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High Pressure Raman Spectroscopy of Nitric Acid

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New high pressure Raman spectroscopy measurements on pure anhydrous HNO_3 and HNO_3-H_2O mixtures up to 38 mol % in water (commercial grade concentration) are reported up to 50 GPa. The main feature is the reversible and progressive transformation of pure solid nitric acid at pressures between 10 and 17 GPa, evidenced by an enhancement of the 1057 cm^{-1} peak assigned to the ν_1 vibrational stretching mode of the NO_3^- group and by the softening of the symmetric stretching NO_2 mode with pressure. The formation of the H bonding by a charge transfer due to a strong interaction between the surrounding molecules is discussed. Two hypotheses are discussed: nitric acid might be pressure autoionized or cross-linked as a reversible polymer-like compound. These two hypotheses are not mutually exclusive. An increase of water concentration in nitric acid shifts the limit of the appearance of the NO_3^- vibrational mode to lower values of the pressure at constant temperature.

Introduction

Research on nitric acid and related compounds has typically been concerned with environmental problems and the physicochemistry of the formation of nitrogen oxides in the Earth's atmosphere.[1,2,3] Nevertheless, nitric acid is known as a powerful oxidizing agent at room temperature and pressure. It takes a prominent part in numerous industrial processes. The concentrated acid is especially known to react explosively with compounds such as ethanol, and its oxidizing properties have been used for military and aerospace applications.[4]

Nitric acid does not seem to be an explosive compound by itself, but, associated with specific compounds, it is used as a powerful propellant. Actually, the chemical mechanism of nitric acid based monergols and propergols is not confidently established, and detonation effects can occur depending on concentration, temperature, pressure, and nature of the mixtures. Moreover, impurities such as water can drastically modify the properties of the acid. Particularly the combustion of nitric acid based monergols and propergols could locally enhance the effect of high pressures and thus modify the behavior of the constitutive products to initiate hazardous effects. To determine pressure induced structural and chemical transformations of the pure nitric acid, a high pressure Raman study of pure nitric and partially hydrated acid has been undertaken.

Gaseous and liquid nitric acid at ambient pressure have been extensively studied by Raman and infrared spectroscopy.[5] By comparison with vibrational spectra measured with isotopically marked molecules of nitric acid (D and ^{15}N), the assignment of the peaks and the structure have been determined by McGraw et al.[6] and Guillory et al.[7] Table 1 summarizes the results of this identification in the liquid and the solid state. The assignment comes primarily from McGraw et al.[6] However, the 677 and 930 cm^{-1} frequencies have been assigned to the NO_2 bending mode and the $O'-NO_2$ stretching mode (O′ is related to the oxygen linked with the hydrogen atom) by Guillory et al. From spectroscopic measurements involving isotopically marked species,[8,9] the planar structure of pure nitric acid with the symmetry point group C_S and nine normal vibrational modes has been deduced.

TABLE 1: Fundamental Vibrational Wavenumbers[a] (cm^{-1}) of the Nitric Acid

mode description	HNO_3 liquid	HNO_3 solid at 14 kbar	HNO_3 solid at 210 K
lattice modes			103 (s), 164 (m)
$O'-NO_2$ bending[b]	611 (m)	625 (w) 642 (m)	627 (vw) 642 (w)
NO_2 bending[c] $O'-NO_2$ stretching[d]	677 (m)	704 (m)	702 (m)
			(709) (m)
NO_2 bending o.p.		778 (w)	
$O'-NO_2$ stretching[c] NO_2 bending[d]	930 (s)	961 (s)	958 (s)
			(977 vw)
ν_1 s-stretching of NO_3^-	1057 (w)	1054 (w)	
NO_2 s-stretching	1298 (s)	1250 (s) in the diamond band	1251 (s) (1342) (w)
ν_3 a-stretching of NO_3^-		1380 (w)	1370 (w)
$\nu(NO_2^+)$	1400 (w)	1416 (m)	1426 (w)
2ν NO_2 bending o.p.	1539 (w)	1550 (w)	1552 (vw)
NO_2 a-stretching	1679 (w)	1660 (w)	1665 (w)

[a] Our results. [b] O′ refers to O−H bond. [c] Reference 7. [d] Reference 6.

The water affinity of nitric acid has been studied by Raman spectroscopy in the liquid, glassy, and solid state to understand the interaction between HNO_3 and H_2O.[10,11] It seems to be generally accepted that the large amplitude of torsional movement of the OH bond plays an important role in the association of neighbor molecules as a function of the temperature and probably of the pressure.[3,12] Evidence in favor of a self-ionization mechanism of liquid nitric acid (reaction 1) has been given by Gillespie et al.,[13] Dunning et al.,[14] and Young et al.[15]

$$2HNO_3 \leftrightarrow NO_2^+ + NO_3^- + H_2O \qquad (1)$$

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TABLE 2: Fundamental Vibrational Wavenumbers[a] (cm^{-1}) of the $LiNO_3$ Salt

mode description[b]	wavenumber (cm^{-1})
$2\nu_2$ out-of-plane	1673
ν_3 a-stretching	1381
ν_1 s-stretching	1066
ν_4 bending	732

[a] Our results. [b] Reference 8.

