Vibrational relaxation of diphenylacetylene at low temperatures

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Abstract

Raman spectra of the $\nu_S(C\equiv C)$ stretching mode of diphenylacetylene dissolved in acetonitrile and methylcyclohexane have been recorded at room temperature and 77 K. The results on vibrational dynamics in liquids at room temperature are compared with those at low temperatures at 77 K. Substantial narrowing of spectra at low temperatures leads to revealing vibrational structure. The results given in this paper are a spectacular example of monitoring structural order going from liquid solutions to frozen matrices at low temperatures by Raman spectroscopy. © 1998 Elsevier Science B.V.

1. Introduction

Raman and IR spectroscopy provide a wealth of information about normal mode assignments and perturbations caused by the interacting environment. In going from isolated molecules in the gas phase through isotropic liquids to the solid state phases of glasses and molecular crystals we can monitor orientational order and changes in dissipation of vibrational energy (vibrational relaxation). In liquid crystal materials we can observe additional mesophases with increasingly higher positional order before approaching the crystal lattice on cooling. Biphenyl derivatives belong to typical nematogenic molecules. For example, it was a major breakthrough when cyanobiphenyl materials were found to exhibit room-temperature nematic phases. The most recent liquid crystal PDLC technology (polymer dispersed liquid crystals) uses fluorinated derivatives of diphenylacetylene.

Many dynamical processes in condensed phase, such as chemical reactions like electron or proton transfer, are strongly affected by the vibrational relaxation properties of the particular material. Molecular crystals have traditionally fulfilled the role of model systems for understanding of the dissipation of excess vibrational energy in condensed phase. Much less is known about vibrational relaxation in glasses and liquid crystal materials.

The dominant contribution to vibrational relaxation in condensed phase comes from: energy relaxation T_1, vibrational dephasing T_2 and inhomogeneous broadening. The first process describes vibrational depopulation permitting an excited vibration to relax by simultaneous emission of two or more acoustic phonons, optic phonons or/and vibrations. The vibrational dephasing is caused by thermally excited modes of the bath. The T_1 and T_2 processes give contribution to the homogeneous vibrational band shape broadening. Inhomogeneous broadening is caused either by static disorder, or by thermally activated slow fluctuations of local density (or con-

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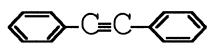
Diphenylacetylene- DPA

Scheme 1.

centration fluctuations in many component systems). In liquids the fast vibrational dephasing accounts for dominant part of the homogeneous line width at ambient temperature [1]. However, under certain circumstances, vibrational line shapes are dominated by inhomogeneous broadening [2].

In some molecular crystals like naphthalene [3] and some glasses [4] the T_2 processes at low temperatures are negligible and the homogeneous line broadening is dominated by T_1 processes. The frequency domain IR and Raman experiments and time domain experiments with a single pulse excitation cannot separate homogeneous and inhomogeneous contributions to the band broadening. Time domain

experiments with two excitation pulses (optical echo) remove the inhomogeneous broadening revealing the homogeneous contributions. The IR [4] and Raman [2] echo experiments show a substantial contribution from inhomogeneous broadening in some glasses at low temperature.

