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Electronic and infrared absorption spectra of $NCCN^+$

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The article is dedicated to the memory of Professor Werner Lindinger.

Abstract

The $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of the $NCCN^+$ cation has been observed in a 5 K neon matrix with origin band at $33{,}522 \pm 23\,cm^{-1}$. The origin of the $B^2\Sigma_u{}^+ \leftarrow X^2\Pi_g$ system is assumed to be the band at $11{,}486 \pm 3\,cm^{-1}$. In the infrared, the $\sigma_u{}^+$ vibrational mode is detected at $1799.5 \pm 1\,cm^{-1}$. Theoretical calculations demonstrate that $D^2\Pi_u$ is a nonlinear shake-up state and possesses *cis*- and *trans*-bent/bent Renner–Teller minima, in contrast to the $X^2\Pi_g$ and $C^2\Pi_u$ states which are linear. The complex vibronic progression in the absorption spectrum in a neon matrix to the $D^2\Pi_u$ state does not provide direct evidence for the two possible isomers. The stretching modes are assigned while the active bending modes coupled by the Renner–Teller effect will require additional studies. In the energy region of the $D^2\Pi_u$ state lie several quartet states. The $D^2\Pi_u$ state forms a conical intersection in C_s symmetry with $B^2\Sigma_u{}^+$ close to its barrier to linearity. The latter state crosses in linear structures also the $C^2\Pi_u$ state and along the *cis*-bending coordinates the $A^2\Sigma_g{}^+$ state. Because the $B^2\Sigma_u{}^+$ state intersects conically with three electronic states, the vibronic and Renner–Teller couplings complicate the assignments of the vibronic progressions observed. (Int J Mass Spectrom 223–224 (2003) 107–114)
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Keywords: $NCCN^+$; Electronic and infrared spectra; Potential energy surfaces

1. Introduction

When hydrogen cyanide was identified in dark interstellar clouds, other aza compounds became a subject of scientific interest due to their possible presence [1]. The observation of a number of asymmetric cyanopolyacetylenes $H(C{\equiv}C)_nCN$ ($n = 1-5$) by means of microwave spectroscopy confirmed that the larger molecules containing cyano groups can indeed exist in space [2,3]. Moreover, some of them have either been identified in the atmosphere of the Saturn's largest satellite Titan or are predicted to occur there [4–7]. In contrast to the asymmetric aza molecules $H(C{\equiv}C)_nCN$, detection of the symmetric $NC(C{\equiv}C)_nCN$ ones by microwave transitions is hampered by the lack of a permanent dipole moment. However, there is every reason to suppose that such molecules are also present in dark interstellar clouds. Cyanogen, the smallest of them, is stable under normal conditions and, therefore, has already been the subject of exhaustive studies. The spectroscopic characterisation of the cation is incomplete.

The first studies of $NCCN^+$ were by photoelectron spectroscopy and provided information on the energy of the electronic states, [8] as well as on the geometry of the lowest two states from a Franck–Condon

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analysis of the vibrational structure in the spectra [9]. Later $NCCN^+$ was produced in a 5 K neon matrix by photoionisation of cyanogen leading to the observation of the absorptions of two dipole-allowed electronic transitions out of the ground state [10]. As a result of the experimental and theoretical [11,12] studies, three excited electronic states, $A^2\Sigma_g{}^+$, $B^2\Sigma_u{}^+$ and $C^2\Pi_u$, in addition to the electronic ground state $X^2\Pi_g$ are known.

The present article reports observation of the fourth excited electronic doublet state, $D^2\Pi_u$, as well as reassignment of the vibrational structure in the $B^2\Sigma_u{}^+ \leftarrow X^2\Pi_g$ band system and the $\sigma_u{}^+$ infrared (IR) fundamental band of $NCCN^+$ in solid neon. Ab initio calculations carried out provide information on the electronic excited states, behaviour of their potential energy functions and anharmonic vibrational frequencies for the $X^2\Pi_g$ electronic ground state of this cation.

