Effects of Dipole Interactions and Solvation on the C=O stretching band of *N,N'*-Dimethylacetamide in Nonpolar Solutions: Infrared, Isotropic and Anisotropic Raman Measurements.

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Abstract

The concentration dependence of the C=O stretching ($\nu_{C=O}$) band of *N,N'*-dimethylacetamide (NdMA) in cyclohexane, *n*-hexane, and CCl_4 has been investigated by infrared (IR) and polarized Raman spectroscopy. For the neat liquid of NdMA, the noncoincidence of the aniso- and isotropic Raman wavenumbers is evident. In the 0.47 M cyclohexane solution of NdMA, the noncoincidence effect almost disappears and the $\nu_{C=O}$ envelopes in both the Raman and IR spectra are asymmetric to the low-wavenumber side. When the concentration of NdMA decreases from 0.33 to 0.023 M, the peak of these bands slightly shift to a higher wavenumber and the band shape becomes symmetric. The shape of the $\nu_{C=O}$ envelope does not show any significant change below 0.023 M. These results suggest that the asymmetric shape of the $\nu_{C=O}$ band observed for the 0.33 M cyclohexane solution is associated with the intermolecular interaction among NdMA molecules, which vanishes at around 0.02 M. Spectral changes for the CCl_4 solution of NdMA show a similar tendency. However, the shape and peak wavenumber of the $\nu_{C=O}$ band observed in a highly diluted CCl_4 solution (≤ 0.023 M) indicated that the solvation effect of CCl_4 is more complicated than those of cyclohexane and *n*-hexane. The analyses of the $\nu_{C=O}$ band, which is sensitive to the intermolecular interactions between solutes and between solute and solvent for NdMA dissolved in nonpolar solvents, would serve to clarify the electronic property of the molecule in a solution.

Introduction

The C=O stretching ($\nu_{C=O}$) and amide I (ν_{am}) vibration bands have been widely used to investigate the interaction and orientation of the functional groups incorporated in macromolecules. For examples, the secondary structures of proteins can be estimated by analyzing the wavenumber and intensities of the ν_{am} bands [1–4]. In the cases where the synthetic polymers contain C=O groups, the interactions and local orientations of the C=O groups can be discussed by monitoring their bands in question [5–11]. It has been considered that two major mechanisms cause a wavenumber shift of the $\nu_{C=O}$ and ν_{am} bands: hydrogen bonding [12, 13] and transition dipole coupling [14–17]. Hydrogen bonding is a donor-acceptor interaction specifically involving a hydrogen atom. In general, a hydrogen bond between X–H and Y, where X is a more electronegative atom and then H and Y have a lone pair of electrons or π electrons, causes a wavenumber shift in the vibrational band associated with X–H and Y groups. The shift in the X-H stretching band is induced by the electrostatic interaction [18, 19] or hyperconjugation [20]. Since the C=O groups can behave as a proton acceptor, the $\nu_{C=O}$ and ν_{am} bands can be used for studying the hydration of polymers [6–10]. On the other hand, it is known that an infrared active vibration can couple via the transition dipole to the same vibration in a neighboring molecule if some degree of short-range order exists due to the large permanent dipole moments of the molecules [14–17]. This causes a noncoincidence of wavenumbers of the IR, isotropic Raman, and anisotropic Raman components in a vibrational band, called noncoincidence effect. Therefore, the orientation of C=O groups has been studied in terms of the noncoincidence effect [4,5].

In the previous paper [21], we reported the interaction between various solvents and the C=O groups of poly(*N*,*N’*-dimethylacrylamide) (pNdMA) or poly(*N*,*N’*-diethylacrylamide) (pNdEA) studied by IR spectroscopy. It is very interesting to explore the solvation of pNdEA from the molecular level, because the polymer shows the thermo-responsiveness in solutions. In several solvents, the shape and peak wavenumber of the $\nu_{C=O}$ band of those polymers deviate from those expected from the experimental results of the monomer model. In some cases, the $\nu_{C=O}$ envelope of the polymer in solutions contains a new band, which is not observed for the monomer model. To explain these characteristic bands for polymer systems, we have to consider the following factors: the accessibility of solvent to the polymer chain (the effect of a steric hindrance on the solvation of the C=O groups incorporated in the polymer chain) and the dipole interactions among the neighboring C=O groups.

The effect of hydrogen bonding on the $\nu_{C=O}$ band of NdMA was minutely investigated in the previous paper [21]. In the present study, therefore, we have focused on the effects of dipole interactions on the wavenumber shift of *N,N'*-dimethylacetamide (NdMA), which can be a model of the side chains of pNdMA and pNdEA. The first systematic report for the noncoincidence effect in NdMA was given by Purkayastha and Kumar [22]. The $\nu_{C=O}$ wavenumber of the isotropic Raman component (ν_{iso}) was lower by ca. 13 cm^{-1} than that of the anisotropic Raman component (ν_{aniso}). They revealed that the wavenumber difference ($\delta\nu = \nu_{aniso} - \nu_{iso}$) decreases with decreasing the concentration of NdMA in C_6H_6, $CHCl_3$, CH_3CN, and CCl_4, indicating that the interaction between solvent and NdMA is larger than that among NdMA molecules in a dilute solution (the mole fraction of NdMA is around 0.05). Thomas and Jones [15] investigated the effects of density on $\delta\nu$ and examined theoretical models of the noncoincidence effect proposed by McHale [23, 24] and Logan [25]. They clarified that the $\delta\nu$ value marginally increases with increasing density of the neat liquid. On the other hand, IR spectra of NdMA in concentrated solutions have not been systematically studied in detail. In the present study, we investigate the concentration dependences of both IR and Raman bands due to the $\nu_{C=O}$ mode in order to establish the assignment of IR bands for the $\nu_{C=O}$ band of NdMA in a condensed phase. The analysis of the $\nu_{C=O}$ band of NdMA in condensed phases is helpful to estimate the effect of the intramolecular interaction between neighboring C=O groups on the $\nu_{C=O}$ bands of pNdMA and pNdEA.

Experimental

NdMA was purchased from Aldrich and purified by distillation. Cyclohexane, *n*-hexane (∞ pure grade, WAKO), and CCl_4 (Aldrich) were dried by use of molecular sieves (4A 1/16, Aldrich). All samples were handled in a hand-made globe box under N_2 atmosphere.

