High Pressure Raman Spectroscopy of 4-Azidobenzoic Acid

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Abstract: With the rapid development of science and technology, people's demand for energy materials is increasing, and researchers' exploration of energy materials is also more and more in-depth. Azide is a kind of nitrogen rich energetic material. In recent years, the research on azide mainly focuses on the synthesis of polynitrogen under the condition of changing pressure. This is because under the action of pressure, the azide group in the azide will hybridize the electronic orbit, and the adjacent azide groups will re combine in the form of single bond, so azide is considered to be an ideal precursor for the synthesis of polynitrogen under high pressure. In this paper, the Raman spectra of 4-azidobenzoic acid at ambient pressure were analyzed, the high-pressure Raman spectra of 4-azidobenzoic acid were measured, and the phase transition of 4-azidobenzoic acid under high pressure was discovered.

Key words: azide; Raman spectra; high pressure; phase transition

1. Introduction

Energy is an important guarantee for social development. With the development of science and the needs of society, single bond polynitrogen has become a research hotspot of energy materials. Nitrogen is a diatomic molecule, in which nitrogen is connected in the form of three bonds, and the bond energy is 954 kJ / mol. The nitrogen in polymerized nitrogen is connected in the form of single bond, and the bond energy between nitrogen and nitrogen is 160 kJ / mol. Theoretically, the decomposition of polymeric nitrogen will form nitrogen, so huge energy will be released due to the existence of energy difference in the process of decomposition, and the energy density is about 38.4 kJ/cm3, which is much higher than that of ordinary energy materials. The decomposition product is nitrogen, which will not cause environmental pollution. Thus, polynitrogen is regarded as a green and clean energy material and is often used as rocket propellant or high explosive. Azide groups of azides combine in the form of double bonds and can form polymeric nitrogen under changing external conditions (temperature or pressure). There are two types of azides, namely organic azides and inorganic azides. The azide groups in these two types of azides are very different, and the main difference lies in the structure. The research shows that the azide in the inorganic azide can form polymeric nitrogen under enough high pressure, but the high experimental pressure limits the practical application. Under normal temperature and pressure, most azide ions are linear, while most azide groups in organic azides are nonlinear. There is a certain angle between the three nitrogen atoms in the azide group. This structural difference makes the two azides exhibit different physical and chemical properties under high pressure. The results show that under the action of pressure, azide will bend or rotate, and the electronic orbital hybridization between adjacent azides will further form polymerized nitrogen. It can be seen that organic azides are more likely to form single bond polynitrogen than that of the inorganic azides under relatively low pressure. 4-azidebenzoic acid is an organic azide, also known as p-azide benzoic acid. At room temperature and pressure, 4-azidebenzoic acid is a white powdery solid, and the molecular formula is C7H5N3O2. In order to understand the phase transition of 4-azidobenzoic acid under high pressure, the structural changes of 4-azidobenzoic acid were analyzed in detail.

2. Experimental Details

(1) Basic principles of Raman scattering

When the light irradiates the material surface, it will scatter, which is elastic scattering and inelastic scattering. There are differences between the scattered light emitted by the two types of scattering. The wavelength of scattered light released by elastic scattering is consistent with the wavelength of excitation light, while another part of scattered light released by inelastic scattering is called Raman scattering.

In Raman scattering, energy is exchanged between molecules and photons. Some incident photons transfer electrons on molecular orbitals from the ground state or excited state to the virtual energy state. Photons gain or lose energy, which changes the frequency of scattered light. The change of frequency depends on the vibration characteristics of chemical bonds. The variation of scattering light frequency affects the number of Raman spectral lines, the size of Raman shift, and the intensity of Raman spectrum. These changes are directly related to the vibrational or rotational energy levels of matter molecules. Therefore, the vibration or rotation information of molecules can be obtained through the changes of Raman spectra.

The analysis of Raman spectrum includes two aspects: qualitative analysis and quantitative analysis. Because different substances have different characteristic frequencies, the changes of molecular structure of substances can be found by qualitative analysis of spectra. Raman spectroscopy is widely used in material identification and molecular structure research. In addition, in terms of quantitative analysis, the amount of substances can be analyzed according to the different absorbance of substances at different wavelengths.

Raman spectroscopy is mainly used in biology, chemistry, physics, materials science and other fields. Whether solid, liquid, gas, colloid or powder, Raman spectroscopy can be used to rapidly characterize the chemical composition and structure of samples. Raman spectroscopy can provide a lot of important information about the structure of polymer materials, including molecular structure and composition, stereoregularity, crystallization and location, intermolecular interaction, surface and interface structure, etc. The intensity, shape, and shift

of Raman peaks are important criteria for Raman spectral analysis, and play an important role in the identification of chemical bonds and functional groups. Therefore, Raman spectroscopy can provide information about the composition, structure and stability of compounds.

