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Calculation of non-fundamental IR frequencies and intensities at the anharmonic level. I. The overtone, combination and difference bands of diazomethane, H_2CN_2

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Abstract

The experimental assignment of IR non-fundamental bands can be assisted by calculation of both frequencies and intensities, as shown in this work on diazomethane. The ab initio B3LYP method is used to obtain the anharmonic force fields up to the fourth order. The anharmonic vibrational wave functions have been calculated using a variation–perturbation algorithm. The dipole moment expansion needed in the evaluation of absolute intensities is limited to the first derivatives. The results, including those for overtone, combination and difference bands disagree with some experimental attributions and complement the available experimental data. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The IR characterisation of any compound usually requires the identification of both fundamental and non-fundamental vibrational modes such as overtones and combination modes. Few criteria are available to attribute the non-fundamental modes. One piece of the experimental information in this delicate assignment is the absolute intensity of each band. From a theoretical point of view, the IR activity of overtone and combination bands can be

explained only by the anharmonicity of the corresponding vibrational wave functions. Therefore calculations at the anharmonic level are necessary to check the experimental attributions. Our purpose in this work is to show, for the example of diazomethane, that calculated anharmonic frequencies and corresponding intensities could complement the experimental interpretation of the IR spectrum.

Diazomethane (H_2CN_2) is an extremely explosive compound, widely used in analytical chemistry. Several IR spectroscopic investigations of diazomethane [1–4] have been published. Some recent publications [5,6] have been devoted to the IR study of this compound, in the frame of a general program on the detection by IR spectroscopy of organic compounds supposed to be present in the atmosphere of Titan viewed as a prebiotic system.

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The interpretation of data obtained from the Voyager Iris spectrum of Titan's atmosphere [6] was supported by earlier experimental work, essentially the paper by Moore and Pimentel [3] on the diazomethane. These authors undoubtedly made the most detailed experimental analysis available. They investigated the spectra of gaseous H_2CN_2 and its related isotopic derivatives in the IR region between 230 and 4000 cm^{-1} . All the parallel and perpendicular fundamental modes of this molecule are discussed as well as some overtones and combinations. The assignments of the observed bands were proposed relying on literature data, without any reference to calculations beyond the harmonic approximation. Moreover the lack of information on both the band intensities and the overlapping between rovibrational structures prevented Moore and Pimentel from giving an exhaustive interpretation of their spectrum. This contribution was partially completed by more recent studies [5,6] including some information on absolute band intensities.

On the other hand, diazomethane has been the subject of a large number of theoretical investigations, essentially about its geometrical structure. However, a relatively restricted number of publications has been devoted to the interpretation of the IR spectrum. To our knowledge, only harmonic vibrational frequencies have been computed [7–9] and an *ab initio* interpretation of the quadratic force field was proposed in 1977 [10].

The aim of the present work is, first, to obtain an accurate *ab initio* anharmonic force field and vibrational structure of the ground electronic state of H_2CN_2 . Secondly, the assignment of overtone, combination and difference bands is investigated to complement experimental results previously obtained and to provide reliable data on the frequency and absolute intensity for each band. The interpretation of the IR spectrum inquires the breakdown of the double harmonic approximation. Another goal of the present paper is to show that the variation–perturbation approach used to solve the vibrational equation is suitable for strongly anharmonic potential surfaces. Diazomethane is an example of a non-rigid molecule as defined by Carsky et al. [11]: the potential

energy hypersurface is very flat in the direction of the CH_2 wagging mode and the harmonic treatment is not suitable, in this case.

2. Theoretical and computational considerations

The approach developed here to compute the vibrational spectrum of diazomethane, consists of four steps: (i) geometry optimisation; (ii) calculation of harmonic, cubic and quartic force constants in the basis of curvilinear coordinates at the optimum geometry; (iii) calculation of the harmonic vibrational spectrum by means of the Wilson method to obtain the vibrational equation in terms of reduced normal coordinates; (iv) variation–perturbation treatment used to solve this equation.

All the molecular electronic wave function calculations were performed using the GAUSSIAN98 [12] package. Post-Hartree–Fock corrections were done in a self-consistent Kohn–Sham calculation with the B3 exchange correction in combination with the LYP correlation correction (i.e. the Becke gradient-corrected exchange form [13] and the Lee et al. [14] correlation form within the GAUSSIAN98 code). This kind of approximation has been shown to yield highly accurate molecular geometries, bond energies and harmonic vibrational frequencies for molecular ground states. The double-zeta plus polarisation (DZ+P) basis set due to Dunning [15] has been used for all the calculations.

The harmonic, cubic and quartic force fields were set up from a least squares fit performed to energies on a grid of 2100 points described in terms of curvilinear coordinates (bond and angle displacements). In the basis of curvilinear coordinates s_k and their conjugate moments p_{s_k} , the quantum mechanical pure vibrational Hamiltonian is written:

$$H = \frac{1}{2} \sum_{i,j} g_{ij}(s) p_{s_i} p_{s_j} + V(s),$$

where g_{ij} is the element of the G matrix described by Wilson et al. [16].

