Vibrational Spectrum of '3-iodo-2-propynenitrile (IC3N)' from accurate CCSD(T)-F12b/MP2-F12 potential energy surface

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REGULAR ARTICLE

Vibrational Spectrum of '3-iodo-2-propynenitrile (IC₃N)' from accurate CCSD(T)-F12b/MP2-F12 potential energy surface

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Abstract

The high-resolution infrared spectrum of IC_3N has been the subject of numerous experimental studies. Relying on a hybrid anharmonic potential CCSD(T) -F12b/ MP2-F12 with cc-pVTZ-F12b basis sets and the application of a pure variational method (VCI), the IR spectrum of IC_3N was calculated between 100 and 4600 cm^{-1}. These calculations allowed us to revisit the entire IR spectrum and assign a large part of its overtones, combinations bands with respect to experimental measurements. As it is shown in this work, the observed bands located at 1031 and 955 cm^{-1} could be explained in terms of Fermi resonance.

Keyword Ab initio CCSD(T)-F12b calculations · 3-iodo-2-propynenitrile molecule · Vibrational configurations interaction · IR spectroscopy

1 Introduction

Substituted cyanopolyynes and in particular halogenated cyanopolyynes have been the subject of numerous experimental works in the middle 60 s and 70 s with respect to their spectroscopic properties. Among these, the first member of the series, and the simplest one, namely halogeno-propynenitrile, has been the subject of both infrared (IR) [1–5] and Raman [6] measurements. Recently, a joint experimental and theoretical work by Guzik et al. [7] studied the photoisomerization of IC_3N linear molecule widely known as iodo-cyanoacetylene or 3-iodo-2 propynenitrile. This molecule is the halogenated analogue of HC_3N molecule extensively studied in the ion–molecule chemistry in Titan's ionosphere. In this article, Guzik et al. explored in depth the middle IR spectrum of gaseous IC_3N in an Ar environment in a spectral region between 400 and 4000 cm^{-1}. Although some interesting findings have been exposed, the complete spectrum interpretation is hampered by limitation of the computational approach chosen which solely relied on the widely applied B3LYP [8] functional. As shown in two previous published studies from our group, on the spectroscopic properties of HC_3N [9, 10]

a quantum dynamic molecular approach DFT/QM is much more adequate than a conventional static approach based on a B3LYP potential energy surface. If the latter treatment is followed by a vibrational second-order perturbative (VPT2) method, the final spectrum interpretation should be considerably more accurate [9], especially when the explicitly correlated CCSD(T)-F12b [10] approximation with an sufficiently large basis set (e.g., aug-cc-pVTZ [11–13]. In this context, it would be meaningful to revisit the IR spectrum of IC_3N by considering a CCSD(T)-F12b approach applied with the adapted basis set cc-pVTZ-F12 family [14, 15], especially developed for such explicitly correlated calculations. In such a manner, adaptive multi-dimensional potential energy surfaces (PES) can be obtained [16–18] that can be treated either by a second-order perturbative method (VPT2), or by a fully variational treatment as the configuration interaction method (VCI). The latter approach, although computationally more expensive, generally provides more consistent and accurate vibrational spectra. The bottleneck of this procedure remains the accurate calculation of extended areas of the potential energy surface by high-level ab initio methods. One way to get around this problem is to develop the PES into a series of terms, expressed in the normal coordinates space q_i, of first (V_i), second (V_{ij}), third (V_{ijk}) that will allow a treatment of the higher-order terms with less sophisticated methods within the framework of density functional theory. Specifically, in this work we performed the calculations of the V_i term of the

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potential using the CCSD(T)-F12b/cc-pVTZ-F12 approach to obtain the best possible geometry parameters and harmonic frequencies. Then, we studied the influence of the obtained second- (V_{ij}) and third-order (V_{ijk}) terms by means of B3LYP/aug-cc-pVTZ method, on the one hand, and on the other hand by means of MP2-F12 [19]/cc-pVTZ-F12b method. In a next step, we analyzed the impact on the calculation of the anharmonic frequencies by a vibrational perturbational method of second order (VPT2). Finally, we interpret the computed vibrational spectrum of IC_3N obtained by a vibrational configuration interaction method (VCI) and compare it to the published experimental data set. The paper is structured as follows: In Sect. 2, we summarize the computational methods applied and the most important details of our calculations. For further information about theory used in the current approach is given in more details in previous published articles [16, 18]. Finally, in Sect. 3 we provide the obtained results to describe, assign and predict the IR spectrum of IC_3N in vacuo.