An extensive study of the self-ionization of liquid acid at different water concentrations[15] showed that the acid self-ionization is the dominant mechanism above 23 mol % of water content. The nitronium ion NO_2^+ and nitrate ion NO_3^- issued from reaction 1 have been identified respectively in the Raman spectrum of pure nitric acid by weak peaks at 1400 and 1057 cm^{-1}. Table 2 summarizes the different frequencies of the nitrate ion NO_3^-.

In the present work, new spectroscopic measurements are reported for nitric acid over a wide range of pressure. In addition, Raman spectra of nitric acid with an increasing concentration of water have been performed in order to investigate the effect of water in the pressure behavior of the acid.

Experimental Method

The measurements have been performed with fresh distilled white nitric acid (CEA Le Ripault, France) and with hydrated nitric acid between 5 and 38 mol % of water in acid (corresponding to the commercial grade form). Pure nitric acid is stored at low temperature in a PTFE container to avoid a rapid aging of the sample which can modify the chemical composition of the acid.

The experiments have been performed in a high pressure membrane type diamond anvil cell made of refractory alloy.[16] The pressure was monitored by a pneumatic ram connected to a pressure generator through a high pressure flexible capillary. The stable hydrated nitric acid is used without further purification or precaution. The diamond anvil cell dried at 373 K over 24 h was then put in a desiccator until its return to room temperature and then loaded in a drybox. The cell is considered to be ready when the intensive Raman band of the ν_1 NO_3^- symmetrical stretching mode at around 1050 cm^{-1} is not observed in the spectrum (the accuracy in the water content is lower than 1% within our experimental conditions). Under these conditions, the acid is considered to be still pure inside the cell. The pressure is measured by the shift of the fluorescence singlet (685.4 nm at 0.1 MPa) of $SrB_4O_7{:}Sm^{2+}$ chips set inside the high pressure chamber.[17] An argon ion laser (514, 514.5 nm) delivered 40 mW power on the sample which is low enough to avoid heating the sample. The diameter, thickness, and volume of the sample are 200 μm, 80 μm, and 2×10^{-3} mm^3, correspondingly. $SrB_4O_7{:}Sm^{2+}$ chips and the stainless steel gasket were mixed with nitric acid during several days. The products did not react with nitric acid. Spectra have been measured with a DILOR XY multichanel spectrometer and an ISA liquid nitrogen cooled CCD detector.

Results and Discussion

High pressure Raman spectra measurements have been performed on pure nitric acid and in 5, 15, 25, and 38 mol % mixtures with water.

A. Pure Nitric Acid. A first set of Raman experiments was performed at ambient conditions of pressure up to the freezing point to compare the measurements with the spectroscopic literature data in the liquid and solid state (Figure 1). Jones et al.[18] claim that pure anhydrous nitric acid exists only in the solid phase. Table 1 summarizes the different frequencies of the pure nitric acid in the liquid and the solid state under pressure at 1.4 GPa and at low temperature at 210 K. In the low frequency range, three peaks have been assumed to be lattice modes at 106 and 164 cm^{-1}. At 210 K, the $O'-NO_2$ (O′ refers to the O−H bond) bending mode (611 cm^{-1} in the liquid state) splits in two distinguishable peaks at 627 and 642 cm^{-1}, and the NO_2 bending mode (677 cm^{-1} in the liquid state) is observed at 707 cm^{-1}. The $O'-NO_2$ stretching mode shifts from 930 to 958 cm^{-1}, and its apparent bandwidth decreases from 53 to 11 cm^{-1}. The NO_2 symmetrical stretching mode shifts to the low frequencies from 1298 to 1251 cm^{-1}, and its apparent bandwidth decreases from 45 to 9 cm^{-1}. We assume that the observed 1426 cm^{-1} band is related to the shifted and enlarged vibrational mode of the nitronium NO_2^+ group (observed at 1400 cm^{-1} in the liquid state). Weak peaks at 977, 1342, and 1370 cm^{-1} are not assigned.