As is usually done for the potential function $V(s)$, the kinetic part of the Hamiltonian can be

written as a Taylor expansion in terms of the curvilinear displacement coordinates set:

$$T = \frac{1}{2} \sum_{i,j} g_{ij}(0) p_{s_i} p_{s_j} + \frac{1}{2} \sum_{i,j,k} g_{ijk} p_{s_i} s_k p_{s_j} + \frac{1}{2} \sum_{i,j,k} g_{iijk} p_{s_i} s_j s_k p_{s_i},$$

with

$$g_{ij}(s) = g_{ij}(0) + \sum_k g_{ijk} s_k + \frac{1}{2} \sum_{k,l} g_{ijkl} s_k s_l + \dots,$$

$$g_{ijk} = \left(\frac{\partial g_{ij}}{\partial s_k} \right)_0 \quad \text{and} \quad g_{ijkl} = \left(\frac{\partial^2 g_{ij}}{\partial s_k \partial s_l} \right)_0.$$

The anharmonic part of the potential includes all the three and four-body terms. In our calculations, both the kinetic and the potential parts of the vibrational Hamiltonian are expressed in the basis of reduced normal coordinates Q_s and conjugated momenta operators P_s . The anharmonic vibrational wave function Ψ_i is expanded as a linear combination of products of harmonic oscillators ($\varphi_{v_s}(Q_s)$), each containing a single normal coordinate Q_s and defined by a single quantum number v_s . For the sake of simplicity, in the next paragraph, harmonic configurations will be indicated by the harmonic frequency(ies) with non-vanishing quantum number(s) in the product. For example, $|\omega_i + \omega_j\rangle$ is the configuration in which all quantum numbers are equal to zero, except $v_i = 1$ and $v_j = 1$.

The variation–perturbation algorithm (CIP-VIB), similar to the CIPSI [17–20] approach developed for electronic calculations is used to solve the vibrational equation. The Hamiltonian representation is first diagonalised within a small space of vibrational configurations and the states to be studied are identified. An iterative process builds a variational subspace S_0 including all the harmonic configurations, which interact with the required vibrational states. The choice of the configurations included in S_0 is made by an evaluation of this contribution to the energy at the second order perturbational level. The multireference vibrational function is then corrected to first order by

the remaining states, which interact weakly. If no selection on harmonic configurations were implemented, for example, in the case of nine fundamental modes up to the third degree of excitation, a space spanned by 262 144 (4^9) configurations would have to be diagonalised. The CIPSI algorithm is particularly appropriate to treat the vibrational problem because only the harmonic configurations having significant weights in the development of any required vibrational states are included in S_0 . Moreover, different limits on levels of excitation can be set in this code depending to the harmonic oscillator of interest. If the anharmonic terms are very strong the eigenvalues and eigenvectors of the corresponding vibrational levels are obtained by diagonalising the Hamiltonian with Davidson's procedure [21–23].

While it is relatively easy to characterise the fundamental vibration, there are few criteria to attribute the overtone, combination and difference bands (hot bands). In this context, knowledge of the absolute intensity is a precious guide especially for the frequency regions with high densities of states. We have modified the CIPVIB algorithm to calculate the infrared absorption intensities of all types of bands. The new code is called CIPVIB_INT01 [24]. The infrared absorption intensity of transition induced between the initial (Ψ_i) and the final (Ψ_f) vibrational states is related to the transition frequency ν_{if} and the electric transition dipole $\langle \Psi_f | \vec{\mu} | \Psi_i \rangle$ by:

$$I_{if} = \frac{8\pi^3}{3\text{ch}} \nu_{if} \langle \Psi_f | \vec{\mu} | \Psi_i \rangle^2 (N_i - N_f),$$

N_i and N_f are the numbers of molecules per volume unit in the states Ψ_i and Ψ_f , respectively. They are calculated assuming a Boltzmann distribution. The other constants have their usual meaning. The dipole moment $\vec{\mu}$ can be expanded as a power series of the normal coordinates Q_s :

$$\vec{\mu} = \vec{\mu}_0 + \sum_s \vec{\mu}_s Q_s + \frac{1}{2!} \sum_{s,t} \vec{\mu}_{st} Q_s Q_t + \dots,$$

where

$$\vec{\mu}_s = \left(\frac{\partial \vec{\mu}}{\partial Q_s} \right)_0 \quad \text{and} \quad \vec{\mu}_{st} = \left(\frac{\partial^2 \vec{\mu}}{\partial Q_s \partial Q_t} \right)_0.$$

The calculation of the intensities of non-fundamental transitions requires to take into account the mechanical and electrical anharmonicity. In our problem, the analysis of the expansion of the vibrational function in terms of harmonic configurations underlines that, for all vibrational states studied (400–3000 cm^{-1}) except in the case of the first overtones ($2\nu_i$) and of the combinations ($\nu_i + \nu_j$), the weight of binary configurations (two excited modes $|2\omega_j\rangle$ or combination of two mono-excited ones $|\omega_i + \omega_j\rangle$) is very weak. So the contribution of the second order derivatives of dipole moment in terms of normal coordinates should be less important than that of the mechanical anharmonicity. In this work, we assume that the dipole moment varies linearly with the normal coordinates Q_s .

