

Is there a correlation between phase transitions of phenylacetylene in liquids and frozen matrices and vibrational dynamics?

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Abstract

Raman spectra of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile and the $\nu_s(\text{C}\equiv\text{C})$ stretching mode of phenylacetylene (PA) in acetonitrile liquid solutions and frozen matrices as a function of temperature have been recorded. Mechanisms of vibrational relaxation and band broadening in liquid and solid phases have been discussed. One of the goals of the paper is to develop the correlation between the phase transitions and mechanisms of vibrational dynamics. The vibrational dephasing of the $\nu_s(\text{C}\equiv\text{C})$ mode of PA and the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile in solution seems to be governed by the coupling of the vibrational modes to internal rotations of the methyl group CH_3 of acetonitrile. The behaviour around the phase transitions between 183 and 218 K with the sudden increase in bandwidths was explained as the result of the changes in the mechanisms of the internal rotation from hindered rotation in periodic potential to almost free rotation for higher temperatures. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Spontaneous and stimulated Raman spectroscopy both in the frequency domain and time domain supply valuable dynamical information on vibrations in the liquid phase and glasses as well as phonons and vibrons in crystals.

Numerous publications have focused on theoretical approaches to understand the mechanisms of

vibrational dynamics in liquids [1–8] and crystals [9–11]. A number of experiments were carried out in liquids and crystals to deduce the relevant relaxation mechanisms. A number of papers have addressed the comparison between the mechanisms of vibrational dynamics obtained from experimental data for liquids and crystals and those predicted from the existing theories [11–14]. For most liquids the existing theories of vibrational dephasing are able to predict reasonably well the experimental results.

In contrast to liquids and crystals there is a limited number of experimental data on vibrational dynamics in glasses [15–17]. The experimental data for glasses have been compared with the predictions of

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the existing theories for liquids [15–17] or the Vogel–Tammann–Fulcher equation for structure relaxation near the glass transition [15,18,19].

A short summary concerning the vibrational dynamics found in liquids seems to be helpful for further discussion:

(1) Vibrational lines are usually homogeneously and inhomogeneously broadened. The contribution from homogeneous and inhomogeneous broadening varies with the vibrational modes, solvent environment due to intra- and intermolecular interactions and thermodynamic state.

(2) Pure vibrational dephasing dominates the homogeneous line width at high temperatures.

(3) Vibration lifetime T_1 (vibrational energy relaxation) and orientational relaxation never dominates the homogeneous broadening but may make significant contributions at intermediate temperatures.

(4) Collisions-induced oscillator frequency perturbations, resonant energy transfer or solvent assisted intramolecular vibrational redistribution are responsible for ‘fast’ changes of the time-dependent frequency of the oscillator and homogeneous contribution to the bandbroadening.

(5) Concentration fluctuations and long-range electrostatic interactions are responsible for ‘slow’ changes and inhomogeneous contribution to the bandbroadening.

The picture that emerges from the studies on vibrational relaxation mechanisms in molecular crystals should be summarised as follows [12]:

(1) Lines of phonons and vibrons are frequently homogeneously broadened.

(2) The inhomogeneity appears in most systems as factor group splitting (Davydov effect) which is due to the different local symmetry of the molecules in the elementary cell.

(3) The inhomogeneity resulting from imperfections is less effective due to the delocalisation of the phonons. However, the imperfections may strongly affect the homogeneous relaxation processes.

(4) The loss of phase coherence described by the dephasing time T_2 depends on several mechanisms such as energy relaxation T_1 , pure dephasing T_2^* , intraband relaxation, and impurity scattering.

(5) At very low temperatures, where processes caused by thermal fluctuations disappear and the

population lifetime T_1 is the only source of homogeneous bandbroadening and therefore determines the total phase relaxation

$$\frac{1}{T_2} = \frac{1}{2T_1} \quad \text{for } T \rightarrow 0.$$

The picture of vibrational dynamics in glasses is much less clear as there is a limited number of experimental data and the existing theories of vibrational dephasing on the equilibrium liquid phase are not able to predict the results below the glass transition [15–17]. A description of vibrational dephasing below the glass transition does not exist yet and is clearly necessary. The results on vibrational dynamics in glasses, which have been obtained so far, may be summarised as follows:

(1) Some results show strong inhomogeneous broadening [15], while another data [16] indicate no contribution from inhomogeneous broadening at low temperatures below the glass transition.

(2) Some data demonstrate the existence of continuous T^2 temperature dependence [15] in the full temperature range, the other ones show discontinuous temperature dependence with strong deviation from the T^2 dependence [20].

(3) The vibrational energy relaxation T_1 dominates the homogeneous line width at lowest temperatures, orientational relaxation does not dominate in any temperature range, but makes non negligible contribution around the glass transition, at higher temperatures pure dephasing dominates the homogeneous line width [15].

