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A Raman Spectroscopic Study of Nitromethane up to 350 °C and 35 GPa

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Abstract: Nitromethane has been studied as a model of the energetic nitro materials. The liquid - transition line has been established by Piermarini [1] and a first solid - solid transition corresponding to the methyl group rotation locking has been evidenced by Cromer [2]. In order to precise the phase diagram of nitromethane, a study has been performed by Raman scattering in the pressure and temperature range of 0 - 35 GPa and 20 - 350°C respectively. From these experimental results three new solid phases of nitromethane called III, IV, V and their stability domain have been located. A first chemical transformation line has been detected by the disappearance of nitromethane Raman modes and by the irreversible formation of a transparent solid (CI). A second chemical transformation (CI - CII), at higher temperature, is observed by the sudden darkening of the sample.

1. INTRODUCTION

The nitromethane, the simplest energetic nitro-compound, has been choosen as a model. Since the study of the phase diagram of the nitromethane appears to be a preliminary stage to deal with a study of the violent decomposition phenomena, we report in this communication results of Raman spectroscopy up to 35 GPa and 350°C. At ambiant pressure and at low temperature the crystal structure of solid nitromethane was determined by Trevino *et al.* [3]. The structure is orthorhombic with four molecules per cell. At pressures between 0.3 and 6.0 GPa at ambiant temperature the structure is the same as the low temperature structure except for a rotation of the methyl group [2]. From the experimental results two chemical transformation have been determined. The first transformed compound CI is obtained from nitromethane with a low transformation rate (several hours). The second compound (CII) at higher temperature is obtained with a higher tranformation rate than CI (some minutes). Moreover three new phase transitions are reported in the *P-T* diagram.

2. EXPERIMENTAL METHOD

The experiments have been performed in a high pressure membrane type diamond anvil cell [4] made of refractory alloy. The pressure was monitored by a pneumatic ram connected to a pressure generator through a high pressure flexible capillary. The stainless steel gasket had an aperture of 0.15 mm in diameter and 0.15 mm in depth. Heating is performed by a coil surrounding the cell and monitored by a thermocouple in contact with the diamond anvils. The pressure was determined by the pressure shift of the $^5D_0$-$^7F_0$ singlet (685.4 nm at 0.1 MPa) of $SrB_4O_7:Sm^{2+}$ chips set inside the high pressure chamber [5]. Raman experiments were carried out in backscattering configuration with an argon ion laser at 514.5 nm wavelength. The laser power was 50 mW in order to avoid any thermal or photochemical effect. The frequencies were measured with a multichanel spectrometer DILOR XY. Plasma lines were used for the frequency calibration. Measurements have been performed at constant temperature and variable pressure for the localization of the solid - solid transitions and at variable temperature for the determination of the irreversible transformations. Nitromethane samples were from commercial purchase (ALDRICH 99+%) and were used without further purification.

3. RESULTS AND DISCUSSION

The *P-T* diagram of nitromethane has been determined (Fig. 1) by the study of the shift of different Raman modes versus static pressure and temperature: $A_1\nu(CN)$ (Fig. 2), $A_1\nu_s(CH_3)$, $A_1\nu_s(NO_2)$ and $B_1\nu_a(NO_2)$ (Fig. 3). Four solid - solid transitions and two irreversible transformations have been determined.

The solid I - solid II transition is located at 3 ± 0.2 GPa at 20°C. It is detected by breaks or discontinuities in the behaviour of the different studied Raman modes. The discontinuity of the linewidth (Γ_{NO}) (Fig. 4) of the $B_1\ \nu_a(NO_2)$ mode versus pressure confirms unambiguously the transition. The solid I - solid II transition line does not run parallel to the temperature axis (Fig. 1). The solid I - solid II transition is reported by Cromer *et al.* [2] at 3.5 GPa at ambiant temperature. But these works were made with too large pressure increments to precisely locate the transition.

The solid II - solid III transition is located at 7.5 ± 0.5 GPa at ambiant temperature. It is particularly detected by the appearance of new bands. The behaviour of Γ_{NO} and of the linewidth (Γ_{CH}) of the $A_1\nu_s(CH_3)$ mode versus pressure confirms the transition. This transition is probably a first order transition with an increase of the molecule number per cell. The solid II - solid III transition is independent of the temperature.

