The A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma^+_{(g)}$ Electronic Transition of CCN^+ and CNC^+

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Dedicated by *J.P.M.* to *Edgar Heilbronner* on the occasion of his 80th birthday as reminder of all the years together in the 'Physikalisch-Chemische Anstalt' and the common SNF projects.

The electronic absorption spectra of the A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma^+_{(g)}$ transition of CCN^+ and CNC^+ have been observed in a 5 K Ne matrix after mass selection of C_2N^+. CCN^+ has the origin band at 462.0(2) nm. The vibrational structure with frequencies 1223(20) and 1725(20) cm^{-1} corresponds to the symmetric and antisymmetric stretching modes in the excited state. The origin band of CNC^+ is observed at 325.7(2) nm, and the system shows extensive vibrational excitation. Calculations of the potential energy functions of CCN^+ and CNC^+ in their X $^1\Sigma^+_{(g)}$ ground state and the A $^1\Pi$ state of CCN^+ followed by variational evaluation of the rovibronic energy levels allows the assignment of the observed spectra. These spectroscopic data open the way to gas-phase studies of the astrophysically important C_2N^+ ions.

1. Introduction. – The C_2N^+ species is expected to be one of the most abundant cations in the interstellar medium though it has not yet been detected [1]. The CNC^+ isomer is predicted to be more stable than CCN^+ by *ca.* 1 eV [2]. It has been suggested that their formation in dense interstellar clouds occurs *via* ion-molecule reactions leading selectively to the formation of one or the other isomer [3]:

$$C^+ + HCN \rightarrow CNC^+ + H$$

$$C^+ + HNC \rightarrow CCN^+ + H$$

The detection of HCN and HNC in the interstellar medium by radio astronomy shows that they are both ubiquitous and abundant [4]. The large rate constant measured for the reaction of C^+ with HCN supports the mechanism [5]. Studies on the chemical reactivity of CNC^+ and CCN^+ with, for example, H_2, CH_4, C_2H_2, NH_3 indicate that CCN^+ is much more reactive than CNC^+ and lead to no doubt about the stability of the latter in the interstellar medium [6][7].

The rotationally resolved infrared gas-phase spectrum of the antisymmetric stretch vibration ν_3 of CNC^+ has been observed [8]. Additional information about the electronic ground state of both isomers was obtained by *ab initio* calculations [2][9][10]. However, the electronic spectra of these ions are unknown. This is of relevance to the observations of absorption features through diffuse interstellar clouds.

In the present study the experimental detection of the A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma^+_{(g)}$ electronic transition of both isomers in a Ne matrix after mass selection of C_2N^+ is reported. *Ab initio*-calculated potential energy function (PEF) for the ground state of CCN^+ and CNC^+, and also for the electronically excited state of CCN^+, has been used for the variational evaluation of the rovibrational levels allowing the assignment of the experimentally observed vibrational progressions.

2. Experiment. – The apparatus used combines mass-selection and matrix-isolation spectroscopy [11]. The C_2N^+ cations were produced in a hot-cathode discharge source from a mixture of cyanogen with He in the ratio 1:4. They passed through an electrostatic lens system, were selected in a quadrupole with unity mass resolution, and codeposited (*ca.* 40 eV kinetic energy) with an excess of Ne on a Rh-coated sapphire substrate cooled to 5 K. A matrix of 150-μm thickness was grown within 4 h. An ion current of 100 nA was maintained for mass 38u (C_2N^+). Absorption spectra in the range of 220–1100 nm were measured by passing the monochromatised light from a halogen or a Xe arc lamp through the matrix in a waveguide arrangement resulting in an absorption length of *ca.* 2 cm. A photomultiplier or a Si diode were used to detect the light. The IR spectra could be measured in the 1200–4000 cm^{-1} range by passing the output of a *Fourier*-transform spectrometer through *ca.* 750 μm of the matrix by reflecting it off the metal surface of the substrate. The measurements were repeated after irradiation of the matrix with the light of a medium-pressure Hg lamp ($E \leq$ 5.4 eV) to neutralize the trapped ions.

