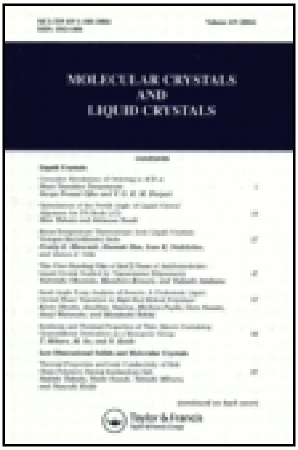

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MOLECULAR MOTION AND CLUSTERING IN MESOPHASES, LIQUID, AND SOLUTIONS OF 4-n-alkyl-4'-cyanobiphenyls

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Abstract The Raman spectral profile of the CN oscillator of 4-n-nonyl-4'-cyanobiphenyl (9-CB) in carbon tetra chloride and chloroform solutions was evaluated in terms of the dynamical processes that cause motional narrowing on the time scale of fractions to several picoseconds. Comparison with corresponding results of the mesophases and liquid of 8-CB, 9-CB, 12-CB, and 8-OCB permits predictions on the general nature of the solutions environment, limiting rates of molecular orientational tumbling, and clustering that can persist in the liquid and polar solution.

INTRODUCTION

Infrared and Raman spectral investigations of liquid crystal systems concentrate, in the majority of cases, on quasi-static properties such as conformational changes,[1] molecular ordering,[2] and other related static system quantities; only relatively few studies have been undertaken with the aim of directly elucidating the time dependence of the atomic and molecular motions as to their influence on conformation and structure.[3,4] In effect, infrared and Raman spectroscopy are eminently suitable to probe, specifically, dynamics of systems that stretch over a time domain of fractions of picoseconds to several picoseconds. The pertinence of this range is readily understood by considering, first, that vibrational bandwidths of suitable internal "probe" oscillators of liquid crystals are of the order of 10 cm^{-1}, which translates to a characteristic time $\tau_c \simeq 0.5$ psec and, second, that the common accuracy of a bandwidth determination amounts to $\pm 0.2\ \text{cm}^{-1}$, which yields an upper limit of the order of $\tau_c \simeq 1/(2\pi c\Delta\nu) = 25$ psec.

It is not difficult to see how molecular motion in such a time frame can influence a purely vibrational oscillator profile. Quite generally, the profile of an oscillator in an amorphous medium is broadened because the n-fold accidentally-degenerate vibrational transition frequency of the oscillator of n isolated molecules (vapor phase) is removed when the assembly is "transferred" into a condensed medium with only <u>local</u> order.[5] More specifically, we recall[6] the general relation between the time autocorrelation C(t) of the stochastic vibrational amplitude m(t) (which is derived by a numerical Fourier transform $\mathfrak{F}\{\}$ of the observed vibrational profile $I(\omega)$) and the autocorrelation function f(t) of the stochastic oscillator transition frequency $\omega(t)$ (which is chosen on appropriate physical grounds):

$$C(t) = \langle m(t)m(0)\rangle\langle|m(0)|^2\rangle^{-1} = \mathfrak{F}\{I(\omega)\}$$

$$= \exp\{-\langle|\omega_1(0)|^2\rangle \int_0^t dt'(t-t')f(t')\}, \qquad (1)$$

$$f(t) = \langle\omega_1(t)\omega_1(0)\rangle\langle|\omega_1(0)|^2\rangle^{-1} . \qquad (2)$$

Here, angular brackets denote the average over the equilibrium system; quantity $\omega_1(t) = \omega(t)-\omega_o$ is the frequency shift off the band center ω_o.

From this, we can simply summarize that the instantaneous oscillator transition frequency $\omega(t)$ - usually the fundamental - fluctuates due to collective perturbative effects which the locally-different environments (the "bath") exert on the energy levels of the oscillator.

