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Chemical Physics 309 (2005) 291-301

Chemical Physics

www.elsevier.com/locate/chemphys

# HCN<sup>2+</sup> dication spectroscopy: theoretical and experimental investigations

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> Received 30 July 2004; accepted 29 September 2004 Available online 22 October 2004

#### Abstract

The present work combines experimental and theoretical investigations of  $HCN^{2+}$  to investigate the spectroscopy and dissociation dynamics of this dication. Its spectrum is a complex blend of overlapping features, consistent with theoretical calculations showing that the low-lying electronic states of  $HCN^{2+}$  exhibit Renner–Teller and vibronic interactions. The double ionisation spectra are dominated by C–N stretching excitations for all the electronic states investigated. Long-lived  $HCN^{2+}$  ions are observed and are believed to be in low vibrational levels of the X  ${}^{3}\Sigma^{-}$  and/or  ${}^{1}\Delta$  and/or  ${}^{1}\Sigma^{+}$  electronic states; some have metastable lifetimes of about 25 ns. The formation of  $H^{+} + CN^{+}$  products is attributed to predissociation by the lowest  ${}^{3}A''$  component resulting from a conical intersection between the X  ${}^{3}\Sigma^{-}$  and  ${}^{3}\Pi$  states. The overall predissociation processes involve vibronic, Renner–Teller and spin–orbit couplings between several electronic states of  $HCN^{2+}$ .

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# 1. Introduction

The hydrogen cyanide molecule is an important constituent of interstellar clouds [1] and planetary atmospheres [2–4], and is possibly a precursor of life on Earth [5]. Its significance in many environments makes knowledge of all its spectroscopic properties very desirable. The neutral molecule and singly charged positive ion have already been studied in depth; here we present a first detailed investigation of the doubly positive ion  $HCN^{2+}$ , using the time-of-flight photoelectron–photoelectron coincidence technique (TOF-PEPECO) and high level calculations.

The existence of HCN<sup>2+</sup> dications with lifetimes of at least microseconds has been known for some time because of the presence of peaks at m/q 13.5 in mass spec-

tra [6]. Some aspects of the dissociation of HCN dications have been investigated by the photoelectron photoion–photoion coincidence (PEPIPICO) technique [7], but without energy selection of the initial states. The isoelectronic species  $N_2^{2+}$  and  $C_2H_2^{2+}$  both show well-resolved spectra in experiments by the TPEsCO and PEPECO techniques [8–10], so we could hope for a similar outcome from work on HCN. However, experience of HCN<sup>+</sup> monocation spectroscopy sounds a warning note.

The photoelectron spectrum of HCN, although measured with good resolution at an early date [11], is notorious for the difficulty of its interpretation. Two electronic states,  $X^2\Pi$  and  $A^2\Sigma^+$  are close in energy (separation 0.4 eV) and interact vibronically, producing a spectrum which cannot be analysed by pattern recognition methods into systems of independent progressions. The spectrum of the two lowest states was explained only after detailed calculations incorporating the vibronic coupling [12] and its modulation by otherwise inactive modes [13]. The second excited state's spec-

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<sup>0301-0104/</sup>\$ - see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.chemphys.2004.09.026

trum has been elucidated more recently [14], and proved to be almost equally complex because of interaction between  $\Pi$  and  $\Sigma$  components. Simple considerations of the orbital occupancy predict that in HCN<sup>2+</sup>, the two configurations involving the outermost orbitals,  $5\sigma^2 1\pi^2$ and  $5\sigma^1 1\pi^3$  will give rise to six electronic states within a few electronvolts. The spectrum may, therefore, be no less complex than that of HCN<sup>+</sup> and could be more complicated.

As shown below, the experimental spectra are structured, but very difficult to interpret. Electronic structure calculations at the highest level are therefore essential for interpretation of the experimental spectra, and even with their input, uncertainty remains. From considerable recent experience in calculations of molecular dication spectra [8,15–18] and successful comparison with experiment, we can perhaps have more confidence in the theoretical results per se than in the fit to the experimental data.

#### 2. Experimental method

The basis of the TOF-PEPECO method [19] is detection and energy analysis of both electrons of each pair ejected in double photoionisation. The light source is a pulsed discharge lamp with helium or neon as the working gas; in its present form it gives ca. 5 ns pulses at 9 kHz repetition rate. Ionisation occurs where wavelength-selected light is focussed into an effusive gas jet at the focus of a long (5.5 m) magnetic bottle time-offlight spectrometer. Further details have been given in recent papers [9,20].

Double ionisation spectra were accumulated at two wavelengths, 30.4 and 25.6 nm, corresponding to the photon energies 40.8 and 48.4 eV. Calibration was by comparison with photoelectron spectra of  $O_2$  taken immediately before and after each run. Because the detection times of all electrons are recorded in the list mode, contact potential changes during long run times could be compensated in the data reduction. Spectra from each few hours of runtime were cross-correlated and optimum shifts determined before addition to form the final spectra. The experimental resolution is a function of electron energy, and also depends on the accuracy of the calibration. The narrowest lines in the spectrum of HCN<sup>2+</sup> at 40.8 eV photon energy are about 50-meV wide.

PEPIPICO spectra (without electron energy analysis) were measured at the same wavelengths in connection with an earlier investigation [7], where the apparatus was described. In essence, ions and ion pairs of all masses were analysed by time of flight, in coincidence with photoelectrons ejected from the molecules by monochromatic light. Under the focus conditions used, the widths of peaks in the ion time-of-flight spectra are directly proportional to the ions' momenta. The conditions of the measurements favour detection of low energy electrons, so the relative intensity of doubly ionised products is exaggerated in the data.

