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Ab-initio calculations of the IR spectra of dicyanodiacetylene (C₆N₂) beyond the harmonic approximation.

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Abstract: On the grounds of a hybrid CCSD(T)/B3LYP/aug-cc-pVTZ anharmonic potential and the use of a variational and variational-perturbational methods, the IR spectra of dicyanodiacetylene C₆N₂ is revisited in the mid-infrared region up to 4500 cm⁻¹. A position and intensity analysis of our theoretical results allow us to assign the fundamental bands together with their combinations and overtones, in the aforementioned range of frequencies. The pure theoretical results are discussed in relation with the pure experimental data. The main objective of this paper is to give an 'a priori' complete IR spectrum of C₆N₂ which can be used as a guide of the low-intensity bands in areas not completely assigned so far.

I-INTRODUCTION

During the past three decades a great deal of experimental and theoretical studies have been devoted to the structural and spectroscopic properties of linear rod-like polyatomic anions, radicals and molecules particularly those which are present (or expected to be) in the interstellar medium.^{1,2,3} Among these investigations, the identification and characterization of interstellar species has often benefitted by a fruitful interplay between theoretical chemistry, experimental spectroscopy and (radio) astronomy works^{4,5,6} giving results of excellent agreement between calculated and experimental data.^{7,8,9,10,11,12,13}

Although diacetylenes have been successfully synthesized since 1860 the synthesis of substituted or disubstituted diacetylenes is a hard to accomplish task since it requires the use of metals catalysts and organometallic substituents.¹⁴ Therefore, the up to date physicochemical and spectroscopic studies of dicyanodiacetylene C_6N_2 (DCDA) are rather limited. Among the investigations reported so far, we highlight the pioneering experimental work of Miller and Lemmon¹⁵ dealing with the Infra-red and Raman spectra of DCDA and more recently the quantum chemical study of its vibrational spectra by Gupta and Coll¹⁶ by means of ab-initio MP2 and Density Functional Theory (DFT) computations. The latter work, however, which is limited to assignments of the fundamental vibrations, reports some notable differences when compared to the Miller's assignments based on symmetry considerations. Given the lack of accurate experimental and theoretical data allowing a detailed knowledge of the vibrational spectra of DCDA between 50 and 4600 cm^{-1} , in this letter we report an exhaustive study of its IR spectrum relying on an arsenal of accurate methods developed to treat the IR vibrational spectra of linear molecules^{11,12} beyond the harmonic approximation for which the accurate determination of the potential function is required.¹⁷ These methods, have been recently improved by taking into account the irreducible representations involved, allowing the diagonalization of larger vibrational spaces in each representation. The application of our variational-perturbational treatment¹⁸, have already allowed the complete assignment of the IR spectra^{19,20,21,22,23,24,25,26,27,28,29} of a great assortment of molecules and also has been successfully used to revisit results from improved experimental studies^{11,12,21,25,29}

The main objective of this work, which extends our previous study on dicyanoacetylene¹¹ is to give an 'a priori' complete computed IR spectrum of C_6N_2 and to revisit the IR spectra

previously reported in the literature. This paper is structured as follows. In section II we describe the computational setup, the results are presented and discussed in section III providing comparison both with the gas phase spectra¹⁵ and the more recent computational studies.^{13,16}

II-COMPUTATIONAL METHODS

Calculations of geometries, energies and harmonic vibrational frequencies of dicyanodiacetylene were performed at CCSD(T) level of theory³⁰ using the aug-cc-pVTZ basis set implemented in the MOLPRO program suite³¹. It is well accepted that this method, after it corrected as suggested by Botschwina⁸ in the case of for cyanopolynes, gives the best structural parameters and therefore accurate harmonic vibrational frequencies. The cubic and quartic force constants to construct the anharmonic potential function are determined from a B3LYP/aug-cc-pVTZ treatment using the Gaussian 09³² package in order to obtain a hybrid quartic force field expressed in the basis of the dimensionless normal modes calculated at the CCSD(T) level as it has been demonstrated by Begue et al.³³