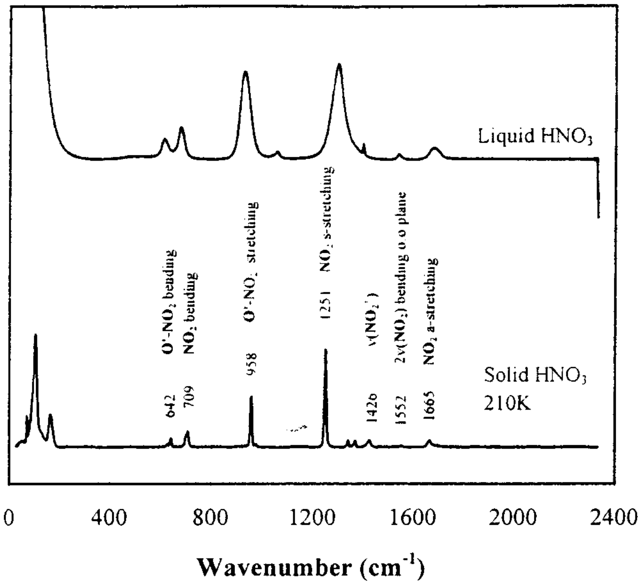

Figure 1. Raman spectra of pure nitric acid at ambient pressure at the liquid state (upper) and the solid state (lower).

The high pressure Raman measurements on pure nitric acid have been measured over a pressure range of 1 to 50 GPa at ambient temperature (Figure 2a−c). We note that peaks are hidden by the strong 1332 cm^{-1} peak from the diamond windows. The pressure freezing point of the pure nitric acid is found at 1.4 GPa and is characterized by the strong shift (48 cm^{-1}) toward lower frequency, observed at 210 K, of the NO_2 symmetrical stretching mode. A new small peak, appearing at 778 cm^{-1}, is not assigned. The behavior of the vibrational modes with pressure will be discussed below, in comparison with previously reported results at ambient pressure.

B. Hydrated Nitric Acid. As for pure nitric acid, a set of Raman measurements has been performed at ambient pressure to compare our results with the spectroscopic literature data. In liquid phase (Figure 3), the ratio between the peaks related respectively to the nitronium ion NO_2^+ and the nitrate ion NO_3^- peaks decreases with increasing concentration of water, in agreement with the equilibrium of reaction 1 and the literature.[4,15,19] Depending on the water concentration, the appearance of the ν_1 NO_3^- symmetrical stretching mode at the liquid−solid transition temperature is different.

