlier studies on the vibronic coupling leading to conical intersections (CONINT) between the X^2B_1 and A^2A_2 states, and a further trio for the B, C, and D states.⁶⁵ We note that all the main peaks of the PES onset between 9.2 and 9.8 eV are interpreted by FC vibrations; this suggests that HT factors may be small in this case, but this is discussed further below.

Figure 6. The onset (Band A) of the photoelectron spectrum of γ -pyrone showing the overlap of the Franck-Condon profiles for the 1^2B_2 (in blue) and 1^2B_1 (in red) ionic states. The inset peaks have Half-Widths at Half-Maximum (HWHM) of 10 and 70 cm^{-1} .



Returning to the present spectra, the most intense vibrational satellites for 1^2B_2 shown in Table III, have a pattern which persists in the other ionic states. The types of vibrational FC modes excited for the 1^2B_1 state have similarities to those for the 1^2B_2 state; in both, the 0-0 bands are intense with several strong fundamentals. Sequences of the a_1 fundamentals with increasing numbers of quanta occur for all the ionic states considered. For 1^2B_2 , the fundamentals 10, 9, 8, 6, 4 and 3 are present, but modes 1 and 2 (C-H stretch) do not occur. Even quanta of some of the low Herzberg-Teller (HT) modes of a_2 , b_1 and b_2 symmetry also occur both here and for other ionic states considered below; a more complete analysis, including HT states, is not possible with our current software, would be expected to participate in the higher energy profile of this and other bands. A full list of harmonic frequencies for the 1^2B_2 state is shown in the supplementary material as SM5.

Table III. The onset and active fundamentals for the 1^2B_2 state, using spectroscopic sequence numbering. The energy of the 0-0 transition is 72942 cm^{-1} , prior to a linear shift for coincidence with the PES. All intensities are given in units of molar absorption coefficient / $\text{dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$. The full list of fundamentals for the state are shown in the supplementary material as SM5.

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	515100	0^0	1244	34330	6^1
397	2780	18^2	1273	1313	$10^1 27^2$

501	208700	10^1	1361	4161	$9^1 10^1$
772	2443	27^2	1396	322500	5^1
860	10560	9^1	1446	11890	4^1
898	1529	$10^1 18^2$	1464	14280	$8^1 10^1$
962	40000	8^1	1503	6014	10^3
1002	56440	10^2	1685	90780	3^1

Table IV. The onset and active fundamentals for the 1^2B_1 state. All intensities are given in units of molar absorption coefficient / $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The full list of fundamentals for the state are shown in the supplementary material as SM6.

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	611000	0^0	1204	119200	6^1
371	1234	18^2	1248	1028	$12^1 13^1$
511	213600	10^1	1287	50970	5^1
681	3359	$17^1 18^1$	1362	1657	$15^1 17^1$
827	39	9^1	1451	16070	4^1
965	93340	8^1	1475	45020	$8^1 11^1$
1021	56490	10^2	1532	9677	10^3
1040	21530	7^1	1550	13060	$7^1 10^1$
1192	1028	$10^1 17^1 18^1$	1638	177100	3^1

The principal fundamentals excited for 1^2B_1 , are modes 10 down to 3, and again excluding C-H stretching modes. The second most intense peak is 10^1 , and this occurs with an increasing sequence of quanta. The three lowest frequencies, all non-symmetric, namely 371 ($5b_1$), 753 ($3a_2$) and 879 ($9b_2$) cm^{-1} , occur with even numbers of quanta. The binary combination bands include several of HT-(non-symmetric) type, such as the modes at 681 cm^{-1} ($17b_1^1 18b_1^1$) and 1028 cm^{-1} ($2a_2^1 3a_2^1$). A triple combination band at low energy related to the former binary 681 cm^{-1} is at 1192 cm^{-1} ($10^1 17^1 18^1$). A full list of the harmonic frequencies in ascending frequency sequence are shown in the supplementary material as SM6.

(b) Vibrational structure of the ionic state (1^2A_2) in the energy range 10.5 to 11.7 eV (Band B).

This IE is assigned to the 1^2A_2 ionic state and is shown with its Franck-Condon analysis in Figure 7. This is the lowest ionic state to show an imaginary frequency (-56 cm^{-1} , $5b_2$). The full list of ascending harmonic frequencies are given in the supplementary material as SM7. The full onset up to $\sim 1000 \text{ cm}^{-1}$, and selected intense peaks are shown in Table V. The most prominent vibrational

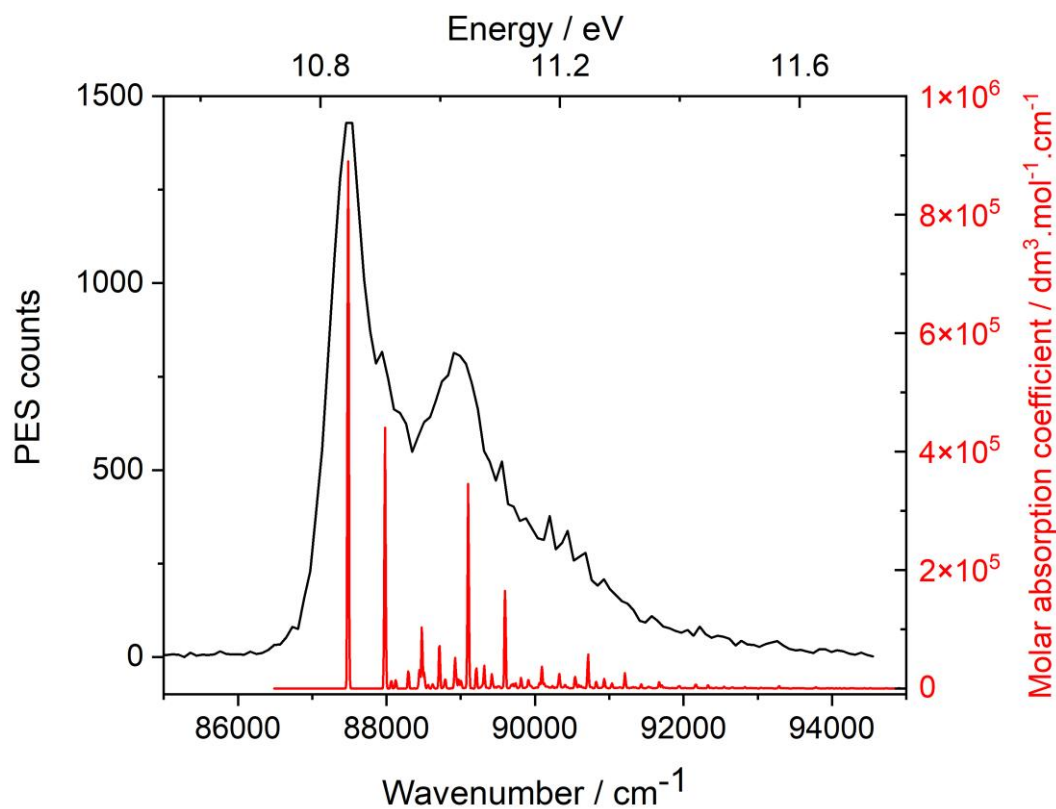
satellites which occur are the a_1 modes 10 down to 3; binary combinations with mode 10 are notable.

All of the low frequency non-symmetric modes 10, 13, 17, occur as even-harmonics.

Table V. The onset and active fundamentals for the 1^2A_2 state. All intensities are given in units of molar absorption coefficient / $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	890200	0^0	1138	7033	$10^1 13^2$
496	440300	10^1	1162	305	13^4
581	11520	13^2	1229	67110	6^1
641	14330	17^2	1307	14270	$9^1 10^1$
811	29040	9^1	1439	36500	5^1
892	154	10^2	1455	10070	$8^1 10^1$
959	21670	8^1	1489	15140	10^3
968	1533	$16^1 17^1$	1521	13000	$7^1 10^1$
993	103000	27^2	1616	233000	4^1
1024	27110	7^1	1804	3317	$9^1 10^2$
1077	5514	$10^1 18^2$	1833	38020	3^1

Figure 7. Band B, the 10.5 to 11.7 eV range of the photoelectron spectrum with the Franck-Condon profiles of the 1^2A_2 ionic states superimposed.