In this paper we present Raman spectra for diphenylacetylene in liquid acetonitrile and methyl-cyclohexane at room temperature and in polycrystalline and glass host matrices at 77 K. The results illustrate that low-temperature Raman spectroscopy is very useful for monitoring structural order going from isotropic liquids to solid state phases at low temperature and vibrational relaxation mechanisms. In this paper we present the isotropic Raman line shape analysis for the C≡C stretching mode of diphenylacetylene in the polycrystalline (acetonitrile) and glass (methylcyclohexane) forming host matrices at 77 K and compare them with the results obtained at room temperatures.
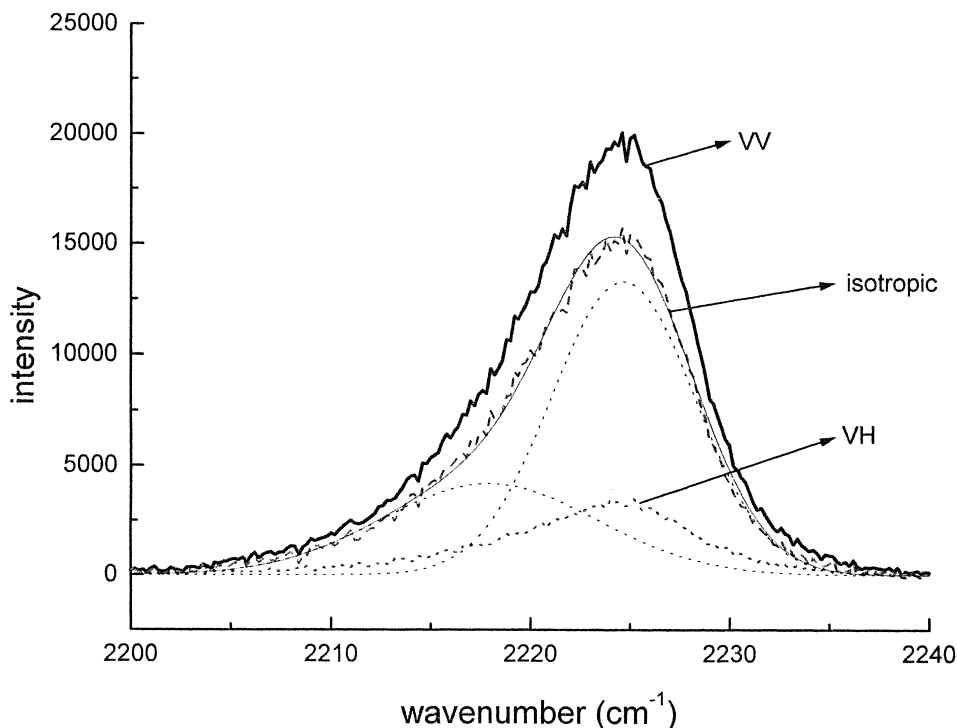

Fig. 1. VV, VH and isotropic Raman spectra of the C≡C stretching mode of diphenylacetylene in acetonitrile ($c = 0.787$ mol/dm^3) at room temperature (- - - - = isotropic band after deconvolution into two Gaussians).

2. Experimental

Spectrograde acetonitrile, methylcyclohexane and diphenylacetylene (DPA) (Scheme 1) were purchased from Aldrich and used without further purification. Solutions of DPA in acetonitrile and methylcyclohexane were made with concentrations varying from 0.045 to 2.1 mol/dm^3. Raman spectra were measured with Ramanor U1000 (Jobin Yvon) and Spectra Physics 2017S argon ion laser operating at 514 nm. The C≡C stretching modes of DPA in acetonitrile and methylcyclohexane were measured. Spectra were recorded at 77 K in a nitrogen bath cryostat. The spectral slit width was 1.5 cm^{-1} both at room temperature and at 77 K. The signal to noise ratio in liquid solutions is about 50:1, whereas in frozen matrices at low temperatures it is lower, about 10:1. The relatively small ratios come from the fact that measurements in the cryostat give always lower intensities of the signals and the presence of liquid nitrogen results in small fluctuations of the scattered light intensities. A polarization analyser and $\lambda/4$ waveplate were used to select polarized (VV) and depolarized (VH) components. The isotropic Raman spectra were calculated according to the relation

$$I_{iso} = I_{VV} - \frac{4}{3} I_{VH} . \tag{1}$$

The depolarization ratio defined as

$$\rho = \frac{I_{VH}}{I_{VV}} \tag{2}$$

was measured for each sample.

The interference filter has been used to purify the laser line by removing additional natural emission lines which interfere with the Raman lines, especially in the case of solid samples.