3. Theory. – The PEFs for the ground states of CCN^+ and CNC^+ were mapped using the CCSD(T) approach in which all valence electrons were correlated [12][13]. The subset of the *spdf* functions of *Dunning*'s cc-VQZ basis [14], comprising 138 contracted Gaussian-type orbitals, was used. All calculations were performed with the MOLPRO program [15]. 22 CCSD(T) Energies for different geometries near the equilibrium structures of CCN^+ and CNC^+ were used to evaluate the PEFs by fitting a quartic polynomial expansion in displacement coordinates, taking the predicted equilibrium geometry as reference to the *ab initio* energies:

$$V(R_1,R_2,\theta) = \Sigma_{\mathrm{ijk}} C_{\mathrm{ijk}} (q_1)^i (q_2)^j (q_3)^k$$

with $q_1 = R_1 - R^e{}_1$, $q_2 = R_2 - R^e{}_2$, $q_3 = \theta - \theta^e$ where R_1 and R_2 are the stretching coordinates and θ is the bond angle. The C_{ijk} coefficients were determined in a least squares fit of the energies.

Variational calculations of the rovibrational states were performed for $J = 0, 1, 2$, with the kinetic energy operator in internal coordinates and bisecting angle [16]. The primitive basis set consisted of products of pre-optimized harmonic oscillator eigenfunctions for the stretching modes, *Legendre* functions for the bending modes and rigid rotor eigenfunctions. The integration was performed numerically for the vibrational, and analytically for the rotational part.

Calculations for the electronically excited states of both cations were carried out with the complete active space self-consistent field (CASSCF) [17][18] and internally contracted multireference configuration interaction (MRCI) [19][20] approaches. In the CASSCF step, all valence orbitals were active. In the MRCI calculations, in which all valence electrons were correlated, reference configurations with a coefficient larger than 0.01 in the CI expansion were used. 22 MRCI Energies for geometries near the equilibrium structure of CCN^+ in the A $^1\Pi$ state were used to evaluate the PEFs. The rovibronic energy levels were obtained from variational *Renner-Teller* calculations on the PEFs [21]. The RHF wavefunctions of the A $^1\Pi_u$ state of CNC^+ are affected by symmetry breaking, *i.e.*, the minimum of the PEFs is found to be a non-centrosymmetric structure. It was not possible to remove this symmetry breaking even with a very large MRCI calculation using more than 4.5×10^6 internally contracted configurations (in C_s symmetry) and the full valence CASSCF wavefunctions as reference (more than 550 configuration state functions in C_s symmetry).

4. Results and Discussion. – The CCSD(T) three-dimensional potential-energy functions (PEFs) of the ground state X $^1\Sigma^+$ of CCN^+ were transformed to a quartic force field in dimensionless normal coordinates. The relevant spectroscopic constants obtained from this force field are given in *Table 1*. The predicted R_e values for CC = 1.381 Å and CN = 1.190 Å agree reasonably well with the 1.3803 and 1.1815 Å distances, respectively, obtained previously in a CI-SDQ approach [2].

Table 1. *Spectroscopic Constants Calculated for the X $^1\Sigma^+_{(g)}$ and A $^1\Pi_{(u)}$ States of CCN^+ and CNC^+*. The constants of the upper component (A′) in the A $^1\Pi$ state of CCN^+ are given in parentheses.

