

# ***Ab initio* Quantum Mechanical Study of Crystalline Nitric Acid Hydrates: Structures and Vibrational Spectra**

S. Bourahla<sup>1\*</sup>, A. Ali Benamara<sup>1</sup>, S. Kouadri Moustefai<sup>2</sup>

<sup>1</sup>Laboratory of Theoretical and Materials Physics, Hassiba Benbouali Chlef University, P.O. Box 151, Hay Es-Salem, Chlef, Algeria

<sup>2</sup>Laboratory of Water and Environment, Hassiba Benbouali Chlef University, P.O. Box 151, Hay Es-Salem, Chlef, Algeria

## ABSTRACT

The vibrational spectra of crystalline nitric acid hydrates have been investigated at the periodic *ab initio* quantum level by using a Gaussian type basis set and the hybrid B3LYP Hamiltonian with CRYSTAL06 code. Using as input the X-ray structures of crystalline nitric acid monohydrate NAM, dihydrate  $\alpha$ -NAD and trihydrate  $\beta$ -NAT, the inner coordinates within each unit cell have been optimized. The calculated structures of these atmospherically relevant systems are used in the evaluation of their vibrational normal modes. The obtained theoretical results show in general a good agreement compared to the observed spectra in the range 4000- 600  $\text{cm}^{-1}$  and 200-20  $\text{cm}^{-1}$  for infrared and Low-Frequency Raman spectra, respectively.

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\*Corresponding author: S. Bourahla<sup>1</sup>  
E-mail: bourahlasaida2001@yahoo.fr

## KEYWORDS

PSCs; Crystalline Nitric Acid Hydrates; IR and Raman spectra; *Ab initio*; B3LYP.

## Introduction

It is well recognized that polar stratospheric clouds (PSCs) are responsible for the ozone depletion. Type I PSCs is important classes of PSCs that is formed during winter and consists mainly of nitric acid hydrates. Polar stratospheric clouds play two essential roles in the chemistry of ozone during winter via two mechanisms which reduce the ozone concentration leading to ozone hole over Antarctic. The first mechanism is the sedimentation of the particles of polar stratospheric clouds removing irreversible nitric acid from the stratosphere. The second one is that clouds surfaces act as sites for heterogeneous chemistry converting relatively inactive chlorine compounds like HCl and ClONO<sub>2</sub> to easily photolysed and reactive chlorine compounds (Lowe and MacKenzie, 2008; Solomon, 1990; Solomon, *et al.*, 1986; Tabazadeh, *et al.*, 2000; Wang and Michelangeli, 2006).

To this end, these atmospherically relevant systems are the subject of study in a number of experimental (Escribano, *et al.*, 2003; Grothe, *et al.*, 2006; Grothe, *et al.*, 2004; Koch, *et al.*, 1996; Maté, *et al.*, 2006; McCurdy, *et al.*, 2002; Peil, *et al.*, 1995; Ritzhaupt and Devlin, 1991; Smith, *et al.*, 1991; Tso and Lew, 1996; Wagner, *et al.*, 2005) or theoretical (Escribano, *et al.*, 2003; McCurdy, *et al.*, 2002; Poshusta and Tseng, 1993; Tóth, 1997; Sullivan, *et al.*, 1999; Bianco, *et al.*, 2008) works. Progress toward understanding the spectroscopic characteristics of these species is not achieved. That because most of the theoretical studies examine the individual molecules and their water aggregates, but not on the crystals or solids that the hydrates form. As regards previous studies, the only theoretical works that specifically deals with the solids is made by (Tóth, 1997) and (Poshusta and Tseng, 1993) on the monohydrate and by (Sullivan, *et*

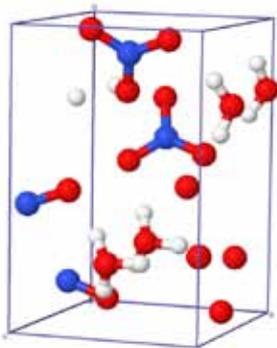
*al.*, 1999) on the trihydrate. Very recent research (Manz, *et al.*, 2002) imputes the interaction of HCl with crystalline NAT. All these papers show an *ab initio* molecular dynamics calculations based on the Car-Parrinello method. (Sullivan, *et al.*, 1999) and (Tóth, 1997) predict the power spectra at the optimized geometry of the crystals.