2 Methods and computational details

The calculation of extended areas of potential energy surface (PES) for a polyatomic system by high level interaction configurations methods is a great challenge in quantum chemistry and needs very time-consuming resources. Different techniques and algorithms developed in our laboratory and reported in the literature [20, 21] offer an accurate representation of PES. They remain, however, less accurate in the case of linear molecules. Therefore, we have chosen the formalism developed by Rauhut et al.[16, 18] for an efficient and fully automatic generation of PES around an equilibrium structure. This method uses an incremental scheme of difference potentials (V_i, V_{ij}, V_{ijk}…called, respectively, 1D, 2D, 3D… terms) spanned by the normal coordinates q_i of the system as originally proposed and described by Carter et al. [22, 23]. The most successful approaches are based on truncated three modes potentials, the many-body expansion of the PES being truncated after the 3D terms as:

$$V(q_{1,\dots,n}) = V_0 + \sum_i V_i(q_i) + \sum_{i<j} V_{ij}(q_i, q_j) + \sum_{i<j<k} V_{ijk}(q_i, q_j, q_k) + \dots \quad (1)$$

with

$$V_i(q_i) = V_i^0(q_i) - V_0 \quad (2)$$

$$V_{ij}(q_i, q_j) = V_{ij}^0(q_i, q_j) - \sum_{r\{i,j\}} V_r(q_r) - V_0 \quad (3)$$

$$V_{ijk}(q_i, q_j, q_k) = V_{ijk}^0(q_i, q_j, q_k) - \sum_{r>s\{i,j,k\}} V_{rs}(q_r, q_s) - \sum_{r\{i,j,k\}} V_r(q_r) - V_0 \quad (4)$$

In the above equations, V_0 represents the total energy at the equilibrium geometry and the quantities with the superscript 0 denote the total energy obtained from the electronic calculations at distorted nuclear configurations.

The conventional CCSD(T) coupled-cluster electronic method is a valuable tool that is considered as capable to provide reliable molecular properties when applied with a rich basis set. Here, its explicitly correlated version [11, 14, 15] known as CCSD(T)-F12b. In the latter implementation, the Marchetti–Werner approach has been used for the scaling of the triple excitations (T). This approach uses extra two-particle basis-functions, which depend on the inter-electronic distance, and it has been shown to the accuracy describe a great variety of properties. In the present case, all structural parameters and harmonic vibrational frequencies have been carried out using a basis set of triple-ζ quality, namely cc-pVTZ-F12 that comprises a large core pseudopotential for I. The calculation of the PES has been based on a multi-level scheme that needs 9288 grid points resulting in 48 single-point calculations for the 1D terms, 956 energy calculations and 8284 energy determinations, respectively, for the 2D and the 3D terms contributions in the case of IC_3N. Taking into account the small size of the system but the presence of a heavy atom, the electronic computations are made at the highest computational level, i.e., CCSD(T)-F12ba for the 1D term (geometry and harmonic frequencies) and MP2-F12 and B3LYP for the 2D and 3D anharmonic contributions. For CCSD(T)-F12b and MP_2-F12 computations, the cc-pVTZ-F12 basis set family developed for explicitly correlated calculations was selected for C and N atoms, while the same basis set with pseudopotential (cc-pVTZ-F12-PP) was used for the I atom [24]. At the DFT level, we used the B3LYP method using an ultrafine grid. For this purpose the aug-cc-pVTZ basis set for C and N and aug-cc-pVTZ-PP for the iodine atom [25]. The IR spectrum of IC_3N is computed at different levels of theory. In a first step, we used the VPT2 method with the complete B3LYP determination of the PES and compare the frequencies obtained for fundamental, overtone and combination bands with those obtained with the hybrid CCSD(T)-F12b/B3LYP and CCSD(T)-F12b/MP2-F12 potential. For electronic computations, we used GAUSSIAN 16 suite [26] of programs, and for VPT2 [27] vibrational calculations, we used the MOLPRO 2018 [28] package. Finally, the VPT2 vibrational results with the hybrid CCSD(T)-F12b/B3LYP PES are obtained with our VPT2-CI program [29–32]. In a second step, we computed the IR spectrum at the VCI level with a complete ab initio PES obtained with the CCSD(T)-F12b/MP2-F12 potential. VCI calculations

