CASCADING THIRD-ORDER RAMAN PROCESS AND LOCAL STRUCTURE FORMATION IN BENZENE/N-HEXANE BINARY LIQUID MIXTURES

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Abstract: The cascading third-order Raman process in benzene/*n*-hexane binary mixtures was studied. We found that the cascading signal intensity showed a significant deviation from the expected quartic dependence at high benzene concentrations. This finding can be interpreted in terms of optical inhomogeneity caused by the domain-structure formation of benzene.

Elucidating microscopic structures in liquids and solutions is an important subject of chemistry because they profoundly affect macroscopic physical properties and chemical reactions in solution. A number of studies, such as the line shape analysis of vibrational spectra [1] and fifth-order two-dimensional Raman spectroscopy [2-4], have been carried out in order to reveal how molecules interact with each other and form local structures. Recently, we demonstrated by six-wave mixing coherent anti-Stokes Raman scattering (SWM-CARS) spectroscopy that the cascading third-order Raman process can be another potential probe for local structures in liquids [5]. In the present work, we applied the cascading third-order Raman scattering to binary mixtures of benzene and *n*-hexane. By examining the concentration dependence of the cascading signal intensity of the 992 cm^{-1} mode (ν_2) of benzene, we investigated local structure formation of benzene in these binary mixtures [6].

Typical SWM-CARS spectra obtained from the binary mixtures in the wavenumber region of 1950—2010 cm^{-1} are shown in Fig. 1 for five different concentrations (30, 50, 64, 80, and 100 volume % of benzene). The peak positions in these spectra are located at around 1980 cm^{-1}, which is twice the fundamental frequency of the ν_2 mode of benzene. Our previous study [5] indicates that the SWM-CARS signal of benzene is attributed to the parallel cascading (PC) third-order process [3,7] where successive CARS processes occur between two different molecular ensembles in a medium. The SWM-CARS signal measured in the present study can also be assigned to the signal originating from this PC process.

The concentration dependence of the cascading third-order signal intensity is shown as a linear plot in Fig. 2(a) and as a logarithmic plot in Fig. 2(b). It is generally accepted that if intermolecular interaction between solute molecules is very weak and the binary mixtures can be regarded as homogeneous both macroscopically and microscopically, the cascading signal intensity is proportional to N^4, where N is the concentration of the solute molecule [2,8]. In contrast, if the effect of intermolecular interactions is not negligible, this simple relation no longer holds, and the cascading signal intensity is expected to depend on the concentration in a more complicated

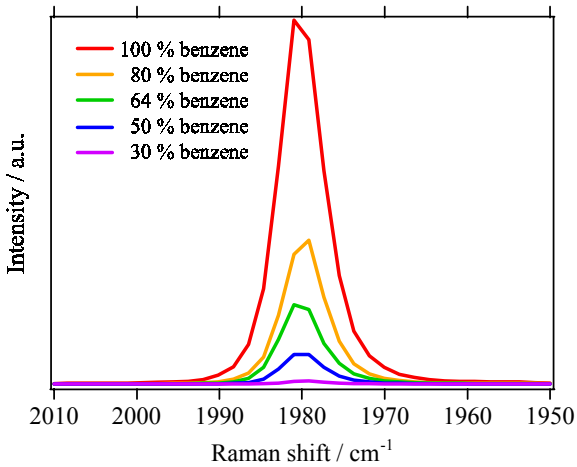

Fig. 1. SWM-CARS spectra of the benzene/*n*-hexane binary mixtures of five different concentrations.

manner. As the solid lines in Figs. 2(a) and 2(b) indicate, the observed cascading signal intensity is fitted well by $I_{\text{cascade}} = AN^{\alpha}, \alpha = 4.3 \pm 0.1$, for concentrations below 6.7 mol dm^{-3}. However, the cascading signal intensity in the higher concentration range shows a significant deviation from the N^4 dependence observed in the low concentration range. We also measured the concentration dependence of the spontaneous Raman intensity of the ν_2 mode of benzene in the same binary mixtures, but no such behaviour was observed. In our previous study, we discovered a nonlinear Raman effect called PCARS, Partially Coherent Anti-Stokes Raman Scattering [9,10]. The concentration dependence study of the PCARS intensity of the ν_2 mode of benzene in *n*-heptane and cyclohexane [10] suggested that microscopic optical inhomogeneity was induced by the formation of domain structures in these liquid mixtures. The unexpected concentration dependence found for the cascading third-order signal intensity can also be explained in terms of the optical inhomogeneity in the benzene/*n*-hexane mixtures. Introducing the phase factor that phenomenologically takes into account the effect of the optical inhomogeneity, we derived an equation that represents the cascading signal intensity for optically inhomogeneous mixtures. The observed concentration dependence of the cascading signal intensity is explained qualitatively by using this equation. The results obtained here show that the cascading process is a good probe for the microscopic structures that are formed in liquids and solutions.

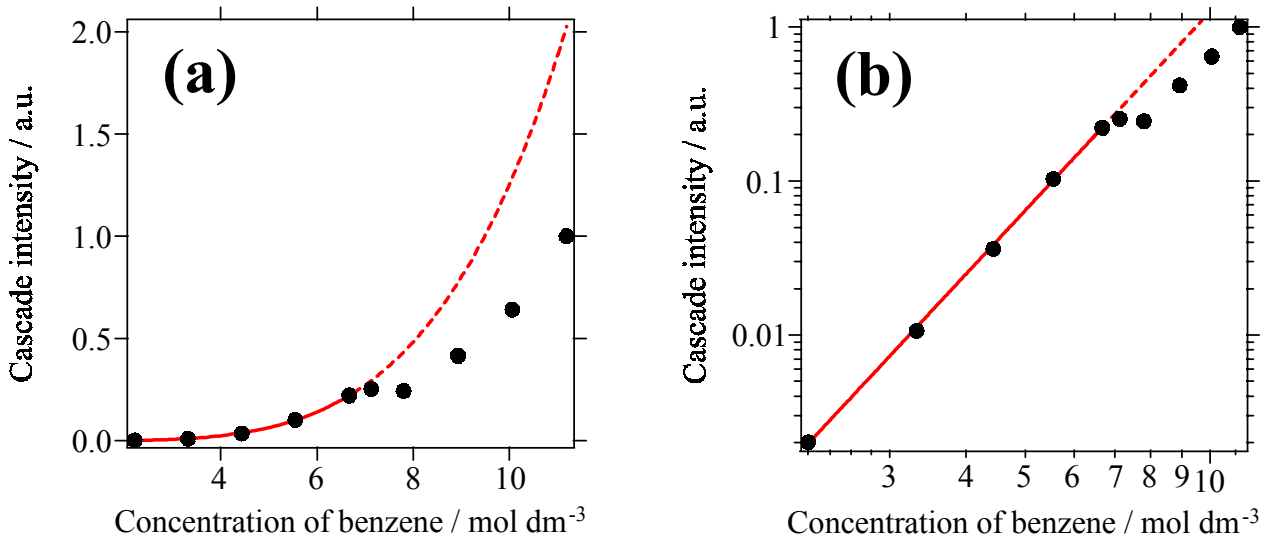

Fig. 2. Concentration dependence of the cascading third-order signal intensity. (a) Linear plot. (b) Logarithmic plot. In both (a) and (b), the solid curves show the fitted results ($I_{\text{cascade}} \propto N^{\alpha}, \alpha = 4.3 \pm 0.1$) obtained below 6.7 mol dm^{-3}. They are extended to the higher concentration range and shown as the dashed curves.

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