IR spectra of NdMA were measured at room temperature (ca. 298 K) by using a Bruker IFS 66V spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector, in which 256 scans were co-added at a resolution of 2 cm^{-1} for a dilute solution and 4 cm^{-1} for a concentrated solution. The CaF_2 cells with 0.006, 0.05 and 0.51 mm of the path length were used to obtain an adequate IR signal under each experimental condition.

Raman spectra were recorded at room temperature (ca. 298 K) by using a JASCO NRS-2100 Raman spectrometer equipped with a CCD detector (Prinston Instrument LN/CCD-1100 PBUVAR). The excitation wavelength of Raman scattering was 514.5 nm from an Ar ion laser (Spectra-Physics 2016). The spectral resolution and laser power at the sample position were 4 cm^{-1} and 200 mW, respectively. Both polarized (I_{VV}) and depolarized (I_{VH}) scattering were measured, and the isotropic spectra were calculated in the usual way ($I_{iso}(\nu)=I_{VV}(\nu) - (4/3)I_{VH}(\nu)$). The anisotropic spectra is assumed to be same with $I_{VH}(\nu)$ ($I_{aniso}(\nu)=I_{VH}(\nu)$).

Nonlinear curve fittings were performed by software composed by one of the authors (Y.K.) [26]. The Levenberg-Marquardt algorithm [27] for a non-linear least square method was used for the curve fitting procedure. The position and number of the peaks used in the curve fitting were estimated by third derivative, and the shape of the decomposed band was assumed to be a Voigt functions. Third derivatives were calculated by the Savitzky-Golay method [28].

Results and Discussion

Raman and IR spectra for a neat liquid of NdMA. Figure 1A shows the $\nu_{C=O}$ bands in the isotropic and anisotropic Raman spectra for the neat liquid of NdMA. The inset of Figure 1A represents Raman I_{VV}

and I_{VH} spectra. The depolarization ration $\rho = I_{VH}/I_{VV}$ is estimated to be ca. 0.2 at around 1634 cm^{-1}, indicating that the 1634 cm^{-1} band is due to a totally symmetric vibration. On the other hand, the ρ value near 1650 cm^{-1} is estimated to be ca. 0.6. The isotropic Raman component is certainly asymmetric to the high-wavenumber side. This phenomenon was also reported for *N,N'*-dimethylformamide (NdMF), which has a very similar chemical structure to NdMA [29, 30]. The peak wavenumber of the isotropic Raman component is observed at 1634 cm^{-1}, whereas that of the anisotropic one appears at 1649 cm^{-1}. On the other hand, the first moments of the aniso- and isotropic components are estimated to be 1648.3 and 1637.5 cm^{-1}, indicating $\delta\nu$ = 10.8 cm^{-1}. These values are in good agreement with that those reported previously [15, 22]. For NdMF, the $\delta\nu$ value determined to be 14.7 cm^{-1} in the neat liquid [29, 30], indicating that the noncoincidence effect observed in NdMA is smaller than that in NdMF. Both NdMA and NdMF have comparable dipole moment derivatives for the symmetric C=O stretching vibration [31] and comparable permanent dipole moments (μ_{NdMA} = 3.80 D [32], μ_{NdMF} = 3.82 D [33]). The density and the dielectric constant of their neat liquids are also similar to each other [33]. Therefore, the difference of $\delta\nu$ between NdMA and NdMF may be attributed to the microscopic orientational order [23-25].

When the dipole interaction leads to orientational order between two polar molecules, the transition-dipole coupling gives rise to two vibrations of the pair: an in-phase and an out-of-phase vibration. Only the in-phase vibration is active in the isotropic Raman spectrum, whereas both components are active in the IR and anisotropic Raman spectra. The $\delta\nu$ value, which is defined as the difference between the first moments of the aniso- and isotropic Raman bands, indicates that NdMA in the neat liquid interacts with each other through the permanent dipoles and a local orientation of the molecules is induced. When $\delta\nu > 0$, the side-by-side antiparallel orientation and/or the head-to-head orientation of the transition dipole moment prevail. Since the positive values for $\delta\nu$ are obtained for both NdMA and NdMF systems, we concluded that the molecules have a similar microscopic orientation in their neat liquid. By comparing the absolute value of $\delta\nu$, however, we inferred that the degree of orientation for NdMA may be lower than that for

NdMF.

The IR and anisotropic Raman spectra contain contributions from both the in-phase and out-of-phase vibrations. Thus, it is expected that the $\nu_{C=O}$ envelopes of NdMA in these spectra consist of multiple components. As seen in Figure 1B, the shape of IR and anisotropic Raman bands is similar to each other. The IR spectra could be satisfactorily fitted by three bands at 1610, 1645, and 1661 cm^{-1} as shown in Figure 2. We uses symmetric functions for the decomposition based on the empirical method proposed by Shelley and Yarwood [34], in which it is assumed that an asymmetric band shape can also be reproduced by the sum of symmetric functions. Mortensen et al. have reported that IR and anisotropic Raman bands with the $\nu_{C=O}$ mode for neat formamide consist of at least two components [35]. They suggested that the low-wavenumber component is due to the hydrogen-bonded molecules and the high-wavenumber component arises from a non-hydrogen bonded monomer, because fromamide can form an intermolecular C=O···H-N hydrogen bond in the neat liquid. The anisotropic profile for the neat NdMF liquid also seems to consist of two independent band [29, 30]. Several research groups pointed out that a weak (O=)C-H···O hydrogen bond can be formed between pairs of NdMF molecules [36]. On the other hand, a pair of NdMA molecules may not form a hydrogen bond. It is, therefore, inferred that the two bands near 1645 and 1661 cm^{-1} in the IR and anisotropic Raman spectra arise from the in-phase and out-of-phase $\nu_{C=O}$ vibrations. The first moment of the decomposed band for the in-phase $\nu_{C=O}$ vibration at 1645 cm^{-1} is higher by ca. 7 cm^{-1} than that of the isotropic Raman profile. It is possible that the bands at 1645 and 1610 cm^{-1} comprise a continuous profile with the asymmetry to the lower wavenumber band.