account for vibrational correlation effects and the use of PES as generated from the SURF program and a basis of VSCF-modals generated from 16 distributed Gaussians. VCI calculations include single (S), double (D), triple (T) and quadruple (Q) excitations. For the irreducible representation, Σ 27,019 configurations (32 S, 504 D, 4820 T and 21,662 Q) have been selected, while 44,774 configurations (18 S, 540 D, 6928 T, 37,288 Q) are required to describe the degenerated irreducible representation Π. An analysis of the modes is carried out to obtain their description (eigenvectors) and to highlight possible resonances.

3 Results and Discussions

3.1 Geometry and harmonic frequencies

We have reported for IC_3N (Fig. 1) in Table 1 the bond lengths and harmonic frequencies calculated in B3LYP and CCSD(T)-F12b with almost identical Gaussian basis sets. The C-I distance is almost identical in the two calculations, but the other bond distances are systematically shorter in the B3LYP calculations. If we turn our attention to the harmonic frequencies, those calculated in CCSD(T)-F12b we will see that they are all lower than those obtained at the B3LYP level. This difference, between 20 and 50 cm^{-1} for the three highest valence modes, is also paradoxically very important (53 and 27 cm^{-1}) for two of the three degenerated angular deformation modes. In fact, only the harmonic frequencies v_4 and v_7 are comparable in the two computational approaches.

For the IC_3N molecule we, thus, find harmonic frequency-differences between CCSD(T)-F12b and B3LYP of the same order of magnitude as expected from the anharmonic correction. This is the reason for which it vital to treat this molecule at the best possible computational level to determine its geometrical structure and its harmonic frequencies.

The CCSD(T)-F12b method applied with the cc-pVnZ-F12 basis ($n=T$ in our case) is as already pointed out by Martin et al. [15] and verified in our previous work on HC_3N [9], one of the reference methods that yield reliable molecular geometries and harmonic frequencies (1D term of the PES) to be used in a second step for the calculation of anharmonic frequencies.

3.2 Calculation of the anharmonic terms

The anharmonicity is obtained taking into account the second- and third-order terms of the potential. Due to the

Fig. 1 IC_3N molecule

Table 1 Computed bond lengths (in Angstroms) and harmonic wavenumbers (in cm^{-1}) for 3-iodo-2-propynenitrile IC3N in vacuo at different levels of theory. Comparison with experimental values

Bond lengths and modes	B3LYP/aug-cc-pVTZ (a)	CCSD(T)-F12b/cc-pVTZ-F12 (a)	Experimental
N≡C	1.157	1.164	
C–C	1.364	1.377	
C≡C	1.208	1.214	
C–I	1.987	1.988	
	ω	ω	N
ν_7^{α}	115	109	(118,134) [c]
ν_6^{α}	323	296	309[a]; (322)[c]; 301[d]
ν_5^{α}	539	486	496[a]; (483)[c]; 493[b];496[d]
ν_4	361	360	364[a]; (349)[c]; 356[d]
ν_3	1025	1006	1031[a];(1037)[c];1031[b]
ν_2	2215	2164	2131[a];(2130)[c];2123[b]
ν_1	2357	2319	2270[a]; (2262)[c];2266[b]

Basis set used in the calculations: aug-cc-pVTZ and cc-pVTZ basis set, respectively, for C and N and pseudo-potential (PP) for I

[α]Double degenerated modes (Π)

[a] ref [5]; [b] ref [7]; [c] ref [6]; [d] ref[4]

high cost of CCSD(T)-F12b calculations, we have chosen to determine the D2 and D3 terms either by DFT (B3LYP) and by a less expensive ab initio method (MP2-F12).