3. Results

Figs. 1 and 2 show the VV, VH and isotropic Raman spectra of the C≡C stretching mode of DPA
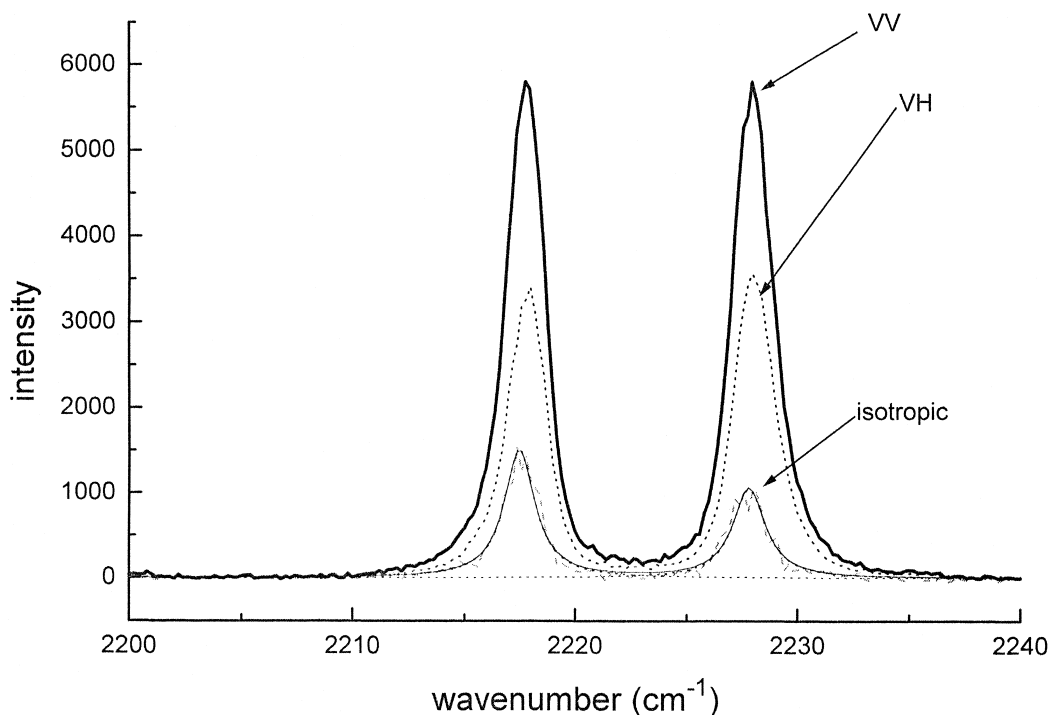

Fig. 2. VV, VH and isotropic Raman spectra of the C≡C stretching mode of diphenylacetylene in acetonitrile ($c = 0.467$ mol/dm^3) at 77 K (————— — = fitting curve of the isotropic band with two Gaussians).

in acetonitrile at room temperature and at 77 K, respectively. The comparison of the Raman spectrum at low temperature to that in liquid solution shows that a new band is produced at the 77 K solid state phase (or the band is split into two components) which does not appear in the liquid phase. The peak position of the C≡C stretching mode of DPA in liquid acetonitrile is observed at 2224.7 cm^{-1}, while at 77 K two bands are observed at 2217.5 and 2227.8 cm^{-1}, respectively. The isotropic Raman line of the DPA band in liquid acetonitrile at room temperature is asymmetric on the low-frequency side. The best reproduction of the experimental band was obtained with two Gaussians: at 2217.9 and 2224.6 cm^{-1}. The isotropic band widths are 10.84 and 7.22 cm^{-1}, respectively. In contrast, at 77 K the isotropic band width at 2217.5 cm^{-1} is 1.66 cm^{-1}, while that at 2227.8 cm^{-1} is 1.77 cm^{-1}. The most striking results are obtained for the depolarization ratios ρ. Indeed, the depolarization ratio of the $\nu_s(C\equiv C)$ mode of DPA in acetonitrile at room temperature is 0.17.

However, in the solid state phase at 77 K the depolarization ratios increase significantly, being equal to 0.56 at 2217.5 cm^{-1} and 0.61 at 2227.8 cm^{-1}.

Figs. 3 and 4 show the VV, VH and isotropic Raman spectra of the C≡C stretching mode of DPA in methylcyclohexane at room temperature and at 77 K, respectively. The peak position of the C≡C stretching mode of DPA in liquid methylcyclohexane is observed at 2224.1 cm^{-1}. In contrast to acetonitrile, only one band for the C≡C mode of DPA in methylcyclohexane at 77 K is observed. The low-temperature band at 2227.6 cm^{-1} is slightly asymmetric on the low-frequency side and was fitted with two Gaussians (isotropic component): at 2225.9 and 2227.8 cm^{-1} with line widths of 8.27 and 2.36 cm^{-1}, respectively. However, in the latter case, the fit with two Lorentzians gives experimental band reproduction of similar quality with the peak positions at 2220.8 and 2227.5 cm^{-1}, and band widths of 6.37 and 2.43 cm^{-1}, respectively. The isotropic Raman line width of the DPA band in liquid methylcy-