(4) The experimental data [15–17,20] demonstrated that above the glass transition additional mechanism or modified vibrational dephasing mechanism turns on.

Temperature-dependent studies in a broad temperature range will become increasingly important in order to monitor vibrational dynamics going from isotropic liquid phase through liquid crystalline phase(s) to glassy or crystal solid state phases at low temperatures.

It will be very important to extend the existing studies on vibrational dephasing to a wider temperature range in order eventually to develop an understanding of the relation between vibrational dynamics and phase transitions like liquid–crystal,

liquid–glass, liquid–liquid crystal transitions at the molecular level.

One of the goals of the proposed work is to develop connections between the phase transitions and mechanisms of vibrational dephasing using as a model system phenylacetylene in acetonitrile. We have found [21] that this system provides the opportunity to monitor different phases from isotropic liquids through glassy plastic crystals, plastic crystals to crystals.

2. Results and discussion

The experimental details has been described in details in our previous paper of this issue [21].

The rather dramatic and sudden changes in line-shapes and widths with solvent and concentration reported in our previous paper [21] must reflect obviously changes in mechanisms of vibrational relaxation due to vibrational dephasing, structural reorganisation and phase transitions. To learn about mechanisms of vibrational dynamics we have monitored the Raman spectra of the stretching mode $\nu_s(\text{C}\equiv\text{C})$ of PA in acetonitrile and the response of the matrix using the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile as a probe in broad temperature range between 298 and 77 K. Temperature-dependent studies may help to find the correlation between the phase transitions and mechanisms of vibrational relaxation. It is well-known that some thermodynamic parameters like entropy, enthalpy or heat capacities show discontinuity as a function of temperature at a phase transition. Although the thermodynamic methods reveal the presence of phase transitions in a material, they are not able to give an insight into mechanisms governing these transitions. If we want to obtain the information at the molecular level we must use other techniques which measure quantities directly correlated with molecular parameters. The results presented in our previous paper [21] show that Raman spectroscopy is very sensitive to the changes in the intermolecular structure around the molecular oscillator and it may monitor reorganisation during transitions from the isotropic liquid phase through liquid crystalline phases with increasingly higher positional and reorientational order to the crystalline or glassy solid phases.

It will be very important to extend these concentration and solvent studies to a wider temperature range in order to find if parameters characterising vibrational dynamics (dephasing relaxation time or band width) show discontinuity at a phase transition. These studies will help to develop an understanding of the relation between phase transitions and vibrational relaxation mechanisms.

In Fig. 1 we have shown the Raman (VV component) band profiles of the stretching mode $\nu_s(\text{C}\equiv\text{C})$ of PA in acetonitrile as a function of temperature in the range between 293 and 77 K. We can see that the broad, structureless, asymmetric band observed in the liquid phase shows the dramatic change between 193 and 185 K and splits into three peaks at around 2105, 2110, and 2116 cm^{-1} .

In Fig. 2 we have shown the line width (FWHH—full width at half height) of the stretching mode $\nu_s(\text{C}\equiv\text{C})$ of PA in acetonitrile as a function of temperature in the range from 77 to 293 K for each component resulting from splitting into three sub-bands, respectively. The broad, structureless bands observed for PA at higher temperatures (Fig. 1) has also been deconvoluted into three components as the conclusion of our previous paper [21] which suggests

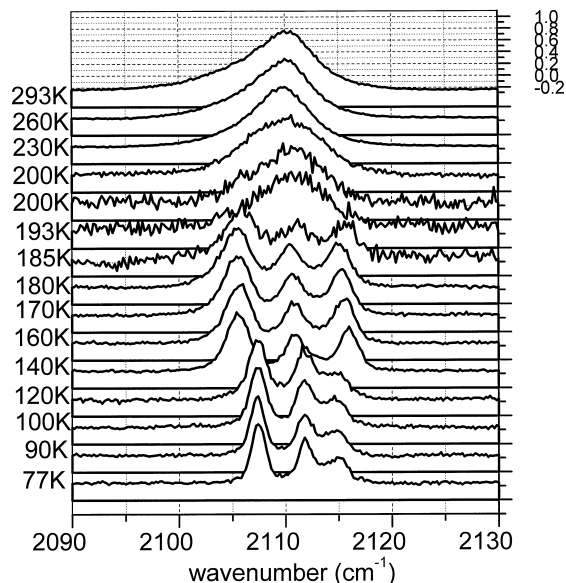


Fig. 1. VV Raman spectra of the $\text{C}\equiv\text{C}$ stretching mode of phenylacetylene in acetonitrile as a function of temperature for PA concentration $c = 0.95 \text{ mol/dm}^3$.