The construction of this accurate quartic hybrid force field^{33,34,35} has been achieved by using energies, gradient and analytical Hessian data on a suitably chosen grid of points and a generalized least-squares procedure as previously reported.^{36,37} The vibrational levels and IR intensities of C₆N₂ are computed thanks to a Configuration Interaction (CI) approach until the hexa-excitations in the area 50-4600 cm⁻¹ by using an efficient iterative variation-perturbation scheme implemented in the VCI-P code³⁸ developed in our group. This code described in detail elsewhere³⁹ allows the treatment of large molecular systems in the mid-IR region. It is based on the original variational-perturbational method previously developed by Pouchan et al.¹⁸ which improves iteratively the primary subspace to be diagonalized, containing the major configurations given by the selection procedure, and correcting, if necessary, these CI energies by considering the contribution given by all other configurations which interact weakly with this primary subspace through a second order perturbation theory. The main advantage of this iterative method is to reduce the configurations space, containing the most important information, which must be diagonalized finally in the CI procedure. At the end of the iterative process, the most pertinent configurations, that describe each state of interest, are added to be diagonalized by the Davidson method.⁴⁰ For

C₆N₂, taking into account the high symmetry ($D_{\infty h}$) of the system, about 20 000 determinants for each irreducible representation $\Sigma+(u,g)$ and $\Pi(u,g)$ are needed to obtain the eigenvalues with a convergence of 1 cm⁻¹ on their diagonalized energies, and the eigenvectors associated. IR intensities are calculated in the same way from the quadratic expansion of the dipole surface. Obtained in the anharmonic mechanical and electrical approximations all active fundamental, overtone and combination bands are also computed⁴¹ using the VCI-P code following the procedure described in the original paper.³⁹

III- RESULTS AND DISCUSSION

In **Figure 1** we show the the CCSD(T)/aug-cc-pVTZ optimized geometry obtained for DCDA. Unfortunately there is no experimental information on the structure of this molecule in the gas phase to compare with. At the B3LYP/ aug-cc-pVTZ level of theory all bond lengths are calculated 0.01 to 0.02 Å **shorter** than those obtained at the CCSD(T) level. It should be interesting to compare the geometry of DCDA with those previously calculated for DCA¹¹ with the CCSD(T) aug-cc-pVTZ method. The lengths of the terminal CN (1.168 Å) and the non-adjacent CC triple bond (1.219 Å) in DCDA are longer than those calculated for DCA (1.159 Å and 1.209 Å respectively). The others CC bond lengths (1.378 Å and 1.366 Å for the bond C₄-C₅ in the center of the molecule) are slightly longer than those of DCA (1.363 Å). These effects can be easily explained by the electron delocalization.

In **Table 1** we list the description of the modes and their irreducible representation. We adopt the Miller and Lemmon's nomenclature¹⁵ to compare more easily our computed values and their vibrational observations. **Also, in Figure 2 we provide a visual aspect of all respective atomic displacements.** All the stretching modes belong to the Σ representation, those belonging to the Π representation are doubly degenerated and correspond to chain bending modes. **Table 2** includes the harmonic fundamental values obtained at CCSD(T) and B3LYP levels with the same aug-cc-pVTZ basis set. Except from ν_{10} , all harmonic frequencies are stronger at B3LYP than at CCSD(T) levels. **The difference between B3LYP and CCSD(T) harmonic frequencies is lower than 10 cm⁻¹ for the lowest frequencies then it reaches 20 to 30 cm⁻¹ for those between 400 to 1200 cm⁻¹. Finally, the respective gap increases to 50 to 60 cm⁻¹ for four out of the five highest ones.** DFT harmonic frequency values of the stretching modes are larger than those computed at the CCSD(T) because in the latter case the bond lengths are longer.

The complete vibrational IR spectrum of DCDA calculated between 50 and 4600 cm^{-1} is listed in **Table 3**. This table contains the anharmonic wavenumbers and the intensity calculated in the hypothesis described in the previous section. Our results are presented, when possible, in comparison with the observed bands reported by Miller and Lemmon to facilitate in depth the discussion on the basis of position and intensity of the calculated and measured bands.

