Enhancement of the Stimulated Raman Scattering of Benzene−Toluene Mixtures under Strong Excitation Condition in the Liquid Phase

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Anomalous enhancement of stimulated Raman scattering (SRS) of the aromatic CH stretching band was observed when the laser-induced plasma was generated in benzene−toluene mixed solvents. Time-resolved spectra of the SRS revealed that the strong excitation condition which led to generation of ionized molecules played an important role in anomalous enhancement. The observed intensity dependence on the mixture ratio meant that the complex formation between benzene and ionized toluene molecules contributed to its enhancement. Results of the theoretical calculation indicated that the Raman cross section of benzene and toluene molecules was remarkably enhanced due to the charge distribution between benzene and toluene cations compared to the Raman cross section in each neutral monomer state. The mechanism of the anomalous enhancement was considered in terms of the formation of cationic benzene−toluene complexes under the strong excitation condition and subsequent change of the Raman cross section due to the charge-resonant interaction in the cationic complexes.

Introduction

Chemical and physical processes induced by irradiation of a strong laser field have attracted much attention for synthesizing chemical compounds,[1] material processing,[2] generating ultrafast X-ray pulses,[3] emerging novel chemical and physical processes under strong laser fields,[4,5] and so on. We have investigated the nonlinear optical phenomena of liquids under strong laser irradiation that lead to the phase transition from liquid to plasma state. We found anomalous enhancement of stimulated Raman scattering (SRS) in the OH stretching band of water molecules, which is induced transiently before the phase transition from liquid to plasma.[6] Our subsequent study revealed that interactions between water molecules and excess electrons transiently generated in water before the phase transition played a key role in the enhancement of the SRS.[7] We have also applied the laser-induced plasma generation technique to organic solvents and observed anomalous enhancement of aromatic CH stretching band of benzene molecules in the presence of toluene molecules.[8] Since such an enhancement is not observed under normal conditions, it is considered that the interactions between the benzene and toluene molecules under the plasma generation condition, where many molecules are excited to higher electronic or ionized states, contribute to the enhancement. However, the states of the benzene and toluene molecules and interactions that contribute to the enhancement have not been clarified yet. The interactions between aromatic moieties in (highly) excited electronic states and/or ionic states have been attracting increasing attention for the past decade.[9−13] However only a little information is available on the interactions between the different kinds of aromatic moieties. Thus, investigations of the enhanced SRS from benzene−toluene mixtures under the strong excitation condition are expected to provide further insight into the enhancement mechanism and information on aromatic−aromatic interactions under their highly excited electronic and/or ionic states in the condensed phase. Here we measured the time-resolved spectra of the enhanced SRS of the CH aromatic band (CH-SRS) emitted from benzene−toluene mixed solvents in more detail under the condition where considerable numbers of molecules are ionized in the condensed phase. From the SRS spectra and theoretical calculation, we discussed the contributing interactions and the mechanism of the enhancement.

Experimental and Calculation Methods

Details of the experimental setup were described elsewhere,[8] so here we only briefly outline the experimental conditions. The second harmonic of a Nd:YAG pulsed laser beam (wavelength: 532 nm, pulse duration 12 ns fwhm, single shot) was focused into benzene (B), toluene (T), and their mixtures with the focusing lens. The excitation power was 15 mJ/pulse and the focal length of the focusing lens was 50 mm. The power density at the beam waist was estimated as 6×10^{12} W cm^{-2} at most from calculation of the beam with a Gaussian spatial profile. After eliminating the strong background of the excitation beam, the SRS in the forward direction with respect to the excitation beam axis was measured by a spectrometer (Jasco, CT-25CS) and streak camera (Hamamatsu Photonics, c4334) to obtain time-resolved spectra of the SRS. All samples were of spectral or analytical grade and they were further purified by filtration.

