

論文の内容の要旨

論文題目 Development of Fast Low Frequency Raman Spectroscopy and its Application to Real-time Tracing of Phase Transitions
(高速低振動数ラマン分光の開発と相転移の実時間観測への応用)

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Introduction

The low frequency region ($< 200 \text{ cm}^{-1}$) of Raman spectra provides valuable information on inter-molecular dynamics in condensed-phase materials. Commercially available multi-channel Raman spectrometers with a holographic notch filter can hardly record this spectral region, because such kind of filters have considerable elimination bandwidths (typically $>200 \text{ cm}^{-1}$) and they eliminate not only Rayleigh scattering but also low frequency Raman scattering as well. Multiple stage monochromators have thus been commonly used for low frequency Raman measurements. These spectrometers are used with single-channel detectors like photomultipliers and require a long measurement time, typically more than 10 minutes. Furthermore, each portion of a spectrum cannot be obtained simultaneously and therefore observed spectra are sensitive to fluctuations in measuring conditions. It is almost impossible to trace real-time Raman spectral changes during phase transitions by using the conventional techniques.

In the present study, I newly develop a multi-channel low frequency Raman spectrometer by using an iodine vapor filter for fast ($< 1 \text{ sec}$) measurements of low frequency Raman spectra. The iodine vapor was first demonstrated in 1970s[1]. Vibronic absorption lines of iodine vapor, which exist in 500-600 nm region, have very narrow bandwidth of 0.03 cm^{-1} . It is possible to use these bands for laser line elimination, if the wavelength of a longitudinal single-mode laser line coincides with that of the iodine absorption line. In spite of its high Rayleigh line elimination efficiency, it was seldom used for low frequency Raman measurements, because the iodine absorption lines cause spike-like artifacts in the observed Raman spectra.

I revisit this technique and combine it with a multi-channel Raman spectrometer. The developed spectrometer records the low frequency ($> 5 \text{ cm}^{-1}$) region with retaining all the advantages of the multi-channel detection, such as short exposure time ($\sim 0.1 \text{ sec}$), simultaneous recording of the whole spectra, and high wavenumber reproducibility. I also applied this new technique to real-time low frequency Raman measurements during phase transitions.

Multi-channel low frequency Raman spectrometer (Chapter 2)

The developed apparatus is shown in Figure 1. A 90° Raman scattering geometry is used for collecting Raman scattering. A heated 10-cm glass cell, which contains a few grams of iodine, is placed in front of a 60-cm F/6.2 polychromator. The Raman scattered light is dispersed by the polychromator and detected with a

liquid nitrogen cooled CCD camera. The read-out time of the detector is about 0.1 sec. The light source is an Ar ion laser (514.5 nm) or a frequency-doubled Nd:YVO₄ Laser (532.2 nm) operating in a single longitudinal mode. The spectral widths of the laser lines are less than 40 MHz, which is one fiftieth of the iodine absorption bandwidth. The operating wavelength of the laser is monitored by the wavelength-meter to set the laser line strictly to the iodine absorption lines (514.5295 nm or 532.0500 nm). The laser line transmittance of the iodine vapor filter is less than 10⁻⁷, while the continuum light transmittance in the same spectral region is 10~50 %. The laser line elimination efficiency is thus over 10⁶.