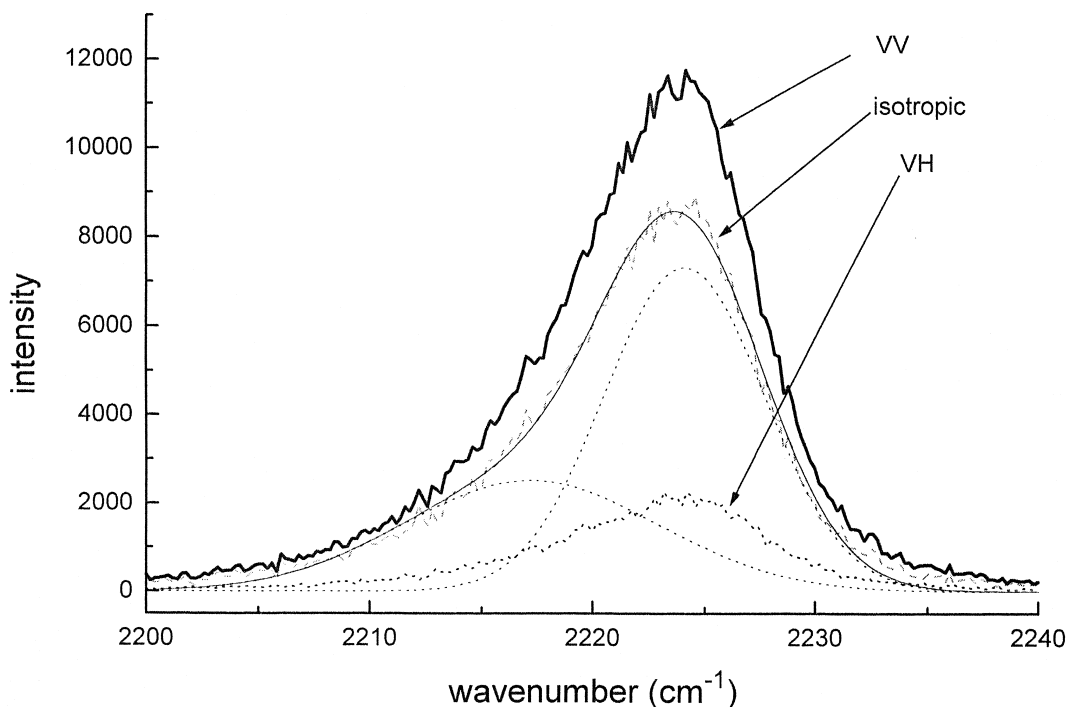Fig. 3. VV, VH and isotropic Raman spectra of the C≡C stretching mode of diphenylacetylene in methylcyclohexane ($c = 0.864$ mol/dm^3) at room temperature.
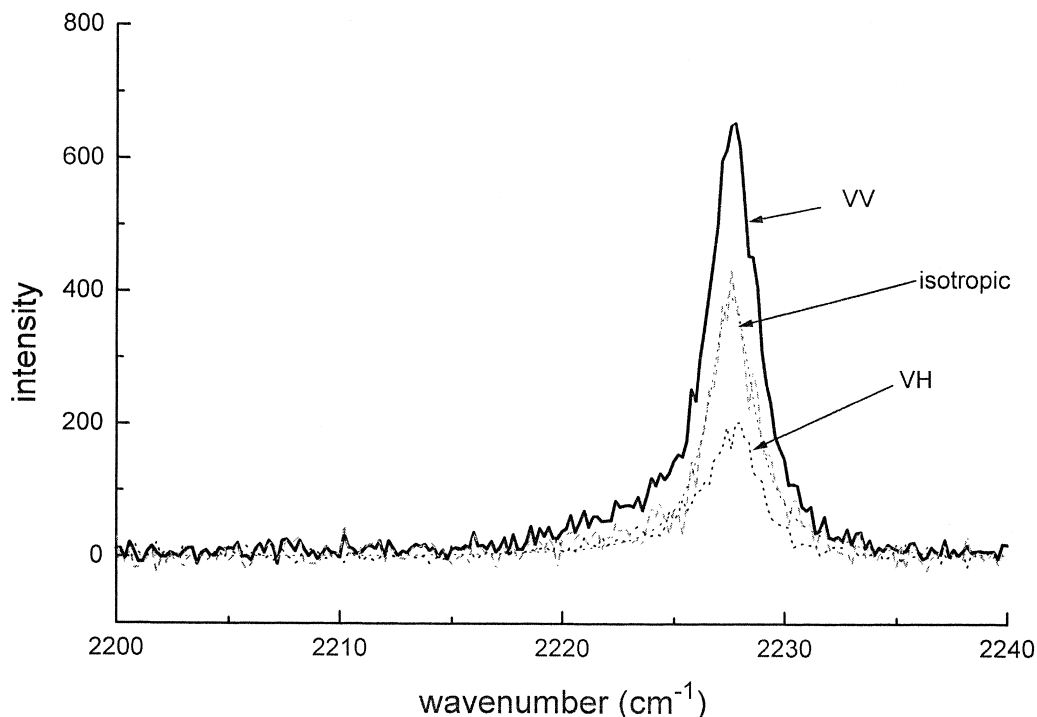
Fig. 4. VV, VH and isotropic Raman spectra of the C≡C stretching mode of diphenylacetylene in methylcyclohexane ($c = 0.203$ mol/dm^3) at 77 K (----= VV band after doconvolution into two Gaussians).