HCN was prepared by heating an intimate mixture of carefully dried NaCN and stearic acid to just above the melting point, 70 °C, in vacuum. Impurity CO<sub>2</sub> was removed by pumping on the condensed product cooled in a CO<sub>2</sub>/acetone slush bath. DCN was prepared by dropwise addition of D<sub>2</sub>O to a mixture of NaCN and P<sub>2</sub>O<sub>5</sub> under nitrogen with collection in a cold trap. It was purified in the same way. The whole apparatus was conditioned with D<sub>2</sub>O before the DCN runs to avoid formation of HCN by isotopic exchange in the gas inlet system. The purity of the DCN was checked by measuring its PES spectrum at 21 eV photon energy; the spectrum was consistent with that of the pure compound [11].

#### 3. Theoretical methods

Electronic correlations are expected to play an important role in the formation and in the metastability of molecular dications. In previous work dealing with triatomic dications, we have shown that highly correlated ab initio methods are needed in the calculations of the potential energy functions (PEFs) and of the properties of such species. [16–18]. Here, the PEFs of the X  ${}^{3}\Sigma^{-}$ ,  ${}^{3}\Pi$ ,  ${}^{1}\Delta$ ,  ${}^{1}\Sigma^{+}$  and  ${}^{\overline{1}}\Pi$  states of HCN<sup>2+</sup> have been mapped using such highly correlated approaches, for instance the complete active space self-consistent field (CASSCF) [21] and the internally contracted multi-reference configuration interaction (MRCI) methods [22,23]. For these calculations, the generally contracted spdf (spd) ccpV5Z basis set of Dunning has been used for C/N (H) atoms, resulting in 156 contracted Gaussian functions [24]. In order to reduce symmetry breaking problems, the CASSCF computations started with the HF molecular orbitals obtained for HCN(X  ${}^{1}\Sigma^{+}$ ). In the active space, all valence molecular orbitals were optimized. In these calculations, electronic states having the same spin multiplicity were averaged together. All valence electrons were correlated. For MRCI calculations, all configurations in the CI expansion of the CASSCF wavefunctions were taken into account as a reference. The calculations were done in  $C_s$  symmetry with wavefunctions corresponding to more than  $31 \times 10^6$  $(54 \times 10^6)$  uncontracted configurations for the singlets (for the triplets). All electronic calculations were performed using the MOLPRO program suite [25].

The three-dimensional PEFs of the HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ,  ${}^{3}\Pi$ ,  ${}^{1}\Delta$ ,  ${}^{1}\Sigma^{+}$  and  ${}^{1}\Pi$ ) have been mapped in the internal coordinates of this dication corresponding to the CN ( $R_{CN}$ ), CH ( $R_{CH}$ ) stretches and to the in-plane bending

angle ( $\theta$ ). For the singlets, the calculations were performed for 22 different geometries around the equilibrium minimum of each electronic state covering the energy ranges up to  $\sim 5000 \text{ cm}^{-1}$  above each minimum. For the triplets, the PEFs have been carried out for 50 different geometries up to energies  $\sim 15,000 \text{ cm}^{-1}$  above the HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ) minimum, so that the equilibrium and the conical intersection regions (see below) are both covered. The calculated energies were fitted to polynomial expansions in displacement coordinates for both the stretches and the bending. The resulting PEF expansions were used to calculate the quartic force fields in internal coordinates, which have been transformed by the *l*-tensor algebra to quartic force fields in dimensionless normal coordinates [26,27]. These data allow us to evaluate a set of spectroscopic properties using secondorder perturbation theory. The PEF expansions were also used in variational calculations using the approach of Carter and Handy [28].

As part of this work, the three-dimensional PEF of the ground state X  ${}^{1}\Sigma^{+}$  of HCN has been generated at the CCSD(T) level of theory and using the same basis set as for the dication calculations. These calculations are not presented here, but the calculated fundamentals differ by less than 20 cm<sup>-1</sup> from the experimental values [29]. This ground-state PEF can be provided on request. It has been used here to evaluate Franck–Condon factors for the direct double photoionisation process.

## 4. Results

## 4.1. Results from TOF-PEPECO experiments

Fig. 1 shows the double photoelectron spectra of HCN at the two photon energies, 40.8 and 48.4 eV. There is clearly a main group of states between 37 and 41 eV, followed by a weaker feature near 45 eV. By comparison with the single ionisation spectrum, we can iden-

tify the main band with states of HCN<sup>2+</sup> from the configurations  $4\sigma^2 5\sigma^2 1\pi^2$  and  $4\sigma^2 5\sigma^1 1\pi^3$ , and the subsidiary band with states from  $4\sigma^1 5\sigma^2 1\pi^3$  or  $4\sigma^1 5\sigma^1 1\pi^4$ .

Resolved structure is visible only at the lower photon energy in Fig. 1 because in the TOF-PEPECO method the energy resolution degrades at higher electron energies. Details of the partially resolved structures are shown for both the HCN and DCN molecules in Fig. 2, and the energies of the distinguishable lines are tabulated in Table 1. Although relative energies of the lines are more precise ( $\pm 0.005 \text{ eV}$ ), the absolute accuracy of the calibrations is not better than  $\pm 0.03 \text{ eV}$ . This means that isotope shifts in ionisation potential between HCN and DCN cannot be used to identify vibrational origins.

The spectra of both  $\text{HCN}^{2+}$  and  $\text{DCN}^{2+}$  are systems of congested vibrational bands, overlying a continuum whose relative intensity increases towards higher energy. There is no unambiguous onset, but a gradual rise in signal from about 37 eV leads to the first clear band(s) near 37.5 eV. At higher energies, sequences of peaks in the spectra of both isotopomers form progressions, from which average spacings can be extracted. In the range 38.5–39.2 eV, there seem to be single progressions with mean intervals of  $1090 \pm 80 \text{ cm}^{-1}$  for both HCN and DCN. The spectra of the isotopomers differ more in the lower energy range, where there are signs of interpenetrating progressions or more complex structures.

