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$D^2\Pi_u, C^2\Pi_u \leftarrow X^2\Pi_g$ Electronic Transitions of $NCCN^+$

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The electronic absorption spectrum of $NCCN^+$ in the gas phase was measured at ~ 15 K in a 22-pole ion trap. The spectra show two band systems assigned to the $C^2\Pi_u-X^2\Pi_g$ and $D^2\Pi_u-X^2\Pi_g$ transitions with origin band maxima at 17 363 (3) and 33 409 (5) cm^{-1} , respectively. Both absorptions show distinct vibrational structure with progressions in ν_2 as well as combinations of double quanta excitations in ν_4 and ν_5 . Rotational structure of the 0_0^0 bands could not be resolved, which indicates that the $C^2\Pi_u$ and $D^2\Pi_u$ states have a lifetime on the order of a hundred femtoseconds because of fast intramolecular processes.

1. Introduction

The major molecules that form the atmosphere of Saturn's moon, Titan, are nitrogen and methane.¹ Small traces of saturated and unsaturated hydrocarbons and cyano compounds were also found during the Cassini mission.^{1,2} Cyanogen is formed when nitrogen and acetylene are reacted by an electrical spark or discharge.³ In the outer atmosphere of Titan, sunlight and high energetic particles from Saturn's magnetosphere⁴ cause similar conditions. Cyanogen cation ($NCCN^+$) can be produced from the ionization of the neutral molecule.⁵ The centrosymmetric nature of $NCCN^+$ does not make it accessible to pure-rotational spectroscopy because it lacks a permanent dipole moment; however, its electronic and vibrational spectrum can be observed, making it of astrophysical interest.

In the inner regions of circumstellar envelopes, many neutral species have been observed through radio-astronomy; however, near the outer edges, UV radiation changes the chemistry, and some positive species are prevalent. This is also true in dark molecular clouds where only long wavelengths of light can penetrate. Small cations can be involved in many ion-neutral reactions to form larger molecules, making for a plethora of chemistry in molecular clouds and circumstellar envelopes.

$NCCN^+$ has a $X^2\Pi_{3/2,g}$ ground state with the $\sigma_u^2\sigma_g^2\pi_u^4\pi_g^3$ electronic configuration. Four excited states $A^2\Sigma_g^+$, $B^2\Sigma_u^+$, $C^2\Pi_u$, and $D^2\Pi_u$ have been known from photoelectron spectroscopy^{6,7} and theory.^{8–10} $NCCN^+$ has been investigated by matrix isolation spectroscopy, where its electronic^{10,11} and infrared¹² spectra have been measured. Transitions from the $X^2\Pi_g$ ground state to the $B^2\Sigma_u^+$, $C^2\Pi_u$, and $D^2\Pi_u$ states are dipole allowed. In neon matrices at 5 K,^{10,11} the observed $C^2\Pi_u-X^2\Pi_g$ and $D^2\Pi_u-X^2\Pi_g$ transitions are broadened by site effects and phonon side bands, making a determination of frequencies and assignments of smaller features difficult. The $D^2\Pi_u-X^2\Pi_g$ transition measured in neon matrices was overlapped by the absorption of CNC ($A^2\Delta_u \leftarrow X^2\Pi_g$), causing difficulties in the assignment of individual bands.¹⁰

Photoelectron⁶ and photoionization¹³ spectra of cyanogen are quite broad; however, well-resolved band systems have been observed by a pulsed-field ionization photoelectron (PFI-PE) measurement⁷ using a molecular beam and synchrotron radiation, although the resolution was still limited to ~ 12 cm^{-1} . In the PFI-PE study, three excited states, $A^2\Sigma_g^+$, $B^2\Sigma_u^+$, $C^2\Pi_u$, have

been recorded; the $D^2\Pi_u$ state has so far only been observed in a neon matrix.¹⁰ The most accurate study of the $B^2\Sigma_u^+$ excited state to date has been via its $B^2\Sigma_u^+-X^2\Pi_g$ transition using cryogenic ion-trapping technology and a 0.3 cm^{-1} resolution laser.¹⁴ The 0_0^0 band could still not be rotationally resolved due to fast intramolecular relaxation resulting in a picosecond lifetime. In the present work, the $C^2\Pi_u-X^2\Pi_g$ and $D^2\Pi_u-X^2\Pi_g$ electronic transitions of mass-selected $NCCN^+$ have been recorded in absorption at ~ 20 K in the gas phase and at a resolution of approximately 5 cm^{-1} . The width of the bands in the observed transitions is limited by lifetime broadening of the excited states. The method used a 22-pole trap to confine and collisionally cool the cyanogen cations to ~ 20 K prior to the measurement of the absorption of laser radiation using a resonant one-color, two-photon dissociation approach.

