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Quantum Chemical Study of the Different Forms of Nitric Acid Monohydrate

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Systems with a 1:1 composition of nitric acid and water were investigated using ab initio quantum chemical methods. We found that the optimized geometry of the complex of a nitric acid and a water molecule is quasi planar with one hydrogen pointing out of the plane. Structural and vibrational data are presented for this complex. We optimized the ionic positions of the bulk and the (100) surface of nitric acid monohydrate crystal using ab initio molecular dynamics with simulated annealing. Some features of the systems and trials of adsorbing HCl, $ClONO_2$, and H_2O on the surface are presented. We did not find specific adsorption that may imply the catalytic effect of the perfect surface on the reactions involved in the depletion of ozone. The systems remained stable during ab initio molecular dynamics performed around 195 K. The only observed change was the reversible proton transfer among the oxonium and nitrate ions in the crystal.

Introduction

The study was motivated by the role of nitric acid hydrates in the depletion of ozone in the stratosphere. Nitric acid hydrates are the main components of polar stratospheric clouds type I. These clouds are formed by crystalline and amorphous nitric acid trihydrate and in a lesser extent by nitric acid monohydrate (NAM). The temperature of the formation is about 195 K and sulfuric acid aerosols seem to be necessary as nucleation centers. Polar stratospheric clouds 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.

Many interesting articles were published about the properties of these clouds and compounds in the past decade. The studies cover the whole range of the physical and physico chemical properties obtained by laboratory and field measurements. The most relevant ones for this study are the articles concerning the composition and phase diagram,[1−5] reactions and adsorption features,[6,7] and spectroscopic properties[8,9] of the polar stratospheric clouds type I.

The topic has been investigated by quantum chemical methods already. Koller and Hadzi[10] studied the structure of the complexes of a nitric acid and one to three water molecules. They used semiempirical and Hartree−Fock ab initio methods. The other study was a periodic Hartree−Fock investigation of nitric acid monohydrate written by Poshusta et al.[11] They calculated properties of a bulk crystal and a clean (100) surface using single point density calculations without performing geometry optimization. Their method demanded very large amount of calculation increasing the number of compromises to make. For example, they applied a basis function set that provides a planar structure for an isolated oxonium ion in contrast to the experimental data.

There are a large number of studies, but there are still a large number of possible questions. It is still not clear whether amorphous or crystalline nitric acid hydrates are the main components of these stratospheric clouds. There is doubt too that both the neutral and ionic species can be found there. It is also a question that a perfect surface of nitric acid hydrates or—as usual—only that with localized crystal defects has catalytic activity. Of course, all of the questions cannot be answered within one ab initio study. We think that our optimized geometries, vibrational frequencies, and density of states help to understand and explain the microscopic behavior of these systems. We also hope that our adsorption trials are of some interest, despite that we did not find specific adsorption positions.

We studied the systems consisting nitric acid and water in 1:1 ratio. This choice is not the most relevant one, since the 1:3 ratio seems to be more important. Unfortunately, the choice of the latter demands several times larger computational effort, because the unit cell[12] of nitric acid monohydrate contains 32 atoms while that one of the trihydrate contains 56 atoms.

Details of the Calculations

Bimolecular Complex of Nitric Acid and Water. Semiempirical quantum Monte Carlo simulations were performed to get a first insight into the energetics of the system consisting of one nitric acid and one water molecule. We used the fragment self-consistent field Monte Carlo method.[13] This method divides the system into two parts, a subsystem and an environment. In the subsystem the exact semiempirical Hamiltonian (here the AM1[14]) is applied while in the environment a simplified one based on coupled strictly localized molecular orbitals is used. The subsystem included both molecules in the present calculation to treat the whole system at the exact AM1 level. Ten simulations were started from different initial configurations and at temperatures between 100 and 300 K. Independently, geometry optimizations were performed by the MOPAC[15] program package starting from the same configurations.

We performed ab initio calculations using the Gaussian 94[16] program package on the basis of the first insight obtained by

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the semiempirical methods. Hartree−Fock (HF), second-order Moller−Plesset (MP2),[17] and density functional calculations were carried out. In the latter case, the exchange functional of Becke[18] and the correlation function of Lee et al.[19] were used (abbr. BLYP). Different basis sets were tested. The presented results are based on the cc-pVDZ set of Dunning.[20]