In addition to spectra of dication states, the TOF-PEPECO method gives complete energy distributions of the electrons emitted in double photoionisation. Fig. 3 shows a two-dimensional map for HCN at 40.8 eV photon energy. Distributions of electrons are shown in the left part of the figure for formation of selected  $HCN^{2+}$  levels. For some of the higher levels, there is a broad peak at 0.15 eV, which presumably represents a contribution from autoionisation of an intermediate state of  $HCN^{+}$  near the photon energy. In formation of the  $HCN^{2+}$  levels below 37.5 eV, the distribution shows only a gentle slope favouring lower electron ener-



hv=40.8 eV

Fig. 1. Overall double photoionisation spectra of HCN at 40.8 and 48.4 eV photon energy.



Fig. 2. Detail of the structured parts of the double photoionisation spectra of HCN and DCN at 40.8 eV photon energy.

Table 1

Energies of distinguishable peaks in the TOF-PEPECO spectra. Where three decimal places are quoted relative precision is  $\pm 0.005$  eV, but absolute accuracy is only  $\pm 0.03$  eV

Line	HCN	DCN
la	37.486	37.517
1b	37.546	37.566
2	37.710	37.738
3a	37.862	37.889
3b	37.936	37.948
3c	38.01	
4	38.104	38.127
5	38.289	38.310
6	38.464	38.47
7	38.572	38.588
8	38.697	38.724
9	38.847	38.858
10	38.974	38.998
11	39.105	39.129
12	39.246	39.29
13	39.36	
14	39.49	
15	39.61	
17	39.73	
18	39.84	
19	39.96	
20	40.08	

gies; most other apparent structures are statistical noise from the low numbers of counts. There is no very clear sign of the characteristic electron energies (0.22, 0.34 and 1.01 eV) from autoionisation of atomic N\* as seen in other compounds with terminal N atoms (N<sub>2</sub> and N<sub>2</sub>O) [9,30], though the first peak near 0.21 eV may possibly be present.

Finally, because the electron collection efficiency is known, the observed ratio of pairs to single electrons

at each photon energy gives the fraction of double ionisation. This is found to be just 0.2% at 40.8 eV and rises to 5.1% at 48.4 eV photon energy.

## 4.2. Results from PEPIPICO experiments

Experiments on HCN and DCN by the PEPIPICO technique were carried out some time ago in connection with a different investigation [7], but only limited results were published at that time. Measurements on both HCN and DCN were made at the same two photon energies used in the current TOF-PEPECO work, so the results refer to exactly the same photoionisation processes. Fig. 4 shows the PEPIPICO signatures of the principal dication dissociation reaction, which produces  $H^+ + CN^+$  in both compounds at 40.8 eV. The diagonal "tails" are due to the decay of metastable dications, whose existence in HCN<sup>2+</sup> has already been remarked upon [31].

From comparison between the simultaneously measured mass spectra and PEPIPICO spectra with the known ion detection efficiency, we can estimate the proportions of different double ionisation channels. Within the double ionisation, the fraction observed as parent  $HCN^{2+}$  ions (rather than ion pairs) is  $8 \pm 2\%$  at both photon energies. The ion pairs produced are almost all  $H^+ + CN^+$  (95%) at 40.8 eV, with just 5%  $CH^+ + N^+$ . At 48.4 eV more different pairs are formed, but the simple H–C cleavage still provides the majority (77%).

From the widths of the ion pair coincidence peaks, the kinetic energy release and aspects of its distribution can be determined [32]; because of kinematic factors, the precision is best in DCN as the peak is wider. At both 40.8 and 48.4 eV photon energy, the total energy release



Fig. 3. Complete photoelectron energy distribution map (right panel) for HCN double photoionisation at 40.8 eV, with projections of the distributions along lines of fixed electron pair energy, corresponding to selected final state energies. The distributions are essentially flat, indicating that direct photoionisation is the major pathway.



Fig. 4. PEPIPICO distributions for the charge separation reactions, at 40.8 eV photon energy, forming  $H^+ + CN^+$  (right) and  $D^+ + CN^+$  (left). The diagonal tails demonstrate the existence of metastable dications with lifetimes of the order of 20 ns (see text).

is sharply peaked at  $5.4 \pm 0.2$  eV. If the products are formed in their electronic and vibrational ground states (or in the almost degenerate first excited state of CN<sup>+</sup>), they must originate in levels of HCN<sup>2+</sup> around 33.1 + 5.4 = 38.5 eV, where 33.1 eV is the lowest dissociation limit for H<sup>+</sup> + CN<sup>+</sup> derived from the standard heats of formation. This result refers to rapid (<10 ns) dissociations into H<sup>+</sup> + CN<sup>+</sup>; the energy release in the slower metastable decays cannot be determined from the data.

From the form of the metastable "tails", it is possible to determine the metastable ions' lifetime [31]. From simple inspection of the arrays, we see a clear tail (Fig. 4), but there is no "V" in the notation of [31]. This indicates that there is no long (microsecond) lifetime component. The form of the tails is quite close to exponential, giving mean lifetimes (after coordinate transformation) of  $34 \pm 5$  ns for DCN<sup>2+</sup> and  $20 \pm 8$  ns for HCN<sup>2+</sup> at 40.8 nm. Although single mean lifetimes fit the tail data well, it is still probable that multiple lifetimes are actually present.

