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Vibronic structure of the cyanobutadiyne cation: I- VUV photoionization study of HC_5N

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We report the vacuum-ultraviolet threshold-photoelectron spectrum of HC_5N recorded over a wide spectral range, from 84 000 to 120 000 cm^{-1}, with a 120 cm^{-1} spectral resolution, better than what was achieved in previous photoelectron studies, and with mass selectivity. The adiabatic ionization potential of cyanobutadiyne is measured at 85 366 ($\pm$ 40) cm^{-1}. Assignment of the vibrational bands of the four lowest electronic states $X^+\ ^2\Pi$, $A^+\ ^2\Pi$, $B^+\ ^2\Sigma^+$ and $C^+\ ^2\Pi$ are performed, supported by high level *ab initio* calculations which are fully detailed in a companion paper (Gans *et al.*, JCP **XX** XX (2019)), and by Franck-Condon simulations. Only vibrational stretching modes are observed in the threshold-photoelectron spectra. The ground state of HC_5N^+ exhibits a vibrational progression in the ν_2 stretching mode involving mainly the elongation of the C≡C triple bonds whereas the A^+ and C^+ excited electronic states show a progression in the stretching mode mainly associated with the elongation of the C≡N bond, *i.e.* ν_4 and ν_3, respectively. The B^+ state appears almost as a vibrationless structure in close vicinity to the A^+ state.

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I. INTRODUCTION

Cyanobutadiyne, H-C≡C-C≡C-C≡N, is a member of the cyanopolyyne family, exhibiting an extended π-conjugated system. Thanks to its strong rotational lines detected by radioastronomy, this compound has been found in numerous extra-terrestrial environments, including molecular clouds[1,2], circumstellar envelopes[3,4], and comets[5]. Models or simulation experiments[6,7] have predicted it to be present in Titan's atmosphere, but so far it has not been observed there. This compound can be ionized by a vacuum-ultraviolet (VUV) radiation field or by electron impact, and the resulting cation can play a role in the gas phase chemical evolution of these media.

Spectroscopic studies on HC_5N are relatively scarce since only small amounts of a pure compound can be produced by chemical synthesis.[8] So far, absorption experiments in cell or matrix environments have been performed in the infrared,[9] mid-UV,[10] and VUV[11] spectral ranges allowing the collection of vibrational band intensities and absorption cross sections. Raman scattering spectra at low temperature have led to the identification of all the vibrational fundamental modes.[12] Concerning the cationic species, the He(I) PhotoElectron Spectrum (PES) at 21.22 eV was measured in 1980 by Bieri and co-workers[13] with a resolving power of 250 (spectral resolution of 350-450 cm^{-1} in the explored range). This work led to identification of the four lowest electronic states of the cation and the determination of the corresponding adiabatic ionization energies with an uncertainty of 20 meV (160 cm^{-1}). A few vibrational frequencies have been derived for the two lowest electronic states ($X^+\,^2\Pi$ and $A^+\,^2\Pi$), but no complete assignment has been performed. Emission spectroscopy experiments were carried out in the same work,[13] using a low energy electron beam to ionize and electronically excite the HC_5N^+ cations. Observation of the $A^+\,^2\Pi \rightarrow X^+\,^2\Pi$ gas phase visible emission spectrum allowed the determination of the $A^+\,^2\Pi$ state radiative lifetime and measurement of the vibrational wavenumbers for four stretching modes (ν_2, ν_3, ν_5, and ν_6) of the cation ground state with an uncertainty of $\pm$ 10 cm^{-1}. Sinclair *et al.* used frequency modulation absorption spectroscopy to record the 0_0^0 band of the $A^+ \rightarrow X^+$ transition with rotational resolution.[14] In their experiment the ions were generated in a cooled hollow cathode modulated discharge coupled to a White absorption cell to increase the optical path. Molecular parameters (rotational and spin-orbit coupling constants) were

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derived from this absorption spectrum for the X^+ and A^+ states.

As for the theoretical studies dedicated to the cation, Lee[15] predicted *via* DFT calculations the linear structure, the vibrational frequencies, the dipole moment and the rotational constant of the ground state of HC_5N^+. Stimulated by matrix isolation spectroscopy experiments performed by Forney *et al.*[16] and Smith *et al.*[17], Cao and Peyerimhoff[18] calculated the vertical transition energies and oscillator strengths for the doublet system of linear HC_5N^+ (starting from the cation ground state) by *ab initio* approaches. As a result, seven doublet states are expected to lie within 6.2 eV (*c.a.* 50 000 cm^{-1}) above the cation ground state energy.

In the present work, an experimental photoionization study from neutral cyanobutadiyne has been performed and the Threshold Photo-Electron Spectrum (TPES) of HC_5N has been recorded between 84 000 and 120 000 cm^{-1}. To support the assignments of the vibronic structures observed in the TPES, a thorough theoretical work has been carried out in order to explore the complicated energy landscape in the region above the ground state of the cation. High level *ab initio* calculations have been conducted, some of them falling beyond the scope of the present experimental study. This complete study is thus presented in a separate paper, to be referred to as Paper II.[19] In the present paper, only the pertinent results of the calculations enabling the understanding of the TPES are reported. The experimental and computational methods are first briefly explained. The vibronic structure of the TPES is then analyzed and discussed in light of the *ab initio* calculations. We would like to point out that as both papers are self-contained, they can be read in any order. We thus encourage the reader to start reading Paper II first, if he prefers to have in mind all theoretical details before discovering the experimental context.