In this study, vibrational spectra of crystalline nitric acid hydrates are calculated using CRYSTAL06<sup>TM</sup> (Dovesi, *et al.*, 2006). It's a first- principles, periodic, all-electron computer program that uses a Gaussian type basis set for representing the electronic crystalline orbitals. The calculation of the force constant matrix via the finite displacements (Pascale and Zicovich-Wilson, *et al.*, 2004) is adopted.

The paper is organized as follows. In section two we summarize the method employed for our calculations. Section three shows the optimized structures which are discussed and compared with experimental results. This last section is also devoted to the vibration analysis, with discussion of various regions of infrared and Raman spectra compared to those previously available in the literature.

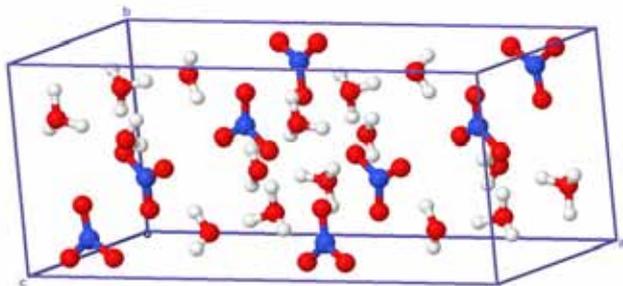
## Materials and Methods

The structure of crystalline nitric acid monohydrate NAM was first determined by (Delaplane, *et al.*, 1975) and has been recently remeasured by (Leburn, *et al.*, 2001) (Fig.1). It has an orthorhombic structure, containing four nitrates and four oxonium ions per unit cell, with space group  $P2_1cn$  ( $C_{2v}^9$ ). In NAM, all HNO<sub>3</sub> and H<sub>2</sub>O molecules are dissociated into NO<sub>3</sub><sup>-</sup> and H<sub>3</sub>O<sup>+</sup> respectively. Every H<sub>3</sub>O<sup>+</sup> is connected by hydrogen-bonding with three NO<sub>3</sub><sup>-</sup> units forming parallel layers.



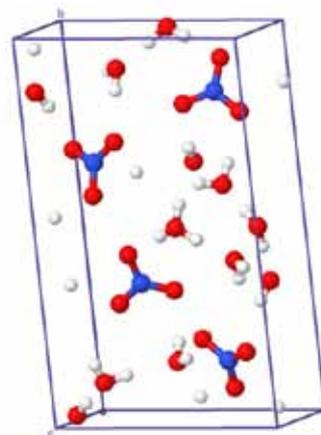
**Figure (1)** Conventional unit cell of crystalline nitric acid monohydrate (NAM). Blue, red and grey balls represent the N, O and H atoms, respectively.

The low temperature phase dihydrate  $\alpha$ -NAD has a monoclinic structure and space group  $P2_1/n$  ( $C_{2h}^2$ ) containing eight nitrates and eight aqua-oxonium ions per unit cell (Leburn, *et al.*, 2001) (see Fig. 2). Every nitrate connects to two oxonium units, which are in a junction with a water molecule. The asymmetric unit contains two independent molecules named A and B. It has a layer structure as in NAM; the layers being bound by weak Van der Waals forces and weak hydrogen bonds, with interatomic distances of the order of 3-3.5 Å for the former and  $\sim 2$  Å for the latter. The asymmetrical geometry of hydrogen bonds leads to important deviations from the ternary symmetry of  $\text{NO}_3^-$ .



**Figure (2)** Conventional unit cell of crystalline nitric acid dihydrate ( $\alpha$ -NAD). Blue, red and grey balls represent the N, O and H atoms, respectively.

In the case of trihydrate, the  $\beta$ -NAT modification is the high temperature phase with an orthorhombic structure of space group  $P2_12_12_1$  ( $D_2^4$ ) with four nitrate and four diaqua-oxonium ions per unit cell (Leburn, *et al.*, 2001; Taeslar, *et al.*, 1975) (Fig.3). Each  $\text{H}_3\text{O}^+$  ion is connected with two water molecules forming the  $\text{H}_7\text{O}_3^+$  unit. The diaqua-oxonium elements are interconnected by weak hydrogen bonds into a helix and the nitrate ions are embedded in this spiral by strong hydrogen bridges. In this way, layers are constructed forming a three dimensional network. For all solid phases, the oxonium  $\text{H}_3\text{O}^+$  roughly agrees with a  $C_{3v}$  symmetry.