#### 4.3. Results from ab initio calculations

#### 4.3.1. Excited states

Fig. 5(a) and (b) gives an overview of MRCI collinear potential energy curves for the electronic excited states of HCN<sup>2+</sup> of singlet (triplet) multiplicity along the  $R_{\rm CH}$  coordinate, where the CN bond length is fixed at 2.53 bohr, corresponding to its equilibrium value in HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ). Fig. 6 presents the same states as Fig. 5 for the collinear configuration where  $R_{\rm CN}$  is varied and  $R_{\rm CH}$  is kept fixed at 2.205 bohr (~ its equilibrium value in HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ )). These PEFs are given relative to the minimum of HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ). The vertical excitation energies are listed in Table 2, where the accuracy is expected to be better than 0.1 eV for such large ab initio calculations. In the 0-8 eV internal energy range, several bound states in both coordinates are found. These electronic states present several avoided crossings such as the one between the 1  ${}^{1}\Sigma^{+}$  and 2  ${}^{1}\Sigma^{+}$  states at  $R_{\rm CH} \sim 4$ bohr responsible for the potential barrier in the lower one (cf. Fig. 5(a)). One can mention also the avoided crossings between the  ${}^{3}\Pi$  states which give rise to the local minima of these electronic states along both  $R_{CH}$  and  $R_{\rm CN}$  coordinates. Additionally, we notice the existence of conical intersections between the electronic states of the dication. The most obvious one is the conical intersection between the X  ${}^{3}\Sigma^{-}$  and the 1  ${}^{3}\Pi$  states along the CN stretch at  $R_{\rm CN} \sim 2.3$  bohr (see Fig. 6(b)). As already mentioned in Section 1, such vibronic interactions are expected, since the lowest molecular orbitals of HCN are close in energy. Nevertheless, the intersection between the two electronic states of HCN<sup>2+</sup> is located at ~0.7 eV above the HCN<sup>2+</sup> (X  ${}^{3}\Sigma^{-}$ ) minimum, which is high enough to allow us to calculate the vibrational structure of the electronic ground state of HCN<sup>2+</sup> without considering this vibronic interaction explicitly (cf. Section 4.3.2). Several other conical intersections can be found between the excited states of  $HCN^{2+}$ , for instance the one between 1  ${}^{1}\Sigma^{-}$  and 2  ${}^{1}\Pi$  at  $R_{\rm CH} \sim 3$  bohr,  $1 {}^{3}\Sigma^{+}$  and  $2 {}^{3}\Pi$  at  $R_{\rm CH} \sim 4$  bohr. Furthermore, all the doubly degenerate states (i.e., all except the  $\Sigma$  states) are expected to split into two components for bent structures because of the Renner-Teller effect. The vibronic and Renner-Teller couplings mix these electronic states together, complicating the mapping of their threedimensional potential energy functions and the calculations of their rovibronic spectra. According to the curves of Figs. 5 and 6, the experimental spectra are expected to



Fig. 5. MRCI collinear potential energy curves of the singlet (a) and triplet (b) electronic states of HCN<sup>2+</sup> along the  $R_{CH}$  coordinate. The  $R_{CN}$  distance is set to 2.53 bohr.



Fig. 6. MRCI collinear potential energy curves of the singlet (a) and triplet (b) electronic states of HCN<sup>2+</sup> along the  $R_{CN}$  coordinate. The  $R_{CH}$  distance is set to 2.205 bohr.

State	$R_{\rm CH}$ (Å)	$R_{\rm CN}$ (Å)	$T (eV)^{a}$	$G_0 \ (\mathrm{cm}^{-1})$	$B_{\rm e}~({\rm cm}^{-1})$	$\alpha_1 \ (cm^{-1})$	$\alpha_2 \ (cm^{-1})$	$\alpha_3 \ (cm^{-1})$
$X^{3}\Sigma^{-}$	1.16	1.34	0 <sup>b</sup>	2381	1.1093	0.0113	-0.0055	0.0135
$^{3}\Pi$	1.16 <sup>d</sup>	1.23 <sup>d</sup>	$0.67^{d}$	_ <sup>c</sup>				
$^{1}\Delta$	1.16	1.36	0.87	2450	1.0920			
${}^{1}\Sigma^{+}$	1.15	1.36	1.28	2479	1.0893	0.0109	-0.0027	0.0127
$^{1}\Pi$	1.21	1.24	2.52	2383	1.2526			

Equilibrium geometries, MRCI vertical excitation energies (*T*), zero point vibrational energies (*G*<sub>0</sub>) and rotational constants (*B*<sub>e</sub>; vibration–rotation terms ( $\alpha_i$ )) of the excited states of HCN<sup>2+</sup>

<sup>a</sup> It corresponds to the energy difference between the minimum of the HCN<sup>2+</sup>(X  $^{3}\Sigma^{-}$ ) state and the minimum of the upper state.

<sup>b</sup> Total MRCI energy at the equilibrium geometry of HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ): -91.94463621 a.u.

<sup>c</sup> Perturbations due to the vibronic interaction between this electronic state and the ground state of  $HCN^{2+}$  (see text).

<sup>d</sup> From the <sup>3</sup>A' component.

Table 2

be very complicated for internal energies > 4 eV. Finally, we remark that the crossings and avoided crossings between the electronic states of  $HCN^{2+}$ , together with the dissociative character of some of them (e.g., the 2 <sup>3</sup> $\Pi$  state) will probably play a crucial role on the metastability of this dication.

## 4.3.2. Spectroscopy

Table 3 lists the quartic force fields of HCN<sup>2+</sup> (X  ${}^{3}\Sigma^{-}$ ,  ${}^{1}\Delta$ ,  ${}^{1}\Sigma^{+}$ ,  ${}^{1}\Pi$ ) in dimensionless normal coordinates. All these electronic states are found to be linear. The conical intersection between the X  ${}^{3}\Sigma^{-}$  and the  ${}^{3}\Pi$  states, mentioned above, is expected to complicate the pattern of rovibrational levels in its vicinity (i.e., the upper levels of X  ${}^{3}\Sigma^{-}$  and of  ${}^{3}\Pi$ ) and should affect the low-lying rovibrational levels of the ground

Table 3

Quartic force fields of HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ,  ${}^{1}\Delta$ ,  ${}^{1}\Sigma^{+}$ ,  ${}^{1}\Pi$ ) in dimensionless normal coordinates (all values are in cm<sup>-1</sup>). See text for more details