In the case of basis sets centered on the nuclei, calculation of intermolecular interactions is biased by the basis set superposition error. It is possible to avoid it by applying the plane wave basis set instead of a Gaussian one, since it describes each point of the three-dimensional space at equal level. The development of the pseudopotentials coupling to the plane wave basis set accelerated the calculations without reasonable loss of the accuracy. These density functional calculations were performed by the program developed by the group of Parrinello.[21] The size of the periodic cell was 12.1711 Å × 9.2500 Å × 7.7895 Å. The ultrasoft pseudopotential of Vanderbilt[22] was applied with an energy cutoff of 40 Ry for the plane wave basis set in the calculation of the wave function. This pseudopotential is not the most accurate one, but it can be used together with a relatively low energy cutoff which helps to treat reasonable large systems. The geometry optimization was performed by the method of Pulay.[23] The code supports to perform ab initio molecular dynamics.[24] We carried out short simulations using a fictive electron mass of 1100 au, 0.1209 fs time step, and an initial temperature distributed randomly over the atoms to check the stability of the optimized geometries and to get data around 195 K that is the interesting temperature in the chemistry of the stratosphere.

The calculations were performed at the $\Gamma = 0$ point. The vibrational analysis was done by finite step method.

Bulk Crystal and Surface. The calculations concerning crystalline NAM were performed using the density functional program mentioned above.[21] The size of the periodic cell was the experimental one[12] in the case of the bulk crystal. An investigation of the energetics of cells with optimized atomic positions belonging to different lattice constants, like in ref 25, demands a large amount of computer time, because the orthorhombic cell of NAM has three independent lattice constants. We neither optimized the lattice constants in a simplified way, since we do not believe that energies belonging to nonoptimized atomic positions provide reasonable basis for any selection. The initial positions of the atoms were the experimental ones described in the standard setting $Pna2_1$ of the space group (group no. 33[26]).

We choose the (100) surface of the crystal similarly to the study of Poshusta et al.[11] One cell thick surface was constructed containing two layers of NAM in the z direction due to the experimental data.[12] The size of this $x-y$ periodic cell was 8.6439 Å × 5.4647 Å × 11.5226 Å.

In the calculations concerning the adsorption of HCl, H_2O, and $ClONO_2$ the cells were enlarged in z direction to 14.2878, 16.9337, and 16.9337 Å, respectively. The initial positions of these molecules were chosen randomly above the surface. The norm conservative pseudopotential of Gödecker et al.[27] was applied for Cl.

The geometry optimization method used at the molecular complex often failed in the calculations of the NAM crystal. In these cases, the steepest descent or the simulated annealing techniques were used to get the minimal energy configurations. The stability tests were performed in a similar way as in the case of the molecular complex using ab initio molecular dynamics.

The other details were identical with the calculations of the bimolecular complex.

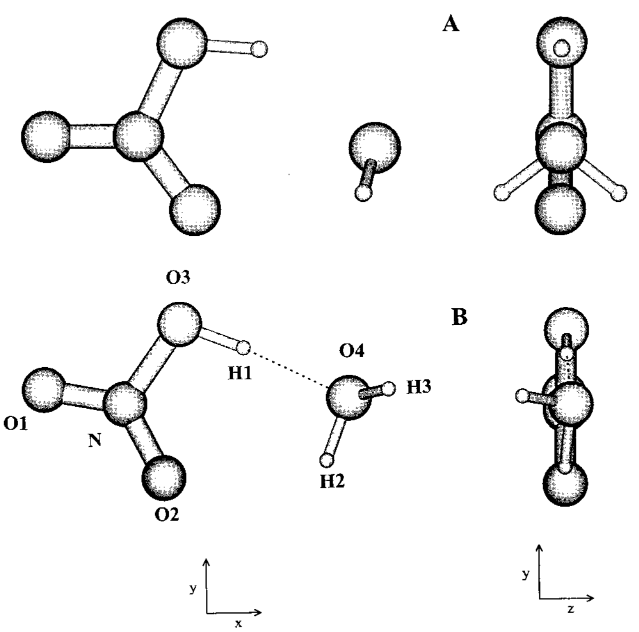

Figure 1. Optimized geometry of the molecular complex of a nitric acid and a water molecule. Two projections are shown both for (A) semiempirical and (B) ab initio (BLYP) calulations.

Results and Discussion

Bimolecular Complex of Nitric Acid and Water. The semiempirical quantum Monte Carlo simulations were started from different initial configurations. After a few hundred steps all calculations reached the equilibrium where the donor of the hydrogen bond is the nitric acid molecule. Independently, either gradient optimization or simulated annealing was performed we got the same structure having the lowest energy as Koller and Hadzi.[10] This nonplanar structure preferred at the semiempirical quantum chemical level can be seen in Figure 1a. Since this geometry is different from the ab initio results, the only important point of these calculations is to confirm the opinion of ref 10 that semiempirical methods fail in the case of this system.

