

Pressure-tuned vibrational resonance coupling of intramolecular fundamentals in ammonium azide (NH_4N_3)

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ABSTRACT

The peculiar behavior of the symmetric stretch of the N_3^- -anion and the bending mode of the NH_4^+ -cation in the high-pressure phase II (above 3 GPa) of the molecular ionic crystal NH_4N_3 has been studied by pressure-dependent Raman spectroscopy up to a pressure of 20 GPa. The spectra in the pressure range above 10 GPa reveal a remarkable intensity transfer between bands and a level repulsion (characteristic of vibrational resonance coupling) that is mediated by hydrogen bonding between the N_3^- and NH_4^+ -ions. These observations may be useful for theoretical studies of the potential energy surface and for studying the nature of hydrogen bonding in ammonium salts. With respect to the biological activity of the ammonium ion, the observed resonance coupling may be relevant to vibrational energy transfer in organic systems.

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1. Introduction

Ammonium salts have attracted substantial interest because some of their properties are markedly different from those of the corresponding alkali metal salts [1]. Anomalies in the spectroscopic, structural, and thermodynamic properties are traced to hydrogen bonding in ammonium salts. On the other hand, the behavior of a number of ammonium salts is significantly different from that of typical hydrogen-bonded neutral compounds [2]. This difference is apparently due to the ionic nature of the salts: the hydrogen-bonding forces are overlaid onto the strong electrostatic forces of attraction. The overlap of forces makes it difficult to distinguish effects ascribed to hydrogen bonding from those ascribed to electrostatic long-range interaction [3]. Thus, the study of intermolecular interactions in this class of solids is of fundamental interest.

The application of pressure is a natural way to study intermolecular interactions in condensed matter. Optical data on ammonium halides at high pressure [4,5] have revealed previously unknown phase transitions. The existence of these previously unknown phase transitions calls their stability at high density into question because these transitions are connected with the critical dynamic

and structural point, as indicated by previous high-pressure neutron diffraction data [6]. In this respect, because pressure can influence all types of hydrogen bonds (from weak to strong), hydrogen bonding is of importance for the high-pressure stability of ammonium-ions, thereby raising the possibility of tuning the hydrogen bonds to the symmetric case.

Ammonium azide can be considered a prototypical ionic hydrogen-bonded system. Its ambient-pressure orthorhombic structure (space group $Pmna$) [7] is related to the CsCl-type structure that is typical for the simplest salts. Hydrogen bonds appear at both end-nitrogen atoms of the linear azido-group N_3^- with $\text{N}-\text{H} \cdots \text{N}$ angles and distances that are indicative of strong hydrogen bonds, as is evident from the neutron diffraction studies [7]. In contrast, the activation energy of reorientation of the ammonium ion (25 kJ/mol) is the highest among ammonium salts (apart from the special case of ammonium fluoride [8]) in accord with the presence of four directional hydrogen bonds. Recent high-pressure Raman spectroscopy studies have revealed a polymorphic phase-transition at a pressure of approximately 3 GPa [9]. The structure of the high-pressure phase II is unknown to date. Here, we report the peculiar behavior of the symmetric stretch of the N_3^- -anion and the bending mode of the NH_4^+ -cation in the high-pressure phase II revealing the pressure-tuned intensity transfer between these modes and the “non-crossing” of their frequencies. This peculiar behavior in ammonium azide is most likely mediated by hydrogen bonding.

The effects of intensity redistribution between different vibrational levels and a large shift in their frequencies arising from

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vibrational resonance coupling are known and observed in both Raman and infrared spectroscopy.

A Fermi resonance in the isolated molecules occurs when two vibrational levels corresponding to a fundamental mode Q_1 at frequency ν_1 and an overtone of a mode Q_2 (or combination of vibrations) at frequency $2\nu_2$ are accidentally degenerate and interact via anharmonic terms of the Hamiltonian of $k_{122}Q_1Q_2^2$ type. This interaction manifests itself in spectroscopic measurements through a frequency shift of both modes from their unperturbed values and through a redistribution of spectroscopic (infrared or Raman) intensity between the perturbed states [10].

Intermolecular interaction affects the Fermi resonance in condensed phases and leads to a splitting of the optical bands into heavily overlapped broad components [11–14], resulting in the controversial interpretation of optical spectra [14–16]. High pressure can cause significant changes in the intermolecular forces; therefore, high pressure has been previously used to study Fermi resonances in molecular crystals. The Fermi resonance can be pressure-tuned because the coupled modes have different pressure dependences that make it possible to observe a bound–unbound phonon transition [17] and resonance coupling that is unobservable at ambient pressure [18,19].

Resonance in molecular crystals containing chemically identical molecules is possible only between the fundamental vibration and the overtone (or combination band) but not between two fundamental modes, since the perturbation term in the potential energy $\partial^2V/\partial Q_1\partial Q_2$ vanishes in a single molecule by definition of normal modes. Thus, the Fermi resonance appears in the crystal only if it exists in the isolated molecule. The main parameter governing the Fermi resonance between a fundamental vibron, ν_1 , and an overtone, $2\nu_2$, or a combination band, $\nu_2 + \nu_2$, in a molecular crystal is the intramolecular anharmonicity $W = -2^{-1/2}k_{122}$. The strength of the resonance can be modulated (enhanced) through intermolecular interactions. The application of hydrostatic pressure can influence the intermolecular interactions and, therefore, influence the strength of the resonance as a result of changes in the bandwidth of the combination band [17] or changes in the frequencies of excitations involved in the resonance [18].