Evaluation of the cartesian components of the dipole moment derivatives with respect to the normal coordinates requires definition of $(3N - 6)$ (or $(3N - 5)$) vibrational coordinates, which may be orthogonal to the six pure rotational and translational coordinates. So the Eckart conditions are satisfied and the roto-translational and vibrational kinetic contributions vanish. The integrated band intensity is related to the $\vec{\mu}_s$ elements by:

$$I_{\text{if}} = \frac{8\pi^3}{3\text{ch}} \nu_{\text{if}} \left\{ \sum_s \vec{\mu}_s \langle \Psi_{\text{f}} | Q_s | \Psi_{\text{i}} \rangle \right\}^2 (N_{\text{i}} - N_{\text{f}}).$$

Evaluation of the transition moment between the two vibrational states $\Psi_{\text{i}} = \sum_k C_{ik} (\prod_s \varphi_{v_{sk}})$ and $\Psi_{\text{f}} = \sum_p C_{fp} (\prod_s \varphi_{v_{sp}})$ implies calculations of integrals such as: $\langle \prod_s \varphi_{v_{sk}} | Q_t | \prod_s \varphi_{v_{sp}} \rangle$. These terms are non-vanishing only for the two harmonic configurations differing by one vibration quantum number (i.e. $\Delta v_t = \pm 1$ and for $s \neq t$, $\Delta v_s = 0$). These calculated intensities must be considered carefully because the first derivatives of the dipole moment seems to be very sensitive to the computed equilibrium geometry and, as a consequence, to the quality of the gaussian electronic basis set. The experimental average absolute intensities published in the literature are roughly estimated and the uncertainty in the values can exceed 50%. Direct comparison between theoretical and experimental values is thus quite difficult, but it is very

interesting to compare the tendencies exhibited by both series of values.

3. Results and discussion

3.1. Potential hypersurface and equilibrium geometry

Since 1949 [25], diazomethane has been accepted, on the basis of experimental evidence, to be an acyclic planar molecule with a C_{2v} symmetry. The nine fundamental vibrational modes of this molecule are described in Table 1 and corresponding experimental data (P, Q, R bands) are given in this table too. However, some theoretical investigations, reported that H_2CN_2 is not planar. Boldyrev et al. [8] found a C_s conformation at the second-order Møller–Plesset perturbation level of approximation including full electron correlation, using the standard 6-31G* basis set (MP2(full)/6-31G*). The potential hypersurface has two minima (C_s conformations) in the CH_2 wagging mode direction, the C_{2v} conformation being an inversion saddle point with an imaginary harmonic frequency. They concluded that the ground vibrational state of this molecule lies above the barrier, which is very low. The quasi-planar structure of diazomethane is confirmed by Kawauchi et al. [9] who performed geometry optimisation at the MP2(full)/6-31G** level. Yet, Boldyrev et al. obtain C_{2v} minima using configuration interaction methods (CISD/6-31G* or QCISD/6-31G*).

The first point to elucidate, before computing the IR frequencies of diazomethane, is thus the structure of its potential hypersurface, especially in the CH_2 wagging direction. Optimisation of diazomethane at the MP2(full)/6-311G** level of theory gives a C_{2v} minimum, the CH_2 wagging harmonic frequency (ω_6) being very low ($\omega_6 = 94 \text{ cm}^{-1}$) compared to the experimental value (406 cm^{-1}). Moreover, while at the MP2(full)/DZ+P level, the C_{2v} conformation is a saddle point on the potential surface ($\omega_6 = 276.11 \text{ cm}^{-1}$), it is a true minimum at the MP4SDQ/DZ+P ($\omega_6 = 297 \text{ cm}^{-1}$), CCSD(T)/DZ+P ($\omega_6 = 264 \text{ cm}^{-1}$) and B3LYP/DZ+P ($\omega_6 = 397 \text{ cm}^{-1}$) levels. These results show that the MP2(full) method is not suit-

Table 1

Experimental data on the fundamental vibrational modes of diazomethane. The numbering of vibrational modes follows Mulliken's recommendations

Symmetry	Symbol	Mode description	Experimental data			
			Ref. [1]	Ref. [2]	Ref. [3]	Ref. [6]
A ₁	ν ₁	ν _s CH ₂	P 3062	3075	P 3063	P 3062
			–	–	Q 3077	–
	ν ₂	ν NN	R 3088	–	R 3087	R 3088
			P 2087	–	P 2090	P 2088
ν ₃	δ CH ₂	Q 2101	Q 2090	Q 2102	–	
		R 2115	–	R 2114	R 2114	
ν ₄	ν CN	P 1401	P 1394	P 1402	P 1402	
		–	–	Q 1414	–	
		R 1429	R 1428	R 1426	R 1430	
		P 839	–	P 1155	–	
B ₁	ν ₅	δ C–N–N (out of plane)	Q 852	Q 1177	–	Q 1175
			R 864	–	R 1185	–
	ν ₆	CH ₂ wagging	920	–	564	Q 557
			487 (I)	–	406	Q 399
ν ₇	ν _{as} CH ₂	456 (II)	–	–	–	
		Q 3140	–	3184.5	–	
		Q 3158	–	–	–	
B ₂	ν ₈	CH ₂ rocking	Q 3175	–	–	–
			1147	Q 1098	1109	Q 1099
			586 (I)	–	421	P 412
ν ₉	δ C–N–N (in plane)	487 (II)	–	–	R 428	
		–	–	–	–	