	$X  {}^3\Sigma^{-a}$	$^{1}\Delta^{b}$	$^{1}\Sigma^{+}$	$^{1}\Pi^{b}$
$\omega_1$	2498.9	2543.5	2557.8	2121.4
$\omega_2$	516.7	579.2 (615.5)	608.7	575.2 (713.7)
$\omega_3$	1307.6	1290.5	1250.6	1483.7
$\phi_{333}$	-570.3	-572.4	-527.4	-898.5
$\phi_{111}$	-1906.7	-2051.7	-2063.0	928.2
$\phi_{223}$	170.1	120.5 (108.2)	84.3	53.5 (7.2)
$\phi_{122}$	993.0	907.7 (843.6)	872.8	-317.9 (-392.7)
$\phi_{133}$	97.0	94.8	83.2	474.0
$\phi_{113}$	-277.7	-266.3	-238.9	-1155.3
$\phi_{2222}$	1345.7	1169.3 (922.4)	1048.8	35.5 (193.8)
$\phi_{3333}$	168.7	154.2	134.7	402.5
$\phi_{1111}$	1120.0	1085.3	1073.7	787.6
$\phi_{2233}$	-59.2	-52.1(-44.0)	-32.8	-258.7 (-226.7)
$\phi_{1333}$	-35.0	-31.2	-23.3	-368.6
$\phi_{1223}$	-117.1	-100.1 (-94.6)	-87.5	423.2 (353.9)
$\phi_{1122}$	-1090.1	-1045.2 (-979.5)	-1001.2	-608.9(-456.3)
$\phi_{1133}$	25.9	20.2	14.1	537.7
$\phi_{1113}$	142.8	125.1	115.1	-582.5

<sup>a</sup> This PEF is mapped well below the conical intersection, so that this quartic force field is valid only close to the equilibrium geometry of  $HCN^{2+}(X^{3}\Sigma^{-})$ .

<sup>b</sup> Between parentheses are given the values for the  ${}^{1}A''$  component.

state slightly. In order to deduce the HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ) spectroscopic properties, we have mapped the 3D-PEF of HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ) close to its equilibrium geometry, well below this conical intersection. For the  $^{1}\Delta$  and  $^{1}\Pi$ states, the quartic force fields of both their  ${}^{1}A'$  and <sup>1</sup>A" components are given in Table 3. However, only the rovibrational spectrum using one component (the  ${}^{1}A''$  one) is presented here without considering the Renner-Teller interaction since the main aim of these calculations is to propose an interpretation for the features observed in the TOF-PEPECO spectra. The differences between the energies of the rovibrational levels given here and those calculated using full treatment of the Renner-Teller and vibronic couplings are expected to be less than  $30 \text{ cm}^{-1}$ . [33] The accuracy of the present theoretical results is comparable with that of the experimental spectra of these and similar polyatomic dications. For example, readers are referred to other recent comparisons between theoretical and experimental results on other triatomic dications [16–18].

From the values given in Table 3, it is evident that there is coupling between the CH stretch and the bending modes for all the investigated electronic states, since both the third and fourth-order force-field terms relative to these modes (for instance  $\phi_{122}$  and  $\phi_{1122}$ ) have large values. Only weak coupling is expected between the two stretching modes except for the  ${}^{1}\Pi$  state, where the  $\phi_{133}$ ,  $\phi_{113}$  and  $\phi_{1113}$  terms are quite large.

Tables 4–6 list the rovibrational theoretical spectra of  $\text{HCN}^{2+}(X^{3}\Sigma^{-}, {}^{1}\Delta, {}^{1}\Sigma^{+}, {}^{1}\Pi)$ . The calculations are carried out for J = 0 and 1 for the  $\Sigma$  electronic states and only for J = 0 for the  $\Delta$  and  $\Pi$  states. For these electronic states, anharmonic resonances can be found between their rovibrational levels even for the ones located as low as 2000 cm<sup>-1</sup>. For example, the two levels of  $\text{HCN}^{2+1}\Sigma^{+}$  located at 1186 and 1240 cm<sup>-1</sup> are mixture of (0,0,1) and (0,2,0) vibrational wavefunctions with equal weights. Such resonances mix the rovibrational wavefunctions of these levels making their assignment by quantum numbers quite difficult. For these reasons the attributions given in Tables 4–6 are only tentative.

Table 4 Rovibrational levels of HCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ). The Franck–Condon factors (FCF) corresponding to the double ionisation from HCN(X  ${}^{1}\Sigma^{+}$ ) are also given

$\overline{\sigma^+ (J=0)}$		$\pi (J=1)$		
$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	FCF	$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )
(0,0,0)	0	0.0256	(0,1,0)	510
(0,2,0)	1009		(0,3,0)	1514
(0,0,1)	1278	0.1936	(0,1,1)	1792
(0,4,0)	2008		(0,5,0)	2508
(0,2,1)	2293		(0,3,1)	2800
(1,0,0)	2348		(1,1,0)	2842
(0,0,2)	2531	0.7056	(0,1,2)	3049
(0,6,0)	2998		(0,7,0)	3495
(0,4,1)	3294		(0,5,1)	3792
(1,2,0)	3328		(1,3,0)	3822
(0,2,2)	3552			
(1,0,1)	3612	0.2704		
(0,0,3)	3766	0.7056		
(0,8,0)	3981			
(2,0,0)	4655	0.0144		
(1,0,2)	4847	$1^{a}$		

<sup>a</sup> Normalized to this value.