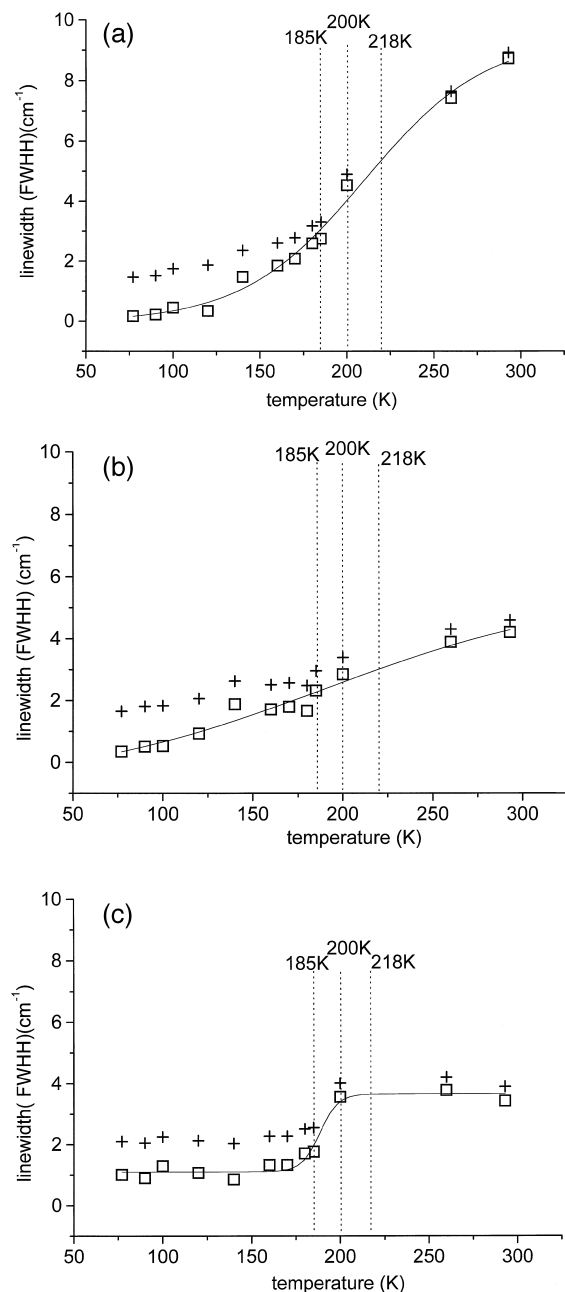


Fig. 2. VV Raman bandwidth $\Delta_{1/2}(\text{FWHH})$ of the $\text{C}\equiv\text{C}$ stretching mode of phenylacetylene in acetonitrile ($c = 0.95 \text{ mol/dm}^3$) as a function of temperature, + – experimental data, □ – experimental data after the slit correction according to Eq. (1), (a) peak at 2105 cm^{-1} , (b) peak at 2110 cm^{-1} , (c) peak at 2116 cm^{-1} .

that the substructure similar to that observed at low temperature persists in the liquid phase although the components are no longer resolvable. The best fit both for the broad band in liquid phase as well as for the three peaks after splitting was found to consist of three Gaussians. The results in Fig. 2 show the experimental line widths without any slit corrections and for comparison after the slit correction. We can see from Fig. 2 that each component shows monotonic gradual increase with temperature from 77 up to around 183 K and shortly after at around 200 K they demonstrate a rapid, significant increase. The most pronounced rise in the line width of about 6 cm^{-1} is observed for the component at 2105 cm^{-1} , which correlates very well with the interpretation from our previous paper, where we ascribed it to the $\nu_s(\text{C}\equiv\text{C})$ oscillator disturbed by H-bond between PA proton and π -electrons of the triple bond $\text{C}\equiv\text{N}$ of acetonitrile and/or $\text{C}\equiv\text{C}$ bond of PA molecules. For the components, which represent species that are not involved in H-bond the changes are much less dramatic: for the component at 2110 cm^{-1} the line width appears to increase in monotonic way without sudden changes between 183 and 200 K, while the component at 2116 cm^{-1} increases in apparently discontinuous manner with the observed rise of about 2 cm^{-1} between 183 and 200 K, which is small in comparison with the changes in the line width for the peak at 2105 cm^{-1} . The best fit of the experimental data in Fig. 2 are obtained with the Boltzmann function

$$\Delta_{1/2}(\text{FWHH}) = (A_1 - A_2) / [1 + \exp(T - T_0)/\Delta T] + A_2, \quad (1)$$

The fitting by the low-temperature power plus the Vogel–Tammann–Fulcher equation

$$\Delta_{1/2}(\text{FWHH}) = A_1 T^\alpha + A_2 \exp[-B/(T - T_0)], \quad (2)$$

which was suggested for dynamic processes near the glass transitions [15,18,19], is much worse than fitting by the Boltzmann function.