(c) Vibrational structure of the ionic states in the range 12.5 to 14 eV (Band C). An expanded version of this range, shown in Figure 8, is a complex profile which seemed likely to contain three ionizations, 2^2B_1 , 1^2A_1 and 2^2B_2 on the basis of the SAC-CI calculations in Table 2. The relatively separated onset peaks between 12.5 and 13.0 eV are characteristic of π -ionizations, and is attributed to 2^2B_1 . The 1^2A_1 envelope is superimposed on the PES after amplifying its intensity by a factor of five relative to the 2^2B_1 ionic state. The CAM-B3LYP calculations (Tables VI and VII) show two of these, 2^2B_1 and 1^2A_1 , differ significantly in calculated intensity. There are several sharper (broader) peaks near 13.6 eV, which do not appear to be from the other two ionizations. The structure and frequencies for 1^2A_1 were determined using the CAM-B3LYP method, as for the earlier ionic states. CASSCF studies led to (both) 2^2B_1 and 3^2B_1 states, as described in the Methods Section II(ii) above. The profiles for these two states differ significantly in character. Whereas the 0-0 band of 2^2B_1 is substantial in intensity, that for 1^2A_1 is relatively weak. Again the vibrations present in each state are C-H deformation, out-of-plane, and ring breathing modes, with no C-H stretching modes participating in the envelope. Both profiles have the characteristic contributions from even quanta of the nonsymmetric modes; one of these for the 1^2A_1 state is of very low frequency, and this leads to the complex set of closely placed vibrations. In contrast, the 2^2B_1 state shows both much stronger, but also more widely spaced vibrations. The positioning of the (unscaled) theoretical set of vibrational peaks on the PES envelope is obvious for the 2^2B_1 state; the 1^2A_1 state, with its small separations better represented by the PES structure above 13.25 eV. The AIE for 2^2B_1 is well determined at 12.646 eV, but that for 1^2A_1 is not clear, and the positioning of it in Figure 8, is based on the SAC-CI, discussed above, at 13.175 eV; this is not the only possible choice of energy. A full list of the harmonic frequencies for the two states in ascending frequency sequence are shown in the supplementary material as SM8 and SM9.

Figure 8. Band C, the 12.5 to 14 eV range of the photoelectron spectrum obtained with $h\nu = 30$ eV, which leads to a resolution ($\Delta E = 11$ meV); the Franck-Condon profiles of the 2^2B_1 and 1^2A_1 ionic states are superimposed; the much lower intensity of the latter has been amplified by a factor of 5 to make more detail apparent.

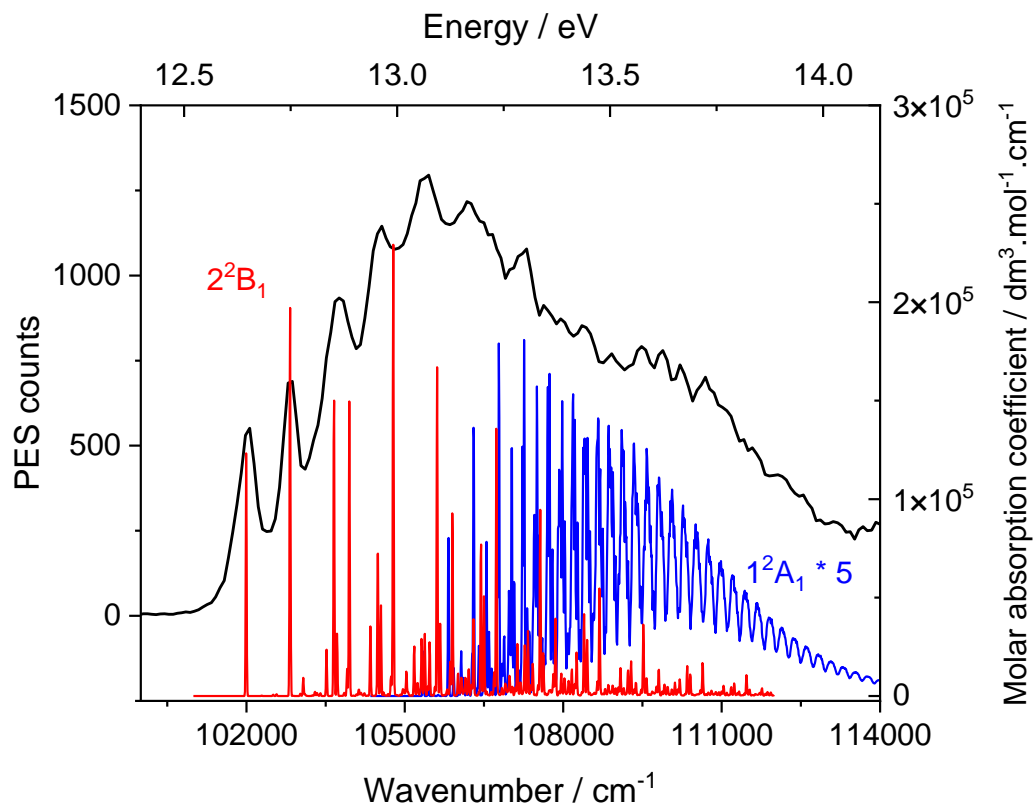


Table VI. The onset and active fundamentals for the 2^2B_1 state. 0-0 transition: 98552 cm^{-1} . All intensities are given in units of molar absorption coefficient / $\text{dm}^3.\text{mol}^{-1}.\text{cm}^{-1}$

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	237900	0^0	1582	257	7^110^1
306	226	18^2	1659	180800	9^2
510	6093	10^1	1712	19240	4^1
653	3498	17^118^1	1725	295	$7^117^118^1$
830	246000	9^1	1803	307	6^110^1
838	141	13^2	1849	67	9^110^2
860	496	16^118^1	1850	2772	8^19^1
1019	195	10^2	1902	19450	7^19^1
1020	2332	8^1	1967	17250	3^1
1072	12800	7^1	1981	68	$9^126^127^1$
1136	200	9^118^2	2026	1218	5^110^1
1151	43	26^127^1	2034	485	12^2
1294	4005	6^1	2105	1326	14^2
1339	103800	9^110^1	2123	5768	6^19^1
1436	550	12^113^1	2169	7952	9^210^1

1483	5242	$9^1 17^1 18^1$	2170	560	$5^1 17^1 18^1$
1516	27210	5^1	2221	709	$4^1 10^1$
1553	2253	$14^1 17^1$	2313	3545	$9^2 17^1 18^1$

Table VII. The onset and active fundamentals for the 1^2A_1 state. Energy of the 0-0 transition: 101868 cm^{-1} . All intensities are given in units of molar absorption coefficient / $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	4512	0^0	1146	2455	6^1
99	735	18^2	1153	1303	$10^2 18^4$
197	161	18^4	1198	12410	$9^1 10^1$
277	88	$17^1 18^1$	1246	4259	$8^1 10^1$
296	57	18^6	1297	2731	$9^1 10^1 18^1$
376	57	$17^1 18^3$	1404	12080	$7^1 10^1$
456	112	17^2	1434	34250	10^3
478	13070	10^1	1440	1825	92
555	34	$17^2 18^2$	1489	1805	$8^1 9^1$
577	2838	$10^1 18^2$	1503	1686	$7^1 10^1 1^2$
720	4542	9^1	1532	5254	$10^3 18^2$
768	1508	8^1	1604	1241	4^1
926	2915	7^1	1623	6249	$6^1 10^1$
956	27060	10^2	1631	1085	$10^3 18^4$
1054	3818	$10^2 18^2$	1646	2717	$7^1 9^1$

(d) **Band D with range 14.0 to 15.2 eV.** The SAC-CI results suggest that a single 2^2A_1 state is present for this energy range. However, we have been able to determine the equilibrium structures for two states under CAS[7,8]SCF conditions and we believe that Band D contains both the 2^2A_1 and 2^2B_2 states; a reasonable fit is shown in Figure 9, but not considered in further detail.