Let us now analyze the IR spectrum in four fingerprint regions. The first is below 600 cm^{-1} where all chain bending modes and their first combinations are expected. The second region is between 600 and 1100 cm^{-1} where only combinations or overtones of the chain bending modes can be observed. The third one lies between 1200 and 2500 cm^{-1} where all the stretching fundamental vibrations and some combinations or overtones should be characterized. The last region is above 2500 cm^{-1} and has not been yet a subject of neither experiment nor theoretical investigations. At this point one must keep in mind that the anharmonicity is lower on the stretching modes (only less than 10 cm^{-1}) than on the bending ones (from 10 to 50 cm^{-1}). This can be easily seen if one compares the harmonic and anharmonic frequencies obtained at the same level of theory.

1- Region below 600 cm^{-1}

In this region the active IR fundamental modes belonging Π_u (ν_{13} , ν_{12} and ν_{11}) are calculated respectively at 67, 292 and 500 cm^{-1} with intensities of 9.9, 11.7 and 7.24 km/mol . These values agree with the observed bands at 61.5 (ν_s); 276 (ν_{vs}) and 490.5 cm^{-1} reported by Miller and Lemmon and confirm their assignments. The inactive IR doubly degenerated Π_g modes ν_{10} , ν_9 ; ν_4 and ν_8 are calculated at 178, 415, 440 and 516 cm^{-1} , respectively. Three of these correspond at the Raman data at 170, 455 and 501 cm^{-1} . Also, a notable difference appears for the fourth (ν_4) bands observed at 571 cm^{-1} and calculated at 440 cm^{-1} in our calculations. Finally, the peak observed in Raman near 468 cm^{-1} and not assigned experimentally could be preferentially associated to this mode.

2- Region 600-1100 cm^{-1}

Only the fundamental ν_7 mode (Σ_u^+ symmetry) active in IR is expected in this spectral region: it is associated to the stretching vibration of single CC bonds. Several other bands of stringer or weaker intensities are observed and should be assigned to combination bands. Our calculations show that for ν_7 a resonance with the combination ($\nu_9 + \nu_{11}$) giving two

bands of which the most intense at 929 cm^{-1} ($I=0.14\text{ km/mol}$) corresponds to that observed at 944 cm^{-1} . Two combinations calculated at 702 and 704 cm^{-1} with high intensities (2.22 and 4.82 km/mol) are assignable to $\nu_{10}+\nu_{11}$ and $\nu_9+\nu_{12}$ respectively and correspond to the strong bands observed in the vapor phase between 714 and 720 cm^{-1} , assigned previously at ν_7 by Miller and coll. Two additional combinations calculated at 605 cm^{-1} and 1009 cm^{-1} respectively assignable to $\nu_8+\nu_{13}$ and $\nu_8+\nu_{11}$ are in agreement with the observed peaks at 565 or 645 cm^{-1} and 1011 cm^{-1} which is experimentally unassigned. In this spectral area our calculation predicts also, four combinations with very weak intensities around 0.05 km/mol situated at 749 cm^{-1} ($\nu_4+\nu_{12}$), 807 cm^{-1} ($\nu_8+\nu_{12}$), 1077 cm^{-1} ($\nu_{12}+2\nu_9$) and 1094 cm^{-1} ($\nu_{13}+2\nu_{11}$), respectively. The latter modes have not reported in the literature up until now.