The solid III - solid IV is located at 13.2 ± 1 GPa at ambiant temperature. It is observed by discontinuities or breaks in the slope of the different Raman modes versus pressure and confirmed by the behaviour of Γ_{NO} and Γ_{CH}. This solid III - solid IV transition is dependent of the temperature and the pressure.

The solid IV - solid V is located at 25 ± 1 GPa at ambient pressure. This transition has not been studied at higher temperature since nitromethane is transformed as soon as about 55°C are reached.

The transformation nitromethane - CI compound is irreversible and slow. Since CI is an amorphous

compound its Raman peak is not distinguishable from the ground.

The CI - CII transformation is irreversible and more rapid than the nitromethane - CI transformation. CII did not give any Raman signal.

From these results, a specific behavior of the nitromethane has been observed. First the stability domain increases with the pressure up to 17 GPa (Fig 1). Second, the unusual negative jump of the wavenumber versus pressure of the $B_1\nu_a(NO_2)$ mode is particulary interesting (Fig 3). The same study performed with deuteried nitromethane does not show such a jump of wavenumber of the $B_1\nu_a(NO_2)$ mode.

4. CONCLUSION

The pressure and temperature dependence of the more intense vibrational Raman modes of solid nitromethane has been studied for the purpose of establish its phase diagram. The nitromethane compression up to 35 GPa at ambiant temperature allowed to show up four solid - solid transitions and two chemical transformations. Some of the reported results show an unusual behavior of nitromethane vs. pressure and temperature.

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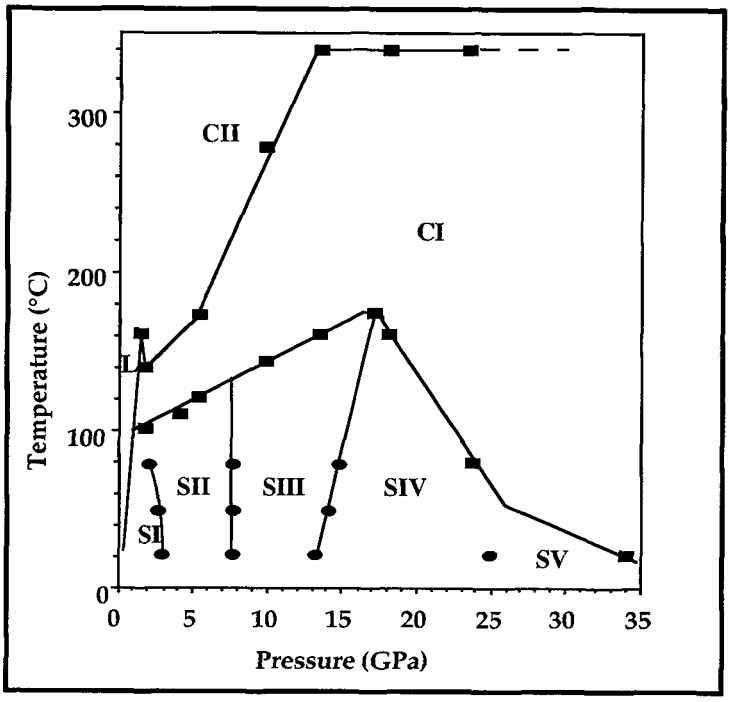

Figure 1: Phase diagram of nitromethane versus static pressure and temperature. The liquid - solid transition is from [1].

