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Vibronic structure of the cyanobutadiyne cation: II- Theoretical exploration of the complex energy landscape of HC_5N^+

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The results of an extensive *ab initio* study of the cyanobutadiyne cation, initially motivated by Threshold-Photoelectron Spectroscopy experiments (see Gans *et al.*, JCP **XX** XX (2019)), are reported in the present paper. Calculations at the Internally-Contracted Multireference Configuration interaction level of theory have been performed to derive the rovibronic properties of the seven lowest electronic states of HC_5N^+ . Equilibrium geometries, rotational constants, vibrational frequencies, electric dipole moments and spin-orbit constants have been calculated and compared with experimental data when available. Adiabatic and vertical ionization energies from the neutral ground state, as well as transition energies within the cation electronic manifold are predicted, using the convergence to the Complete Basis Set limit. The accurate description of the complex energy landscape up to 32 000 cm^{-1} above the ionization potential allows to perform Franck-Condon simulations of the photoionization spectrum to the $X^+ {}^2\Pi$, $A^+ {}^2\Pi$, $B^+ {}^2\Sigma^+$, and $C^+ {}^2\Pi$ states, and allows to simulate the $A^+ {}^2\Pi \rightarrow X^+ {}^2\Pi$ emission spectrum. The vibronic perturbations occurring on the excited potential energy surfaces are revealed and discussed, in particular for the 3 ${}^2\Pi$ surface which presents a double-well topography.

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INTRODUCTION

The present paper is the second one of a series dealing with the vibronic structure of the cyanobutadiyne cation (HC_5N^+) up to several eV above the cationic ground state. The first paper¹ (hereafter referred to as Paper I) was focused on the Threshold PhotoElectron Spectrum (TPES) of HC_5N investigated by synchrotron-based experiments. It has been recorded on the DESIRS beamline of the SOLEIL synchrotron facility and covers the 84 000 – 120 000 cm^{-1} range with a 120 cm^{-1} spectral resolution. The assignment of the vibronic structures observed in the TPES has been achieved with the support of the high-level *ab initio* calculations detailed in the present paper. These calculations turned out to be challenging mainly because of the multiconfigurational features characterizing such π conjugated systems. Let us recall indeed the linear structure of the parent neutral system HC_5N , which exhibits an alternation of single and triple bonds

The reorganization of this π structure upon ionization depends on the concerned cationic state, introducing important multiconfigurational effects, as shown by the analysis of the wavefunctions. Another computational challenge comes from the complex energy landscape of cyanobutadiyne cation resulting from numerous potential energy surface crossings. The experimental TPES exhibits four vibrationally resolved electronic states of the cation ($\text{X}^+ {}^2\Pi$, $\text{A}^+ {}^2\Pi$, $\text{B}^+ {}^2\Sigma^+$, and $\text{C}^+ {}^2\Pi$) very close in energy with other electronic states predicted by the *ab initio* calculations but unobservable through single-photon ionization within the electric dipolar approximation. The density of states gives rise to several state crossings, which complicate the topography of the potential energy surfaces (PES) in some regions of the coordinate space. In addition, as HC_5N^+ is linear, the degenerate electronic states are also affected by the Renner-Teller effect.

So far, only few theoretical papers have investigated the electronic and vibrational structures of the HC_5N^+ cation. In 1996, Lee² used unrestricted BLYP theory with 6-311G* and 6-311G** basis sets to compute the geometry, vibrational frequencies, and dipole moments of the ground state of several cyano- and dicyanopolyacetylene cations, including cyanobutadiyne. Tatchen and Marian³ performed spin-orbit calculations for the $\text{X}^+ {}^2\Pi$ electronic ground state using an effective one-electron mean-field spin-orbit hamiltonian.

Later on, Lee and Adamowicz⁴ calculated the vertical transition energy at the CASSCF and CASPT2 levels of theory for the lowest $\pi \rightarrow \pi^*$ electronic excitation, corresponding to the $A^+ {}^2\Pi \leftarrow X^+ {}^2\Pi$ transition. Cao and Peyerimhoff⁵ extended this work to the higher doublet excited electronic states by performing multireference configuration interaction (MRCI) calculations to predict the vertical electronic transition energies and oscillator strengths of transitions from the $X^+ {}^2\Pi$ cationic ground state towards the seven lowest excited states. The goal of the study was to provide reliable information on the electronic absorption spectrum of several linear isoelectronic species such as HC_5N^+ cation for which measurements had been recorded by Maier's group⁶ in rare gas matrix experiments. No vibrational frequencies were determined for the excited electronic states

In Paper I, only the outlines of the calculations were described and the presented *ab initio* results were restricted to adiabatic photoionization threshold calculations for the four lowest electronic states, and to vibrational structure calculations of interest for the TPES. The theoretical study is more complete and detailed here. It extends to the seven low-lying states and investigates more properties, which may be helpful for further spectroscopic studies of the cation. This includes the characterization of the spin-orbit coupling, the Renner-Teller effect and the electronic excitation properties (energies and transition electric dipole moments). It also discusses the topography of the PES and includes a Franck-Condon simulation of the absorption spectrum of the cation. All these results are presented and discussed in the present paper, where they are also compared with previous theoretical studies when available (comparison with experimental results was done in Paper I).

The paper is organized as follows. We present the method of calculations in Section II. The results are developed and discussed in Section III. They include the calculated equilibrium properties (geometries, vibrational frequencies, dipole moments and spin-orbit constants), ionization and transition energies. Finally, the investigation of the topography of the crossing potential energy surfaces is discussed.

METHODS OF CALCULATION

A. Electronic problem

All calculations were performed with the MOLPRO program package^{7,8} running on the HYDRA and VEGA clusters of the ULB/VUB computer center in Brussels (Belgium).

As pointed out in our previous works on the cyano- and dicyanoacetylene cations,^{9–12} such linear π -bonded systems require high-level multireference *ab initio* methods to describe their excited electronic structure. We have adopted for this purpose the accurate Internally Contracted MultiReference Configuration Interaction (ic-MRCI) method,^{13,14} using molecular orbitals (MOs) which are optimized for the multireference wavefunction by a State Averaged Complete Active Space Self-Consistent Field (SA-CASSCF) calculation.^{15,16} The state averaging has been used systematically for the calculation of excited states of a given symmetry. As MOLPRO only works with abelian group symmetries, we have also applied the state averaging to ensure the exact two-fold degeneracy of the potential energy surfaces of $\Lambda \neq 0$ electronic states, using the symmetry of an abelian subgroup of $C_{\infty v}$ (C_{2v} and C_s for linear and bent geometries, respectively).

The complete active space (CAS) has been defined based on test-calculations, which showed that the multiconfigurational character of the states of interest essentially resulted from the mixing between the four low-lying π orbitals, in agreement with our observations on similar systems.^{9–12} We thus adopted a CAS(13,9) in all calculations, which means that according to C_{2v} labelling, 13 electrons are distributed into 9 active MOs (one a_1 , four b_1 , and four b_2 , correlating to one σ and four π in $C_{\infty v}$ symmetry), in addition to a core of twelve doubly-occupied a_1 (σ) MOs. These active MOs are drawn in Figure 1, by order of decreasing stability from 13σ to 4π . The lone pair of the N atom is clearly represented by the 13σ MO, while the four π MOs describe the delocalization of the π structure along the nuclear chain, with a combination of bonding and antibonding features between adjacent atoms. One clearly sees that the bonding characters of the $C - C$, $C \equiv C$, and $C \equiv N$ bonds are well represented by this set of MOs. Antibonding contributions are also included, with an increasing number of nodal planes (0 to 3) from 1π to 4π , respectively. Higher energy valence MOs (14σ to 19σ and 5π to 6π) bring additional antibonding contributions, but according to our test-calculations, they do not participate to the multiconfigurational

FIG. 1. Isocontour profiles of the CASSCF valence molecular orbitals of HC_5N^+ (isocontour step values of 0.02).

mixing and have been excluded from the CAS.

This CAS has been used in all SA-CASSCF calculations, but also in the building step of the multireference wavefunctions at ic-MRCI level. However the core of doubly excited MOs has been reduced from 12 to 6 MOs in order to include all valence electrons in the single and double excitation process. The ic-MRCI wavefunctions are expanded over 10 to 90 millions of contracted configuration state functions depending on the state and the basis set. The efficient MRCIc code,¹⁷ allowing the contraction of the single excitations in addition to the double ones, has been used for all calculations performed on the lower state of a given symmetry.

All ic-MRCI energies were corrected for the contributions of unlinked clusters by means of the Davidson correction¹⁸ adapted to a relaxed reference,¹⁹ leading to a level of calculation denoted below as ic-MRCI+Q.