	CCN^+		CNC^+	
	X $^1\Sigma^+$	A $^1\Pi$	X $^1\Sigma^+_{(g)}$	A $^1\Pi_{(u)}$
R^e_{CC}/Å	1.381	1.257		
R^e_{CN}/Å	1.190	1.270	1.246	1.263
B_e/cm^{-1}	0.3945	0.4078	0.4523	0.4391
ω_1/cm^{-1}	1109.5	1146.3	1284.0	
ω_2/cm^{-1}	94.7	384.6 (461.6)	38.7	
ω_3/cm^{-1}	2167.3	1918.4	2018.0	
ε		0.1807		
α_1/MHz	57.2	82.1	59.6	
α_2/MHz	– 259.6	– 58.0 (– 32.4)	– 642.1	
α_3/MHz	99.5	112.8	122.9	
x_{11}/cm^{-1}	2.5	– 8.0	– 5.0	
x_{22}/cm^{-1}	4.0	– 7.5 (– 4.3)	127.7	
x_{33}/cm^{-1}	– 17.0	– 40.3	– 14.4	
x_{12}/cm^{-1}	29.6	12.9 (6.9)	49.9	
x_{13}/cm^{-1}	– 48.9	– 15.2	– 28.0	
x_{23}/cm^{-1}	– 17.7	– 5.3 (– 9.8)	– 48.4	

The rovibrational levels for $J = 0$, 1 and 2 have been obtained variationally up to 3000 cm^{-1} [22]. These data will be of interest when the gas-phase spectra are measured. The fundamental vibrational frequencies are $\nu_1 = 1088$ cm^{-1}, $\nu_2(J = 1) = 108$ cm^{-1}, and $\nu_3 = 2189$ cm^{-1}. The CI-SDQ approach yielded $\omega_1 = 1146$ cm^{-1}, ω_2 $(J = 1) = 153$ cm^{-1} and $\omega_3 = 2205$ cm^{-1} [2]. In the isoelectronic C_3 the corresponding experimental frequencies are $\nu_1 = 1226.6$ cm^{-1}, $\nu_2 = 63.41$ cm^{-1}, and $\nu_3 = 2040.019$ cm^{-1} [23], whereas in C_2B^-, calculated with the same approach as in the present work, they are $\nu_1 =$ 1014.7 cm^{-1}, $\nu_2 = 125.4$ cm^{-1}, and $\nu_3 = 1935.4$ cm^{-1} [24]. The frequencies of the bending modes of all three molecules are small, reflecting the shallow behavior for these parts of the PEFs.

The three-dimensional PEFs for the excited A $^1\Pi$ state of CCN^+ have been generated in a similar way as for the ground state but using the MRCI energies. The transition energy T_e is found to be 2.74 eV. *Table 1* lists the equilibrium distances, rotational constant, harmonic wavenumbers, and the *Renner-Teller* parameter, $\varepsilon = (\omega_{2-}^2 - \omega_{2+}^2)/(\omega_{2+}^2 + \omega_{2-}^2)$. The ω_{2+} and ω_{2-} signify the harmonic bending wavenumbers of the lower and the higher *Renner-Teller* components, respectively. The mean value of ω_2 is 423 cm^{-1}. The 328-cm^{-1} difference between the ω_2 values of the ground and the excited state is much larger than in the case of C_2B^- (204 cm^{-1} [25]) or C_3 (245 cm^{-1} [26]). The ε parameter 0.1807 is much smaller than in C_2B^- (0.4244) [25]. In *Table 2*, the vibronic levels for $J = 0$, 1 and 2 ($J = \mathrm{P}$) are given for energies up to 3000 cm^{-1}. The Π (1,0,0) fundamental transition is predicted to be at 1153 cm^{-1}, Σ^+ (0,1,0) at 334 cm^{-1}, Σ^- (0,1,0) at 490 cm^{-1}, and Π (0,0,1) at 1791 cm^{-1}. *Fig. 1* shows the two-dimensional contour plots of the PEFs for the ground and the excited states of the linear CCN^+ along the stretching coordinates. The excited state equilibrium bond lengths are predicted to be shorter by 0.124 Å for R_{CC}^e and longer by 0.080 Å for R_{CN}^e than in the electronic ground state.