The optimized geometries were similar to each other in the ab initio calculations. Selected geometrical parameters are shown in Table 1. The table contains information also on the isolated species. The final geometry of the calculation at the BLYP level can be seen in Figure 1b together with the numbering of the atoms. We found in all cases of the applied ab initio methods, that the atoms are close to be on one plane except one hydrogen of the water molecule. The distance of the dangling H3 atom was 0.5−0.6 Å from the plane of the nitric acid molecule in the different ab initio calculations.

The N−O3 bond is shorter, the O3−H1 bond is longer, and the N−O3−H1 angle is larger in the monohydrate than in the isolated nitric acid. The changes can be explained well by the spherical and electrostatic effects of the hydrogen bond. Elongation of the N−O1 and N−O2 bonds was detected as a consequence of the reduced π character in these bonds due to the decreased N−O3 distance.

Koller and Hadzi got a fully planar geometry for the bimolecular complex of nitric acid and water using 4-31G basis function set. We performed some simulations at lower quality of basis function sets than the cc-pVDZ set. Worsening the basis set provided the fully planar geometry. This dependence on the quality of the basis function set forced us to study the system using plane wave basis set in the density functional formalism. The optimized geometry of the BLYP/PW method corresponds well to our other ab initio results. The planar

TABLE 1: Selected Geometrical Parameters and Binding Energies of the Nitric Acid Monohydrate Complex[d]

	HF		MP2		BLYP		BLYP/PW		experimental	HF(4-31G)[c]
Distances (Å)										
N−O1	1.173	*1.170*	1.216	*1.211*	1.220	*1.214*	1.259	*1.255*	*1.190−1.206*[a]	
N−O2	1.192	*1.186*	1.231	*1.222*	1.241	*1.229*	1.281	*1.270*	*1.206−1.226*[a]	
N−O3	1.319	*1.333*	1.384	*1.416*	1.428	*1.471*	1.448	*1.489*	*1.396−1.406*[a]	1.349
O3−H1	0.965	*0.951*	0.998	*0.977*	1.012	*0.985*	1.026	*1.001*	*0.960−0.964*[a]	0.994
O3−O4	2.757		2.708		2.732		2.747			2.567
O4−H2	0.946	*0.944*	0.970	*0.966*	0.979	*0.975*	0.993	*0.992*	*0.957*[b]	
O4−H3	0.944		0.966		0.975		0.993			
Angles (deg)										
N−O3−H1	106.72	*105.19*	104.11	*102.06*	104.33	*102.11*	104.09	*102.32*	*102.0−102.9*[a]	108.91
H2−O4−H3	107.25	*105.85*	105.36	*103.85*	105.57	*104.17*	105.36	*103.82*	*104.52*[b]	
O3−H1−O4	177.31		174.59		174.62		173.81			170.58
E(binding) (kJ/mol)										
	−76.2		−43.1		−34.2		−32.2			−79.5

[a] Reference 28−30. [b] Reference 31. [c] Reference 10. [d] The values printed in italics belong to the isolated nitric acid or water molecules. The numbering of the atoms are defined in Figure 1.

TABLE 2: Harmonic Frequencies for the Nitric Acid Monohydrate Complex and for the Isolated Nitric Acid and Water Molecules

approximative description	HF		MP2		BLYP		BLYP/PW		experimental
moving of H_2O around the H bond	345		462		387		733		
O1,O2−N−O3 bend (NO_2 rocking)	726	*688*	648	*583*	594	*523*	771	*631*	*580*[a]
O1−N−O2 bend (NO_2 bend)	796	*789*	692	*656*	619	*563*	824	*740*	*647*[a]
N out of plane (NO_2 wagging)	811	*921*	788	*777*	730	*720*	888	*786*	*763*[a]
O1,O2−N−O3−H1 torsion (NO_2 twisting)	929	*499*	894	*491*	831	*408*	988	*546*	*458*[b]
N−O3 str	1149	*1128*	950	*897*	855	*825*	1289	*829*	*879*[c]
NO_2 sym str	1567	*1589*	1350	*1332*	1252	*1274*	1323	*1246*	*1326*[d]
N−O3−H1 bend	1602	*1476*	1520	*1344*	1402	*1220*	1621	*1325*	*1303*[d]
H2−O4−H3 bend (H_2O bend)	1739	*1754*	1640	*1661*	1570	*1593*	1634	*1646*	*1595*[e]
NO_2 antisym str	1950	*1952*	1856	*1884*	1668	*1685*	1863	*1717*	*1708*[c]
O3−H1 str	3806	*4098*	3338	*3740*	3102	*3571*	3219	*3530*	*3550*[c]
H_2O sym str	4144	*4145*	3813	*3827*	3629	*3638*	3657	*3674*	*3657*[e]
H_2O antisym str	4254	*4254*	3947	*3962*	3749	*3760*	3780	*3821*	*3756*[e]

[a] Reference 32. [b] Reference 33. [c] Reference 34. [d] Reference 35. [e] Reference 31. [f] Those of the isolated molecules are printed in italics. The experimental ones belong to the isolated molecules.

geometry seems to be a failure of the insufficient quality of the applied basis set in ref 10.