Dunning's correlation consistent cc-pVnZ and aug-cc-pVnZ basis set series (VnZ and AVnZ for short, respectively) have been used.^{20,21} The AVTZ basis set has been employed in all geometry optimization and harmonic frequency calculations. Single point calculations using larger basis sets were performed at the ic-MRCI+Q/AVTZ equilibrium geometries and complete basis set (CBS) extrapolations were carried out using the VnZ basis set series, with $n = Q, 5$ and 6 . As in previous works,^{10,12,22} the CASSCF and dynamical correlation energies were extrapolated separately, using the $E_{\text{CAS}}(\text{CBS}) + A \cdot e^{-B \cdot n}$ and $E_{\text{CAS}}(\text{CBS}) + C \cdot n^{-3}$ functionals, respectively. Such extrapolations led to the prediction of converged values of the energy difference properties (ionization and transition energies).

B. Vibrational problem

Harmonic vibrational frequencies were calculated by numerical differences using a home-made program interfaced with MOLPRO. It is dedicated to linear molecules and exploits the C_{2v} and C_s abelian subgroup symmetries for linear and bent structures, respectively. These symmetries are explicitly taken into account in the ic-MRCI calculations, which lead to an important gain of computer time compared with the generic procedure implemented in MOLPRO for any kind of symmetry by setting the no-symmetry option (C_1 subgroup) for multireference calculations. The block-diagonal form of the cartesian Hessian matrix also allows a separate diagonalization for the σ and π_x (or π_y) frequencies, and only one of the π blocks needs to be calculated, as π_x and π_y frequencies are degenerate. Apart from computer time saving, the major advantage of this symmetry-adapted procedure is that it ensures the explicit separation of the A' and A'' Renner-Teller (RT) components of the $\Lambda \neq 0$ electronic states. In contrast, when the calculation is carried out without symmetry, the frequencies of the two RT-components are calculated from two successive roots of the Hamiltonian matrix. For a molecule having more than one vibrational coordinate which breaks the electronic degeneracy (a linear molecule larger than triatomic, for instance), it may happen that some of these coordinates stabilize the A' component more than the A'' one, while other ones produce the opposite effect. In such a case, finite differences determined from a given root of the Hamiltonian erroneously mix the energies of the A' and A'' PESs. Such a situation occurring in the Π and Φ excited states of HC_5N^+ motivated us to develop the symmetry-adapted code. We showed that calculations performed using C_1 symmetry, as

ing the standard MOLPRO code, led to incorrect results, with a mix-up of the π frequencies arising from the A' and A'' electronic components, and deviations of up to 20 cm^{-1} of the individual frequency values.

Exploratory variational calculations using the Vibrational Mean Field Configuration Interaction approach (VMFCI) were also performed using the CONVIV program²³ to highlight possible anharmonic couplings between vibrational modes.

C. Spin-orbit coupling

The spin-orbit (SO) splittings of the $\Lambda \neq 0$ states have been determined by means of the state-interacting method,²⁴ in which the Breit-Pauli spin-orbit Hamiltonian (BPSOH) is diagonalized in the basis of the non-relativistic (Λ, S) wavefunctions of all the states calculated in this work. The non-diagonal matrix elements were calculated with the corresponding ic-MRCI wavefunctions, using the effective Hamiltonian approach implemented in MOLPRO.²⁴ The diagonal matrix elements were replaced by the corresponding ic-MRCI+Q energies in order to improve the zeroth-order energies.

D. Computer codes

Apart from the MOLPRO program already referenced above, other computer codes have been used to analyze the results. Orbital isocontour maps and normal vibrational displacement vectors were drawn by means of the MOLDEN program.²⁵ Franck-Condon spectrum simulations were carried out by means of the Pgopher software, using our *ab initio* results as input data.²⁶

III. RESULTS AND DISCUSSION

A. Electronic structure of $\text{HC}_5\text{N}/\text{HC}_5\text{N}^+$

The ground state of neutral HC_5N arises from the closed-shell configuration:

- $(\alpha) [\dots] 13\sigma^2 1\pi^4 2\pi^4 3\pi^4 (\text{X } ^1\Sigma^+)$,

where $[\dots]$ stands for a closed-shell core of twelve σ MOs and (α) denotes the ground configuration of the neutral system. The configurations of the cation will be labelled by

numbers following their energy order, starting from the ground configuration (1), which results from the ejection of an electron from the HOMO of (α):

- (1) [...] $13\sigma^2 1\pi^4 2\pi^4 3\pi^3 (X^+ {}^2\Pi)$.

Extracting an electron from the HOMO-1, HOMO-2 and HOMO-3 leads to the low-lying excited configurations, from which single spin-doublet electronic states arise:

- (2) [...] $13\sigma^2 1\pi^4 2\pi^3 3\pi^4 ({}^2\Pi)$,
- (3) [...] $13\sigma^1 1\pi^4 2\pi^4 3\pi^4 ({}^2\Sigma^+)$, and
- (4) [...] $13\sigma^2 1\pi^3 2\pi^4 3\pi^4 ({}^2\Pi)$.

As already pointed out by Cao and Peyerimhoff⁵ and confirmed by our calculations, there is a fifth configuration close in energy to (4), leading to five excited states:²⁷

- (5) [...] $13\sigma^2 1\pi^4 2\pi^4 3\pi^2 4\pi^1 ({}^2\Pi(\times 3) \oplus {}^2\Phi \oplus {}^4\Pi)$.

This configuration corresponds to a $3\pi \rightarrow 4\pi$ single excitation from (1), but, in the framework of the ionization process, it is a bielectronic excitation from (α). A total of six ${}^2\Pi$ states thus arise from the low-lying configurations of the cation, which suggests, as confirmed by the results, that state mixing will occur and that avoided crossings will affect the corresponding PESs. The five MOs (13σ , 1π , 2π , 3π , and 4π) govern the electronic structure of the cation and define the CAS (see Figure 1). Their shape will be useful for discussing the observed equilibrium properties of the calculated electronic states.

B. Equilibrium properties

1. Characterization of the equilibrium structures

Geometry optimizations were carried out at the ic-MRCI+Q/AVTZ level of theory on the PESs corresponding to all of the states arising from configurations (α) and (1) to (5). Eight stationary points were located and characterized on these PESs: two corresponding to the ground states of HC_5N and HC_5N^+ and seven to excited states of the cation. Let us note that no minimum has been found on the $5 {}^2\Pi$ PES, as explained in section III E 1. The analysis of the ic-MRCI wavefunctions at equilibrium of each state provides the weights of

TABLE I. Analysis of the ic-MRCI wavefunctions of HC_5N and HC_5N^+ in terms of electronic configurations.^a

System	State ^b	Label ^c	Weight ^d
HC_5N	$1^1\Sigma^+$	X	79% (α) + 4% (β)
HC_5N^+	$1^2\Pi$	X^+	53% (1) + 22% (2)
	$2^2\Pi$	A^+	34% (2) + 18% (1) + 18% (4) + 4% (5)
	$1^2\Sigma^+$	B^+	79% (3) + 3% (10) + 3% (11)
	$1^4\Pi$	-	74% (5) + 3% (9)
	$3^2\Pi(\text{Min}_1)$	-	67% (5) + 6% (2)
	$3^2\Pi(\text{Min}_2)$	C^+	62% (4) + 11% (6) + 7% (5)
	$1^2\Phi$	-	73% (5) + 3% (7)
	$4^2\Pi$	-	71% (5) + 3% (7) + 3% (8)

^a See text for the definition of the electronic configurations: (1) to (11) for HC_5N^+ , (α) and (β) for HC_5N ;

^b States are listed in adiabatic energy order (see Tables V and VI), and numbered accordingly within each symmetry manifold;

^c Spectroscopic labels (only for the experimentally observed states);

^d Weights at the equilibrium geometries of the corresponding states. Only configurations with a contribution higher than 3% are considered.

the main contributing electronic configurations, as reported in Table I. The weight of a configuration (in %) is calculated as the sum of squares of the contributing MRCI coefficients. A threshold of 3% is used for eliminating the less important configurations. A set of secondary configurations is adding up to the configurations list already presented:

- (6) [...] $13\sigma^2 1\pi^4 2\pi^3 3\pi^3 4\pi^1$,
- (7) [...] $13\sigma^2 1\pi^4 2\pi^2 3\pi^4 4\pi^1$,
- (8) [...] $13\sigma^2 1\pi^3 2\pi^3 3\pi^3 4\pi^2$,
- (9) [...] $13\sigma^2 1\pi^4 2\pi^3 3\pi^2 4\pi^2$,
- (10) [...] $13\sigma^1 1\pi^4 2\pi^4 3\pi^3 4\pi^1$,
- (11) [...] $13\sigma^1 1\pi^4 2\pi^4 3\pi^2 4\pi^2$,

for HC_5N^+ and,

- $(\beta) [\dots] 13\sigma^2 1\pi^4 2\pi^4 3\pi^2 4\pi^2$

for HC_5N .

