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Quantum molecular dynamic approach to modeling the vibrational spectra of propynitrile and its 1:1 complexes with water.

Claude POUCHAN

CNRS, UMR 5254, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, Université de Pau et des Pays de l'Adour, F-64000 Pau, France.

*corresponding author: 00 33 5 59 40 78 50,

claude.pouchan@univ-pau.fr

[ORCID Number: 0000-0003-3841-4922](https://orcid.org/0000-0003-3841-4922)

Abstract

We present here a quantum molecular dynamic approach from *DFT* molecular dynamics (*DFT/MD*) trajectories around 150K, 300K, 450K and 600K to compute the IR spectra of the propynitrile (or cyanoacetylene) molecule HC_3N , the simplest linear cyanopolyne detected in interstellar clouds and circumstellar envelopes of stars. The *DFT/MD* results in fair agreement with the experimental data for the isolated molecule are close to those obtained, for all the valence modes, from an effective second order treatment (*VPT2*) at the *CCSD(T)* level of theory. This *DFT/MD* simulation is used to predict the IR spectra of the 1:1 complexes with water and analyse the shifts expected for the micro-hydrated molecule.

Keywords: Density functional theory; *DFT* Molecular Dynamic Simulation; IR spectroscopy; propynitrile or cyanoacetylene molecules; complexes 1:1 with water

1. Introduction

Vibrational spectroscopies (Infrared and Raman) and IR spectroscopy particularly are commonly used in laboratories to identify and know the quality of a product. To do this, it is sufficient to choose the most intense characteristic bands without worrying about the globality and the complexity of all the signals appearing in the spectrum. Indeed, all the IR bands of a molecule are not easy to assign because we can find in addition to fundamental bands, overtones and combinations whose position and intensity varies according to the physical state of the product which can be gaseous, liquid, in solution, solid or trapped in a matrix [1]. To help in the full identification of an IR spectrum, and to take into account the effects of the environment, modelling through theoretical chemistry methods must be used very often [2]. When we are only interested in the fundamental bands, quantum mechanics methods easily provide harmonic frequencies that are corrected by scale factors to take into account the anharmonicity and thus get closer the calculated spectrum to the observed data [3]. When we want to know in order to explain or predict the whole spectrum (fundamentals, overtones, combinations) and to account for the effects due to the environment (liquid, solution, solid, adsorption...) we must use much more sophisticated quantum methods. Two main types of methods make it possible to obtain a theoretical IR spectrum that can be classified into 'static' and 'dynamic' methods and whose main characteristics are briefly recalled in the paragraph 'Methods and Computational Details'

Several 'static' models have been developed and implemented to explicitly take into account anharmonicity. In particular, for small molecules converged rovibrational levels can be obtained by fully variational treatments, as Vibrational Configuration Interaction (VCI) [4-9] or (VCI-P) [10-12] methods when the configuration interaction is guessed by a perturbative treatment and more recently Vibrational Coupled Cluster method (VCC) [13,14]. However, to conveniently handle large isolated systems it becomes unavoidable to introduce some approximations concerning both the form of the potential and the rovibrational treatment. Today to modelling vibrational spectra in the mid infrared region the most successful approaches are based on truncated three-mode potentials by using the effective second order perturbative (VPT2) [15] treatment, fast and easy, which tends to correct the numerical instabilities of a traditional perturbative approach due to the presence of random degeneracy.

Beside these static approach and starting from the pioneer work of Wilson et al.[16], vibrational spectra can be calculated in an alternative way using a 'molecular dynamic' approach and statistical mechanic models based on the Fourier transform analysis of the time correlation function of atomic dipole moments. These molecular dynamic (MD) approaches in principle yield to a full description of the modes activated at a given energy or

temperature and describe their couplings and finally allow the complete description of the IR properties as position and intensity for all bands. Although several quantum corrections to the classical time-correlation functions have been proposed, they don't affect the calculated wavenumbers but only the shape and the width of the bands [17].