2. Experimental

The apparatus employed combines mass selection with matrix isolation spectroscopy [13]. The ions were generated in a hot cathode discharge source from a mixture of cyanogen and helium in a ratio of 1:4. Ion currents between 200 and 240 nA were attained. The $C_2N_2{}^+$ cations were co-deposited with excess of neon onto a rhodium-coated sapphire substrate maintained at 5 K during 4 h. The regions 220–1100 nm and 1200–4000 cm^{-1} were then scanned using wave-guide (path length ∼2 cm) and reflection (path length ∼750 μm) techniques for the two regions, respectively. After the matrix had been irradiated with a medium pressure mercury lamp (∼5.4 eV), the usual procedure to eliminate cations, the spectra were recorded anew.

3. Theoretical

Six-dimensional potential energy functions (PEFs) have been generated by the RCCSD(T) approach [14,15] for the upper A″ component of the $X^2\Pi_g$ electronic ground state of $NCCN^+$ and its isomer $CNCN^+$. Parts of their PEFs for the electronically excited doublet and quartet states have been calculated by state averaged CASSCF method [16,17]. The correlation consistent cc-pVTZ or cc-pVQZ atomic orbital basis sets of Dunning have been used [18,19]. All computations have been performed with the MOLPRO program suite [20]. In the computations of the electronic ground state all valence electrons were correlated, whereas in the CASSCF wavefunctions the lowest 7a′ molecular orbitals were not active.

This limitation has been imposed by the large number of CSFs resulting for complete valence space. In the present approach with 9a′ and 4a″ active molecular orbitals, the CASSCF wavefunctions comprised more than 490,000 CSFs in C_s symmetry. All states with the same multiplicity were averaged together with equal weights. The aim of the electronic structure calculations was to qualitatively describe the characteristics of the electronic states, particularly the location of possible conical intersections leading to vibronic couplings. The nuclear motion problem was solved only for the A″ component of the electronic ground state of both isomers by a second order perturbation theory, using spectroscopic constants from a quartic force field in dimensionless normal coordinates (Table 1). These computations showed that the stretching modes are coupled with the bending modes and the solution of the nuclear motion problem with a reduced dimensionality—for linear structure only—did not yield anharmonic vibrational transition energies accurate enough to distinguish between the $NCCN^+$ and $CNCN^+$ isomers for the asymmetric stretching mode. A full six-dimensional treatment

Table 1
Anharmonic vibrational frequencies (cm^{-1}) for the $X^2\Pi_g$ ground states of $NCCN^+$ and $CNCN^+$ obtained at the RCCSD(T)/VQZ level

Mode	$NCCN^+$, $X^2\Pi_g$	$CNCN^+$, $X^2\Pi$
1. $\sigma_{(g)}{}^+$	2300	2033
2. $\sigma_{(g)}{}^+$	808	963
3. $\sigma_{(u)}{}^+$	1789	1731
4. $\pi_{(g)}$	537	465
5. $\pi_{(u)}$	240	163

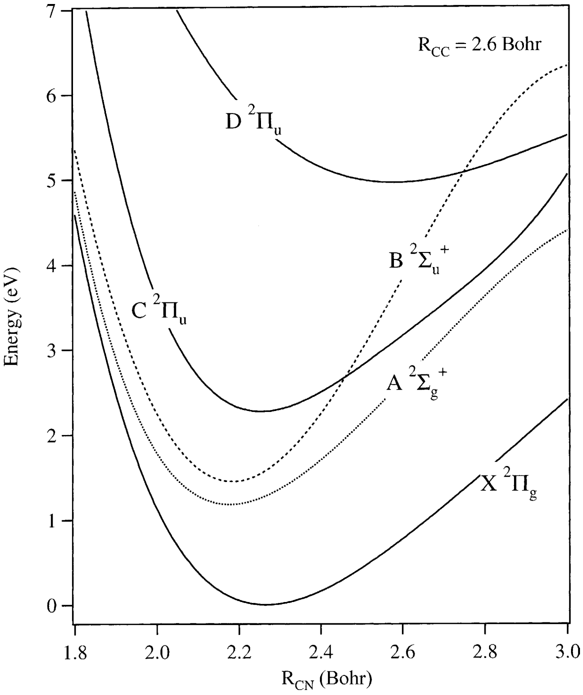

Fig. 1. One-dimensional cuts of the collinear centrosymmeric part of the CASSCF potential energy functions of the NCCN$^+$ electronic excited states along the CN coordinate.