Region $1200\text{-}2500\text{ cm}^{-1}$

This region is the one where all other stretching modes described by $(\sum u^+)$ and $(\sum g^+)$ irreducible representation are expected. The former $(\sum u^+)$ (ν_5 and ν_6) is IR-active and the latter $(\sum g^+)$ (ν_1, ν_2, ν_3) is only observable in Raman (see Fig 2). The ν_3 mode corresponding to the third single CC bond is only observable in Raman and gives a weak polarized peak at 1287 cm^{-1} very well reproduced in our calculation (1282 cm^{-1}). For the modes that can be assigned to vibrations of CC and CN triple bonds, a resonance should be between the C=C stretching mode ν_6 and the combination ($\nu_3+\nu_7$) corresponding to the single CC mode. This coupling gives two bands computed at 2126 and 2164 cm^{-1} which presents a weak intensity (0.22 and 1.35 km/mol respectively). The calculated splitting between the two bands (38 cm^{-1}) is in line with the gap observed in the vapor phase between the peaks at 2097 and 2150 cm^{-1} . The ν_5 CN antisymmetric intense stretching (47.2 km/mol) calculated at 2309 cm^{-1} is observed at 2266 cm^{-1} whereas the complex combination $\nu_3+\nu_8+\nu_{11}$ computed at 2341 cm^{-1} with an intensity of 0.75 km/mol could be assigned to the large band centered around $2290\text{-}2295\text{ cm}^{-1}$. **The two CC and CN symmetric stretching modes ν_2 and ν_1 , active in Raman, are respectively calculated at 2221 and 2292 cm^{-1} in agreement with the bands experimentally observed at 2183 and 2286 cm^{-1} . We should also note that for three out of these four computed fundamental modes a gap around 40 cm^{-1} towards the high wavenumbers is observed relatively to the experimental values which have been determined either in CCl_4 or hexane solutions.** Finally, we also found in this spectral area a

combination band $\nu_3+\nu_9+\nu_{11}$ significantly intense (1.41 km/mol) at 2243 cm^{-1} corresponding to the broad band observed at 2221 cm^{-1} .

3- Region above 2500 cm^{-1}

This spectral area has been slightly explored in the experimental study and none IR band is reported. The Raman band observed in solution near 2570 cm^{-1} is calculated at 2586 cm^{-1} and is assignable to the combination $\nu_6+\nu_9$. Except the combination band $\nu_4+\nu_5$ calculated at 2754 cm^{-1} with an intensity around 0.5 km/mol all others calculated combinations until 4500 cm^{-1} present very weak intensity.

IV- CONCLUSIONS

In this study, we have carried out accurate and systematic theoretical computations concerning the vibrational spectra of dicyanodiacetylene C_6N_2 in the mid-infrared region, for the first time. On the basis of a hybrid CCSD(T)/B3LYP/aug-cc-pVTZ quartic force field and by means of pure variational and variational-perturbational approaches, we propose a complete ab-initio modeling of the IR spectrum of C_6N_2 which allows to assign fundamental, combination and overtone bands in the spectral region between 50 and 4500 cm^{-1} . Our original theoretical results give a new interpretation of the assignment of the bands observed by Miller and Lemmon in their experimental study. We hope that this accurate theoretical study shall prove useful to revisit the experimental IR spectra of dicyanodiacetylene in the whole mid-infrared region.

V- ACKNOWLEDGEMENTS

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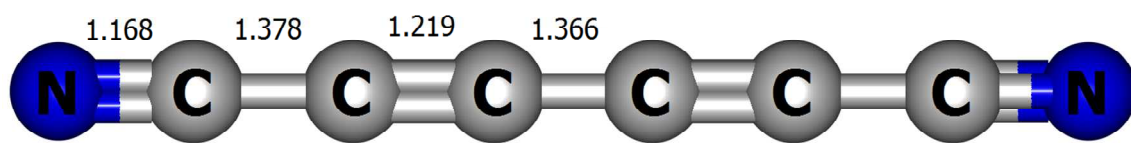


Figure 1. Equilibrium geometry of DCDA obtained at CCSD(T)/aug-cc-pVTZ level of theory.