This work aims to compare the spectra obtained by the two approaches for an isolated molecule and a molecule interacting with water in order to describe, as a first approximation, the effects of the environment related to micro-hydration. For MD simulations, DFT has been applied for the description of the electronic structure and gradients 's computations using the very popular Becke three parameter hybrid functional (B3LYP) [18] and a localized Gaussian type basis set [6-31+G(p,d)] known to give excellent IR spectra for organic molecules [19]. The DFT/MD results based on the propagation of the density matrix will be compared, for the valence modes, to the computed data obtained at CCSD(T)/aug-cc-pVTZ anharmonic wavenumbers issued from a VPT2 treatment also known to provide excellent results in the static method when the couplings between the normal modes are not very important.

The molecule chosen for this study is a linear system the propynenitrile HC_3N since it is the simplest cyanopolyne discovered in interstellar environments. Detected in the atmosphere of Titan it was identified by means of the knowledge of the fundamental bands and has been extensively studied by means of careful laboratory studies of high resolution infra-red spectra since 1990 [20-24]. Recently, Bizzochi et al. [25] re-investigate the IR spectrum up to 1100 cm^{-1} and improve all the data by an extensive list of highly accurate rest frequencies. Taking into account these experimental data, our objective will be to know what is the most appropriate approach to modelling the experimental spectrum.

After a brief description of the computational methods applied (section 2), the DFT/MD results obtained for the propynenitrile will be discussed and compared both with the experimental data and the results issued from CCSD(T)/VPT2 computations. A first approach of the IR spectra for the complexes $\text{HC}_3\text{N}:\text{H}_2\text{O}$ will complete this theoretical study. (section 3).

2. Methods and Computational details

Structural optimization, harmonic frequencies, IR intensities, and anharmonic frequencies issuing from second order perturbative approach (VPT2) and ab-initio molecular dynamic simulations were performed with Gaussian

09 program [26]. Spectral analysis from the MD simulations was obtained using the VAMD (Vibrational Assignments in Molecular Dynamic) program developed in our group and described in reference [27].

Electronic structure calculations were performed at the DFT level using the most common three parameter hybrid functional of Becke (B3LYP) [18] and a valence double zeta Pople basis set including diffuse and polarization functions, 6-31+G(d,p). This model chemistry was chosen since it has been previously shown that, for the prediction of harmonic and anharmonic force constants and in the case of small organic [18,28,29] and radical [30], systems it is able to recover the results obtained using the more expensive CCSD(T) [31]/Aug-ccp-VTZ [32] approach.

2.1. Static treatment of anharmonicity

The static approach used to compute anharmonic effects using the perturbative (VPT2) approach is briefly recalled. From a minimum energy structure of a given system, a quartic force field is built in which the third and fourth derivatives are computed by 6N-11 (N=number of atoms) numerical differentiations of analytical or numerical (in case of CCSD (T) calculations) second derivatives from a least square fitting procedure [33]. In the quartic approximation, the potential is given by:

$$V = \frac{1}{2!} \sum_i \omega_i q_i^2 + \sum_{i,j,k} k_{ijk} q_i q_j q_k + \sum_{i,j,k,l} k_{ijkl} q_i q_j q_k q_l$$

where q_i the i -th dimensionless normal coordinate, and ω_i , k_{ijk} , k_{ijkl} the harmonic, cubic and quartic force constant respectively expressed in cm^{-1} . Note that only the anharmonic force constants involving the tri-mode interactions ($k=1$) are determined by numerical differentiation.

Next, the vibrational frequencies can be evaluated in the VPT2 approach by using the well-know formula of Willets and coworkers [34] derived from second order perturbation theory:

From a technical point of view, it can be shown [35] that the best setup is obtained using a step size of 0.01\AA for the numerical differentiation of harmonic frequencies. For DFT computations very tight convergence criteria for structural optimizations and fine grids for integral evaluation (that is at least 99 radial and 590 angular points) are necessary.