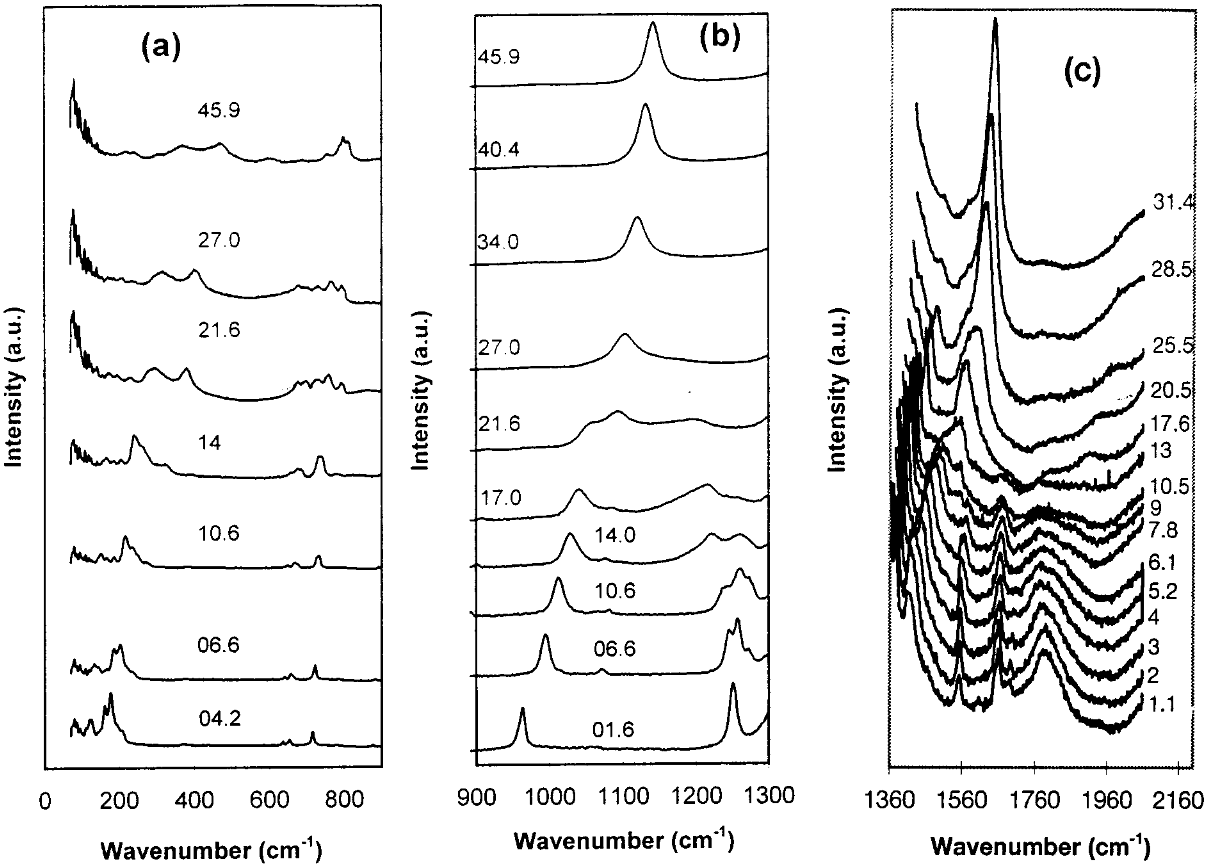

Figure 2. Raman spectra of pure nitric acid for different pressures (GPa) at ambient temperature: (a) 70−900 cm^{-1} range, (b) 900−1300 cm^{-1} range, and (c) 1350−2000 cm^{-1}. It is worthwhile to notice the behavior of the 1550 cm^{-1} peak between 6 and 11 GPa.

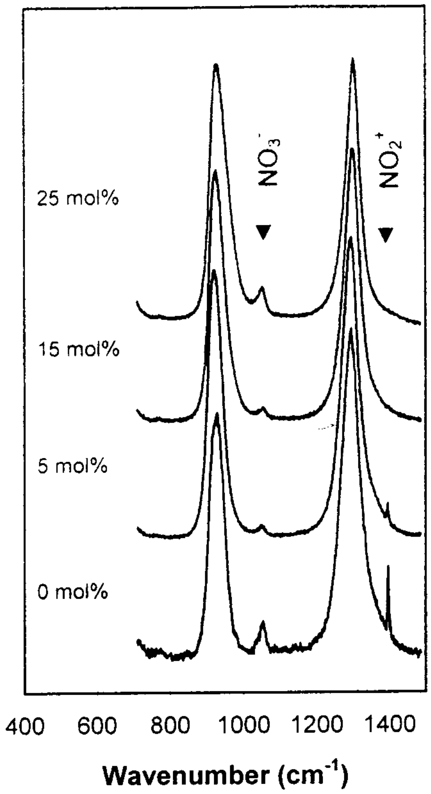

Figure 3. Raman spectra at ambient conditions of liquid nitric acid for four concentrations in water (0, 5, 15, and 25 mol %).

Two types of mixtures can be distinguished. First, at 38 mol % in water concentration (and probably at higher concentration), the liquid−solid transition at 210 K is evidenced by the vanishing of the 1303 and 957 cm^{-1} vibrational modes corresponding to the intramolecular NO_2 symmetrical stretching mode and the $O'-NO_2$ stretching mode of the nitric acid. Compared to the pure nitric acid, the $O'-NO_2$ stretching mode is shifted by 24 cm^{-1} to the higher frequencies. A splitting of the ν_1 stretching mode is observed at 1056 and 1045 cm^{-1}. At 210 K, two weak peaks at 738 and 720 cm^{-1}, assigned respectively to the ν_4 bending mode (Table 2) of the NO_3^- group and the NO_2 bending mode of the nitric acid, appear in the Raman spectrum. The vanishing of the nitric acid NO_2 symmetrical stretching and the $O'-NO_2$ stretching vibrational modes has also been reported in the equimolecular mixture $HNO_3{\cdot}H_2O$ by Herzog-Cance et al.[10] They observed single strong peaks at 1060 and 740 cm^{-1}, assigned to ν_1 NO_3^- symmetrical stretching and ν_4 NO_3^- bending modes in the solid phase of nitric acid $HNO_3{\cdot}H_2O$. Second, below 38 mol % in water, the liquid−solid transition is similar to the pure nitric acid liquid−solid transition. The NO_2 symmetrical stretching and the $O'-NO_2$ stretching modes are still present and shifted toward lower and higher frequencies in the spectra, respectively. The only difference comes from the ν_1 NO_3^- symmetrical stretching peak intensity which increases with the water concentration.

High pressure Raman spectra of acid−water solutions have been measured up to 50 GPa for 38 mol % (Figure 4 and Figure 5) and up to 20 GPa for 5, 15, and 25 mol % in water. Figure 6 shows the differences between Raman spectra for four different water concentrations in the acid at 4 GPa. The shift of the NO_2 symmetrical stretching mode frequency is reported as a function of the concentration and the pressure (Figure 7). The behavior of the vibrational modes with pressure will be discussed