In addition, Tables 4–6 give the Franck–Condon Factors (FCFs) corresponding to the direct double ionisation HCN<sup>2+</sup> SS HCN(X  $^{1}\Sigma^{+}$ ). Only FCFs for the

Table 5

Rovibrational levels of HCN<sup>2+</sup>(<sup>1</sup> $\Delta$ ) and HCN<sup>2+</sup>(<sup>1</sup> $\Pi$ ) (in cm<sup>-1</sup>) using the <sup>1</sup>A' component of these electronic states (without considering the Renner–Teller interaction). We are also giving the Franck–Condon factors (FCF) corresponding to the double ionisation from HCN(X <sup>1</sup> $\Sigma$ <sup>+</sup>). See text for more details

$HCN^{2+}(^{1}A)$	Δ)		$HCN^{2+}(^{1})$	Π)	FCF 0.261			
$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	FCF	$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	FCF			
(0,0,0)	0	0.020	(0,0,0)	0	0.261			
(0,2,0)	1152		(0,2,0)	972	0.0049			
(0,0,1)	1258	0.183	(0,0,1)	1358	0.740			
(0,4,0)	2304		(0,4,0)	1905				
(1,0,0)	2333	0.009	(1,0,0)	1931	0.216			
(0,2,1)	2420	0.009	(0,2,1)	2297	0.0049			
(0,0,2)	2495	0.510	(0,0,2)	2743	1 <sup>a</sup>			
(0,4,1)	3447		(1,2,0)	2802	0.0541			
(0,0,6)	3452		(0,6,0)	2882				
(1,0,1)	3568	0.580	(0,4,1)	3267				
(1,2,0)	3573	0.009	(1,0,1)	3337	0.019			
(0,0,3)	3664	0.383	(1,2,1)	3670	0.002			
(0,2,2)	3726		(1,4,0)	3750				
(1,4,0)	4569		(2,0,0)	3852	0.078			
(2,0,0)	4577	0.111	(0,8,0)	3890				
(0,1,2)	4586		(0,0,3)	4147	1			
(1,2,1)	4694		(1,2,1)	4228	0.005			
(0,2,3)	4713		(0,6,1)	4294				
(1,0,2)	4769	$1^{a}$						
(0,0,4)	4817		(0,0,4)	5554	0.394			
(1,6,0)	4893		(3,0,0)	5871	0.589			
(0,0,4)	4972		(1,0,4)	6544	0.044			

<sup>a</sup> Normalized to this value.

#### Table 6

Rovibrational levels of  $HCN^{2+(1\Sigma^{+})}$  (in cm<sup>-1</sup>). The Franck–Condon factors (FCF) corresponding to the double ionisation from  $HCN(X^{1}\Sigma^{+})$  are also given

$\overline{\sigma^+ (J=0)}$			$\pi (J=1)$		
$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	FCF	$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	
(0,0,0)	0	0.017	(0,1,0)	606	
(0,2,0)	1186		(0,3,0)	1783	
(0,0,1)	1240	0.153	(0,1,1)	1859	
(1,0,0)	2341	0.007	(1,1,0)	2930	
(0,2,1)	2358		(0,3,1)	2947	
(0,0,2)	2417	0.546	(0,1,2)	3026	
(0,4,0)	2490		(0,5,0)	3120	
(1,2,0)	3493		(1,3,0)	4076	
(0,2,2)	3516		(0,3,2)	4099	
(0,0,3)	3546	0.484	(0,1,3)	4150	
(1,0,1)	3589	0.425	(1,1,1)	4187	
(0,2,2)	3652		(0,5,1)	4273	
(0,6,0)	3754		(0,7,0)	4391	
(2,0,0)	4592	0.068	(2,1,0)	5175	
(1,4,0)	4627		(1,5,0)	5203	
(1,2,1)	4665		(1,3,1)	5243	
(0,0,4)	4682	0.007	(0,1,4)	5279	
(1,0,2)	4748	0.017	(1,1,2)	5336	
(0,2,3)	4763		(0,3,3)	5377	
(1,0,2)	4812		(1,1,2)	5431	
(0,4,2)	4902		(0,5,2)	5532	
(0,8,0)	5029		(0,9,0)	5670	
(2,2,0)	5725				
(0,2,4)	5742				
(2,0,1)	5781	$1^{a}$			
(1,4,1)	5800				
(0,0,5)	5812				
(1,2,2)	5883				
(1,0,3)	5891				

<sup>a</sup> Normalized to this value.

levels located <6000 cm<sup>-1</sup> relative to the vibrational zero point energies (ZPE) are given, since the PEFs calculated here are not valid above this energy. For the HCN(X  ${}^{1}\Sigma^{+}$ ) state we have used our own calculated PEF.

The analysis of the FCFs shows that long progressions in CN stretching, but insignificant CH excitation should be observed experimentally, despite the fact that both CH and CN bonds are longer in HCN<sup>2+</sup> than in HCN neutral (cf. Table 2). There is considerable CN extension in the  $\pi^{-2}$  states resulting in long progressions with very weak HCN<sup>2+</sup>(0,0,0)  $\leftarrow$  HCN X  $^{1}\Sigma^{+}(0,0,0)$ transitions, making unambiguous determination of the double ionisation potentials very difficult. For instance, the first strong line in both HCN and DCN spectra (near 37.5 eV) is (at least) a doublet and the third strong line is a triplet. Because the calculated FCF is so small, the first significant peak in the spectra at  $37.49 \pm 0.02$  (HCN) and  $37.52 \pm 0.02$  (DCN) is probably not the (0,0,0)-(0,0,0) transition. (This is the lower energy component of the doublet). This effect should be less strong in the  $\sigma^{-1}\pi^{-1}$  states. For energies >2000 cm<sup>-1</sup> above the ZPE, the overlap between the PEFs of HCN X and Tables 7 and 8 give the calculated rovibrational spectra of DCN<sup>2+</sup>(X  ${}^{3}\Sigma^{-}$ ,  ${}^{1}\Delta$ ,  ${}^{1}\Sigma^{+}$ ,  ${}^{1}\Pi$ ). The isotopic shifts are calculated to be in the ranges of ~500–520 cm<sup>-1</sup> for  $v_1$ , ~100–120 cm<sup>-1</sup> for  $v_2$  and ~60–70 cm<sup>-1</sup> for  $v_3$ , values which are consistent with those observed for the neutral DCN and DCN<sup>+</sup> cation [11,34]. Since the FCFs correspond mostly to the excitation of the CN stretching mode ( $v_3$ ) and the isotopic shift for this mode is smaller than our experimental resolution, the TOF-PEPECO spectra of HCN and DCN have similar shapes with relatively few differences (cf. Fig. 2).