The linear CNC^+ isomer also possesses a very shallow bending part of the PEF ($\omega_2 = 38.7$ cm^{-1}) in its electronic ground state. The R_{CN} bond length is found to be 1.246 Å, in good agreement with the CI-SDQ value of 1.243 Å [2]. The rovibrational energy levels have been evaluated variationally for $J = 0$, 1, and 2 [22]. The fundamental vibrational frequencies are found to be $\nu_1 = 1278$ cm^{-1}, ν_2 ($J = 1$) = 100 cm^{-1}, and $\nu_3 = 1958$ cm^{-1}. In the CI-SDQ approach, $\omega_1 = 1335$ cm^{-1}, ω_2 ($J = 1$) = 165 cm^{-1}, and $\omega_3 = 2040$ cm^{-1} were obtained [2]. The vibrational wavenumber for ν_3 of

Table 2. *Variationally Calculated Rovibronic Energy Levels* ($J = P$, in cm^{-1}) *in the A $^1\Pi$ state of CCN^+*

$J = 0$				$J = 1$		$J = 2$	
Σ^+ (ν_1,ν_2,ν_3)		Σ^- (ν_1,ν_2,ν_3)		Π (ν_1,ν_2,ν_3)		Δ (ν_1,ν_2,ν_3)	
(0,1,0)	334	(0,1,0)	490	(0,0,0)	0	(0,1,0)	404
(0,3,0)	1026	(0,3,0)	1363	(0,2,0)μ	696	(0,3,0)μ	1058
(1,1,0)	1499	(1,1,0)	1644	(0,2,0)$\varkappa$	927	(0,3,0)$\varkappa$	1354
(0,5,0)	1671	(0,5,0)	2210	(1,0,0)	1153	(1,1,0)	1565
(0,1,1)	2121	(0,1,1)	2268	(0,4,0)μ	1361	(0,5,0)μ	1696
(1,3,0)	2205	(1,3,0)	2522	(0,4,0)$\varkappa$	1788	(0,1,1)	2187
(0,7,0)	2279	(2,1,0)	2786	(0,0,1)	1791	(0,5,0)$\varkappa$	2203
(2,1,0)	2652			(1,2,0)μ	1870	(1,3,0)μ	2237
(0,3,1)	2803			(0,6,0)μ	1985	(0,7,0)μ	2303
(0,9,0)	2830			(1,2,0)$\varkappa$	2085	(1,3,0)$\varkappa$	2516
(1,5,0)	2888			(2,0,0)	2294	(2,1,0)	2713
				(0,2,1)μ	2478	(0,3,1)μ	2833
				(1,4,0)μ	2538	(0,9,0)μ	2849
				(0,8,0)μ	2582	(1,5,0)μ	2908
				(0,6,0)$\varkappa$	2628		
				(0,2,1)$\varkappa$	2697		
				(2,2,0)μ	2928		
				(1,4,0)$\varkappa$	2950		