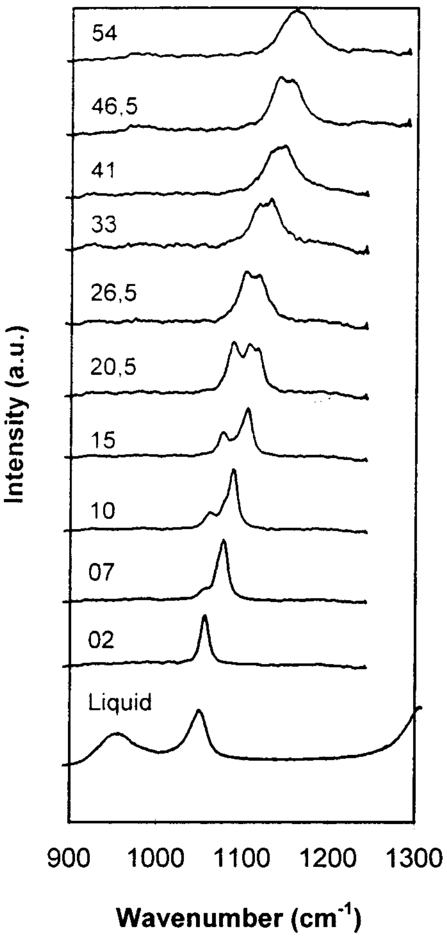

Figure 4. Raman spectra of solid nitric acid (38 mol % of water) as a function of the pressure (GPa) in the 900−1300 cm^{-1} range.

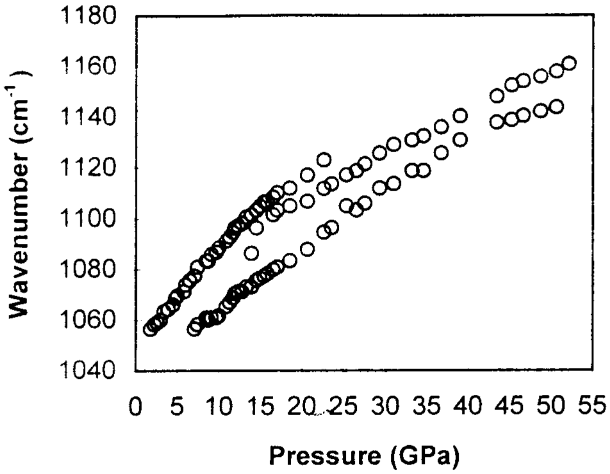

Figure 5. Pressure variation of the selected Raman-active mode ν_1 NO_3^- symmetrical stretching of solid nitric acid (38 mol % of water).

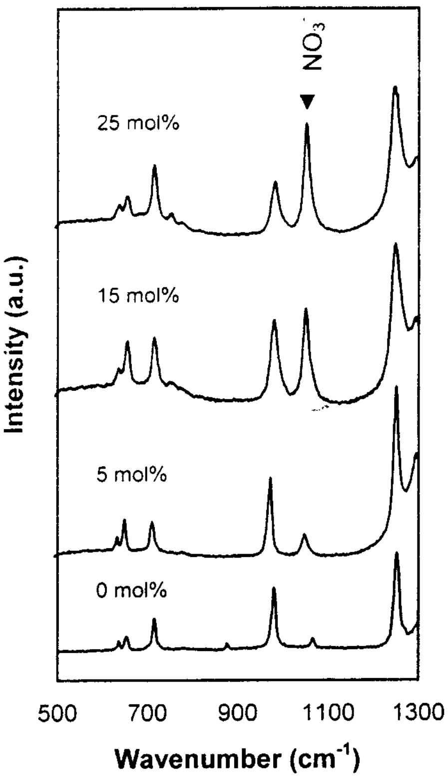

Figure 6. Pressure Raman spectra of solid nitric acid for four concentrations in water (0 mol %, 5 mol %, 15 mol %, and 25 mol %) at 4 GPa.

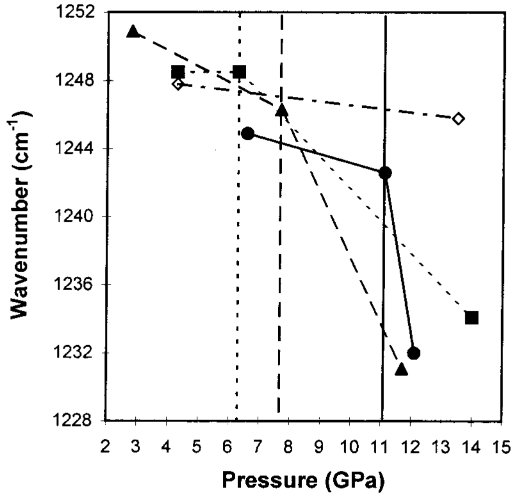

Figure 7. Pressure dependences of the selected Raman-active NO_2 symmetrical stretching mode in function of concentrations in water (●, 0 mol %; ▲, 5 mol %; ■, 15 mol %; and ◇, 25 mol %).

below in comparison with previously reported room measurements.[10] Figure 8(a−d) shows the pressure shift of the vibrational modes of the pure nitric acid.