**Figure (3)** Conventional unit cell of crystalline nitric acid trihydrate ( $\beta$ -NAT). Blue, red and grey balls represent the N, O and H atoms, respectively.

The present calculations have been performed with CRYSTAL06<sup>TM</sup> (Dovesi, *et al.*, 2006). A periodic ab initio program, in which the crystalline wave functions, are expanded as linear combination of atom-centered Gaussian orbitals (LCAO) with  $s$ ,  $p$ ,  $d$  and  $f$  symmetry. This code can be used either as an all-electron code or in combination with pseudo-potentials. All calculations presented are all-electron calculations. The B3LYP Hamiltonian (Becke, 1993) has been adopted, which contains a hybrid Hartree-Fock/density-functional exchange-correlation term. This method is widely and successfully used in molecular quantum chemistry as well as in solid-state calculations. It has been shown that B3LYP provides geometries and vibrational spectra in much better agreement with experiment than local density functional (LDA) or gradient-corrected functional (GGA) (Montanari, *et al.*, 2006; Pascale and Tosoni, *et al.*, 2004; Pascale and Zicovich-Wilson, *et al.*, 2004; Ugliengo, *et al.*, 2004; Zicovich-Wilson, *et al.*, 2004). In particular, this method does not show the large overestimation of the OH bond strength in OH groups and the related red shift of the OH stretching affecting most of the other functionals (Pascale and Tosoni, *et al.*, 2004; Ugliengo, *et al.*, 2004).

About this work, the basis sets 21G, 6-21G\* and 6-21G\* for H, O, N, respectively (Binkley, *et al.* 1980; Dovesi, *et al.*, 1990), have been used and the exponents of the most diffuse  $sp$  and  $d$  orbitals are (0.37, 0.8) for O and (0.28, 0.8) for N.

The level of accuracy in evaluating the Coulomb and Hartree-Fock exchange series is controlled by five parameters (Dovesi, *et al.*, 2006), for which standard values have been used (i.e., 6 6 6 6 12). The DFT exchange-correlation contribution to B3LYP is evaluated by numerical integration over the unit cell volume (Pascale, *et al.*, 2004). Further, details about the grid generation and its influence on the accuracy and cost of calculation can be found in (Pascale, *et al.*, 2005). The reciprocal space was sampled according to a regular sublattice with shrinking factor equal to 8, 3 and 4 for NAM,  $\alpha$ -NAD and  $\beta$ -NAT respectively. The geometry of these phases, that is inner coordinates, has been optimized

within an iterative procedure based on the total energy gradients evaluated analytically (Doll, 2001; Doll, *et al.*, 2001). Convergence in the geometry optimization process is tested on the root mean square (RMS), the absolute value of the largest component of both the gradients and the estimated nuclear displacements. The thresholds for the maximum and the RMS forces and the maximum and the RMS atomic

displacements on all atoms have been set to (in atomic units) 0.00045, 0.00030 and 0.00180, 0.00120, respectively. About the calculations of vibrational spectra, we refer to previous paper (Pascale and Zicovich-Wilson, *et al.*, 2004) for more explicit formulation of the method.

We have performed manipulation and visualization of structures with the MOLDRAW program (Ugliengo, 2006).

### 3. Results and Discussion

#### 3.1. Geometries of NAM, $\alpha$ -NAD and $\beta$ -NAT

**Table1.** Selected Structural Parameters of Crystalline Nitric Acid Hydrates (Interatomic distances in Å, angles in degrees).