2.2. Vibrational analysis from ab-initio Molecular dynamic simulations.

Ab-initio molecular dynamic simulations were performed using the Atom-centered Density Matrix (ADMP) formalism [36-38] which uses localized Gaussian basis sets, thus allowing for sampling on the same potential used for the static methods. This is of particular importance when both the potential energy surface and the

observables are sensitive to the choice of the DFT computational level and, in particular, it allows for the use of hybrid functionals [18, 39-41]. Furthermore, in our case, this choice let to a direct comparison of the results of anharmonic calculations obtained from static and dynamic approaches. Molecular dynamic simulations were performed in the microcanonical subspace [42] with a time-step of 0.2 fs over an overall period of 10 ps, the initial nuclear velocities being set to perform simulations averaging the temperatures of 150K, 300K, 450K and 600K. A suite of programs developed in our lab is used to perform the spectral analysis from ADMP DFT trajectories [27]. Several papers report in detail a simple procedure [43, 44] to get the IR spectrum as Fourier transform of the dipole autocorrelation function [45] that is:

$$I(\bar{\nu}) \propto \int dt \langle \dot{M}_0 \dot{M}_t \rangle e^{i\omega t}$$

M being the total dipole moment, \dot{M} the derivative $\frac{dM}{dt}$ and $I(\bar{\nu})$ the intensity at the $\bar{\nu}$ wavenumber.

To assign the vibrational bands we used the Fourier Transform of Time Correlation Function (FTTCF) of the velocity (V(t)) obtained together with the dipole moment at each time step of the simulation, this function projected along the normal modes or better the internal or local modes giving as described in reference [27] a good representation of the band assignment.

This procedure has been used in our computational strategy to modelling successfully DFT/MD infra-red spectra for gaseous and micro-hydrated forms of nucleobases [46-50]

3. Results and discussions

3-1 Propynenitrile as exemple of linear molecule.

At B3LYP/6-31 G+(d,p) and CCSD(T)/Aug-cc-pVTZ levels the calculated geometries are very similar for C₁-C₂ (1.211 Å vs 1.204 Å) and C₂-H₃ (1.067 Å vs 1.063 Å). A small difference of about 0.01 angstroms can be noted for the other two lengths C₁-C₄ (1.373 Å vs 1.386 Å) and C₄-N₅ (1.167 Å vs 1.157) Å. It should be emphasized the weak influence of the triple excitation at CCSD level for the computed bond lengths.

Table 1 reports the harmonic vibrational wavenumbers obtained at different levels of theory. The harmonic values obtained at the CCSD and DFT levels for the valence vibrations ν_1 , ν_2 , ν_3 , ν_4 and the CCH bending mode ν_5 are in fairly good agreement. However, it should be noted that for ν_7 and ν_6 modes, the B3LYP values are overestimated by about 12 and 16 % respectively compared to CCSD frequencies. Except for the modes ν_5 and

ν_1 (this latter associated with the CH valence mode), the introduction of triple excitations reduces harmonic frequencies by 3 to 5%, bringing them closer to the experimental data.

Table 2 reports the anharmonic vibrational values obtained for the five modes ν_1 , ν_2 , ν_3 , ν_4 and ν_5 from VPT2 and DFT/MD approaches. At VPT2 level, modes ν_6 and ν_7 that have large differences according to their CCSD or B3LYP harmonic determination are decoupled from the other five modes to compute anharmonic wavenumbers. In addition, it should be noted that the quartic force constants are not often adapted for the description of the soft modes that are here ν_6 and ν_7 leading to inappropriate VPT2 results to describe these modes. As reported by Handy and coworkers [51], the simplest VPT2 treatment generally provides, in absence of strong anharmonic couplings, reasonable vibrational wavenumbers of stretching motions: this can be the case for HC_3N . Also the comparison between VPT2 and DFT/MD values appears quite reasonable to describe the five highest modes (valence modes ν_1 to ν_4 and the bending mode ν_5) reported in Table 2, against the experimental data [23-25]. At the VPT2 level, the CCSD(T) wavenumbers are much closer to the experimental values than the DFT results. The mean average deviation varies from 11 to 48 cm^{-1} . Molecular dynamic simulations show a relative weak influence of temperature with an average deviation ranging from 26 cm^{-1} (300K) to 19 cm^{-1} (600K). As a general rule, the CCSD(T)/VPT2 and B3LYP/MD frequencies lead to convergent results in fair agreement with the experimental data with a more favorable mean average deviation for the CCSD(T)/VPT2 static determination (11 cm^{-1}) than for the B3LYP/MD dynamic one (19 cm^{-1}).