Changes in the $\nu_{C=O}$ Band of NdMA in Solutions by Dilution. The Raman and IR spectra for the neat liquid of NdMA revealed that the dipole interaction creates a local orientational order of NdMA molecules. The local order of NdMA should be destroyed in the mixture with nonpolar solvents. Figure 3 shows the concentration dependence in the $\nu_{C=O}$ vibration region of Raman I_{VV} and IR spectra for NdMA in cyclohexane. In both spectra, the $\nu_{C=O}$ envelopes drastically change by dilution. The peak of the IR band shifts from 1645 to 1670 cm^{-1} with the decreases in χ from 1.0 to 0.048. Note that in the IR band at χ = 1.00 a shoulder is observed at around 1662 cm^{-1} (see the second derivative spectrum shown in Figure 3B). The similar tendency is observed for the changes in the Raman spectra: the peak is located at 1673 cm^{-1} at χ = 0.048 (0.47 M) and a small band is detected at around 1650 cm^{-1} as a shoulder (Figure 3D). The existence of the band near 1650 cm^{-1} can also be interpreted as an asymmetric of the $\nu_{C=O}$ envelope to the low-wavenumber side. For NdMF-CCl_4 mixture, for example, it was reported that the asymmetry of the isotropic $\nu_{C=O}$ profile moves from the higher to the lower wavenumber side by dilution [29, 37]. It is generally expected that the IR and both Raman bands coincide at infinite dilution [15, 22]. At χ = 0.048, the peak wavenumber and shape of the $\nu_{C=O}$ envelope in the Raman spectrum are almost identical with those in the IR spectrum. This suggests that the dipole interaction among NdMA is weakened and the transition dipole coupling disappears by dilution with cyclohexane. This observation is in good agreement with the result reported previously [15].

The spectral changes shown in Figure 3 indicate that the vibrational coupling between molecules diminishes with decreasing concentration of NdMA in cyclohexane. The change in the $\nu_{C=O}$ wavenumbers in the Raman I_{VV} spectra reflect the variation of the orientational order and the solvation of NdMA. Figure 4 depicts the concentration dependences of the two $\nu_{C=O}$ wavenumbers in the Raman I_{VV} spectra (ν_h and ν_l) measured for the cyclohexane and CCl_4 solutions. The wavenumbers were estimated by third derivatives of the spectra. The concentration dependences of ν_h and ν_l for the cyclohexane solution of NdMA are clearly deferent from those for the CCl_4 solution. In CCl_4, the ν_h band does not show a wavenumber shift in the range $0.16 \le \chi \le 1.00$, whereas the ν_l wavenumber monotonically increases. In the cyclohexane solution, both the ν_h and ν_l bands show a higher wavenumber shift. Although cyclohexane and CCl_4 have similar dielectric constants (2.02–2.24) [33], the solvation effect on the $\nu_{C=O}$ bands is clearly different from each other. To clarify the solvation effect of CCl_4 on the $\nu_{C=O}$ band, we measured IR spectra of NdMA in a highly diluted solution.

Changes in the $\nu_{C=O}$ wavenumber in a highly diluted solution. Figure 5 shows the $\nu_{C=O}$ envelope in IR spectra of NdMA in cyclohexane and *n*-hexane solutions with the concentrations less than 0.5 M. It is evident that the $\nu_{C=O}$ envelope of NdMA is unimodal and asymmetric to the low-wavenumber side in the 0.33 M (0.46 M) cyclohexane (*n*-hexane) solution. When the concentration of NdMA decreases, the peak wavenumber of the band slightly shifts to a higher wavenumber and the band shape becomes symmetric. The band shape does not change at the concentrations below 0.023 M. For the *n*-hexane solution, a similar trend is observed (Figure 5B). These results imply that the asymmetric shape of the $\nu_{C=O}$ band observed in *n*-hexane and cyclohexane with the concentrations above 0.023 M is associated with the intermolecular interaction among NdMA molecules, which vanishes at around 0.023 M. Note that the average distance between the NdMA molecules in the 0.023 M solution is estimated to be about 3.5 nm.

The concentration dependence of the $\nu_{C=O}$ envelope for the CCl_4 solution of NdMA, which is shown in Figure 6A, is deviated from those for the cyclohexane and *n*-hexane. Two bands near 1660 and 1650 cm^{-1} are clearly observed at a concentration of 0.47 M. The relative intensity of the band near 1650 cm^{-1} gradually decreases by dilution. Further dilution causes no remarkable spectral change as shown in the inset of Figure 6A. The band at around 1650 cm^{-1} may contain a contribution from the intermolecular interaction among NdMA molecules. This is again an indication that the intermolecular interaction among NdMA disappears at around 0.023 M in nonpolar solvents. However, the shape and peak wavenumber of the $\nu_{C=O}$ band for the highly diluted CCl_4 solution are significantly different from those for the cyclohexane and *n*-hexane solutions. The peak wavenumber of the $\nu_{C=O}$ band observed for the 0.023 M CCl_4 solution is located at 1662 cm^{-1}, while those for the 0.023 M cyclohexane and *n*-hexane solutions appear at 1673–4 cm^{-1}. Moreover, the $\nu_{C=O}$ band observed in the CCl_4 solution is significantly broader than those in cyclohexane and *n*-hexane. Surprisingly, the $\nu_{C=O}$ envelope of NdMA for the highly diluted CCl_4 solutions seems to consist of at least two bands. Figure 6B shows the second derivative and curve fitting results for the $\nu_{C=O}$ envelope of NdMA in CCl_4 at 0.0013 M, indicating that the two bands exist at 1662 and 1652 cm^{-1}. As described in the previous section, the Raman noncoincidence effect is not observed in this concentration range. That is, the origin of these two bands may not be concerned with the transition dipole coupling, which arises from the off-diagonal terms of vibrational Hamiltonian of coupled oscillator systems [30]. To explain the existence of two $\nu_{C=O}$ bands for NdMA in CCl_4 at 0.0013 M, the diagonal effect should be considered, which is due to the molecular interaction between NdMA and CCl_4.