## 5. Discussion

According to these calculations, only the X  ${}^{3}\Sigma^{-}$ ,  ${}^{3}\Pi$ ,  ${}^{1}\Delta$  and  ${}^{1}\Sigma^{+}$  states of HCN<sup>2+</sup> are likely to be seen in the experimental data below 40 eV (see Table 2). The spectra show resolved lines, on a continuum which grows stronger at higher energy. At 48.4 eV photon energy, some new peaks appear at 39.5 eV and above.

Table 7

Rovibrational levels of  $DCN^{2+}\!(X\ ^3\Sigma^-)$  and  $DCN^{2+}\!(^1\Sigma^+)$ 

These may be due to the  ${}^{1}\Pi$  state, which should lie in the 40–41 eV energy range. The spectra of Fig. 2 are quite difficult to analyse even using our highly accurate ab initio calculations mainly because of ambiguity in the position of the  $(0,0,0) \leftarrow (0,0,0)$  transitions (even using isotopic shifts) and the overlap between all the vibrational progressions. Fig. 7 gives a tentative partial simu-

tional progressions. Fig. 7 gives a tentative partial simulation of the experimental spectrum using our computed energies of the rovibrational levels and FCFs (cf. Tables 4-6) and assuming 50 meV experimental resolution. The double ionisation energies can not be computed accurately (typically within  $\pm 0.1$  eV even with the most accurate theoretical methods as the ones used in the present  $\text{HCN}^{2+}$   $X^{3}\Sigma^{-}(0,0,0) \leftarrow \text{HCN}$ Here, the work).  $X^{1}\Sigma^{+}(0,0,0)$  transition was put at 37.2662 eV and we have used the  $T_{\rm e}$  values of Table 2 to position the other excited states. We emphasize that these simulations are not unique, despite the good accord between the simulated and the measured spectra. To go further we need at least calculations of all the rovibronic levels with inclusion of all the couplings (such as Renner-Teller and vibronic interactions), and of the FCFs for all the electronic states. Better resolved experimental spectra will also be needed. Nevertheless, the present comparison shows good agreement on vibrational spacings,

$X^{3}\Sigma^{-}$				$^{1}\Sigma^{+}$			
$\sigma^+ (J=0)$		$\pi (J=1)$		$\sigma^+ (J=0)$		$\pi (J=1)$	
$(v_1, v_2, v_3)$	Energy $(cm^{-1})$	$(v_1, v_2, v_3)$	Energy $(cm^{-1})$	$(v_1, v_2, v_3)$	Energy $(cm^{-1})$	$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )
(0,0,0)	0	(0,1,0)	405	(0,0,0)	0	(0,1,0)	479
(0,2,0)	803	(0,3,0)	1204	(0,2,0)	956	(0,3,0)	1436
(0,0,1)	1212	(0,1,1)	1623	(0,0,1)	1166	(0,1,1)	1650
(0,4,0)	1599	(0,5,0)	1996	(1,0,0)	1804	(1,1,0)	2271
(1,0,0)	1804	(1,1,0)	2196	(0,4,0)	1911	(0,5,0)	2391
(0,2,1)	2027	(0,3,1)	2433	(0,2,1)	2128	(0,3,1)	2611
(0,6,0)	2388	(0,7,0)	2782	(0,0,2)	2311	(0,1,2)	2799
(0,0,2)	2405	(0,1,2)	2821	(1,2,0)	2734	(1,3,0)	3202
(1,2,0)	2581	(1,3,0)	2968	(0,6,0)	2866	(0,7,0)	3345
(0,4,1)	2832	(0,5,1)	3233	(1,0,1)	2950	(1,1,1)	3421
(1,0,1)	2998	(1,1,1)	3396	(0,4,1)	3088	(0,5,1)	3570
(0,8,0)	3170	(0,9,0)	3562	(0,2,2)	3280	(0,3,2)	3765
(0,2,2)	3229	(0,3,2)	3639	(0,0,3)	3436	(0,1,3)	3928
(1,4,0)	3351	(1,5,0)	3735	(2,0,0)	3539	(2,1,0)	3994
(2,0,0)	3570	(2,1,0)	3949	(1,4,0)	3665	(1,5,0)	4132
(0,0,3)	3580	(0,1,3)	4000	(0,8,0)	3820	(0,9,0)	4298
(0,6,1)	3628	(0,7,1)	4026	(1,2,1)	3888	(1,3,1)	4359
(1,2,1)	3787	(1,3,1)	4180	(0,6,1)	4045	(0,5,2)	4525
(0,10,0)	3948	(0, 11, 0)	4337	(1,0,2)	4077	(1,1,2)	4553
(0,4,2)	4041	(0,5,2)	4446	(0,4,2)	4243	(0,3,3)	4726
(1,6,0)	4115	(1,7,0)	4497	(0,2,3)	4411		
(2,0,1)	4176	(2,1,1)	4579	(2,2,0)	4446		
(2,2,0)	4322	(2,3,0)	4698	(0,0,4)	4543		
(0,2,3)	4412	(0,9,1)	4811	(1,6,0)	4595		
(0,8,1)	4417	(0,3,3)	4825	(0,8,1)	4671		
(1,4,1)	4567			(0, 10, 0)	4771		
(0,12,0)	4720			(1,4,1)	4825		
(0,0,4)	4739						
(1,0,2)	4754						

Table 8

Rovibrational levels of  $DCN^{2+}(^1\Delta)$  and  $DCN^{2+}(^1\Pi)$  (in  $cm^{-1})$  using similar approach for  $HCN^{2+}(^1\Delta)$  and  $HCN^{2+}(^1\Pi)$ 