Parameters	NAM			$\alpha$ -NAD						$\beta$ -NAT		
	this work	Exp. <sup>a, b</sup>	Dev(%)	this work (mol.A, mol.B)	Exp. <sup>b</sup> (mol.A, mol.B)	Dev(%) (mol.A)	Dev(%) (mol.B)	Dev(%) (mol.A)	Dev(%) (mol.B)	this work	Ref <sup>b, c</sup>	Dev(%)
<b>NO<sub>3</sub><sup>-</sup></b>												
N-O1(Å)	1.265	1.252	+1	1.293	1.306	1.286	1.279	+0.5	+2.2	1.244	1.256	1
N-O2(Å)	1.265	1.251	+1.1	1.232	1.232	1.222	1.223	+1	+0.7	1.252	1.285	+2.6
N-O3(Å)	1.261	1.249	+0.9	1.277	1.263	1.235	1.253	+3.4	+0.8	1.251	1.267	+1.3
O1NO2(°)	119.9	120.0	–	120.1	117.4	119.3	119.7	+0.7	-1.9	120.7	120.0	-0.6
O2NO3(°)	120.3	120.0	–	121.9	123.7	123.5	122.3	-1.3	+1.1	118.5	118.1	–
O3NO1(°)	119.8	119.9	–	118.0	116.8	117.4	118.0	+0.5	-1.	120.7	121.9	1
<b>H<sub>3</sub>O<sup>+</sup></b>												
O-H1(Å)	1.059	0.93	+13.9	1.083	1.188	0.99	0.92	+9.4	+12.7	0.82	1.014	+2.4
O-H2(Å)	1.054	0.87	+21.1	1.059	1.039	0.93	0.91	+13.9	+14.2	0.86	1.028	+19.5
O-H3(Å)	1.059	0.97	+9.2	1.048	1.037	0.81	0.85	+29.4	+23.1	0.88	1.127	+28.1
H1OH2(°)	104.3	103	+1.2	107.6	103.7	111	111	-3.1	-6.6	105	103.2	-1.7
H2OH3(°)	108.6	115	+5.5	109.6	109.6	108	110	+1.5	–	103	108.6	+5.4
H3OH1(°)	106.6	117	-8.9	105.5	106.9	117	114	-9.8	+6.2	115	110.9	-3.6
<b>H-bond</b>												
(NO <sub>3</sub> <sup>-</sup> , H <sub>3</sub> O <sup>+</sup> )												
O...H(Å)	1.564	1.71	-8.5	1.672	1.779	1.55	1.69	+1.9	+5.3	1.78	1.690	-5.1
O...O(Å)	2.620	2.590	+1.1	2.685	2.790	2.55	2.606	+5.3	+7	2.626	2.716	+3.4
(H <sub>2</sub> O, H <sub>3</sub> O <sup>+</sup> )												
O...H(Å)	–	–	–	1.568	1.568	1.64	1.55	-4.4	+1.1	1.71	1.673	-2.1
O...O(Å)	–	–	–	2.624	2.624	2.559	2.460	+2.5	+6.7	2.576	2.699	+4.8
(H <sub>2</sub> O, H <sub>3</sub> O <sup>+</sup> )												
O...H(Å)	–	–	–	–	–	–	–	–	–	1.59	1.673	+5.2
O...O(Å)	–	–	–	–	–	–	–	–	–	2.482	2.699	+8.7
(NO <sub>3</sub> <sup>-</sup> , H <sub>3</sub> O <sup>+</sup> )												
O...OH(°)	174.1	168	+3.6	168.5	169.5	172	174	-2	-2.6	177	174.4	-1.5
(H <sub>2</sub> O, H <sub>3</sub> O <sup>+</sup> )												
O...OH(°)	–	–	–	174	174	174	176	–	-1.1	171	174.8	+2.2
(H <sub>2</sub> O, H <sub>3</sub> O <sup>+</sup> )												
O...OH(°)	–	–	–	–	–	–	–	–	–	177	174.8	-1.2

<sup>a</sup>Delaplane, *et al.*, 1975; <sup>b</sup>Leburn, *et al.*, 2001; <sup>c</sup>Taelsarm *et al.*, 1975.

Selected geometrical parameters are presented in Table 1 compared with experimental work (Delaplane, *et al.*, 1975; Leburn, *et al.*, 2001; Taeslar, *et al.*, 1975). The N-O bond lengths are well reproduced, as the N-O-N angles, with about 3% a maximum. The agreement of the  $\text{H}_3\text{O}^+$  parameters is less satisfactory, since the deviation of O-H bond lengths and the H-O-H angles are in the ranges 9%-20% and 1%-9% respectively. The hydrogen bond parameters are well estimated with deviation about 8%. The large differences between experimental results and our calculated geometries are due to the difficult theoretical treatment of the weak interaction existed in these systems. Previous ab initio based Car-Parrinello molecular dynamics calculations for crystalline nitric acid trihydrate (Sullivan, *et al.*, 1999) reported large overestimation of the structural parameters compared to experiment. In this case, the O-H bond lengths are overestimated by about 30%. This difference noted in this

study will come of use when the vibrational spectra will be compared with those obtained from this method (see section 3.2.1).