II. METHODS

A. Experimental details

The experiment was carried out at the SOLEIL synchrotron facility operating in the multibunch mode with the double imaging photoion-photoelectron coincidence spectrome-

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ing DELICIOUS III[20] coupled to the SAPHIRS chamber installed on the monochromatized branch of DESIRS VUV beamline.[21] HC_5N was synthesized prior to the experimental campaign according to the chemical procedure developed by Trolez and Guillemin in 2005[8] and was stored at −80°C. Manipulation of the pure HC_5N sample was performed at a controlled temperature of −12°C by means of a chiller. The vapour pressure (P_{vap} = 4.6 mbar at −12°C) was introduced into the SAPHIRS vacuum experimental chamber *via* an effusive jet allowing for a moderate consumption of product (*c.a.* 2 mg per hour) compatible with the small amounts available, and allowing the continuous recording of energy scans lasting several hours.

The molecules were ionized by the VUV synchrotron radiation from DESIRS, which was set to provide energy resolution between 0.72 and 0.22 Å. Removal of the high harmonics from the undulator was achieved using a gas filter filled with Argon. The VUV flux was monitored by a VUV photodiode (AXUV, IRD) and was used to normalize all of the spectra. The absorption lines of Argon observed as dips in the ion yield allowed for absolute spectral calibration with an accuracy of 20 cm^{-1}. Ions and electrons were detected in coincidence by Wiley-MacLaren and velocity map imaging devices to record two types of spectra: Threshold PhotoElectron (TPE) spectra and HC_5N^+ ion yield spectra. Since no fragmentation occurs in the present energy range, all spectra are given for the parent mass only, *i.e.* $m/z = 75$. TPE spectra were recorded between 84 000 and 120 000 cm^{-1} with 40 cm^{-1} steps, with an extraction field E of 88 V/cm, which is a compromise between resolution and maximum kinetic energy of the detected electrons *(i.e.* 3.7 eV kinetic energy). In these conditions, the overall energy resolution of the TPE spectra is 15 meV (120 cm^{-1}). The ionization threshold values extracted from the TPES were corrected from the estimated Stark-induced shift ($6 \times \sqrt{E} = 56$ cm^{-1}).

For the HC_5N^+ total ion yield spectrum, all electrons must be detected within the explored spectral range due to the coincidence scheme. Therefore for the above conditions, the upper energy limit for full ion detection is 110 000 cm^{-1}. For the total ion yield, the energy resolution is given by the photon energy resolution, which was set to 0.72 Å and 0.22 Å for photon energies below or above 12.5 eV (i.e. 101 000 cm^{-1}). An additional scan with an extraction field of 264 V/cm (yielding an electron bandwidth of 10.8 eV, and therefore an energy range for full transmission of up to $h\nu = IE_{adia} + 10.8$ eV) was also performed to record a reliable HC_5N^+ ion yield up to 120 000 cm^{-1}. Due to limited beamtime access, this

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scan was performed with a larger energy step (*c.a.* 807 cm^{-1}). Note that for this scan, the energy resolution corresponds to ~ 30 cm^{-1}, much smaller than the energy steps of the scan, but detector saturation prevented us from degrading the resolution due to the consequent gain in photon flux.

B. Computational details

All calculations were performed with the MOLPRO program package[22,23] running on the HYDRA and VEGA clusters of the ULB/VUB computer center in Brussels (Belgium). The accurate Internally Contracted MultiReference Configuration Interaction (ic-MRCI) method[24,25] has been used with molecular orbitals (MOs) optimized for the multireference wavefunction by a State Averaged Complete Active Space Self-Consistent Field (SA-CASSCF) calculation.[26,27] The Davidson correction has been applied to all energies, leading to a level of theory denoted by the ic-MRCI+Q acronym. Geometry optimizations were carried out at the latter level of theory using the Dunning's aug-cc-pVTZ basis set (AVTZ for short)[28,29] on the potential energy surfaces corresponding to all states investigated in the study. Linear geometry was found for all states. Harmonic frequency calculations were determined at the same level of theory for the four lowest electronic states of the cation, *i.e.* $X^+\ ^2\Pi$, $A^+\ ^2\Pi$, $B^+\ ^2\Sigma^+$, and $C^+\ ^2\Pi$. Let us note that our *ab initio* calculations predict the existence of two minima on the third potential energy surface of $^2\Pi$ symmetry. They are referred to as 3 $^2\Pi(Min_1)$ and 3 $^2\Pi(Min_2)$ in Paper II, where it is demonstrated that the photoionization process only populates one of them, Min_2, which is thus assigned to the observed C^+ state. This assignment is fully confirmed by the good agreement obtained with our TPES results. Vertical and adiabatic ionization and transitions energies were calculated using a Complete Basis Set (CBS) extrapolation procedure, detailed in Paper II.[19] These energies were also corrected to take the zero-point energy (ZPE) contributions into account.

Figure 1 illustrates the atomic displacements of the stretching modes (ν_1 to ν_6) for the four lowest electronic states of the HC_5N^+ cation. Only the stretching modes are presented here since it will be shown that they are the only ones observed in our experiments. A similar figure for the bending modes is available in Paper II.[19] As shown in Figure 1, the ν_1 mode is mainly associated with the CH stretch for all four electronic states, whereas the ν_2, ν_3, and

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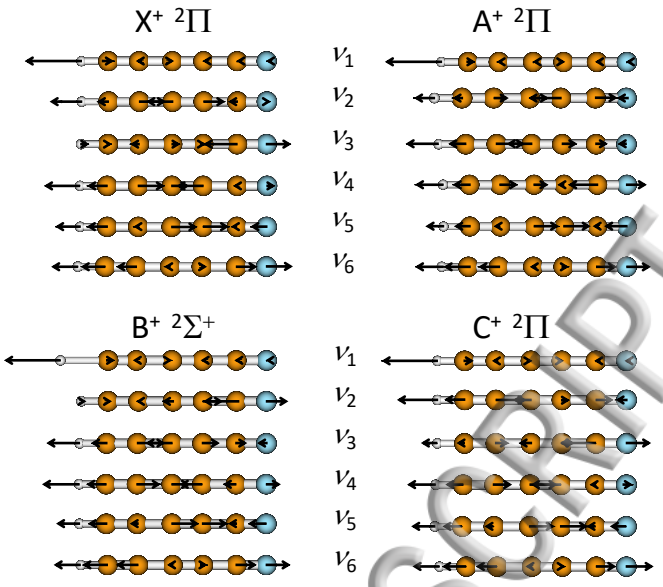


FIG. 1. Illustration of the atomic displacements for each vibrational stretching mode of the X^+, A^+, B^+, and C^+ electronic states of HC_5N^+ cation. The N atom appears in blue color. Mass-weighted normal coordinates have been calculated at the ic-MRCI+Q/AVTZ level of theory. The corresponding frequencies are reported in Table II. Atomic displacements are scaled by a factor of 0.3 for the CH-stretching modes and by a factor of 0.8 for the other modes.