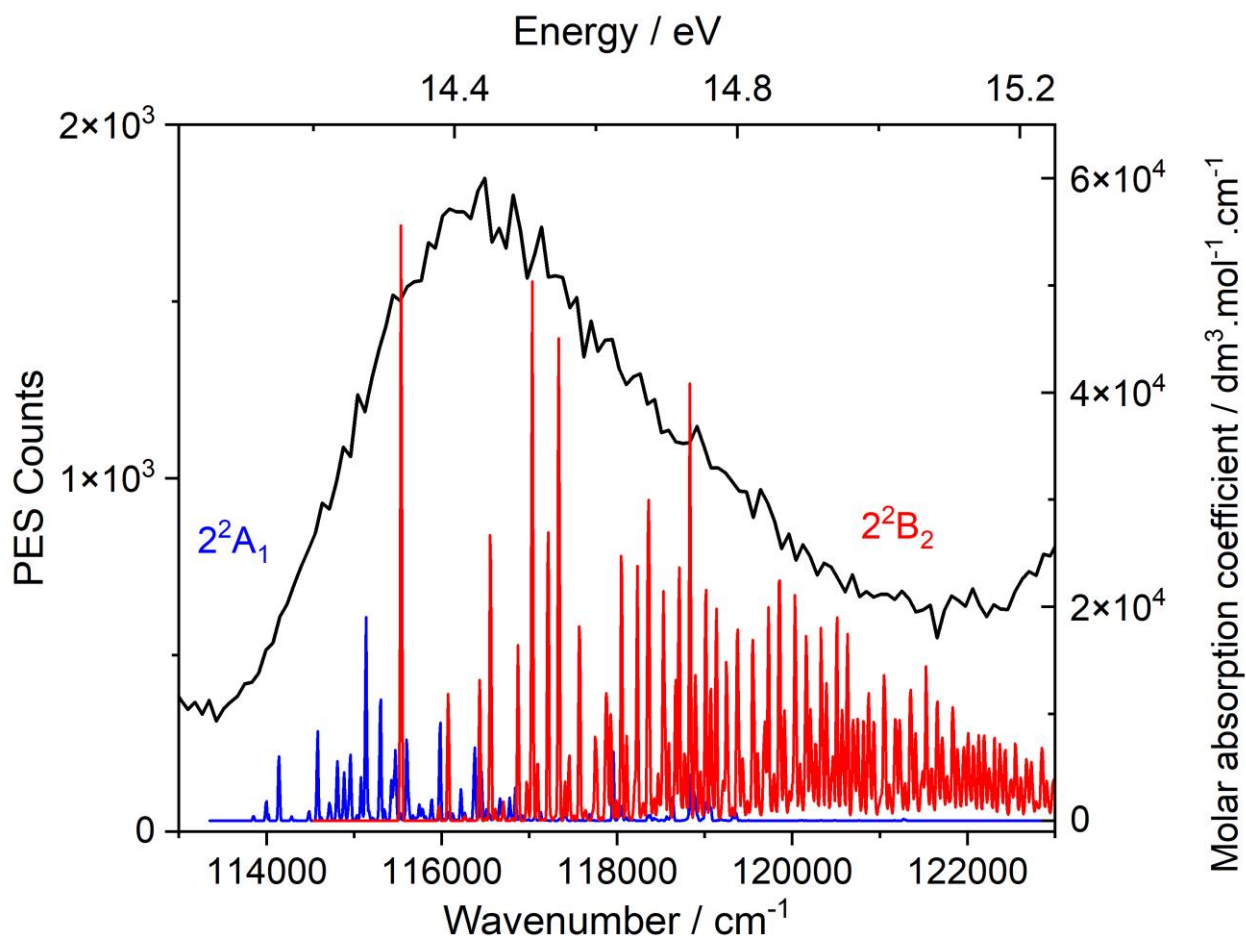
Table VIII. The onset and active fundamentals for the 2^2B_2 state. Energy of the 0-0 transition: 111441 cm^{-1} . All intensities are given in units of molar absorption coefficient / $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	113300	0	1499	134100	5^1
557	25520	10^1	1635	31560	4^1
1024	26780	8^1	1931	46460	3^1
1362	35860	6^1	2057	44110	$10^1 5^1$

Table IX. The onset and active fundamentals for the 3^2B_1 state. Energy of the 0-0 transition: 111441 cm^{-1} . All intensities are given in units of molar absorption coefficient / $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

Energy / cm^{-1}	Intensity	Spectroscopic sequence	Energy / cm^{-1}	Intensity	Spectroscopic sequence
0	1169	0^0	1906	75	8^2
476	70	10^1	1988	146	$8^1 9^1$
771	5053	9^1	2017	656	$9^2 4^1$
953	471	8^1	2029	1199	$6^1 9^1$
1035	424	7^1	2069	65	7^2
1246	248	$9^1 10^1$	2158	11430	$5^1 9^1$
1259	328	6^1	2200	89	$8^1 9^1 10^1$
1387	3074	5^1	2212	129	$6^1 7^1$
1533	426	4^1	2281	152	$7^1 9^1 10^1$
1541	9695	9^2	2293	108	11 14
1724	1995	$8^1 9^1$	2304	1507	$4^1 9^1$
1799	293	3^1	2312	10990	6^3
1805	1629	$7^1 9^1$	2315	64	$9^2 27^2$
1842	62	$9^2 17^2$	2340	1146	$5^1 8^1$
1863	137	$5^1 10^1$	2422	961	$5^1 7^1$