Two limiting cases can be established easily: A completely rigid system ($f(t) = 1$) obviously leads to a Gaussian band profile[7], of full width at half peak height FWHH = $2(2\ln 2)^{1/2}<|\omega_1(0)|^2>^{1/2}$, that depends solely on static bath parameters (besides eigenparameters of the oscillator: mass, frequency, anharmonicity). In contrast, a very mobile bath generates a Lorentzian band since, at many succeeding time instants t_j, $\omega(t)$ can "sample" all the different local environments of energy $E^i(t_j) = \hbar\omega_1^i(t_j)$, $i,j = 1, 2, \ldots$ within their (squared) width $<|\omega_1(0)|^2>$. In this fast repetition limit, the original coherence of $\omega_1(t)$ drops "instantaneously": $f(t) = \delta(t/\tau)$, where δ is a delta function. This obviously leads in Eq.1 to a purely exponential $C(t)$[8] and thus to a Lorentzian oscillator profile of $\mathcal{F}\{C(t)\}$, with FWHH = $2<|\omega_1(0)|^2>^{1/2}\tau$, that is now (in addition) determined by the dynamical bath parameter τ contained in $f(t)$ ("modulation time").[9]

Real systems of interest here are neither completely rigid nor extremely mobile but somewhere in between these limits. In such a situation, we have recently shown[10] that a useful and convenient choice of modulation function $f(t)$ of Eq.2 is the so-called 'fractional', 'extended', or 'stretched' exponential[11,12]

$$f(t) = \exp\{-(t/\tau)^{\alpha}\} \ ; \ 0 < \alpha \leqslant 1. \qquad (3)$$

Insertion of Eq.3 into Eq.1 yields

$$C(t^*) = \exp\{-<|\omega_1(0)|^2>(\tau^2/\alpha)[t^*\gamma(1/\alpha,t^{*\alpha})-\gamma(2/\alpha,t^{*\alpha})]\}, (4)$$

where γ is an incomplete gamma function and $t^* = t/\tau$ is a reduced time.

Depending on the size of dispersion parameter α, interesting conclusions on the nature of the dynamical processes can be drawn. If $\alpha \approx 1$, the "modulation event" which switches $\omega_1(t)$ of the probe oscillator from one value to another occurs essentially randomly, meaning that the history of the dynamics of the system at some previous time point $t' < t$ has no influence on the event at $t = t$. On the other hand, for $\alpha < 1$, the modulation event at $t = t$ depends on the previous state of the system such that some relatively slower motion, for instance a trans/gauche transition within a $(CH_2)_n$ residue of the alkyl chain, can only take place after several faster motions "happen to move in the right way"[13] (say, after C-C torsions coupled with CH_2 deformations have led to a $(CH_2)_n$ configuration that favors a trans/gauche conversion). This "constrained-sequential-hierarchical" model does not support the notion of a relaxation time (of the entire chain of the various dynamical processes) but leads, instead, to a scale-invariant distribution of relaxation times ("fractal time").[12,13]

In the following, we shall discuss some new Raman and infrared solution data of the CN oscillator profile of 4-n-nonyl-4'-cyanobiphenyl (9-CB) and relate them, in the frame of Eq.4, to corresponding results on molecular motion and clustering of the mesophases and the liquid.[14] Furthermore, we shall present a useful spectral diagnostic on the persistence of "local" phase memory of smectic and nematic configurations upon transition into the corresponding liquids for n-CB and related compounds that have or lack a nematic phase.

EXPERIMENTAL

All material-related, Raman-spectral, data-acquisition, and computational procedures were as previously described.[14] Infrared solution spectra were taken with standard commercial equipment and absorption cells. Slit corrections were not deemed necessary.

RESULTS AND DISCUSSION

MESOPHASES AND LIQUID

The mode of the CN stretching fundamental of 9-CB peaks at 2226.5 cm^{-1} for the liquid (95 C) and at 2227.5 cm^{-1} for the smectic (45 C) and nematic (49 C) phases. Its experimental band profile $I(\omega)$, bandwidth, and correlation function $\tilde{F}\{I(\omega)\}$ are not only identical in the three phases but are also independent of the type of spectroscopy (infrared, Raman-VV and VH polarization). This signifies, first,[15] that any molecular reorientational motions that have components normal to the CN bond direction (molecular "tumbling", for instance) are on a time scale of $\tau \gtrsim (\pi c \Delta\nu)^{-1} \sim 10^{-10}$ sec, where $\Delta\nu =$ 0.1 cm^{-1} is the absolute error of a bandwidth determination under optimal conditions. Second, we can draw certain generalizations of spectral diagnostic nature concerning alkyl/alkoxy cyanobiphenyls when such a system traverses phase transitions to the *liquid*. We predict:

(i) If the liquid crystal possesses a smectic and a nematic phase, the band profile of the probe oscillator remains essentially *identical* when the *nematic* → *liquid* phase transition is traversed.

