

Low-temperature phosphorescence of dicyanoacetylene in rare gas solids

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A strong visible $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ luminescence was observed upon the UV excitation of cryogenic rare gas (argon, krypton, and xenon) matrices doped with dicyanoacetylene (NC₄N). Spectra and lifetimes of this phosphorescence have been measured. A detailed analysis of resolved vibronic bands is presented.

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Dedicated to Professor Elena V. Savchenko

Introduction

Dicyanoacetylene (dicyanoethyne, 2-butyne dinitrile, NC₄N, Fig. 1) is a rod-shaped molecule, first synthesized by Moureu and Bongrand [1]. Its IR and Raman vibrational spectroscopy was thoroughly studied [2–5], as were the mid-UV [6,7] and vacuum-UV [8] electronic transitions. Electronic luminescence (phosphorescence) has so far been found for several cyanoacetylene-family molecules dispersed in solid rare-gas matrices, namely for NC₄N [9] and HC₅N (cyanodiacetylene) [10], for another isoelectronic pair: NC₂N (cyanogen) [11] and C₃N[−] (cyanoacetylide anion) [12], and finally for NC₆N [13]. Such emission, on the other hand, is not occurring for HC₃N (cyanoacetylene). The study presented here has been carried out with the goal of revisiting the topic investigated by Smith *et al.* [9], by giving a detailed account of NC₄N phosphorescence in solid rare gases. Smith *et al.* limited their description to the most intense vibronic bands (0–0, and 3 elements of the ν_1 '' progression) in Ar. We were also interested in comparing the NC₄N phosphorescence to that of HC₅N, recently measured by Turowski *et al.* [10] in Ar, Kr, and Xe.

Experimental

NC₄N was prepared following the method described by Miller and Lemmon [14], starting from the methyl ester of acetylene dicarboxylic acid (Aldrich, 99%). Inert gases — either argon (Multax 5.0 grade), krypton (Linde 4.0) or xenon (Messer 4.8) were doped with NC₄N at a typical ratio of 1:1000, and solidified onto a sapphire substrate inside a closed-cycle helium refrigerator *Displex* DE-202 (Air Products). Purity of samples was checked with standard FTIR absorption spectroscopy. All spectra were routinely measured at 15 K. The luminescence studies were accomplished with an Edinburgh FL 900 CDT fluorometer equipped with a high-pressure xenon lamp, grating monochromators, and a photon-counting detection system. The spectral resolution was 0.2–0.4 nm; wavenumber differences (leading to vibronic spacings) were measured with an accuracy of approx. 20 cm^{−1}. Edinburgh FL 900 CDT time-resolved fluorometer, featuring a pulsed nitrogen discharge lamp, was employed for luminescence lifetime measurements.

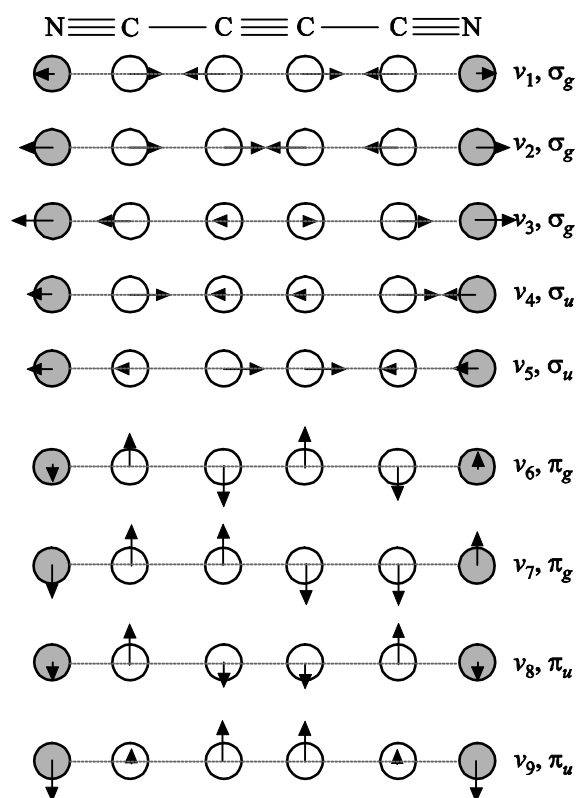


Fig. 1. Displacement vectors for fundamental vibrational modes of NC_4N in its ground electronic state, as derived with a harmonic density functional theory computation B3PW91/aug-cc-pVTZ.