able to describe the potential surface of diazomethane. Instead of a double-well potential surface in the direction of the CH₂ wagging mode, B3LYP method leads to a very flat potential around the C_{2v} minimum. The difference between the true and the harmonic potentials is so large that a Taylor expansion up to the fourth order is necessary to reproduce the potential energy. The harmonic and anharmonic potential constants reported in Table 2 confirm the strong anharmonicity of this hypersurface. Some potential constants involving the CH₂ wagging mode (ϕ_{663} , ϕ_{661} and ϕ_{666}) are large, and show the anharmonicity of the surface in this direction. The other large terms (ϕ_{111} , ϕ_{771} and ϕ_{1177}) confirm the anharmonicity effects on the two CH₂ stretching modes. The last point is the relatively strong coupling at the third order between the ω_2 and ω_4 modes ($\phi_{224} = 159 \text{ cm}^{-1}$). Optimised bond lengths and angles obtained for the ground state of diazomethane are reported in Table 3. These results are very close to the experimental values proposed by Sheridan [26] and confirm the

well-known tendency of B3LYP method to give very accurate geometrical parameter.

3.2. Infrared spectrum

We now discuss theoretical results obtained on the vibrational modes at the anharmonic level in order to assign all the IR experimental bands observed for the diazomethane.

3.2.1. Fundamentals modes

The nine harmonic (ω_s) and anharmonic (ν_s) fundamental vibrational modes computed using B3LYP electronic energy surface are reported in Table 4. Each attribution is completed by calculated absolute intensity at both the harmonic and the anharmonic levels. The algebraic values of the first derivative terms of the dipole moment $\vec{\mu}_s$ at the equilibrium geometry are also given because they are needed in the evaluation of anharmonic intensities as shown in the previous section. Note that the only non-vanishing cartesian component

Table 2
Quadratic (ω_s), cubic^a (ϕ_{cub}) and quartic^b (ϕ_{quar}) potential constants (cm^{-1}) of H_2CN_2 obtained at the B3LYP level, with respect to dimensionless normal coordinates Q_s .

Parameter	B3LYP	Parameter	B3LYP
$\omega_1(\text{A}_1)$	3183	ϕ_{222}	90
$\omega_2(\text{A}_1)$	2222	ϕ_{113}	21
$\omega_3(\text{A}_1)$	1413	ϕ_{111}	230
$\omega_4(\text{A}_1)$	1214	ϕ_{771}	791
$\omega_5(\text{B}_1)$	580	ϕ_{654}	76
$\omega_6(\text{B}_1)$	397	ϕ_{653}	68
$\omega_7(\text{B}_2)$	3317	ϕ_{651}	20
$\omega_8(\text{B}_2)$	1100	ϕ_{983}	22
$\omega_9(\text{B}_2)$	418	ϕ_{982}	32
		ϕ_{917}	117
		ϕ_{847}	22
ϕ_{663}	361	ϕ_{817}	79
ϕ_{662}	89	ϕ_{431}	76
ϕ_{661}	103	ϕ_{432}	61
ϕ_{904}	24	ϕ_{666}	81
ϕ_{554}	24	ϕ_{111}	22
ϕ_{884}	40	ϕ_{777}	24
ϕ_{883}	73	ϕ_{665}	9
ϕ_{881}	28	ϕ_{663}	30
ϕ_{444}	38	ϕ_{442}	10
ϕ_{443}	64	ϕ_{117}	147
ϕ_{442}	45	ϕ_{662}	14
ϕ_{334}	38	ϕ_{365}	13
ϕ_{333}	22	ϕ_{197}	23
ϕ_{332}	35	ϕ_{187}	15
ϕ_{331}	36	ϕ_{698}	9
ϕ_{224}	159	ϕ_{665}	43
ϕ_{223}	57		

^a Only cubic force constants over 20 cm^{-1} are reported.

^b Only quartic force constants over 10 cm^{-1} are reported.

Table 3

Optimised and experimental geometry (lengths in Å and angle in degrees) for the H_2CN_2 ground state

	B3LYP	Experimental
$r_{\text{C-N}}$	1.2993	1.300 ^a
$r_{\text{N-N}}$	1.1434	1.139 ^a
$r_{\text{C-H}}$	1.0870	1.075 ^a
θ_{HCN}	117.78	117.0 ^a

^a Data from Ref. [26].