Compared with the vibrational wavenumber of the $\nu_{C=O}$ band in gas phase [38], the wavenumber is lower by 28 cm^{-1} for the CCl_4 solution and by 16–17 cm^{-1} for the cyclohexane and *n*-hexane solutions at a concentration below 0.023 M. The result suggests that the low-wavenumber shift of the $\nu_{C=O}$ band in CCl_4 is larger than that expected by the dielectric constant of CCl_4 (the dielectric constant of *n*-hexane, cyclohexane, and CCl_4 is 1.89, 2.02, and 2.24, respectively.). This large shift may be concerned with the fact that the atomic polarizability of chlorine is larger than that of carbon [33]. In fact, it has been suggested by quantum chemical calculations that the low-wavenumber shift of the $\nu_{C=O}$ band of acetone observed for the CCl_4 solution is attributed to the atomic quadrupoles of the chlorine atoms generated by the covalent bonds with the carbon atom [39]. However, the existence of the two $\nu_{C=O}$ bands of NdMA in the highly diluted CCl_4 solution cannot be explained by the effect of atomic quadrupoles of the chlorine atoms of CCl_4. There are two possibilities to understand the splitting of the $\nu_{C=O}$ band of NdMA in the highly diluted CCl_4 solution; a heterogeneous solvation of NdMA and/or a coordination of NdMA through interactions between NdMA and CCl_4. To examine these possibilities, further experiments may be needed with the aid of quantum chemical calculations.

Effects of Dipole Interaction and Solvation on the $\nu_{C=O}$ Band of NdMA.

Referring to the experimental results, we divide the concentration region of NdMA-nonpolar solvent mixtures into three for explaining the spectral changes: $c > 0.47$ M, 0.47 M $\geq c > 0.0023$ M, $c \leq 0.0023$ M. In $c > 0.47$ M, the change in the $\nu_{C=O}$ band is mainly caused by the transition dipole coupling. The disappearance of noncoincidence effects may be concerned with a drastic change in the dielectric constant of the mixture. Since NdMA has a large dielectric constant of 38.85 [33], the dielectric constant of the mixtures is strongly dependent upon the concentration of NdMA. In the concentration range below 0.47 M, the dielectric constant of the mixture is very close to that of nonpolar solvent [40]. In 0.47 M $\geq c > 0.0023$ M, NdMA molecules weakly interact with each other, and this interaction gives rise to a minor band at a lower wavenumber side of the $\nu_{C=O}$ band. When $c \leq 0.0023$ M, the interaction among NdMAs become weak, and the $\nu_{C=O}$ band does not show a concentration dependence. The solvation effect of $CC1_4$ on the $\nu_{C=O}$ band of NdMA is significantly different from those of cyclohexane and *n*-hexane. The characteristic solvation effect of CCl_4 may also occur in the higher concentration range, which causes the difference between the $\nu_{C=O}$ wavenumbers observed for the cyclohexane solution and those for the CCl_4 solution as seen in Figure 4.

Conclusion.

The effects on dipole interactions among NdMA molecules on the $\nu_{C=O}$ band have been investigated. For the neat liquid of NdMA, the noncoincidence of the $\nu_{C=O}$ wavenumbers in IR, isotropic and anisotropic Raman wavenumbers is evident. The $\delta\nu$ value of 10.8 cm^{-1} was obtained, indicating that NdMA in the neat liquid interacts with each other through the permanent dipoles and a local orientation (the side-by-side antiparallel orientations and/or the head-to-head orientations) of the molecules is induced. The concentration dependence of the $\nu_{C=O}$ band of NdMA has been investigated for the cyclohexane, *n*-hexane, and CCl_4 solutions. At a concentration of 0.45 M in the cycrohexane solution of NdMA, the noncoincidence effect almost disappears and the $\nu_{C=O}$ envelopes in both the Raman and IR spectra are asymmetric to the low-wavenumber side. When the concentration of NdMA decreases from 0.33 to 0.023

M, the peak of the band slightly shifts to a higher wavenumber and the band shape becomes symmetric. The band shape does not show any changes at a concentration range below 0.023 M. These results suggest that the asymmetric shape of the $\nu_{C=O}$ band observed for the 0.46 M *n*-hexane and 0.33 M cyclohexane solutions is associated with the intermolecular interaction among NdMA molecules, which vanishes at 0.023 M. The dipole coupling, which is observed in the highly concentrated solutions, may become weak or absence from the intermolecular-interacting NdMAs in the concentration range of $0.33 \geq c$. The interesting result will be the subject of the theoretical study on the intermolecular interaction. In the CCl_4 solution, changes in the $\nu_{C=O}$ band are similar to those observed for the *n*-hexane and cyclohexane solutions. However, the shape and peak wavenumber of the $\nu_{C=O}$ band observed in a highly diluted solution (≤ 0.023 M) are different from those observed in the other nonpolar solvents. The peak wavenumber of the $\nu_{C=O}$ band observed for the 0.023 M CCl_4 solution is estimated to be 1662 cm^{-1}, while those for the cyclohexane and *n*-hexane solutions appear at 1673–4 cm^{-1}. Compared with the vibrational wavenumber of the $\nu_{C=O}$ band in gas phase, the wavenumber is lower by 28 cm^{-1} for the CCl_4 solution and by 16–17 cm^{-1} for the cyclohexane and *n*-hexane solutions in the concentration range lower than 0.023 M. Moreover, the $\nu_{C=O}$ envelope of NdMA in the highly diluted CCl_4 solutions consists of at least two bands at 1662 and 1652 cm^{-1}. These results suggest that the solvation effect of CCl_4 on the $\nu_{C=O}$ envelope of NdMA is more complicated than that expected from the dielectric constant of the solvent. The characteristic solvation of CCl_4 may also affect the wavenumbers of the aniso- and isotropic Raman bands at a higher concentrated solution of NdMA.

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Figure Legends

Fig 1. (A) Isotropic (solid line) and anisotropic (dotted line) Raman components of the $\nu_{C=O}$ vibration for the neat liquid of NdMA. The inset depicts Raman I_{VV} and I_{VH} spectra. (B) Normalized $\nu_{C=O}$ bands in the anisotropic Raman (open circle) and IR (solid line) spectra.

