

C_5N_2 revisited: mass-selective matrix isolation and DFT studies

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Received 30 May 2001; in final form 5 November 2001

Abstract

Experiments employing mass-selected ion deposition in neon matrices confirm that a spectrum with origin near 440 nm, which we have previously reported, indeed corresponds to the C_5N_2 mass, as tentatively assigned. The spectrum consistently appears when mass 88 is deposited, but is absent when other C_mN_n species are selected. We discuss the observed spectra in light of the recently reported theoretical density functional calculations, as well as new calculations which we have carried out. Taking into consideration computed band frequencies, observed isotopic shifts, and spectroscopic selection rules, consistent assignments for all the nine observed vibrational frequencies of the carrier can be proposed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Several years ago, in the course of experiments designed to generate various cyano-carbon radicals and ions in low temperature matrices, and characterize them spectroscopically, we have detected a new spectrum with origin near 440 nm. The spectrum appeared with appreciable intensity in absorption, and excitation in this region produced a very intense laser induced fluorescence

with extensive vibrational structure. Even though the carrier appeared to be only a minor component among the products of our discharge source, and its infrared spectrum was not observed, the fluorescence was sufficiently intense to observe the ^{13}C and ^{15}N isotopic bands in natural abundance. Careful studies using isotopically enriched samples then strongly suggested that the carrier is a linear, centrosymmetric molecule with two equivalent nitrogens, and with at least five carbon atoms. Based on this evidence, we have tentatively assigned the spectrum to the linear C_5N_2 species [1].

Recently reported DFT calculations seemed to provide a strong support for our assignment of the spectrum to the linear NC_5N carrier [2]. Unfor-

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tunately, the conclusions of the authors are somewhat impaired by several factors. In the first place, they attribute several bands occurring with appreciable intensity in the spectrum to symmetry forbidden transitions. Even more importantly, though, they dismiss numerous weaker bands in the spectrum, suggesting that these are due to a different carrier. They do not realize that in selective laser excitation studies it is very easy to establish unambiguously which bands do or do not belong to the spectrum, and these must then be accepted or dismissed as a package.

On the experimental front, Kołos [3,4] has recently reported a series of elegant studies of various C_mN_n species. By using methods similar to those we have used to isomerize dicyano-acetylene to the mono- and di-isocyano species, he succeeded in producing analogous isomers of a dicyano-di-acetylene, (CNC_4CN) and (CNC_4NC), and characterized them by IR spectroscopy. Interestingly, he also observed in his experiments our 440 nm ‘mystery’ emitter. In this study, at least three different methods were employed: electrical discharge through gaseous C_6N_2 in argon during the sample deposition, a so-called ‘cold window radial discharge’, and in situ 193 or 248 nm laser photolysis. While formation of a C_5N_2 fragment in the case of the gas phase discharge could be expected, in view of the matrix cage effect is its formation in the latter two experiments somewhat more surprising, and the question arises if the spectrum could be due to for instance the $CNCCCNC$ di-isonitrile, which fits our original requirements: linear, centrosymmetric, at least five carbon atoms, and two equivalent nitrogens. Unfortunately, simultaneous measurements of the relative intensities of the CNC_4NC infrared bands, and of the 440 nm spectrum were not carried out in his experiments.

In order to remove the remaining uncertainties, and resolve this question, we have now taken advantage of our new apparatus for the deposition of mass-selected ions. In the present work we describe experiments where electron impact ionization of C_6N_4 was used to deposit various C_mN_n ions. The experiments show that the 440 nm bands consistently appear whenever mass 88 is deposited, but are absent when various other fragment ions were

selected. We have also carried out additional density functional calculations on several isomers of C_5N_2 and a few other fragments. The present work demonstrates, that based on the computational results, it is possible to propose a reasonable assignment of all the nine experimentally observed frequencies of the ‘mystery’ emitter, which does not require violation of any spectroscopic selection rules.

2. Experimental

The apparatus used in our experiment to deposit mass-selected ions is quite similar to Maier’s setup [5], and has been described in a previous paper [6] with additional details appearing in our recent study of the vibrational spectra of cyano-acetylene and related ions [7].