μ_s^i ($i = x, y, z$) belongs to the same irreducible representation as the normal coordinate Q_s . The expansion coefficients of the mono-excited variational vibrational wave function on the harmonic configurations are reported in Table 4 to justify

Table 4

Calculated harmonic (ω_s) and anharmonic (ν_s) fundamental frequencies are given in cm^{-1} . Algebraic values of the only component of the first derivatives of the dipole moment μ_s with respect to the normal coordinate at the equilibrium geometry are in u.a. Calculated harmonic (I_{ω_s}) and anharmonic infrared intensities (I_{ν_s}) (in km mol^{-1}) are compared to experimental values (I_{exp}). The expansion coefficients of the mono-excited variational vibrational wave function on the mono-excited harmonic configurations $|\omega_s\rangle$ are reported to support our assignments

	ω_s	ν_s	μ_s	I_{ω_s}	I_{ν_s}	$ \omega_1\rangle$	$ \omega_2\rangle$	$ \omega_3\rangle$	$ \omega_4\rangle$	$ \omega_5\rangle$	$ \omega_6\rangle$	$ \omega_7\rangle$	$ \omega_8\rangle$	$ \omega_9\rangle$	I_{exp}^a
$\nu_1(\text{A}_1)$	3184	3066	0.1230	14.76	13.75	0.89	0.01	0.03	0.02	–	–	–	–	–	4.6 ± 0.8
$\nu_2(\text{A}_1)$	2222	2167	−0.5947	344.92	327.07	0.00	0.93	0.02	0.03	–	–	–	–	–	171.3 ± 20.1
$\nu_3(\text{A}_1)$	1415	1416	0.1810	31.94	29.17	0.03	0.00	0.89	0.05	–	–	–	–	–	12.0 ± 1.1
$\nu_4(\text{A}_1)$	1215	1193	−0.0388	1.46	0.48	0.02	0.01	0.03	0.92	–	–	–	–	–	3.1 ± 0.7
$\nu_5(\text{B}_1)$	580	576	−0.0418	1.70	0.87	–	–	–	–	0.96	0.03	–	–	–	–
$\nu_6(\text{B}_1)$	397	417	−0.3713	134.44	134.41	–	–	–	–	0.04	0.91	–	–	–	35.5
$\nu_7(\text{B}_2)$	3318	3179	−0.0556	3.02	2.83	–	–	–	–	–	–	0.91	0.02	0.02	–
$\nu_8(\text{B}_2)$	1101	1104	−0.0414	1.67	1.66	–	–	–	–	–	–	0.00	0.96	0.00	–
$\nu_9(\text{B}_2)$	419	420	0.0272	0.74	0.73	–	–	–	–	–	–	0.00	0.01	0.96	–

^a Data from Ref. [6].

our attributions and facilitate the interpretation of the anharmonic intensities computed for each mode.

Our results are in good agreement with the experimental data and assignments of Moore and Pimentel [3]. The three fundamental modes ν_1 , ν_7 and ν_2 related respectively to both symmetric and asymmetric CH_2 stretching and N–N stretching clearly exhibit strong anharmonicity. Inclusion of the kinetic anharmonic terms in the vibrational hamiltonian produces a relatively large shift to lower frequencies. For the two CH_2 stretching (ν_1 and ν_7) and the CH_2 rocking (ν_8) modes, we find 3066, 3179 and 1104 cm^{-1} instead of 3103, 3173 and 1113 cm^{-1} without anharmonic kinetic corrections. The effect on the N–N stretching frequency is of the same order ($\nu_2 = 2167\text{ cm}^{-1}$ instead of $\nu_2 = 2187\text{ cm}^{-1}$). At the harmonic level of approximation, the absolute intensities of the four fundamental bands $\omega_1, \omega_2, \omega_3, \omega_6$ are expected in the order $I_{\omega_2} > I_{\omega_6} > I_{\omega_3} > I_{\omega_1}$. These results are in good agreement with the experimental data of Khelifi et al. [6]. However, these authors attributed the two bands at $412, 428\text{ cm}^{-1}$ to the rotational P and R branches of the out of plane CNN bending mode (ν_9). We do not agree with this assignment. The development coefficients reported in Table 4 shows without any ambiguity, that this IR band corresponds to the out of plane CH_2 wagging mode (ν_6), as first proposed by Moore and Pimentel. The attribution of the two modes (ν_9, ν_6) by Khelifi et al. has to be reversed. Moreover, these authors do not take into account the symmetry of the vibrational transitions and propose perpendicular rotational branches for the totally symmetric ν_1 mode (A_1). Two others important points can be extracted from the intensity calculations: (i) Even the modes with very weak estimated intensities are observed in the IR spectrum; (ii) our multimodes variational approach of the vibrational problem will probably lead to a strong intensity redistribution from the fundamental to the overtone and combination modes, as shown by the development coefficients of the mono-excited states (see Table 4). It can be predicted that many overtone and combination bands will borrow intensity from the four intense fundamental modes ($\nu_6, \nu_3, \nu_2, \nu_1$).