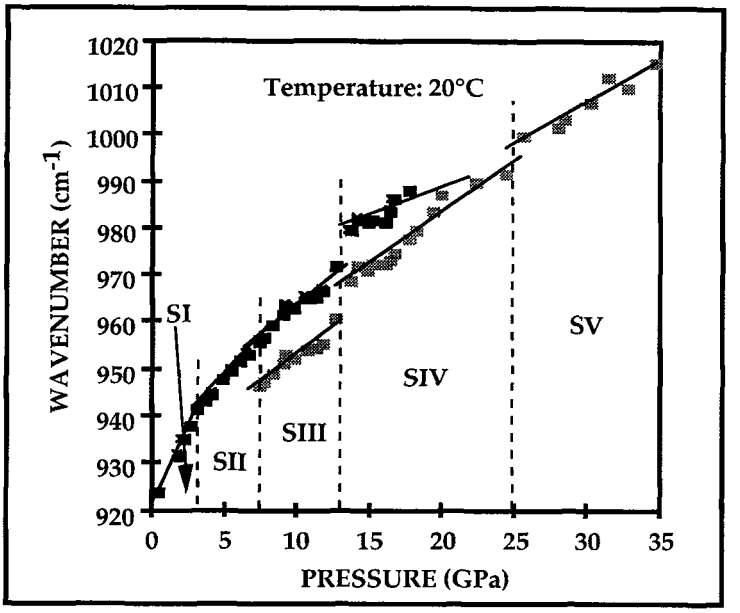

Figure 2: Effect of pressure on the $A_1\nu(CN)$ mode of nitromethane at ambient temperature.

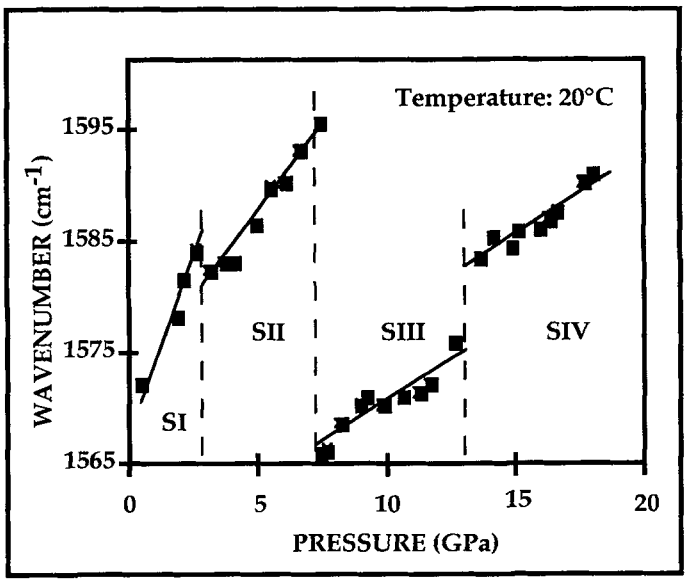

Figure 3: Effect of pressure on the $B_1\nu_a(NO_2)$ mode of nitromethane at ambient temperature.

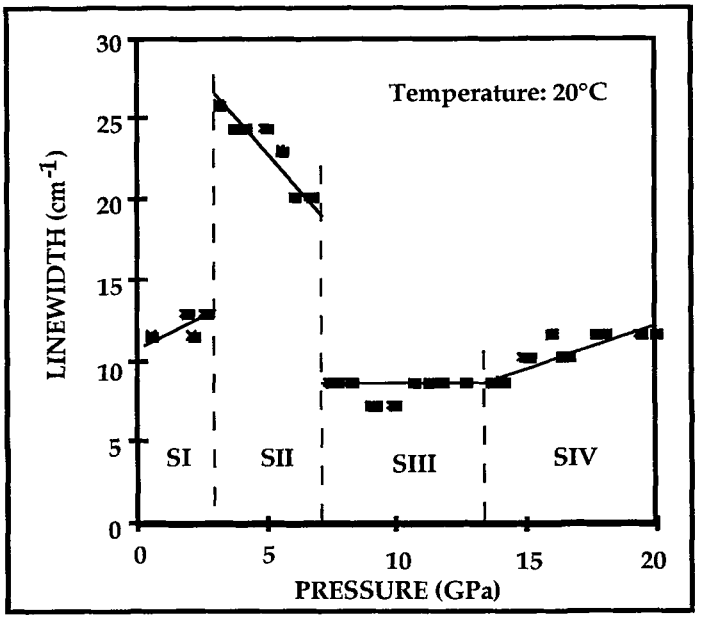

Figure 4: Evolution of the linewidth (Γ_{NO}) of the nitromethane $B_1\nu_a(NO_2)$ mode at ambient temperature. The spectral resolution is 7 cm^{-1}.