2. Method

The cyanogen cations were created using electron impact (15 eV) of the neutral molecular gas. The apparatus employed was described previously.¹⁴ The experiment incorporates a magnetic bender, which separates cations and neutrals after they exit the source from a 0.5 mm pinhole. The bender also serves as a kinetic energy selector from the wide energy distribution of an electron impact source. The ions were passed into a hexapole, subsequently mass-selected by a quadrupole filter and then injected into a 36 mm long 22-pole ion trap, based on the design given in ref 15. The mass resolution was set to ± 2.5 u. The trap was filled with approximately 3000 ions in 20 ms. There the ions undergo collisions with cryogenically cooled helium gas (ca. 8 K) for 60 ms, thermalizing their rotational and vibrational degrees of freedom.

The ions were probed using a one-color, two-photon technique. In this the ions were first excited by one photon from a tunable optical parametric oscillator (OPO) laser and subsequently fragmented by a second photon. The laser beam was directed through the center of the trap. After resonance excitation, the dissociation products were released from the ion trap by lowering the exit potential. A second quadrupole mass filter analyzes and detects fragment ions. The $C^2\Pi_u-X^2\Pi_g$ and $D^2\Pi_u-X^2\Pi_g$ transitions were obtained by monitoring CN^+ and C_2^+ mass channels as a function of photon energy. The power curve of the OPO laser was fitted to a higher order polynomial, and the intensities of the recorded absorption features are scaled accordingly. The laser bandwidth was 5 cm^{-1} within the visible

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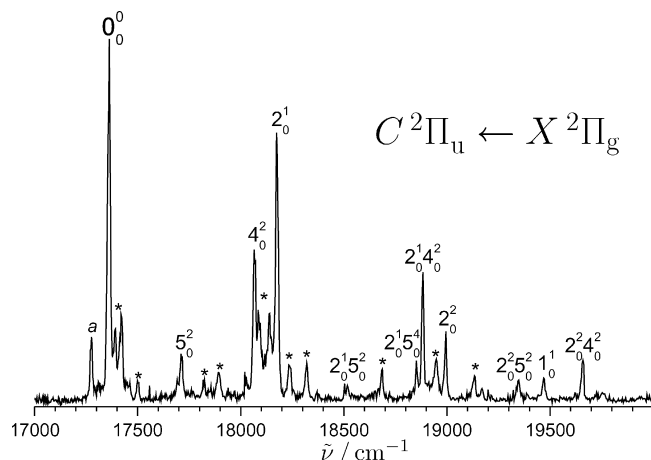


Figure 1. The origin band and assigned vibrational excitations within the C²Π_u–X²Π_g transition of NCCN⁺.

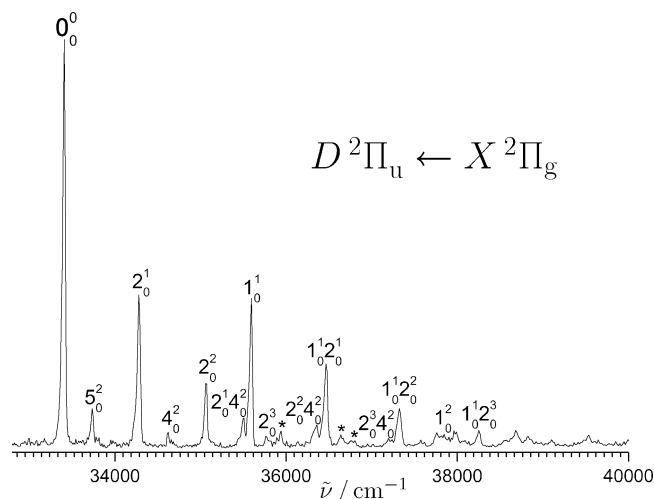


Figure 2. The electronic spectrum of the D²Π_u–X²Π_g transition of NCCN⁺ with the assignments of vibrational excitations.

region, while in the UV it was 8 cm^{−1}. The 0₀⁰ band of the C²Π_u–X²Π_g transition was also recorded with a 0.15 cm^{−1} bandwidth dye laser, without resolving the rotational structure further.