In the lower frequency range (Figures 2a and 8a), the intensity of one of the external modes, initially observed at 210 cm^{-1} (4 GPa), progressively increases with pressure and a change in dν/dP is observed above 15 GPa.

In the 600 to 850 cm^{-1} range, the splitting of the NO_2 and of the $O'{-}NO_2$ bending modes (Figure 8b) occurs at about 11 GPa. A new important feature is that the ν_4 NO_3^- bending mode of the NO_3^- group, observed in the solid equimolecular mixture $HNO_3{\cdot}H_2O$ at low temperature by Herzog-Cance et al.,[10] is observed in the pressure spectrum of the pure nitric acid above 11 GPa. At the same time, a change in dν/dP of the ν_1 NO_3^- symmetrical stretching mode is observed at around 11 GPa. These observations indicate the onset of significant changes in the nitric acid at this pressure. In the 950 to 1300 cm^{-1} range (Figure 8c), the NO_2 symmetrical stretching mode (1250 cm^{-1} at 1.4 GPa) and the $O'{-}NO_2$ stretching mode (961 cm^{-1} at 1.4 GPa) progressively give place to a strong peak assigned to the ν_1 symmetrical stretching of the NO_3^- group (1054 cm^{-1} at 1.4 GPa). At the same time, the NO_2 symmetrical stretching mode observed at 1250 cm^{-1} at 1.4 GPa shifts to lower frequencies