We also calculated the Raman activities of benzene and toluene molecules and their complexes. All their geometries were fully optimized without symmetry constraints using the density functional theory (DFT), employing hybrid B3LYP.[14]

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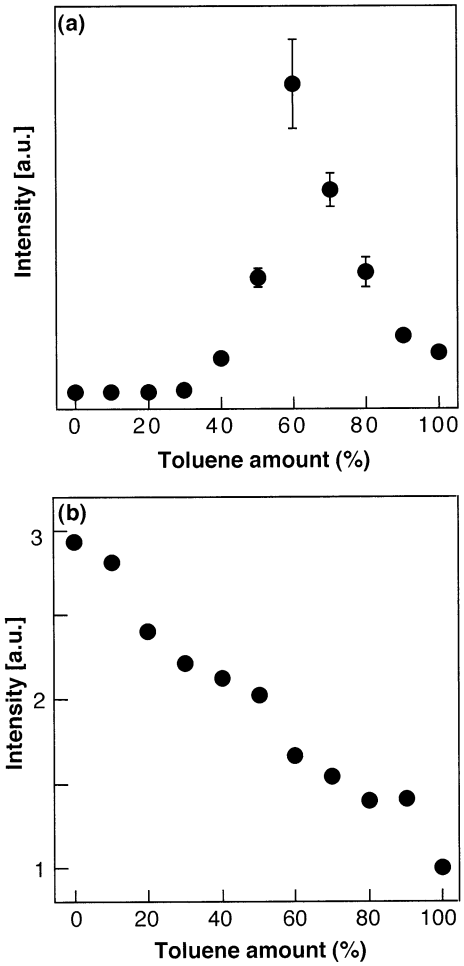

Figure 1. (a) Intensity dependence of SRS (CH stretching mode) on the toluene amount (%). 0% indicates the sample consists of only benzene. (b) Intensity dependence of Raman scattering on the toluene amount (%) when a laser-induced plasma was not generated. The intensity at each concentration is normalized by that for 100% toluene sample.

The cc-pVDZ basis set was employed.[15] All calculations were performed using the Gaussian 98 package.[16]

Results and Discussion

In normal SRS phenomena, only the most intensive Raman band is selectively enhanced and only this SRS peak can be observed. In pure benzene or toluene solvents, since the breathing mode of the aromatic ring (ν1-SRS) around 1000 cm^{-1} is the strongest band, only this band and its higher order Stokes band dominate the spectra. In contrast, when a laser-induced plasma is formed in a benzene−toluene mixture, an aromatic CH stretching mode at around 3060 cm^{-1} (CH-SRS) newly appears beside ν1-SRS.[8] Because the CH-SRS is prominent only in the mixed solvents, both benzene and toluene molecules are considered to play an important role for the enhancement of the CH-SRS.

Figure 1a shows the intensity dependence of the SRS in the CH-SRS on the mixing ratio. We found that the SRS intensity is sharply increased at around the mixing ratio B:T = 60:40. To investigate whether the enhancement of the Raman cross section of the benzene and toluene is induced by simply mixing both solvents, the Raman intensities of benzene−toluene mixed solvents were also measured under a normal condition, i.e., a laser-induced plasma was not generated. These results are shown in Figure 1b. Under the normal condition, the Raman intensity of the CH stretching band is monotonically decreased with increasing mixing ratio of toluene. Since the Raman cross section of the CH stretching mode of benzene was estimated to be about 3 times higher than that of toluene under the normal condition, this result is considered to represent normal behavior. Thus, we can consider that the strong excitation condition that leads to the plasma (ionized molecules and electrons) generation and the interaction between benzene and toluene molecules are crucial to the anomalous enhancement of the CH-SRS. It is worth noting that the CH-SRS has considerable intensity even in pure toluene (Figure 1a). On the other hand, it has hardly any intensity in pure benzene though the Raman intensity of the CH stretching mode of benzene is about 3 times larger than that of toluene under the normal condition. Thus, we can also consider that the toluene molecules are in some specific states due to the strong laser irradiation and that they play a key role in the enhancement of the SRS intensity.

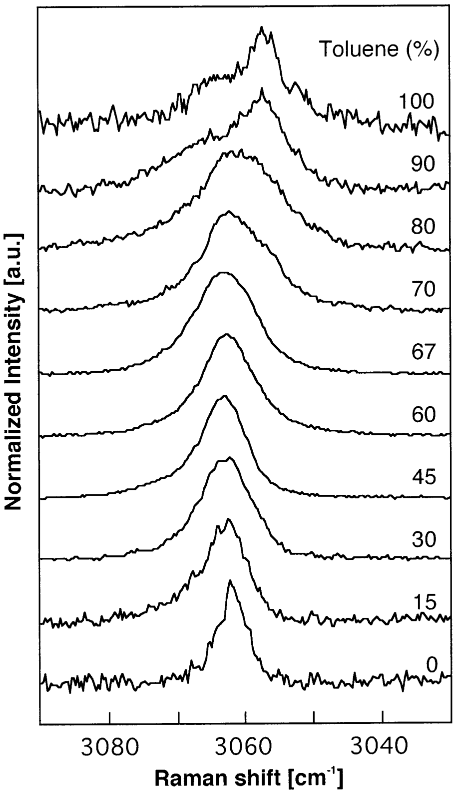

Figure 2. The SRS spectra of CH stretching mode of the benzene−toluene mixture at various mixing ratios.

