Vibrational infrared and Raman spectra of dicyanoacetylene

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Abstract—The Raman and infrared spectra for solid C_4N_2 are reported. New assignments are given for $\tilde{\nu}_1$ (2333 cm⁻¹), $\tilde{\nu}_2$ (2267) and $\tilde{\nu}_3$ (640 cm⁻¹). These assignments are supported by a Normal Coordinate Analysis using eight force constants. Extinction coefficients for the infrared active fundamentals are also reported. Our results suggest C_4N_2 to be a likely candidate to explain the 478 cm⁻¹ band in the Titan's emission recorded by the Voyager mission.

INTRODUCTION

The identification of several hydrocarbons in the thermal emission spectrum of Titan [1, 2] one of the moons of Saturn, has renewed interest in the study of vibrational spectra of these molecules. Among the positively identified species are also three nitriles [3], namely, hydrogen cyanide (HCN), cyanogen (C_2N_2) and cyanoacetylene (HC₃N) which are believed to be the photochemical products of methane (CH_4) and nitrogen (N₂) mixtures in Titan's atmosphere. Laboratory experiments on electrical discharges through CH₄N₂ mixtures reveal several complex nitriles [4-6], suggesting thereby, that other (yet unidentified) nitriles may also contribute to the thermal emission from Titan. Further, in view of their relatively high boiling points, it is conjectured that some of the nitriles may exist in a condensed phase in Titan's atmosphere. As a part of our program to understand the chemistry of Titan we have undertaken investigations of the quantitative infrared spectra of condensed phases of hydrocarbons and their nitrile derivatives which are relevant to Titan's atmosphere. In this report we present results on dicyanoacetylene (C_4N_2) which is the most likely candidate for the 478 cm^{-1} peak in the Titan's emission recorded by the Voyager IRIS mission.

Earlier work on the vibrational spectra of C_4N_2 was restricted to the infrared absorption of the vapor and the Raman of the liquid phase [8, 9]. To our knowledge there is no report on the infrared and Raman spectra of solid C_4N_2 . Further, there is no published data on the extinction coefficients of any of the infrared absorption bands which are required for atmospheric modeling. The present study adds to the assignments of the vibrational modes of C_4N_2 . The extinction coefficient data obtained in our studies will be utilized in model emission spectrum calculations.

EXPERIMENTAL

 C_4N_2 was prepared by a method similar to the one employed by MOUREU and BONGRAND [10]. Approximately 2 g of acetylene dicarboxamide ($H_2NOCC\equiv CCONH_2$) was mixed with 15 g phosphorus pentoxide (P_2O_5) and 20 g sand and ground thoroughly for 10 min. The mixture was placed in a 200 ml flask and the entire system was evacuated to ~ 20 microns then backfilled to ~ 20 torr with helium. The flask was heated to 220°C in a silicone bath which immediately resulted in the formation of $C_4 N_2$ crystals in a collection tube kept at liquid N_2 temperature. Water and CO_2 were the major impurities detected by the infrared spectra of the sample. Purification of the sample was achieved by first distilling off CO_2 and leaving the $C_4 N_2$ vapor in contact with P_2O_5 for an additional 2 hr to remove the water vapor.

The infrared spectra of the sample were recorded on a Perkin-Elmer 1800 FT i.r. under ~ 1 cm⁻¹ resolution. The gas phase spectrum was recorded in a 10 cm cell at ~ 55 torr pressure. A solid film of the sample was obtained by controlled deposition of the material on a KRS-5 substrate attached to the cold finger of a closed cycle cryocooler (Air Products 202). The deposition temperature was 70 K and the sample was annealed at 90 K for ~ 30 min before recording the spectra. The Raman spectra of liquid C₄N₂ contained in a 3 mm i.d. tube were recorded on a Spex 1401 Dual monochromator with Kr laser lines at 6417 Å and 5612 Å as the exciting radiations. The solid phase of C₄N₂ was obtained in the same tube by flowing cold N₂ gas across the tip of the tube. The spectral traces are reproduced in Figs 1 and 2.