The calculated states are listed by order of increasing adiabatic energies (see sections III C and III D 1). The second column of Table I gives the standard numbering of the states, by energy order for each orbital and spin symmetry. The third column provides the corresponding spectroscopic labels, introduced by Bieri *et al.*²⁸ for X^+ , A^+ , B^+ , and C^+ . The multireference character of most states clearly appears when looking at the fourth column of the table, which reports the configuration weights. This character, already pointed out in previous works on cyanopolyynes cations,⁹⁻¹² comes from the mixing between the π orbitals forming such linear chains (see Fig. 1). The configuration mixing is important within the $^2\Pi$ state manifold, as already postulated before. The competition between configurations (4) and (5) is of particular interest. It leads to the formation of two minima in the third PES of $^2\Pi$ symmetry. These minima will be referred to as $3^2\Pi(\text{Min}_1)$ and $3^2\Pi(\text{Min}_2)$, respectively. As indicated in Table I, the latter minimum has been assigned to the C^+ state observed in the TPE spectrum, according to the successful Franck-Condon factor simulation presented in Paper I.¹ We refer the reader to Figure 3 of Paper I and to the related text. This simulation reproduces very satisfactorily the vibrational progressions of the X^+ , A^+ , B^+ , and C^+ states, and, in the case of C^+ , it thus confirms the observation of the vibration within the $3^2\Pi(\text{Min}_2)$ potential well. This assignment is furthermore consistent with the fact that, according to the electric dipole approximation, single-photon ionization implies a single electron excitation process. This is actually the case for the $(\alpha) \rightarrow (4) \text{Min}_2$ excitation, unlike for the $(\alpha) \rightarrow (4) \text{Min}_1$ excitation.

Let us note that the good agreement between the simulated and experimental spectra rests on a set of complementary *ab initio* results, detailed in the next sections:

- (i) the ionization energy values, which give the energy positions of the 0-0 origin bands,
- (ii) the vibrational frequency values of the cationic states, which predict the energy spacings within the progression series with respect to the 0-0 origin, and
- (iii) the FCF values, which provide relative values of the band intensities.

The latter quantities require the calculation of the vibrational overlap integrals between the neutral ground state and the cationic states of interest, taking the Dushinski rotation matrix into account. These integrals depend on the calculated geometries and on the harmonic eigensolutions of both states. The use of the harmonic approximation has been found sufficient for an unambiguous identification of most of the observed vibrational features. Larger deviations in the predicted intensities of the C^+ states bring to light the existence of vibronic couplings induced by the double well shape of the $3^2\Pi$ PES, as discussed in section III E 5.

2. Geometries and rotational constants

The equilibrium properties (bond distances and rotational constants B_e) have been calculated at the ic-MRCI+Q/AVTZ level for all stationary points. The results are reported in Table II. We refer to (1) in section I for the definition of the atom numbering.

As confirmed by the calculated vibrational frequencies (see next section), the global minima of all calculated states correspond to linear geometries, except for the $1^4\Pi$ state, for which the linear form is a local minimum. This state is indeed split into a couple of Renner-Teller planar bent states ($1^4A'$ and $1^4A''$), among which the $^4A''$ component is the global minimum, as detailed in section III B 3. The geometries of the local and global minima are both reported in Table II.

The results are compared with the available theoretical and experimental values from the literature, but as it is the first time that the equilibrium properties of the excited states of the cation are calculated, the comparison is limited to the ground state properties.

The ic-MRCI+Q results are in good agreement with the available experimental values, noting however that theoretical values are equilibrium properties while experimental ones are $v = 0$ vibrationally averaged ones. For the ground state of HC_5N , the deviation with the microwave spectroscopy results³¹ is 0.3% for the rotational constant and $< 0.9\%$ for the bond distances. For the cation, the deviation of the calculated rotational constants with respect to the frequency modulation spectroscopy values³² is 0.3% and 0.02% for the X^+ and A^+ states, respectively.

On the theoretical side, the results on the neutral ground state can be compared with CCSD(T) calculations. Deviations of our calculated ic-MRCI bond distances with the VTZ, VQZ and VTZ corr CCSD(T) results^{29,30} are $< 1\%$, $< 0.8\%$ and $< 0.5\%$, respectively.

TABLE II. Equilibrium bond distances (in Å) and rotational constants B_e (in MHz) of the ground state of HC_5N and of the low-lying states of HC_5N^+ .

		HC_5N						B_e
State	Method ^a	H–C ₁	C ₁ ≡C ₂	C ₂ –C ₃	C ₃ ≡C ₄	C ₄ –C ₅	C ₅ ≡N	
$X^1\Sigma^+$		1.061	1.203	1.371	1.215	1.376	1.155	1327.1
	CCSD(T) /VTZ ^b	1.064	1.216	1.372	1.219	1.377	1.168	1317.1
	CCSD(T) /VTZ corr. ^a	1.063	1.209	1.366	1.213	1.371	1.161	1330.1
	CCSD(T) /VQZ ^c	1.064	1.212	1.370	1.216	1.376	1.165	–
	Exp. ^d	1.0569	1.2087	1.3623	1.2223	1.3636	1.1606	1331.3313
		HC_5N^+						B_e
$X^+2\Pi$		1.0712	1.234	1.317	1.229	1.352	1.174	1341.0
	UB3LYP /TZVP ^e	1.07	1.23	1.32	1.24	1.34	1.17	–
	UBLYP /6-311G** ^f	1.078	1.240	1.325	1.251	1.339	1.188	1325.8
	B3LYP /6-311G* ^g	1.074	1.230	1.322	1.239	1.338	1.173	1342.4
	Exp. ^h	–	–	–	–	–	–	1337.56
$A^+2\Pi$		1.070	1.230	1.383	1.216	1.342	1.202	1314.8
	Exp. ^g	–	–	–	–	–	–	1314.55
$B^+2\Sigma^+$		1.066	1.216	1.351	1.216	1.343	1.151	1349.2
$1^4\Pi$		1.070	1.273	1.263	1.329	1.273	1.221	1322.2
$1^4A''$ planar bent ⁱ		1.079	1.324	1.247	1.316	1.299	1.192	1342.8, 1338.2 ^j
$3^2\Pi(\text{Min}_1)$		1.070	1.261	1.279	1.319	1.292	1.207	1321.7
$3^2\Pi(\text{Min}_2) (C^+)$		1.068	1.212	1.380	1.241	1.381	1.199	1292.9
$1^2\Phi$		1.070	1.271	1.265	1.330	1.283	1.211	1322.6
$4^2\Pi$		1.070	1.266	1.273	1.327	1.285	1.212	1320.4

^a This work, unless specified, from ic-MRCI+Q/AVTZ calculations;

^b From Ref. 29 ; CCSD(T)/VTZ corr values are corrected for systematic errors in similar systems;

^c From Ref. 30;

^d Microwave spectroscopy;³¹ B_0 and r_0 from a substitution structure;

^e From Ref. 34;

^f From Ref. 2;

^g From Ref. 5;

^h Frequency modulation absorption spectroscopy;³² B_0 value;

ⁱ Renner-Teller component of the $1^4\Pi$ state (see section III.B.3). The values of the bending angles are 140, -176, 180, -165, and 175 degrees, for the $\angle\text{HC}_1\text{C}_2$, $\angle\text{C}_1\text{C}_2\text{C}_3$, $\angle\text{C}_2\text{C}_3\text{C}_4$, $\angle\text{C}_3\text{C}_4\text{C}_5$, and $\angle\text{C}_4\text{C}_5\text{N}$ angles, respectively.

^j $B \simeq C$ rotational constants corresponding to rotation about the inertial axes perpendicular to the quasi-linear frame. b lies within the molecular plane and c is perpendicular to it. The value of A is 400039 MHz.

The VTZ corr values involve a correction for systematic overestimates of the bond distances evaluated from similar systems using CCSD(T). Our ic-MRCI+Q results are in better agreement with these corrected values. We pointed out similar discrepancies resulting from the monoreference correlation treatment of the CCSD(T) approach in our paper on HC_3N^+ .¹⁰ This shows again that multiconfigurational effects are important for representing the π electron delocalization along the molecular chain.

For the ground state of the cation, the deviations with the DFT results are larger but still reasonable ($< 0.9\%$, $< 1.8\%$, and $< 1\%$ with UB3LYP/TZVP,³ UBLYP/6-311G**,² and B3LYP/DZVP,⁵ respectively).