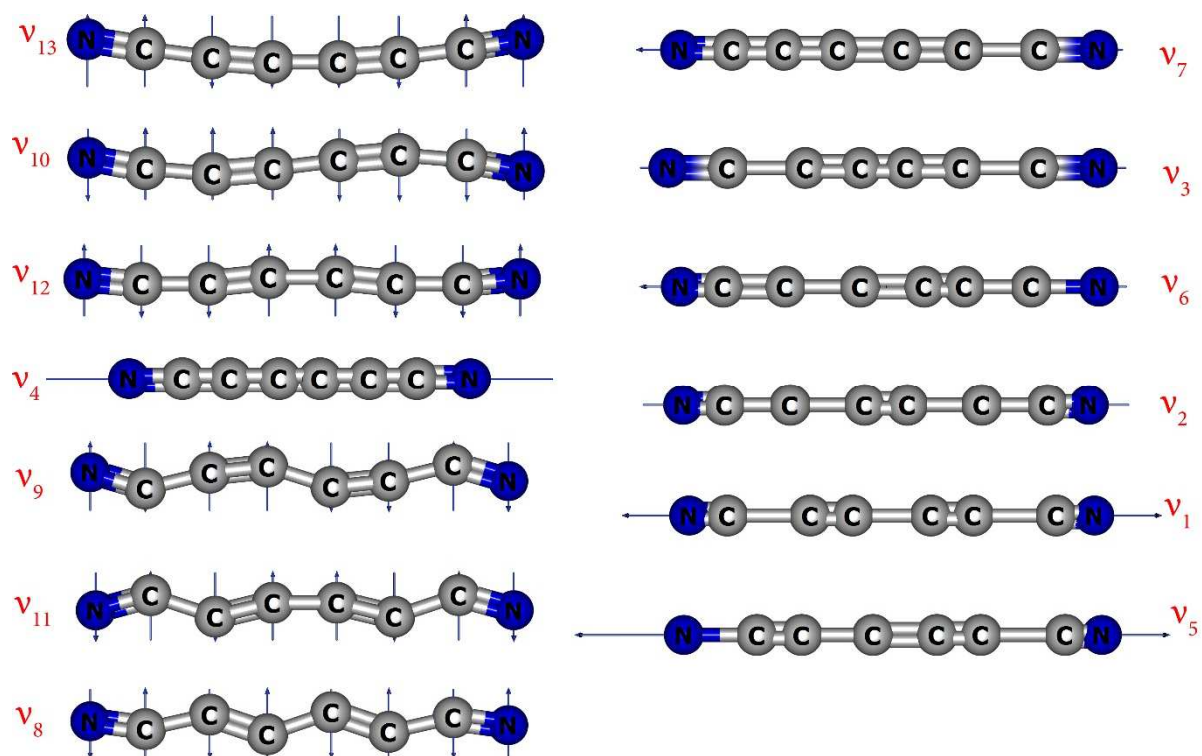


Figure 2. Schematic representation of the harmonic vibrational modes computed at B3LYP/aug-cc-pVTZ level of theory.

Description of the modes	Nomenclature	Symmetry
Chain bending sym CCC	ν_{13}	Π_u
Chain bending asym CCC	ν_{12}	Π_u
Chain bending CCN,,CCC	ν_{11}	Π_u
Chain bending CCN,CCC	ν_{10}	Π_g
Chain bending CCN,,CCC	ν_9	Π_g
Chain bending CCC	ν_8	Π_g
C-C stretching	ν_7	Σ^+_u
C \equiv C asym stretching	ν_6	Σ^+_u
C \equiv N asym stretching	ν_5	Σ^+_u
C-C stretching	ν_4	Σ^+_g
C-C stretching	ν_3	Σ^+_g
C \equiv C sym stretching	ν_2	Σ^+_g
C \equiv N sym stretching	ν_1	Σ^+_g

Table 1: Description of the modes and Nomenclature for C_6N_2

Nomenclature is similar to those adopted by Miller and Lemmon¹⁵

CCSD(T) /aug-cc-pVTZ	B3LYP /aug-cc-pVTZ	Mode number
56	65	v ₁₃
176	170	v ₁₀
301	308	v ₁₂
459	475	v ₄
468	489	v ₉
515	542	v ₁₁
561	591	v ₈
893	925	v ₇
1283	1332	v ₃
2125	2186	v ₆
2218	2283	v ₂
2301	2317	v ₁
2307	2358	v ₅

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Table 2 : Harmonic wavenumbers calculated respectively at CCSD(T) and B3LYP levels with the same aug-cc-pVTZ basis set.