### 3.2. Vibrational Spectra

CRYSTAL06™ (Dovesi, *et al.*, 2006) program decompose automatically the reducible representations built on the basis of the Cartesian coordinates of the unit cell, thereby providing the symmetry attribution for the normal modes present in these systems. The obtained results, detailed below, are compared with earlier experiments (Tso and Leu, 1996; Smith, *et al.*, 1991) as well as recent experiments (Grothe, *et al.*, 2006; Grothe, *et al.*, 2004) in the range 4000- 600  $\text{cm}^{-1}$  and 200-20  $\text{cm}^{-1}$  for IR and Low-Frequency Raman spectra, respectively.

**Table 2.** Predicted Infrared Spectra ( $\text{cm}^{-1}$ ) of Crystalline Nitric Acid Hydrates.

Normal modes	NAM ( $\text{v}/\text{cm}^{-1}$ )				$\alpha$ -NAD ( $\text{v}/\text{cm}^{-1}$ )			$\beta$ -NAT ( $\text{v}/\text{cm}^{-1}$ )			
	this work	Exp. <sup>f</sup>	Exp. <sup>e</sup>	Dev(%)	this work	Exp. <sup>f</sup>	Dev(%)	this work	Exp. <sup>e</sup>	Exp. <sup>d</sup>	Dev(%)
$\nu_3(\text{H}_2\text{O})_{\text{a-s}}$	–	–	–	–	3396	3494	2.8	3343	–	3370	0.8
$\nu_1(\text{H}_2\text{O})_{\text{s-s}}$	–	–	–	–	3100	3262	5	3218	–	3220	–
$\nu_3(\text{H}_3\text{O}^+)_{\text{a-s}}$	2479	2226	2230	11.3	2868	2714	5.7	2808	2702	2750	2.1
$\nu_1(\text{H}_3\text{O}^+)_{\text{s-s}}$	2866	2644	2644	8.4	2189	2260	3.1	2710	2236	2410	12.4
$\nu_4(\text{H}_3\text{O}^+)_{\text{a-s}}$	1824	1663	1671	9.7	1857	1737	6.9	1881	1731	1825	3.1
$\nu_3(\text{NO}_3^-)_{\text{a-s}}$	1454	1269	1316	14.5	1516	1450	4.5	1461	1452	1380	5.9
$\nu(\text{NO}_3^-)$	–	–	–	–	1377	–	–	–	–	–	–
$\nu(\text{H}_3\text{O}^+)$	–	–	–	–	1300	1258	3.3	–	–	–	–
$\nu_2(\text{H}_3\text{O}^+)_{\text{s-s}}$	1356	1116	1115	21.5	1227	1258	2.4	1336	1262	–	5.9
$\nu_1(\text{NO}_3^-)_{\text{s-s}}$	–	–	–	–	1044	1025	1.8	–	–	–	–
$\nu(\text{H}_2\text{O})$	–	–	–	–	954	–	–	–	–	–	–
$\nu(\text{H}_3\text{O}^+)$	–	–	–	–	887	876	1.2	–	–	–	–
$\nu_2(\text{NO}_3^-)_{\text{s-s}}$	818	816	813	–	776	809	4.1	835	804	821	1.7
$\nu_4(\text{NO}_3^-)_{\text{a-s}}$	733	730	735	–	737	743	0.8	777	743	735	5.7
$\nu_{\text{L}}(\text{H}_3\text{O}^+)$	710	700	702	1.4	691	672	2.8	638	669	602	6

<sup>d</sup> Tso and Leu, 1996; <sup>e</sup> Smith, *et al.*, 1991; <sup>f</sup> Grothe, *et al.*, 2004.

#### 3.2.1. Case of IR Spectra

The predicted IR spectra are compared for different phases of crystalline nitric acid hydrates and to the experimental data (Table 2). The O-H stretching vibrations of water molecules are present as expected in the normal modes analysis of  $\alpha$ -NAD and  $\beta$ -NAT. The deviation of the corresponding frequencies to symmetric  $\nu_1$  and asymmetric  $\nu_3$  stretching is about 5% for  $\alpha$ -NAD (Grothe, *et al.*, 2004). They coincide

very well with the experimental results (Tso and Leu, 1996) for  $\beta$ -NAT; however a concrete difference about 10% is noted in the results of ref (Sullivan, *et al.*, 1999). This deviation is ascribed to the exploitation of pseudopotentials and the approximation used to treat exchange and correlation terms.