Bond lengths are found to vary significantly (up to 9.5%) from one state to another. As in the case of HC_3N^+ ,¹⁰ the changes can be rationalized in terms of the main configuration changes reported in Table I and of the bonding/antibonding characters of the involved MOs (see Fig. 1). Ejecting an electron from a given MO induces indeed a weakening of its features (bonding or antibonding) and accordingly a change of the corresponding bond lengths (extension or contraction, respectively). The relative magnitude of these effects on the different bonds were verified by an analysis of the overlap Mulliken atomic populations. The following trends, already pointed out for X^+ and A^+ ,³² can be drawn for the ionization towards different states of the cation:

- (i) $\text{X} \rightarrow \text{X}^+$: an electron is ejected from 3π , which exhibits bonding triple bonds and antibonding single bonds (see Fig. 1), with as a result an extension of the formers and a contraction of the latters. The rotational constant value increases by 1% because the contractions are globally larger than the extensions.
- (ii) $\text{X} \rightarrow \text{A}^+$: the bonding regions of 2π , which lose an electron, cover the C_1C_2 , C_2C_3 , and C_5N bonds, which are stretched (4% for C_5N), while the C_4C_5 bond contracts. The net result is an elongation of the structure, with a 0.9% decrease of the B_e value.
- (iii) $\text{X} \rightarrow \text{C}^+ (= 3^2\Pi(\text{Min}_2))$: the electron ejected from the fully bonding 1π MO induces a stretch of all bonds, in particular of C_3C_4 (2%) and C_5N (4%). The B_e value decreases consequently by 2.6%.
- (iv) $\text{X} \rightarrow 3^2\Pi(\text{Min}_1)$, $1^2\Phi$ and $4^2\Pi$: spectacular geometry changes characterize all states arising from configuration (5), as a result of the superposition of two effects: the loss of

a 3π electron and a $3\pi \rightarrow 4\pi$ excitation. All states obey to the same trends: increase of all triple bond lengths (by more than 5%, 9%, and 5% for C_1C_2 , C_3C_4 , and C_5N , respectively) and decrease of the single bond lengths (by more than 7%). Due to a compensation of both opposite effects, the net extension of the structures is small, and the B_e value decreases by less than 0.5%.

The non-planar geometry of the $^4A''$ state, reported in Table II (see footnotes), corresponds to a quasi-linear structure, as confirmed by the large value of the A rotational constant related to the rotation about the inertial axis a which lies along the molecular frame. The values of the equilibrium bending angles characterize the zig-zag shape of the chain, presenting an alternation of positive and negative angle values. The main deviation from linearity comes from the HC_1C_2 bending of 140 degrees, and to a lesser extent from the $C_3C_4C_5$ bending of 165 degrees. The fact that the rotational constants $B \simeq C$ characterizes moreover a near prolate asymmetric top.

3. *Vibrational frequencies*

Table III reports the results of harmonic vibrational frequencies calculated at the ic-MRCI+Q/AVTZ level of theory using the symmetry adapted procedure explained in section II B. The calculations were performed at the linear equilibrium geometries of all states. The normal coordinate displacements of the bending frequencies of the four low-lying states of the cation are depicted in Figure 2, while those of the stretching frequencies were already shown in Paper I¹ to illustrate the vibrational signatures of our TPE spectrum. Apart from the differences mentioned in Paper I between the stretching normal modes of the considered states, one observes that the bending coordinates are quite similar in all the considered states, except for the B^+ state, in which ν_7 , ν_8 , and ν_9 correspond to quasi pure C_4C_5N , HC_1C_2 and $C_2C_3C_4$ local bendings, respectively, while in the other states they mainly contribute to ν_9 , ν_7 , and ν_8 , respectively. We also note that the frequencies of B^+ are globally higher than those of the other states, as indicated by the high value of the ZPE. This is a consequence of the strengthening of the π structure by the three closed π MOs.

As already pointed out, the linearity characterizes the global minima of all states except the $1^4\Pi$ state. This is confirmed by the real frequencies calculated for all modes in the case of linear global minima. In the case of the $1^4\Pi$ state, an imaginary frequency, marked in

TABLE III. Calculated harmonic vibrational frequencies (in cm^{-1}) of HC_5N^+ .^a

	$X^+ \ ^2\Pi$	$A^+ \ ^2\Pi$	$B^+ \ ^2\Sigma^+$	$1 \ ^4\Pi$	$3 \ ^2\Pi(\text{Min}_1)$	$3 \ ^2\Pi(\text{Min}_2)$ (C^+)	$1 \ ^2\Phi$	$4 \ ^2\Pi$
ν_1 (σ)	3403	3412	3456	3407	3397	3433	3388	3393
ν_2 (σ)	2300	2350	2339	2339	2742	2214	2208	2278
ν_3 (σ)	2121	2210	2282	1937	1841	2170	1810	1829
ν_4 (σ)	1985	1999	2141	1507	1637	2102	1605	1667
ν_5 (σ)	1238	1097	1244	1282	1296	1229	1308	1307
ν_6 (σ)	639	618	654	485	636	608	641	640
ν_7 (π) ^b	(803, 693) [750, 0.15]	(695, 705) [700, -0.02]	847	(775, 296i) ^c – ^d	(772, 411) [618, 0.56]	(748, 763) [756, -0.02]	(550, 550) [550, 0.00]	(414, 821) [650, -0.60]
ν_8 (π) ^b	(607, 546) [577, 0.11]	(554, 545) [549, 0.02]	776	(586, 386) [496, 0.39]	(555, 375) [474, 0.37]	(535, 527) [531, 0.01]	(491, 491) [491, 0.00]	(398, 605) [512, -0.40]
ν_9 (π) ^b	(446, 468) [457, -0.05]	(476, 475) [476, 0.0]	566	(472, 353) [417, 0.28]	(462, 315) [396, 0.37]	(457, 446) [452, 0.03]	(423, 423) [423, 0.00]	(249, 437) [356, -0.51]
ν_{10} (π) ^b	(260, 261) [261, 0.00]	(277, 277) [277, 0.00]	264	(270, 285) [277, -0.06]	(254, 264) [259, -0.04]	(270, 262) [266, 0.03]	(281, 281) [281, 0.00]	(228, 264) [247, -0.15]
ν_{11} (π) ^b	(106, 110) [108, -0.04]	(104, 107) [105, -0.03]	106	(118, 108) [113, 0.09]	(93, 71) [82.8, 0.25]	(112, 113) [112, 0.00]	(97, 97) [97, 0.00]	(70, 102) [88, -0.36]
ZPE ^e	7996	7950	8617	– ^d	7604	7994	7323	7409

^a Calculations performed at the ic-MRCI+Q/AVTZ level;

^b Modes of π symmetry of the Π and Φ electronic states are characterized by two different frequencies

($\omega(A')$, $\omega(A'')$) corresponding to the A' and A'' Renner-Teller components, respectively. The numbers

between squared brackets correspond to zeroth-order RT bending frequency ω_0 and Renner parameter ϵ ,

respectively (see text);

^c The frequency of the A'' RT component is imaginary;

^d Not calculated for a linear-bent RT effect;

^e ZPE calculated using the ω_0 values for the bending modes of the $\Lambda \neq 0$ states.

bold, indicates that the Renner-Teller (RT) splitting induces the non-linearity of one of its components, as detailed below.

The RT effect has been characterized for all the $\Lambda \neq 0$ states (Π and Φ) for which the two-fold degeneracy is lifted upon planar bending, according to the $C_{\infty v} \rightarrow C_s$ symmetry correlation rule: Π or $\Phi \rightarrow A' \oplus A''$. The resulting pair of states will be referred to as a RT pair below.

The frequencies have been calculated independently for each component of the RT pairs using our symmetry-adapted procedure. For the stretching modes (ν_1 to ν_6), belonging to the σ symmetry, both electronic components remain degenerate and are characterized by the same frequency reported in Table III. On the contrary, the bending modes (ν_7 to ν_{11}), of

FIG. 2. Mass-weighted normal coordinates of the bending modes of the X^+ , A^+ , B^+ and C^+ states of HC_5N^+ , calculated at the ic-MRCI+Q/AVTZ level of theory. The corresponding frequencies are reported in Table III. Atomic displacements are scaled by a factor of 0.5 for the CH-bending modes and by a factor of 0.8 for the other modes.

π symmetry, are lifting the degeneracy, and the RT components A' and A'' are characterized by different frequencies reported as $(\omega(A'), \omega(A''))$ in the table. One observes that all ${}^2\Pi$ and ${}^2\Phi$ states are characterized by pairs of real frequencies and thus belong to the linear-linear RT case of splitting. This means that both PESs of the RT-pair (${}^2A'$ and ${}^2A''$) have a minimum at linear geometry.

In contrast, a linear-bent RT splitting occurs in the case of the ${}^4\Pi$ state, for which all modes have real frequencies except the $\omega(A'')$ frequency of ν_7 , which is imaginary. The global minimum of the ${}^4A'$ PES is thus a linear structure, while the one of the ${}^4A''$ PES corresponds to a planar bent structure located in the direction of the $\nu_7(A'')$ normal coordinate. As for most of the calculated states (see Figure 2), ν_7 mainly corresponds to the HC_1C_2 bending

tion. This is confirmed by the equilibrium value of this angle (140 degrees) reported in Table II for the bent equilibrium geometry of this state. The linear geometry of the 4Π state is a saddle point on the $4A''$ PES, calculated at the ic-MRCI+Q/AVTZ level to be 573 cm^{-1} higher in energy than the planar bent minimum.