3.2.2. Overtone and combination bands

Calculated anharmonic frequencies, intensities and analysis of the variational wave functions of active overtone and combination transitions are given in Tables 5 and 6, respectively.

In Table 5, we first report the results obtained for the overtones of the ν_6 and ν_9 modes that might be found in the same region of the IR spectrum. The only active bands expected are ($2\nu_6$) and ($3\nu_6$). Our results underline that ($2\nu_9$) and ($3\nu_9$) should be not detectable, confirming the results of Moore and Pimentel, in disagreement with the attribution of Khelifi et al. Note that generally, the intensity decrease in one series is usually rapid [27] as in the ν_6 case ($I_{\nu_6} = 134.41$; $I_{2\nu_6} = 4.21$; $I_{3\nu_6} = 0.33$ and $I_{4\nu_6} = 0.00\text{ km mol}^{-1}$). The analysis of the variational wave function attributed to the ($2\nu_6$) mode exhibits strong participation of the two harmonic configurations ω_2 (0.03) and ω_3 (0.26) modes which are responsible for relatively weak intensity of this band. On the contrary, the overtone ($2\nu_9$) mode is weakly coupled leading to an almost forbidden transition. The other important point is the variation of the intensities in the ν_4 series ($I_{\nu_4} = 0.48$; $I_{2\nu_4} = 5.08$; $I_{3\nu_4} = 0.00\text{ km mol}^{-1}$). The intensity of ($2\nu_4$) is greater than that of ν_4 and is attributable to the participation of the four A_1 harmonic fundamental configurations ($|\omega_1\rangle, |\omega_2\rangle, |\omega_3\rangle, |\omega_4\rangle$) in the development of the variational wave function of the ($2\nu_4$) state. In conclusion, our results predict four active overtone transitions ($2\nu_6, 3\nu_6, 2\nu_8$ and $2\nu_4$) in the IR spectrum in agreement with the experimental data [3,4]. Note that Crawford [1] assigns the band at 852 cm^{-1} (Q rotational branch) to the parallel ν_4 branch. Our calculations confirm the ($2\nu_6$) attribution for this band, the (ν_4) mode being proposed at 1175 cm^{-1} in the other experimental studies [2,3,6] and at 1193 cm^{-1} in our calculations.

There are few experimental results concerning the combination bands, which are in general weaker than the fundamental ones. First, the band centre observed at 1987 cm^{-1} (see Table 6) is attributable to the ($\nu_4 + 2\nu_6$) combination [3] ($2.15\text{ km mol}^{-1}, 2032\text{ cm}^{-1}$). Neither of the ($\nu_4 + 2\nu_8$) and ($\nu_4 + \nu_8$) transitions proposed by Crawford et al. [1] can appear in the IR spectrum, because they do have vanishing calculated intensity. In the

Table 5

Calculated anharmonic (ν_i) frequencies (in cm^{-1}) and infrared intensities (I_{ν_i}) (in km mol^{-1}) of overtone transitions are compared to experimental data (ν_{exp} , I_{exp}). The expansion coefficients of the associated variational vibrational wave functions on the mono-excited harmonic configurations $|\omega_s\rangle$ are reported to identify the source of transition intensity

	Symmetry	ν_{exp}	ν_i	I_{ν_i}	$ \omega_1\rangle$	$ \omega_2\rangle$	$ \omega_3\rangle$	$ \omega_4\rangle$	$ \omega_5\rangle$	$ \omega_6\rangle$	$ \omega_7\rangle$	$ \omega_8\rangle$	$ \omega_9\rangle$	I_{exp}^a
$2\nu_6$	A_1	Q 852 ^b	843	4.20(9)	0.01	0.03	0.26	0.04	–	–	–	–	–	11.6 ± 1.2
$3\nu_6$	B_1	P 1268 ^b R 1299 ^b	1299	0.33(0)	–	–	–	–	0.01	0.11	–	–	–	1.5 ± 0.3
$4\nu_6$	A_1	–	1733	0.00(2)	0.01	0.00	0.07	0.00	–	–	–	–	–	–
$2\nu_9$	A_1	P 839 ^a R 865 ^a	853	0.00(5)	0.00	0.00	0.01	0.01	–	–	–	–	–	–
$3\nu_9$	B_2	P 1272 ^a R 1300 ^a	1303	0.00(0)	–	–	–	–	–	–	0.01	0.01	0.03	–
$2\nu_8$	A_1	Q 2294 ^c	2233	0.11(8)	0.00	0.03	0.04	0.01	–	–	–	–	–	–
$3\nu_8$	B_2	–	3400	0.00(1)	–	–	–	–	–	–	0.01	0.01	0.01	–
$2\nu_4$	A_1	P 2290 ^a Q 2317 ^b R 2330 ^b	2391	5.08(0)	0.19	0.11	0.03	0.19	–	–	–	–	–	7.4 ± 0.8
$3\nu_4$	A_1	–	3608	0.00(4)	0.00	0.01	0.01	0.04	–	–	–	–	–	–

^aData from Ref. [3].

^bData from Ref. [6].

^cData from Ref. [1].