3-1 Propynenitrile in interaction with water.

The study of 1:1 complexes of propynenitrile with water is undertaken to simulate as a first approximation the study of hydration and explain the expected vibration frequency shifts on the IR spectra. These calculated displacements will be compared to the experimental values from FT-IR matrix isolation spectroscopy reported by Borget et al [25]. For these 1:1 complexes, two structures are possible (fig 2). The most stable is the formation of a hydrogen bond between the oxygen in the water and the hydrogen of HC_3N (OH structure), the other about 2 kcal mol^{-1} less stable combines the hydrogen in the water with the nitrogen in HC_3N (NH structure). From a Boltzmann population point of view at 300K the former represents 96%. To best modelize the hydrogen bonds, calculations are also performed using the B3LYP-D/6-31G+(d,p) method. From a static point of view, the quartic force field is calculated on all complexes modes (molecule + water) but not by coupling for HC_3N the two lowest deformation modes (ν_6 and ν_7) as for the study of the isolated molecule. From a dynamic

point of view, DFT or DFT-D/MD calculations are performed with energies corresponding to temperatures around 300K and 450 K for the OH structure where the largest band shifts relative to the isolated molecule are expected and around 300K for the NH structure. All theoretical results are reported in Tables 3 and 4 for each of the complexes and compared to the experimental data reported by Borget et al [25].

When examining Tables 3 and 4, we can note a slight improvement brought by the consideration of dispersion effects (DFT-D better than DFT) as well as the relatively small influence of temperature in dynamic simulations with the exception of the ν_1 mode for the OH form largely affected by the hydrogen bond. The results provided by DFT-D/VPT2 and DFT-D/MD approaches are both qualitatively reliable, but globally, the mean average deviation (MAD) between theory and experiment is better for molecular dynamics (respectively 19 and 13 cm^{-1} for OH and NH forms) than for the static DFT/VPT2 approach (42 and 52 cm^{-1} respectively). However, we can emphasize that this difference is mainly due to the incorrect description of the ν_2 mode in the DFT or DFT-D/VPT2 computations. When we look at the displacements of the IR bands of the OH and NH forms relatively to the isolated molecule, we can see that the largest shifts concern the OH form. Indeed for this form the wavenumber of the CH valence mode (ν_1) is downshifted by about hundred cm^{-1} (-98 to -115 cm^{-1} according to our calculations) while the frequency of the CCH bending mode ν_5 is upshifted from 95 to 100 cm^{-1} . These results are in excellent agreement with the experimental values reported by Borget et al (-96 and +93 cm^{-1} respectively). The large decrease observed for the CH stretching mode is likely due to the presence of hydrogen bond which increase the CH bond with respect to the isolated molecule, whereas the upshift of the bending mode is essentially due to the coupling between the bending mode ν_5 and the CC valence mode ν_4 . The frequencies of the other modes are little modified by the presence of the hydrogen bond except for ν_3 upshifted of about ten cm^{-1} (13 cm^{-1} in our calculations versus 10 cm^{-1} experimentally). For the NH structure, the shifts brought by solvation are lower and never exceed about ten cm^{-1} as confirmed by our calculations.