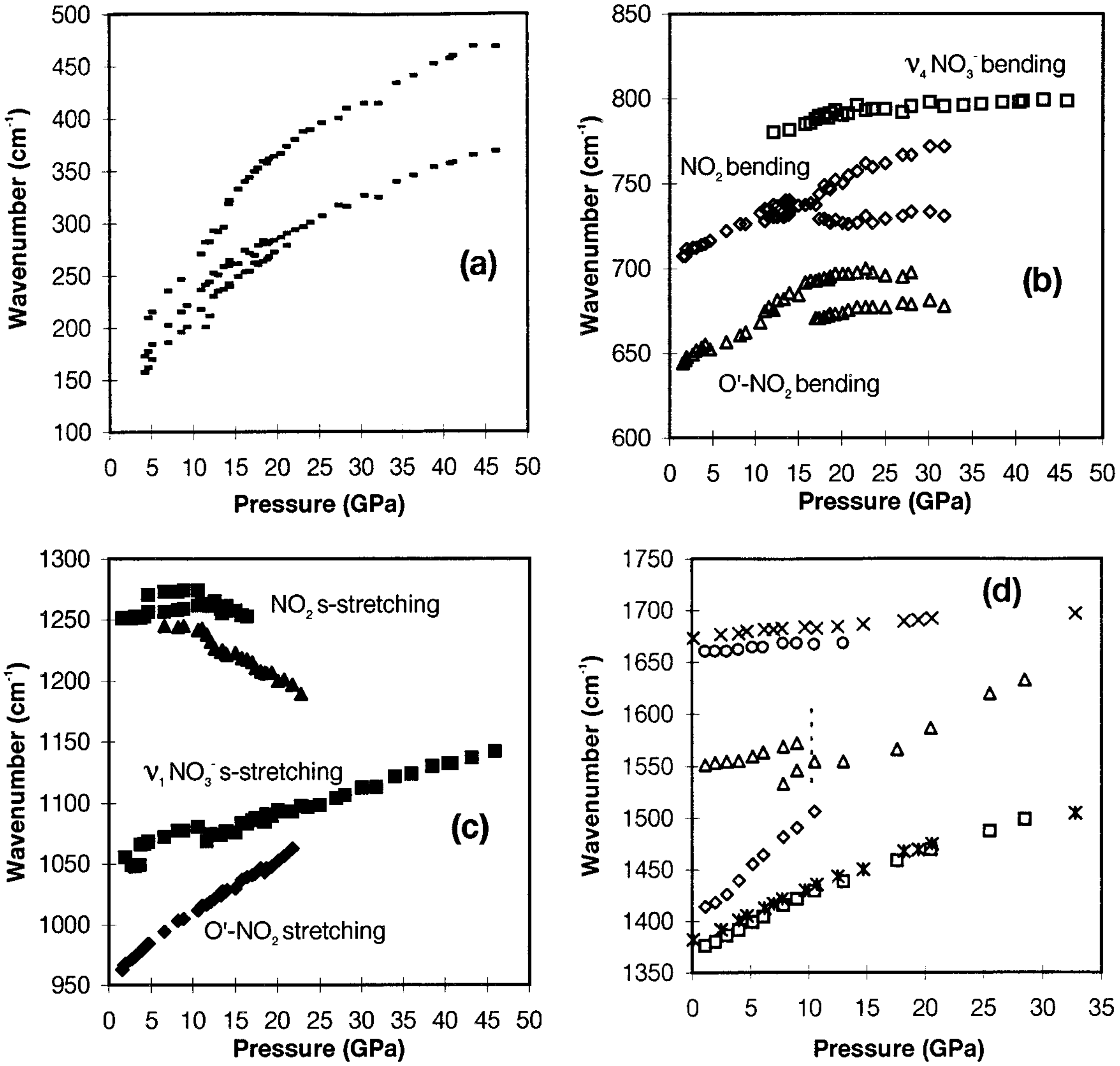

Figure 8. Pressure dependences of the selected Raman-active modes of HNO_3 between (a) 100−500 cm^{-1}, (b) 600−850 cm^{-1} (△, O′-NO$_2$ bending mode; ◇, NO$_2$ bending mode; and □, ν_4 NO$_3^-$ bending mode), (c) 900−1300 cm^{-1} (◆, O′−NO$_2$ stretching mode; ■, ν_1 NO$_3^-$ stretching mode; and ▲, NO$_2$ symmetrical stretching mode), and (d) 1350−1700 cm^{-1} (□, ν_3 NO$_3^-$ a-stretching mode; ◇, ν(NO$_2^+$); △, second overtone NO$_2$ bending out of plane; and ○, NO$_2$ antisymmetrical stretching mode and $*\nu_3$ LiNO$_3$ a-stretching mode and × 2 ν_2 LiNO$_3$).

with a slope of −1 cm^{-1}/GPa and, above 11 GPa, − 4.5 cm^{-1}/GPa. Above 23 GPa, this NO$_2$ symmetrical stretching mode completely disappears and the ν_1 symmetrical stretching mode of the nitrate ion is the major peak in the 900−1400 cm^{-1} range. The O′−NO$_2$ stretching mode increases as a function of pressure with a slope of 4.5 cm^{-1}/GPa and disappears in the ν_1 NO$_3^-$ symmetrical stretching band.

The frequency variation in the 1350−1750 cm^{-1} range is reported in Figure 8d. Four vibrational modes are found at 1.4 GPa corresponding respectively to (1) a weak peak at 1380 cm^{-1} (this peak is assumed to correspond to the 1370 cm^{-1} peak observed in the low temperature solid acid whose assignment corresponds to the ν_3 NO$_3^-$ antisymmetrical stretching band in comparison with a high pressure spectroscopic study of LiNO$_3$ (cf. Figure 8d); (2) the NO$_2^+$ stretching mode at 1416 cm^{-1}; (3) the second overtone of the NO$_2$ out of the plan bending mode at 1550 cm^{-1}; and (4) the NO$_2$ antisymmetrical stretching mode at 1660 cm^{-1}. The second overtone of the NO$_2$ out of plane bending mode at 1550 cm^{-1} disappears between 7 and 9 GPa while a new peak appears at a 25 cm^{-1} lower wavenumber and becomes progressively dominant in the spectrum above 13 GPa. Above 11 GPa, the NO$_2$ antisymmetrical stretching mode disappears (see Figure 2c). It is worthwhile to note that a weak negative frequency shift of the second overtone of the NO$_2$ out of the plane bending mode is observed as a function of pressure.

It is known that the molecule of pure nitric acid is planar under room conditions with a C_S symmetry. According to Stern et al.[4] and Luzzati et al.,[20] the structure is monoclinic. Luzzati suggests that twinning and disordering occur in the crystal owing to the position of the hydrogen atoms. The molecular crystal formed by van der Waals bonds is strengthened under high pressure. This effect is evidenced by the strong shift of the external modes (more than 200 cm^{-1} between 5 and 45 GPa compared with the main value of 40 cm^{-1} for the internal modes).

The NO$_2$ and O′−NO$_2$ bending modes between 600 and 800 cm^{-1} shift toward higher frequencies (40 cm^{-1}), corresponding to a closing of the NO$_2$ and O′−NO$_2$ angles and the deformation of the plane of the molecule. Above 17−18 GPa, a splitting is observed showing that the progressive closing of the NO$_2$ and O′−NO$_2$ angles leads to two active Raman modes corresponding to two distinguishable molecular forms which disappear above 30 GPa. It is supposed that the complete symmetrization of the

NO_3^- group is then achieved in the whole compound. The mean equivalence of the ONO angles in the NO_3^- group could explain the weak effect of the pressure above 30 GPa, since only the NO_3^- vibrational modes are active above this pressure. Simultaneously, the pressure weakening of the NO_2 symmetrical stretching mode is observed from 10 to 23 GPa. Above this pressure, the peak disappears, leaving the Raman activity only to the NO_3^- group in the compound.

The charge transfer via the H-bonding of the proton toward the neighboring nitric acid molecules is expected to lead to the symmetrization of NO_3^-, by the strengthening of the NO_2^+ stretching mode (1416 cm^{-1} at 1.4 GPa) and the vanishing of the second overtone NO_2 out-of-plane vibrational bending mode (1550 cm^{-1} at 1.4 GPa) to the benefit of a 25 cm^{-1} lower frequency new peak. Above 15 GPa, this last new frequency is always present in the spectrum.