The O-H symmetric  $\nu_1$  and asymmetric  $\nu_3$  stretching vibration of the oxonium ions  $\text{H}_3\text{O}^+$  differences are in the range of 2% -12%, in the case of NAM and  $\beta$ -NAT, however it's about 5% for  $\alpha$ -NAD phase. The difference between

our calculated  $\text{H}_3\text{O}^+$  frequencies and those in the gas phase (Escribano, *et al.*, 2003; McCurdy, *et al.*, 2002; Tóth, 1997) is explained by the fact that, in crystal the oxonium O-H bonds are weakened because of partial proton transfer from this ion to the nitrate.

The deviation between the calculated asymmetric  $\nu_2(\text{H}_3\text{O}^+)_{\text{a-s}}$ , symmetric  $\nu_4(\text{H}_3\text{O}^+)_{\text{s-s}}$  bending and experimental assignments (Grothe, *et al.*, 2004; Smith, *et al.*, 1991; Tso and Leu, 1996) is about 7%, in the case of dihydrate and trihydrate phases, excepting in NAM which is overestimated by about 20%. This large difference is probably a consequence of uncertainty in the X-ray data. The frequency associated to librational mode  $\nu_{\text{L}}(\text{H}_3\text{O}^+)$  is closer to those obtained by the literature (Grothe, *et al.*, 2004; Smith, *et al.*, 1991; Tso and Leu, 1996).

In the case of nitrate ion, generally  $\alpha$ -NAD shows a splitting of the asymmetric stretching  $\nu_3$  because the nitrate ion in the crystal is distorted by interactions with the oxonium ion. Therefore, the  $D_{3h}$  symmetry of nitrate is lowered and the degeneration of this band is lifted, as shown in Table 2. The obtained frequencies are estimated by about 6% for  $\alpha$ -NAD and  $\beta$ -NAT, but it is about 14% for NAM phase compared to ref (Grothe, *et al.*, 2004; Smith, *et al.*, 1991; Tso and Leu, 1996).

Due to the  $D_{3h}$  symmetry of the isolated ion, symmetric stretching  $\nu_1(\text{NO}_3^-)$  is an IR inactive mode in the gas phase, which is the case of NAM and  $\beta$ -NAT, because the nitrate ions maintain their symmetry. As mentioned above, this band is very characteristic for  $\alpha$ -NAD, where the distortions lower the symmetry of the nitrate ion to  $C_{2v}$ . The corresponding frequency is in a good agreement with the results of (Grothe, *et al.*, 2004). Grossly, the vibrational modes, associated with symmetric  $\nu_2$  and asymmetric  $\nu_4$  bending motions in  $\text{NO}_3^-$

occur at frequencies, closer to those mentioned in (Grothe, *et al.*, 2004; Smith, *et al.*, 1991; Tso and Leu, 1996).

The obtained frequencies for  $\alpha$ -NAD crystal, 1300  $\text{cm}^{-1}$  and 887  $\text{cm}^{-1}$ , are associated to  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  motion, respectively. In another way, we have opted for frequencies about 1377  $\text{cm}^{-1}$  and 954  $\text{cm}^{-1}$  due to  $\text{NO}_3^-$  and 954  $\text{cm}^{-1}$  due to  $\text{H}_2\text{O}$  motion respectively in the aim to complete the fundamental frequencies of the water molecule, oxonium and nitrate ions. We can conclude that the calculated IR vibrations frequencies reproduce well the experimental spectra.

### 3.2.2. Case of Low-Frequency Raman Spectra

The low frequency region of the Raman spectrum is more suited for the spectroscopy phase analysis, since it exhibits additional bands resulting from the crystal lattice. The unit cell of the hydrate contains a certain number of nitrate, oxonium, and water molecules, which are interconnected by hydrogen bonds forming networks of different structures. The intermolecular vibrations of these structures involve the relative motions of the molecules or ions as a whole within the crystal lattice. For a unit cell with  $P$  molecules there are  $3(2P-1)$  intermolecular vibrations:  $3(P-1)$  are translational modes and  $3P$  are librational modes. Water ice librational modes are peaking in the region 300-650  $\text{cm}^{-1}$  (Takasu and Nishio, 2003). Water ice shows a stretching mode at 210  $\text{cm}^{-1}$  and deformation mode at 60  $\text{cm}^{-1}$  (Takasu, *et al.*, 2003). Nitric acid hydrates includes ions with higher reduced masses but similar force constant, and thus, shift the vibrations to low frequencies by about 30% (Grothe, *et al.*, 2006). One notes that the only calculations of low frequency vibrations of nitric acid hydrates have been performed by (Escribano, *et al.*, 2003). These results are not comparable with ionic