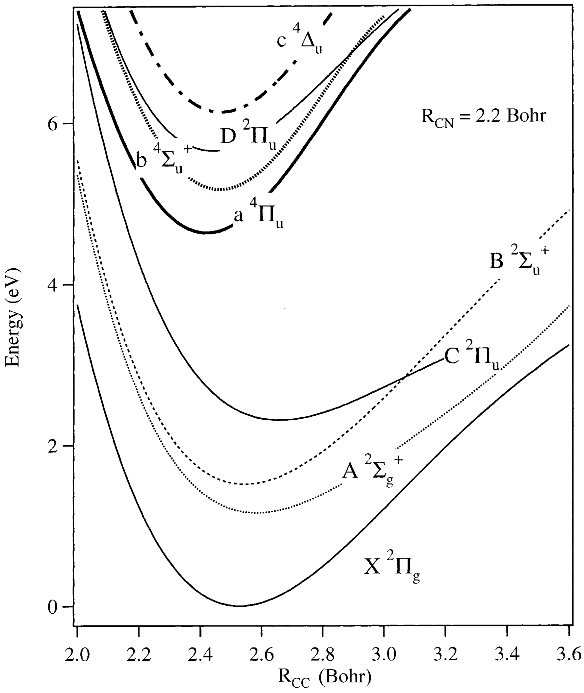

Fig. 2. One-dimensional cuts of the collinear centrosymmeric parts of the CASSCF potential energy functions of the NCCN$^+$ electronic excited states along the CC coordinate.

of the Renner–Teller problem in electronically degenerate states of tetra-atomic molecules remains a challenging theoretical problem particularly if conical intersections lead to additional vibronic coupling.

The one-dimensional cuts of the CASSCF PEFs for linear geometries along the CN stretch (Fig. 1) and CC stretch (Fig. 2) show that the $B^2\Sigma_u{}^+$ state PEF crosses that of $C^2\Pi_u$, and its A′ component forms a conical intersection leading to vibronic coupling between both electronic states. Another conical intersection has been located between the $B^2\Sigma_u{}^+$ and $A^2\Sigma_g{}^+$ states for the *trans*-bending coordinate. In Fig. 3, the CASSCF PEFs of both states cross around 140° at the NCCN$^+$ ground state equilibrium bond lengths (cf. Table 2). On the other hand, the PEFs do not cross either along the *cis*-bending coordinate (Fig. 4) or along the NCC-bending coordinate (Fig. 5) in the investigated geometry region of the six-dimensional PEFs.

The two-dimensional parts of the PEFs displayed in Fig. 6 for the $X^2\Pi_g$ and $D^2\Pi_u$ states along the CN

Table 2
Equilibrium geometry, electronic configuration and excitation energies of the lowest excited states of NCCN$^+$

State	R_e(CC) (Bohr)	R_e(CN) (Bohr)	Electronic configuration	T (eV) calculated	T_0 (eV) experiment
$X^2\Pi_g$	2.53	2.26	$\sigma_u{}^2\sigma_g{}^2\pi_u{}^4\pi_g{}^3$	0[a]	0
$A^2\Sigma_g{}^+$	2.58	2.18	$\sigma_u{}^2\sigma_g{}^1\pi_u{}^4\pi_g{}^4$	1.16	1.13 [8]
$B^2\Sigma_u{}^+$	2.54	2.19	$\sigma_u{}^1\sigma_g{}^2\pi_u{}^4\pi_g{}^4$	1.45	1.42[b]
$C^2\Pi_u$	2.66	2.25	$\sigma_u{}^2\sigma_g{}^2\pi_u{}^3\pi_g{}^4$	2.27	2.11 [10]
$D^2\Pi_u$	2.44	2.58	$\sigma_u{}^2\sigma_g{}^2\pi_u{}^4\pi_g{}^2\pi_u{}^1$	4.3	4.16[b]

[a] CASSCF total energy at the equilibrium geometry of the $X^2\Pi_g$ state: −184.4183213 a.u. (VQZ basis set).