DISCUSSION

Vibrational assignments

 C_4N_2 is a centrosymmetric linear molecule (point group $D_{\infty h}$) containing conjugated triple bonds. The 13 fundamental frequencies are classified among the symmetry species of $D_{\infty h}$ as follows:

$$\begin{split} \Gamma &= 3 \, \Sigma_g^+ \quad + \quad 2 \, \Sigma_u^+ \quad + \quad 2 \pi_g \quad + \quad 2 \pi_u . \\ \tilde{v}_1 \,, \tilde{v}_2 \,, \tilde{v}_3 \qquad \tilde{v}_4 \,, \tilde{v}_5 \qquad \tilde{v}_6 \,, \tilde{v}_7 \qquad \tilde{v}_8 \,, \tilde{v}_9 \end{split}$$

The Σ species involve bond stretches whereas π modes are (perpendicular) bending vibrations; the g modes are Raman active and the u modes are infrared active. In the condensed phase the selection rules are expected to be relaxed.

Our infrared spectrum of the vapor and the Raman spectrum of the liquid generally agree with those of MILLER and HANNAN [8] and MILLER *et al.* [9] as far as the fundamental modes are concerned. Thus, the assignments of 504 cm⁻¹ and 263 cm⁻¹ Raman frequencies to $\tilde{\nu}_6$ and $\tilde{\nu}_7$ respectively (π_g species) and of 471 cm⁻¹ and 107 cm⁻¹ (estimated) infrared frequencies to $\tilde{\nu}_8$ and $\tilde{\nu}_9$ respectively (π_u species) are justified. The splitting of the observed π_g and π_u peaks in the solid phase lend further support to these assignments. However, the previous assignment of 692 cm⁻¹ to $\tilde{\nu}_3$



Fig. 1. Infrared absorption spectrum of the thin film of solid C₄N₂ at 90 K.↑Indicate fundamental modes
* Indicate CO₂ impurity and possibly cryopumped oil on the substrate window. The channel fringes in the background are due to interference effects.



Fig. 2. Raman spectrum of (A) solid C_4N_2 and (B) liquid C_4N_2 . * Grating ghost.

(C-C sym-St) is questionable. Our Raman spectral traces for $C_4 N_2$ (liquid or solid) do not reveal this band even though the 263 cm⁻¹ peak (marked by the previous authors as relatively weaker) is clearly observed in our spectra. However, our Raman spectral traces give weak features at ~ 640 cm⁻¹ and 980 cm⁻¹ that were not previously reported. In as much as minor impurities in the sample may be responsible for some of the reported weak features, the 640 cm⁻¹ and 980 cm⁻¹ peaks appear to be in the appropriate range for C-C symmetric stretches. The results of a normal coordinate analysis reported in the next section prefer the assignment of 640 cm⁻¹ peak to $\tilde{v}_3(\Sigma_q^+)$. The assignment of the corresponding C-C asymmetric stretch, \tilde{v}_5 (Σ_u^+) to 1160 cm⁻¹ (i.r.) is also in line with the results of normal cordinate analysis. It is likely that the 980 cm⁻¹ weak Raman line is the first overtone of $\tilde{v}_6(\pi_a)$.

In the triple bond region the infrared spectrum of the solid phase exhibits a strong peak at 2244 cm^{-1} which is clearly assigned to \tilde{v}_4 (C=N antisymmetric stretch). The Raman spectra of liquid, as well as solid phase, exhibit strong peaks at $\sim 2330 \,\mathrm{cm}^{-1}$ and $\sim 2270 \,\mathrm{cm}^{-1}$ along with a sharp medium peak at ~ 2300 cm⁻¹. MILLER et al. [8,9], assigned the former pair to the Fermi resonance doublet arising from the interaction of $2\tilde{v}_5$ and \tilde{v}_2 (C=N symmetric stretch); consequently \tilde{v}_2 was given a frequency $(\sim 2290 \text{ cm}^{-1})$ which is the average of the observed strong peak frequencies and \tilde{v}_1 (C=C St) was assigned a value 2119 cm^{-1} which is one of the extremely weak Raman peaks in the spectra. The presence of 2304 cm⁻¹ peak (which is almost exactly equal to $2\tilde{v}_5$) in the Raman spectra precludes the possibility of Fermi resonance. It appears more appropriate to assign the 2333 cm⁻¹ to \tilde{v}_1 (C=C St) and 2267 cm⁻¹ to \tilde{v}_2 (C=N symmetric stretch) rather than the reverse order. First, $C \equiv C$ has a lower reduced mass than $C \equiv N$. Second, the reverse assignment would require a large potential interaction between the two $C \equiv N$ groups. However, this leaves the weak Raman lines at 2137 cm⁻¹ and 2119 cm⁻¹ unaccounted for. An examination of the infrared spectrum of a relatively thick film of C_4N_2 reveals weak features at 2140 cm⁻¹ and 2120 cm⁻¹ which strongly suggest that they originate from some impurity (to the extent of ~ 0.5% or less). The major features of the vibrational infrared and Raman spectra of C_4N_2 , therefore, seem to be appropriately assigned (Table 1). Further check on these assignments is provided by a normal coordinate analysis discussed below.