The energy of the hydrogen bond is shown in Table 1. The values indicate an intermediate strength. The hydrogen bonds are quasi linear in all cases. The distance of the two oxygen atoms forming the hydrogen bond is similar to the values found in water dimers. Our trials to optimize the geometry where the water molecule donates the hydrogen did not lead to success.

Nitric acid monohydrate does not exist as a complex of neutral molecules, but as ion pair in crystalline and glassy form. We tried to analyze the proton transfer between the acid and the water molecules. We could not isolate the ion pair. Despite the different methods applied in searching local minima, our trials starting from the ionic case turned spontaneously into the molecular complex. It corresponds well to the previous study[10] where stable ions were not found, except the hydration of the ions was included. We could isolate the ion pair only in one case, where a low level basis function set was applied together with a symmetry constraint of planarity. We did not derive any conclusion from the energetics of this single case, since such constraints are far from reality.

Both our semiempirical and ab initio results suggested that the rotation barrier of the water molecule is rather low around the hydrogen bond. It reduces the feasibility of a search for one optimized configuration, since the thermal motion causes rotation. We performed ab initio molecular dynamics to investigate the behavior of nitric acid monohydrate under the conditions of interest for stratospheric chemistry. The system consisted of one water and one nitric acid molecule. The molecular dynamics proved our intuition that the rotation of the water molecule is rather free. We detected two full rotations in the total simulation time of 0.725 ps. The rotation of the water molecule cannot be projected onto one angle variable. At least two variables are necessary to describe it. For example, one should be the angle between the planes of the two molecules and the other should be the angle between the dipole vector of the water molecule and the plane of the nitric acid molecule. We did not find it feasible to calculate the rotation barriers, since two variables cause a loss of clearness.

The harmonic frequencies calculated for the isolated molecules and for the complex can be seen in Table 2. The lowest five frequencies of the complex are omitted from Table 2, since their uncertainty is rather large in the harmonic approximation.

In the case of the intramolecular vibrations of the water molecule, we found small red shifts for the stretching and bending frequencies. Despite the shifts, the water molecule remains rather intact, which indicates correctly that this molecule is the acceptor of the hydrogen bond. The changes of the frequencies belonging to the internal motions of the nitric acid molecule lead to the same conclusion as the observed changes of the bond lengths. The O1−N and O2−N bonds are weaker and the O3−N bond is stronger in the complex than in the isolated molecule.

Three frequencies can be related to the hydrogen bond. The H1−O3 bond is weaker in the monohydrate, as it is shown by the 300−400 cm^{-1} red shift. It is interesting that the difference of the in plane motion of the H1 atom (N−O3−H1 bend, 200 cm^{-1} blue shift) is smaller than the difference in the out of plane motion. The out of plane motion of the H1 atom (termed as the twisting of the NO_2 group or as the O1,O2−N−O3−H1

TABLE 3: Calculated and Experimental Bond Lengths and Angles for Nitric Acid Monohydrate Crystal

	calcd		
	bulk	(100) surface	X-ray[12]
bond lengths (Å)			
N−O	1.303, 1.305, 1.315	1.302−1.318	1.254, 1.257, 1.258
H−O	1.029, 1.050, 1.054	1.037−1.056 (inner)	
		1.032−1.038 (outer)	
hydrogen bond	1.590−1.598	1.517−1.607 (inner)	
		1.605−1.662 (outer)	
H−O−H angle (deg)	104.4, 105.9, 107.7	102.9−105.2 (inner)	
		108.4−109.5 (outer)	

torsion) shows an astonishingly large blue shift. It can be explained by the quite free out of plain motion of H1 in the isolated nitric acid molecule, while in the complex the hydrogen bond hinders this motion. On the other hand, the increasing π character of the N−O3 bond enforces the atoms to stay in a plane. The first frequency shown in Table 2 refers to the rotation of the water molecule around the hydrogen bond.