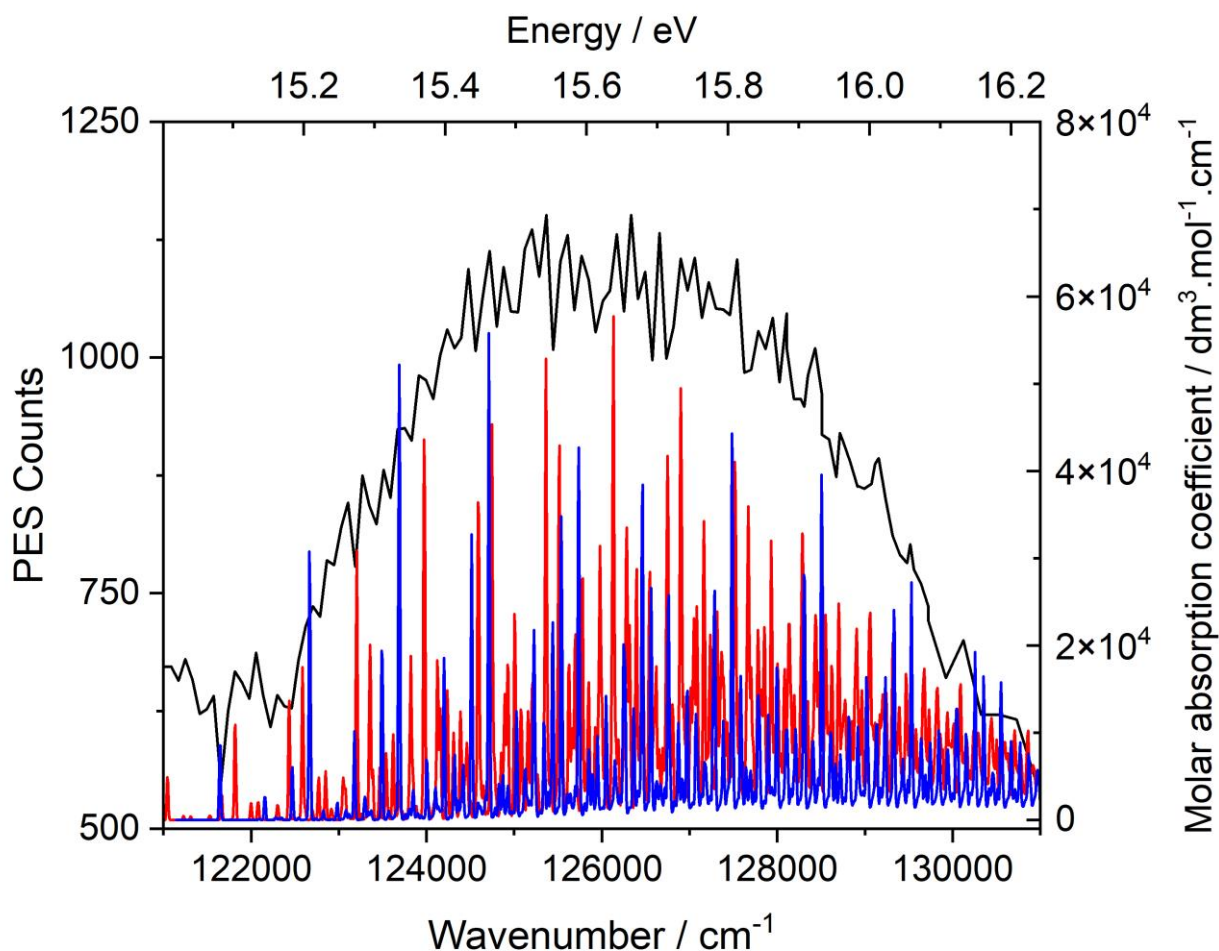
Figure 9. Band D, the 14.0 to 15.2 eV range of the photoelectron spectrum obtained with $h\nu = 30 \text{ eV}$, which leads to a resolution ($\Delta E = 11 \text{ meV}$). This band is thought to contain both 2^2B_2 and 2^2A_1 . The two theoretical profiles have been placed arbitrarily, rather than attempt an assignment.



(d) Band E with range 15.1 to 16.2 eV.

This band is shared by the 3^2B_1 and 3^2B_2 states, as shown by the SAC-CI study above. The 3^2B_2 state is dominated by the fundamental mode 9, and in various combinations. The vibrational structure is superimposed on the PES for this state in Figure 10; the onset and range up to circa 2440 cm^{-1} is shown in Table IX. However, it is clear that the a_1 fundamentals, 10 down to 3, all occur but with the exception of mode 9 have generally low intensity. The principal vibrational energy lies in overtones, especially of mode 6, and combination bands. There are 50 vibrational state combination bands, with molar absorption coefficient $> 10^4$ units ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and the most intense vibration, 9472 with intensity 4580 units, is some 5857 cm^{-1} above the 0^0 band. A full list of the harmonic frequencies for the 3^2B_1 states in ascending frequency sequence are shown in the supplementary material as SM10.

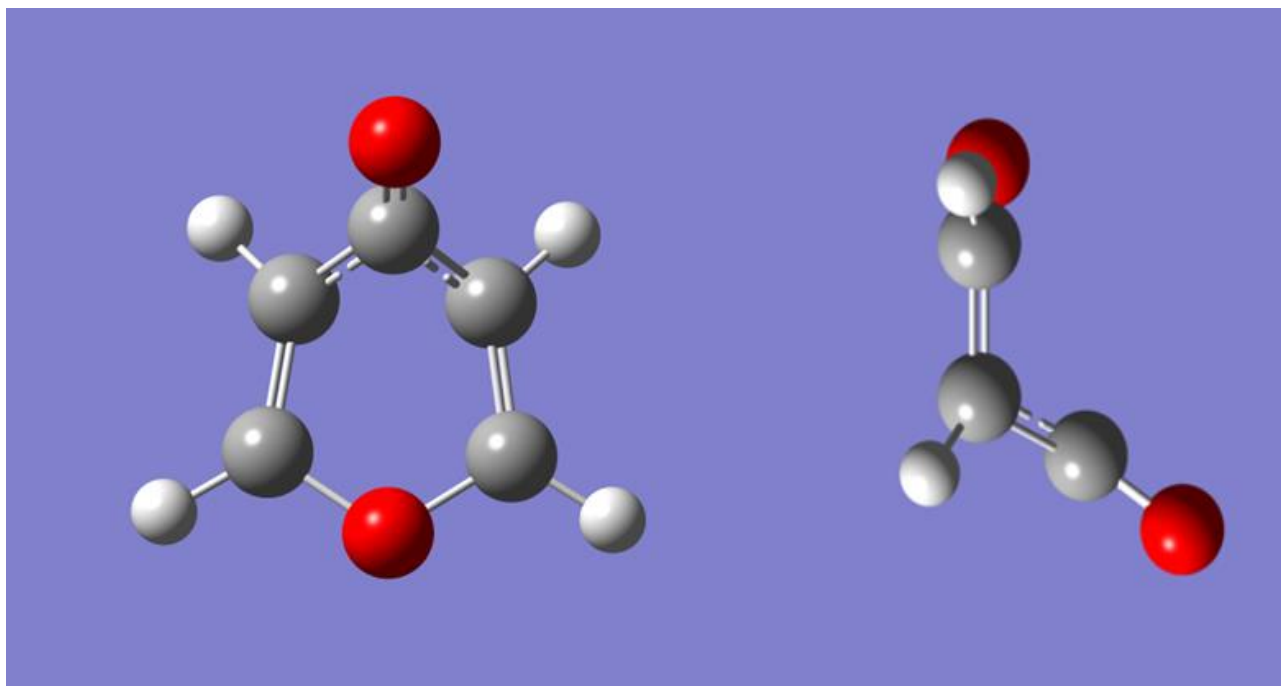
Figure 10. Band E, the 15.1 to 16.2 eV range of the photoelectron spectrum obtained with $h\nu = 30$ eV, which leads to a resolution ($\Delta E = 11$ meV). The Franck-Condon profiles of the 3^2B_1 (red) and 3^2B_2 (blue) ionic states are superimposed.



(e) **The transition state between the 1^2B_2 and 1^2B_1 ionic states.** This was performed by the combined synchronous transit and quasi-Newton methods for finding transition states (QST2 procedure) implemented in G-16.^{66,67} The Cartesian coordinates for the equilibrium structures of the two states were input, using the CAM-B3LYP procedure with the 6-311G(d,p) basis set. The coordinates between the two sets of corresponding atoms are interpolated to generate a range of intermediate points. The energies of these points were determined by the same method as used for the equilibrium structures. The TS from these two states has C_s symmetry, is strongly buckled and resembles the cyclohexane boat configuration, as shown in Figure 11. The structure shows the

necessary negative vibration frequency (-288 cm^{-1} of A' symmetry). The coordinates, and the variation in bond lengths and angles between the two input states and the TS, which are often substantial, are shown in the supplementary material as SM11.

Figure 11. The C_s symmetry transition state lying between the 1^2B_2 and 1^2B_1 ionic states. shown in two projections with similarities to the boat form of cyclohexane.



(f) Herzberg-Teller effects.