The strength of the RT effect can easily be evaluated in the case of the linear-linear RT splitting that affects the 2Π and 2Φ states. A first indication is provided by the magnitude of the frequency difference in a RT pair, but the ϵ parameter is a better indicator of this strength. It has been evaluated, as in our work on HC_3N^+ ,¹⁰ by means of an harmonic single-mode vibronic approach.²⁷ This simplified method, neglecting anharmonicity and inter-mode vibronic coupling provides for each mode the zeroth-order bending frequency ω_0 and the ϵ parameter. Both values are reported between square brackets in Table III. A comparison of the absolute values of ϵ in the different states shows that the RT effect is very weak for the A^+ , $C^+(3^2\Pi(\text{Min}_2))$, and $1^2\Phi$ states. For the latter state, it is even negligible ($\epsilon < 0.01$). It is also weak for the X^+ state, except for the ν_7 and ν_8 modes. In contrast, it is strong for $3^2\Pi(\text{Min}_1)$ and $4^2\Pi$ states that lie in a perturbed region. It is also important to note the occurrence of positive and negative values of ϵ . Its sign depends on the energy order of the $2A'$ and $2A''$ states in the RT splitting: a positive value indicates that the energy of the $2A''$ PES is more stable than the one of the $2A'$ PES, or in other words that $\omega(2A') > \omega(2A'')$. The opposite is true when ϵ is negative, respectively. The occurrence of positive and negative values of ϵ for different modes of the same state is observed here for all states except for $4^2\Pi$. This implies that the use of a symmetry-adapted calculation of the frequencies is mandatory, as done here.

The comparison of the stretching frequencies of Table III with those extracted from our TPE spectrum has already been discussed in Paper I,¹ where a Franck-Condon factor (FCF) simulation of the spectrum has facilitated the identification despite the harmonic approximation (see section III.B and Figure 3 of Ref. 1). The neglect of anharmonicity implies that most of the calculated values overestimate the experimental values, but the discrepancies are smaller than 30 cm^{-1} for most of the observed modes, except for ν_2 and ν_4 for which they reach 120 cm^{-1} , noting however the uncertainty of 80 cm^{-1} on the TPES values. The existence of stronger anharmonic effects is likely for these modes, considering that they form with ν_3 a cluster of close lying harmonic levels around 2000 cm^{-1} , which

are involved in combinations of coupled bond stretching vibrations, as shown by the normal coordinates pictures depicted in Figure 1 of Ref. 1. This point has been investigated in the case of the X^+ state by means of 2- and 3-mode variational calculations performed using the CONVIV program.²³ They actually show qualitatively that the anharmonic coupling is important, mainly between ν_2 and ν_4 , which may explain the larger discrepancies observed for ν_2 but not for ν_3 .

Previous theoretical works only provide the harmonic frequencies of the X^+ state calculated with UBLYP/6-311G**² and B3LYP/6-311G*⁵. The former works, limited to the stretching frequencies, are in excellent agreement (within 10 cm^{-1}) with the experimental findings, although they did not include anharmonic corrections. The latter ones are closer to our ic-MRCI+Q values. Note however that the bending frequencies calculated with DFT faced with the symmetry issue of the RT components and cannot be compared to our symmetry adapted results.

4. *Electric dipole moments*

The electric dipole moment of linear molecular chains is aligned along the internuclear Z -axis and its projection μ_{ez} on this axis is reported for all states in Table IV. This quantity provides two interesting classes of information: its absolute value gives the modulus of the permanent electric dipole moment vector, while its sign indicates how the electronic charges are distributed along the molecular chain, noting that the HCCCCCN nuclear frame is oriented toward positive Z values. As the dipole moment of a charged system depends on the origin of the coordinate system, we must specify that the calculations are performed with the centre of mass as the coordinate origin.

All $A \neq 0$ states ($^2\Pi$, $^2\Phi$, and $^4\Pi$) are characterized by a large negative value of μ_{ez} of about -6.5 D , while the $^2\Sigma^+$ state has a smaller value of opposite sign ($+2.4\text{ D}$). Similar results were obtained for HC_3N^+ ,¹⁰ and the interpretation is the same. The 13σ orbital (9σ in HC_3N^+) is localized on the CN σ bond and on the nitrogen lone pair (see Fig. 1), which results in a large negative contribution to the dipole moment value. In contrast the delocalized π MOs give smaller positive values, and the sign of μ_{ez} thus results from the compensation between these opposite sign effects.

TABLE IV. Calculated equilibrium properties of the low-lying states of HC_5N^+ : electric dipole moment (in D) and spin-orbit constant A_{SO} (in cm^{-1}); this work, unless specified.

HC_5N			
State	Method	$\mu_{e,z}$ ^a	A_{SO} ^b
$X^1\Sigma^+$	ic-MRCI+Q/AVTZ	-4.600	—
	CCSD(T)/VTZ ^c	4.407 ^d	—
	Exp. ^e	4.33 ± 0.03^d	—
HC_5N^+			
$X^+2\Pi$	ic-MRCI+Q/AVTZ	-6.937	-39.2/-40.4/-41.2
	SDCI/TZVP ^f	—	-40.79
	UBLYP/6-311G* ^g	-6.015	—
	Exp.	—	-35.71, ^h 95 ⁱ
$A^+2\Pi$	ic-MRCI+Q/AVTZ	-6.408	-41.3/-42.3/-42.9
	Exp.	—	-32.58, ^h 17 ⁱ
$B^+2\Sigma^+$	ic-MRCI+Q/AVTZ	+2.391	—
$1^4\Pi$	ic-MRCI+Q/AVTZ	-6.457	-33.93/-35.79/-36.60
$3^2\Pi(\text{Min}_1)$	ic-MRCI+Q/AVTZ	-6.458	14.5/14.9/15.2
$3^2\Pi(\text{Min}_2)$	ic-MRCI+Q/AVTZ	-4.562	-37.2/-36.5/-37.04
$C^+1^2\Phi$	ic-MRCI+Q/AVTZ	-6.497	38.7/39.9/41.35
$4^2\Pi$	ic-MRCI+Q/AVTZ	-6.418	34.6/35.9/36.8

^a Projection of the permanent electric dipole moment vector μ_e along the internuclear axis (OZ);

^b This work, otherwise specified; calculated using BPSOH/ic-MRCI and VTZ/VQZ/V5Z basis sets.

Positive and negative signs of A_{SO} indicate regular and inverted splitting patterns, respectively;

^c From Ref. 29;

^d Modulus of μ_e ;

^e Microwave spectroscopy;³¹

^f From Ref. 3 ; spin-orbit calculation performed at UB3LYP/TZVP geometry using the full one- and

two-electron no-pair spin-orbit Hamiltonian;

^g From Ref. 2;

^h Frequency modulation absorption spectroscopy;³²

ⁱ Laser induced fluorescence in isolated matrix.³³

5. Spin-orbit constants

Spin-orbit A_{SO} constants of the Π and Φ states have been estimated by the spin-orbit splitting of their Ω components, calculated at the ic-MRCI+Q/AVTZ equilibrium geometries. For that purpose, the 30×30 BPSOH matrix involving the SO-components of the 7 lowest electronic states of the cation (four $^2\Pi$, one $^2\Phi$, one $^2\Sigma^+$, and one $^4\Pi$ states) has been diagonalized, as explained in section II C. The calculations were performed using the

VnZ basis sets. The A_{SO} values converge to within less than 1 cm^{-1} along the VnZ series ($n=T, Q, 5$), as shown in Table IV, where the results are reported. The sign of the constant indicates a regular ($A_{SO} > 0$) or inverted ($A_{SO} < 0$) splitting of the $^2\Pi$ and $^2\Phi$ states. As expected, all states arising from a π^3 configurations (X^+ , A^+ , and C^+) are inverted. States arising from configuration (5) are regular, except the $^4\Pi$ state which is inverted. The order of magnitude of the splitting is almost the same for all states (between 37 and 42 cm^{-1}), except the $3^2\Pi(\text{Min}_1)$ value, which is only 15 cm^{-1} . Our X^+ state value compares very well (within 0.4 cm^{-1}) with the theoretical value of Tatchen *et al.*,³ obtained using the full no-pair spin-orbit Hamiltonian and the SDCI/TZVP level of calculation. However, the deviations from the experimental values of Sinclair *et al.*³² are larger (5 cm^{-1} for X^+ and 7 cm^{-1} for A^+). Smith *et al.*³³ also derived A_{SO} values for X^+ and A^+ from laser induced fluorescence matrix isolation spectroscopy, but their values (95 and 17 cm^{-1} , respectively) seem to be out of range (see Table IV).