In Table 2, we list the anharmonic VPT2 values computed at three different approximation levels, namely B3LYP, CCSD(T)-F12b/B3LYP, CCSD(T)F12b /MP2-F12. In the last two methods, the 1D term is computed at the CCSD(T)-F12b level, while the 2D and 3D terms are computed at the B3LYP and MP2-F12 levels, respectively. These numerical data are followed by an approximate assignment of the frequencies at the VPT2 level.

The average deviation between the calculated anharmonic frequencies in CCSD(T)-F12b/B3LYP and CCSD(T)-F12b/MP2-F12 is of the order of 7 cm^{-1}, with the largest deviations observed for the v_3 (19 cm^{-1}), v_5 (11 cm^{-1}) and v_7 (7 cm^{-1}) modes and their combinations. However, this deviation never exceeds 20 cm^{-1} for all the fundamental modes, their overtones and their combinations, thus making possible the global interpretation of a spectrum in the mid-IR, whatever the DFT or ab initio (MP2 in our case) determination of the 2D and 3D terms of the potential.

If we now compare, at the VPT2 level, the B3LYP and CCSD(T)-F12b/B3LYP frequencies, we can see that the average difference between the calculated frequencies is about 50 cm^{-1} with a maximum up to 100 cm^{-1}. We can thus deduce that for IC_3N it is inadequate to attempt the global interpretation of the spectrum from B3LYP computations, especially in the spectral regions where the density of states

Table 2 Computed frequencies (in cm^{-1}) for fundamental, overtone and combinations bands calculated at VPT2 level with the three different PES (a, b, c):

B3LYP[a]	CCSD(T)-F12b/B3LYP[b]	CCSD(T)F12b / MP2-F12b[c]	Approximate Assignment[d]
2318	2280	2276	ν_1
2182	2131	2128	ν_2
992	973	992	ν_3
356	355	358	ν_4
534	481	492	ν_5
323	297	300	ν_6
106	101	108	ν_7
Overtones			
4621	4544	4540	$2\nu_1$
4352	4251	4245	$2\nu_2$
2009	1970	1978	$2\nu_3$
711	709	715	$2\nu_4$
1067	981	993	$2\nu_5$
650	600	603	$2\nu_6$
209	209	225	$2\nu_7$
Combinations			
4482	4393	4380	$\nu_1+\nu_2$
3330	3273	3270	$\nu_1+\nu_3$
3192	3122	3120	$\nu_2+\nu_3$
2674	2635	2633	$\nu_1+\nu_4$
2537	2487	2485	$\nu_2+\nu_4$
1364	1344	1349	$\nu_3+\nu_4$
2845	2753	2763	$\nu_1+\nu_5$
2711	2606	2616	ν_{2+5}
1539	1467	1481	$\nu_3+\nu_5$
890	836	849	$\nu_4+\nu_5$
2638	2572	2571	$\nu_1+\nu_6$
2500	2421	2422	$\nu_2+\nu_6$
1333	1287	1279	$\nu_3+\nu_6$
679	651	656	$\nu_4+\nu_6$
858	777	794	$\nu_5+\nu_6$
2420	2376	2381	$\nu_1+\nu_7$
2283	2227	2233	$\nu_2+\nu_7$
1111	1086	1090	$\nu_3+\nu_7$
462	457	469	$\nu_4+\nu_7$
641	583	603	$\nu_5+\nu_7$

B3LYP with an aug-cc-pVTZ basis set for C and N and pseudopotential (PP) for I

CCSD(T)-F12b/ B3LYP for D1 /D2; D3 terms, respectively

CCSD(T)-F12b/MP2-F12 for D1/D2;D3 terms calculated with cc-pVTZ-F12 developed for explicitly correlated calculations

The approximate assignment is given at VPT2 level

becomes important (between 2600 and 2000 cm^{-1} or around 1000 cm^{-1}). On the other hand, all calculated frequencies at the CCSD(T)-F12b/MP2-F12 level reproduce very well the experimental data, except from the v_3 mode that will be examined more closely in the following pages.