As indicated above, we are currently unable to evaluate the HT vibrational coupling in cationic systems, HT calculations using the Pisa software are limited to singlet and triplet states. This is important to the present study, since the calculated onset of the γ -pyrone PES shows pairs of ionic states in very close proximity, as shown in Figures 6 and 8. It is evident that the vibrational states calculated for each state in isolation must overlap. Using the FC calculated data, the most probable separation shown in Figure 6 gives a reasonable interpretation of the most intense peaks observed. The Born-Oppenheimer approximation, implicit in Franck-Condon processes,^{68,69} is based on the fact that the separation of electronic states is generally large compared to typical spacings associated with nuclear motion. When this condition is violated, residual coupling occurs, via the nuclear kinetic energy operator, which causes transitions between the adiabatic electronic states.^{70,71} The resultant ‘diabatic states’ can cross, in contrast to

‘adiabatic states’ which are subject to the non-crossing rule. We have previously shown the effect of including HT effects in some singlet states; generally the intensities of these HT states are relatively low when compared with the 0-0 bands of the corresponding FC states. But they do allow odd-quanta (i.e. 1-, 3- etc.) of non-symmetric modes to participate, and that may be happening in the current ionic states.^{72,73,74,75}

As stated, we cannot perform the necessary HT analysis for these ionic states. However, we have found that a transition state lies between the two separate state minima for 1^2B_2 and 1^2B_1 , as described above. A conical intersection of any type necessarily causes a complete breakdown of the Born-Oppenheimer approximation,^{68,69} and this provides direct evidence of the vibronic coupling between these two states.

IV. CONCLUSIONS

This study offers a new approach to the bonding of the γ -pyrone in its ground state, via the ‘atoms in molecules’ procedure. Here, direct integration of the electron density between the constituent atoms is performed, and the boundaries of the atomic basins are defined in terms of local minima in the electron density. The σ -electron polarization is considerable. The polarity of the C-O and C=O bonds are similar, such that the observed and calculated dipole moment arises from a delicate balance between the O₁ and C₄O polarization. Using high order symmetry adapted coupled cluster methods, we give a good account of the main groupings of ionization. The sequence of state adiabatic ionization energies is: $1^2B_2 < 1^2B_1 < 1^2A_2 < 1^2A_1 < 2^2B_1 < \text{others including } 3^2B_1$. The electron density contours of the lowest ionization (1^2B_2) show a complex structure far removed from that of the classical carbonyl group lone-pair ionization.

The first vibrational analysis of the photoelectron spectrum for γ -pyrone, enabled by a much higher resolution PES using synchrotron radiation, shows that the lowest ionization region, Band A in Figures 2 and 6, is clearly two overlapping ionizations, 1^2B_1 and 1^2B_1 . This order of states only appears at the CI level. A transition state, determined late in the investigation, between the two onset states 1^2B_2 and 1^2B_1 established that vibronic coupling between these two states does indeed happen.

All the π -electron ionizations, which lie in Bands A to E have been analyzed by Franck-Condon methods; bearing in mind the density of calculated theoretical vibrational states do not contain contributions from Herzberg-Teller processes, the envelopes are reasonably well reproduced. Even higher resolution with higher count rates would be beneficial in finalizing the experimental envelopes. Unexpectedly, the overlap of the 1^2B_2 and 1^2B_1 ionic state vibrational envelopes does not lead to degradation of the higher energy one. That phenomenon was observed numerous times in our studies of the halogenobenzenes previously, and the profile of the higher energy state(s) could only be interpreted by increasing the apparent vibrational line (band) width.^{64,65} For example, in the case of iodobenzene, in order to simulate the observed spectra, different bandwidths are required for different states. That increase for the A^2A_2 and B^2B_2 states was attributed to internal conversion between these two states; the lowest state X^2B_1 shows a highly resolved spectrum. Study of the band separations between the four lowest IE of the 4-mono-halogenobenzenes gave a good demonstration of the effect; the reader is referred to Figure 2 in the iodobenzene study.⁶⁴ The fluorobenzene results extend several earlier studies on the vibronic coupling leading to conical intersections between the X^2B_1 and A^2A_2 states, and a further trio of B, C, and D states.⁶⁵ However, since the super-position of the two FC profiles gives a reasonable account of the PES, vibronic coupling is not obvious in the current cases of 1^2B_2 and 1^2B_1 where it might have been anticipated. The discovery that a transition state lies between the two equilibrium geometry ionic structures, provides the necessary evidence.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional information on each of the following:

1. Table SM1. Peak positions from the multi-peak analysis for the combined lowest band, assigned to the combined $^2B_2 + ^2B_1$ and 2A_2 ionizations.
2. Figure SM2. The equilibrium structures of the γ -pyrone ionic states.
3. Table SM3. The integrated electron density in the atomic basins.
4. Table SM4. The higher energy region of the photoelectron spectrum of γ -pyrone determined with the scaled symmetry-adapted cluster CI (SAC-CI) theoretical pole strength intensities.
5. Table SM5. The

ascending sequence of harmonic frequencies for the 1^2B_2 state with the normal mode labels. 6. Table SM6. The ascending sequence harmonic frequencies for the 1^2B_1 state with the normal mode labels. 7. Table SM7. The ascending sequence harmonic frequencies for the 1^2A_2 state with the normal mode labels. 8. Table SM8. The ascending sequence harmonic frequencies for the 2^2B_1 state with the normal mode labels. 9. Table SM9. The ascending sequence harmonic frequencies for the 1^2A_1 state with the normal mode labels. 10. Table SM10. The ascending sequence harmonic frequencies for the 3^2B_1 state with the normal mode labels. 11. Table SM11 and Figure SM11 for the transition state lying between the 1^2B_2 and 1^2B_1 states.

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DATA AVAILABILITY OF ARTICLE OR SUPPLEMENTARY MATERIAL.

The data that support the findings of this study, including its supplementary material, will be available from the corresponding author upon reasonable request.

AUTHOR DECLARATIONS The authors have no conflicts to disclose.

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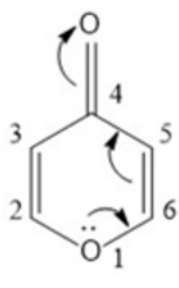
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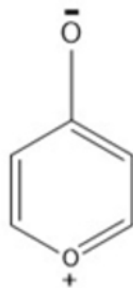
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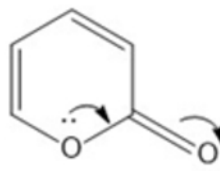


A

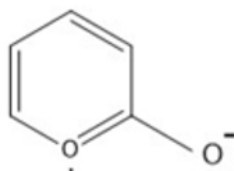


B

4H-pyran-4-one (1A,1B)



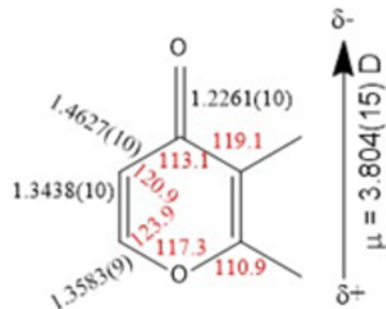
C



D

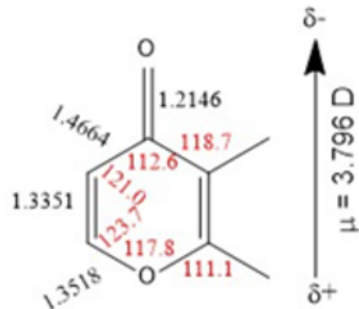
2H-pyran-2-one (2C,2D)