Bulk Crystal and Clean Surface. We optimized the ionic positions for the bulk crystal using the experimental lattice constants. The optimized geometry shows the same feature as the experimental one. It suggests that omitting the lattice constants optimization does not produce a serious error. Selected geometrical parameters of the bulk crystal are shown in Table 3. Delephane et al.,[12] who determined the experimental geometry, proposed 0.909 Å for the O−H bond length and 107.8° for the H−O−H angle, but these values contain large uncertainty due to their determination using X-rays. There are some other data omitted from Table 3. BLYP/PW calculations of an isolated oxonium ion suggests 1.003 Å for the bond length and 113.8° for the H−O−H angle, while the experimental angle is 115.3°. In other crystals of H_3O^+ a mean value of 109° was found. The BLYP/PW value of the N−O bond length is 1.322 Å for an isolated NO_3^- ion. The experimental structure of the NAM crystal shows less symmetric intramolecular geometry than in the isolated case. This feature remains detectable in our optimized geomety. The intramolecular geometrical parameters kept their splitting into triplets found in the experiment. Quantum chemical calculations are less accurate in the calculation of the intermolecular distances than in the intra ones. The omitting of the optimization of the lattice constants should bias mostly the intermolecular parameters. Despite this, we obtained reasonable agreement in the hydrogen bond length with the values customary.

The (100) surface was constructed from the crystal where the positions of the ions were optimized assuming $x-y$ periodicity. The optimized geometry is shown in Figure 2. The easiest cut of the crystal can be performed parallel to the (100) surface, since in this direction puckered layers should be removed from each other, which ones are bonded through weak forces. Large Coulomb interactions and hydrogen bonds should be destroyed in all other directions. Poshusta et al. chose the same surface of the crystal on the basis of the calculation of the elastic constants.

The indistinguishable four NO_3^- or H_3O^+ ions of the bulk crystal split into two-two different ones. We termed the ions inner and outer where outer means the position closer to the surface. We observed only small surface reconstruction. The spacing between the two layers increased with 0.2 Å. This is similar to the general trend, that the spacing among the layers close to the surface is usually larger than in the bulk crystal. Some geometrical parameters of the surface are shown in Table 3. The intramolecular changes of the nitrate anion were not large. In the case of the oxonium ions, the two different positions mean rather different structures. The outer ones changed to the direction of the ideal tetrahedron, while the inner ones become less planar. The difference appears also in the intermolecular structure. The hydrogen bonds of the outer oxonium ions are longer than those of the inner ones.

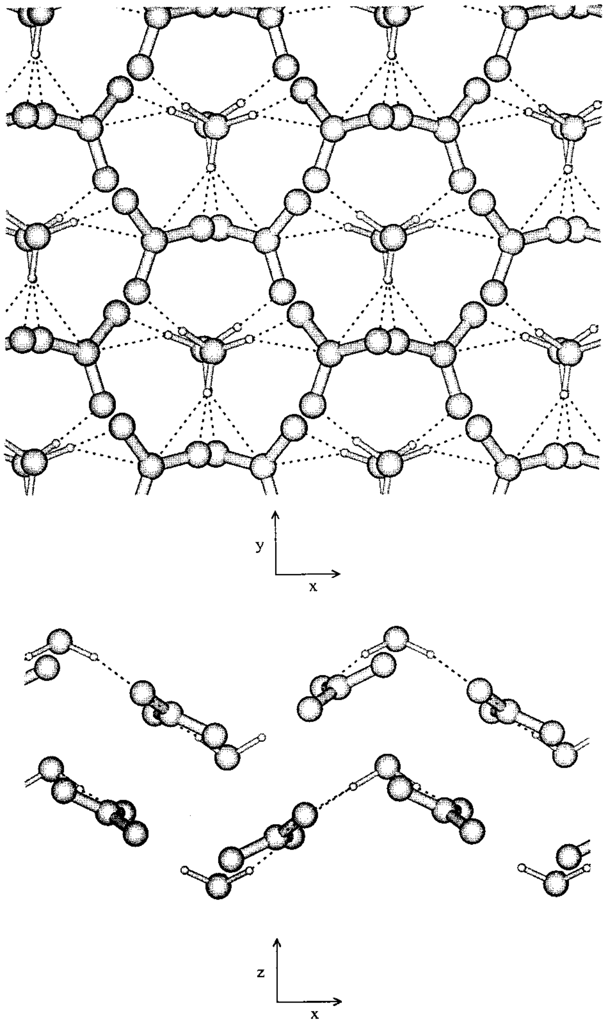

Figure 2. Optimized geometry of the (100) surface of nitric acid monohydrate crystal.