clohexane at room temperature is also asymmetric on the red side and the best fit of the experimental band was obtained with two Gaussians at 2217.2 and 2224.1 cm^{-1}. The isotropic band widths are 11.41 and 7.21 cm^{-1}, respectively.

Again, the depolarization ratio of DPA in liquid methylcyclohexane solutions is small ($\rho = 0.19$), while at the solid state phase at 77 K ρ increases remarkably ($\rho = 0.31$). However, it should be noticed that the low-temperature depolarization ratio of DPA in methylcyclohexane is much lower than that in acetonitrile.

4. Discussion

The results presented in this paper have three important findings: (1) change of the depolarization ratios with decreasing temperature; (2) substantial narrowing of the C≡C band observed both in acetonitrile and methylcyclohexane with decreasing temperature, contrary to the expectation that inhomoge-

neous broadening should give a significant contribution at low temperatures; and (3) appearing of additional bands of diphenylacetylene in acetonitrile matrices (or splitting of the bands into two bands).

The DPA molecule is a rod-like, cylindrically symmetric molecule. Being related to its molecular shape, the molecular polarizability is anisotropic as well. The average polarizability $\bar{\alpha}$ and polarizability anisotropy $\bar{\gamma}$ characterize the isolated molecule and do not depend on the laboratory frame of reference, and as a consequence, on orientational order. The parameter $\bar{\gamma}$ is zero for fully isotropic molecules. For vibrations that are not totally symmetric $\bar{\alpha} = 0$ and they are represented by depolarized bands. In our case, both $\bar{\gamma}$ and $\bar{\alpha}$ differs from zero and the υ_s(C≡C) vibrations of DPA are represented by polarized bands, because they belong to the totally symmetric representations A$_g$ and A$_1$, respectively.

However, the depolarization ratio $\rho = I_{VH}/I_{VV}$ depends on the reference frame and it can be treated as a measure of orientational order. In isotropic liquids, when an ensemble of differently oriented

molecules contributes to the measured signal, the depolarization ratio is ρ is expressed as

$$\rho = \frac{3\bar{\gamma}^2}{45\bar{\alpha}^2 + 4\bar{\gamma}^2}. \tag{3}$$

However, if the molecules within a sample are aligned, the macroscopic properties of the sample are anisotropic as well, so that eventually dichroism and birefringence may occur. In partially ordered systems like liquid crystals and other mesophases or perfectly ordered crystals which structures differ from the one of an isotropic liquid, Eq. (3) is not longer valid. Thus, going from zero indicating random orientation to perfect alignment the depolarization ratio measured as $\rho = I_{VH}/I_{VV}$ must change because averaging over all molecules of the sample yields a specification of the degree of order. The Raman spectra that in isotropic liquids depend on the Legendre polynomial of the second order P_2 are influenced additionally by the ordering parameters of the next level, such as the P_4 term [5].

From what was said before it should be clear that the degree of order depends on temperature. Our results show marked difference between the depolarization ratios in solution and frozen matrices, giving evidence of increasing degree of order of DPA going from liquid solutions to frozen matrices for both polar and nonpolar solvents. However, the depolarization ratios of DPA in acetonitrile are ~ 0.6 and they are as much as twice greater than in methylcyclohexane. This illustrates the higher order of alignment in a polar, polycrystalline matrix than in a nonpolar, glassy one. In order to determine if DPA liquid solutions differ from isotropic liquids having nematic-like alignment in the liquid phase it would be advantageous to compare the depolarization ratios in the gas phase with those in the liquid phase. Unfortunately, such data are not available.