[b] Present study.

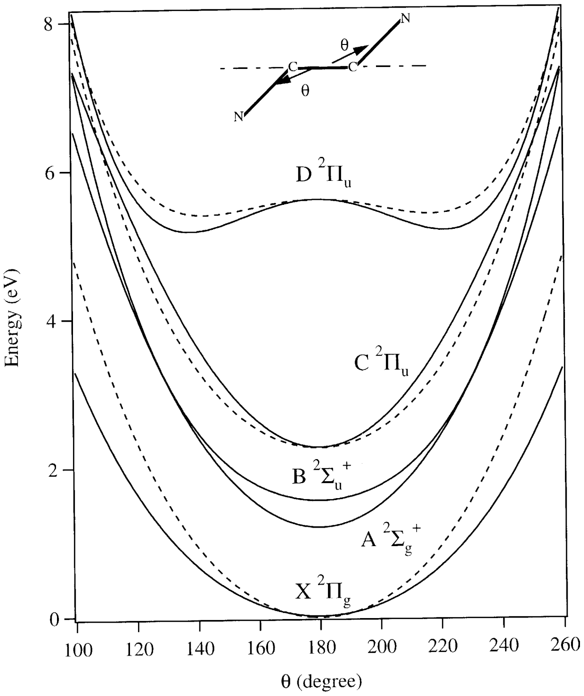

Fig. 3. One-dimensional cuts of the *trans*-bending centrosymmeric part of the CASSCF potential energy functions of the NCCN$^+$ electronic excited states along the CCN angle. The A′ states are drawn with full lines, the A″ states with dashed lines.

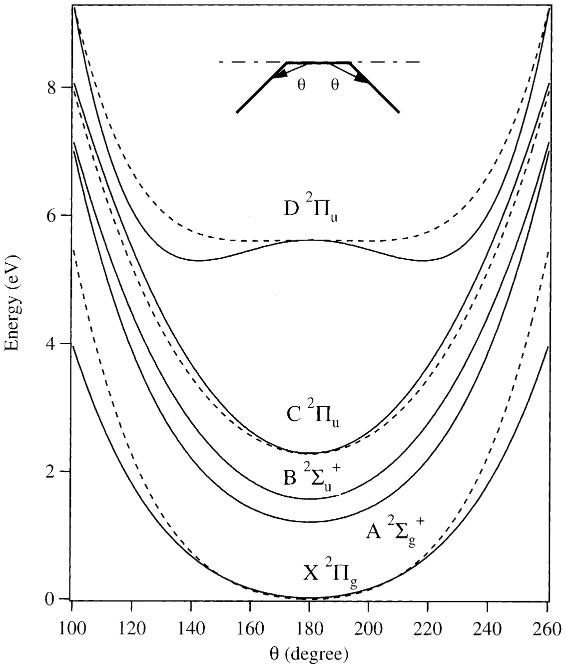

Fig. 4. One-dimensional cuts of the *cis*-bending part of the CASSCF potential energy functions of the NCCN$^+$ electronic excited states along the CCN angle. The A′ states are drawn with full lines, the A″ states with dashed lines.

and CC distances in linear centrosymmetic structure of NCCN$^+$ are common to both electronic Renner–Teller components. In the $D^2\Pi_u$ state both CN and CC distances differ strongly from the electronic ground state (Table 2).

4. Results and discussion

The trapping of the mass-selected $C_2N_2^+$ ions in a neon matrix gave rise to a number of absorptions in the 220–1100 nm region. Some of these (C_2, CN, CNC and N_2^+) are due to impurities and fragmentation of the deposited ions, which hit the matrix substrate with ~50 eV kinetic energy, as well as to products of reactions between them. Other absorptions resemble those reported in the previous matrix study [10], and belong to the known $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ and $C^2\Pi_u \leftarrow X^2\Pi_g$ electronic transitions of NCCN$^+$.