C. Vertical and adiabatic ionization energies

Vertical and adiabatic ionization energies (IE_v and IE_a , respectively) were determined at the ic-MRCI+Q level of theory for all the cationic states of interest, using the hierarchical VnZ basis set series (with $n= Q, 5$, and 6), and the individual energies were extrapolated to the CBS limit (see section II A). The VnZ energies of all states were calculated at their corresponding AVTZ equilibrium geometries (see Table II), for evaluating the adiabatic energies. Those of the cationic states were also calculated at the AVTZ equilibrium geometry of the X state of HC_5N , for determining the vertical energies.

The results are reported in Table V, which shows the convergence of the ionization energies toward the CBS limit. The CBS+ZPE values refer to CBS values of IE_a corrected for the zero point energy (ZPE) difference between the considered cationic state and the neutral ground state. We refer to Table III for the cationic ZPE values and to the value of 8360 cm^{-1} , calculated at the same level of theory for the neutral state.

The adiabatic values are compared to our experimental TPES values and to the photoelectron spectroscopy values of Bieri *et al.*³⁴ There are no theoretical values of ionization energies to our knowledge in the literature. The deviations with respect to the TPES values for the four low-lying states are given in parenthesis, showing that the CBS extrapolation

TABLE V. Vertical and adiabatic ionization energies (in cm^{-1}), from ic-MRCI+Q/ VnZ calculations^a extrapolated to the CBS limit. Deviations to the TPES experimental values of Ref. 1 are given in parentheses.

		$X^+ \ ^2\Pi$	$A^+ \ ^2\Pi$	$B^+ \ ^2\Sigma^+$	$1^4\Pi$	$3^2\Pi(\text{Min}_1)$	$3^2\Pi(\text{Min}_2)$	(C^+)	$1^2\Phi$	$4^2\Pi$
$IE_{\text{adia.}}$	AVTZ	83970 (-1396)	101410 (-1106)	105434 (-1638)	106403	110407	111698 (-1033)		112663	116532
	VQZ	84364 (-1002)	101843 (-673)	105635 (-1437)	106967	110917	112205 (-526)		112958	116970
	V5Z	84584 (-782)	102109 (-407)	105843 (-1229)	107283	111203	112484 (-247)		113216	117216
	V6Z	84675 (-691)	102212 (-304)	105932 (-1140)	107417	111324	112604 (-127)		113326	117320
	CBS	84809 (-557)	102372 (-144)	106060 (-1012)	107607	111495	112772 (41)		113480	117467
	CBS + ZPE	84445 (-921)	101962 (-554)	106317 (-755)	- ^b	110739 (-1992) ^c	112406 (-325)		112443	116950
	Exp.	85366 ^d 85253 ^e	102516 ^d 102432 ^e	107072 ^d 107110 ^e			112731 ^d 112595 ^e			
$IE_{\text{vert.}}$	CBS	85725	103226	106439	118432	-	113580		124074	121011
$IE_{\text{vert.}} - IE_{\text{adia.}}$	CBS	916	854	379	10825	-	808		10594	3544

^a This work, unless specified ; ic-MRCI+Q/ VnZ ionization energies are calculated at the ic-MRCI+Q/AVTZ equilibrium geometries of the considered states (see Table II); extrapolation to CBS from VQZ, V5Z and V6Z energies as explained in the text.

^b ZPE has not been calculated for a linear-bent RT effect;

^c Calculated with respect to the C^+ state TPES value of 112731 cm^{-1} .

^d TPES values.¹.

^e Photoelectron spectroscopy.³⁴

improves the convergence to the experimental values (within $\simeq 300 - 900 \text{ cm}^{-1}$ at the CBS + ZPE level). Deviations are negative, which means that calculated IE values are underestimated. This comes from the fact that the energy of the neutral ground state converges more slowly than the one of the cationic states, which involve one fewer electron. Such energy differences that imply the correlation energy balance between two systems that differ in the number of electrons are demanding, and the agreement can be considered as very

satisfactory. Let us also note that the ZPE correction is a negative energy contribution, except in the case of the B^+ state for which the ZPE value is larger than that for the X neutral state. The CBS value for this state deviates more from TPES than the other states, but this is compensated by the positive ZPE correction, leading to a CBS + ZPE estimate lying within our *ab initio* error bar. For the C^+ state, we have here the opportunity to confirm that the observed vibrational structures arise from the $3^2\Pi(\text{Min}_2)$ and not from the $3^2\Pi(\text{Min}_1)$ potential well, owing to the deviations from the TPES values of 325 and 1993 cm^{-1} , respectively.

The difference between vertical and adiabatic ionization is also given in the last row for the CBS values only. This difference is small (800-900 cm^{-1}) and smaller than the ZPE values for the states identified in our TPE spectrum (X^+ , A^+ , B^+ , and C^+), see Table III. The difference is however considerably larger ($> 10000 \text{ cm}^{-1}$) for the states arising from configuration (5). This is consistent with the important geometry differences pointed out before (see section III B 2), which explains why the energies reached on the PESs of the cation vertically from the X state are far from the bottom of the corresponding potential wells. The difference is however smaller (3500 cm^{-1}) for the $4^2\Pi$ state, which also belongs to configuration (5), because of avoided crossings (ACs) as detailed in Section III E 2. Although the $4^2\Pi$ and $1^2\Phi$ states have similar geometries, these ACs also imply the inversion of the ionization energy order of $4^2\Pi$ and $1^2\Phi$ when going from adiabatic to vertical, which means that a state crossing must occur at intermediate geometries.

D. Electronic transitions in HC_5N^+ cation

1. Transition energies

Vertical and adiabatic transition energies (TE_v and TE_a , respectively) to the excited states of the cation were calculated using the same CBS extrapolation procedure as for the ionization energies. TE_a values are directly obtained by simple differences of the adiabatic ionization energies of Table V, while TE_v values result from energy differences between excited and ground state cationic energies, calculated at the equilibrium geometry of X^+ .

The results are reported in Table VI.

The convergence toward CBS being quite similar for all states, it is illustrated for the

TABLE VI. Vertical (TE_v) and adiabatic (TE_a) transition energies (in cm^{-1}), from ic-MRCI+Q/ VnZ calculations extrapolated to the CBS limit.

	Method ^a	TE_v	TE_a
$X^+ \ ^2\Pi$		0	0
$A^+ \ ^2\Pi$	AVTZ	18726	17440
	VQZ	18681	17479
	V5Z	18702	17526
	V6Z	18715	17537
	CBS	18728	17563
	CBS + ZPE ^b		17517
	Theory	17502 ^c , 17360 ^d	
	Exp.		17150 ^e , 17179.5 ^f , 17077.5 ^g
$B^+ \ ^2\Sigma^+$	AVTZ	21871	21464
	CBS	21844	21251
	CBS + ZPE ^b		21872
	Theory	19922 ^c	
	Exp.		21706 ^e
$1 \ ^4\Pi$	AVTZ	28110	22433
	CBS	28227	22798
$3 \ ^2\Pi(\text{Min}_1)$	AVTZ	-	26437
	CBS	-	26686
	CBS + ZPE ^b		26294
$3 \ ^2\Pi(\text{Min}_2)$ (C^+)	AVTZ	29178	27728
	CBS	29232	27963
	CBS + ZPE ^b		27961
	Theory	28794 ^c	
	Exp.		27365 ^e
$1 \ ^2\Phi$	AVTZ	33852	28693
	CBS	33692	28671
	CBS + ZPE ^b		27998
	Theory	32746 ^c	
$4 \ ^2\Pi$	AVTZ	30767	32562
	CBS	30853	32658
	CBS + ZPE ^b		32505
	Theory	28955 ^c	

^a This work, unless specified ; transition energies are obtained from ic-MRCI+Q/ VnZ calculations performed at the ic-MRCI+Q/AVTZ equilibrium geometries of the considered states (see Table II); extrapolation to CBS has been carried out as explained in the text using the VQZ, V5Z and V6Z energies;

^b CBS values corrected for the ZPE contributions estimated from the ic-MRCI+Q/AVTZ harmonic frequencies calculated in this work;

^c From Ref. 5; MRCI+Q/DZVP calculations performed at the B3LYP/6-311G* equilibrium geometry of the ground state;

^d From Ref. 4; CASPT2/DZVP calculations performed at the UHF/4-31G equilibrium geometry of the ground state;

^e Calculated as the difference of TPES adiabatic ionization energies (this work, Table 1 of Paper I¹)

state only. One sees that the energy improvement from AVTZ to CBS is smaller for TE values ($< 400 \text{ cm}^{-1}$), as compared with IE values ($< 1200 \text{ cm}^{-1}$), see Tables V and VI. As already pointed out, IE values result from energy differences between systems having a different number of correlated electrons and are thus more demanding to compute than TE values which correspond to energy differences within the same system. Unfortunately, the extrapolation increases slightly the deviation with respect to the experimental TE values in the case of the A^+-X^+ and C^+-X^+ transitions. This comes from the more important basis set improvement of the ground state energy.