The vibrational frequencies were calculated for the NAM crystal containing either hydrogens or deuteriums. The frequencies are schematically presented in Figure 3 together with those of the isolated H_3O^+ and NO_3^- ions. The figure does not show any kind of infrared spectra, since equally large Gaussian functions were added to each frequency independently the infrared activity and intensity. We compared the results to the experimental ones.[8,9] We obtained a red shift in the stretching frequencies of the oxonium ions provided in two groups of frequencies, one at 2950−3000 cm^{-1} and another at 2450−2700 cm^{-1}. The experimental spectra show maxima around 2640 and 2230 cm^{-1}. Our bending frequencies of the oxonium

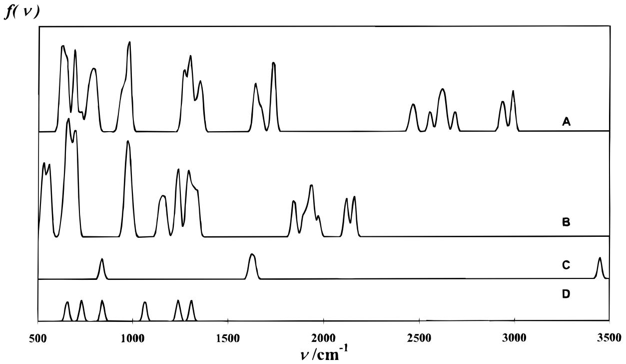

Figure 3. Schematic representation of the vibrational frequencies obtained by density functional method with plane wave basis set: (A) nitric acid monohydrate crystal; (B) nitric acid monohydrate crystal (deuterated); (C) isolated H_3O^+; (D) isolated NO_3^-.

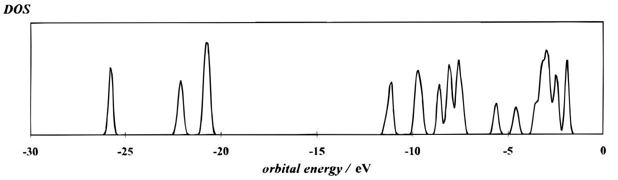

Figure 4. Schematic representation of the valence orbital energies in nitric acid monohydrate crystal obtained by density functional method with plane wave basis set.

ions are close to the isolated case. The experimental data suggest different positions for the symmetric and asymmetric bends where the former appears around 1130 cm^{-1}. Our calculation suggests more symmetric oxonium ions than indicated by the experiments. The frequencies appearing around 750−820 cm^{-1} (520−570 in the deuterated calculation) can be assigned as the torsional and librational[9] modes. In the case of the nitrate ion, we found a larger difference between the symmetric and asymmetric stretching frequencies than suggested in the experiment. It corresponds to the calculated unequal N−O bond lengths shown in Table 3. The bending frequencies of the nitrate groups appear at 630−700 cm^{-1}. Besides the fundamental frequencies of the oxonium and nitrate ions, we obtained frequencies around 1270 and 940 cm^{-1} that can be connected to the hydrogen bonds in a similar way as it was done in the case of the bimolecular complex for the NO_2 twisting.

Poshusta et al.[11] discussed the density of states in detail. We show a schematic representation of the density of states of the valence orbitals for the bulk crystal in Figure 4. The values are presented in a same manner as the vibrational curves using Gaussian functions. The low energy part of the spectrum consists of three bands. We also found an about 10 eV large gap in the intermediate region. The largest occupied orbital has an energy of about −2 eV. Our density of states seems to be similar in the most important features to the Hartree−Fock one. It is not worthwhile to describe further details, since the absolute value of the energy is not informative. It highly depends on the quality of the applied basis set. It means the cutoff value of the kinetic energy for the plane waves, the size of the periodic box, and the applied pseudo potential in the present calculation.

We performed short molecular dynamics for the bulk crystal and the (100) surface. Proton transfers were observed from the oxonium ions to the nitrate ions, but the protons got back to the original oxonium ions. We performed simulated annealing starting from a configuration with transferred proton and we got the original bulk crystal consisting of oxonium and nitrate ions. On the basis of our calculations on the bimolecular complex, on the crystal, and on the previous studies[10,11] the proton transfer may occur without large barrier. In amorphous and crystalline phases the ionic form is preferred, since the ions are bonded to the neighbors with three hydrogen bonds where the proton acceptors are the oxygens of the nitrate ion. It is possible that the thermal motion locally transfers one of the hydrogens of a oxonium ion to the next nitrate ion. This behavior corresponds well to the traces of nitric acid molecules found in the vibrational spectra of the NAM crystal.[8,9]

Adsorption of HCl, H_2O, and $ClONO_2$. The catalytic activity of a surface can rise from the arrangement of a perfect surface or of localized crystal defects. Modeling the latter is rather arbitrary, since large number of different defects can be constructed. Unfortunately, the reactions occur mostly on these defects. To test, if there is any effect of the perfect crystal surface in the regeneration process of the active chlorine species, we studied the adsorption of the reservoir molecules (HCl and $ClONO_2$) and H_2O on the (100) surface of nitric acid monohydrate. It is presumed, that the catalytic surface activates the components of the following reactions:

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \qquad (1)$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (2)$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \qquad (3)$$

The outer plane of the (100) crystal surface is formed by oxonium ions, but not only their molecular orbitals can interact with molecules tending to adsorb. The puckering of the (100) surface creates possible adsorption holes where the orbitals of the nitrate ions may play important roles, too.