Results and discussion

Strong NC_4N luminescence was emitted upon the excitation of $\tilde{A}^1\Sigma_u^- - \tilde{X}^1\Sigma_g^+$ or $\tilde{B}^3\Delta_u^- - \tilde{X}^1\Sigma_g^+$ transitions in all investigated matrices. Its lifetime was long, as expected for the $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ phosphorescence — and was found to depend on the environment, being as long as 1.25 s in solid Ar, 52 ms in krypton, and just 2.5 ms in xenon. Qualitatively, the phosphorescence intensity was found to grow in the Ar, Kr, Xe order. The wavenumber of a vibrationless origin (0_0^0 band), 25659 cm^{-1} in Ar (red-shifted from that value by 344 cm^{-1} in Kr, and by 452 cm^{-1} in Xe), is approx. 50 cm^{-1} higher than measured by Smith *et al.* [9] with a Fourier transform instrument. The reason for this discrepancy, larger than our estimated absolute calibration error, is not clear; it may possibly originate in the pulsed method of matrix deposition employed by Smith *et al.* (a technique known to produce particularly well-relaxed arrangements of dopant molecules in cryogenic solids). Despite certain efforts, we did not detect any fluorescence, i.e., any emission originating from excited singlet electronic states. As already recognised by Smith *et al.*, the main vibronic progression is governed mostly by a triple-bond stretching frequency of about 2300 cm^{-1} (Fig. 2), which corresponds to the fully symmetric mode ν_1 (cf. Fig. 1). This general spectral pattern, resembling the one observed for related linear cyanides NC_2N , NC_6N or HC_5N (see Introduction), suggests a linear emitting state, $\tilde{a}^3\Sigma_u^+$. Of note,

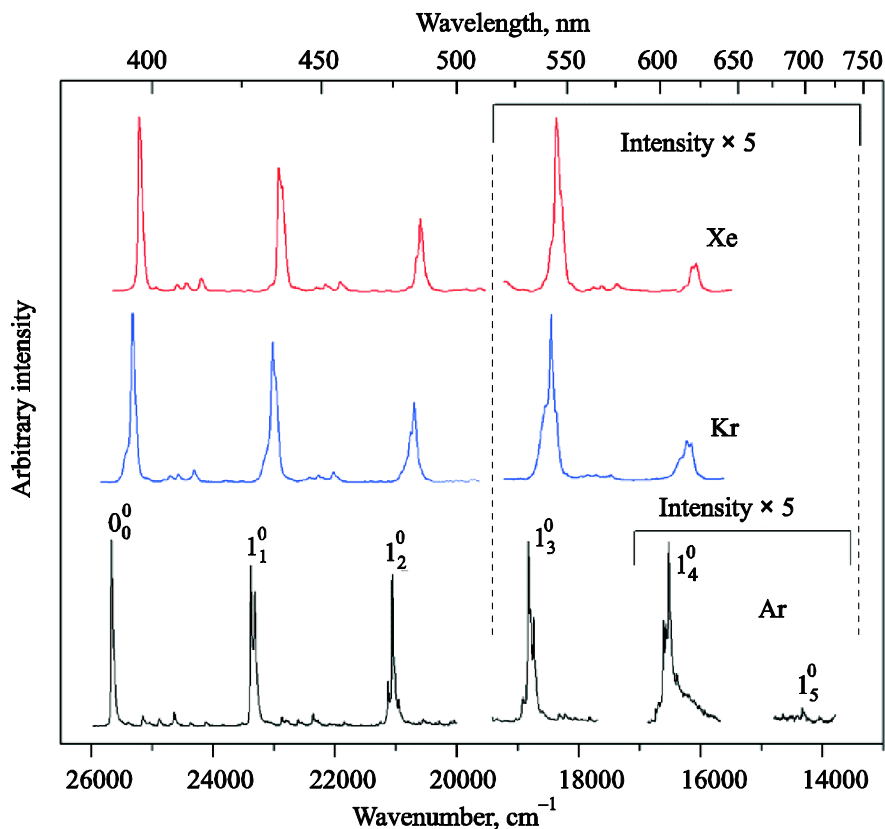


Fig. 2. NC_4N phosphorescence in solid rare gases (15 K).

the spectrum is by far dissimilar to that reported by Vuitton *et al.* [15] for a seemingly similar case of diacetylene, HC₄H; there, phosphorescence is dominated by the progression of bands spaced with a bending mode frequency of ca. 630 cm⁻¹. These findings are in agreement with the theoretically predicted geometry of the corresponding lowest triplet states: bent in the case of HC₄H [16] and linear for NC₄N [17].