(2) Experimental method

The samples used in the experiment were purchased from Sigma. The pressure in the experiment was obtained by the symmetrical diamond anvil device, and the anvil surface diameter was 500μm. During the experiment, T301 stainless steel sheet was selected as the high-pressure sealing gasket material, and the gasket thickness was about 55μm. The sample chamber diameter is about 160μm. Put the sample and ruby ball into the sample chamber. The pressure in the sample cavity is determined by the relationship between the linear red shift of Ruby Fluorescence R1 line and the change of pressure. The pressure transmission medium is a mixture of methyl alcohol with a volume ratio of 4:1. The Raman spectrum was measured by Horiba iHR550 spectrometer. The laser wavelength was 785 nm and the integration time was 60 seconds.

3. Result analysis

(1) Raman spectra at ambient pressure

Due to the similar characteristic frequencies of organic groups in different compounds, the Raman spectra of 4-azidobenzoic acid at ambient pressure were analyzed according to the characteristic frequencies of organic groups in benzoic acid, phenyl azide compounds and other organic azide compounds.

Figure 1 shows the Raman spectra of 4-azidobenzoic acid obtained from 0 to 1700cm-1 at ambient pressure. In the spectra range of 0-320cm-1, the Raman peak of 4-azidobenzoic acid is an external mode vibration (E). In Figure 1, 561 cm-1, 678cm-1 and 1291/1307cm-1 refer to the in-plane bending vibration mode (β N3), out of plane bending vibration mode (γ N3), and symmetric stretching vibration mode (νS N3) of azide group, respectively. Raman characteristic peaks of benzene ring in 4-azidobenzoic acid appeared at 1013cm-1, 1123cm-1, 771cm-1, 1606cm-1, 693 / 826 / 844cm-1 and 1179cm-1 correspond to the ring bending vibration mode (δRing), ring breathing (R), C-C stretching vibration mode (ν C-C), C-H out of plane bending vibration mode (γ C-H) and C-H plane bending vibration modes (β C-H), respectively. The Raman peaks of 4-azidobenzoic acid at 359cm-1, 398cm-1, 516 / 633cm-1, 1418cm-1 and 1505cm-1 are attributed to the OC = O in-plane bending vibration mode of carboxyl group (β OC=O), COOH out of plane bending vibration mode (γ COOH), O-H out of plane bending vibration mode (γ O-H), C=O stretching vibration mode (ν C=O) and C-O stretching vibration mode (ν C-O), , respectively.