ν_4 modes describe the elongation and contraction of the CC and CN bonds, with different combinations depending on the electronic state. It is interesting to note for instance that the local C≡N stretch is dominantly described by the ν_2 mode in the B^+ state, by the ν_3 mode for the X^+ and C^+ states, and by the ν_4 mode for the A^+ state. This is consistent with a decrease of the C≡N bond strength along the $B^+ \rightarrow X^+/C^+ \rightarrow A^+$ series, as indicated by the decrease of the C≡N stretching frequency (from 2339 to 1999 cm^{-1}) accompanied by an increase of the bond length (from 1.151 to 1.202 Å, see Table II of Paper II[19]). The frequencies of the normal modes involving the CN stretching vibration consequently shift down below those of C≡C triple bonds, thus explaining the mode numbering changes.

In addition, the ν_5 and ν_6 modes are mostly assigned to the stretching motion of the two C-C single bonds.

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III. RESULTS AND DISCUSSION

A. TPE spectrum and HC_5N^+ ion yield

Figure 2 displays the TPE spectrum of HC_5N in the 84 000–120 000 cm^{-1} range (i.e. 10.5–15 eV) with a typical resolution of 120 cm^{-1}. The corresponding HC_5N^+ ion yield is presented in the upper panel as two different scans, the first one between 84000 and 111 000 cm^{-1} with a moderate extraction field and the second one up to 120 000 cm^{-1} with a higher extraction field and a step scan of 100 meV (*i.e.* 807 cm^{-1}).

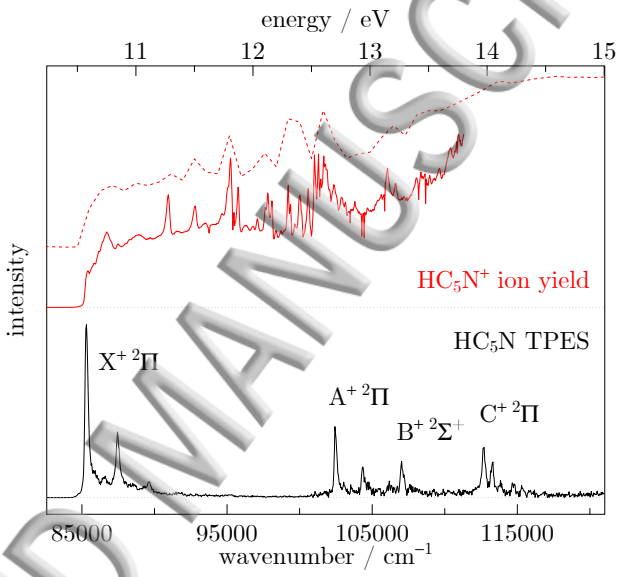


FIG. 2. HC_5N^+ ion yield (upper panel; continuous and dashed red curves) and TPE spectrum of HC_5N (lower panel; black curve) between 84 000 and 120 000 cm^{-1}. Depletion lines observed in the ion yield are due to absorption transitions of atomic species present in the gas filter. The red continuous line curve corresponds to a moderate extraction field that allows for detection of ions in coincidence with the photoelectron with 3.7 eV maximum kinetic energy. The red dashed ion yield displays the same signal but with a higher extraction field and a lower spectral resolution, in order to cover the full range up to 120 000 cm^{-1}.

Up to 110 000 cm^{-1}, the HC_5N^+ ion yield exhibits sharp autoionization structures due to Rydberg states converging to excited vibronic states of HC_5N^+. Above this energy, the ion yield is structureless. Note that in this region the HC_5N^+ ion yield corresponds to the total ion yield since the opening of the dissociative ionization channels occurs at higher energy,

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TABLE I. Experimental adiabatic ionization energies of HC_5N toward the four lowest electronic states of the cation measured in the present work, and comparison with the theoretical values calculated in Paper II[19] at the CBS limit and corrected for the ZPE. All values are given in cm^{-1}.

E_i/hc / cm^{-1}	$X^+\,^2\Pi$	$A^+\,^2\Pi$	$B^+\,^2\Sigma^+$	$C^+\,^2\Pi$
IE_{adia}^{calc}	84 445	101 962	106 317	112 406
IE_{adia}^{exp} (this work)	85 366 ± 40	102 516 ± 40	107 072± 40	112 731± 40
IE_{adia}^{exp} (Ref.[13])	85 253 ± 160	102 432 ± 160	107 110 ± 160	112 595± 160
IE_{adia}^{calc}-IE_{adia}^{exp} (this work)	- 921	- 554	- 755	- 325

above 129 000 cm^{-1}.[30]

In the TPE spectrum, four distinct electronic states are observed, as already pointed out by Bieri *et al.*[13]. The experimental adiabatic ionization energies from the neutral ground state to these ionic states can be determined from the energy of the main intense structure for each region. Indeed, even though the excitation process is vertical, starting from the neutral ground state geometry, the equilibrium geometry of the cationic states does not change significantly (see Table II of Paper II[19]) and the first peak of the TPES for each electronic state, corresponding to the 0_0^0 band, is the most intense. To good approximation, the energy of the origin band (0_0^0) can thus be associated with the adiabatic value, neglecting the rotational structure. These results are reported in Table I and they are compared with the adiabatic energies IE_{adia} previously measured by Bieri and co-workers,[13] as well as with the values calculated in the present work and presented in Table IV of Paper II.[19] Our experimental values lie within the 160 cm^{-1} (*i.e.* 20 meV) uncertainty of Bieri *et al.*[13] They agree well with the calculated values of Paper II within $\simeq 500-1000$ cm^{-1}.