$\text{DCN}^{2+}(^{1}\Delta)$		$\mathrm{DCN}^{2+}(^{1}\Pi)$			
$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )	$(v_1, v_2, v_3)$	Energy (cm <sup>-1</sup> )		
(0,0,0)	0	(0,0,0)	0		
(0,2,0)	916	(0,2,0)	805		
(0,0,1)	1194	(0,0,1)	1036		
(1,0,0)	1801	(0,4,0)	1575		
(0,4,0)	1838	(0,2,1)	1769		
(0,2,1)	2117	(1,0,0)	1824		
(0,0,2)	2364	(0,0,2)	2108		
(1,2,0)	2689	(0,6,0)	2314		
(0,6,0)	2764	(1,2,0)	2529		
(1,0,1)	2971	(0,4,1)	2602		
(0,4,1)	3044	(0,2,2)	2809		
(0,2,2)	3292	(0,0,3)	2862		
(0,0,3)	3511	(0, 8, 0)	3071		
(2,0,0)	3536	(1,0,2)	3216		
(1,4,0)	3584	(0,6,1)	3310		
(0,8,0)	3693	(1,2,1)	3373		
(1,2,1)	3867	(0,2,3)	3528		
(0,6,1)	3975	(2,0,0)	3586		
(2,0,1)	4120	(0,4,2)	3625		
(0,4,2)	4224	(0, 8, 0)	3885		
(2,2,0)	4398	(1,2,2)	3914		
(0,2,3)	4443	(0,0,4)	3963		
(1,6,0)	4484				
(0,10,0)	4623				
(0,0,4)	4636				
(1,0,2)	4691				

confirming the dominance of the CN stretching mode excitation during the double photoionisation of HCN. The spacings calculated between the higher levels of CN progressions ( $v_3 \ge 3$ ) agree well with the observed spacings of the resolved lines. Moreover, these simulations suggest that the lines up to about 38 eV probably arise from the two lowest electronic states. Intermediate



Fig. 7. HCN TOF-PEPECO spectrum of Fig. 2 together with the calculated spectra (see text for more details). We have added  $\sim$ 50 meV to the  ${}^{1}\Pi$  T<sub>e</sub> value (cf. Table 1) in order to match better the TOF-PEPIPICO spectrum for the  ${}^{1}\Pi$  state.

lines at 38–38.75 eV must be blends of lines from the lower states with a dominant contribution of  ${}^{1}\Delta$ . Above 38.8 eV the main contributor is  ${}^{1}\Sigma^{+}$ . Finally, we cannot exclude the excitation of odd and/or even quanta of bending in the experimental spectra specially when anharmonic and/or vibronic and/or Renner–Teller interactions are involved, as we have already observed such excitation in the simple photoionisation of triatomic molecules [35–39].

We turn now to the analysis of the PEPIPICO spectra (Fig. 4), in light of the potential energy curve calculations. In Figs. 8 and 9, we show how the singlet and triplet electronic states of  $HCN^{2+}$  lying in the 0–4 eV internal energy range evolve along the  $R_{\rm CH}$  and  $R_{\rm CN}$ coordinates. The triplets cross the singlets at several  $R_{\rm CH}$  and  $R_{\rm CN}$  distances thus allowing spin-orbit predissociation processes to occur. The spin-orbit selection rules are relaxed for bent geometries so that the conversion of the  $HCN^{2+}$  ions from one multiplicity to the other is feasible leading to the dissociation products. By examining the curve of Figs. 8 and 9, one can see that breaking the CH bond should be much easier than breaking CN, since the potential barrier of the X  ${}^{3}\Sigma^{-}$ along the  $R_{CH}$  coordinate (~1.67 eV) is smaller that along  $R_{\rm CN}$  (~2.31 eV). The height of this barrier may be less for bent structures of the dication, which is consistent with the estimation of the PEPIPICO barrier height of  $\sim 1.3 \pm 0.2$  eV {i.e.,  $38.5 \pm 0.2$  eV (Section 4.2) - 37.2 (IP of HCN<sup>2+</sup> X<sup>3</sup> $\Sigma^{-}$ )}. The HCN<sup>2+</sup>  $\rightarrow$  H<sup>+</sup> + CN<sup>+</sup> reaction is expected to take place at least along the lowest <sup>3</sup>A" PEFs resulting from the  $X^{3}\Sigma^{-}-{}^{3}\Pi$  conical intersection. The metastable HCN<sup>2+</sup> ions observed experimentally are probably formed in the low-lying vibrational levels of the X  $^{3}\Sigma^{-}$  and/or  $^{1}\Delta$ and/or  ${}^{1}\Sigma^{+}$  electronic states.



Fig. 8. Interaction between the singlets and the triplets along the  $R_{CH}$  distance. The  $R_{CN}$  distance is set to 2.53 bohr.



Fig. 9. Interaction between the singlets and the triplets along the  $R_{\rm CN}$  distance. The  $R_{\rm CH}$  distance is set to 2.205 bohr.

#### 6. Conclusion

Our experimental resolution has allowed the observation of vibrationally resolved spectra of HCN<sup>2+</sup> with very complex structures due to vibronic and Renner-Teller interactions. The comparison between the experimental and calculated spectra showed that the observed structures are mainly due to the CN mode excitations and to combination modes involving minor contributions from the CH stretch, despite the longer  $R_{\rm CH}$  and  $R_{\rm CN}$  distances in the dication relative to the neutral HCN X  ${}^{1}\Sigma^{+}$ . We stress the difficulty in this case of locating the HCN<sup>2+</sup>(0,0,0)  $\leftarrow$  HCN(0,0,0) transitions because of relatively small FCFs for the direct double ionisation. Metastable  $HCN^{2+}$  dications are found to be formed in the low lying ro-vibrational levels of X  $^3\Sigma^-$  and/or  $^1\Delta$  and/or  $^1\Sigma^+$  electronic states. The efficient  $HCN^{2+} \rightarrow H^+ + CN^+$  dissociation occurring for internal energies greater than  $\sim 1.3 \pm 0.2$  eV takes place along the lowest <sup>3</sup>A" PEFs and probably involves vibronic, Renner-Teller and spin-orbit couplings.

## Acknowledgements

M.H. thanks the NERSC (UC Berkeley, USA) for computational time. We acknowledge the financial support of the EPSRC for the experimental part of the work.

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