Table 6

Calculated anharmonic (ν_i) frequencies (in cm^{-1}) and infrared intensities (I_{ν_i}) (in km mol^{-1}) of combination transitions are compared to experimental data (ν_{exp} , I_{exp}). The expansion coefficients of the variational vibrational wave functions on the mono-excited harmonic configurations $|\omega_s\rangle$ are reported to identify the source of the transition intensity

	Symmetry	ν_{exp}	ν_i	I_{ν_i}	$ \omega_1\rangle$	$ \omega_2\rangle$	$ \omega_3\rangle$	$ \omega_4\rangle$	$ \omega_5\rangle$	$ \omega_6\rangle$	I_{exp}^a
$\nu_5 + \nu_6$	A_1	Q 975 ^b	988	0.45(5) (3.20) ^c	0.00	0.00	0.10	0.00	–	–	11.0 ± 1.4
$\nu_3 + \nu_6$	B_1	–	1907	6.05(0)	–	–	–	–	0.00	0.25	–
$\nu_4 + 2\nu_6$	A_1	P 1975 ^b Q 1987 ^b R 1997 ^b	2032	2.15(2)	0.00	0.07	0.00	0.00	–	–	–
$\nu_4 + \nu_5 + \nu_6$	A_1	–	2191	2.58(7)	0.00	0.08	0.00	0.00	–	–	–
$\nu_3 + \nu_4$	A_1	–	2615	1.16(0)	0.00	0.06	0.14	0.00	–	–	–
$\nu_2 + \nu_6$	B_1	2400– 2650 ^d	2643	0.21(0)	–	–	–	–	–	–	–
$\nu_2 + \nu_4$	A_1	P 3241 ^b Q 3245 ^a R 3266 ^b	3307	2.26(6)	0.00	0.16	0.00	0.00	–	–	2.1 ± 0.2

^aData from Ref. [6].

^bData from Ref. [3].

^cSee text for difference bands intensities in the same region of the IR spectrum.

^dData from Ref. [1].

region between 2400 and 2650 cm^{-1} , they suppose a perpendicular band system due to superimposed combinations of ν_2 with the low-frequency bending modes ν_6 , ν_9 and ν_5 and the combination ($\nu_3 + \nu_8$).

Of these four transitions, only the ($\nu_2 + \nu_6$) combination (2643 cm^{-1}) has a non-vanishing but weak calculated intensity (0.21 km mol^{-1}). In our calculations, the ($\nu_3 + \nu_4$) combination (2615 cm^{-1})

exhibits a participation of the two harmonic configurations of the ω_2 (0.06) and ω_3 (0.14) modes and may be responsible for the intensity observed in this region (1.16 km mol^{-1}). The last combination band reported experimentally around 3250 cm^{-1} is calculated as the $(\nu_2 + \nu_4)$ transition. This result agrees with the proposition of both Moore et al. and Khelifi et al. but disagrees with the assignment of Crawford ($\nu_3 + 2\nu_5$). Moreover, two other combinations have non-negligible intensity: (i) the binary combination $(\nu_3 + \nu_6)$ (6.05 km mol^{-1}) whose activity is essentially due to the participation of the $|\omega_6\rangle$ harmonic configuration in the wave function; (ii) the ternary combination $(\nu_4 + \nu_5 + \nu_6)$ (2.59 km mol^{-1}) in the region of the very strong ν_2 fundamental band and whose intensity is attributable to the participation of the harmonic configuration ω_2 (see Tables 4 and 6).

3.2.3. Difference transitions (hot bands)

We turn, now, to the transitions in which the initial state is not the vibrational ground state. The statistical population of these vibrational states is given by the Boltzmann factor and it rapidly decreases with the corresponding frequency ν_i and is very sensitive to the temperature. The temperature dependence is a precious aid in locating such experimentally transitions. The only possible hot

transitions at 300 K are from the three mono-excited states of the ν_6 , ν_9 and ν_5 modes (lowest frequencies).

All the investigated transitions from the ν_9 state are very weak. The frequencies and the absolute intensities of the nine active difference bands relative to the ν_6 and ν_5 modes are reported in Table 7, together with the most important contributions to these intensities. Five of these transitions corresponding to a ν_6 initial state have been observed experimentally [1,3]. The calculated frequencies for both $(3\nu_6 - \nu_6)$ and $(\nu_4 + 3\nu_6 - \nu_6)$ are very close to the experimental values and the anharmonicity effects on these bands are of the same order as the experimental ones (52 cm^{-1} between $(3\nu_6 - \nu_6)$ and $(2\nu_6)$; 43 cm^{-1} between $(\nu_4 + 3\nu_6 - \nu_6)$ and $(\nu_4 + 2\nu_6)$). The intensity of the $(2\nu_6 - \nu_6)$ (426 km mol^{-1}) transition is relatively strong ($12.66 \text{ km mol}^{-1}$) at 300 K and the anharmonicity effect on this transition, with respect to the very intense fundamental mode ν_6 is relatively weak (9 cm^{-1}). The lack of experimental data in this spectral region at 300 K explains that this band has never been identified and it would be interesting to resolve and analyse the IR spectrum around $400\text{--}500 \text{ cm}^{-1}$. Around 1000 cm^{-1} , two hot bands $(\nu_3 - \nu_6)$ and $(\nu_5 + 2\nu_6 - \nu_6)$ have been assigned experimentally. Our investigations show that only the