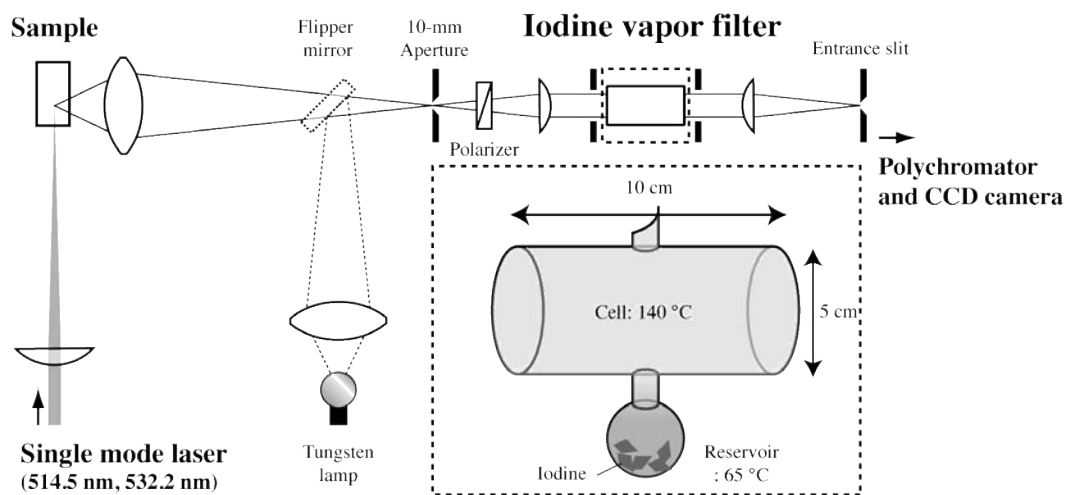


Figure 1. Schematic diagram of the developed multi-channel low frequency Raman spectrometer

Because the observed Raman spectra contain spike-like artifacts due to the iodine absorptions, the intensity correction of the spectra is extremely important. It is necessary to measure the transmittance spectrum of the iodine vapor filter with good wavelength reproducibility. A flipper mirror is used to introduce continuum light from a tungsten lamp into the filter before and after each measurement. The intensity corrected spectrum is obtained by dividing observed Raman spectrum by the continuum light spectrum. The artifact from iodine vapor no longer exists in the corrected spectrum.

Results and Discussions

① Low frequency Raman measurements of L-cystine (Chapter 2)

In order to evaluate Rayleigh scattering elimination efficiency, Raman spectra of microcrystalline powder L-cystine, which is often used for testing Raman spectrometers, are measured (Figure 2 (a)). Thanks to a high Rayleigh scattering elimination efficiency of the iodine vapor filter, the remaining Rayleigh scattering at 0 cm⁻¹ has nearly the same area intensity as that of the intense S-S stretching Raman band at 498 cm⁻¹. The Rayleigh scattering makes almost no interference in the Raman spectra, even though both the Stokes and anti-Stokes sides are simultaneously recorded. The low frequency Raman spectra can be recorded with a small Rayleigh gap (-5 cm⁻¹ to 5 cm⁻¹), and many Raman bands including as low as 9.8 cm⁻¹ band of L-cystine are measurable. Note that these low frequency Raman bands are very difficult to detect by using conventional methods. Because of multi-channel detection, the measurement time is determined only by the exposure and read-out time of the detector. As shown in Figure 2 (b), 0.1 sec exposure, which is as short as the read-out time, is enough to measure a high S/N low frequency Raman spectra of L-cystine. It means sub-second real-time low frequency Raman measurements are possible by using this apparatus. If the CCD camera having shorter

read-out time is used, the measurement time can be shortened.