The origin of forces stabilizing mutual orientation still remains unclear. Long-range electrostatic attractive/dispersive, inductive or dipole–dipole interactions seem to be insufficient to explain the order, at least in the case of nonpolar DPA in nonpolar methylcyclohexane. The detailed analysis of the vibrational relaxation mechanisms reflecting the dynamic fluctuations about average force may be helpful to elucidate the origin of forces resulting in increasing order.

The results presented in this paper show substantial band narrowing with decreasing temperature. In recent years a considerable amount of experimental and theoretical information has been accumulated on the vibrational dynamics in liquids using conventional IR and Raman spectroscopy [1,6–8], ultrafast coherent spectroscopy methods such as coherent anti-Stokes Raman spectroscopy [9], Raman echo [2], and IR echo [4]. However, much less work has been carried out on the mechanism of vibrational dephasing at low temperatures for crystals and glasses. Vibrational dynamics is characterized by two relaxation times — the phase relaxation time T_2 and the energy relaxation time T_1. In most liquids one finds $T_1 > T_2$. Thus, the observed effective vibrational dephasing time T_2^* $((T_2^*)^{-1} = (T_2)^{-1} + (2T_1)^{-1})$ determined from the homogeneous line width of the mode in conventional IR and Raman spectroscopy is frequently equal to the pure vibrational dephasing time T_2. However, in many cases other line-broadening effects such as inhomogeneous broadening, energy resonance transfer or isotope multiplicity may also contribute to the measured IR and Raman line width and the observed line shape represents a convolution of homogeneous (rapid limit) and inhomogeneous (static limit) contributions. The time-resolved coherent Raman spectroscopy using single excitation pulse techniques provides information about the same dephasing time T_2 as conventional linear vibrational spectroscopy and like it suffers from the same inability to separate the various contributions to the observed line shape. Two or more excitation pulses techniques like IR echo [4] or Raman echo [2] can extract the homogeneous vibrational line shape, even when the line shape is broadened significantly by inhomogeneous contributions. Vibrational relaxation in the crystal and glass phases can be vastly different from its liquid counterpart. Not only the energy relaxation T_1 but also the phase relaxation T_2 can differ due to the effects of interactions of the solute with the solvent molecules and different time scale of these processes. The dynamics of vibrational relaxation T_1 and T_2 proceed on a much slower time scale and the relation $T_1 > T_2$ may not be fullfilled. Additionally, it can be expected that the rigid environment of the solute leads to significant inhomogeneous band broadening in glasses. Although a general outline of the dynamics in glasses

has been developed [10–12] the fundamental issues of vibrational dynamics remain to be clarified. There is a limited number of papers on vibrational relaxation in glasses. The recent results [4] which are the first ones on the temperature dependence of vibrational dephasing in organic glasses show that at low temperatures below the glass transition temperature the energy relaxation T_1 is the dominant contribution to the homogeneous line width and the contributions from pure dephasing are negligible. Above 50 K pure dephasing T_2 and orientational relaxation make the major contributions to the IR line width, while above 150 K pure dephasing overwhelms the other contributions to the homogeneous line width. The comparison of the IR echo and IR absorption results shows that at low temperatures below 150 K, the vibrational line of tungsten hexacarbonyl in 2-methylpentane is dominated by inhomogeneous broadening and the homogeneous contribution is negligible. Above 150 K the homogeneous line width begins to approach the measured absorption line width and at 200 K the homogeneous and inhomogeneous contributions to the absorption line are of equal magnitude.

The results obtained in this paper are in contrast to those obtained by Tokmakoff and Fayer [4] for $W(CO)_6$ in 2-methylpentane glass solution where the IR absorption band at low temperature is much broader than that at room temperature and the width decreases monotonically with temperature increase. Our results may be a manifestation that for DPA inhomogeneous broadening does not dominate in any temperature range and the homogeneous broadening due to the pure dephasing T_2 and/or energy relaxation T_1 give contribution both around 77 K and at room temperature. However, the results obtained by Tokmakoff and Fayer [4] show that the energy relaxation contribution to the line width appears mildly temperature dependent over the whole temperature range and temperature dependence of T_1 is insignificant in comparison to the temperature dependence of pure dephasing. Moreover, it has been shown [13] that the C≡C stretching mode of acetylene in liquid CCl_4 solution has exceptionally long energy relaxation life time T_1 ($T_1 = 240$ ps) and gives negligible contribution to the band broadening. This value can be modified by the phenyl substituent in DPA but it seems that the DPA band broadening in the whole temperature range comes rather from the pure de-