3.3 Analysis of the computed IR spectra

The calculated spectrum in the mid-IR between 100 and 4600 cm^{-1} is shown in Table 3. Obtained at the VCI level from the ab initio CCSD(T)-F12b/MP2-F12 determination of the PES, the spectrum is analyzed according to the position of the bands and their intensity in comparison to the experimental data. Note that, apart the v_3 mode, all of the intensities calculated for the combination modes and overtones feature a considerably lower intensity than the fundamental modes. Between the spectral range of 3000 and 4600 cm^{-1}, overtones of the v_1 and v_2 modes as well as the combination bands between them and with v_3, should be expected. These modes calculated at 4538, 4382, 4249, 3308 and 3164 cm^{-1} have weak intensities of the same order of magnitude and have not been observed experimentally. The region between 2800 and 2400 cm^{-1} has been the subject of the recent studies in Ar matrix. The five bands observed, respectively, at 2754, 2718, 2619, 2562 and 2476 cm^{-1} are calculated at 2768, 2706, 2628, 2574, and 2496 or 2435 cm^{-1}. We assign them to the $v_1 + v_5$, $v_2 + v_4 + 2v_7$, $v_2 + v_5$, $v_1 + v_6$, $v_2 + v_4$ or $v_2 + v_6$ combination bands, respectively. The calculated intensities are also in the same ratio as those observed. Only the band calculated at 2642 cm^{-1} and of non-negligible intensity (0.94 km/mol) is not observed in matrix. Hence, we attribute this band to the combination $v_1 + v_4$.

Around 2000 cm^{-1}, the fundamental bands v_1 and v_2 corresponding to the CN and CC triple bond and, respectively, calculated at 2275 and 2129 cm^{-1} with intensities of 159.7 and 0.96 km/mol are observed in the gaseous state at 2270 and 2131 cm^{-1}. Three other bands are calculated in this region at 2233, 2090 and 1990 cm^{-1}. Only the second band assigned at $2v_3 + v_7$ is observed in the solid state (2087 cm^{-1}) and in matrix (2074 cm^{-1}). The other two calculated bands with respective intensities of 0.1 and 0.55 km/mol are assigned at $v_2 + v_7$ and $2v_3$, respectively. Turning our attention in the spectral range between 1900 and 1050 cm^{-1}, four combination bands of null or very low intensity have been obtained at 1447, 1396, 1271 and 1074 cm^{-1}. These absorption bands are assigned to the combinations of the v_3 mode with v_4, v_5, v_6 and v_7; it is not surprising that they could not be observed.

Around 1000 cm^{-1}, a Fermi resonance appears between the v_3 mode and the first overtone ($2v_5$) of the angular deformation vibration. This resonance causes a band splitting into two bands located, respectively, at 1027 and 958 cm^{-1}. The first of these bands is preferentially assignable to the v_3 mode and has a much higher intensity than the second which concerns preferentially the $2v_5$ overtone. It is under the

Table 3 Anharmonic spectrum of IC$_3$N computed at the VCI (SDTQ) level with the CCSD(T)-F12b/MP2-F12 potential energy surface. All calculations are carried out with the cc-pVTZ-F12 basis set for C and N. PP is added for the iodine atom