3. Results and Discussion

The absorption spectra are the C²Π_u–X²Π_g and D²Π_u–X²Π_g transitions of NCCN⁺ presented in Figures 1 and 2. Because the temperature of the ion is ca. 15 K, the population of the Ω = 1/2 spin–orbit component in the ground state is negligible as A_{so} = −57.2 cm^{−1},⁷ therefore, all photoinduced excitations occur from Ω = 3/2, and ΔΩ = 0 transitions (Hund's case a) are observed. Both C²Π_u and D²Π_u excited states are Renner–Teller active, resulting in a complex pattern.

Using the PFI-PE⁷ and photoionization¹³ data, the photofragmentation dynamics in NCCN⁺ are deduced. The lowest thermodynamic process is NCCN⁺ + hν → C₂⁺ + N₂ (4.09 ± 0.02 eV), and there is also an energetically higher fragmentation channel, NCCN⁺ + hν → CN⁺ + CN (7.05 ± 0.02 eV). In the N₂ loss pathway, the energy required for dissociation is slightly below the D²Π_u–X²Π_g transition of NCCN⁺; however, sequential absorption of two photons from the laser radiation in the C²Π_u–X²Π_g system is energetically sufficient to produce fragmentation products.

3.1. C²Π_u–X²Π_g Transition. The C²Π_u–X²Π_g transition arises from the excitation of a bonding π_u electron to the π_g

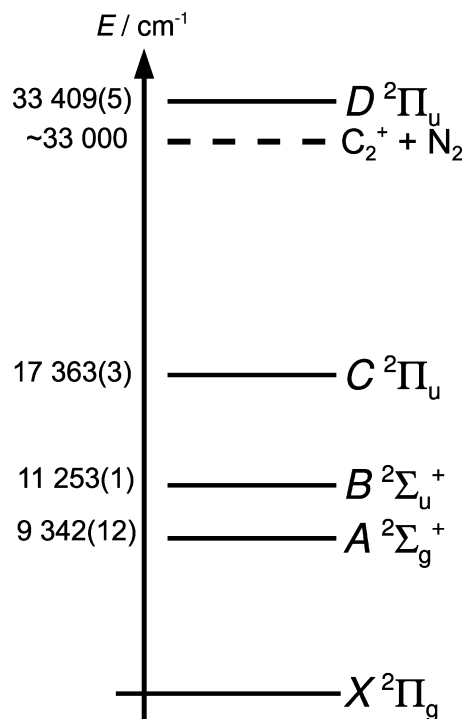


Figure 3. Energy level diagram of NCCN⁺ giving the ν = 0 levels of the states inferred from the electronic transition (B,¹⁴ C, and D) and from the PFI-PE study (A).⁷ Thermodynamic threshold is at ~33 000 cm^{−1}.

(HOMO) orbital, giving a σ_u²σ_g²π_u³π_g⁴ electronic configuration. The most intense peak farthest to the red at 17 363 ± 3 cm^{−1} is the origin band (Figure 1). This is outside the error limit of the PFI-PE value of 17 393 ± 12 cm^{−1}.⁷ There is a small absorption feature at 17 276 cm^{−1} (a in Figure 1) to the red of the 0₀⁰ band, which is most probably due to a symmetry-allowed transition to the vibrational manifold in the B²Σ_u⁺ state. In the absorption spectrum in a 5 K neon matrix, a band red-shifted by ~100 cm^{−1} from the 0₀⁰ origin transition is also observed,¹¹ thus excluding the possibility that the peak a is a hot band. In the PFI-PE data, it is wrongly assigned to the C²Π_{(3/2),u}–X²Π_{3/2,g} transition, and, in the same study,⁷ the doublet structure was assumed to be a vibrational progression in ν₂ (C–C stretch) of the C²Π_u state caused by the spin–orbit components, Ω' = 1/2 and 3/2. The origin bands of the B²Σ_u⁺–X²Π_g and C²Π_u–X²Π_g systems are separated by ~6000 cm^{−1} (Figure 3), making vibronic coupling probable for the absorption band a in Figure 1. This is similar to that in the B²Σ_u⁺–X²Π_g transition, where the B²Σ_u⁺ excited-state lifetime is on the order of picoseconds,¹⁴ presumably due to internal conversion to the nearby A²Σ_g⁺ (Figure 3).