Finding an appropriate precursor for the desired $C_5N_2^+$ (mass 88) species is not an easy task. Synthesis of the linear C_6N_2 is non-trivial [8]; C_4N_2 is easier to prepare but its yield of mass 88 in the electron impact source was still < 100 pA. In spite of its low vapor pressure, the commercially easily available and inexpensive tetracyanoethylene (TCNE, Aldrich, 98%) turned out to be quite a convenient source of the $C_mN_n^+$ ions. To increase its pressure, we have heated the finger containing the C_6N_4 precursor compound to 80 °C. Under these conditions the pressure in the source rose from 1×10^{-6} to about 1×10^{-5} mbar, with the resulting mass spectrum being shown in Fig. 1. In this way one could obtain a steady mass 88 current of about 40 pA, which was quite stable over many hours, and allowed deposition of the samples overnight with 12–20 h being the typical deposition times. To avoid matrices developing a net positive charge, which could interfere with the further deposition of positively charged ions, the matrix was simultaneously sprayed with an electron current, typically a factor of 3 higher than the positive ion current, during the deposition.

The infrared absorption spectra were obtained on a BRUKER IFS 120 HR Fourier transform spectrometer with a glowbar as an IR source and a liquid nitrogen cooled mercury–cadmium–telluride

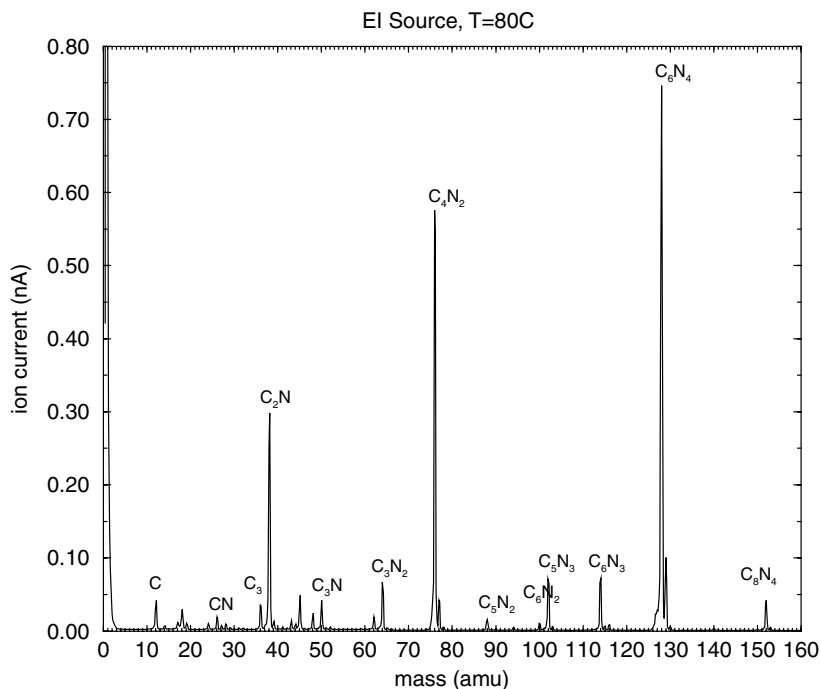


Fig. 1. Quadrupole mass spectrum produced with the electron-impact ionization source using C_6N_4 .

(MCT) detector. The spectra were measured with a reflection geometry, with the beam passing twice through the samples. In most cases both the reference spectrum prior to sample deposition, and the matrix sample spectra afterwards were recorded using 0.06 cm^{-1} resolution. For the FT-visible absorption spectra a 1 cm^{-1} resolution was usually adequate. They were measured with a tungsten lamp source and either a silicon or gallium-phosphide diode as detector.

To obtain the laser excitation spectra, the samples were irradiated using an Ar^+ laser (multiline-UV) pumped, tunable ring dye laser operating with a stilbene-3 dye. The laser output was first intensity stabilized, modulated at 1.4 kHz by a chopper, and loosely focused onto the matrix. The fluorescence collected by a parabolic mirror was directed via suitable filters to eliminate or reduce the scattered laser light to a photomultiplier, whose phase and frequency sensitive signal was detected by a lock-in amplifier. While recording the spectra, the laser frequency was step-tuned by turning a three-plate birefringent filter.