As in Table V, CBS+ZPE values refer to $TE_a(\text{CBS})$ values corrected by the ZPE of Table III.

Comparison with direct spectroscopic values^{32,33,35} is limited to the A^+ state, with deviation of less than 450 cm^{-1} . Indirect estimates can also be obtained by differences of our TPES IE_a values. Comparison with other theoretical work is limited to TE_v values obtained at a lower level of theory.^{4,5} The agreement is reasonable (within 2000 cm^{-1}) and the energy order is the same. However, let us recall the energy inversion between $1^2\Phi$ and $4^2\Pi$ states from vertical to adiabatic transition.

2. Electronic transition dipole moments

Electronic transition electric dipole moments between the four lowest electronic states of the cation are reported in Table VII. These values have been calculated at the ic-MRCI/AVTZ level at the equilibrium geometries of the considered states. The geometry dependency is found to be small, which demonstrates the validity of the Franck-Condon approximation. The intensity of an electronic transition being proportional to the square of the corresponding transition moment value, one can predict the relative intensities of the different electronic transitions which may be observed in future absorption or emission spectroscopy experiments. The $X^+ \leftrightarrow A^+$ transition is clearly the most intense, followed by the $A^+ \leftrightarrow C^+$ and $X^+ \leftrightarrow C^+$ transitions, about 40 and 80 % weaker, respectively. Probabilities of transitions between $B^+ \ ^2\Sigma^+$ and any of the $^2\Pi$ states are more than 95 % weaker and are suspected to be unobservable.

TABLE VII. Square of the transition dipole moments (in Debye²), from ic-MRCI/AVTZ calculations performed at the equilibrium geometries of the different HC₅N⁺ electronic states.

	geometry			
	X ⁺	A ⁺	B ⁺	C ⁺
$\langle X^+ \mu A^+ \rangle^2$	17.72	22.77	20.70	22.69
$\langle X^+ \mu B^+ \rangle^2$	0.10	0.10	0.10	0.09
$\langle X^+ \mu C^+ \rangle^2$	4.08	3.81	3.14	3.68
$\langle A^+ \mu B^+ \rangle^2$	0.09	0.08	0.09	0.08
$\langle A^+ \mu C^+ \rangle^2$	12.15	13.30	13.22	16.31
$\langle B^+ \mu C^+ \rangle^2$	0.04	0.03	0.04	0.04

3. Franck-Condon simulations of vibronic transitions in HC₅N⁺ cation

To test and exploit the stretching vibrational frequencies calculated in the present paper, we have performed Franck-Condon Factor (FCF) simulations of the A⁺ → X⁺ emission spectrum in order to compare with other available experimental spectra. As explained in Paper I¹, only stretching vibrational modes of the HC₅N⁺ cation were observed in the TPE spectrum and not all of them were seen. The same situation is encountered in the A⁺ ↔ X⁺ system of the cation.^{33,34} Bieri *et al.*³⁴ recorded the gas-phase emission spectrum of HC₅N⁺ formed electronically excited in the A⁺ state from neutral cyanobutadiyne by interaction with an electron beam. The explored range spanned roughly 2500 cm⁻¹ below the vibrationless state of A⁺. Smith *et al.*³³ investigated the A⁺ → X⁺ transition by Laser-induced Fluorescence (LIF) spectroscopy in neon matrix environment in a range completing the data of Bieri *et al.*³⁴ Figure 3 shows the results for the emission spectrum of Bieri *et al.*³⁴ The calculated spectrum, taking into account the FCF simulations and the instrumental resolution (*FWHM* of 50 cm⁻¹), reproduces remarkably well the experimental spectrum. It confirms the assignment for the ν_6 , ν_5 and $2\nu_6$ bands. It enables proposal of an alternative assignment for the ν_3 band which had been attributed to the ν_4 band by Bieri *et al.*³⁴ In addition, a very weak combination band $\nu_5 + \nu_6$ is identified and proposed.

Figure 4 displays equivalent results for the LIF spectrum of Smith *et al.*³³ with a better spectral resolution (20 cm⁻¹) provided by the laser source. The agreement between the sim-

culated spectrum and the experimental one is quite good for the band positions. It confirms almost all of the assignments except for the ν_1 band and the $\nu_2 + \nu_4$ combination band which are instead assigned to $\nu_2 + \nu_5$ and $2\nu_3$ bands, respectively. The simulations validate the quality of our *ab initio* results, already pointed out in Section III B 1.

FIG. 3. Comparison of our calculated spectrum (lower panel) with the experimental $A^+ \rightarrow X^+$ emission spectrum of Bieri *et al.* (upper panel).²⁸ The black labels are reported from Ref. 28 and the star symbol corresponds to the position of the strong Lyman- α emission line of hydrogen which has been removed for the sake of clarity. In the lower panel, the calculated black sticks have been convoluted with a gaussian-line shape ($FWHM = 50 \text{ cm}^{-1}$) to reproduce the experimental bandwidth. The red labels are deduced from our FCF calculation (see text).

E. Topography of the crossing potential energy surfaces

We are back now to the perturbed energy region 3 eV above the ground state of the cation, where our calculations predict state mixing and potential surface crossings. This situation results from the existence of numerous interacting states with different equilibrium geometries (see Section III B 2). The potential wells of two states having similar geometries are usually well nested into each other, without surface crossings in the vicinity of the surface minima. In contrast, states with staggered minima will cross at an intermediate geometry at

FIG. 4. Comparison of our calculated spectrum (lower panel) with the experimental $A^+ \rightarrow X^+$ LIF spectrum of Smith *et al.* (upper panel).³³ The black labels are reported from Ref. 33 and the red ones are deduced from our FCF calculation (see text). In the lower panel, the calculated black sticks have been convoluted with a gaussian-line shape ($FWHM = 20 \text{ cm}^{-1}$) to reproduce the experimental bandwidth.

energies between their respective minima. Of course, if the considered states have the same symmetry and as long as the adiabatic approximation holds, avoided crossings will occur. However, if the interaction at the crossing is symmetry-forbidden, a conical intersection may nevertheless happen, depending on symmetry conditions.

1. Crossing pattern

The situation that we have described is encountered here, where the PESs corresponding to the states arising from configurations (2), (3) and (4) ($A^+ {}^2\Pi$, $B^+ {}^2\Sigma^+$, and $3 {}^2\Pi$) crosses the PESs of states ($4 {}^2\Pi$, $5 {}^2\Pi$, $1 {}^2\Phi$, and $1 {}^4\Pi$) arising from configuration (5). The geometry difference characterizing the states that belong to these two sets of configurations (see Table II) explains the observed crossings and in particular the existence of a double well in the $3 {}^2\Pi$ PES. This is illustrated in Figure 5, where cuts through the PESs computed at the ic-MRCI+Q/AVTZ level are shown. The seven potential energy curves (PECs) drawn on this figure give a complete overview of the crossing pattern. The ground electronic state

FIG. 5. Cuts through lowest excited PESs of HC_5N^+ computed at the ic-MRCI+Q / AVTZ level of theory and connecting linearly the equilibrium geometries of the $3^2\Pi(\text{Min}_1)$ and the $3^2\Pi(\text{Min}_2)$ (C^+) minima. The coloured points locate local minima along the connecting path. See text for details.

($\text{X}^+ 2^2\Pi$) is not represented because it lies outside of the crossing region.

The origin of the energy scale is the minimum of the X^+ state and the coordinate axis corresponds to a path linearly connecting the equilibrium geometries of the two minima of the $3^2\Pi$ PES, Min_1 and Min_2 , indicated on the abscissa axis. All bond distances were thus adjusted linearly between their equilibrium values at both minima. Sixteen points have been calculated along this path, which is representative of the crossing pattern, as all states of the two sets of crossing states have geometries which are close to those of Min_1 and Min_2 , respectively.

The positions of the minima of the interacting $2^2\Pi$ states can be visualized on the figure. The double well $3^2\Pi$ PES is highlighted by a bold blue line, with each minimum indicated by a blue point. The minimum on the $4^2\Pi$ yellow curve is shown by a yellow circle at about 4 eV. However no minimum appears on the $5^2\Pi$ light blue curve, which explains

Our geometry optimization did not converge, as pointed out in Section IIIB 1. Eight surface crossings occur between the adiabatic PESs: two of them, marked by open circles and noted as $AC_{(1)}$ and $AC_{(2)}$, correspond to avoided crossings (AC) between $^2\Pi$ states, while the others, marked by open squares and noted as $CI_{(1)}$ to $CI_{(6)}$, are explicit crossings between states of different spin and/or orbital symmetries, but potentially leading to conical intersections (CI) upon deformations away from linearity.