In Fig. 2 the characteristic temperatures at which the phase transitions occur are plotted obtained by the differential scanning calorimetry (DSC) measure-

ments from our previous paper [21] for PA in acetonitrile at the same concentration as for the results from Fig. 2. We have found a glass-like transition at 183 K from a crystalline to a plastic crystal and a plastic crystal–a glassy plastic crystal transition at 200 K followed by a melting from a glassy plastic crystal to isotropic liquid transition at 218 K [21]. Thus, the sudden line width changes for PA in acetonitrile correlate with the phase transitions. The maximum peak positions of the peaks at 2105 and 2116 cm^{-1} are also sensitive to the transitions at 183, 200 and 218 K (Fig. 3). There is another sudden shift at about 125 K. However, this temperature was beyond the DSC scans. However, the static frequency shifts are not of our concern here. Changes like these are not unique and were reported in the literature for the other systems, for example plastic crystals and glassy plastic crystals [13]. However, it is important to remember that the broadening of Raman lines is only the probe in order to rationalize the molecular mechanisms themselves by which solvent influence intramolecular dynamics. Knowing the magnitude of broadening at phase transitions is informative, but it does not tell us which kinds of motions by the solvent molecules are most efficient in dissipating vibrational energy or vibrational dephasing.

The Arrhenius plot of the line width versus temperature will help to estimate the activation energy ΔE of the vibrational relaxation mechanism. When

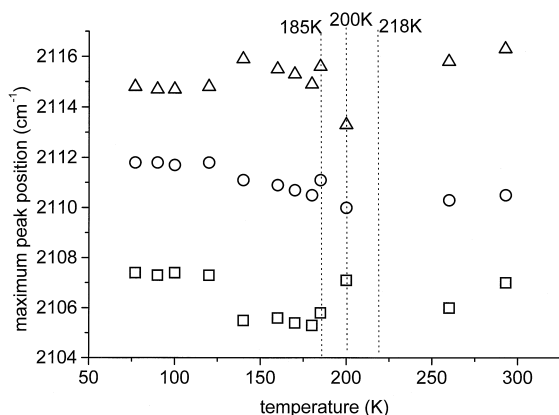


Fig. 3. VV Raman maximum peak positions of the $\text{C}\equiv\text{C}$ stretching mode of phenylacetylene in acetonitrile ($c = 0.95 \text{ mol/dm}^3$) as a function of temperature.

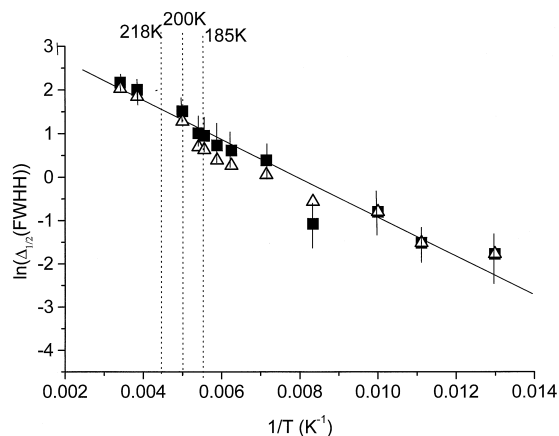


Fig. 4. Logarithm of the VV Raman bandwidth $\Delta_{1/2}(\text{FWHH})$ of the $\text{C}\equiv\text{C}$ stretching mode of phenylacetylene in acetonitrile ($c = 0.95 \text{ mol/dm}^3$) as a function of temperature: ■ – experimental data for the peak at 2105 cm^{-1} (fitting with 3 Gaussians, the slit correction according to Eq. (1) in Ref. [21]), Δ – experimental data (fitting with 3 Lorentzians, the slit correction obtained by subtracting the slit width from the experimental bandwidth).

an Arrhenius plot is linear, it indicates that only a single low energy mode is involved in the temperature dependence of the relaxation process, and the slope of the plot gives the frequency of the mode coupled to the relaxing vibrational mode.

Figs. 4 and 5 show the Arrhenius plot for the peak at 2105 and 2110 cm^{-1} of the stretching mode $\nu_s(\text{C}\equiv\text{C})$ of PA in acetonitrile, respectively. As we can see the linear plot does fit quite well with the experimental data in the temperature range from 77 to 293 K. Assuming approximately linear plot, the experimental data for the peaks at 2105 , 2110 , and 2116 cm^{-1} yield a thermal activation energy of 310 ± 108 , 190 ± 74 , and $112 \pm 34 \text{ cm}^{-1}$ respectively. As the Arrhenius plot is likely to be sensitive to the way of fitting and the deconvolution procedure correcting the finite slit width of the Raman spectrometer we plotted in Figs. 4 and 5 the results for the experimental band widths obtained from the Gauss and Lorentz profiles, which are in fact the same within the experimental error, but the deconvolution procedure is different in each case. For the Gaussian profiles we used Eq. (1) from Ref. [21], while for the Lorentzian profiles we subtracted the slit width from the total band width, which is justified because the spectrometer band profile is also