To obtain further insight into the enhancement mechanism, we investigated the spectra and time courses of the CH-SRS while varying the mixing ratio. Figure 2 shows the change of the CH-SRS spectra at various mixing ratios. We can see that the Raman shift of the SRS almost corresponds to that of benzene molecules at B:T = 40:60 where the intensity of the CH-SRS reaches its maximum, indicating that the benzene molecules have a dominant role as a Raman scattering entity. It should be noted that the Raman frequency at B:T = 40:60 is slightly higher than that in pure benzene. Another interesting point is that a broad shoulder peak, which is not observed under the normal condition, appears in the higher wavenumber region in the pure toluene spectrum. The appearance of the shoulder peak indicates that some of the toluene molecules are in a specific structure or state that induces the frequency shift. We discuss the reason for these changes in the spectra in the latter part of this paper.

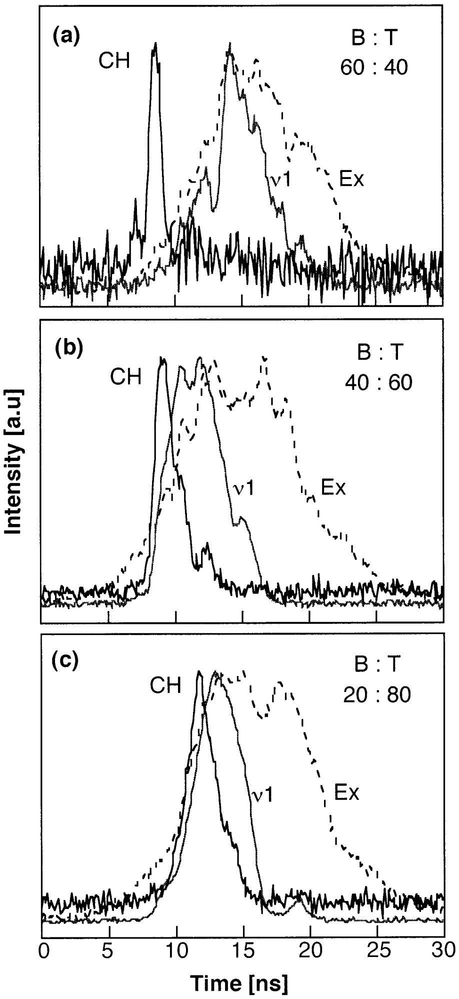

Figure 3. Simultaneous measurements of the time courses of the CH stretching mode (CH), breathing mode ($\nu1$), and the excitation beam (Ex) at the following mixing ratios. (a) benzene (B):toluene (T) = 60:40, (b) B:T = 40:60, and (c) B:T = 20:80.

Then, we measured the time course of the CH-SRS. Figure 3 compares the time courses of CH-SRS (CH), $\nu1$-SRS ($\nu1$), and the excitation beam (Ex) at the mixing ratios (benzene (B): toluene (T)) = (60:40, benzene-rich), (40:60, at the maximum intensity of CH-SRS), and (20:80, toluene-rich). We can also observe the plasma continuum emission (data not shown). It becomes dominant about 5−10 ns after the onset of the irradiation of the excitation beam due to the recombination of ions and electrons.[8] Before the plasma continuum emission becomes dominant, the time course of the $\nu1$-SRS agrees with that of the excitation beam at all measured mixing ratios. The latter part of the $\nu1$-SRS is diminished because the focusing region is drastically perturbed due to the phase transition from the liquid to plasma (gas) states and the excitation beam is strongly scattered. In contrast, the CH-SRS is enhanced only at the very early stage of the excitation and its intensity is more rapidly decreased than that of $\nu1$-SRS. The condition for the enhancement of CH-SRS lasts only a few nanoseconds at most. These results indicate that the condition for the CH-SRS enhancement is achieved only at the very early stage of the phase transition from the liquid to plasma, where there are many ionized molecules and electrons but they are in the condensed phase. Compared with the time course of the $\nu1$-SRS, we find that the time course of the CH-SRS is completely different with that of the benzene $\nu1$-SRS mode (Figure 3a). However, the time course of CH-SRS becomes similar to that of $\nu1$-SRS of toluene (Figure 3b,c). In addition, the duration of the CH-SRS becomes longer on increasing the amount of toluene. These features indicate that toluene molecules play a key role in the onset of the CH-SRS enhancement.