Assignment	ν (VCI) (cm^{-1})	I (in km/mol)	Experimental gas/(solid)	Experimental [Ar matrix]
$2\nu_1$	4538	–		
$\nu_{1+}\nu_2$	4382	0.15		
$2\nu_2$	4249	0.30		
$\nu_{1+}\nu_3$	3308	0.16		
$\nu_{2+}\nu_3$	3164	0.14		
$\nu_{1+}\nu_5$	2768	0.06		2754 [0.1]
$\nu_{2+}\nu_{4+}2\nu_7$	2706	–		2718 [0.05]
$\nu_{1+}\nu_4$	2642	0.94		
$\nu_{2+}\nu_5$	2628	0.25		2619 [0.7]
$\nu_{1+}\nu_6$	2574	–		2562 [0.05]
$\nu_{2+}\nu_4$	2496	1.0		2476 [0.5]
$\nu_{2+}\nu_6$	2435	0.07		
$\nu_{1+}\nu_7$	2375	–		
ν_1	2275	159.7	2270; (2262)	2266 [100]
$\nu_{2+}\nu_7$	2233	0.1		
ν_2	2129	0.96	2131; (2130)	2123 [13]
$2\nu_{3+}\nu_7$	2090	–	(2087)	2074 [0.7]
$2\nu_3$	1990	0.55		
$\nu_{3+}\nu_5$	1447	–		
$\nu_{3+}\nu_4$	1396	–		
$N_{3+}\nu_6$	1271	–		
$\nu_{3+}\nu_7$	1074	–		
$0.6(\nu_3)_+0.4(2\nu_5)$	1027	1.3	1031; (1037)	1031 [0.8]
$0.4(\nu_3)_+0.6(2\nu_5)$	958	0.08	(958;959)	955 (0.06)
$\nu_{4+}\nu_5$	860	**–**		847 [0.13]
$\nu_{5+}\nu_6$	798	2.0		
$2\nu_4$	718	–		
$\nu_{4+}\nu_6$	668	–		
$2\nu_6$	609	0.45		
$\nu_{5+}\nu_7$	597	1.8		
ν_5	492	5.9	496; (483);[496]	493–494 [5.2]
$\nu_{6+}\nu_7$	411	0.26		
ν_4	358	1.88	364; (349);[356]	
ν_6	300	12.0	309; (322);[301]	
$2\nu_7$	210	0.47		
ν_7	101	4.2	106;(118,134);[126]	

effect of this resonance that these modes are in perfect agreement with the experimental values located at 1031 cm^{-1} and 955 cm^{-1} in the gaseous state and in argon matrix.

The band observed at 847 cm^{-1} corresponds to the $v_4 + v_5$ combination calculated at 860 cm^{-1} while the $v_5 + v_6$, $2v_6$, and $v_5 + v_7$ vibrations calculated at 798, 609, and 597 cm^{-1}, respectively, and of nonzero intensity are not experimentally reported.

Below 500 cm^{-1}, we calculate, respectively, the modes v_4 and v_5, v_6 and v_7 corresponding to the CI valence vibration and the doubly degenerate angular deformations. The values obtained of 358 cm^{-1} and 492, 300 and 101 cm^{-1} are in perfect agreement with the various experimental data reported in the literature and in particular those obtained in the gaseous state (364, 496, 309 and 106 cm^{-1}).

Finally, let us note that two other bands not observed experimentally, which feature weak intensities at 411 and 210 cm^{-1}. These bands correspond, respectively, to the combination $v_6 + v_7$ and to the overtone $2v_7$.

4 Conclusions

In this study, we have carried out, for the first time, accurate theoretical computations concerning the vibrational spectrum of 3-iodo-2-propynenitrile IC_3N in the mid-infrared region. On the basis of CCSD(T)-F12b/MP2-F12 potential energy surface and by means of a pure vibrational configurations interaction method (VCI), we propose a complete ab initio modeling of the IR spectrum of IC_3N which allows to assign all fundamental, combinations and overtones between 100 and 4600 cm^{-1}. Our original results give a new interpretation of the assignments of all the observed bands and explains by the existence of a Fermi resonance the presence of the two bands observed at 1031 and 955 cm^{-1}.

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