Observed frequencies	Calculated frequencies and Intensities		Assignment
	$\nu(\text{cm}^{-1})$	$I(\text{km/mol})$	
	4620	0.04	$\nu_1 + \nu_5$
	4421	0.05	$\nu_1 + \nu_6$
	4347	0.05	$\nu_2 + \nu_6$
	3420	0.15	$\nu_3 + \nu_6$
	3206	0.11	$\nu_1 + \nu_7$
	3117	0.17	$\nu_2 + \nu_7$
	2775	0.23	$\nu_5 + \nu_9$
	2761	0.18	$\nu_2 + \nu_{11}$
	2754	0.49	$\nu_4 + \nu_5$
2697(Raman)			
	2615	0.14	$\nu_1 + \nu_{12}$
	2586	0.00	$\nu_6 + \nu_9$
2570(Raman)			
	2565	0.13	$\nu_4 + \nu_6$
	2513	0.15	$\nu_5 + \nu_{10}$
2290-2295 (m)	2341	0.75	$\nu_3 + \nu_8 + \nu_{11}$
2266 (s)	2309	47.2	ν_5
2235/2286(Raman)	2292	0.	ν_1
2221 (vw)	2243	1.41	$\nu_3 + \nu_9 + \nu_{11}$
2183(Raman)	2221	0.	ν_2
2150 (vw)	2164	1.35	$0.8(\nu_3 + \nu_7) + 0.3\nu_6$
2097 (m)	2126	0.22	$0.8\nu_6 + 0.3(\nu_3 + \nu_7)$
1287 (Raman)	1282	0.	ν_3
	1094	0.05	$\nu_{13} + 2\nu_{11}$
	1077	0.05	$\nu_{12} + 2\nu_9$
1011 (vw)	1009	0.15	$\nu_8 + \nu_{11}$
944 (w)	929	0.14	$0.5\nu_7 + 0.5(\nu_9 + \nu_{11})$
	873	0.10	$0.5\nu_7 + 0.5(\nu_9 + \nu_{11})$
	807	0.04	$\nu_8 + \nu_{12}$
	749	0.05	$\nu_4 + \nu_{12}$
714-720 (s)	704	4.82	$\nu_9 + \nu_{12}$
	702	2.22	$\nu_{10} + \nu_{11}$
645-650 (s)	658	0.0	$\nu_{13} + 2\nu_{12}$
565 (s)	605	0.50	$\nu_8 + \nu_{13}$
501 (Raman)	516	0.0	ν_8
490.5 (vs)	500	7.24	ν_{11}
571,468(Raman)	440	0.0	ν_4
455 (Raman)	415	0.0	ν_9
276 (vvs)	292	11.7	ν_{12}
170 (Raman)	178	0.0	ν_{10}
61.5 (vs)	67	9.9	ν_{13}

Table 3: Observed and anharmonic ($\nu(\text{cm}^{-1})$) wavenumbers calculated at CCSD(T)/B3LYP level with the aug-cc-pVTZ basis set. Intensities (km/mol) are calculated within the anharmonic mechanical and electrical scheme. The main assignment is given from the variational method.

Table 3: Observed and anharmonic ($\nu(\text{cm}^{-1})$) wavenumbers calculated at CCSD(T)/B3LYP level with the aug-cc-pVTZ basis set. Intensities (km/mol) are calculated within the anharmonic mechanical and electrical scheme. The main assignment is given from the variational method.

CAPTIONS FOR FIGURE AND TABLES:

Figure 1. Equilibrium geometry of DCDA obtained at CCSD(T)/aug-cc-pVTZ level of theory.

Table 1: Description of the modes and Nomenclature for C_6N_2 . Nomenclature is similar to those adopted by Miller and Lemmon¹⁵

Table 2: Harmonic wavenumbers calculated respectively at CCSD(T) and B3LYP levels with the same aug-cc-pVTZ basis set.

Table 3: Observed and anharmonic ($\nu(\text{cm}^{-1})$) wavenumbers calculated at CCSD(T)/B3LYP level with the aug-cc-pVTZ basis set. Intensities (km/mol) are calculated within the anharmonic mechanical and electrical scheme. The main assignment is given from the variational method.

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