However, a group of three bands (at 11,486, 11,770 and 12,000 cm^{-1}) to the red from the reported origin band of the $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ electronic transition of NCCN$^+$, as well as a system of bands starting at 33,522 cm^{-1} and expanding to the UV, have been observed for the first time.

Bands of the system lying in the near IR region have a triplet site structure (Fig. 7). The first transition overlaps with the band associated with vibrational excitation as part of the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ electronic transition of the C_2 molecule. The bands of the latter absorption consist of four components (site structure) in the spectra measured. Strong absorptions due to CN, as seen in the figure, might obscure some members of the $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ system. The group of bands in the UV overlaps with the $A^2\Delta_u \leftarrow X^2\Pi_g$ and the $B^2\Sigma_u^- \leftarrow X^2\Pi_g$ electronic transitions of CNC [21,22] (Fig. 8). The unknown bands of the UV and near IR band systems disappear after photobleaching

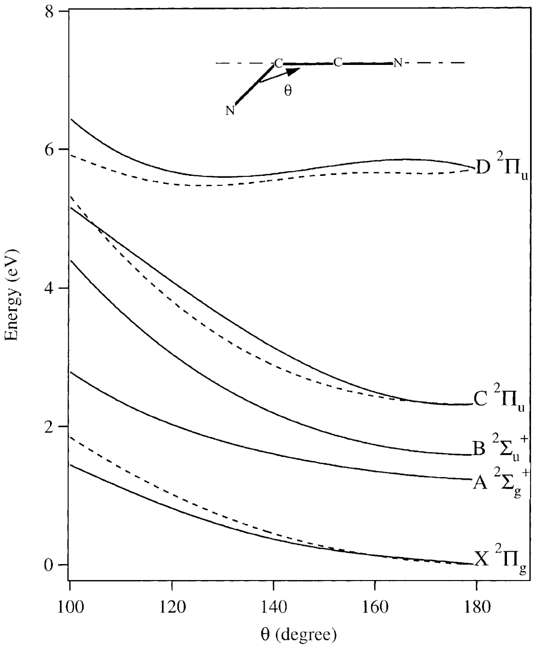

Fig. 5. One-dimensional cuts of the NCC bending part of the CASSCF potential energy functions of the NCCN$^+$ electronic excited states for the NCC angle. The A′ states are drawn with full lines, the A″ states with dashed lines.

which indicates that the carrier is ionic. They vanish after the same period of exposure to 5.4 eV radiation from the medium pressure mercury lamp as the $C^2\Pi_u \leftarrow X^2\Pi_g$ absorptions of NCCN$^+$. In view of this and the mass selection, the assignment of the bands to absorption of the NCCN$^+$ cation is indicated. In addition, an absorption band at 1799.5 cm^{-1} is observed in the IR region. It also vanishes after UV irradiation and is, therefore, attributed to the $C_2N_2^+$ cation.

4.1. $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ electronic transition

In the previous matrix study the band lying at 12,269 cm^{-1} was reported to be the origin of the $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ electronic transition of NCCN$^+$, though the authors were not entirely sure [10]. Fig. 7 shows that the site structure of this band is similar to the ones observed at 11,486, 11,770 and 12,000 cm^{-1}. It appears that the band at 11,486 cm^{-1} is the origin of the $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ electronic transition of the NCCN$^+$ cation as no other bands are observed to the red which would be displaced by the appropriate