Conclusion

We have investigated the vibrational infra-red spectra of propynenitrile and its 1:1 complexes with water in the framework of quantum mechanics. Building on a B3LYP/6-31G+(d,p) level of theory, two different approaches have been tested to account for vibrational anharmonicity: a static calculation with second order vibrational perturbation theory (DFT/VPT2) and a dynamic through quantum molecular dynamics (DFT/MD). Comparing the results of these anharmonic quantum-mechanical approaches with experimental data reveals that if the

perturbative treatment at the CCSD(T) /VPT2 level of theory offers a more reliable description of both stretching modes for the isolated molecule, the DFT/MD approach (extremely time consuming however) is better than the DFT/VPT2 (fastest when the quartic force constants are obtained) one, by using the same basis set, to describe the IR spectra of propynenitrile and its two 1:1 complexes with water.

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TABLE 1: Computed harmonic wavenumbers (in cm⁻¹) for propynenitrile in vacuo at different levels of theory. Comparison with experimental values

Mode	Main Assignment	CCSD(T)/ aug-cc- pVTZ	CCSD / Aug-cc- pVTZ	B3LYP /6- 31+G(d,p)	Experimental
		ω	ω	ω	ν
ν_7	$\delta(\text{C-CC-N})^a$	218	226	244	222 ^c
ν_6	$\delta(\text{CCN})^a$	487	509	563	504 ^d ; 499 ^c ; 500 ^b
ν_5	$\delta(\text{CCH})^a$	664	702	706	667 ^d ; 663 ^c ; 664 ^b
ν_4	$\nu(\text{C-C})$	875	883	907	862 ^c ; 861 ^b
ν_3	$\nu(\text{C}\equiv\text{C})$	2100	2164	2174	2077 ^d ; 2079 ^c
ν_2	$\nu(\text{CN})$	2306	2393	2374	2269 ^d ; 2274 ^c
ν_1	$\nu(\text{CH})$	3445	3472	3474	3316 ^d ; 3327 ^c

^a Double degenerated modes

^b ref [24] ; ^c ref [23]; ^d ref [25]

TABLE 2: Wavenumbers (in cm-1) calculated for prpynenitrile in vacuo following VPT2 and DFT/MD approaches. Comparison with experimental values

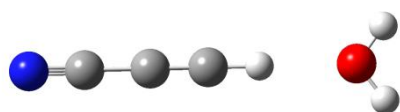
Mode	VPT2 ^a :CCSD(T)/ aug-cc-pVTZ	VPT2 : B3LYP /6- 31+G(d,p)	DFT/MD			Experiment
	ν	ν	T=300K	T=450K	T=600K	
ν_7	218 ^a	244 ^a	252	251	248	222 ^c
ν_6	487 ^a	563 ^a	567	559	563	504 ^d ; 499 ^c ; 500 ^b
ν_5	657	698	652	652	657	667 ^d ; 663 ^c ; 664 ^b
ν_4	867	897	903	900	903	862 ^c ; 861 ^b
ν_3	2078	2145	2093	2088	2083	2077 ^d ; 2079 ^c
ν_2	2279	2344	2252	2247	2242	2269 ^d ; 2274 ^c
ν_1	3337	3365	3363	3354	3346	3316 ^d ; 3327 ^c

^a Order 2 : CCSD(T)/aug-cc-pVTZ – Orders 3 and 4 : B3LYP/6-31+G(d,p)

Modes ν_7 and ν_6 are totally decoupled from others: their harmonic values are reported in the table 2

^b Ref [24]; ^c Ref [23]; ^d Ref [25]

TABLE 3: Wavenumbers (in cm-1) calculated following VPT2 and DFT/MD approaches for HC3N:H2O (OH form). Comparison with experimental values



Mode	VPT2/B3LYP				DFT or DFT-D/MD			Experiment ^a
	ω_{DFT}^b	ν_{DFT}	$\omega_{\text{DFT-D}}^c$	$\nu_{\text{DFT-D}}$	DFT 450K	DFT- D 450K	DFT-D 300K	
ν_7	307	-	306		260	260	282	
ν_6	646	-	645		538	540	555	506
ν_5^c	874	-	879	-	738	742	752	760
ν_4	910	901	906	894	899	895	900	
ν_3	2161	2132	2157	2116	2090	2088	2085	2067