**Table3.** Predicted Low-Frequency Raman Spectra ( $\text{cm}^{-1}$ ) of Crystalline Nitric Acid Hydrates.

NAM ( $\text{v}/\text{cm}^{-1}$ )			$\alpha$ -NAD ( $\text{v}/\text{cm}^{-1}$ )			$\beta$ -NAT ( $\text{v}/\text{cm}^{-1}$ )		
this work	Exp. <sup>§</sup>	Dev(%)	this work	Exp. <sup>§</sup>	Dev(%)	this work	Exp. <sup>§</sup>	Dev(%)
45	50	+10%	34	31	-9.7%	29	35	+17%
68	57	-19%	56	—	—	48	55	12.7%
87	75	-16%	70	81	+13.6%	61	63	+3%
91	86	-5.8%	83	88	+8%	71	74	+4%
111	102	-8.8%	99	98	-1%	91	94	+3.2%
124	118	-5%	128	113	-13.3%	105	109	+3.7%
130	129	-0.8%	134	—	—	118	115	+2.6%
160	143	-12%	146	—	—	126	—	—
172	—	—	155	—	—	154	—	—
—	—	—	—	—	—	169	—	—

<sup>§</sup> Grothe, *et al.*, 2006.

solids because they are based just for the uncharged clusters of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ .

As described in the section devoted to the structural models, NAM contains three different kinds of hydrogen bonds with six independent vibrations giving rise to 18 intermolecular modes. According to (Grothe, *et al.*, 2006), for every hydrogen bond, there should be at least two intense bands; one stretch and one deformation mode of  $\text{NO}_3^- \dots \text{H}_3\text{O}^+$ . Generally for all modes, the differences between calculated and experimental frequencies are less than 10%, excepting for four modes for which the differences are +10% (45, 50), -19% (68, 57), -16% (87, 75) and -12% (160, 143) as shown in table 3.

For the low temperature modification  $\alpha$ -NAD, there are seven different hydrogen bonds per unit cell, only three are quite strong hydrogen bridges forming the layers. It should be noted that from the 14 bands, only six bands should present considerable intensity (Grothe, *et al.*, 2006). In Table 3 the computed modes are overestimated by about 13% a maximum.

In the case of high temperature modification  $\beta$ -NAT, six bands can be recognized, probably related to the bridges which embed the nitrate ions, and one band due to the weak interactions inside the helix (Grothe, *et al.*, 2006). The comparison between our results and those in ref (Grothe, *et al.*, 2006) shows a good agreement than the other phases of crystalline nitric acid hydrate, excepting for two modes which are overestimated by about 17% (29, 35) and 13% (48, 55) (Table 3).

In the three cases, the differences between our calculated Low-Frequency Raman spectra and experimental results are probably related to the temperature effect, where the crystal lattice is expanded with increasing temperature. Some results of the Low-Frequency Raman spectra are not observed in the available spectra on the literature recorded to the present phases of nitric acid hydrates. The accordance between the present results of Low-Frequency Raman spectra and those in literature is qualitatively good.

## 4. Conclusion

Crystalline nitric acid hydrates are theoretically studied using a Gaussian type basis set and the hybrid B3LYP Hamiltonian with CRYSTAL06 code. The equilibrium structures of crystalline nitric acid monohydrate NAM, dihydrate  $\alpha$ -NAD and trihydrate  $\beta$ -NAT are well estimated and compared to those in literature. From these structures, the infrared and Low-Frequency Raman spectra were calculated. The present results allow us to make some remarks in particularly the assignment of the stretching modes of  $\text{H}_2\text{O}$  in  $\alpha$ -NAD and  $\beta$ -NAT phases. The lifting of asymmetric stretching degeneration of  $\text{NO}_3^-$  and the symmetric stretching vibration of  $\text{NO}_3^-$  in  $\alpha$ -NAD where distortion lower the symmetry of the nitrate ion from  $D_{3h}$  to  $C_{2v}$

Furthermore, the calculated Low-Frequency Raman spectra correlate marginally with the differences in the networks of hydrogen bonds, which are the framework of particular hydrates structures. Finally, the predicted IR spectra are in a good agreement with experiment compared to Low-Frequency Raman spectra.

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