Table 7

Symmetry, calculated anharmonic (ν_i) frequencies (in cm^{-1}) and absolute intensities (I_{ν_i}) (in km mol^{-1}) attributed to difference bands. The most important contribution(s) to intensities are given in percent with the corresponding integrals between harmonic configurations

	Symmetry	ν_i	I_{ν_i}	ν_{exp}	Contributions to intensity ^a	%
$2\nu_6 - \nu_6$	B_1	426	12.66		$\langle 2\omega_6 O_6 \omega_6 \rangle$	94
$3\nu_6 - \nu_6$	A_1	895	0.10	Q 905 ^b	$\langle 2\omega_3 + \omega_6 O_3 \omega_3 + \omega_6 \rangle$	79
$\nu_3 - \nu_6$	B_1	994	2.74	Q 928 ^c	$\langle 2\omega_6 O_6 \omega_6 \rangle$	92
$(\nu_5 + 2\nu_6) - \nu_6$	A_1	1000	0.00	P 990 ^b R 1015 ^b	–	–
$(\nu_3 + \nu_5 + \nu_6) - \nu_5$	B_1	1916	0.17		$\langle \omega_3 + \omega_5 + 2\omega_6 O_6 \omega_3 + \omega_5 + \omega_6 \rangle$ $\langle \omega_3 + \omega_5 + 2\omega_6 O_6 \omega_3 + \omega_5 + 3\omega_6 \rangle$	26 21
$(\nu_4 + 3\nu_6) - \nu_6$	A_1	2075	0.18	Q 2035 ^b	$\langle 2\omega_3 + \omega_6 O_3 \omega_3 + \omega_6 \rangle$	99
$2\nu_3 - \nu_6$	B_1	2421	0.14		$\langle 2\omega_6 O_6 \omega_6 \rangle$ $\langle 2\omega_3 + \omega_6 O_3 \omega_3 + \omega_6 \rangle$	66 32
$(2\nu_8 + 2\nu_9) - \nu_5$	B_1	2577	0.14		$\langle 3\omega_6 + \omega_5 O_6 2\omega_6 + \omega_5 \rangle$	51
$(2\nu_3 + \nu_6) - \nu_6$	A_1	2767	0.22		$\langle \omega_3 + \omega_5 + 3\omega_6 O_6 \omega_3 + \omega_5 + 2\omega_6 \rangle$ $\langle 2\omega_3 + \omega_6 O_3 \omega_3 + \omega_6 \rangle$	47 96

^a The notation O_s stands for the operator $\mu_s Q_s$.

^b Data from Ref. [3].

^c Data from Ref. [1].

first one has an intensity (2.74 km mol^{-1}), in accordance with Crawford and Fletcher [1]. Moreover, this band (994 cm^{-1}) is superposed with the very weak ($\nu_5 + \nu_6$) combination (988 cm^{-1} and 0.45 km mol^{-1}). We thus conclude that the P and R rotational branches observed by Moore and Pimentel [3] correspond undoubtedly to the ($\nu_3 - \nu_6$) band. In the interval $2400\text{--}2700 \text{ cm}^{-1}$, some difference transitions have a non-negligible intensity ($0.2\text{--}0.3 \text{ km mol}^{-1}$). They have not been reported in the literature because they occurred in a region with more intense combination bands.

To complete this analysis, it is interesting to examine the terms which cause each hot transition intensity. Surprisingly, in all cases, the most important contributions come from either the mode ω_6 or ω_3 even if they do not strongly participate in the definition of the transition (e.g. $(2\nu_8 + 2\nu_9) - \nu_5$). For some difference transitions such as $(2\nu_6 - \nu_6)$, $(\nu_3 - \nu_6)$, $((\nu_4 + 3\nu_6) - \nu_6)$ and $(2\nu_3 + \nu_6) - \nu_6$, only one term is predominant; other contributions such as the cross terms are negligible and in these cases, it would not be necessary to know the sign of the dipole moment first derivatives. On the other hand, for some hot bands like $(2\nu_6 - \nu_6)$, many terms have the same weight and our approach is quite suitable for this type of problem.

4. Conclusion

To our knowledge, few studies have been devoted to calculations of IR absolute intensities implementing variational vibrational wave functions, at the anharmonic level. The first reason is the lack of experimental data in this field. It is easier to characterise IR bands by their frequencies than by their intensities. Although the comparison between experimental and theoretical intensities is difficult, the interpretation of IR non-fundamental bands can be complemented by theoretical calculations of both frequencies and intensities, as shown in this paper on diazomethane as an example. The contributions of first derivatives of dipole moment to the intensities, implemented in this study will be completed, in a second contri-

bution, by calculations on diazomethane and its deuterated compounds including the second derivatives of dipole moment.

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