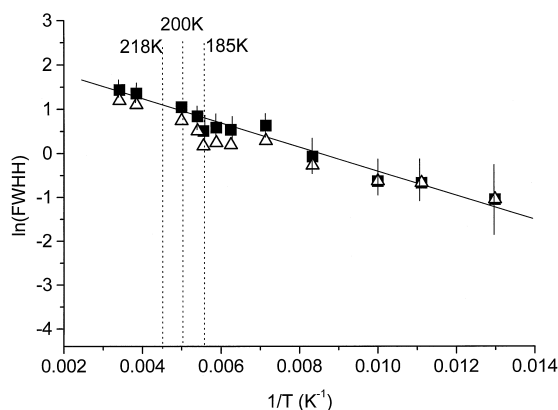


Fig. 5. Logarithm of the VV Raman bandwidth $\Delta_{1/2}(\text{FWHH})$ of the $\text{C}\equiv\text{C}$ stretching mode of phenylacetylene in acetonitrile ($c = 0.95 \text{ mol/dm}^3$) as a function of temperature: ■ – experimental data for the peak at 2110 cm^{-1} (fitting with 3 Gaussians, the slit correction according to Eq. (1) in Ref. [21]), Δ – experimental data (fitting with 3 Lorentzians, the slit correction obtained by subtracting the slit width from the experimental bandwidth).

Lorentzian. We can state from the comparison that both procedures provide very similar results.

The activation energy for the peak at 2105 cm^{-1} covers the range of the ν_{16a} (B_2) (boat vibration of the phenyl ring in PA at 349 cm^{-1}) [22] and the bending mode ν_8 (E)($\text{C}-\text{C}\equiv\text{N}$) at 375 cm^{-1} in acetonitrile [23], respectively. The activation energies for higher frequency peaks cover the range of translational and librational optic phonons at much lower energies than the ν_8 and ν_{16} modes. The vibrations which we have obtained to be preferentially coupled to phenylacetylene serve to emphasise the striking connection with our earlier suggestion about the origin of the components observed in the low temperature spectra of PA. Clearly, both ν_8 and ν_{16} vibrations may strongly perturb the T-shaped geometry of the H-bond complex, although the influence of the large-amplitude bending vibration ν_8 of acetonitrile seems to be dominant in this kind of coupling.

Having reached the point, when we suspect which solvent modes are preferentially coupled to the stretching mode $\nu_s(\text{C}\equiv\text{C})$ of PA in acetonitrile, we have studied the response of these modes to the interaction with PA solute molecules. In this paper we will confine ourselves to presenting the results for the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile.

Fig. 6 shows the Raman (VV component) band profiles of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile in PA–acetonitrile system at concentration $c = 0.95 \text{ mol/dm}^3$ as a function of temperature in the range between 293 and 120 K. We can see that the broad, structureless, symmetric band at 379 cm^{-1} observed in the liquid phase shows the dramatic change at 200 K and becomes split into two peaks, shifted blue to around 390, and 400 cm^{-1} at 120 K. The band of small intensity at 357 cm^{-1} corresponds to the ν_{16a} (B_2) (boat) vibration of the phenyl ring in PA. In view of these results and our earlier interpretation about the importance of H-bond interaction, one might have imagined that the peaks reflect H-bonded and non H-bonded species of acetonitrile. With this possibility in mind, we have recorded the spectra of neat acetonitrile in the same spectral region and have found the similar splitting for of acetonitrile in the absence of PA, which makes clear that the splitting has another origin. Generally, the factors leading to splitting are similar to those discussed in our previous paper [21] for the $\nu_s(\text{C}\equiv\text{C})$ mode of PA:

(1) A factor group splitting [11] of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile.

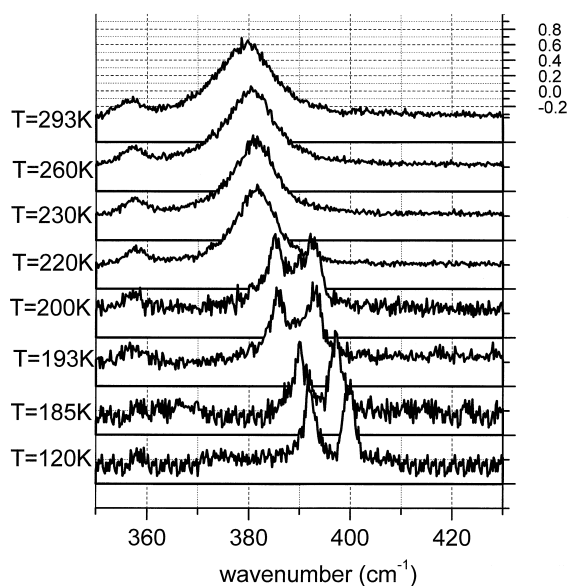


Fig. 6. VV Raman spectra of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile as a function of temperature for PA concentration $c = 0.95 \text{ mol/dm}^3$.