B. Vibrational structures observed in the TPE spectrum

The higher resolution used in the present experiment as compared to Bieri *et al.*[13] (120 cm^{-1} vs 350-450 cm^{-1}) allowed some of the vibronic features of the TPE spectrum to be resolved. In HC_5N and its cation, the ν_2, ν_3, and ν_4 stretching modes are very close in energy and differ slightly between the X, X^+, A^+, B^+, and C^+ electronic states (see

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wavenumber values in Ref. 9 for the neutral and in Table II for the cation). The assignment of vibronic transitions involving these modes is thus ambiguous as mentioned by Bieri *et al.*[13] To facilitate the identification, we have calculated by means of the Pgopher software[31] the multidimensional Franck-Condon factors (FCF) of each ionizing transition ($X^+ \leftarrow X$, $A^+ \leftarrow X$, $B^+ \leftarrow X$, and $C^+ \leftarrow X$) using the equilibrium geometries and the harmonic normal mode solutions resulting from our *ab initio* calculations (see Paper II[19]). The strength of each electronic transition has been manually adjusted to reproduce the intensities of the origin bands ($v^+ = 0 \leftarrow v = 0$) observed in the experimental spectrum.

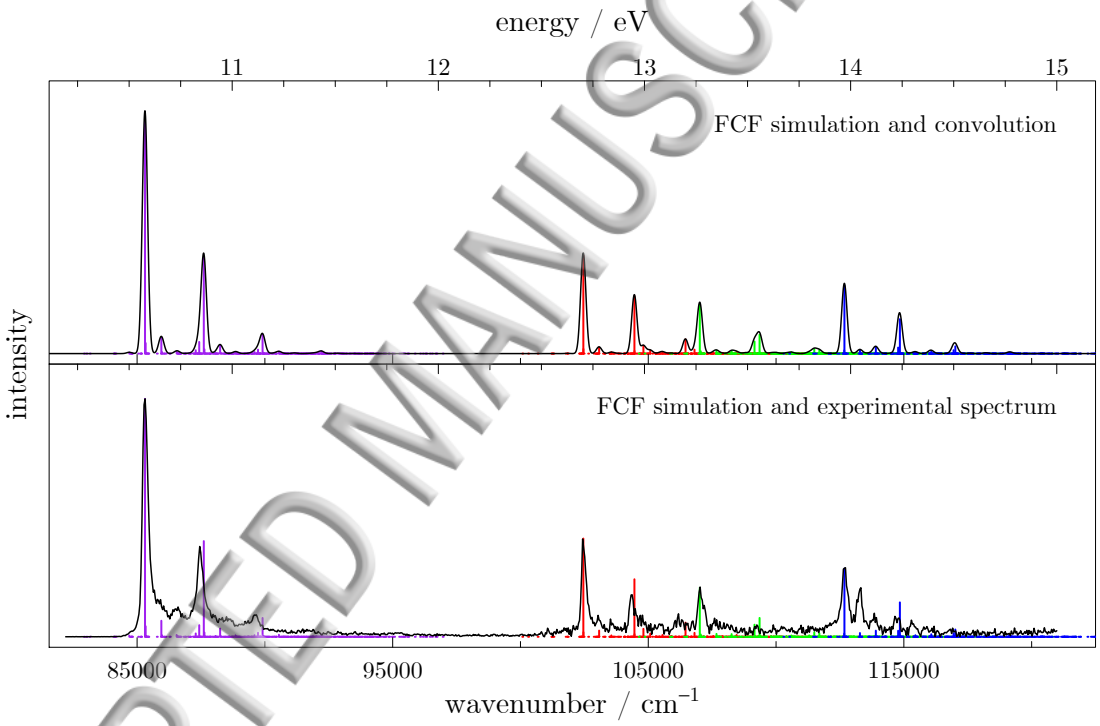


FIG. 3. Calculated photoelectron spectrum of HC_5N toward the X^+, A^+, B^+, and C^+ cationic states displayed as purple, red, green, and blue stick spectra, respectively. The vibrational progression of each electronic transition has been shifted to match the experimental origin bands. See text for details.

Upper panel; black line: convolution of the stick spectra with a gaussian function of 240 cm^{-1} (FWHM). Lower panel; black line: experimental TPE spectrum.

Only the stretching modes were considered since the linear geometry of cyanobutadiyne is conserved upon ionization and the calculated bending frequencies do not change sig-

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nificantly from the neutral ground state to the cationic excited states (see Table II and Paper II[19]). Hence the transitions involving bending mode excitations are expected to be unobservable. The complete FCF simulation of the TPE spectrum is displayed in Figure 3. The corresponding convoluted spectrum is shown in black in the upper panel. In the lower panel, the same stick spectrum is compared with the experimental TPE spectrum. It is clear that the vibrational structures of each ionizing transition are well reproduced and the agreement between the calculated and experimental spectra is quite good. From this comparison, it is straightforward to conclude that the vibrational structures of the observed ionizing transitions can be ascribed to the stretching modes.