3. Results and discussion

3.1. FT-absorption and laser excitation spectra

A matrix resulting from deposition of an ≈ 40 pA current of mass 88, with a simultaneous 120 pA current of electrons over 16 h resulted in an infrared spectrum exhibiting besides weak precursor bands only a few relatively broad bands due to easily identifiable matrix isolated impurities, in particular CO_2 and H_2O . In the visible, very weak origin bands of the 440 nm spectrum which we have previously assigned to the C_5N_2 fragment were present with a marginal signal to noise. The presence of the spectrum was, however, clearly confirmed with the much more sensitive laser excitation method using the tunable cw dye laser. As shown in Fig. 2, a laser scan in this region revealed two rather strong lines at 22762.5 and 22784.8 cm^{-1} , exactly the previously observed frequencies for the two sites of the 440 nm carrier in a neon matrix [1]. Their intensity is not changed dramatically upon annealing or bombardment

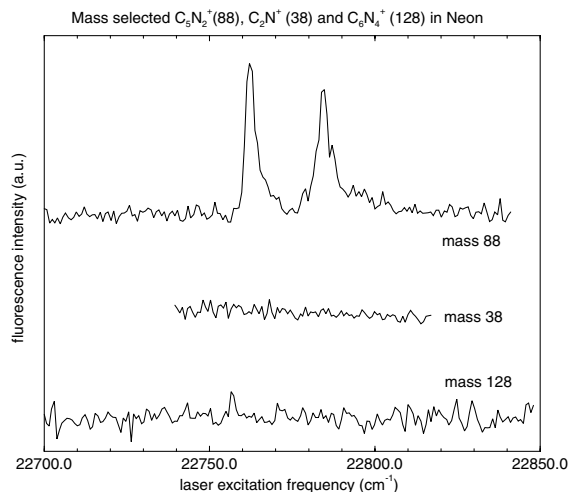


Fig. 2. Laser excitation scans of the C_5N_2 origin region from various neon matrices. The two characteristic sites of the '440 absorber', at more exactly 22784.8 and 22762.5 cm^{-1} in solid neon, appear only in the spectra of mass 88 and the signal is not changed dramatically after annealing with electron bombardment, pointing to a neutral species as the carrier.

with electrons, in contrast to the peaks of the related ionic species observed recently in the infrared [7], which provides some support for assignment to the *neutral* C_5N_2 .

The presence of the bands is, however, not yet a 100% proof that its carrier is C_5N_2 . One could certainly argue that another of the numerous C_nN_m fragments produced in the discharge manages to get 'around the corner' from the source to the matrix – after all we clearly see evidence that over the 16 h deposition, some of the TCNE precursor reaches the sample. Alternatively, the matrix is continuously sprayed by electrons, which could easily break up the TCNE to produce various fragments.

In order to test these possibilities, we have investigated matrices resulting from the selection and deposition of several other $C_nN_m^+$ ions, using the same TCNE precursor and production conditions. For example, deposition of mass 38, instead of 88, resulted in a strong, sharp infrared band at 1969.9 cm^{-1} , which is readily assigned to the CNC^+ (mass 38) ion, known to absorb at 1974.07 cm^{-1} in the gas phase [9]. However, in spite of a comparable deposition time, no trace of

the 440 nm spectrum could be detected, as shown in Fig. 2. In a similar experiment, we have selected a heavier ion, the 128 amu TCNE parent ion. The deposited matrix exhibited absorptions due to the $C_6N_4^+$ cation, as confirmed by our DFT calculations [10], but again a scan in the 440 nm region showed no absorptions. Quite consistently, the visible spectrum was present when ions of mass 88, corresponding to C_5N_2 were deposited, but completely absent when other masses were selected. In the mass 88 matrices, laser excitation of either of the two sites showed the previously reported, complex fluorescence spectrum extending throughout the visible range.

An important question which needs to be addressed is the relative weakness of the observed 440 nm spectra. In our previous discharge experiments very strong visible absorption spectra were observed, even though we were never able to detect any infrared bands attributable to its carrier, which clearly was present only in minor quantities. Should the selective deposition of a 40 pA current over many hours not produce an exceedingly strong fluorescence? There are several answers to this question.

In the first place, we have deposited ionic species rather than neutrals. While one might expect that charge recombinations in matrices continuously sprayed with electrons should very effectively produce the neutrals, our own experiments indicate that this is not the case. When CS_2^+ was selectively deposited, the ion was seen, but in spite of the large infrared oscillator strength of its IR absorptions, the neutral was not detected. A similar situation was found for C_2N^+ and also $C_4N_2^+$ and in several other experiments. It is therefore possible, or even very likely, that the matrix contains large quantities of the $C_5N_2^+$ ions, but only very few of them were neutralized. One might then inquire why no infrared spectrum due to the ions is seen. Here, however, the answer is relatively simple. In all the cases where we have seen infrared spectra with an acceptable signal to noise ratio, the deposited integrated current was considerably larger than in the $C_5N_2^+$ case.