This graph generates many comments which are developed in the next subsections.

2. *Avoided crossings and diabaticity*

$AC_{(1)}$ and $AC_{(2)}$ arise from the adiabatic mixing of the $3\ ^2\Pi$ state with the $4\ ^2\Pi$ and $5\ ^2\Pi$ states, respectively. The evolutions of the weights of the most relevant configurations (2), (4), (5), and (6) along the reaction coordinate are illustrated in Figure 6. The most spectacular effect is the occurrence of sharp jumps at points $AC_{(1)}$ and $AC_{(2)}$, in the (b), (c), and (d) panels. These surface hoppings are induced by configuration switches between $3\ ^2\Pi$ and $4\ ^2\Pi$ at $AC_{(1)}$ and between $4\ ^2\Pi$ and $5\ ^2\Pi$ at $AC_{(2)}$. The complementary patterns on the (b) and (c) panels indicate a configuration exchange between (4) and (5), which cross diabatically. Configuration (2), which describes the A^+ state, also contributes to the electronic changes, as shown in (a), with a progressive gain of weight when approaching the $3\ ^2\Pi(\text{Min}_1)$ region.

The sharp configuration exchanges just pointed out indicate a quasi-diabatic behaviour of the involved electronic states, confirmed by the very small value of the Hamiltonian off-diagonal matrix element at $AC_{(1)}$ and $AC_{(2)}$ ($< 50\text{ cm}^{-1}$), and explained by a bielectronic interaction involving three different orbitals (1π , 3π , and 4π).

3. *Conical interactions*

The existence of explicit crossings $CI_{(1)}$ to $CI_{(6)}$ (see Figure 5) and their positions with respect to the topography of the different PESs merits special attention, because they are related to the formation of conical intersections, which may complicate the interpretation of the rovibrational spectra. Crossing point $CI_{(1)}$ is of major concern in this context, as it

FIG. 6. Weight evolutions of the configurations (2), (4), (5), and (6) for the $3^2\Pi$, $4^2\Pi$, and $5^2\Pi$ states of HC_5N^+ along the connecting path adopted in Figure 5.

involves the B^+ and C^+ states, which are experimentally observed. On a theoretical point of view, this is a $^2\Sigma^+ / ^2\Pi$ crossing, exactly like the A^+ / B^+ crossing in HC_3N^+ .¹¹ These states obey the following $\text{C}_{\infty v} \rightarrow \text{C}_s$ correlation rules upon planar bending of the molecular frame: $^2\Pi \rightarrow ^2\text{A}' \oplus ^2\text{A}''$ and $^2\Sigma^+ \rightarrow ^2\text{A}'$. The pair of $^2\text{A}'$ states so formed repel each other at non-linear geometries, forming a conical intersection. This is a typical case of accidental conical intersection, sometimes referred to by analogy as a pseudo-Jahn-Teller effect.¹¹ $\text{CI}_{(1)}$ is thus the top of a double cone and belongs to the intersection seam of the CI. It is also a point of the $^2\text{A}''$ PES and there is a triple degeneracy at this geometry. The $^2\text{A}''$ PES is not perturbed by the symmetry breaking and goes through the double cone without deformations (see Fig. 8 of Ref. 11 to visualize this specific topography). It is important to note that the linear equilibrium geometries of both crossing states (B^+ and C^+) are linked

through a connecting path on the lower $^2A'$ PES.

Crossing $CI_{(2)}$ between the $B^+ ^2\Sigma^+$ and $1 ^2\Phi$ PESs is expected to lead to a similar result, as the correlation rule $^2\Phi \rightarrow ^2A' \oplus ^2A''$ is the same as in the case of a $^2\Pi$ state. The consequence on B^+ is probably less important because the crossing happens at higher energy, but it may be decisive for $1 ^2\Phi$, as it occurs close to its equilibrium geometry.

Intersection point $CI_{(3)}$ corresponds to a $^2\Pi/^2\Phi$ crossing, obeying the correlation rule $^2\Pi/^2\Phi \rightarrow (^2A' \oplus ^2A'')/(^2A' \oplus ^2A'')$, which leads to a topography even more complex, in which two conical intersections ($^2A'/^2A'$ and $^2A''/^2A''$) share the same intersection seam.

4. *Spin-orbit crossing states*

The three last crossing points $CI_{(4)}$ to $CI_{(6)}$ imply doublet to quartet spin change, and as far as spin-orbit interaction is ignored, the crossing is possible. However spin-orbit interaction, even if it is weak, can intermix the (Λ, S) components of the crossing states and lead to avoided crossings between the spin-orbit states that have the same value of the $\Omega = \Lambda + \Sigma$ quantum number, where Σ is the projection of the spin vector on the internuclear axis. Similar mixings also occur at crossing points $CI_{(1)}$ to $CI_{(3)}$, involving states of the same spin, as shown in our HC_3N^+ paper,¹¹ where a theoretical analysis of the spin-orbit mixing in the vicinity of a conical intersection is presented.

5. *Vibronic perturbations in the C^+ state*

The above results can now be used to explain in more detail the vibrational assignment of the C^+ state TPES spectrum proposed in Paper I (see Figures 3 and 4 of Ref. 1 and related discussion). This assignment was made, supported by the FCF simulation using our *ab initio* calculations, considering that the C^+ signature was originated from vibrations in the $3 ^2\Pi$ (Min_2) potential well, ignoring thus the double well shape of this PES. Observation of vibrations in a single well is a reasonable zeroth-order approximation, given the quasi-diabatic behaviour of the surface crossing. Vibronic perturbations may nevertheless occur, but are expected to be weak and to affect only vibrational states that have a non-zero wave-

function in the localized region where the crossing occurs. A projection of the coordinates of the crossing path of Figure 5 on the normal coordinates of the stretching modes of the $3^2\Pi(\text{Min}_2)$ well gives the following contributions of the different modes: 0 % ν_1 + 21 % ν_2 + 18 % ν_3 + 9 % ν_4 + 1 % ν_5 + 50 % ν_6 . It follows that among the vibrational signatures predicted by our FCF simulation, ν_6 is likely to be perturbed by vibronic interactions, and ν_3 also but to a lesser extent. The intensities of the calculated stick spectrum are actually in poor agreement for these two modes with the maximum peak intensities of the TPES. The intensity of the 6_0^1 band is underestimated by about a factor of 12, while the intensity of the 3_0^1 band is overestimated by a factor of about 2. We attribute these discrepancies to the vibronic perturbations induced by the surface crossing, which have not been taken into account by the single state harmonic approach. We note however the remarkable intensity predictions (within less than 10 %) made for the other states of the cation, which are vibronically unperturbed.

IV. CONCLUSIONS

In the present paper of this series dedicated to the photoionization of the cyanobutadiyne molecule, an extensive *ab initio* study has been performed to understand the complex energy landscape up to 32 000 cm^{-1} above the ionization potential. The electronic properties of the seven low-lying electronic states of the cation have been calculated at a high level of *ab initio* theory which allows an accurate description of the multiconfigurational effects that affect the excited electronic structure. Convergence to the CBS limit has been applied to the determination of accurate ionization and transition energies. The first goal of this work was to provide a theoretical support to the interpretation of the threshold-photoelectron spectrum of HC_5N , presented in the first paper of this series (Paper I).¹ In these experiments the first four electronic states of the cation (X^+ , A^+ , B^+ , and C^+) are populated by single-photon ionization processes. The assignment of the vibrational structures that appear in this spectrum have been established in Paper I thanks to the theoretical results detailed in the present paper. The second goal of this work was to provide a more complete survey of the excited electronic structure of the cation. We have thus extended our theoretical study beyond the scope of the TPES experiment, by characterizing additional high energy states, unattainable by single-photon photoelectron spectroscopy. However these states indirectly

contribute however to the understanding of the vibronic perturbations affecting the TPE spectrum of the C^+ state. In addition to the properties directly related to our photoelectron experiments (ionization energies and vibrational frequencies), we have calculated additional properties which may be helpful to guide further spectroscopy experiments dedicated to the cyanobutadiyne cation. These properties, calculated for all considered states, include the rotational constants, permanent and transition electric dipole moments, spin-orbit constants, transition energies, and Renner-Teller parameters. The accuracy of the calculations is demonstrated through the good agreement between FCF simulations and experimental spectra, both for the photoionization and emission processes. This work contributes to the global knowledge of the photoionization of cyanopolynes and the electronic structure of the corresponding cations of astrophysical interest.^{10–12,36–39}

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$X^+ 2\Pi$ $A^+ 2\Pi$

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$B^+ 2\Sigma^+$ $C^+ 2\Pi$

Connecting path

$3^2\Pi(\text{Min}_2)$ $3^2\Pi(\text{Min}_1)$ $3^2\Pi(\text{Min}_2)$ $3^2\Pi(\text{Min}_1)$