The obtained features of the CH-SRS enhancement are summarized as follows. (1) The enhancement is prominent in the presence of both benzene and toluene molecules. (2) The enlargement of the Raman cross section is not induced by simply mixing the two neutral solvent molecules. (3) The Raman shift of the CH-SRS is close to that of benzene molecules when the SRS intensity reaches its maximum. (4) The slight enhancement of the CH-SRS is observed in pure toluene though the Raman intensity is weaker than that of benzene. In addition, a specific shoulder peak appears in the higher wavenumber region in pure toluene. (5) The CH-SRS is transiently enhanced only at the early stage of the plasma generation and this lasts only a few nanoseconds at most.[8] Considering these features of the CH-SRS, we assumed that transiently generated ionized species under the plasma generation condition contribute to the enhancement of the CH-SRS. In the very early stage of laser-induced plasma generation in liquid, considerable numbers of ionized molecules and electrons are generated by multiphoton ionization in the condensed phase (i.e., before the phase transition from liquid to plasma). The onset and the duration of the CH-SRS have a strong relation to the toluene amount. In addition, the ionization potential of toluene molecules is 0.4162 eV lower than that of benzene molecules,[17,18] so we assumed that the transiently generated toluene cations play a dominant role as a trigger entity to induce the enhancement of the Raman cross section of the CH stretching band. On the other hand, because the Raman shift of the CH-SRS at its intensity maximum is similar to that of benzene, not only the toluene molecules but also the benzene molecules are considered to significantly contribute to the CH-SRS enhancement. Thus, we also consider the possibilities that the subsequent interaction between ionized toluene molecules and benzene molecules can also contribute to the CH-SRS enhancement. Once a toluene monomer cation is generated, it interacts with a neighboring neutral benzene or toluene molecule and forms stable dimers due to the charge resonance interactions.[12,13,19,20] In the condensed phase, such transient dimer species are reported to last at least 100−500 ps.[11]

From the viewpoint of pulse shortening of the SRS compared to the duration of the excitation beam, it is worth comparing this to previous studies describing the intense light burst phenomenon observed in the *backward* SRS.[21,22] In that phenomenon, the initiation of the backward SRS pulse by self-focusing and growth of the backward-traveling SRS pulse played a dominant role to produce an intense SRS pulse with shortened duration. On the other hand, in forward-traveling SRS, such pulse generation is generally prevented by pump saturation.[21] Actually, in the present work measuring the forward-traveling SRS, such an intense burst was not observed for the $\nu1$-SRS. The time course of the $\nu1$-SRS rather accords with the time course of the excitation beam and differs from that of the transiently enhanced CH-SRS. In addition, the enhancement of the CH-SRS was prominent only when both benzene and toluene coexist. Thus, in the present case observed in the *forward* SRS of the CH stretching mode, not the self-focusing effect but the transiently generated species such as dimer ions before the phase transition from liquid to plasma (gas) phase are considered to play a dominant role for the transient enhancement of the CH-SRS. However, such weakly bonded species are considered to be easily broken when the phase transition from liquid to plasma

TABLE 1: Calculated Values of the Raman Shift and Intensity of Benzene and Toluene Molecules and Their Ions and Ionic Complexes

	benzene	benzene$^+$	toluene	toluene$^+$
Raman shift [cm^{-1}]	3190	3218	3184	3216
Raman activity [Å^4/amu]	729	588	608	500

	(benzene−toluene)$^+$		(toluene−toluene)$^+$	
	benzene	toluene	toluene	toluene
Raman shift [cm^{-1}]^a)	3215	3209	3210	3210
Raman activity [Å^4/amu]	1362	508	844	844
activity change [%]^b)	+86.9	−16.5	+38.8	+38.8
Raman cross-sectional change^c)	5.49	0.84	1.39	1.39
charge distribution [%]	38.9	61.1	50.0	50.0
δE [kcal/mol]^d)	−23.8		−17.3	