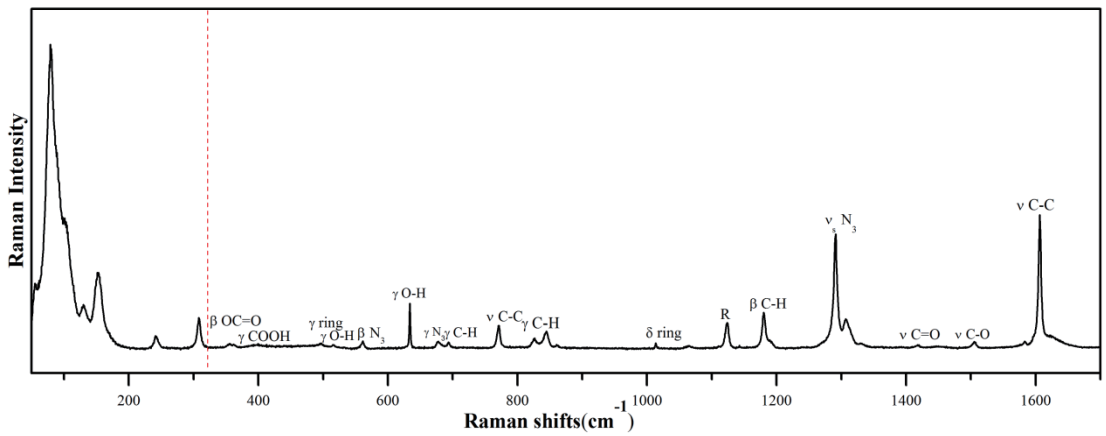

Fig. 1 Raman spectra of 4-azidobenzoic acid at ambient pressure

(2) High Pressure Raman spectroscopy analysis

The maximum pressure of high-pressure Raman scattering experiment of 4-azidobenzoic acid is 6 GPa. Fig. 2 and Fig. 3 show the Raman spectra of 4-azidobenzoic acid at different pressures and the curves of the positions of Raman peaks with pressure in the frequency range of 60-1800cm-1. The Raman spectra in the frequency range of 50-350 cm-1 showed the change of the lattice modes of 4-azidobenzoic acid. It can be seen from Figure 2 that at 1.0 GPa, two new external vibration modes appeared at 104 cm-1 and 183 cm-1, indicating the occurrence of phase transition of 4-azidobenzoic acid, and 4-azidobenzoic acid changed from phase I to phase II. At the same time, two new Raman internal modes appear at 773 cm-1 and 1149 cm-1, which are consistent with the changes of the external modes. The new Raman peaks at 1149 cm-1 and 773 cm-1 are ring-C stretching vibration mode and C-C stretching vibration mode, indicating that the benzene ring was deformed during the phase transition. The change of pressure in the experiment has a certain influence on the structural stability of aromatic compounds. In general, in the organic compound benzene, the change of pressure will have a great impact on the structural stability of the ring compound, and the pressure increases the interaction between adjacent carbon atoms, resulting in the deformation of the benzene ring. Therefore, in the vibrational spectra, some vibration modes related to benzene ring, such as ring deformation vibration mode (γ Ring), C-H out of plane bending vibration mode (β C-H), ring breathing vibration mode, C-C deformation vibration mode□γ C-C) and C-C stretching vibration mode (ν C-C). The deformed benzene ring will further change the molecular structure of the substance under the action of pressure. At the same time, it can also be seen from Figure 3 that at 1 GPa, the curve of Raman frequency versus pressure appears discontinuous, which proves the existence of phase transition.

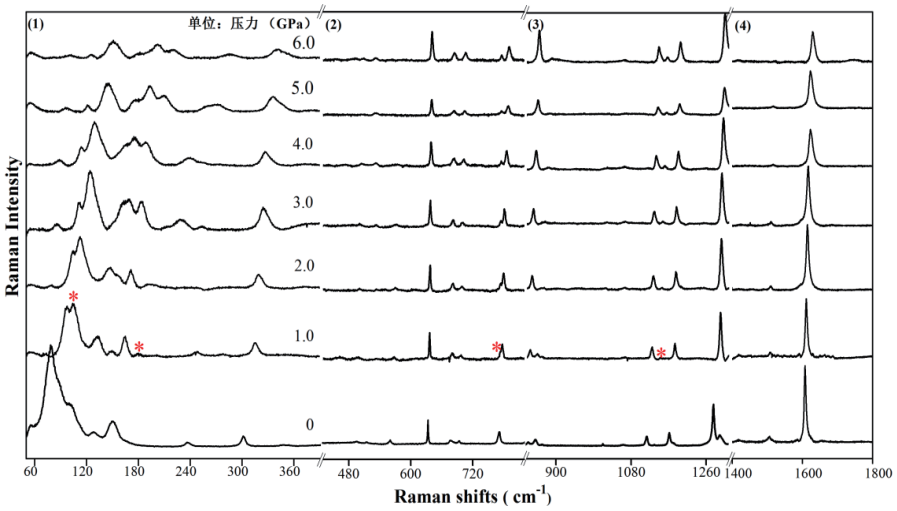

Fig. 2 Raman spectra of 4-azidobenzoic acid at different pressures in the frequency range of 60-1800cm-1

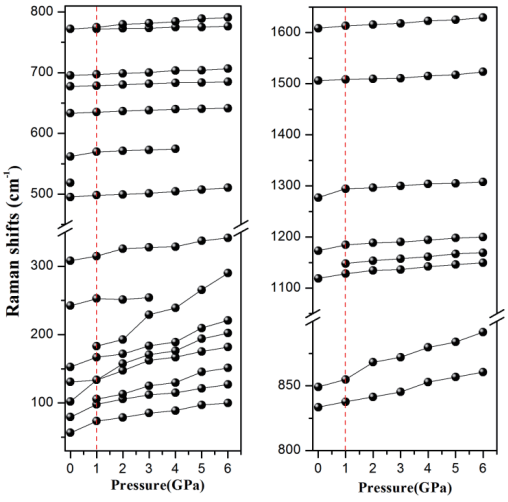

Fig. 3 Raman peak position versus pressure curve with frequency in the range of 0-1700cm-1

4. Conclusion

The Raman spectra of 4-azidobenzoic acid at ambient pressure were analyzed and identified. In the high-pressure Raman scattering experiment of 4-azidobenzoic acid, the maximum pressure is 6 GPa. The Raman peaks below 320 cm-1 are external modes, two new external modes appear at 1.0 GPa, and two new Raman internal modes appear at the same time, indicating that the structural phase transition of 4-azide benzoic acid occurs, which is caused by the deformation of benzene ring under the action of pressure.

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