Microwave substitution structure



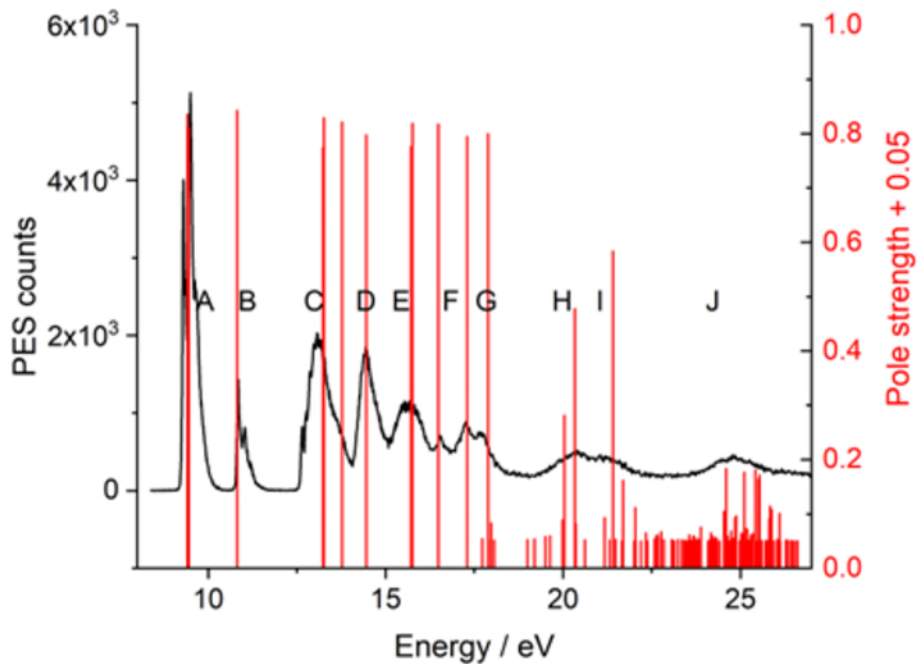
Rotational constants (MHz):
A, 5859.17; B, 2715.09; C, 1855.55

Equilibrium structure CAM-B3LYP 6-311G(d,p)

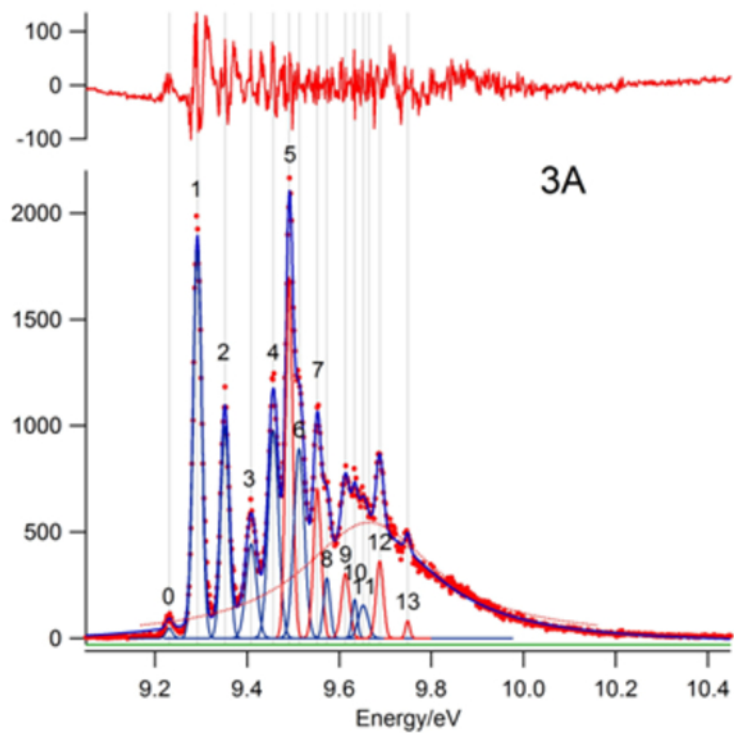


Rotational constants (MHz):
A, 5903.36; B, 2741.65; C, 1872.20

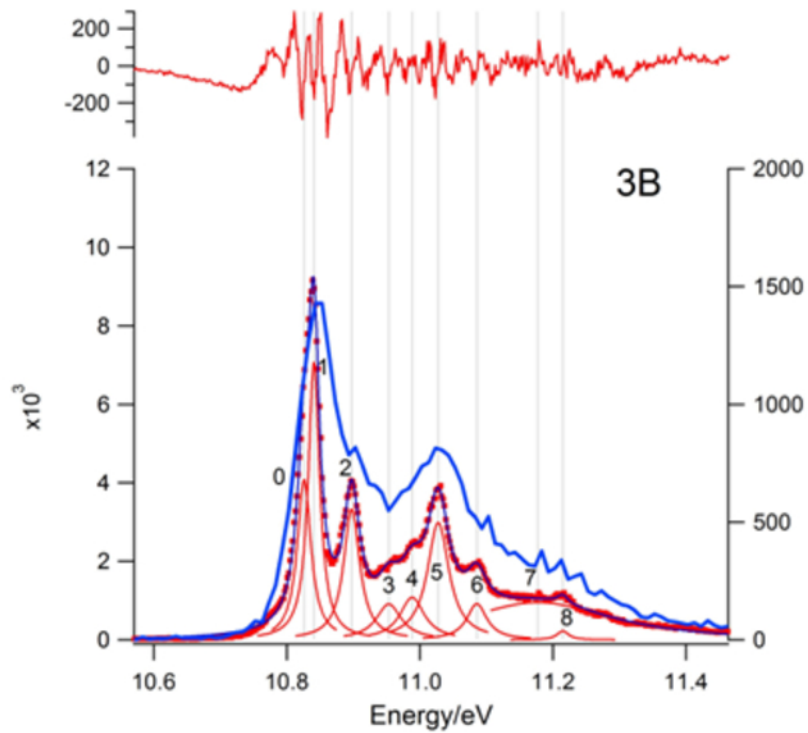
Palmer et al Figure2



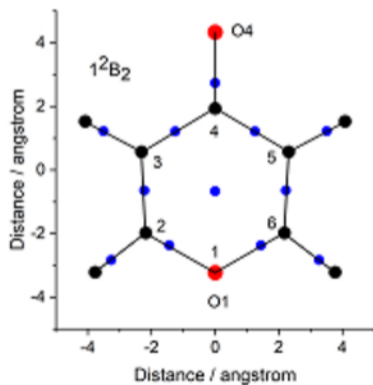
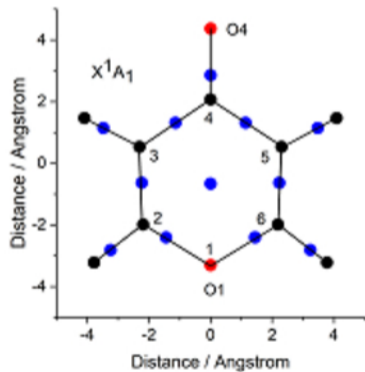
Palmer et al Figure3A



