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journal homepage: www.elsevier.com/locate/saaStudy the effect of Li^+ on the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of acetonitrile by Raman Spectroscopy[☆]Dongfei Li^{a,b,c}, Naicui Zhai^d, Shichong Xu^a, Mingzhe Zhang^b, Chenglin Sun^{b,c,*}, Haibo Li^{a,**}^a Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, Jilin Province, PR China^b State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, Jilin Province, PR China^c College of Physics, Jilin University, Changchun 130012, Jilin Province, PR China^d Institute of Translational Medicine, The First Hospital of Jilin University, Changchun 130061, Jilin Province, PR China

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ABSTRACT

Raman spectra of the solution of LiClO_4 in acetonitrile (CH_3CN) at different concentrations have been measured. With increasing the concentration of Li^+ , it was noted that several vibrational modes of CH_3CN had significant changes in Raman shifts and some new Raman peaks emerged due to the $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex formation. In addition, Fermi resonance phenomenon between the ν_2 and $(\nu_3 + \nu_4)$ Raman bands of $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex was observed. Based on the Bertran's equations, Fermi resonance parameters of free CH_3CN and $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex at different concentrations have been calculated, respectively. Compared the Fermi resonance coupling coefficients W of free CH_3CN with $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex at different concentrations, the free CH_3CN had a little smaller value, which indicated that the $\nu_2/(\nu_3 + \nu_4)$ Fermi resonance in $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex was much stronger than the $\nu_2/\nu_3 + \nu_4$ Fermi resonance in CH_3CN . From the detailed analysis of the effect of Li^+ on the spectral features of CH_3CN , the effect mechanism of Li^+ coordination to CH_3CN at the nitrogen of the CN group on the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN has been elucidated.

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1. Introduction

The interaction between the solute and solvent in solution, especially the ions and solvent molecules in electrolyte-solutions, has been investigated extensively by vibrational spectroscopy, such as Raman, IR and FTIR for a few decades [1–9]. Investigation of the solute-induced frequency shifts can provide useful information on solute-solvent interactions, particularly for the case of water, thus, it has attracted much attention recent years [10–12]. Another notable example is the interaction between the nitrile-containing molecules and cations, particular the acetonitrile (CH_3CN) molecule [13,14]. Acetonitrile is an important polar solvent that is also of interest because

of the potential usefulness of the nitrile moiety as a vibrational probe of environment [15–18]. Its suitability as reporters of the local environment is due to the sensitivity of the CN stretching frequency to intermolecular interactions. The origin of CN frequency shifts in complex formed between the acetonitrile molecules and cations is still a topic of current study. A key issue involves the effect of cations to the nitrogen of the nitrile group, which result in a blue shift of the CN stretching frequency. In early work, Coetzee et al. [19] not only studied the effect of a variety of anions on the C – H stretching frequency of CH_3CN , but also gave a detailed analysis on the cations (such as Li^+ , Na^+ , and Mg^{2+} et al.) affect the C – C and particularly the C ≡ N stretching frequencies by IR spectroscopy. Although the frequency shifts of the C ≡ N and C – C groups in acetonitrile can be explained by the interaction of donor and acceptor between the salt cations and acetonitrile, other important features of the vibrational spectra have not been analyzed. Especially, the effect of the interaction between the ions and acetonitrile molecule on the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN is still not clear. Recently, with the development of time-resolved vibrational spectroscopic techniques, more and more researchers have performed their experimental research on Fermi resonance by two-dimensional IR (2DIR) and infrared pump-probe. Kwon et al. [4] have studied the effect of ion-molecule interaction on the Fermi resonance in acetonitrile by using FTIR, IR pump-probe and 2DIR experiments, and it was observed that the Li^+ ion could enhance the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN . However, there is

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still little information available in literature about using the Raman spectroscopy to study the effect mechanism of complex $\text{CH}_3\text{CN}\cdots\text{Li}^+$ formation on the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN , and more detailed features of the vibrational spectra of CH_3CN solution with dissolved Li^+ should be analyzed.

In the present work, vibrational characteristics of CH_3CN solutions of LiClO_4 have been studied by means of Raman spectroscopy. Blue shifts of ν_2 , ν_8 and combination ($\nu_3 + \nu_4$) are observed resulting from interaction of CH_3CN with Li^+ , while other vibrational bands are relatively immune to the donor-acceptor interaction. According to the Bertran's equations, Fermi resonance parameters of free CH_3CN and $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex at different concentrations have been calculated, respectively. Compared with the Fermi resonance parameters of the free CH_3CN and $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex at different concentrations, it was found that the Fermi resonance coupling coefficient W of free CH_3CN had a little smaller value, which implied that the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN was enhanced due to $\text{CH}_3\text{CN}\cdots\text{Li}^+$ complex formation. Finally, we gave a qualitatively analysis about the effect mechanism of Li^+ coordination to CH_3CN at the nitrogen of the CN group on the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN based on the detailed spectral analysis.

2. Experimental Methods

The samples of CH_3CN and LiClO_4 were obtained commercially (Aladdin Chemical Company) and used without further purification. Stock solution of LiClO_4 and CH_3CN were prepared at various concentration. Raman spectra were collected by using a confocal microscope Raman spectroscopy system (Renishaw InVia Raman microscope). The 514 nm laser (Spectra-Physics 160 M argon ion laser) was used to excite the CH_3CN sample with dissolved LiClO_4 at different concentrations. An Olympus microscope with 50 \times objective lenses enables measurements with back scattering geometry. For Rayleigh rejection, the scattered light passed through an edge filter. The laser power was 5 mW and exposure time (CCD integration times) of 50s were used to collect all Raman spectra. The spectra wavenumbers were calibrated with the Si line and are believed to be accurate to 1 cm^{-1} . All the experimental data, which were processed with the OriginPro 8.0 software systems, were obtained at atmospheric pressure and room temperature.