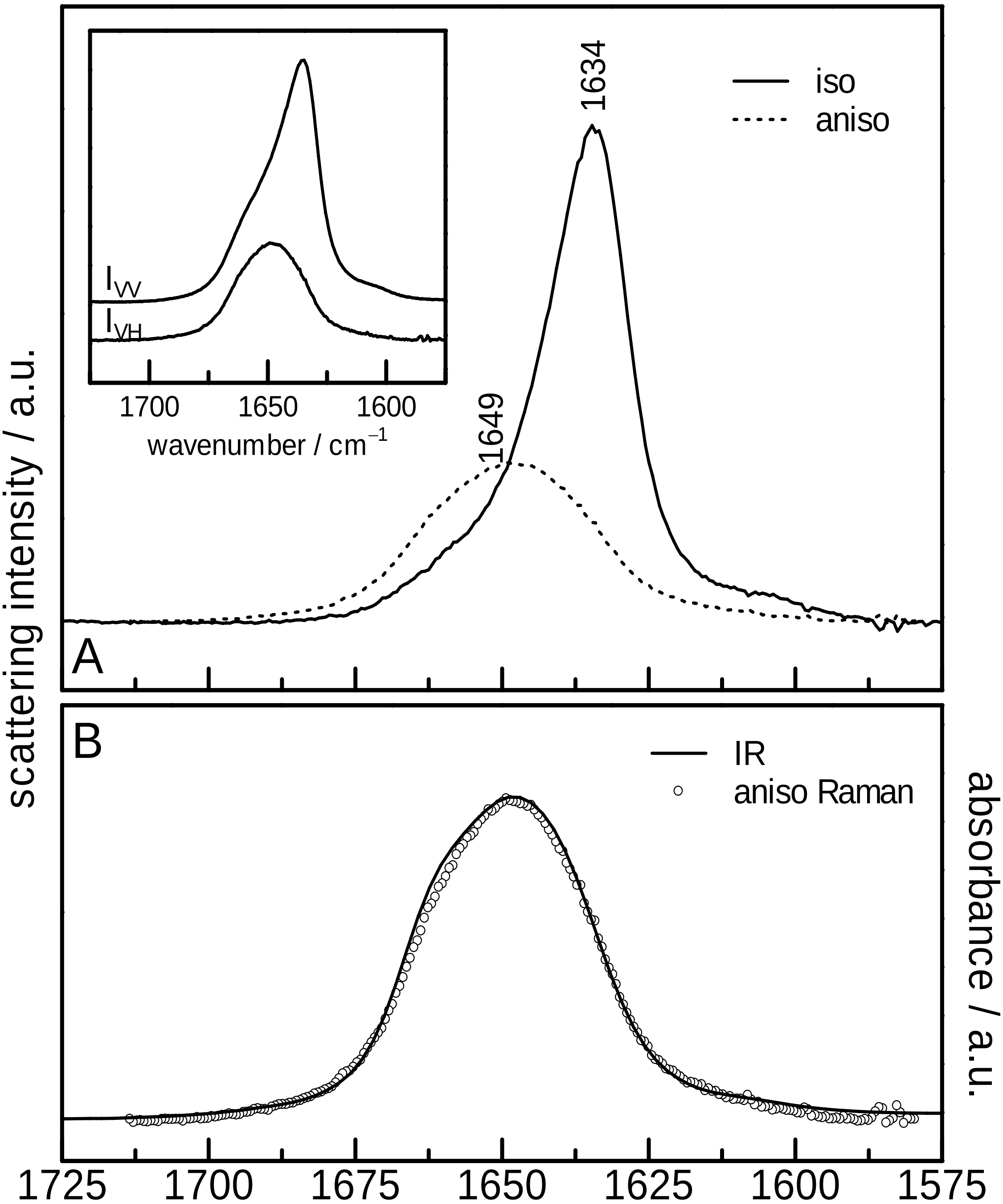
Fig 2. The $\nu_{C=O}$ envelope in the IR spectrum for the neat NdMA liquid (open cirvle) together with the curve fitting result (solid lines).

Fig 3. Concentration dependence of the $\nu_{C=O}$ band in IR spectra (A) and their second derivatives (B). The changes in Raman I_{VV} spectra (C) and their second derivatives (D). The mole fraction of NdMA, χ, is varied from 0.048 to 1.00.

Fig 4. The ν_h (filled symbol) and ν_l (open symbol) wavenumbers in cyclohexane (circle) and CCl_4 (square) plotted against χ, which are estimated by third derivative of the $\nu_{C=O}$ envelope in Raman I_{VV} spectra.

Fig 5. (A) The $\nu_{C=O}$ band in IR spectra of the cyclohexane solution of NdMA in a concentration range from 0.023 to 0.33 M. The inset represents the IR spectra at 0.023 and 0.0055 M. (B) The $\nu_{C=O}$ band in IR spectra of the *n*-hexane solution of NdMA in a concentration range from 0.017 to 0.46 M.

Fig 6. (A) The $\nu_{C=O}$ band in IR spectra of the CCl_4 solution of NdMA in a concentration range from 0.013 to 0.47 M. The inset represents the IR spectra at 0.023 and 0.0044 M. (B) The second derivative and curve fitting result for he $\nu_{C=O}$ band in IR spectra of NdMA observed in CCl_4 at 0.0013 M.



1634
iso
aniso
1649
I_VV
I_VH
1700
1650
1600
wavenumber / cm–1
A
B
IR
aniso Raman
scattering intensity / a.u.
absorbance / a.u.
1725
1700
1675
1650
1625
1600
1575
wavenumber / cm–1

Figure 1.