Palmer et al Figure 3B

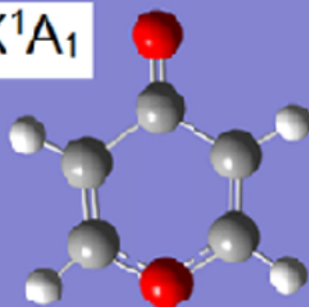


Palmer et al Figure 4

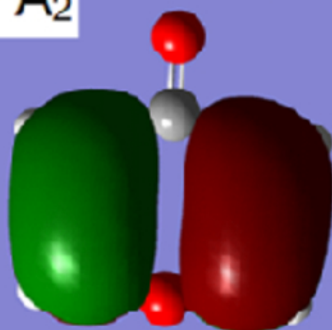


Palmer et al Figure 5

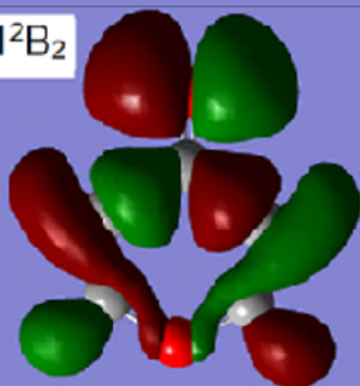
X^1A_1



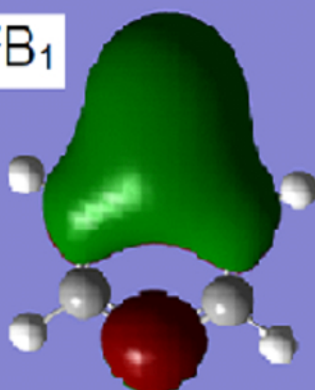
1^2A_2



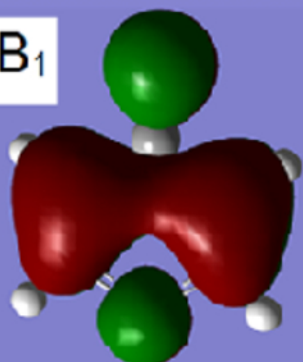
1^2B_2



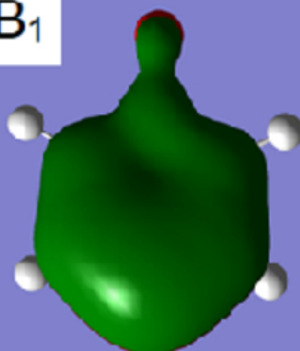
2^2B_1



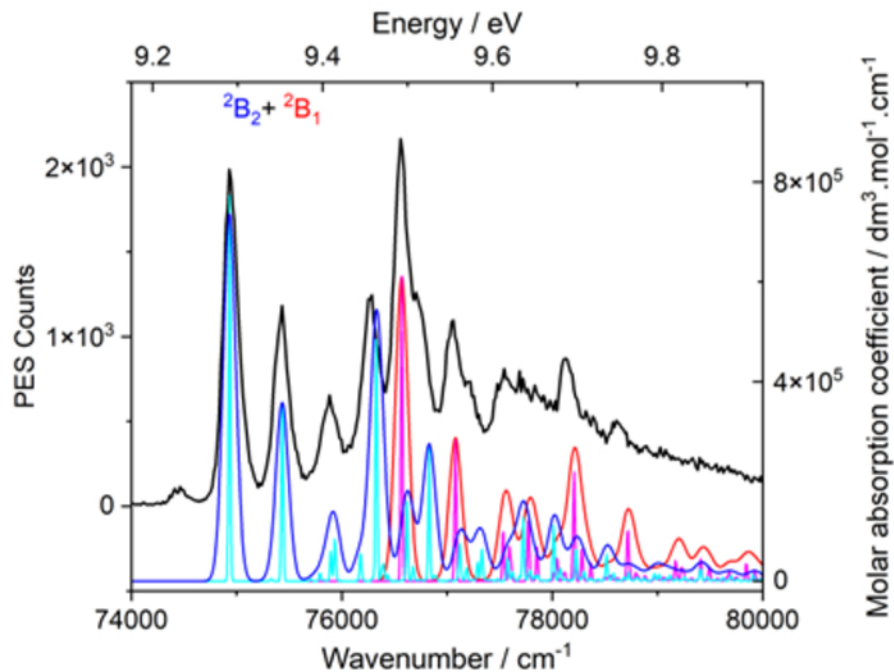
1^2B_1



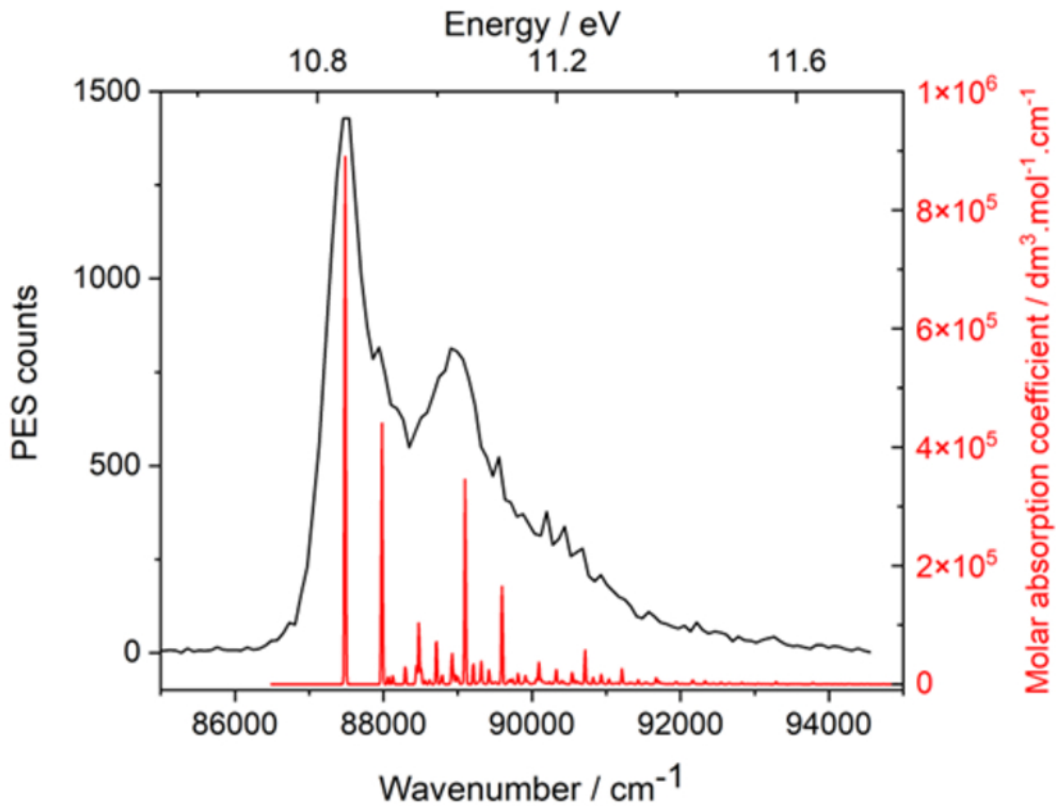
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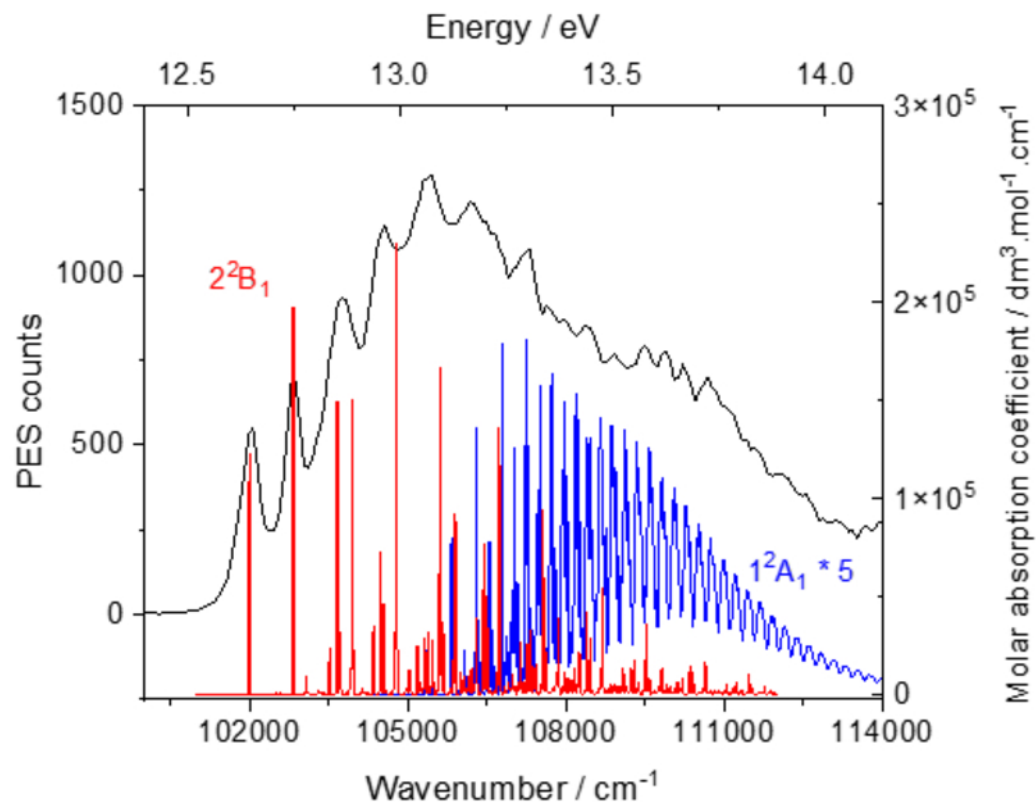
Palmer et al Figure 6