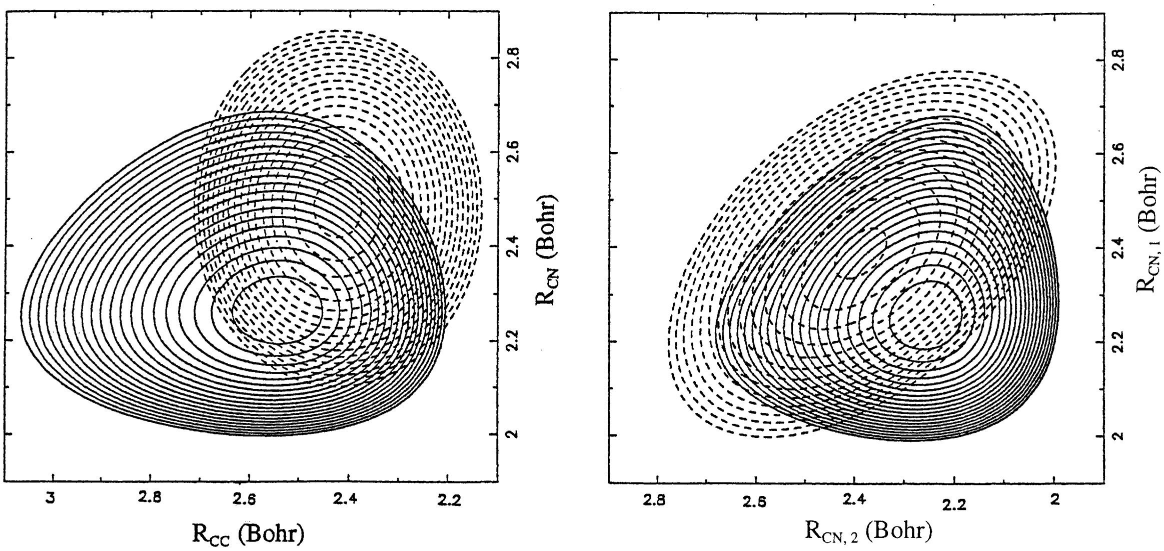

Fig. 6. Collinear two-dimensional plots of the potential energy functions (500 cm^{-1} intervals) for the $X^2\Pi_g$ state (full line) and for the $D^2\Pi_u$ state (broken line) of the NCCN$^+$ cation along the both CN distances (right trace), and the CN and CC distances (left trace). The third R_i in each plot has been kept fixed at its equilibrium value (cf. Table 2).

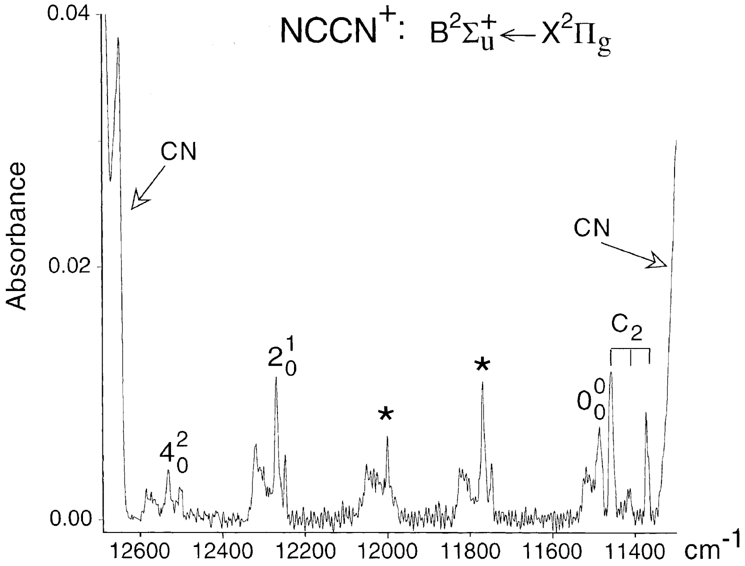

Fig. 7. Electronic absorption spectrum of the $B^2\Sigma_u{}^+ \leftarrow X^2\Pi_g$ electronic transition of NCCN$^+$ recorded after 4 h of mass-selected co-deposition with neon to form a 5 K matrix.

interval. This differs from the energy obtained computationally by only 2%.