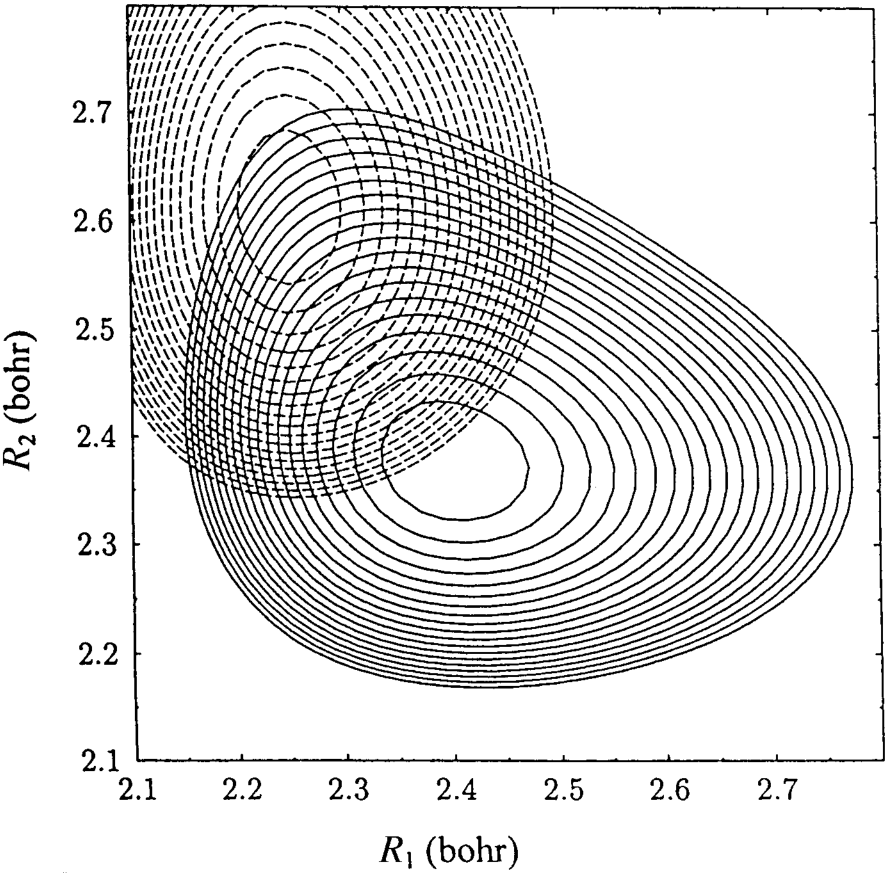

Fig. 1. *Two-dimensional contour plots of the potential-energy functions along the stretching coordinates for the* $X\ ^1\Sigma^+$ (dashed lines) *and* $A\ ^1\Pi$ (full lines) *states of* CCN^+. The contours are separated by 250 cm^{-1}. R_1 corresponds to R_{CN} and R_2 to R_{CC}.

1958 cm^{-1} is in good agreement with the experimental gas-phase value of 1974.07 cm^{-1} [8]. The MRCI equilibrium bond length R_{CN} in the A $^1\Pi_u$ state of CNC^+ is predicted to be 1.263 Å, *i.e.* longer by 0.017 Å than in the ground state. The MRCI excitation energy T_e is 4.18 eV.

The absorption spectrum observed after codeposition of mass-selected C_2N^+ with excess of Ne to form a matrix at 5 K shows the known absorptions of both C_2N isomers [27]. CCN has origin bands at 470.5 nm (A $^2\Delta \leftarrow$ X $^2\Pi$), 445.7 nm (B $^2\Sigma^- \leftarrow$ X $^2\Pi$), 375.2 nm (C $^2\Sigma^+ \leftarrow$ X $^2\Pi$), and 365.9 nm (D $\leftarrow$ X $^2\Pi$), and CNC at 330.0 nm (A $^2\Delta_u \leftarrow$ X $^2\Pi_g$) and 288.5 nm (B $^2\Sigma_u^- \leftarrow$ X $^2\Pi_g$) in a Ne matrix. Furthermore, the electronic B $^2\Sigma^+ \leftarrow$ X $^2\Sigma^+$ transition of CN at 386.7 nm was observed strongly. This is formed during deposition by fragmentation of the C_2N^+ ions. Additionally two new systems are observed with origins at 462.0 and 325.7 nm (*Figs. 2* and *3*). Irradiation of the matrix with a Hg lamp ($E \leq 5.4$ eV) leads to the disappearance of these peaks in the absorption spectrum, indicating the ionic character of the absorbers. In different experiments, the intensities of these absorptions did not correlate and thus they are assumed to originate from two different ions.

In the IR range the excitation of two vibrations is observed at 1452.4 and 1973.0 cm^{-1}. The former corresponds to the antisymmetric stretching mode ν_3 of CNC in good agreement with the 1453 cm^{-1} frequency measured previously in an Ar matrix [27]. The IR band at 1973.0 cm^{-1} disappears during the irradiation as is expected for an ionic species. This is the ν_3 mode fundamental of CNC^+, observed previously in the gas phase at 1974.07 cm^{-1} [8]. In the Ne matrix, it is observed with two maxima (solid state artefact – site structure) at 1973.0 and 1969.9 cm^{-1}. CCN^+ could not be identified in the IR spectrum. This might be related to the weaker IR intensities for the CCN^+ vibrational excitations than for CNC^+, as theory predicts [9].