The next most intense peak in the C²Π_u–X²Π_g system is the 2₁⁰ transition at 18 174 cm^{−1}. This corresponds to a vibrational frequency of 811 ± 3 cm^{−1} for the ν₂ C–C stretch in the C²Π_u state (Table 1). This differs significantly from the neon matrix value of 740 ± 10 cm^{−1},¹¹ whereas in the PFI-PE a tentative assignment of 788 ± 10 cm^{−1} was made.⁷ If the assignment of the transitions 2₁⁰ and 4₂⁰ in the neon matrix spectrum is interchanged, ν'₂ = 844 ± 10 cm^{−1} is obtained, although still outside the error limits with the ν'₂ inferred here.

The two peaks to the red of the 2₁⁰ transition are assigned to double excitations in ν₄ and ν₅ (bending modes); 4₂⁰ is centered around 18 065 cm^{−1} and 5₂⁰ at 17 710 cm^{−1}. From these frequencies, ν'₄ = 351 cm^{−1} and ν'₅ = 173.5 cm^{−1} are inferred.

TABLE 1: Band Maxima ($\pm 3\text{ cm}^{-1}$) Observed in the $\text{C}^2\Pi_u - \text{X}^2\Pi_g$ Transition of NCCN^+ and the Assignments Made

assignment	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$
a	17 276			18 236	
0_0^0	17 363			18 320	
	17 390		$2_0^1 5_0^2$	18 517	1154
	17 423			18 683	
	17 500		$2_0^1 5_0^4$	18 852	1489
5_0^2	17 710	347	$2_0^1 4_0^2$	18 884	1521
	17 821			18 948	
	17 891		2_0^2	18 995	1632
	18 026			19 137	
4_0^2	18 065	702	$2_0^2 5_0^2$	19 344	1981
	18 085		1_0^1	19 468	2105
	18 140		$2_0^2 4_0^2$	19 659	2296
2_0^1	18 174	811			

TABLE 2: Experimentally Determined Vibrational Frequencies (in cm^{-1})

	NCCN^a		NCCN^+			
	$\text{X}^1\Sigma_g^+$	$\text{X}^2\Pi_g^b$	$\text{A}^2\Sigma_g^{+b}$	$\text{B}^2\Sigma_u^{+c}$	$\text{C}^2\Pi_u^d$	$\text{D}^2\Pi_u^d$
ν_1	2330(3)	2262(10)	1860(40)	2287(1)	2105(3)	2188(5)
ν_2	846(6)	956(10)	838(10)	1066(1)	811(3)	870(5)
ν_3	2158(1)	1818(20)				
ν_4	503(6)			390 ^e	351 ^e	607 ^e
ν_5	234(3)		277 ^e	273 ^e	174 ^e	164 ^e

^a Reference 16. ^b Reference 7. ^c Reference 14. ^d This work. ^e Obtained from double quanta excitations. Calculated¹⁰ $\text{X}^2\Pi_g$ state frequencies are: ν_1 (σ_g^+ : $\text{C}\equiv\text{N}$ sym. str.) = 2300, ν_2 (σ_g^+ : $\text{C}-\text{C}$ str.) = 808, ν_3 (σ_g^+ : $\text{C}\equiv\text{N}$ asym. str.) = 1789, ν_4 (π_g : deform.) = 537, and ν_5 (π_u : deform.) = 240.

Using the interchanged values of 4_0^2 and 2_0^1 bands in the neon matrix, ν_4 of $\sim 370\text{ cm}^{-1}$ is obtained. There is also a progression in $2_0^1 4_0^2$ and $2_0^1 5_0^2$, where $\nu' = 1$ and 2 (Figure 1). The 1_0^1 ($\text{C}\equiv\text{N}$ symmetric stretch) can be clearly associated with the $19\,468\text{ cm}^{-1}$ absorption peak, $\nu'_1 = 2105\text{ cm}^{-1}$ thus changing only by 7% from that of the ground state of NCCN^+ (Table 2). Several weaker bands within the electronic spectrum, marked as “*”, are apparently due to the complicated nature of this Renner–Teller state. These weak transitions are artificially enhanced by the power of the laser used in the two-photon experiment. An assignment of these features will require a high-level ab initio treatment.