ν_2	2367	2330	2364	2324	2251	2252	2253	2263
ν_1	3354	3220	3339	3201	3294	3294	3248	3219
MAD. ^d		44		42	37	36	19	

^a Ref [25]

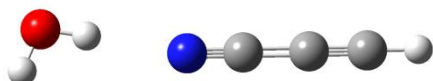
^b B3LYP/6-31+G(d,p) calculations

^c B3LYP-D/6-31+G(d,p) calculations

^d MAD. for Mean Average Deviation (in cm^{-1}) for the valence modes only

^e Not converged values

TABLE 4: Wavenumbers (in cm^{-1}) calculated following VPT2 and DFT-D/MD approaches for HC₃N:H₂O (NH form). Comparison with experimental values



Mode Assignment	VPT2		Molecular Dynamics	Experiment ^a
	$\omega_{\text{DFT-D}}^b$	$\nu_{\text{DFT-D}}$	DFT-D 300K	
ν_7	232	-	221	
ν_6	568	-	572	
ν_5	719	706	680	670
ν_4	910	901	903	
ν_3	2176	2146	2097	
ν_2	2380	2340	2258	2273
ν_1	3463	3342	3367	3312
MAD. ^c		52	13	

^a Ref [25]

^b B3LYP-D/6-31+G(d,p) calculations

^c MAD. for Mean Average Deviation (in cm^{-1})



Fig 1 : Propynenitrile atomic numbering

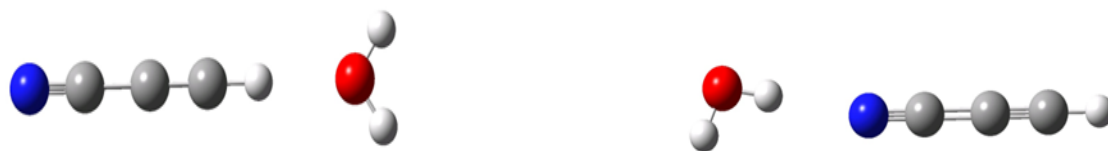


Fig 2: OH and NH forms of the 1 :1 complex between HC₃N and H₂O

Caption for Tables:

TABLE 1: Computed harmonic wavenumbers (in cm-1) for propynenitrile in vacuo at different levels of theory. Comparison with experimental values

TABLE 2: Wavenumbers (in cm-1) calculated for propynenitrile in vacuo following VPT2 and DFT/MD approaches. Comparison with experimental values

TABLE 3: Wavenumbers (in cm-1) calculated following VPT2 and DFT/MD approaches for HC₃N:H₂O (OH form). Comparison with experimental values

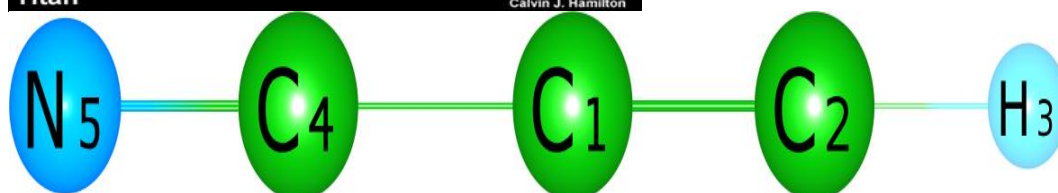
TABLE 4: Wavenumbers (in cm-1) calculated following VPT2 and DFT-D/MD approaches for HC₃N:H₂O (NH form). Comparison with experimental values

Caption for Figures:

Fig 1 : Propynenitrile atomic numbering

Fig 2 : OH and NH forms of the 1 :1 complex between HC₃N and H₂O

Graphical Abstract:



Highlighths

- Propynitrile HC_3N is a molecule of astronomical importance detected in interstellar clouds
- We compare static (VPT2) and dynamic (DFT/MD) approaches to modelize the IR spectrum in vacuo.
- IR spectra of 1:1 complexes with water are studied by DFT/MD to analyze the shifts expected by the environment