(2) A factor group splitting of the translational and librational modes of lower frequency coupled to the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile.

(3) Splitting due to tunneling through periodic barrier for internal rotations of the methyl group [24–26].

(4) The interaction between the upper state of an allowed transition and a near resonant optically inactive state [27].

(5) Shift of vibrational components of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending of acetonitrile due to the coupling with phonons of lower frequency modes of acetonitrile and/or PA.

(6) Coexistence between crystalline and amorphous mesophases.

It is worth pointing out that the temperature of 200 K at which the splitting begins to be observed for the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile does not match the temperature of 185 K for the $\nu_s(\text{C}\equiv\text{C})$ mode of PA. It may have a more deeper physical meaning such as a different origin of splitting or it may simply denote that the subbands of PA are still too broad to be resolvable. This explanation seems to be reasonable as the magnitude of splitting is about 10 cm^{-1} for acetonitrile and only 5 cm^{-1} for PA. In this paper we will confine our discussion to mechanisms of vibrational dynamics and the origin of the splitting observed for the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ bending mode of acetonitrile is not of our concern here. Additional studies are needed to discover the factors determining the splitting in acetonitrile and they will be a subject of a separate paper.

Fig. 7 shows the line width (FWHH—full width at half height) of the bending mode of acetonitrile $\nu_8(\text{C}-\text{C}\equiv\text{N})$ as a function of temperature in the range from 120 to 293 K for each band resulting from splitting into the two components, respectively. The broad band at room temperature and each of the components after splitting are perfectly Lorentzians in their shapes, which indicates that vibrational relaxation processes are purely homogeneous. The line widths for both components increase in apparently discontinuous manner with the sudden rise of about 6 cm^{-1} between 183 and 200 K.

So what kinds of insights can one gain from all of this analysis to this point?

At very low temperatures, where processes caused by thermal fluctuations disappear, the population

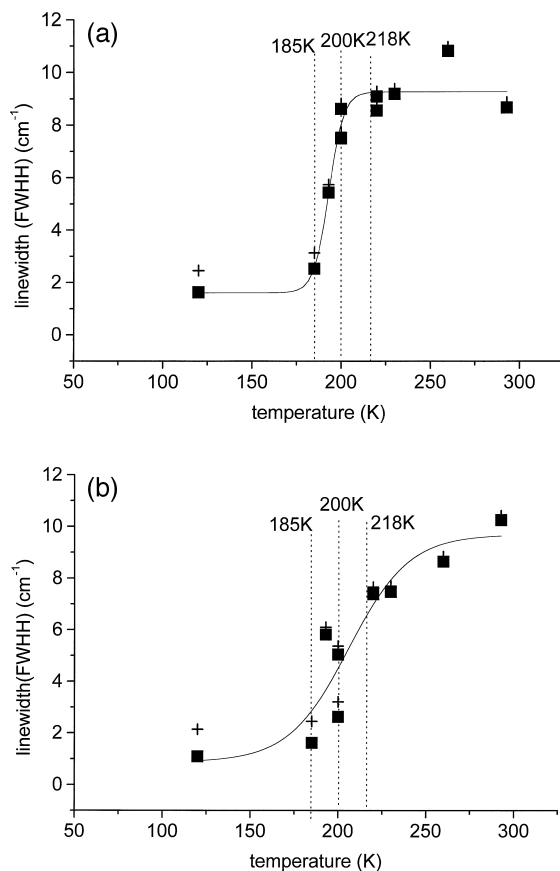


Fig. 7. VV Raman bandwidth $\Delta_{1/2}(\text{FWHH})$ of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile as a function of temperature for PA concentration $c = 0.95\text{ mol/dm}^3$, + – experimental data, ■ – experimental data after the slit correction according to Eq. (1) in Ref. [21], (a) peak at 390 cm^{-1} , (b) peak at 400 cm^{-1} .

lifetime T_1 is the only source of homogeneous band-broadening and therefore determines the total phase relaxation ($1/T_2 = 1/2T_1$ for $T \rightarrow 0$). Extrapolations of our results to $T \rightarrow 0$ with the Boltzmann function (Fig. 2) give the values close to zero (-0.016 , -0.032) for the peaks at 2105 and 2110 cm^{-1} and 1.1 cm^{-1} for the peak at 2116 cm^{-1} of the $\nu_s(\text{C}\equiv\text{C})$ mode of PA. The corresponding values for the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile (Fig. 7) are 1.6 and 0.87 cm^{-1} for the peaks at 390 and 400 cm^{-1} . Comparison of these figures with the bandwidths at around the phase transitions between 183 and 200 K confirms that this channel of vibrational relaxation is negligible both for PA and aceto-

nitrile at the phase transitions temperatures. Since we consider VV and VH components of Raman spectra (because the isotropic component disappears for PA at around 200 K whereas for the completely depolarized band of acetonitrile purely vibrational spectra cannot be determined by the VV–VH polarization experiments), we need to ask what role reorientational relaxation can be playing in the bandbroadening. We have found that the direct reorientational broadening contribution due to rotations of the entire molecules is less than 10% at room temperature estimated from the comparison between IR, isotropic Raman spectra and VH Raman spectra. Thus, at low temperatures this source of relaxation is negligible. However, the reorientational contribution may enter indirectly through vibrational dephasing from the coupling between vibrations and internal rotations.