A comparison of the calculated A ${}^1\Pi_{(u)} \leftarrow \mathrm{X}\,{}^1\Sigma^+_{(g)}$ transition energies for both $\mathrm{C_2N^+}$ isomers with the observed spectrum allows the assignment of the band systems with origins at 462.0 and 325.7 nm. In the case of CCN^+, the transition energy is predicted to be $T_e = 2.74$ eV which compares well with the experiment: $T_0 = 2.68$ eV (462.0 nm band). The transition energy $T_e = 4.18$ eV calculated for CNC^+ is comparable with the experimental value $T_0 = 3.81$ eV (325.7 nm system).

The A ${}^1\Pi \leftarrow \mathrm{X}\,{}^1\Sigma^+$ absorption of CCN^+ shows besides the strong origin band the weak excitation of two vibrations in the upper electronic state with spacings of 1223 and 1725 cm^{-1} (*Fig. 2*). All bands are broad (*ca.* 150 cm^{-1}) but structured in an identical way with distinct zero phonon lines. In view of the *ab initio* results, the 1223 cm^{-1} frequency corresponds to ν_1, and 1725 cm^{-1} to ν_3, calculated at 1153 and 1791 cm^{-1}, respectively (*Table 3*). A comparison of the calculated values with the experiment is indicated in *Fig. 2*.

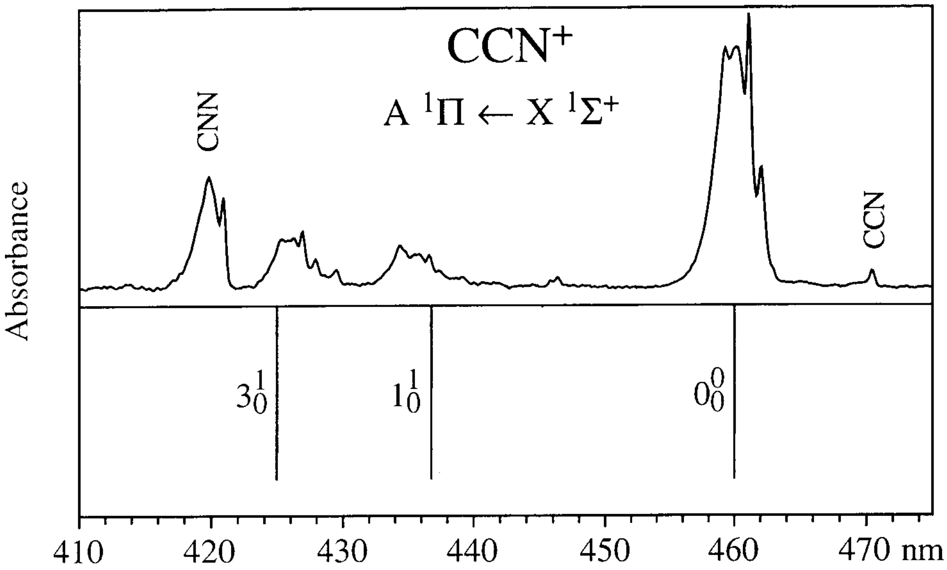

Fig. 2. *The A ${}^1\Pi \leftarrow X\,{}^1\Sigma^+$ electronic transition of CCN^+ observed in a Ne matrix at 5 K after mass selection* (upper trace). The lower trace shows the calculated vibronic transitions with the band origin shifted to coincide with the experiment.