The corresponding assignments are shown in Figure 4. Transition to the X^+ state exhibits a vibrational progression involving the ν_2 mode, and combination bands with the ν_5 mode. These findings can be interpreted in terms of bond length changes upon ionization from the neutral ground state. Indeed, *ab initio* calculations (see Table II of Paper II[19] and atom labelling adopted in this work) predict that the main geometry changes in the ($X^+ \leftarrow X$) transition are a shortening of the C_2-C_3 single bond ($\Delta R(C_2\text{-}C_3) = -0.054$ Å) and a lengthening of the $C_1{\equiv}C_2$ triple bond ($\Delta R(C_1{\equiv}C_2) = +0.031$ Å). These geometry changes are well described by the ν_2 vibrational normal mode (see Figure 1). For the ($A^+ \leftarrow X$) transition, observation of a progression in the ν_4 mode agrees with the shortening of the C_4-C_5 single bond ($\Delta R(C_4\text{-}C_5) = -0.034$ Å) and the lengthening of the $C_5{\equiv}N$ triple bond ($\Delta R(C_5{\equiv}N) = +0.047$ Å), both changes are associated to the ν_4 mode (see Figure 1). For the ($C^+ \leftarrow X$) transition, the main change in geometry predicted by the calculations concerns the lengthening of the $C_5{\equiv}N$ triple bond ($\Delta R(C_5{\equiv}N) = +0.044$ Å) and, to a lesser extent, that of the $C_3{\equiv}C_4$ triple bond ($\Delta R(C_3{\equiv}C_4) = +0.026$ Å). This explains the observation of a progression in the ν_3 mode only for this excited electronic state. For all these excited electronic states, the assignments of other vibrational modes (mainly ν_5 and ν_6) are also tentatively proposed, with a weaker intensity. Note that the intensity of the assigned ν_6 mode for the C^+ cation state is much higher than expected. It does not seem to be induced by autoionization processes, since in this spectral region, neither the absorption spectrum[11] nor the ion yield exhibit Rydberg structures. We attribute this disagreement to the existence of vibronic couplings revealed by our *ab initio* calculations, but not taken into account by our FCF simulation. These vibronic interactions are induced by an avoided

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crossing that affects specifically the ν_6 mode of the C^+ state (see Section III.E.5 of Paper II[19] for more details).

The case of the ($B^+ \leftarrow X$) transition is more peculiar because only a few vibrational signatures emerge above the spectral noise. The 0-0 transition is indeed about four times weaker than in the ($X^+ \leftarrow X$) transition. Our simulation predicts a band system involving the ν_2 mode, from which only the 0-1 band emerges above the spectral noise. A second band involving ν_4 is even weaker and is not visible in the TPE spectrum. A tentative assignment of the ν_2 mode is thus proposed in Figure 4.

The experimental vibrational wavenumbers derived from the TPE spectrum are reported in Table II along with previous experimental values,[15,18] and *ab initio* values calculated in Paper II.[19] The agreement with theory is very good, within 100 cm^{-1} or less for most states. Values for the stretching modes of the B^+ and C^+ electronic states are measured for the first time.

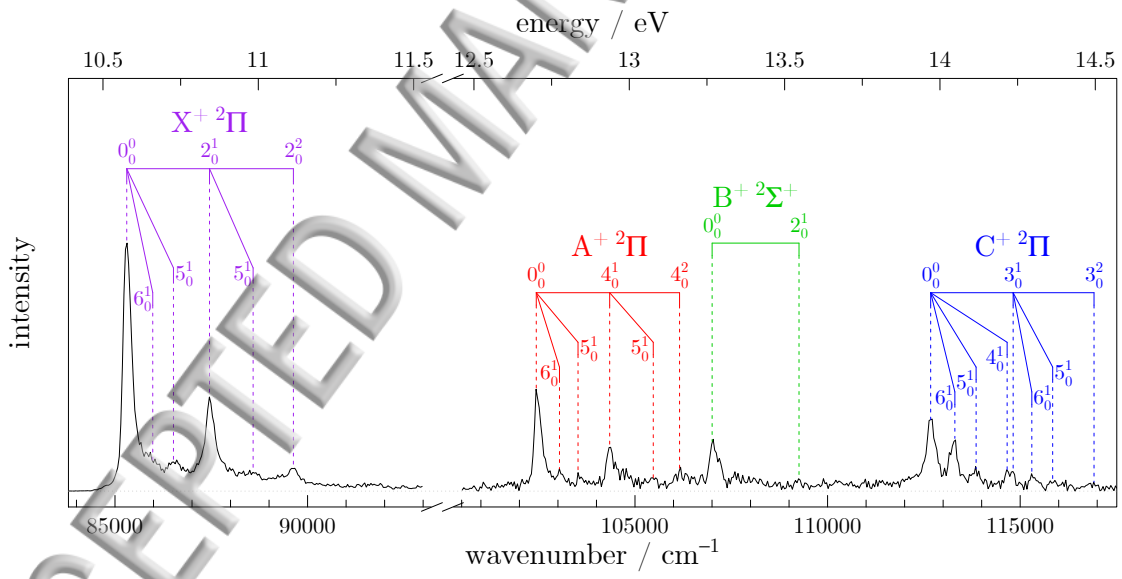


FIG. 4. TPE spectrum of HC_5N with the vibrational band assignments according to *ab initio* and Franck-Condon factor calculations. The mode labelling is the same as that used in Figure 1.

