# A study on the Fermi resonance of phenol under the effects of pressure and temperature by Raman spectroscopy

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HIGHLIGHTS

- Raman spectra of phenol at different pressures and temperatures were measured.
- Fermi coupling coefficients were calculated based on the FR theory.
- Fermi coupling coefficient turnover between 1.912 and 2.244 GPa was observed.
- Fermi coupling coefficient exhibited monotonic reduction as the temperature decreased.
- A conformation evolving induced by pressure and temperature on FR was analyzed.

GRAPHICAL ABSTRACT
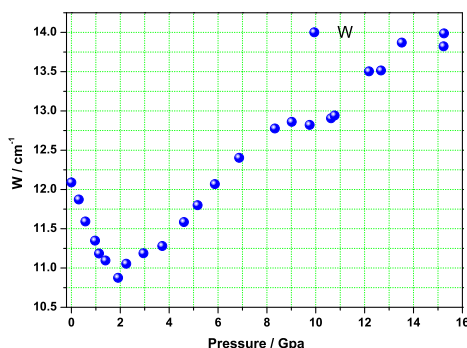
ABSTRACT

The v_1–v_{18a} Fermi resonance (FR) of phenol were investigated by pressure-dependent Raman spectroscopy from atmospheric up to $P = 15.2$ GPa and temperature-dependent Raman spectroscopy from 40 down to $T = -180$ °C, respectively. In the case of pressure, we found the Fermi coupling coefficient W, which were calculated based on the FR theory, exposed a value turnover between 1.912 and 2.244 GPa in the process of increasing the pressure. This turnover phenomenon of the Fermi coupling coefficient W has been ascribed to the crystal structure of phenol evolving towards a more symmetric structure with pressure, from a structure like a pseudo-threefold helical chain at ambient pressure to like a ribbon arrangement at 1.912 GPa, then to adopt a herringbone arrangement at much higher pressure. On the other hand, we also found the Fermi coupling coefficient W exhibited monotonic reduction without turnover points appearing by decreasing the temperature. The tendencies of the Fermi coupling coefficient W with temperature were in good agreement with the pressure dependence of the Fermi coupling coefficient W in the region of ambient to 1.912 GPa, indicating that the effect of pressure and temperature on the FR of phenol in this region might be the same. A conformation evolving induced by pressure and temperature on the v_1 and v_{18a} FR of phenol have been analyzed.

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Introduction

The phenomenon of Fermi resonance (FR), which is a consequence of the vibrational modes of similar energy and symmetry mixing, is commonly observed in complex molecules [1–5]. It is

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the large perturbation between near-degenerate vibrational levels produced by anharmonicity. FR is first recognized in Carbon dioxide (CO_2) and explained by Fermi in 1931 [6]. Phenomenologically, this perturbation is revealed by the occurrence of two strong Raman/Infrared lines of about equal intensities in a wavenumber region where only one strong line, or possibly one strong line and one very weak line, are expected. This effect has been observed before in gas, liquid and solid as a function of temperature, pressure and solvent. Despite several decades of study, there is still debate over the details of the interactions giving rise to this resonance. Recently, a significant body of studies has revisited the FR in efforts to correlate variations in its component frequencies and intensities with model parameters [7–13], local structures [14,15], isotopic substitution [7–9,13,16] or experimental conditions (density) [15–17]. Most of these studies agree well on the conditions for the occurrence of FR that must be satisfied with the two vibrational states of a molecule which not only must have the same symmetry and almost the same energy, but also exist with a fairly large anharmonic coupling constant that contributes to a strong mixing of the unperturbed eigenfunctions. FR plays an important role in molecular spectra, energy transfer, internal conversion, and reaction dynamics [18,19]. Furthermore, it can also cause an accelerated rate to population or energy transfer between the vibrational modes, thus influencing the dynamical behavior of molecules and the fate of chemical reactions [20]. Since FR is very important in spectrum analysis, the studies of FR remain an active area of research, both experimentally and theoretically [21–24]. The investigation of FR will help researchers not only better understand details in chemical reactions but also know what we are looking at, if we are going to use certain bands as guidelines to understand molecular interaction.