The resonance coupling between different molecular species forming the molecular crystal, in contrast to crystals formed by one type of molecular species, may occur between the normal vibrational modes, Q_1 and Q_2 , for which the cross term is nonzero as a result of the intermolecular interaction. The idea of the resonant vibrational coupling involving states of two distinct chemical species (“intermolecular Fermi-resonance”) was utilized for the analysis of Raman spectroscopy data on cobalt porphyrin complexes (vibrational coupling between solute and solvent molecules) [20] and for the explanation of the infrared intensity enhancement of the C–N stretch of HCN in a mixed ordered overlayer of HCN and CO on a Cu(1 0 0) surface (coupling between the C–O stretch of CO molecule and the C–N stretch of HCN) [21].

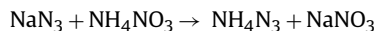
Coupled-mode interaction involving only fundamental lattice phonons has been observed by Raman studies of covalent crystals. Such vibrational coupling occurs when two modes of the same symmetry have similar frequencies of vibrations. The coupling can be tuned by the application of an external electrical field (e.g., in SrTiO₃, where one of the coupled modes is strongly electric-field dependent [22]), as well as by the change of temperature (e.g., SbSI [23]) or pressure (e.g., zirconia) [24], resulting in the spectacular intensity transfer and anti-crossing (level repulsion) of coupled lattice phonons.

Thus, despite the considerable attention that vibrational resonance mode coupling has received in both theoretical and experimental studies in the literature, a resonance between two fundamental intramolecular vibrations of different molecular species constituting a crystal similar to our case of ammonium azide

has been neither extensively considered theoretically nor studied experimentally to date.

2. Experimental

Ammonium azide, NH₄N₃, was prepared by the metathetical reaction between sodium azide and ammonium nitrate and purified by sublimation, as previously reported in the literature [25]



A powdered sample of NH₄N₃ was loaded into a diamond anvil cell with a tungsten gasket. The diamond anvils had flat culets that were 600 μm in diameter. To avoid sample contamination, the sample loading was performed in a glove box in an atmosphere of pure nitrogen containing <0.1 ppm of oxygen and water. Dry silicon oil was used as a pressure transmitting medium. The pressure on the sample was determined by using the pressure-dependent fluorescence lines of a ruby chip [26] that was mounted in contact with the sample.

A HeNe laser with a power of 25 mW was used for the excitation of Raman spectra. Raman spectra were recorded with an imaging spectrometer, HR460 (focal length 460 mm), equipped with a 900 grooves/mm grating, that provides a resolution of approximately 1 cm^{-1} . The spectrometer was equipped with notch filters and a cooled charge-coupled device array detector. Raman scattering spectra were calibrated using Ne lines; the uncertainty in the calibration is $\pm 1 \text{ cm}^{-1}$.

3. Results and discussion

Representative Raman spectra of NH₄N₃ in both phases are shown in Fig. 1. The internal vibrational modes were assigned by analyzing the known Raman and infrared data on NH₄N₃ and ammonium halides [9]. The spectra of the external (lattice) modes (Fig. 1a) and the internal vibrations of the N₃ anion (Fig. 1b) at low pressures are in good agreement with previous studies [27]. At a pressure of approximately 3 GPa, the multiplication of lattice modes (Fig. 1a and d) indicates a phase transition to the high-pressure phase II. The single $\nu_1(\text{N}_3)$ peak (Fig. 1b, spectrum at 3.5 GPa) implies that azide anions occupy equivalent crystallographic positions in the high-pressure phase II. The spectrum of internal vibrations indicates that the N₃⁻ and NH₄⁺ ions maintain their identity in the high-pressure phase II, and the spectral peculiarities indicate a preservation of hydrogen bonding, although its strength is modified at the phase transition [9]. As the pressure increases up to pressures close to 20 GPa, the frequencies of all the observed lattice excitations monotonically increase (Fig. 1d), indicating the absence of further major phase transitions.

Hereafter, we will focus on the pressure dependence of the N₃⁻ anion symmetrical stretch [$\nu_1(\text{N}_3)$] and the NHN angle-bending of the NH₄⁺ cation [$\nu_4(\text{NH}_4)$] in the high-pressure phase II. At pressures below 12 GPa, the frequency of the N₃⁻ stretching linearly increases with pressure, with a pressure coefficient of approximately 2.8 $\text{cm}^{-1}/\text{GPa}$. In contrast, the NH₄⁺ bending frequency linearly decreases with pressure at a rate of approximately $-0.6 \text{ cm}^{-1}/\text{GPa}$ (Fig. 2). Since the bending motion associated with the $\nu_4(\text{NH}_4)$ -mode has components along N–H···N bond, the decrease of the frequency with pressure is attributed to the strengthening of hydrogen bonding. Similar behavior is observed in the $\nu_4(\text{NH}_4)$ bending mode of ammonium halides (e.g., NH₄Cl [28]) at high pressures.

A remarkable resonance behavior is observed at pressures above 12 GPa. Initially, as the pressure increases, a weak high-frequency peak attributed to the $\nu_4(\text{NH}_4)$ vibration (below 12 GPa, its intensity

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