Table 1 reports the main vibronic frequencies observed for the NC₄N phosphorescence in rare gas solids, together with corresponding spectral assignments. A more detailed table is available as the [Supplemental Material](#). The selection rules for spin-forbidden, orbitally-allowed $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ transitions predict the occurrence of a vibrationless band, and of those vibronic features, which involve totally symmetric modes, such as ν_1 . A closer inspection of the distance separating the strongest groups of bands reveals that its change is not monotonic, and hence not governed solely by the anharmonicity of ν_1 . The reason for this stems from multiple cases of Fermi resonance. While the first (0_0^0) band of the progression consists of a single strong component, the second one is doubled due to the $\nu_1/2\nu_5$ anharmonic interaction — as discovered in the gas-phase Raman spectrum by Miller and Hannan [3], and further studied in

solid Ar by Smith *et al.* [9]. The third group of strong bands consists of as many as three components, for which the possible explanation involves a resonance between two overtone modes and a combination mode, namely $2\nu_1$, $4\nu_5$, and $\nu_1 + 2\nu_5$. If this is the case then the fourth group may originate from the interacting modes $3\nu_1$, $2\nu_1 + 2\nu_5$, $\nu_1 + 4\nu_5$.

When comparing the spectral shifts that accompany the transition from one solid matrix to another, it can clearly be seen that bending modes are usually more strongly altered by the environment than the stretching ones. Moreover, certain bands that appear prominently in Ar, are weak or missing in Kr and in Xe (see Fig. 3). This applies in particular to the spectral features associated with the centrosymmetric zig-zag bending mode ν_6 . The bands ν_6 , $2\nu_6$, and $3\nu_6$ are of medium intensities in Ar, while in Kr only the $2\nu_6$ is of a comparable strength, ν_6 being barely visible, and $3\nu_6$ — absent. The symmetry of ν_6 is π_g whereas the $2\nu_6$ overtone, a $\pi_g \times \pi_g$ product, contains a totally symmetric (and thus orbitally allowed) component. The appearance (albeit weak) of π_g -symmetry modes in argon (ν_6 , ν_7 , $2\nu_6 + \nu_7$, $3\nu_6$, ...) may indicate a slight distortion of the NC₄N molecule from linearity, imposed by the argon lattice.

Table 1. Vibronic assignments for the $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ phosphorescence of NC₄N in solid rare gases at 15 K. See [Supplemental Material](#) at for a complete list of spectral features.

Ar			Kr			Xe			Assignment
Wavenumber, cm ⁻¹		Int. ^b	Wavenumber, cm ⁻¹		Int. ^b	Wavenumber, cm ⁻¹		Int. ^b	
ν	$\Delta\nu^a$		ν	$\Delta\nu^a$		ν	$\Delta\nu^a$		
25659	0 ^c	vs	25315	0	vs	25207	0	vs	0 ₀
25392	267 ^c	vw	25068	247	vw	24937	270	vw	7 ₁
25144	515	w	24807	508	vw	24703	504	vw	6 ₁
25037	622 ^c	w	24697	618	w	24594	613	w	3 ₁
24875	784	w	24558	757	w	24444	763	w	6 ₁ 7 ₁
24697	962	vw	24373	942	vw	24254	953	vw	8 ₂
24630	1029	w	24307	1008	w	24190	1017	w	6 ₂
24366	1293 ^c	w	24050	1265	vw	23947	1260	vw	6 ₂ 7 ₁
24114	1545 ^c	w	23804	1511	vw	23669	1538	vw	6 ₃
23844	1815	w	23541	1774	w	23425	1782	w	6 ₃ 7 ₁
23597	2062	vw				23171	2036	w, sh	6 ₄
23519	2140	w				23069	2138	w, sh	2 ₁
23376	2283	vs	23021	2294	vs	22916	2291	vs	1 ₁
23305	2354	m	22958	2357	s, sh	22858	2349	s, sh	5 ₂
21125	4534	s	20760	4555	s, sh	20654	4553	s, sh	5 ₄
21049	4610	vs	20692	4623	s	20594	4613	s	1 ₂
20952	4707	m							1 ₂ 5 ₂
18822	6837	w	18446	6869	w	18362	6845	w	1 ₃
16518	9141	w	16146	9169	vw	16069	9138	vw	1 ₄
14325	11334	vw							1 ₅

Comment: ^awavenumber relative to the 0–0 band; ^bs – strong, m – medium, w – weak, v – very, sh – shoulder; ^cbands featuring phonon sidebands, redshifted by ca. 40 cm⁻¹ (see Supplemental Material).