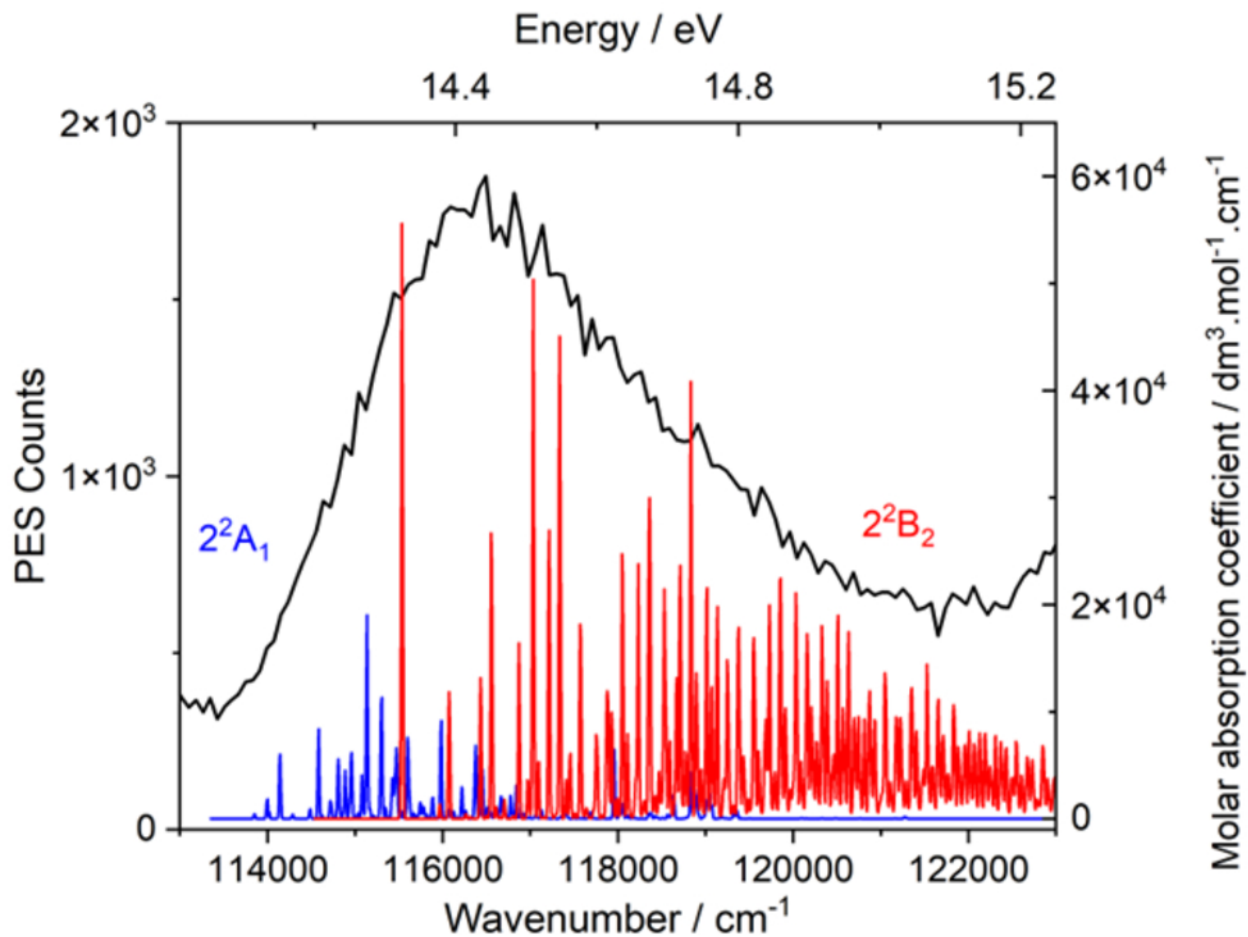
Palmer et al Figure 7



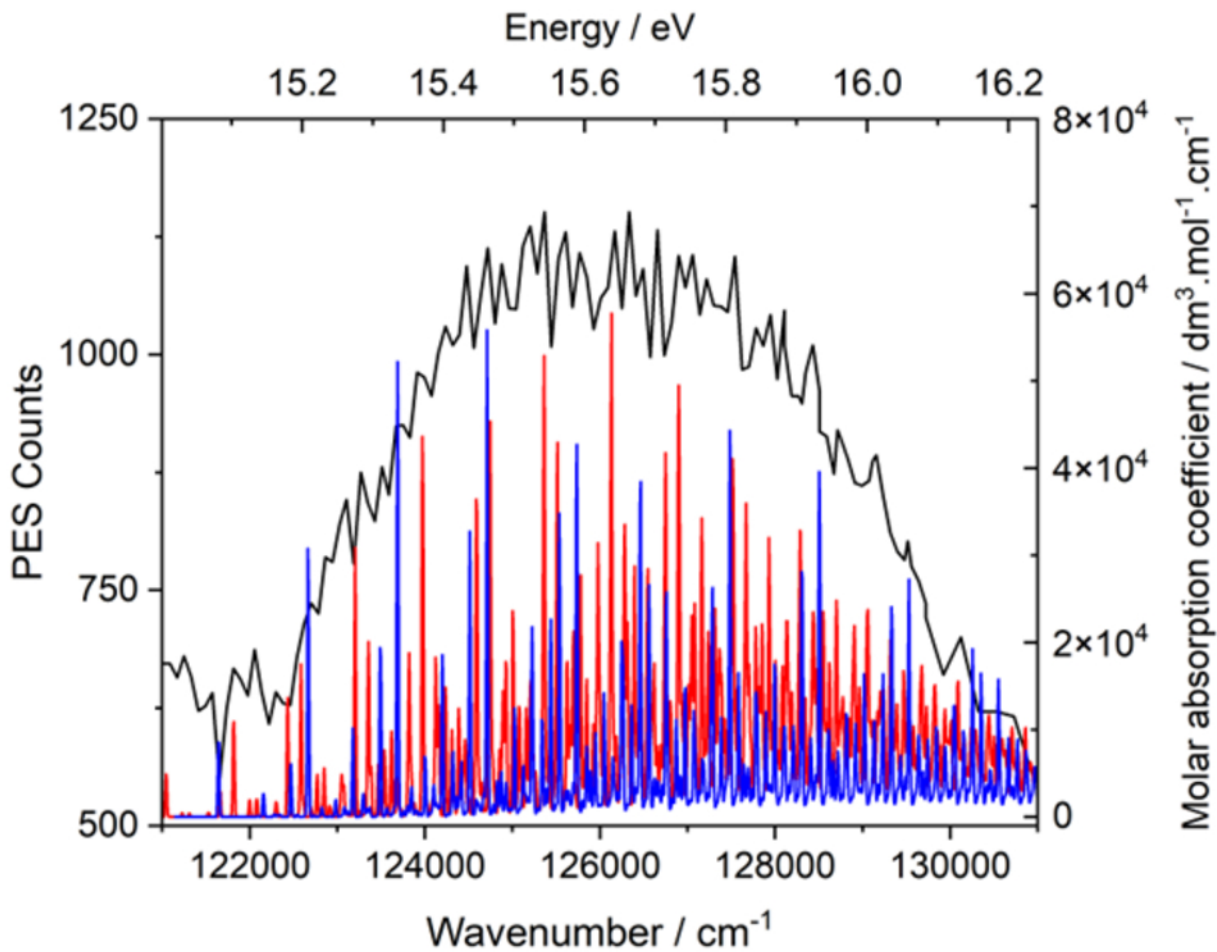
Palmer et al Figure 8



Palmer et al Figure 9



Palmer et al Figure 10



Palmer et al Figure 11