The symmetrized G elements for different species given by MILLER and HANNAN [8], were ascertained to be correct as were the force constants for the bending vibrations. In view of the conjugation, a more elaborate set of stretching force constants is desirable. In our work the following force constant matrix of a general valence force field was employed in

	C≡N		C≡C	C(C-C		
	d_1	d_2	R	r_1	r_2		
d_1	f_1	f_2	f_3	f_4	0		
d_2		f_1	f_3	0	f_4		
R			f_5	f_6	f_6		
r_1				f_7	f_8		
r,					fs		

which the only interaction constant ignored is between nonadjacent C=N and C-C stretches. Initial rough estimates of the diagonal force constants were made by assuming noninteracting modes which were then refined by a FPERT program [11] to obtain agreement between calculated and observed frequencies to within ± 5 cm⁻¹. These resulting constants are given below:

$f_1 = 18.20 \text{ md/A}$	$f_5 = 17.91 \text{ md/A}$
$f_2 = 0.48 \text{ md/Å}$	$f_6 = 1.36 \text{ md/Å}$
$f_3 = -0.55 \text{ md/Å}$	$f_7 = 7.16 \text{ md/\AA}$
$f_4 = 1.00 \text{ md/Å}$	$f_8 = 0.13 \text{ md/Å}.$

Table 2 gives the potential energy distribution for each frequency among different force constants

Raman Infr		ared				
Liquid	Solid	Vapor	Solid	\tilde{v} (Calculated)	Assignment	
2333	2331			2327	\tilde{v}_1 C=C St	
2267 640	2270 640			2271	$\tilde{v}_2 C \equiv N S \cdot St$ $\tilde{v}_3 C - C S \cdot St$	Σ_{g}
		2241 1154	2244 1160	2241 1156	$\dot{v}_4 C \equiv N A \cdot St$ $\dot{v}_5 C - C A \cdot St$	Σ_u^+
504	507				\tilde{v}_{4} In phase	
	503				bending	π.
263	266				ν̈́-	<i>g</i>
200	262	471	478*		v. Out of	
		107	770		phase bending \tilde{v}_9	π"

Table 1. Fundamental vibrational frequencies (cm⁻¹) of C_4N_2

*Split into 3 components in the spectrum of the sample annealed at 155 K.

Mode	f_1	f2	f_3	f4	f_5	<i>f</i> 6	fı	<i>f</i> 8
v ₁	0.16		-0.03	-0.04	0.76	-0.16	0.3	
v ₂	0.75	0.02	0.03	-0.02	0.18	0.02	0.01	
v ₃	0.07		—	0.04	0.10	0.09	0.70	0.01
V4	0.9	-0.02	_	-0.07			0.18	
v ₅	0.11		_	0.06			0.85	-0.01

Table 2. Potential energy distribution in stretching modes of C_4N_2

for the C₄N₂ molecule. A few general remarks on these results are in order. First, the single and triple bond stretching force constants ($f_{C-C} \sim 7 \text{ md/A}, f_{C=C}$, $f_{C=N} \sim 17-19 \text{ md/A}$) are within the limits expected for conjugated systems [8]. Second, the interaction constants f_4 and f_6 are of similar magnitudes as expected. Third, the interaction constants f_2 and f_8 between equivalent, but non-neighboring bonds, are small fractions (less than 2.5%) of the diagonal force constants. The physical significance of the negative sign on f_3 is not clear to us, but it illustrates a definite, though small, coupling between the C=C and the C=N stretches. The extent of coupling among the modes is illustrated in table 2 where, for example, the v_1 mode derives $\sim 70\%$ contribution from the C=C stretch and as much as 31 % from the C-C stretch. This set of force constants may not be unique, but the values reported here are reasonable estimates, and reproduce the vibrational frequencies well.