phasing mechanism. With this assumption, the results presented here can be compared with the predictions of a number of theories for the temperature effect on vibrational dephasing in liquids: translational diffusion model of Lynden—Bell [14], which obtains the vibrational dephasing band width $\Gamma \propto \rho\eta/T$, hydrodynamic model of Oxtoby [15] with $\Gamma \propto \eta T$, the isolated binary collision models of Fischer–Laubereau [16] and Schweizer–Chandler [17], which predict a temperature dependence of $\Gamma \propto \eta T/\rho$ and $\Gamma \propto \rho T^{3/2}\rho(\sigma)$, respectively. All the theories, except the first model, predict a decrease in the homogeneous line width with decreasing temperature as we observe for the results in this paper. However, none of the hydrodynamic theories, which include viscosity η as an approximation for the collision frequency can describe the results in this paper. The viscosity in liquid acetonitrile and in methylcyclohexane increases by many orders of magnitude between room temperature and 77 K and overcomes the temperature effect. It would lead to an increase of the band width at temperatures below the phase transition temperature contrary to the results observed in this paper. The temperature effect on the vibrational line width in our results seems to be reproduced, at least partially, with the relation $\Gamma \propto \rho T^{3/2}\rho(\sigma)$, where the vibrational dephasing mechanism is approximated by the fast, repulsive, hard collision interactions based on the Enskog collision time. Assuming mild temperature dependence for the radial distribution function $g(\sigma)$ we obtain the ratio of the isotropic Raman band widths $\Gamma(77)/\Gamma(298)$ at 77 and 298 K should be equal to $(77/298)^{3/2} = 0.13$. It is in reasonable agreement with the experimental ratios of $1.66/10.84 = 0.15$ and $1.77/7.22 = 0.24$ for DPA in acetonitrile, respectively. For DPA in methylcyclohexane the experimental ratio is $2.36/7.21 = 0.32$ which is greater than the theoretical prediction.

If we take into account the instrumental band broadening (1.5 cm^{-1}) and calculate the experimental band widths after the deconvolution procedure corrected for finite slit width according to the formula [18]

$$\Delta_{1/2}^{t} = \Delta_{1/2}^{a}\left[1 - 2\left(s/\Delta_{1/2}^{a}\right)^2\right]^{1/2}, \qquad (4)$$

where the subscripts t and a denote 'true' and 'apparent', respectively, and s is the spectral slit width, the experimental ratios of the band widths at 77 and 298 K are 0.06, 0.13 and 0.25 cm^{-1}, respectively.

To, summarize, the mechanisms of vibrational relaxation of DPA at low temperatures seem to be dominated by the homogeneous, hard collision repulsion interactions. This conclusion is in agreement with the results on the mechanisms of band broadening of DPA in liquid solutions [19].

The third issue that arises from the results of this paper is the interpretation of the splitting of the DPA spectra in acetonitrile frozen matrices. Let us try and understand the origin of these additional bands or the splitting of the band into two components.

We can exclude that the splitting reflects the molecular spectral properties of DPA molecules, like Fermi resonance, that are revealed from the broad bands of liquid solutions due to narrowing at low temperature. Indeed, the splitting is determined by solvent, not by the properties of individual molecules. It exists in polycrystalline acetonitrile and disappears in methylcyclohexane that forms glassy matrices.

One possibility is that the two bands of DPA in acetonitrile represent different conformers like planar and nonplanar structures. DPA in the S_0 state is known to be in a planar structure having D_{2h} symmetry in the crystalline state and it is suggested that the most probable geometry in solutions is the same [20,21]. However, it is possible that in solution a twist around the C-phenyl bond occurs, leading to a nonplanar structure that is stabilized in rigid environment. However, our results for phenylacetylene which will be published in a subsequent paper, where such conformers do not exist, exclude such a possibility.

Another possibility is that DPA forms complexes with acetonitrile, which are stabilized at low temperatures. The bands at 2217.5 and 2224.7 cm^{-1} could be assigned to the free DPA and DPA complexed with acetonitrile, respectively.