The HCl, $ClONO_2$, and H_2O molecules were put at random positions over the surface. At first, we optimized the geometry by simulated annealing. The optimized geometries can be seen in Figure 5. The minimum energy positions were similar for the three molecules. They lay above the surface at the point where the puckering of the layers constructs a hollow. They did not penetrate into the hollow. All the three molecules adsorbed parallel to the surface. The distances of the adsorption planes, defined as the center of mass of the molecules, were 2.4, 3.2, and 2.4 Å far from the plane of the outermost atom of the surface. One of the hydrogen atoms of the water molecule and a part of the nitrate group of chlorine nitrate moved out from the aforementioned planes toward the surface. Despite these small displacements, the atoms were far from the surface. The smallest distances between the atoms of the molecules and the surface were 3.3 (H−H), 3.6 (Cl−H), and 3.9 Å (O−H) for the HCl, $ClONO_2$, and H_2O molecules, respectively. These intermolecular distances are longer than usual in the case of chemisorption or hydrogen bond. The changes in the intramolecular geometries, in the harmonic frequencies, and in the density of states were within the statistical uncertainty as against the isolated ones. Therefore, we concluded that the geometrical and electronic structure of the isolated molecules remained intact during the adsorption. The adsorption energies of the HCl, $ClONO_2$, and H_2O molecules were −15, −120, and −39 kJ/mol, respectively.

We were interested in the possible changes, like chemisorption or decomposition, occurring at nonzero temperature, e.g., at 195 K. The systems were heated to this temperature and were let to move in ab initio molecular dynamics. We did not find any reasonable changes in the adsorption positions or in the geometries of the molecules during the 0.5 ps long simulations.

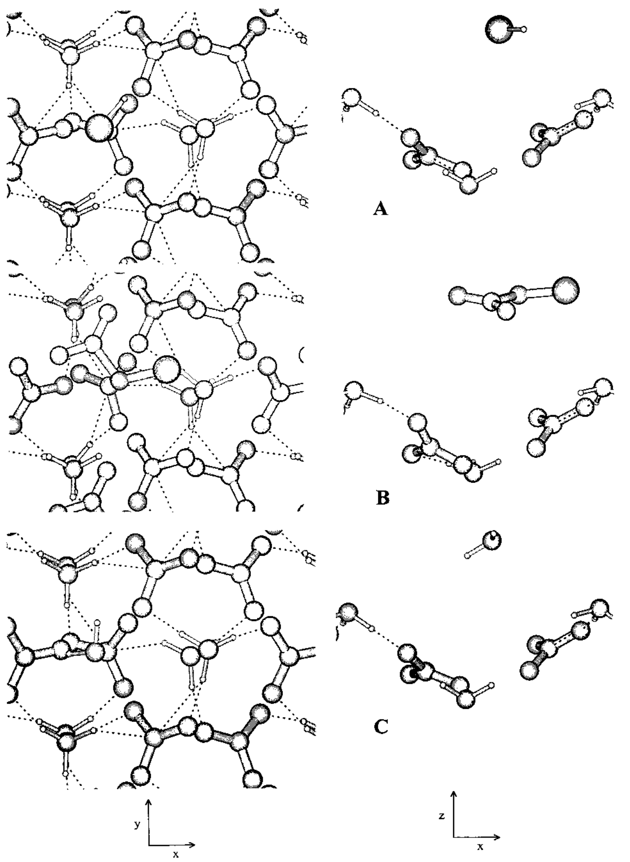

Figure 5. Optimized adsorption positions on the (100) surface of nitric acid monohydrate crystal for (A) HCl, (B) $ClONO_2$, and (C) H_2O.

The facts imply that the surface of the perfect crystal of nitric acid monohydrate does not act catalytically in the aforementioned reactions. Probably, the catalytic sites of the polar stratospheric clouds type I are at the defects of the nitric acid hydrate crystals or at the amorphous parts.