Table 3. *Observed Bands in the Electronic Absorption Spectrum of CCN^+* (zero phonon lines ±0.2 nm) *and CNC^+* (maxima ±0.2 nm)

Wavelength/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1}	Assignment
			CCN^+
462.0	21637	0	0_0^0 A $^1\Pi \leftarrow$ X $^1\Sigma^+$
437.3	22860	1223	1_0^1
427.9	23362	1725	3_0^1
			CNC^+
325.7	30694	0	0_0^0 A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma_{(g)}^+$
324.7	30789	95	
318.8	31359	665	2_0^2
314.7	31767	1073	1_0^1
313.4	31899	1205	
309.1	32343	1649	$1_0^1 2_0^2$
307.6	32500	1806	
303.4	32950	2256	1_0^2
301.9	33114	2420	

The vibrational pattern in the A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma_{(g)}^+$ electronic transition of CNC^+ is more complex (*Fig. 3*). Besides the origin band at 325.7 nm, four strong vibronic bands are discernible. These are broad (*ca.* 300 cm^{-1}) and show two maxima. The shape of the bands is the result of phonon broadening and site structure. The vibrational pattern is due to the excitation of the symmetric stretching mode in the excited state, the double excitation of the degenerate bending mode, and their combinations (*Table 3*). In *Table 4*, a comparison of the observed spectroscopic constants with the *ab initio* values is given for the two C_2N^+ isomers.

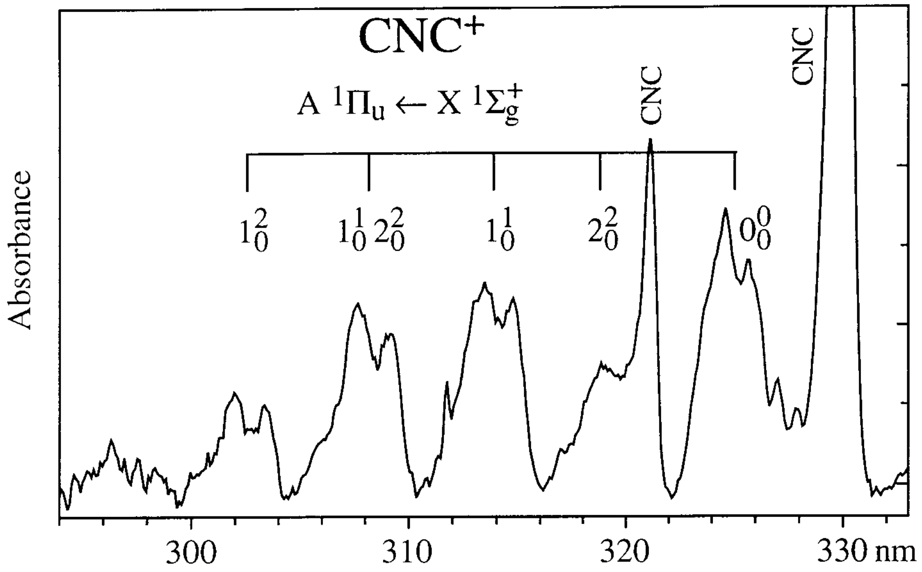

Fig. 3. *The A $^1\Pi_{(u)} \leftarrow$ X $^1\Sigma_{(g)}^+$ electronic transition of CNC^+ observed in a Ne matrix at 5 K after mass-selected codeposition*

Table 4. *Comparison of the Experimental Transition Energies* (T_0) *and Vibrational Frequencies with Calculated Transition Energies* (T_e) *and Vibrational Frequencies*

			Experiment	Calculations
CCN^+	A $^1\Pi$	$T_{0/e}$/eV	2.68	2.74
		$\tilde{\nu}_1$/cm^{-1}	1223(20)	1153
		$\tilde{\nu}_3$/cm^{-1}	1725(20)	1791
CNC^+	X $^1\Sigma^+_{(g)}$	$\tilde{\nu}_3$/cm^{-1}	1973.0(1.0)	1958
	A $^1\Pi_{(u)}$	$T_{0/e}$/eV	3.81	4.18

5. Conclusions. – IR and UV spectra of the CCN^+ and CNC^+ ions in the X $^1\Sigma^+_{(g)}$ and A $^1\Pi_{(u)}$ states in a neon matrix are presented. *Ab initio* calculations were carried out for these species at the CCSD(T) and the MRCI levels of theory. The assignment of the electronic transition and the vibronic features in these spectra is made. The presently reported electronic spectra in Ne matrices provide the necessary data for gas-phase measurements on these astrophysically important species to be undertaken.

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