The splitting that we observe for DPA may correspond to the in-phase and out-of-phase $v_s(C\equiv C)$ vibrations shown in Scheme 2. Indeed, ab initio normal mode analysis shows [22] that the band at 2224.1 cm^{-1}, which is empirically assigned to the C$\equiv$C stretch, involves a considerable contribution (20–30%) of the C–Ph stretch.
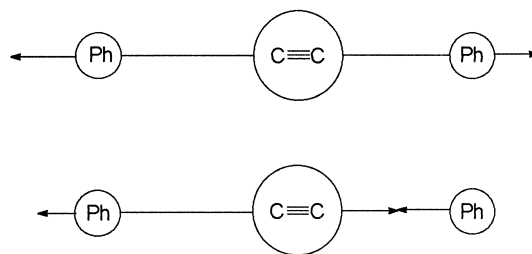
Scheme 2.

The in- and out-of-phase vibrations would be able to explain the origin of two bands in DPA (Scheme 2). However, with this explanation it would be difficult to understand the dependence on solvent and concentration. In this case a similar band structure should be observed both in acetonitrile and methycyclohexane, contrary to the experimental results.

We think, that the Raman spectra for DPA illustrate rather changes in structural order that occur with temperature and concentration. Strong evidence conforming this conclusion comes from the marked difference in depolarization ratios between the isotropic components in solution and frozen matrices. As it is well known a spectrum of nonlinear, isolated molecule contains $3N - 6$ internal vibrations, and six external degrees of freedom (translation and rotation). In the solid state at low temperatures, intermolecular interactions modify somewhat the states of isolated molecule. The external degrees of freedom are modified, essentially leading to the appearance of new bands in the low-frequency region. The vibrations are modified only slightly, preserving the main features of that in isolated molecules. However, the interactions in rigid environment may lead to appearance of forbidden bands, splitting of degenerate modes due to the disappearance of symmetry elements at the crystal site. Moreover, the interactions between the Z molecules in the crystal unit cell creates coupling of the corresponding molecular modes, giving rise to Z components appearing in the spectra as splitting. This splitting is known in the literature as correlation field or factor group splitting. Additionally, each Z component may be split into M bands due to the interaction between the M translationally equivalent molecules, where M is the number of crystal unit cells. However, in molecular crystals where the intermolecular potential

is much weaker than the intramolecular potential, the M splitting effect is small, typically of $10^{-2}-T^3$ cm^{-1}, and cannot be observed with the resolution of conventional IR and Raman spectrometers.

The two bands of DPA in crystalline host matrix (acetonitrile) are the effect of splitting into Z components as a result of interaction within the unit cell. In nonpolar glassy methylcyclohexane this order disappears and this is the reason why only one band is observed.

5. Conclusions

In this paper the results on the vibrational dynamics of diphenylacetylene in frozen matrices at 77 K are presented and compared with the results in liquid solutions at room temperature. We observe a substantial narrowing in the Raman line widths of the C≡C stretching mode of diphenylacetylene with decreasing temperature. The results obtained above clearly demonstrate the existence of a homogeneous component to the Raman line in DPA at 77 K and negligible contribution from inhomogeneous broadening. The homogeneous isotropic Raman band broadening is dominated by pure dephasing due to the hard-sphere repulsive interactions.

The second major result of this paper is the appearance of the additional bands of DPA in acetonitrile at 77 K. The observed splitting of the C≡C band in DPA corresponds to the interactions between the Z molecules in the crystal unit cell which create coupling of the corresponding molecular modes giving rise to Z components known as correlation field or factor group splitting. The other vibrational modes of diphenylacetylene show no factor group splitting within the resolution of the Raman spectrometer.

The results illustrate that Raman band shape analysis provides an excellent method to monitor structural order going from random orientation isotropic liquids through partially ordered phases to increasing alignment in solid state phases.

The here presented results and current interpretations clearly ilustrate that more elaborated methods to estimate the experimental values of the ordering parameters and additional supplementary evidence from crystallographic data for these systems are required. Taking into account that diphenylacetylene derivatives are particularly interesting to the recent liquid crystal technologies and because they offer a wide range of electronic structures going from the ground state S_0 and the electronically excited states S_1 and T_1, radical ions DPA$^+$ and DPA$^-$, respectively, the here presented results may give some contribution to understand their spectral properties at the molecular level.

6. Unlinked references

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Acknowledgements

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