Phenol (C_6H_5OH, monohydroxybenzene) is an economically important chemical reagent and used in a wide variety of synthetic processes. It is also being used in many industries, such as textile, paper mills, herbicides and fungicides production. It is a member of the monoalcohol series and, as its hydroxyl group is slightly acidic (pK_a at 298 K is 9.99 in aqueous solution), it is often referred to as carbolic acid. Phenol is one of the molecular species which has been a subject of most extensive, both experimental as well as theoretical, spectroscopic investigations in vapor, liquid and solid phases. The vibrational spectrum of phenol has been examined by a number of spectroscopic techniques which include UV–vis, IR and Raman spectra of the vapor, liquid and solid Evans [25] and William Wilson et al. [26] have reported the Raman spectra and infrared spectra of phenol (vapor, liquid and solid phases) and given a more complete vibrational assignment. They found that there was an FR between the in-plane ring deformational vibration v_1 at approximately 999 cm^{-1} and the CH in-plane bending mode at approximately 1025 cm^{-1}. Most recently, numerous investigations of the Raman spectrum of liquid phenol have been performed with the goal of elucidation of the hydrogen-bonding and other structural properties of this complex liquid. Since phenol is the simplest aromatic alcohol and has the chromophore of an aromatic amino acid, hydration of phenol molecules has been studied as a natural first step to understand hydrogen bonding that represents solute–solvent interaction in biological systems. Contrary to the extensive studies, there is not much information available on the FR of phenol, and especially, little is known about the FR of phenol under the effects of pressure and temperature.

In the present work, we investigate the v_1–v_{18a} FR of phenol under high pressure and lower temperature, respectively, performed by Raman spectroscopy. In light of the FR standard theory, we have calculated the values of FR parameters, such as the Fermi coupling coefficient W, of the Raman bands v_1 and v_{18a} of phenol under high pressure and lower temperature, respectively, and studied their variations with the pressure and temperature. The

most irregular behavior is given by pressure. From ambient to 1.912 GPa the Fermi coupling coefficient W keeps reducing, but at 2.244 GPa the reduction pattern is inverted. The behavior of the Fermi coupling coefficient W of the phenol is associated with a conformation evolving towards a more symmetric structure with pressure. In the temperature case, it only exhibits monotonic reduction of the Fermi coupling coefficient W by decreasing the temperature, which associates to the structural changes of the phenol with the temperature. Besides, it is also found that the relatively modest temperature dependent FR coupling coefficient W is quite similar to that in the pressure region from ambient to 1.912 GPa. Finally, we give a detailed analysis for the effects of pressure and temperature on the v_1–v_{18a} FR of phenol, respectively.

Experimental methods

Phenol were purchased from Sigma Aldrich and used without further purification. The sample was prepared by heating crystalline phenol above its melting temperature of 313 K and then loading it, as a liquid, into a preheated Merrill–Bassett diamond-anvil cell [27] that had been equipped with 400 μm culet diamonds and a tungsten gasket. The sample with a small ruby chip (~10 μm) was loaded in a 200 μm hole drilled in a 250 μm thick T301 gasket pre-indented to 80 μm thickness. Pressure calibration was done by the usual method of measuring the shift of the fluorescence line of ruby added to the sample chamber [28–31]. No pressure-transmitting liquid medium was used in the experiment. We monitored the separation between the R_1 and R_2 components of the ruby fluorescence line, which was found to remain invariant even at the highest pressure, indicating a negligible nonhydrostatic component.

All Raman spectra of the samples were recorded using a Renishaw in via Raman Microscopic instrument. Laser excitation at 514.5 nm was provided by a Spectra-Physics Model 160 argon ion laser. A Leica microscope with ×20 objective lenses enables measurements with backscattering geometry. The spectral resolution was approximately 1 cm^{-1}. Radiant power was approximately 3.6 mW at the sample spot, and the typical accumulation time was 30 s for a single spectral measurement. Frequency calibration of the Raman spectrum was realized using the characteristic 520 cm^{-1} line of silicon. The Raman spectra of the phenol were measured at different temperatures in a Linkam thms600 system.

Results and discussion

1. Raman spectra of phenol at different pressures

Fundamental Raman modes of phenol are identified and assigned on the basis of the literature [25,26]. Raman spectra of phenol ranging from 970 to 1090 cm^{-1} and the pressure dependence of corresponding modes are illustrated in Fig. 1(a). As shown in Fig. 1(a), two Raman bands at approximately 999 cm^{-1} and 1025 cm^{-1} are assigned, respectively, to the in-plane ring deformational vibration v_1 and the CH in-plane bending mode in phenol. In the pressure range from ambient pressure to 15.2 GPa, both of the vibrational frequencies v_1 and v_{18a} of phenol increase when the pressure is increased. This is due to the contraction of molecular distances with increasing the pressure, as expected. Besides, we also calculate the integrated intensities ratio R between Raman integrated intensities of FR doublet at different pressures, which are presented in Fig. 1(b). As shown in Fig. 1(b), from ambient to approximately 1.912 GPa the value of the integrated intensities ratio R keeps increasing, but at 2.244 GPa the increased pattern is inverted. The change exposes the integrated intensities ratio R turnover between 1.912 and 2.244 GPa for the in-plane ring