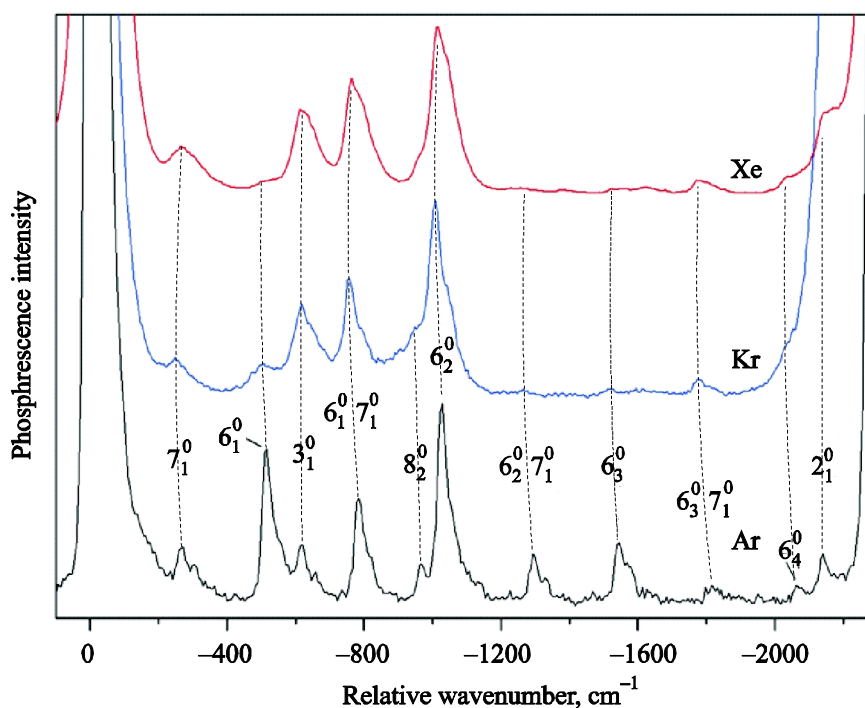


Fig. 3. Short-wavelength part of the NC_4N phosphorescence in solid rare gases (15 K). Relative abscissa scale, drawn with respect to vibrationless origins positioned at: $25\,659\text{ cm}^{-1}$ in Ar, $25\,315\text{ cm}^{-1}$ in Kr, $25\,207\text{ cm}^{-1}$ in Xe.

NC_4N and HC_5N (cyanoacetylene) are similar, being linear, isoelectronic, and of comparable sizes; a nitrogen atom of the dicyano- is replaced by CH in the monocyano-species. Both molecules feature a number of mutually alike vibrations. In fact the $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, \nu_7, \nu_8, \nu_9$ modes of NC_4N are close to respective HC_5N vibrations $\nu_2, \nu_4, \nu_6, \nu_3, \nu_5, \nu_8, \nu_{10}, \nu_9, \nu_{11}$ (neglecting the obvious lack of a symmetry center in the latter). It is therefore interesting to compare their phosphorescence. Indeed, the above-mentioned environment-dependent compartment found for the ν_6 mode of NC_4N , is similarly observed for the corresponding ν_8 mode of HC_5N , where it may also be rationalised in terms of a small matrix-induced nonlinearity of the molecule.

Dramatic changes between solid Ar and Kr have also been reported for the intensity of bending modes in the phosphorescence of other linear chains: HC_4H [15] and C_3N^- [12]. Particularly interesting is the case of C_3N^- , for which nontotally symmetric modes appeared in Kr, and were absent in Ar (a behavior opposite to that of NC_4N). The chain size, similar for NC_4N and HC_5N , but quite different for C_3N^- , is obviously a critical factor determining the arrangement and possible distortions of the molecule within a given host lattice.

The main vibronic progressions concern the mutually similar vibrations ν_1 of NC_4N and ν_2 of HC_5N [10]. Fermi-type resonances of $2\nu_5$ with either of these modes are observed. Such an anharmonic interaction is weaker in the case of HC_5N ; consequently the vibrational progression is for HC_5N less perturbed than in the case of NC_4N .

Conclusions

The phosphorescence of NC_4N in rare gas matrices, induced by the absorption to excited singlet states, is very intense. This qualitative observation, together with the absence of any measurable fluorescence, suggests an efficient intersystem crossing between the excited states. The triplet state lifetime, of the order of seconds in Ar, is reduced in heavier host solids due to the external heavy atom effect [18], especially pronounced in Xe. The vibronic structure of the phosphorescence is complex, due to Fermi resonances between totally symmetric modes and lower-symmetry overtones. Exploration of different host media allows for detailed analyses of vibronic bands and highlights the matrix effects.

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