[a] The Raman shift in the table is at the gravity center. [b] Comparison with neutral benzene or toluene molecules. [c] Relative intensity of the Raman cross section compared to that of neutral toluene molecule (1.00). The products of the experimentally obtained value of Raman intensity and activity change are indicated. For example, the Raman intensity of pure benzene is 2.94 times larger than that of neutral toluene. Thus, the expected Raman cross section of benzene molecules in (benzene−toluene)$^+$ is estimated as 2.94 × 1.869. [d] The degree of energy stabilization due to charge resonant interaction by the complex formation compared with the sum of a neutral benzene molecule and toluene cation in (benzene−toluene)$^+$ and the sum of a neutral toluene molecule and toluene cation in (toluene−toluene)$^+$.

(gas) phase takes place. We consider that strong perturbation induced by the phase transition leads to deformation of the transiently generated species and results in the hindrance of the stimulation process of the SRS and the considerable shortening of the duration of the CH-SRS compared to that of the excitation beam.

Next we examined the possibilities that such ionic species can contribute to the SRS enhancement in terms of the changes in Raman activity. To estimate the effect of the charge redistribution in the dimer cations to the change of Raman cross sections of component molecules, we calculated Raman activities of (toluene)$^+$, (benzene)$^+$, (toluene−benzene)$^+$, and (toluene−toluene)$^+$ to evaluate the change of Raman cross sections compared to those of neutral species. The Raman activities of the neutral benzene and toluene molecules, benzene, and toluene cations, and (benzene−toluene)$^+$ and (toluene−toluene)$^+$ dimer cations are listed in Table 1. The optimized geometries of (toluene−benzene)$^+$ and (toluene−toluene)$^+$ complexes are shown in Figure 4. We noted several features as follows. (1) The Raman cross section of the aromatic CH stretching mode decreases about 20% when neutral benzene and toluene simply become cations. Thus, the contribution of the cation monomers of benzene and toluene to the CH-SRS enhancement is negligible. (2) When dimers (benzene−toluene)$^+$ and (toluene−toluene)$^+$ are formed and charge delocalization due to the charge-resonant interaction takes place, the Raman cross section of the component benzene molecules in the hetero dimer ion (benzene−toluene)$^+$ is about twice as large as that in neutral species. In contrast, no remarkable change appears in the Raman cross section of toluene between the toluene molecules in the neutral state and in (benzene−toluene)$^+$ heterodimer. This theoretical result well explains the experimental results that Raman shift of the enhanced CH-SRS is close to that of benzene molecule though both benzene and toluene molecules are necessary for the enhancement. Since the Raman cross section of benzene is originally higher than that of toluene molecules (Figure 1b), the enhancement of the Raman activity of the benzene molecules is considered to dominate the CH-SRS spectrum. The probability that we can find a positive charge in the benzene molecule in the (benzene−toluene)$^+$ heterodimer is estimated to be approximately 39%, which is in good agreement with that estimated from perturbation theory (36%).[12] In the homodimer cation (toluene−toluene)$^+$, the Raman cross section of toluene is as about 1.5 times as large as that in the neutral species. Since the SRS intensity shows an exponential dependence on the Raman cross section, these changes in Raman cross sections are considered to remarkably contribute to the drastic increase of SRS intensity of the aromatic CH mode. (3) The Raman shifts of both benzene and toluene cations increase compared to those of neutral species. In the (benzene−toluene)$^+$ and (toluene−toluene)$^+$ dimers, a similar tendency is also seen. Although the degree of the Raman shift of the observed CH-SRS is smaller than that obtained by the theoretical calculations, the tendency in the Raman shift corresponds to the observed spectral features (Figure 2) qualitatively. This result also supports the basic idea that such transient ionic species contribute to the CH-SRS enhancement. To check whether we can explain the intensity dependence of the CH-SRS on the mixing ratio, we did a curve fitting using the following relation, based on the assumption that both dimer cations contribute to the enhancement:

$$I_{\mathrm{CH-SRS}} \propto \exp(\alpha[\mathrm{B}][\mathrm{T}]^{+} + \beta[\mathrm{T}][\mathrm{T}]^{+}) \tag{1}$$

where α and β are fitting parameters representing the weight of the contribution from (benzene−toluene)$^+$ and (toluene−toluene)$^+$, respectively. The fitting parameters are considered to be proportional to the products of the Raman cross section and the number of each corresponding component. This result is indicated in Figure 5. The steep dependence of the SRS intensity on the mixing ratio is not well represented by relation 1. Thus, we should consider another factor.