It is also conceivable that during the neutralization process, the neutral isomerizes or fragments, since the ion–electron recombination frees

some 10 eV of energy. In fact, Leroi and coworkers [11] have in their experiments explained the lack of an infrared CS_2^+ absorption, and the presence of a rather strong CS signal by exactly such a dissociative electron attachment process.

Finally, and perhaps most importantly, when one considers the structure of the TCNE parent, one would not expect a linear C_5N_2 to form readily in the course of its fragmentation, since the longest carbon atom chain present within its molecule contains only four carbon atoms. The most abundant ion in our source is the well-known and very stable C_4N_2^+ cation, and one possibility would be that the C_5N_2 species are formed by its reactions. Such reactions, however, would seem to be likelier to produce branched or perhaps even cyclic species, rather than the linear centrosymmetric species which is responsible for the 440 nm absorption. In other words, it is possible that many or even most of the deposited mass 88 ions are not the desired linear species, but its structural isomers. Obviously, the presence of several structural isomers would ‘dilute’ the signal, and make experimental observation of their spectra considerably more difficult.

It should also be noted that both theoretical calculations, as well as the relative scarcity of the ion in the discharge mass spectrum, suggest that the C_5N_2 species are relatively unstable. It may be noted that formation of C_5N_2 on the surface of a matrix or during its annealing process may be greatly facilitated. Matrices resulting from gas phase discharges invariably contain large quantities of carbon atoms, and their reactions, for instance, with the C_4N_2 and an efficient carbon atom insertion [12] might produce the linear isomer. Similarly, in the in situ NC_6N photolysis experiments of Kołos performed during deposition, the particular chemistry affordable on the matrix surface likely facilitated the production of NC_5N ; again the much larger mobility of carbon atoms compared to di- and poly-atoms. After the in situ photoisomerization to NC_5NC via the matrix cage effect, a carbon atom was photolyzed away, mobile enough, particularly on the surface of the matrix, to escape the matrix cage, leading to the NC_5N .

In summary, in spite of some outstanding problems and questions, the unflinching appearance

of the 440 nm spectrum when mass 88 is deposited, and its consistent absence when ions of other masses are selected require assignment to a carrier with a C_5N_2 elemental composition, in agreement with our previous tentative conclusion.

3.2. Density functional calculations

Density functional calculations appear to perform well for compounds of the type studied here, as recently exemplified by cyano- and dicyanopolyacetylenes [13]. Our calculations were carried out on a dual Pentium-III Linux PC with 1 GB of RAM using the GAUSSIAN 98 program package [14]. In our density functional computations the UB3LYP hybrid functional was used. For all light atoms H, C and N all electrons were treated explicitly, using the relatively large 6-311++G(3d, 3pd) basis set with two diffuse and four polarization functions on each atom. The frequencies are all scaled with the factor 0.97.

There were several reasons to repeat the DFT calculations of Tittle et al. First of all, our experimental isotopic shift data consist not only of the normal and all ^{13}C and ^{15}N species calculated by Tittle et al., but also of 13 further isotopomers [1]. Secondly the theory must also be consistent with the complete spectrum of the molecule including the five molecular frequencies between 1000 and 600 cm^{-1} dismissed by Tittle et al. Thirdly, we have employed a much larger basis set to hopefully get a clear picture which of the multitude of isomers and spin states is the true ground state. We calculated all three linear centrosymmetric isomers of C_5N_2 in their triplet and open-shell singlet states.

Table 1
DF-theoretical vibrational frequencies (cm^{-1}) and IR intensities^a (km/mol) $^3\Sigma_g^-$ ground state of NCCCCN, scale factor = 0.97 for frequencies

$\nu_1(\sigma_g)$	2054.6(0.0)	$\nu_7(\pi_g)$	457.8(0.0)
$\nu_2(\sigma_g)$	1647.9(0.0)	$\nu_8(\pi_g)$	175.4(0.0)
$\nu_3(\sigma_g)$	528.4(0.0)	$\nu_9(\pi_u)$	485.2(4.4)
$\nu_4(\sigma_u)$	2027.2(1.3)	$\nu_{10}(\pi_u)$	401.7(6.8)
$\nu_5(\sigma_u)$	1651.9(30)	$\nu_{11}(\pi_u)$	74.6(7.2)
$\nu_6(\sigma_u)$	1021.5(1.6)		

^a The IR intensities are given in parentheses.