The same low value of $d\nu/dP$ of the external and internal modes at high pressure (i.e., 3 cm^{-1}/GPa in comparison with 9 cm^{-1}/GPa and 5 cm^{-1}/GPa, respectively, at low pressure) involves the homogenization between intramolecular and intermolecular modes. The high pressure splitting of the NO_2 bending and $O'-NO_2$ bending modes, confirms the hypotheses of the proton transfer between neighboring molecules. The splitting disappears beyond 30 GPa where only one structure is distinguishable (the NO_3^- vibrational mode is only active above this pressure).

Two hypotheses can be considered. First, the proton transfer above 11 GPa, locally occurring on a ps time scale, could be explained by an electron overlap mechanism and short range order up to 23 GPa. Above 23 GPa, HNO_3 involves classical electrostatic interaction with a long range interaction and a longer time scale. At higher pressure, solid nitric acid presents long range electrostatic behavior. This finding supports the statement that the reinforcement of the NO_3^- anion may be attributed to an increasing donor strength. It is confirmed by the observation at 23 GPa of the NO_2^+ vibrational band at 1600 cm^{-1}, corresponding to an ionization of the solid nitric acid as NO_3^-, NO_2^+. The second hypotheses could be the progressive cross-linking of H-bonded deformed chains of acid as is the case for the pressure behavior of solid halogenated acids.[21,22] Moreover, the spectrum of acetic acid[23] shows broad IR absorption at 200 cm^{-1} extended to low frequency which is characteristic of disordered crystal formed of H-bonded monomers. In the same manner, propanoic acid shows a broad IR absorption characteristic of a chain structure. The overall structure of solid formic acid at low temperature is illustrated by H-bonded acid molecules forming planar chains with different polymeric forms.[24]

According to reaction 1, water is always in equilibrium with liquid acid. Therefore, the chemical effect of water impurities should not be neglected when explaining the chemical behavior of pure solid nitric acid. To confirm the role of water, pressure Raman measurements have been performed as a function of increasing water concentration. The intensity of the NO_3^- peak in the Raman spectra increases with water concentration (Figure 6). Above 25 mol % of water, only the 1050 and 730 cm^{-1} modes are present in the spectrum and it is assumed that they arise from the ionization in the solid state as NO_3^-, H^+. The spectra of water−acid mixtures as a function of pressure show that the transformation of high pressure nitric acid is improved by the addition of water. Figure 7 shows the pressure-induced negative frequency shift of NO_2 symmetrical stretching peak at different water concentrations. The breaking of the negative slope of the NO_2 symmetrical stretching mode observed at 11 GPa in pure nitric acid is located at lower pressures as the concentration in water increases. This feature confirms the prior statement of the proton transfer mechanism in the transformation of solid nitric acid under high pressure, enhanced by the presence of water.

Conclusions

The complete and reversible high pressure transformation of solid nitric acid has been observed by Raman spectroscopy. This has been evidenced by the progressive frequency lowering of the NO_2 symmetrical stretching vibrational mode,[25] the strong increase of the intensity of the ν_1 NO_3^- symmetrical stretching vibrational mode, and the reinforcement of the NO_2^+ mode at 1400 cm^{-1}. The transformation is assumed to be complete above 23 GPa with the formation of intermolecular $-O'\cdots H$ bonds. Two nonexclusive hypotheses have been proposed. The first one would be an autoionization of the nitric acid, in comparison with the autoionization of the liquid acid, and the second, the formation of an H-bonded polymer-like compound between the NO_3^- groups. The former is similar to the high pressure behavior of the solid halogenide or carboxylic acids. The addition of water up to 25 mol % moves the transformation toward lower pressures, without modifying the hypothesis. Above 25 mol % the behavior of the solid acid solutions is expected to be similar to the liquid.

In a previous study it has been shown that the initiation of the chemical decomposition of nitromethane occurred at the so-called 7.5 GPa solid II−solid III transition, characterized by a strong negative wavenumber shift of the NO_2 symmetrical (30 cm^{-1}) and (19 cm^{-1}) modes.[26] Therefore, the hazardous reactivity of nitric acid in propellant mixtures, whatever the expected assumption for the high pressure 10−25 GPa solid−solid transformation, would be expected in the vicinity of the pressure freezing (1.5 to 3 GPa) of the pure or weakly hydrated acid characterized by a strong shift to the lower wavenumbers (50 cm^{-1}) of the NO_2 symmetrical stretching mode. It would be interesting to confirm this conclusion by the study of a model mixture of pure nitric acid and a nitro-alkane compound known for its weak propensity to explode.

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