In view of these results the pure vibrational dephasing and/or inhomogeneous broadening give dominant contribution to bandbroadening and they represent the main vibrational relaxation channel for PA in acetonitrile. Since the lineshape of the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile is purely Lorentzian in the full temperature range the inhomogeneous broadening can be excluded from considerations. The most interesting lesson which comes from the comparison between Figs. 2 and 7 is the similarity – both in terms of the behaviour in the full temperature range and magnitudes of the sudden rise during the phase transitions. It may suggest the same pattern of vibrational dephasing. Clearly, the magnitude of the sudden broadening of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ acetonitrile band, which occurs at the phase transitions between 183 and 200 K, correlates very well with nearly identical broadening for the peak at 2105 cm^{-1} of the $\nu_s(\text{C}\equiv\text{C})$ mode of PA. This additional, sudden broadening around 183–200 K may come from the same source of fluctuations of the vibrational level frequencies. What we discovered in our previous paper [21] was that the peak at 2105 cm^{-1} represents the H-bonded complex resulting from interaction with acetonitrile. The Arrhenius plot in Fig. 4 shows that this interaction leads to the coupling between the stretching $\nu_s(\text{C}\equiv\text{C})$ mode of PA and the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile. It is interesting to notice that the splitting of about 10 cm^{-1} observed in acetonitrile corresponds very well to 2B distance in the rotational spectrum, where B is the

rotational constant for internal rotations of the CH_3 group of acetonitrile around the C_{3v} symmetry axis [24,25]. It gives strong evidence that the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ is coupled with this kind of internal rotation, which seems to look quite natural in terms of geometry of the molecule and the symmetry of the vibration. Since the stretching $\nu_s(\text{C}\equiv\text{C})$ mode of PA is coupled to the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile, we might have guessed the influence of CH_3 internal rotation not only on acetonitrile vibration, but also on the PA mode. Thus, varying with temperature fluctuations in energy of the internal rotor induced by thermal excitations may lead to vibrational dephasing of both vibrations. Moreover, the sudden increase at the phase transi-

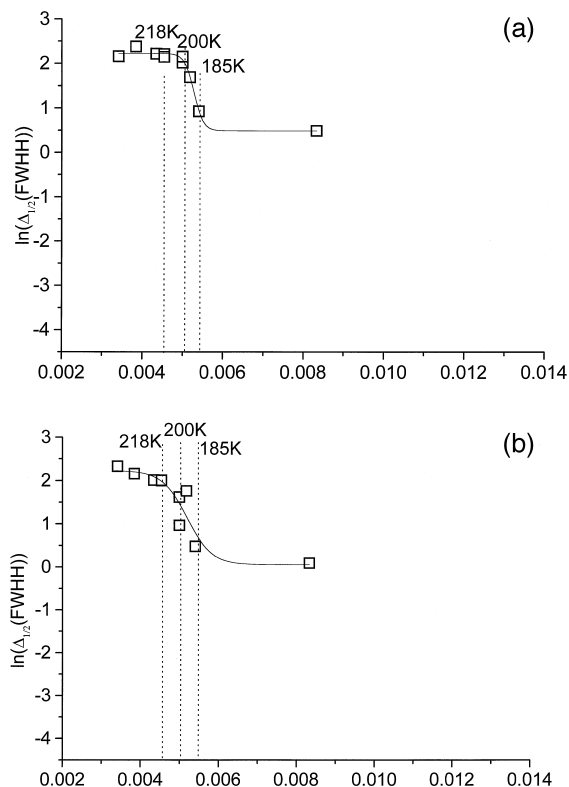


Fig. 8. Logarithm of the VV Raman bandwidth $\Delta_{1/2}(\text{FWHH})$ of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile as a function of temperature for PA concentration $c = 0.95\text{ mol/dm}^3$: \square – experimental data for the peak (a) at 390 cm^{-1} , (b) at 400 cm^{-1} (fitting with 2 Lorentzians, the slit correction by subtracting the experimental slit width).