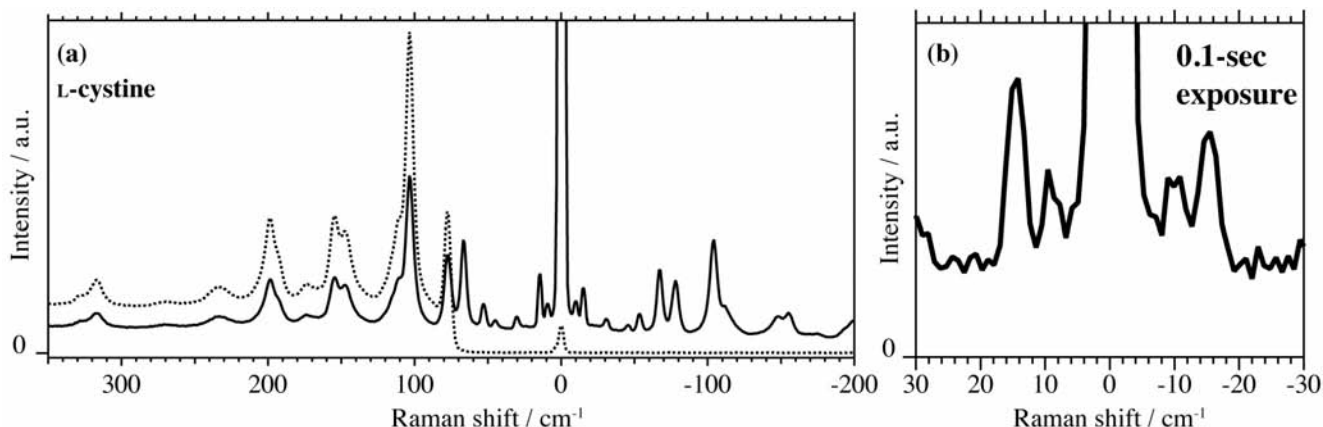


Figure 2. (a) Raman spectra of L-cystine measured by the developed multi-channel spectrometer using an iodine vapor filter (solid line) and using a typical edge filter (dotted line). Each spectrum is obtained with the same exposure time (10 sec) and the same spectral resolution (1.7 cm⁻¹). (b) Low frequency region of the Raman spectrum of L-cystine obtained with 0.1-sec exposure. Laser power: 50 mW (at the sample point) Excitation: 532 nm

② Real-time low frequency Raman spectral changes during the melting process of anthracene (Chapter 3)

Next I applied the developed technique to monitoring the quick melting of an anthracene crystal. The low frequency Raman bands of anthracene are thoroughly studied by using polarized Raman measurements of a single crystal [2]. A small piece of crystalline anthracene in a 1-mm glass capillary is quickly heated by using a heating gun. The Raman spectral change is continuously measured in 0.2 seconds (Figure 3(a)). Three Raman bands in both Stokes and anti-Stokes sides are assigned as a librational lattice vibration of anthracene crystal. After heating, these bands gradually shift to lower frequency side and disappear in 15 seconds, which corresponds to the change of the crystal structure and its disappearance (melting).

In the multi-channel measurements, Stokes and anti-Stokes sides of Raman spectra are simultaneously measured, and the intensity ratios of both sides, which correspond to the temperatures, are obtained accurately. The temperature estimated from the anti-Stokes/Stokes intensity ratio of the lattice vibrational Raman bands are plotted in Figure 3(b). There is a plateau in the temperature profile, and it has almost the same as the melting point of anthracene (491 K). This profile is consistent with known melting process. It is interesting that even after the temperature rise over the melting point, the lattice vibrational bands remain for a few seconds (10~15 sec). Because the temperature is estimated from the lattice, this result indicates that the remaining crystal has temperatures higher than the melting point (super heating).

③ Melting processes of an ionic liquid compound bmimCl (Chapter 4)

Finally, I applied this developed technique to the melting of bmimCl (1-butyl-3-methyl-imidazolium chloride), which is a prototype of imidazolium-based ionic liquids. It is known that bmimCl has crystal polymorphism due to the *trans-gauche* rotation isomerism of butyl chain in the cation [3]. In solid phase the butyl conformation is either in the *trans* or *gauche* form, while in the liquid phase the two conformers coexist. In order to understand how bmimCl forms liquid, it is important to study the conformation changes of the butyl chain during the melting. The multi-channel low frequency Raman measurement can simultaneously record

both lattice vibrational bands in the low frequency region and the marker bands of the *trans* and *gauche* conformations (625 cm^{-1} and 603 cm^{-1} respectively).

A small piece of crystalline bmimCl is heated quickly and the Raman spectral changes are measured in 0.5 sec (Figure 4). The low frequency Raman bands below 200 cm^{-1} gradually changes after heating and sharp spectral features disappear after 54 sec, while the marker band of *trans* isomer does not appear. The *trans* isomer band appears only a few seconds after the disappearance of the lattice vibrational bands. This result indicates that the lost of the crystal structure and the butyl chain conformational change do not simultaneously occur.

Conclusion

A newly constructed multi-channel low frequency Raman spectrometer using an iodine vapor filter is described. It records down to 5 cm^{-1} in both the Stokes and anti-Stokes sides simultaneously with a short ($\sim 0.2\text{ sec}$) measurement time. It is shown that this new technique can detect real-time low frequency spectral changes, and can be applied to investigate structural changes during the phase transitions.