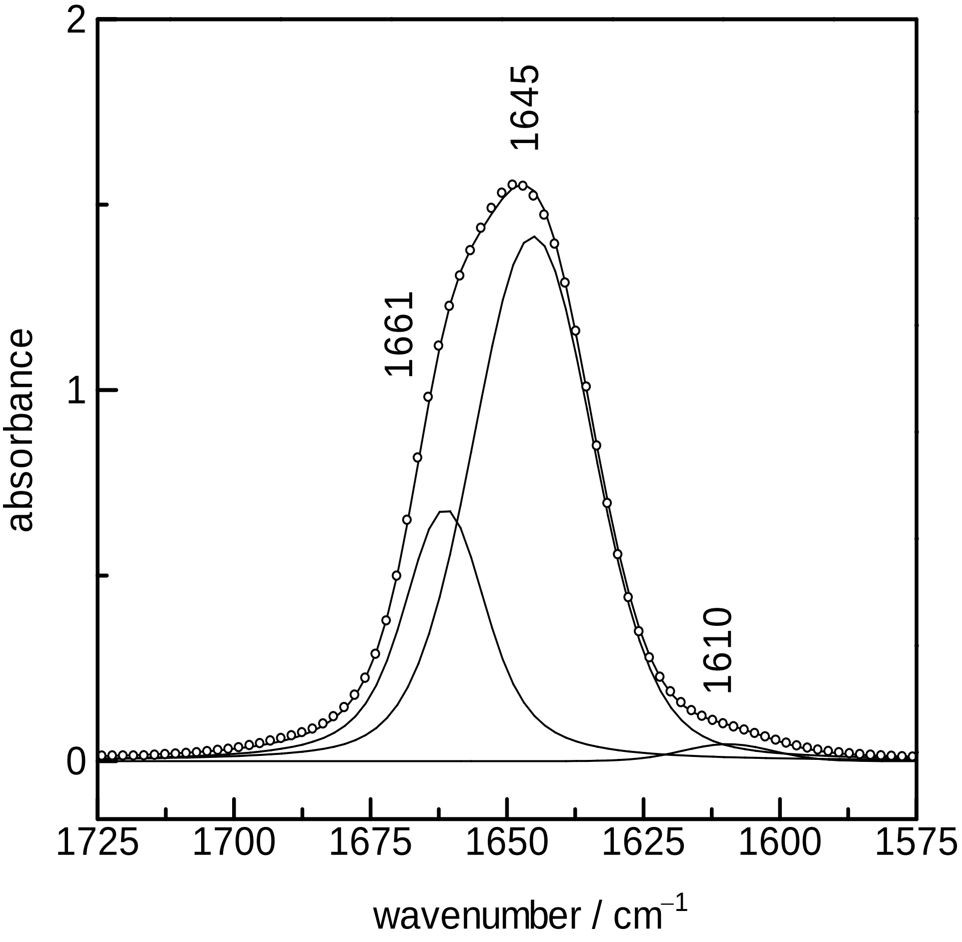

2
1
0
absorbance
1645
1661
1610
1725
1700
1675
1650
1625
1600
1575
wavenumber / cm^{-1}

Figure 2

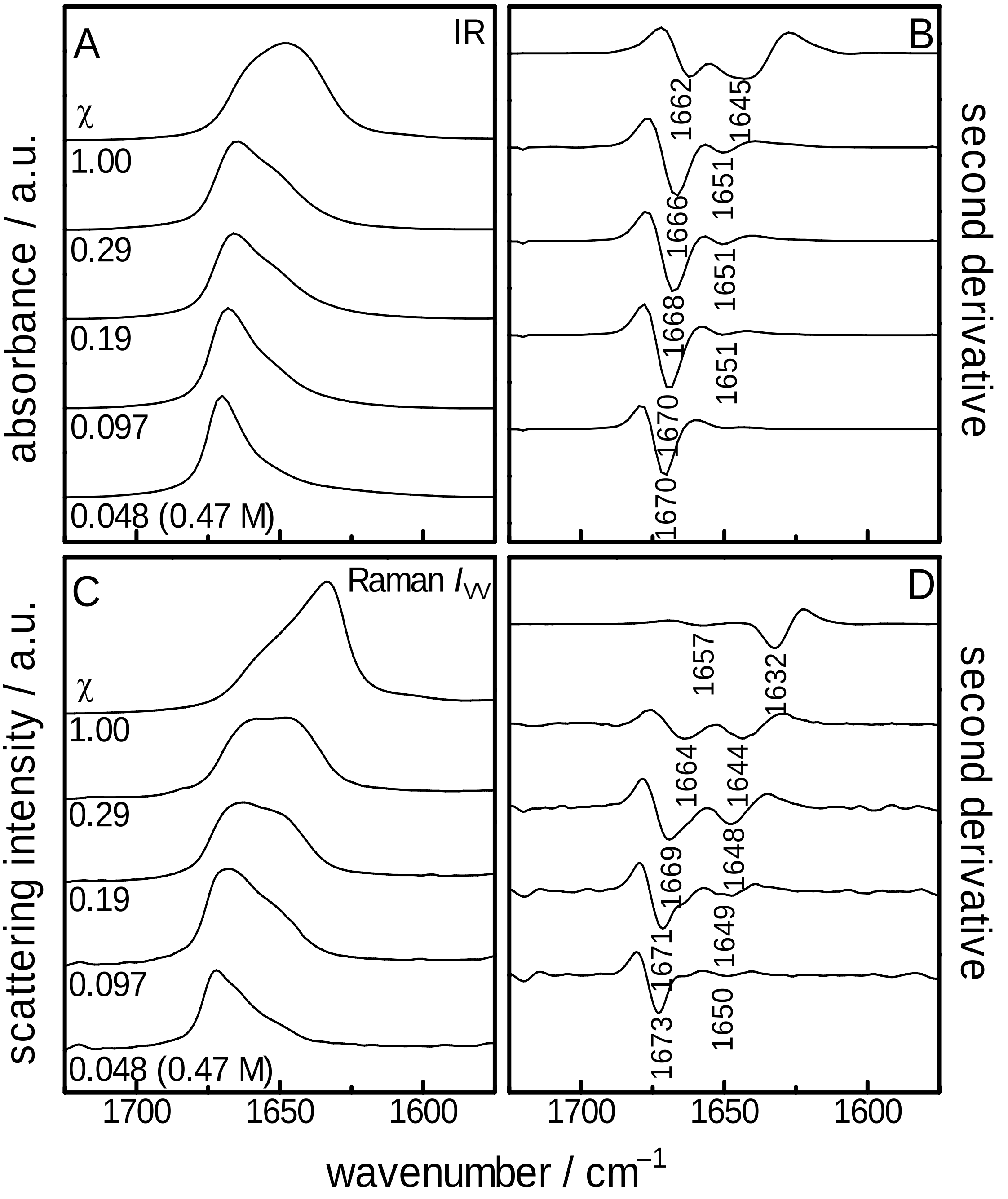

A
IR
χ
1.00
0.29
0.19
0.097
0.048 (0.47 M)
absorbance / a.u.
B
1662
1645
1666
1651
1668
1651
1670
1651
1670
second derivative
C
Raman I_{VV}
χ
1.00
0.29
0.19
0.097
0.048 (0.47 M)
scattering intensity / a.u.
D
1657
1632
1664
1644
1669
1648
1671
1649
1673
1650
second derivative
1700
1650
1600
1700
1650
1600
wavenumber / cm^{-1}