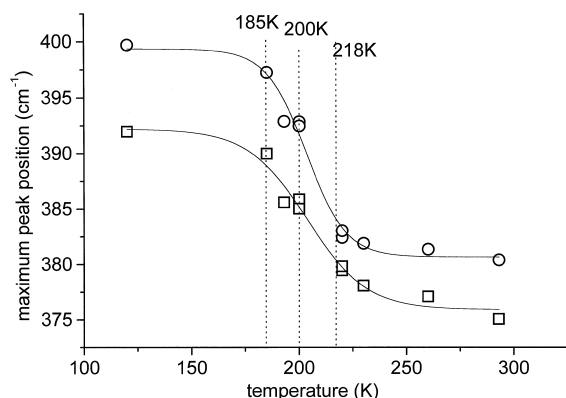


Fig. 9. VV Raman maximum peak positions of the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile as a function of temperature for PA concentration $c = 0.95 \text{ mol/dm}^3$.

tions may indicate the change of the mechanism for the internal rotation from hindered rotation in periodic potential to almost free rotation for higher temperatures. This pattern of behaviour, which reveals from the discussed results works very well also for the peaks at 2110 and 2116 cm^{-1} of PA (Fig. 2b and 2c), which show much less pronounced changes in the region of the phase transitions because the oscillators have quite different activation energy than the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile and are supposed to be coupled with internal rotation of acetonitrile much weaker than the 2105 cm^{-1} oscillator.

In contrast to the stretching $\nu_s(\text{C}\equiv\text{C})$ mode of PA, the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile deviates from Arrhenius behaviour much more evidently around the phase transitions (Fig. 8). Also the changes in the maximum peak positions are much more pronounced in the region of the phase transitions between 183 and 218 K (Fig. 9)

3. Conclusions

We have examined vibrational dynamics of the stretching $\nu_s(\text{C}\equiv\text{C})$ mode of phenylacetylene and the $\nu_8(\text{C}-\text{C}\equiv\text{N})$ mode of acetonitrile in solutions in temperature range from 77 to 293 K. One of the goals of the paper was to identify the mechanism of vibrational relaxations in the full range of tempera-

tures with a special emphasis on the range around the phase transitions occurring between 183 to 218 K.

We have found that bandbroadening of the $\nu_s(\text{C}\equiv\text{C})$ mode of PA in acetonitrile solutions is dominated by pure dephasing in the whole temperature range. For temperatures between 77 to around 125 K the vibrational energy relaxation T_1 makes non negligible contribution for the peak at 2116 cm^{-1} ascribed to the $\nu_s(\text{C}\equiv\text{C})$ oscillator which is not involved in H-bond. For the $\nu_s(\text{C}\equiv\text{C})$ oscillators at 2105 and 2110 cm^{-1} , which are engaged in H-bond, the T_1 relaxation is negligible in the whole temperature range. The orientational relaxation resulting from the rotations of the whole molecules are also negligible. The mechanism of vibrational dephasing of the $\nu_s(\text{C}\equiv\text{C})$ oscillator involved in H-bond, which is reflected by the spectacular bandbroadening of about 6 cm^{-1} around the phase transitions, comes from the coupling with the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile. The oscillator at 2116 cm^{-1} shows much less spectacular change around the phase transitions, while the oscillator at 2110 cm^{-1} is independent of the phase transitions between 183 and 218 K.

We have found that the $\nu_s(\text{C}\equiv\text{C})$ vibration of PA in acetonitrile shows approximately Arrhenius behaviour with a thermal activation energy of 310 ± 108 , 190 ± 74 , and $112 \pm 34 \text{ cm}^{-1}$ for the peaks at 2105, 2110, and 2116 cm^{-1} , respectively. The activation energy for the peak at 2105 cm^{-1} covers the range of the $\nu_{16a}(\text{B}_2)$ (boat) vibration of the phenyl ring in PA at 349 cm^{-1} and the bending mode $\nu_8(\text{E})(\text{C}-\text{C}\equiv\text{N})$ at 375 cm^{-1} in acetonitrile, respectively. The activation energies for higher frequency peaks cover the range of translational and librational optic phonons at much lower energies than the ν_8 and ν_{16} modes.

The vibrational line widths both for the $\nu_s(\text{C}\equiv\text{C})$ vibration of PA and the bending mode $\nu_8(\text{E})(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile in PA solution can be fitted by the Boltzmann function $\Delta_{1/2} = (A_1 - A_2)/[1 + \exp(T - T_0)/\Delta T] + A_2$. The vibrational dephasing of the $\nu_s(\text{C}\equiv\text{C})$ mode of PA and the bending mode $\nu_8(\text{C}-\text{C}\equiv\text{N})$ of acetonitrile in solution seems to be governed by the coupling of the vibrational modes to internal rotations of the methyl group CH_3 of acetonitrile. The behaviour around the phase transitions between 183 and 218 K with the sudden increase in the bandwidths has been explained as the result of

the changes in the mechanisms of the internal rotation from hindered rotation in periodic potential to almost free rotation for higher temperatures.

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