Table 2

Experiment vs. theoretical vibrational frequencies for the ground state of NCCCCCN

Argon matrix (All containing σ_g)			UB3LYP, $^3\Sigma_g^-$ ground state, scale factor 0.97			
$\nu(\text{C}_5\text{N}_2)$	$\Delta\nu(^{13}\text{C}_5\text{N}_2)$	$\Delta\nu(\text{C}_5^{15}\text{N}_2)$	Theor. assign.	$\nu(\text{C}_5\text{N}_2)$	$\Delta\nu(^{13}\text{C}_5\text{N}_2)$	$\Delta\nu(\text{C}_5^{15}\text{N}_2)$
2071.4	56.9	20.0	$\nu_1(\sigma_g)$	2054.6	57.0	19.0
2030.9	54.8	19.8	$2\nu_6(2\sigma_u)$	2043.0	54.5	23.3
1639.5	54.1	8.5	$\nu_2(\sigma_g)$	1647.9	54.6	9.5
870.9	30.1	3.9	$2\nu_7(2\pi_g)$	915.6	31.5	3.7
859.3	29.3	2.6	$\nu_9 + \nu_{10}(2\pi_u)$	886.9	32.1	2.3
801.5	29.3	2.4	$2\nu_{10}(2\pi_u)$	803.4	28.2	2.9
748.5	28.6	0.8	$\nu_7 + 2\nu_8(3\pi_g)$	808.6	26.6	4.4
605.7	19.5	0.5	$\nu_7 + \nu_8(2\pi_g)$	633.2	21.2	3.1
527.8	10.1	9.7	$\nu_3(\sigma_g)$	528.4	9.7	10.1

As found by Tittle et al. with the smaller basis set, the NCCCCCN isomer is found to be significantly lower in energy than the other two linear configurations. Whereas Tittle et al., however, find the triplet and open-shell singlet states of NCCCCCN to be very close in energy and both in excellent agreement with experimental frequencies and isotope shifts of the four frequencies which they treat, our larger basis set calculations predict $E = -299.9401491$ a.u. for the triplet and $E = -299.9098864$ a.u. for the open-shell singlet, or a difference of 6641 cm^{-1} or 18.99 kcal/mol , indicating that the $^3\Sigma_g^-$ state is the true ground state. Thus, below we compare the experimental frequencies and isotopic shifts with those calculated for the $^3\Sigma_g^-$ state.

The computed NC_5N frequencies and infrared intensities are listed in Table 1. All the IR-active vibrations are predicted to be rather weak, explaining the experimental difficulty in observing its vibrational spectrum, and finding IR bands correlating with its strong visible transition. The observed NC_5N frequencies as well as the all ^{13}C and all ^{15}N isotopic shifts are listed in Table 2, and compared with the corresponding computed values. As already mentioned in our previous paper, the fluorescence spectrum is dominated by a series of prominent groups of bands or ‘polyads’ attributable to Fermi resonance. Based on the theoretical results, the two resonant levels, observed at 2071 and 2030 cm^{-1} , must be assigned to ν_1 and $2\nu_6$, respectively, both of σ_g symmetry, with computed frequencies of 2055 and 2043 cm^{-1} . They cannot be attributed to ν_1

and ν_4 as proposed in [2], since the latter mode is of σ_u species, and will be strictly forbidden by symmetry. As shown in Table 2, also other vibrational frequencies observed in the spectrum can be reasonably assigned to computed vibrational modes, without violating the spectroscopic selection rules.

4. Summary

Mass-selective ion deposition in neon matrices shows conclusively that the carrier of a spectrum we have previously assigned to neutral linear NC_5N species indeed has this elemental composition. The spectrum near 440 nm invariably appears when ions of mass 88 are deposited, but is conspicuously absent when ions of other masses, e.g. 38 or 128, are deposited. We also demonstrate that with the help of theoretical results obtained by density functional calculations, a reasonable and consistent assignment of all nine ground state vibrational intervals observed in the spectrum can be proposed.

Acknowledgements

Research funding from the Deutsche Forschungsgemeinschaft as well as support from the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank the EU for financial support within the Research Training Network *Reactive Intermediates*.

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