Figure 3

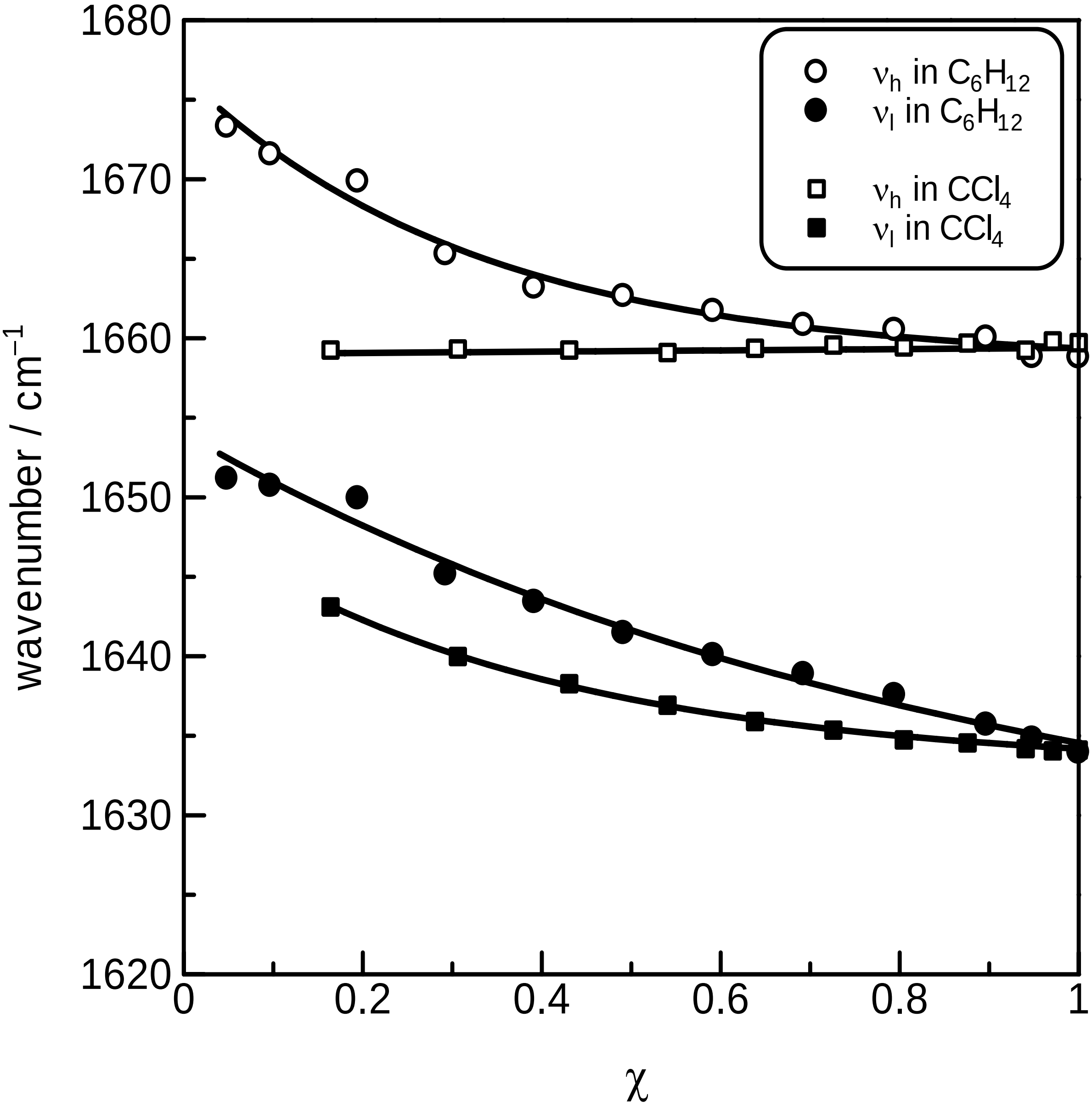

1680
1670
1660
1650
1640
1630
1620
0
0.2
0.4
0.6
0.8
1
wavenumber / cm^{-1}
χ
ν$_h$ in C$_6$H$_{12}$
ν$_l$ in C$_6$H$_{12}$
ν$_h$ in CCl$_4$
ν$_l$ in CCl$_4$