The first and the second vibronic bands in the $B^2\Sigma_u{}^+ \leftarrow X^2\Pi_g$ spectrum (marked with asterisks in Fig. 7) correspond to spacings of 283 and 514 cm^{-1}, respectively. These intervals are too small for any of the stretching modes (Table 1) and could only correspond to the single excitation of the bending modes which are normally forbidden by symmetry. However, in the spectrum they are intense. Thus, in view of the

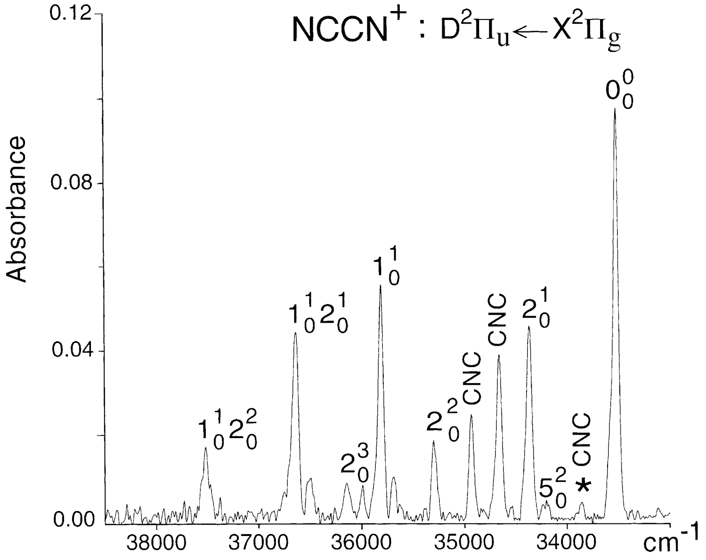

Fig. 8. Electronic absorption spectrum of the $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of NCCN$^+$ recorded after 4 h of mass-selected co-deposition with neon to form a 5 K matrix.

calculations which indicate conical intersections between the $B^2\Sigma_u{}^+$ and three other electronic states, it is suggested that these bands arise due to coupling between vibrational modes of the $A^2\Sigma_g{}^+$ and the $B^2\Sigma_u{}^+$ electronic states. This situation seems to be similar to that observed previously for the isoelectronic $C_4{}^-$ ion [23]. A detailed prediction of the levels accessible as result of this interaction is not feasible at present. Besides these absorptions, excitations of one quantum of the ν_2 and two quanta of the ν_4 modes can be seen (Table 3).

4.2. $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition

The first band (at 33,522 cm^{-1}) of the system detected in the UV region is close to the value calculated for the $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of the $NCCN^+$ cation. Furthermore, the calculations show that the $CNCN^+$ cation, the presence of which cannot a priori be ruled out because the absorptions of the neutral CNCN are observed in the IR, possesses no state in the region where the electronic transition occurs (Table 4). Therefore, the band system is assigned to the $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of the $NCCN^+$ cation. The difference between the experimental and theoretical excitation values is 3.5%. As can be seen from the dominant electron configuration given in Table 2, the $D^2\Pi_u$ state is classified as a shake-up one.

The next two strongest absorptions present in the spectrum of the $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of the $NCCN^+$ cation are assigned to excitations of the ν_1 and ν_2 stretching modes. Considerable differences in the CN and CC bond lengths for the $X^2\Pi_g$ and the $D^2\Pi_u$ electronic states (Table 2) are predicted by the calculations and account for the Franck–Condon activity of these stretching modes. Although the structure of the bending and the combination levels cannot be properly distinguished due to the complex bent/bent Renner–Teller problem in the $D^2\Pi_u$ electronic state, a tentative assignment of the weak features on either side of the 2_0^1 band (Fig. 8) to double excitations of the ν_4 and ν_5 bending vibrations is suggested. Some combination bands involving these modes are also present (Table 5). The feeble absorption marked with an asterisk in the figure cannot belong to the $NCCN^+$ cation because it persists after exposure to the UV irradiation. Moreover, this band is also observed following mass-selected deposition of the C_2N^+ ions (the published article does not report spectra for this region) [21]. It appears that the band belongs to the $A^2\Delta_u \leftarrow X^2\Pi_g$ electronic transition of CNC, the origin of which is at 30,303 cm^{-1} in solid neon [21].

