A PERIODIC AB INITIO QUANTUM MECHANICAL CALCULATION OF VIBRATIONAL SPECTRUM OF CRYSTALLINE NITRIC ACID HYDRATES

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ABSTRACT

The vibrational spectrum of crystalline nitric acid hydrates have been investigated at the periodic ab initio quantum level by using a high quality Gaussian type basis set and the hybrid B3LYP Hamiltonian with CRYSTAL06 code. The X-ray structures of crystalline nitric acid monohydrate NAM and dihydrate α-NAD were taken as input values for the ab initio calculation. We kept the cell parameters fixed to the observed values and the inner coordinates within each unit cell have been optimized. The obtained structures of these atmospherically relevant systems are used in the prediction of their vibrational frequencies. It is shown that the mean difference with respect to the experimental infrared spectra is about 10% in the range 4000-600 cm^{-1}.

Keywords: PSCs; Crystalline Nitric Acid Hydrates; Vibrational frequencies; Ab initio; B3LYP.

1 INTRODUCTION

Since the discovery of the ozone hole and the mechanisms that led to the ozone destruction over Antarctica there has been an increasing interest in the evolution and composition of polar stratospheric clouds (PSCs) which play a crucial role in the destruction of stratospheric ozone in the polar winters. Nitric acid hydrates are the components of polar stratospheric clouds (PSCs) type I. These last play two essential roles in the chemistry of ozone during winter. Both mechanisms 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. This denitrification enforces the ozone destruction, since stratospheric nitric acid photolyzes to NO_X radicals, which inactivates the active chlorine compounds. The active chlorine compounds, atomic Cl, ClO and HOCl react by the O_3 molecules. The other mechanism, in which polar stratospheric clouds type I are involved, is connected to the chlorine reservoir molecules, to HCl and $ClONO_2$. The regeneration of the active chlorine species from the reservoir molecules occurs on the presence of these clouds. The surface of the clouds acts as heterogeneous catalytic surfaces [1-3]. Nitric acid hydrates are the subject of study in number of experimental [4-7] and theoretical [8-10] works.

In the present work, the structural and vibrational properties of crystalline nitric acid monohydrate NAM and dihydrate α-NAD are calculated using CRYSTAL06 code[11].

We present in this article the calculated theoretical structures of NAM and α- NAD crystals. The interest in this optimized geometrical structure lies both in its comparison to the experimental geometry, when it is available, and also in that it provides the basis for further calculations on these systems, like eventual studies on the reactivity of their surfaces, of key importance in atmospheric chemistry, or like the prediction of their infrared spectra, which again can be compared to experimental measurements. In the first section we present a brief discussion of the numerical method. In the following sections, the results on the structures of NAM and α-NAD are described. Then we present the full calculated vibrational spectrum, along with an analysis and comparison with those previously available in the literature. Finally, in the last section, the main conclusions are summarized.

2 COMPUTATIONAL METHODS

For the present calculations, a development version of the CRYSTAL06 program is used [11]. CRYSTAL is a periodic ab initio program in which the crystalline wave functions are expanded as a 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. For H, O and N, 21G, modified 6-21G* and 6-21G* have been used. The B3LYP Hamiltonian has been adopted, which contains a hybrid Hartree-Fock/ density-functional exchange-correlation term and is widely and successfully used in molecular quantum chemistry as well as in solid-state calculations [12, 13]. We refer to ref. [14] for details about the frequency calculations after the optimization of NAM and α-NAD structures. Manipulation and visualization of these structures have been performed with MOLDRAW program [15].

3 STRUCTURE

The structure of crystalline nitric acid monohydrate NAM was first determined by Delaplane et al [16] and has been recently remeasured by Leburn et al [17]. 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_3 and H_2O molecules are dissociated into NO_3^- and H_3O^+ respectively. Every H_3O^+ is connected by hydrogen-bonding with three NO_3^- units forming parallel layers. .

The low temperature phase dihydrate α-NAD has a monoclinic structure and space group $P2_1/n$ (C_{2h}^2) containing eight nitrates and eight aquaoxonium ions per unit cell [17]. Every nitrate connects two oxonium units, which are in a junction with a water molecule each. It has a layer structure as in NAM; the layers are bound by weak Van der Waals forces and weak hydrogen bonds. The asymmetrical geometry of hydrogen bonds leads to important deviations from the ternary symmetry of NO_3^- . .

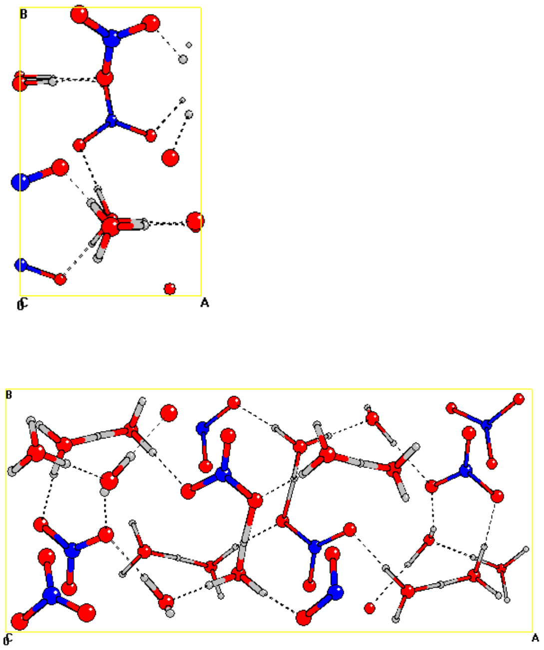

Figure1. View of the atomic arrangement in a unit cell of crystalline nitric acid hydrates: (a) monohydrate, (b) dihydrate. (N: blue, O: red, H: grey).