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TABLE II. Calculated and experimental vibrational wavenumbers for the stretching modes of HC_5N^+. All the values are in cm^{-1} and the experimental uncertainties are given in parenthesis.

mode	$X^+\,^2\Pi$		$A^+\,^2\Pi$		$B^+\,^2\Sigma^+$		$C^+\,^2\Pi$	
	Calc.[a]	Exp.[a]	Calc.[a]	Exp[a]	Calc.[a]	Exp[a]	Calc.[a]	Exp[a]
ν_1	3403	-	3412	-	3456	-	3433	-
	3305[b]							
	3381[c]							
ν_2	2300	2190 (80)	2350	-	2339	2218(80)	2214	-
	2189[b]	2190(10)[d]						
	2278[c]							
ν_3	2121	-	2210	-	2282	-	2170	2141(80)
	2082[b]	2070(10)[d]						
	2156[c]							
ν_4	1985	-	1999	1890(80)	2141	-	2102	1985(80)
	1929[b]			1870(160)[d]				
	1998[c]							
ν_5	1238	1220(80)	1097	1115(80)	1244	-	1229	1180(80)
	1221[b]	1220(10)[d]						
	1251[c]							
ν_6	639	670(80)	618	610(80)	654	-	608	628(80)
	628[b]	630(10)[d]		600(160)[d]				
	643[c]							

[a] this work[19] unless specified. Calculated values obtained at the ic-MRCI+Q/AVTZ level of theory within the harmonic approximation;
[b] DFT calculations from Lee[15];
[c] DFT calculations from Cao and Peyerimhoff[18];
[d] Bieri *et al.*[13]

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Concluding remarks

The present experimental study provides additional information on the vibronic structure of the HC_5N^+ cation up to 33 000 cm^{-1} above the ionization potential thanks to improved resolution compared to the previous study by Bieri *et al.*[13] High-level *ab initio* calculations coupled with Franck-Condon simulations provides the reliable assignment of vibrational modes of the four lowest electronic states of the cation. Only stretching vibrational mode excitations have been observed with a non-negligible intensity in the TPE spectrum, corresponding to elongation of the C≡N and C≡C triple bonds. This new information, as well as the refined values of the adiabatic ionization threshold values for the $X^+\ ^2\Pi$, $A^+\ ^2\Pi$, B^+, $^2\Sigma^+$ and $C^+\ ^2\Pi$ electronic states, will be very helpful for the analysis of the VUV absorption spectrum of HC_5N recently measured with the VUV Fourier-Transform spectrometer of the DESIRS beamline,[32] and assigment of various Rydberg series converging to these excited cationic states. That work will be presented in a forthcoming paper.