Table 3
Positions of the band maxima (±0.2 nm) observed for the $B^2\Sigma_u{}^+ \leftarrow X^2\Pi_g$ electronic transition of $NCCN^+$ in a 5 K neon matrix and the suggested assignment

λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$(cm^{-1})	Assignment
870.6	11,486.4	0	0_0^0
868.2	11,518.3	32	
851.2	11,747.5	261	[a]
849.6	11,769.6	283	
845.6	11,826.0	340	
834.6	11,982.2	496	[a]
833.3	12,000.2	514	
829.8	12,051.0	565	
816.5	12,247.8	761	2_0^1
815.0	12,269.6	783	
811.7	12,319.1	833	
799.9	12,502.1	1016	4_0^2
798.0	12,531.6	1045	
794.6	12,585.5	1099	

[a] Arise as result of vibronic interaction between the $B^2\Sigma_u{}^+$ and $A^2\Sigma_g{}^+$ electronic states.

Table 4
Calculated equilibrium geometry, electronic configuration and vertical excitation energies of the lowest excited states of $CNCN^+$

State	R_e(CN) (Bohr)	R_e(CN) (Bohr)	R_e(NC) (Bohr)	Electronic configuration	T_0 (eV) calculated
$X^2\Pi$	2.32	2.36	2.30	$\sigma^2\sigma^2\pi^4\pi^3$	0[a]
$^2\Sigma^+$	–	–	–	$\sigma^2\sigma^1\pi^4\pi^4$	0.43
$^2\Sigma^+$	–	–	–	$\sigma^1\sigma^2\pi^4\pi^4$	2.22
$^2\Pi$	–	–	–	$\sigma^2\sigma^2\pi^3\pi^4$	3.89
$^2\Delta$	–	–	–	$\sigma^2\sigma^1\pi^4\pi^3\pi^1$	5.34
$^2\Pi$				$\sigma^2\sigma^2\pi^4\pi^2\pi^1$	5.37

[a] CASSCF total energy at the equilibrium geometry of the $X^2\Pi$ state: −184.38490823 a.u. (VQZ basis set).

Table 5
Positions of the band maxima (±0.2 nm) observed for the $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transition of $NCCN^+$ in a 5 K neon matrix and the suggested assignment.

λ (nm)	$\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	Assignment
298.3	33,521.9	0	0_0^0
292.4	34,202.1	680	5_0^2
291.0	34,366.9	845	2_0^1
289.5	34,536.4	1015	4_0^2
287.2	34,819.0	1297	5_0^4
283.3	35,300.7	1779	2_0^2
280.1	35,696.6	2175	$2_0^1 5_0^4$
279.3	35,807.2	2285	1_0^1
277.9	35,989.1	2467	$2_0^2 5_0^2$
276.7	36,140.6	2619	2_0^3
274.1	36,489.2	2967	$1_0^1 5_0^2$
273.0	36,631.6	3110	$1_0^1 2_0^1$
266.6	37,513.6	3992	$1_0^1 2_0^2$

4.3. *IR spectrum*

The band observed in the IR region at 1799.5 cm^{-1} is assigned to ν_3 (σ_u^+) fundamental of $NCCN^+$ by comparison with anharmonic vibrational frequencies calculated for the $X^2\Pi_g$ ground states of $NCCN^+$ and $CNCN^+$ isomers (Table 1).

5. Conclusion

Dicyano compounds and their cations can be expected to occur in interstellar clouds but are not accessible for identification by microwave spectroscopy. Thus, their IR and electronic spectra are of importance and may be the way to search for these molecules in space. The object of this study, $NCCN^+$, is one of the smallest dicyano compounds. Observation of its $B^2\Sigma_u^+ \leftarrow X^2\Pi_g$ and $D^2\Pi_u \leftarrow X^2\Pi_g$ electronic transitions with origin bands at 11,486 cm^{-1} and 33,522 cm^{-1}, respectively, as well as of its asymmetric stretching mode in the electronic ground state at 1799.5 cm^{-1}, provides a valuable aid for future gas phase measurements.

Several conical intersections in the electronic excited states of the $NCCN^+$ ion have been located by ab initio calculations at CASSCF level of theory. The electronically degenerate $^2\Pi$ states form linear/linear ($X^2\Pi_g$ and $C^2\Pi_u$ states) and *cis*-bent/bent as well as *trans*-bent/bent ($D^2\Pi_u$) Renner–Teller pairs. The quartet states have been calculated to lie above the $C^2\Pi_u$ state.

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