Figure 4

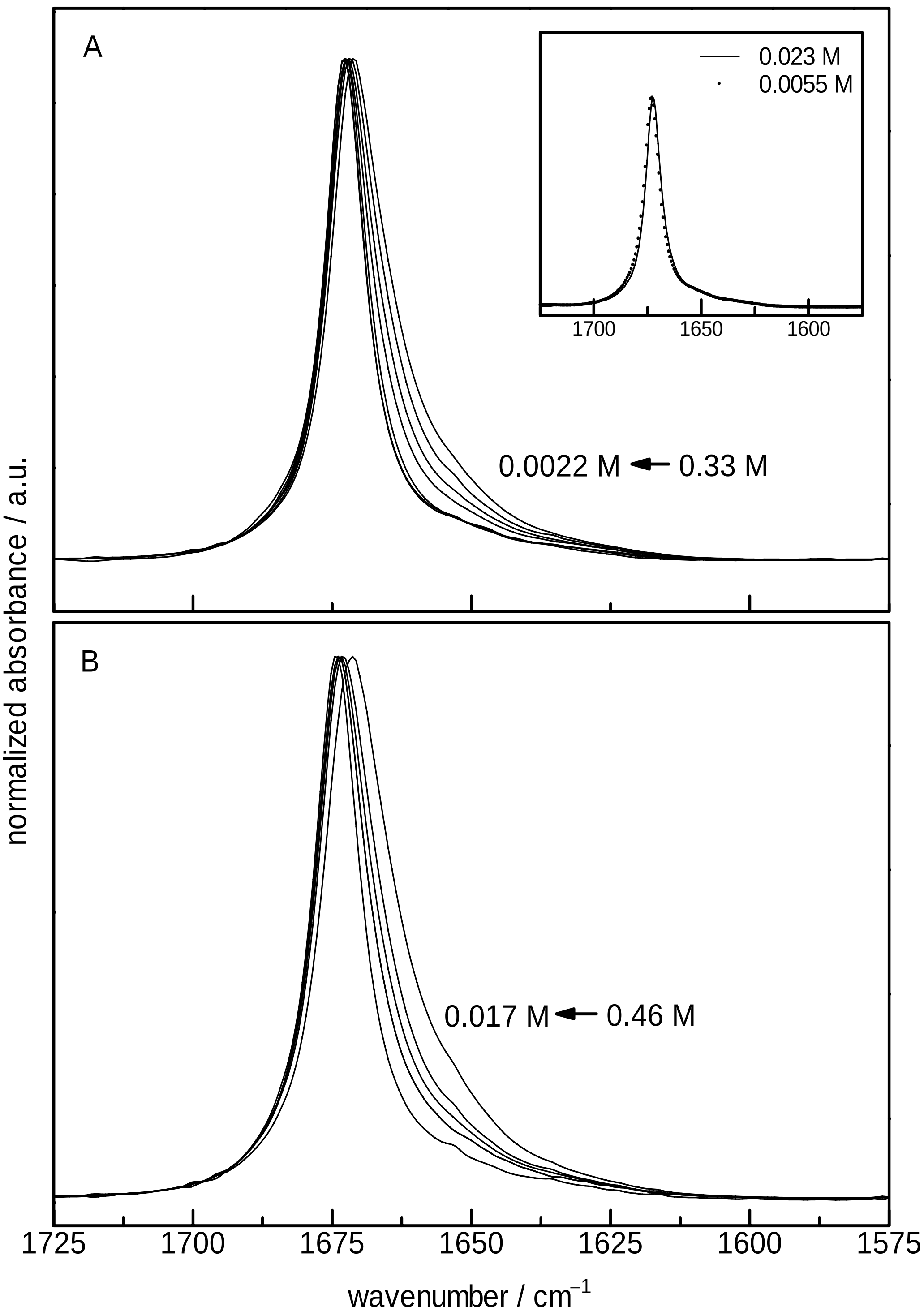

A
0.023 M
0.0055 M
1700
1650
1600
0.0022 M
0.33 M
B
0.017 M
0.46 M
normalized absorbance / a.u.
1725
1700
1675
1650
1625
1600
1575
wavenumber / cm^{-1}

Figure 5

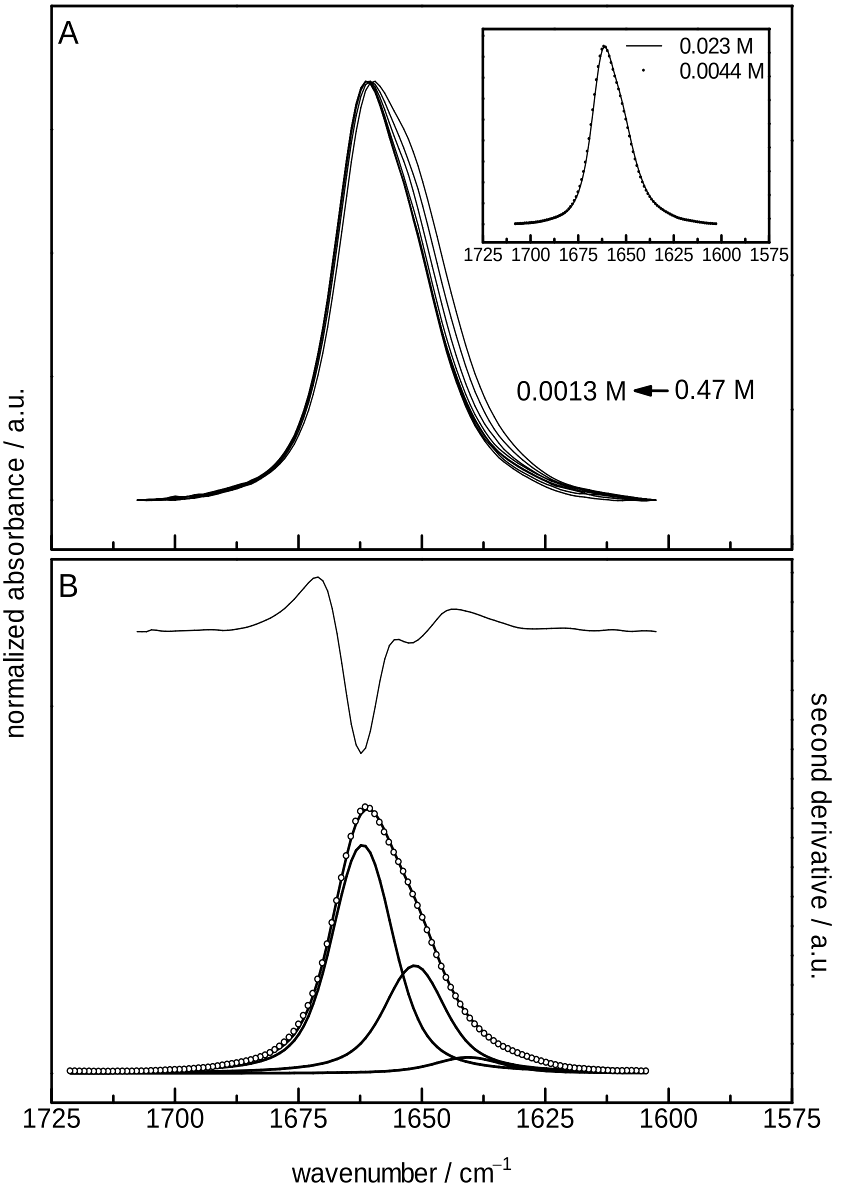

A
0.023 M
0.0044 M
1725 1700 1675 1650 1625 1600 1575
0.0013 M ← 0.47 M
normalized absorbance / a.u.
B
second derivative / a.u.
1725
1700
1675
1650
1625
1600
1575
wavenumber / cm^{-1}

Figure 6