[1] G.E. Devlin, J.L. Davis, L. Chase and S. Geschwind, *Appl. Phys. Lett.* **19** (1971) 138-141.

[2] M. Suzuki, T. Yokoyama and M. Ito, *Spectrochim. Acta A* **24** (1968) 1091-1107.

[3] H. Hamaguchi and R. Ozawa, *Adv. Chem. Phys.* **131** (2005) 85-104.

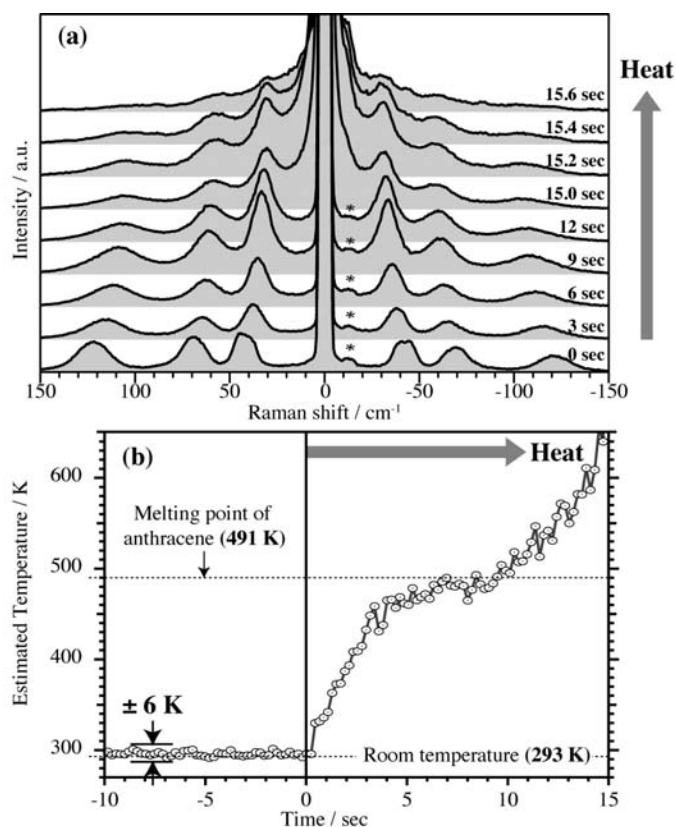


Figure 3. (a) Low frequency Raman spectral change of anthracene during the melting

Each spectrum was obtained in 0.2 sec (515 nm excitation).

*: Spontaneous emission from Ar^+ laser.

(b) Temperature estimated from anti-Stokes/Stokes ratio of lattice vibrational Raman bands

The temperatures without heating fluctuate around $\pm 6\text{ K}$ from the room temperature.

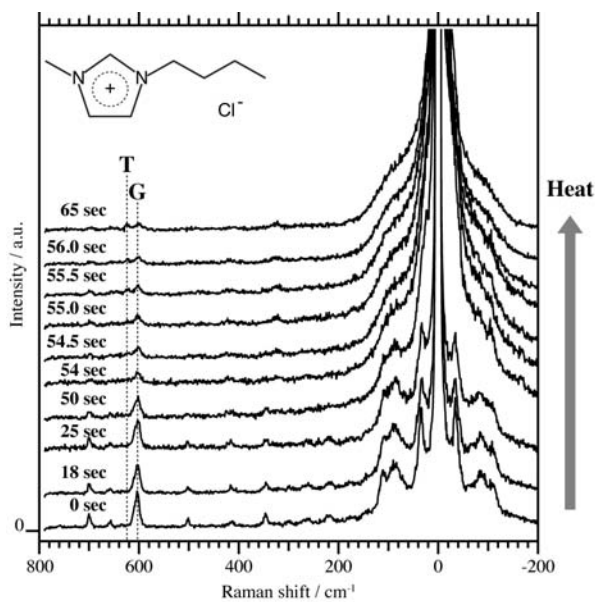


Figure 4. Raman spectral change of bmimCl during the melting

Excitation: 532 nm, exposure: 0.5 sec

T and G in the graph indicate the positions of marker bands of butyl chain conformer of bmim⁺ (*trans* and *gauche* respectively).