Conclusion

We obtained some new features and details of the systems with 1:1 composition of nitric acid and water. We found that the optimized geometry of the complex of a nitric acid and a water molecule is quasi planar, only one hydrogen atom is out of the plane. This results is in contradiction with the previous quantum chemical trials on this complex. We compared and explained the changes in the geometrical parameters and vibrational frequencies against the isolated molecules.

In the case of the bulk crystal and clean surface, we could reproduce the experimental structure within the accuracy of the method. We could optimize the geometries to get reliable vibrational spectra that corresponds well to the experimental data and explains it. We detected reversible proton transfer from the oxonium to the nitrate ions.

Our adsorption trials imply that the perfect (100) surface of nitric acid monohydrate crystal has no catalytic effect on the reactions regenerating the active chlorine species from the reservoir molecules.

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References and Notes

(1) Arnold, F. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96,* 339.

(2) Worsnop, D. R.; Fox, L. E.; Zahniser, M. S.; Wofsy, S. C. *Science* **1993**, *259,* 71.

(3) Molina, M. J.; Zhang, R.; Woolridge, P. J.; McMahon, J. R.; Kim, J. E.; Chang, H. Y.; Beyer, K. D. *Science* **1993**, *261,* 1418.

(4) Fox, L. E.; Worsnop, D. R.; Zahniser, M. S.; Wofsy, S. C. *Science* **1995**, *267,* 351.

(5) Koop, T.; Luo, B.; Biermann, U. M.; Crutzen, P. J.; Peter, T. *J. Phys. Chem. A* **1997**, *101,* 1117.

(6) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1992**, *96,* 2682.

(7) Abbatt, J. P. D.; Molina, M. J. *J. Phys. Chem.* **1992**, *96,* 7674.

(8) Ritzhaupt, G.; Devlin, J. P. *J. Phys. Chem.* **1991**, *95,* 90.

(9) Smith, R. H.; Leu, M.; Keyser, L. *J. Phys. Chem.* **1991**, *95,* 5924.

(10) Koller, J.; Hadzi, D. *J. Mol. Struct.* **1991**, *247,* 225.

(11) Poshusta, R. D.; Tseng, D. C.; Hess, A. C.; McCarthy, M. I. *J. Phys. Chem.* **1993**, *97,* 7295.

(12) Delaplane, R. G.; Taesler, I.; Olovsson, I. *Acta Crystallogr.* **1975**, *B31,* 1486.

(13) Tóth, G.; Náray-Szabó, G. *J. Chem. Phys.* **1994**, *100,* 3742.

(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107,* 3902.

(15) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10,* 209.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.2; Gaussian, Inc.: Pittsburgh, 1995.

(17) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46,* 618.

(18) Becke, A. D. *Phys. Rev. A* **1988**, *38,* 3098.

(19) Lee, C. L.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37,* 785.

(20) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98,* 1358.

(21) Hutter, J.; Ballone, P.; Bernasconi, M.; Focher, P.; Fois, E.; Gödecker, S.; Parrinello, M.; Tuckerman, M. *CPMD*, Version 3.0, MPI für Festkörperforschung; Stuttgart and IBM Research Laboratory: Zürich, 1990−1996.

(22) Vanderbilt, D. *Phys. Rev. B* **1990**, *41,* 7892.

(23) Császár, P.; Pulay, P. *J. Mol. Struct.* **1984**, *114,* 31.

(24) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55,* 2471.

(25) Langel, W.; Parrinello, M. *J. Chem. Phys.* **1995**, *103,* 3240.

(26) Hahn, T. *International Tables of Crystallography*; Kluwer Academic Publishers Group: Dordrecht, The Netherlands, 1989.

(27) Gödecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54,* 1703.

(28) Millen, D. J.; Norton, J. R. *J. Chem. Soc.* **1960**, 1523.

(29) Cox, A. P.; Riveros, J. M. *J. Chem. Phys.* **1965**, *42,* 3106.

(30) Cox, A. P.; Waring, S. *Trans. Faraday Soc.* **1971**, *67,* 3441.

(31) *CRC Handbook of Chemistry and Physics,* 75th ed.; Lide, D. R., Ed.; CRC Press Inc.: Boca Raton, FL, 1994.

(32) Maki, A. G.; Olson, W. B. *J. Mol. Spectrosc.* **1989**, *133,* 171.

(33) Hoy, A. R.; Bunker, P. R. *J. Mol. Spectrosc.* **1979**, *74,* 1.

(34) McGraw, G. E.; Bernitt, D. L.; Hisatsune, I. C. *J. Phys. Chem.* **1965**, *42,* 237.

(35) Perrin, A.; Lado-Bordowsky, O.; Valentini, A. *Mol. Phys.* **1989**, *67,* 249.