Extinction coefficients

The evaluation of the extinction coefficient

 $\left(=\frac{1}{t}\ln\frac{I_0}{I}\right)$ requires a knowledge of the thickness of the sample. In our studies the sample thickness was estimated by obtaining the transmission of the sample in the (2.0 to $0.6 \,\mu$ m) region. In this region the sample has no strong characteristic absorptions and the spectrum exhibits channel fringes due to the interference between multiply reflected and transmitted radiation through the sample film. In order to obtain good quality fringes (for better thickness measurements) a uniform sample deposition over the crosssection of the substrate is required. This was achieved by directing the gas molecules on to the substrate through a set of 8 equally spaced holes ($\sim 0.5 \text{ mm dia.}$) on a cylindrical disc (~ 2.5 cm dia.) attached to the sample container. An appropriately placed mask with a 6 mm central hole enabled us to obtain the spectra through the most uniform region of the film. The sample deposition was made in short pulses, a typical pulse being ~ 2 ml at 20 torr. The sample thickness, t. was obtained by measuring the spacing between adjacent fringes {maxima or minima $\Delta \tilde{v}$ (cm⁻¹)} and

Table 3. Extinction coefficients in the regions of infrared active fundamental modes of $C_4N_2^*$

Frequency	α (cm ⁻¹)	Frequency	α (cm ⁻¹)	Frequency	α (cm ⁻¹)
460	0	1153	14	2236	0
462	0	1154	16	2237	0
464	0	1155	24	2238	6
466	32	1156	39	2239	80
468	37	1157	50	2240	240
470	51	1158	112	2241	648
472	87	1159	166	2242	1058
474	156	1160	187	2243	1592
476	1398	1161	151	2244	1798
478	2378	1162	105	2245	1627
480	1694	1163	61	2246	1149
482	1187	1164	29	2247	848
484	672	1165	18	2248	572
486	238	1166	9	2249	431
488	104	1167	3	2250	300
490	96	1168	3	2251	228
492	63	1169	5	2252	171
494	37	1170	3	2253	120
496	36	2230	0	2254	93
498	22	2231	0	2255	66
500	0	2232	0	2256	48
1150	1	2233	0	2257	36
1151	2	2234	0	2258	33
1152	9	2235	0	2259	31
				2260	32

*Values of α below 30 cm⁻¹ are unreliable.

employing the following relationship:

$$t = \frac{1}{2\Delta \tilde{\mathbf{v}} \cdot \mathbf{n}}$$

where *n* is the refractive index of the sample. The value of *n* employed in our calculations (n = 1.46) refers to that of a liquid in the visible region [12]. Since there is not strong dispersion in the visible and near infrared regions, this value is expected to be accurate to within 5%. A detailed error analysis suggests that the extinction coefficients (Table 3) in the region of absorption bands in the infrared and possibly correct to within 15%, the largest error being in the thickness measurement.

It was noticed that annealing the sample at ~ 155 K produced sharper bands; however, the integrated extinction coefficient over the band profile is independent of temperature.

The absorption feature at ~ 478 cm^{-1} is of interest in the modeling of Titan's atmosphere. In the spectrum of the sample at 90 K this band has 3 components (481.0 cm⁻¹, 477.6 cm⁻¹, and 472 cm⁻¹). (See Fig. 1 insert). However, convolving this spectrum with a 4.4 cm⁻¹ spectral slit width (as was employed in the Voyager IRIS instrument) results in a single band peaked at 477.6 cm⁻¹ which matches the emission peak recorded by the Voyager instrument under identical resolution. Definite identification of C₄N₂ solid on Titan requires detailed radiative transfer calculations for which the data on both the refractive index as well as the extinction coefficients are necessary. This work is underway in our laboratory.

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