As mentioned above, the duration of the CH-SRS is a few nanoseconds. However, the characteristic time for recombination between dimer cations and photoejected electrons is theoretically estimated to be a few hundred femtoseconds.[23] This estimated value is much shorter than that observed here. However, time-resolved spectroscopy has revealed that such dimer cations can exist rather stably in the liquid phase and last at least a few hundred picoseconds.[11] In the liquid phase, there are abundant solvent molecules surrounding dimer cations and photoejected electrons. The surrounding solvent molecules may effectively shield the charges from each other. We can consider that the coexistence of such surrounding solvent molecules (here, benzene or toluene) also plays an important role in sustaining the dimer cations stably. Then, we assumed that at least another neutral molecule interacts with the dimer cations and is indispensable to prevent recombination between the dimer cations and photoejected electrons. We fitted the following relation to the experimental data again.

$$I_{\mathrm{CH-SRS}} \propto \exp(\alpha([\mathrm{B}][\mathrm{B}][\mathrm{T}]^{+}) + \beta([\mathrm{B}][\mathrm{T}][\mathrm{T}]^{+}) + \gamma([\mathrm{T}][\mathrm{T}][\mathrm{T}]^{+})) \tag{2}$$

Here, α, β, and γ are fitting parameters. The second term represents both cases where a neutral benzene molecule is attached to the (toluene−toluene)$^+$ homodimer cation and a neutral toluene molecule is attached to the (benzene−toluene)$^+$ heterodimer one. This result is also shown in Figure 5. The steep dependency of the SRS intensity on the mixing ratio is well explained by relation 2 ($\alpha = 35.3\%$, $\beta = 52.6\%$, and $\gamma = 12.1\%$). Although further detailed investigation is required to confirm the contribution of the dimer cations, the time-resolved spectroscopic study and the theoretical calculation suggest that