The X-ray geometry was taken as input value for the ab initio calculation. We kept the cell parameters fixed to the observed values and the inner coordinates within each unit cell have been optimized. Some of the most relevant interatomic distances and angles are presented in Table 1, compared with the experimental observations of refs [16] and [17]. Figure 1a and 1b displays the structures of monohydrate and dihydrate crystals of nitric acid respectively. .

The N-O bond lengths are quite well reproduced, as are the N-O-N angles, with a maximum deviation of only 0.02 Å and 0.5° respectively. The H_3O^+ parameters are overestimated by 0.07Å for O-H bond lengths and by 2° for H-O-H angle.

Table1. Selected Structural Parameters of Crystalline Nitric Acid Hydrates

Parameters	NAM		α-NAD	
	Ref 16,17	this work	Ref 17	this work
NO_3^-				
N-O1	1.252	1.265	1.286	1.293
N-O2	1.251	1.265	1.222	1.232
N-O3	1.249	1.261	1.235	1.277
O1NO2	120.0	119.9	119.3	120.1
O2NO3	120.0	120.3	123	121.9
O3NO1	119.9	119.8	117.4	118.0
H_3O^+				
O-H1	0.93	1.059	0.99	1.083
O-H2	0.87	1.054	0.93	1.059
O-H3	0.97	1.059	0.81	1.048
H1OH2	103	104.3	111	107.6
H2OH3	115	108.6	108	109.6
H3OH1	117	106.6	117	105.5

4 VIBRATIONAL SPECTRUM

A fully comprehensive understanding of the spectroscopic characteristics of these species, however, is not yet achieved, partly because most of the theoretical studies deal with the individual molecules and their water aggregates, and not on the crystals or solids that the hydrates form. The only theoretical works that specifically deal with the solids are by Poshusta et al[9] and Tóth[10] on the monohydrate.In the present work, IR vibrational spectra of crystalline nitric acid monohydrate (NAM) and low temperature modification of dihydrate (α-NAD) were calculated using CRYSTAL06 [11] program. The obtained results are compared with experiment of Grothe et al [15] in the range 4000-600 cm^{-1}. The O-H stretching vibrations of water are present as expected in the normal modes analysis of α-NAD. The frequencies corresponding to asymmetric ν_3 and symmetric ν_1 stretching of water are red shifted by 5% a maximum compared to experimental result [7]. For the two hydrates, the O-H stretching vibrations of the oxonium ions H_3O^+ asymmetric ν_3 and symmetric ν_1 are overestimated by about 10% in the case of NAM; however, it’s about 5% for α-NAD phase. The difference between the calculated asymmetric ν_2 and symmetric ν_4 bending and experimental assignments [7] is in the range 3% - 9%, excepting the asymmetric ν_2 in NAM which is overestimated by about 17%. In the case of nitrate ions, the symmetric stretching ν_1 (NO_3^-) is an IR inactive mode, which is not observed in the case of NAM, where the nitrate ions maintain their D_{3h} symmetry. This band is very characteristical for α-NAD where distortions lower the symmetry of the nitrate ion to C_{2V}. The corresponding frequency is in a good agreement to Grothe et al [7]. Modes associated with symmetric ν_2 and asymmetric ν_4 bending motions in NO_3^- occur at frequencies closer to those obtained by Grothe et al [7]. .

Table2. Predicted Infrared Spectra of Crystalline Nitric Acid Hydrates

Normal modes	NAM		α-NAD	
	this work	Ref 7	this work	Ref 7
$\nu_3(H_2O)_{a\text{-}s}$			3396	3494
$\nu_1(H_2O)_{s\text{-}s}$			3100	3262
$\nu_3(H_3O^+)_{a\text{-}s}$	2479	2226	2868	2714
$\nu_1(H_3O^+)_{s\text{-}s}$	2866	2644	2189	2260
$\nu_4(H_3O^+)_{a\text{-}s}$	1824	1663	1857	1737
$\nu_3(NO_3^-)_{a\text{-}s}$	1454	1269	1516	1450
$\nu_2(H_3O^+)_{s\text{-}s}$	1356	1116	1227	1258
$\nu_1(NO_3^-)_{s\text{-}s}$			1044	1025
$\nu_2(NO_3^-)_{s\text{-}s}$	818	816	776	809
$\nu_4(NO_3^-)_{a\text{-}s}$	733	730	737	743

5 CONCLUSION

The crystalline structure of the nitric acid hydrates, species of key relevance in atmospheric processes, has been determined by application of the ab initio program CRYSTAL06. The obtained geometry is well estimated compared to experiment. The analysis of these normal modes provides an adequate tool to discuss the assignment of the spectra. We have found in general a good agreement with the observed spectra, being particularly successful the assignment of the stretching modes of H_2O and the symmetric stretching vibration of $NO_3^{\,-}$ in α-NAD.

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