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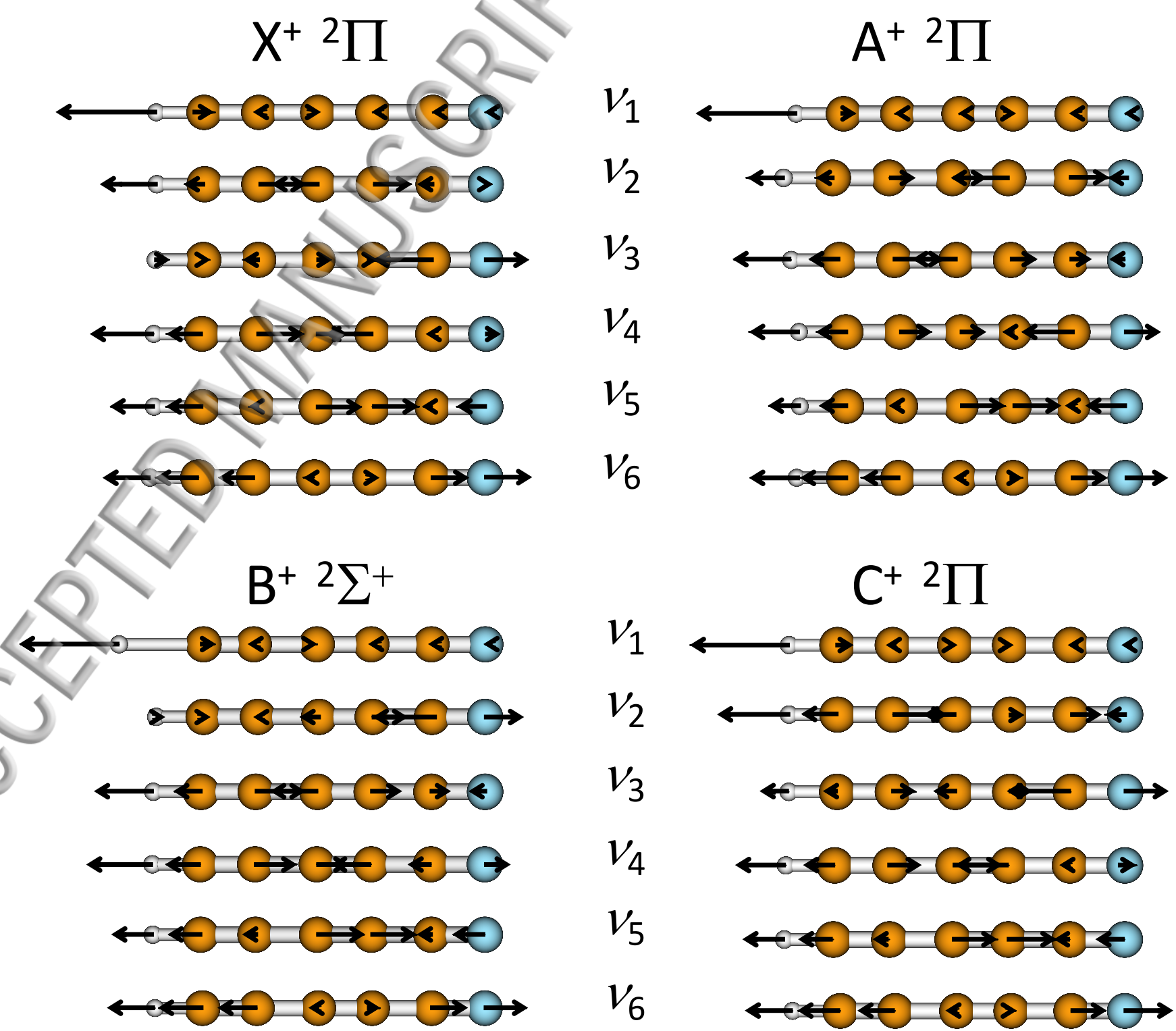
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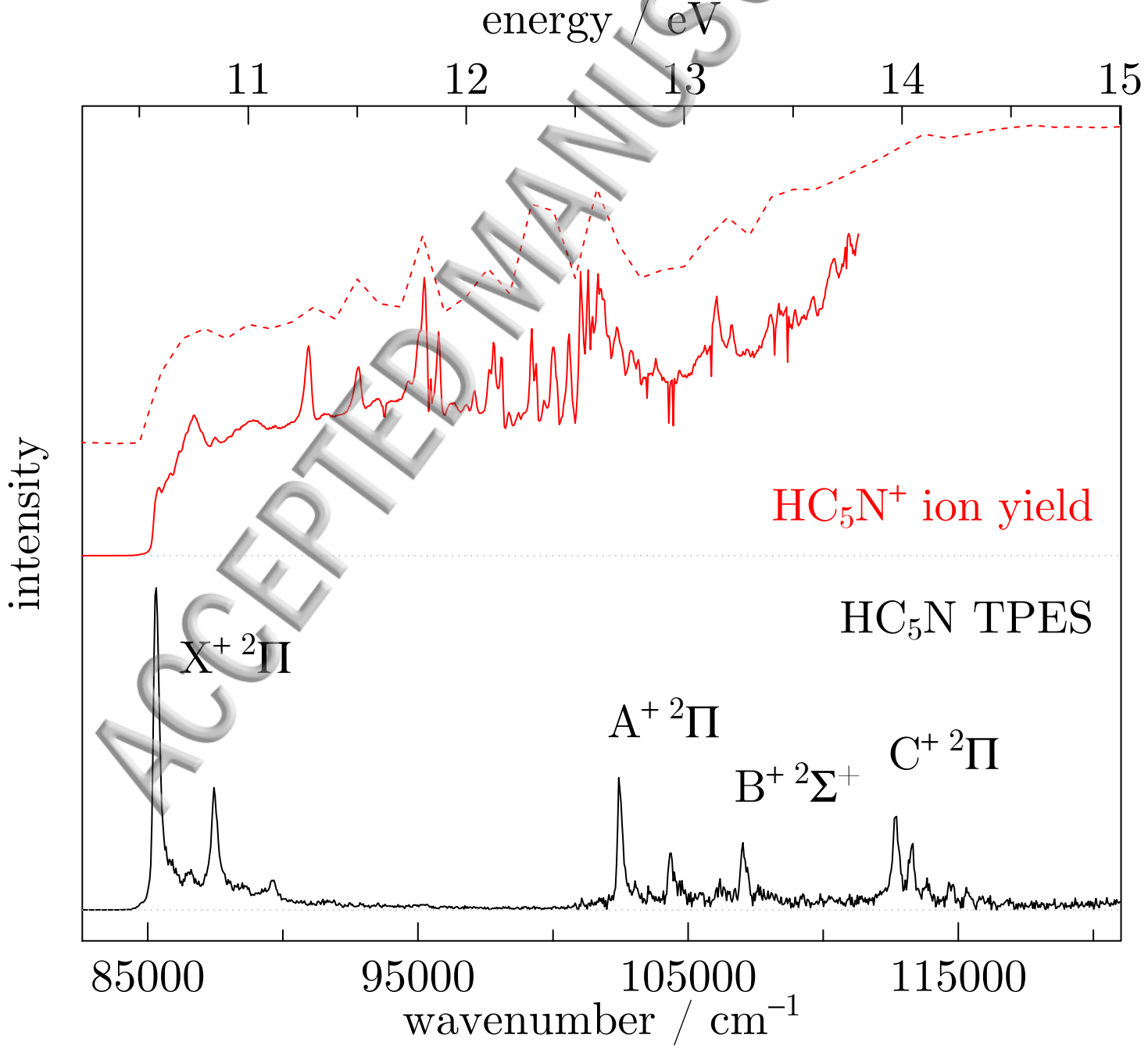