3. Results and Discussion

Fig. 1 shows the Raman spectra of CH_3CN , LiClO_4 , and CH_3CN with dissolved LiClO_4 (0.7 M). The acetonitrile molecule belongs to the C_{3v}

point group and has twelve fundamental vibrational modes. These include four nondegenerate vibrations (a_1 symmetry) and four doubly degenerate vibrations (e symmetry), all of which are active both in infrared and Raman spectrum. The Raman vibrational modes and corresponding vibrational assignments of CH_3CN are summarized in Table 1 [4,13,20,21]. It is well known that, in the harmonic approximation, the combination/overtone are forbidden in Raman spectrum. However, in the case of CH_3CN , a significant Raman band at $\sim 2293\text{ cm}^{-1}$, which has been assigned to the combination of the C—H bending mode (ν_3) and the C—C stretching mode (ν_4), can be observed in Fig. 1(c). This phenomenon can be attributed to the $\nu_2/\nu_3 + \nu_4$ Fermi resonance of CH_3CN . Fermi resonance occurs when two molecular vibrational modes of the same symmetry and comparable vibrational frequencies are perturbed by the anharmonic term in the Hamiltonian [22–24]. As a result, the energy levels of both vibrations are changed and mixed, leading to changes in the observed frequencies and intensity transfer from a (bright) fundamental to an overtone or combination mode, which is otherwise dark or has a negligible spectral intensity [25]. Therefore, the forbidden vibrational transition of ($\nu_3 + \nu_4$) combination of CH_3CN can be observed as a prominent Raman peak in Fig. 1(c).

Raman spectra of the solution of LiClO_4 in acetonitrile at different concentrations are shown in Fig. 1S (Supplement materials) and Fig. 2. Fig. 1S shows the Raman spectra in the ν_1 and ν_5 regions for pure CH_3CN and CH_3CN solutions of LiClO_4 at different concentrations. As can be seen from Fig. 1S, C—H stretching modes of CH_3CN show no significant changes in frequency with increasing the concentrations of LiClO_4 . Fig. 2(a) and Supplementary Figs. 2S and 3S show that, with increasing the concentration of Li^+ , the C=N bending vibrational mode ν_8 of CH_3CN shifts to higher wavenumbers gradually, which can be attributed to the interaction between Li^+ and CH_3CN molecule and correspondingly making a slight decrease of the CN bond length. In addition, Fig. 2(a) also shows that a new Raman peak located at $\sim 390\text{ cm}^{-1}$ arising gradually with increasing the concentration of Li^+ without remarkable shift. This new Raman peak can be attributed to the ν_8 C=N bending band of CH_3CN complexed with Li^+ . With increasing the concentration of Li^+ , more and more Li^+ can form the complex with the CH_3CN , thus, the spectral intensity of new Raman peak located at $\sim 390\text{ cm}^{-1}$ become stronger. Detailed analysis of Fig. 2(a) and curve fitting are presented in Supplementary Figs. 2S–3S.

In Fig. 2(b), two Raman bands located at ~ 918 and $\sim 932\text{ cm}^{-1}$ can be observed, respectively. As is shown in Fig. 2(b), the Raman band located at $\sim 932\text{ cm}^{-1}$ is a new Raman peak arisen gradually with increasing the Li^+ concentration. According to the Kwon et al. [4], the new Raman peak

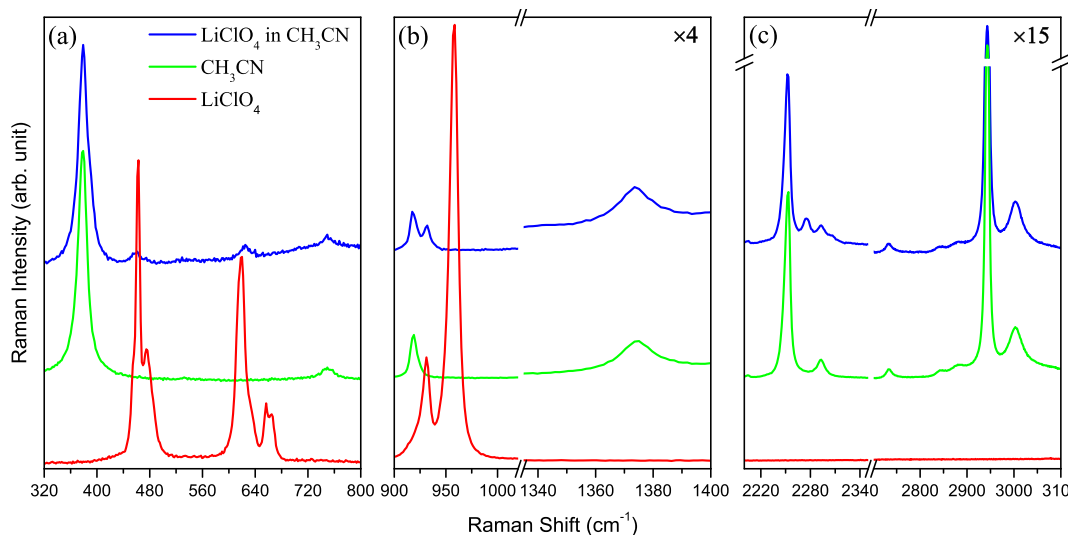


Fig. 1. Raman spectra of CH_3CN , LiClO_4 and LiClO_4 dissolved in CH_3CN solution (0.7 M). For clarity, the spectra were divided into three parts: (a) $320\text{--}800\text{ cm}^{-1}$; (b) $900\text{--}1400\text{ cm}^{-1}$; (c) $2220\text{--}3100\text{ cm}^{-1}$.

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