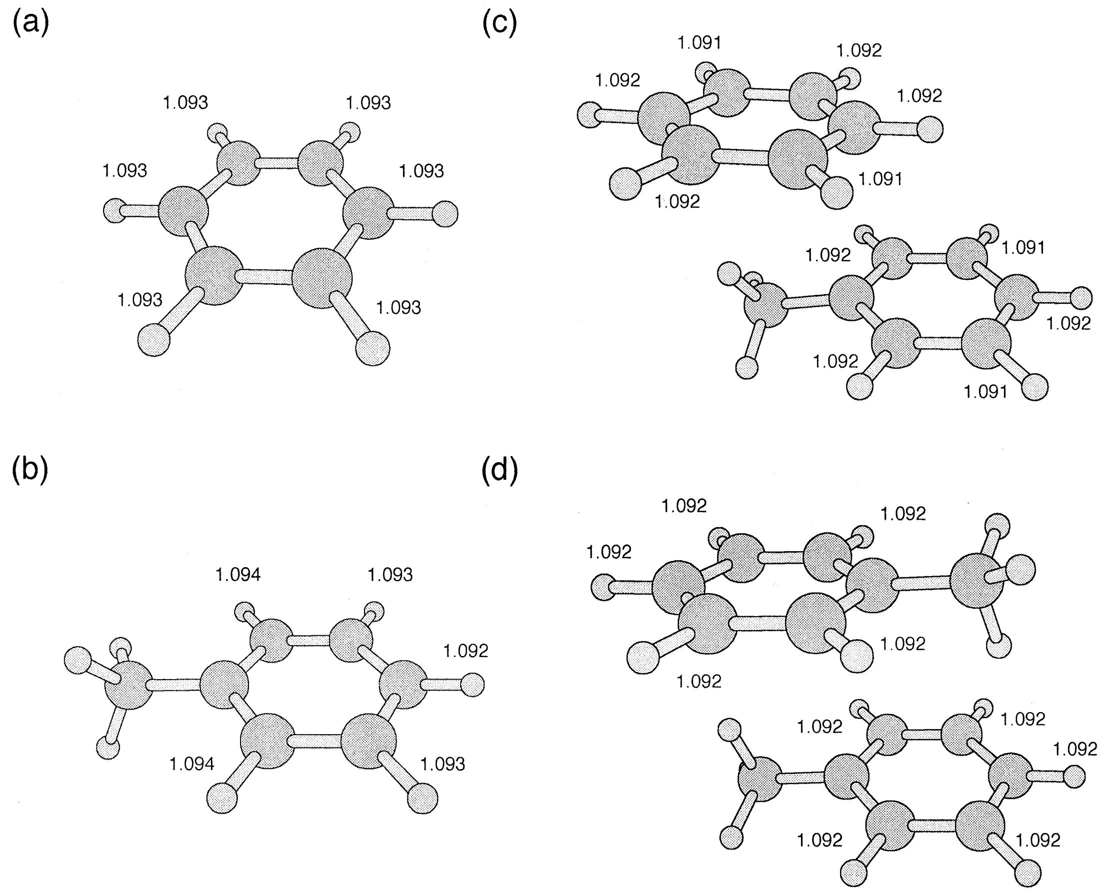

Figure 4. Optimized geometries of (a) neutral benzene monomer, (b) neutral toluene monomer, (c) (toluene−benzene)$^+$ dimer, and (d) (toluene−toluene)$^+$ dimer. The lengths of the CH bonds (Å) in each species are also indicated. The distance between toluene and benzene molecules in (toluene−benzene)$^+$ and toluene molecules in (toluene−toluene)$^+$ are estimated as 3.2 and 3.5 Å, respectively.

the transiently generated dimer cations with solvent molecules play an important role in the anomalous enhancement of the CH-SRS.

Conclusion

We found anomalous enhancement of the SRS of the aromatic CH stretching mode (CH-SRS) when a laser-induced plasma was generated in benzene and toluene mixtures and we considered the mechanism of the enhancement. The CH-SRS was observed only at the very early stage of the plasma generation and it lasted only a few nanoseconds at most. The CH-SRS was prominent when both benzene and toluene molecules were present. We found that the time course of the CH-SRS was strongly affected by the number of toluene molecules. In contrast, the Raman shift of the CH-SRS is close to that of benzene molecules. These characteristic features suggested the transient enhancement of the Raman activity of CH stretching mode, especially in benzene molecules, was induced due to intermolecular interactions between benzene and toluene molecules. We considered the mechanism of the anomalous enhancement in terms of the contribution from transiently generated homo- and heterodimer cations, such as (toluene−toluene)$^+$ and (benzene−toluene)$^+$. Theoretical calculation of the Raman activities of such dimer cations revealed that the enhancement of the Raman activities took place by forming such dimer cations due to the charge resonant interaction. The intensity dependence of the CH-SRS on the mixing ratio also suggested that the solvent molecules played an important role to prevent recombination and stabilize the transiently formed dimer cations that contributed to the SRS emission. Laser-induced plasma generation in the liquid phase is expected to provide new ways to induce and investigate intermolecular interactions involving molecules in highly electronic excited or ionic states, which are almost unobserved under the normal condition.

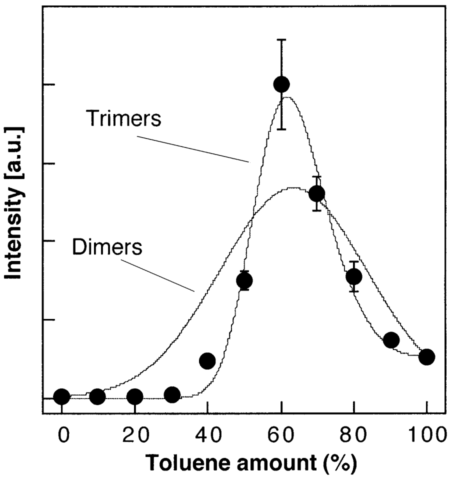

Figure 5. Curve fittings for the intensity dependence of CH-SRS on the mixing ratio. Two kinds of fitting curves are shown. One is the least-squares fitting on the assumption that dimer complexes ((benzene−toluene)$^+$ and (toluene−toluene)$^+$) contribute to the enhancement of the SRS (relation 1 in the text). The other is the least-squares fitting on the assumption that trimer complexes contribute to the SRS enhancement (relation 2 in the text).

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