3.2. $\text{D}^2\Pi_u - \text{X}^2\Pi_g$ Transition. In the $\text{D}^2\Pi_u - \text{X}^2\Pi_g$ transition, electronic excitation occurs from the π_g (HOMO) to the π_u (LUMO) orbital with the $\sigma_u^2\sigma_g^2\pi_u^1\pi_g^1\pi_u^1$ electronic configuration dominating the $\text{D}^2\Pi_u$ state. The strongest peak to the red at $33\,409\text{ cm}^{-1}$ is the origin band of the $\Omega' = \Omega'' = 3/2$ spin–orbit component (Figure 2). In the absorption spectrum in a 5 K neon matrix,¹⁰ the 0_0^0 band is at $33\,522 \pm 5\text{ cm}^{-1}$, blue-shifted by $\sim 110\text{ cm}^{-1}$ relative to the gas phase. The origin band in the gas phase has a full-width half-maximum of $\sim 30\text{ cm}^{-1}$, which is broadened due to a fast internal process and/or predissociation as the fragmentation threshold for the dissociative product formation is exceeded.

The next two strongest features present in the $\text{D}^2\Pi_u - \text{X}^2\Pi_g$ system are assigned to the 2_0^1 ($\text{C}-\text{C}$ stretch) and the 1_0^1 ($\text{C}\equiv\text{N}$ symmetric stretch) transitions, which are located at $34\,279$ and $35\,597\text{ cm}^{-1}$ (Table 3). There is a clear vibrational progression in ν_2 , where $\nu' = 1, 2$, and 3 are observed (Figure 2). Treating this as a diatomic vibration, one obtains ω_e and $\omega_e x_e$ in the $\text{D}^2\Pi_u$ excited state to be 952 ± 5 and $42 \pm 3\text{ cm}^{-1}$, respectively. In the gas-phase spectrum, there are two weak bands to the red and blue of the 2_0^1 transition, which have been tentatively

TABLE 3: Vibrational Band Maxima ($\pm 5\text{ cm}^{-1}$) Observed in the $\text{D}^2\Pi_u - \text{X}^2\Pi_g$ Transition of NCCN^+ and the Suggested Assignments

assignment	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$
0_0^0	33 409	
5_0^2	33 736	327
2_0^1	34 279	870
4_0^2	34 623	1214
2_0^2	35 060	1651
$2_0^1 4_0^2$	35 496	2087
1_0^1	35 597	2188
2_0^3	35 762	2353
	35 929	2520
$2_0^2 4_0^2$	36 334	2925
$1_0^1 2_0^1$	36 466	3057
	36 627	3218
	36 788	3379
$2_0^3 4_0^2$	37 212	3803
$1_0^1 2_0^2$	37 324	3915
1_0^2	37 832 ^a	4423
$1_0^1 2_0^3$	38 251	4842

^a $\pm 50\text{ cm}^{-1}$.

attributed to the 5_0^2 ($33\,736\text{ cm}^{-1}$) and 4_0^2 ($34\,623\text{ cm}^{-1}$) vibrational excitations. The present data show that the assignment of the 5_0^2 and 4_0^2 bands in a neon matrix is not correct.¹⁰ In the latter, the system is overlapped by the $\text{A}^2\Delta_u \leftarrow \text{X}^2\Pi_g$ transition of CNC. Therefore, the gas-phase values are the reliable ones: $\nu'_4 = 607(5)\text{ cm}^{-1}$ and $\nu'_5 = 164(5)\text{ cm}^{-1}$. In Table 2 are collected the best values for the vibrational modes with error limits determined for the cation in its different electronic states by different techniques. There are also two combination progressions in the gas-phase spectrum (Figure 2), one with $2_0^1 4_0^2$ and the other in $1_0^1 2_0^1$, where $\nu' = 1, 2$, and 3.

4. Conclusions

The centrosymmetric cyanogen and its cation occur in the interstellar medium or terrestrial environments; however, they cannot be probed by mm-wave spectroscopy. The presently measured gas-phase electronic transitions provide the means of identifying the cation spectroscopically in such inaccessible media. The $\text{C}^2\Pi_u - \text{X}^2\Pi_g$ and $\text{D}^2\Pi_u - \text{X}^2\Pi_g$ absorption spectra of NCCN^+ in the gas phase have been observed with 0_0^0 bands at 575.9 and 299.3 nm , respectively. The absorption features yield the vibrational frequencies of several of the fundamental modes in the excited states. Because of the short lifetimes in the $\text{C}^2\Pi_u$ and $\text{D}^2\Pi_u$ excited states, the 0_0^0 bands could not be rotationally resolved; the bandwidths imply lifetimes of a hundred femtoseconds. The short lifetimes are attributed to fast intramolecular processes, made feasible due to the presence of several low-lying excited electronic states.

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