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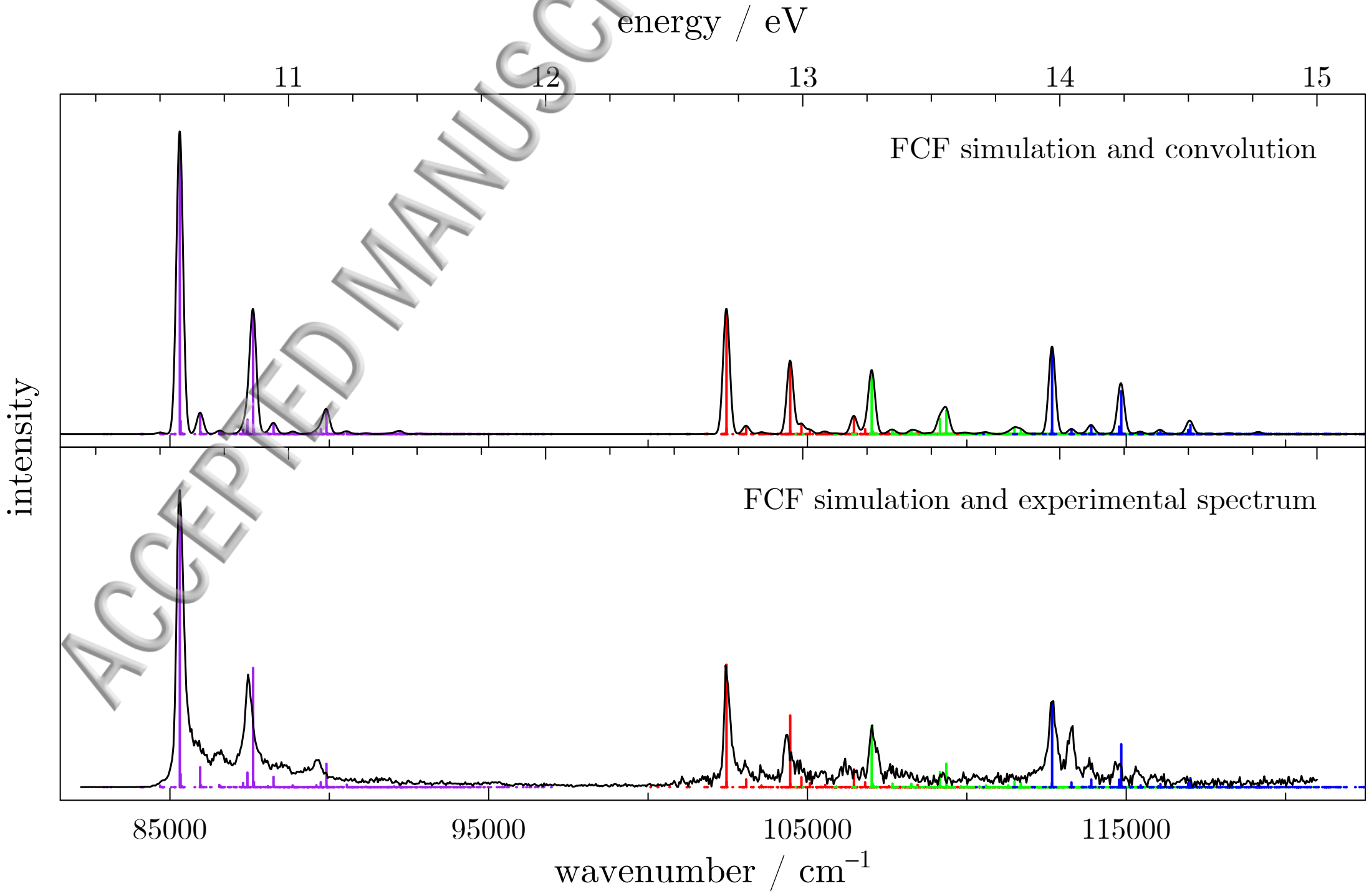
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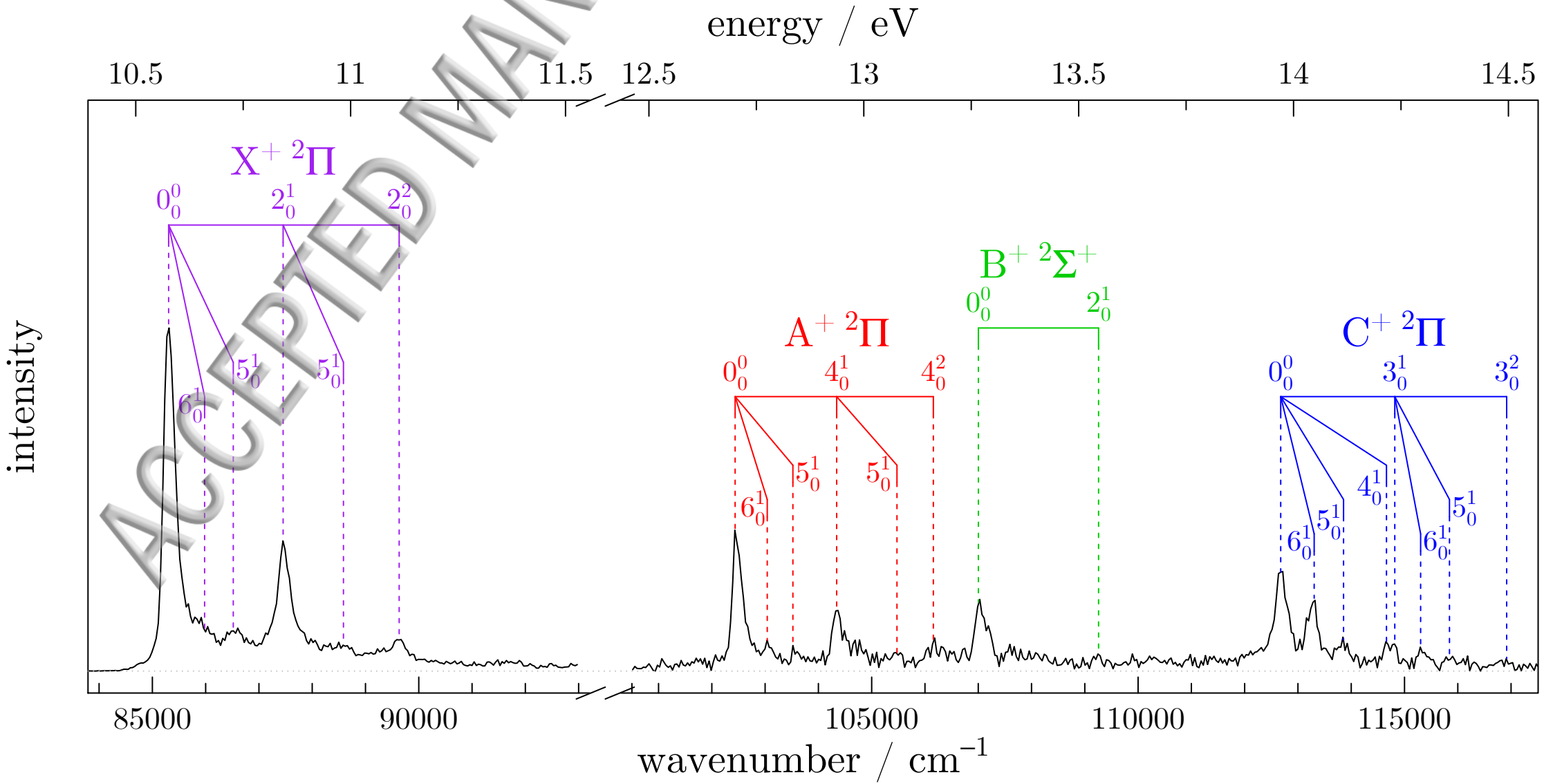
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