(ii) If a nematic phase is missing, appropriate probe oscillator profiles undergo *band narrowing* when the *smectic* →

liquid phase transition is traversed.

These predictions are based on ideas of Gray[16] on mesophase stabilities as they depend on the lateral and terminal cohesions within liquid crystal systems: If the smectic phase breaks up to yield directly the liquid without passing through a nematic phase, the parallel molecular configurations, which are maintained in the smectic by strong cohesive lateral forces, are overcome by the randomizing effects of the kinetic energy; hence, the remaining terminal interactions are unlikely to re-establish a significant distribution of nearly aligned molecular configurations in the liquid.[16a] Consequently, the components of fast molecular motions which modulate the oscillator phase in the vibrational dephasing process, for instance torsional oscillations, encounter lower potential barriers due to the generally increased intermolecular separations: Thus, band narrowing ("motional narrowing") ensues by the faster loss of the coherence of the intermolecular potential, as we described in the Introduction. On the other hand, once a smectic phase goes over into a nematic phase, the relations between the lateral and terminal cohesive forces must by such that a near-parallel molecular arrangement is maintained in the nematic phase (although the regular layered structure is destroyed).[16b] Therefore, a significant distribution of microscopic configurations that remember the arrangement of the nematic parent phase may well exist in the liquid. In such a situation, the interchain separations and the rapid intra/interchain mobilities will rarely vary sufficiently strongly between the nematic and liquid phases to be registered by the environment-coupled probe oscillator.

Evidently, the above picture holds for 9-CB, 8-OCB, 8-CB on one hand, and 12-CB on the other.[17] The first three systems possess a smectic and a nematic phase: No bandwidth changes are observed[4,14] during the nematic to liquid phase transition; for 8-CB this has been verified with several other system oscillators, not only with the CN mode.[1c] Whether all mesomorphic systems behave accordingly, for instance those possessing short methylene chains (nematics),[18] or whether spectral changes during mesophase transitions can be resolved by more precise spectral techniques than ours, remains to be seen: It would certainly be of interest and importance.

SOLUTIONS

Figure 1 shows the experimental Raman CN-profile of 9-CB in its liquid phase (95 C, upper spectrum) and dissolved to 0.02 mol/l in CCl_4 (24 C, lower spectrum). In both cases, $\tilde{F}\{C(t);Eq.4\}$ with $\alpha = 1$ (smooth profile) is fitted to the experimental $I(\omega)$. Clearly, the fit for the pure liquid phase is very poor, as to be expected.[14] On the other hand, the theoretical fit to the experimental $I(\omega)$ for the dilute solution in CCl_4 leads to a value of dispersion parameter $\alpha \approx 1$. Furthermore, the result is <u>independent</u> of the spectral method (infrared, Raman-VV or VH) within the maximum accuracy of the data ($\pm$ 0.1 cm^{-1}).

First, this shows that the cybotactic groups of the liquid of 9-CB must have broken up in the dilute CCl_4-solution since $\alpha \approx 1$ predicts instantaneous modulation events ("binary collisions")[15] that occur completely at random, such as a positional fluctuation of a CCl_4 molecule within a "solvation sphere" around the CN group. Second, we can conclude that even the <u>isolated</u> 9-CB molecule does not undergo tumbling motion at a time scale faster than $\sim 10^{-10}$ sec.[15]

We found that only <u>near-complete</u> solvation of 9-CB by CCl_4, a nonpolar solvent, neutralizes the strong intermolecular association of the molecules. For instance, the dynamics of a more concentrated (0.1 mol/l) 9-CB/CCl_4 solution can no longer be simulated satisfactorily with $\alpha \approx 1$. In addition, the situation for the polar solvent $CHCl_3$ is entirely different: Here, Eq.4 with $\alpha = 1$ fails for the entire concentration range from neat 9-CB to 0.02 mol/l in $CHCl_3$. Further, whereas dissolution of 9-CB in nonpolar CCl_4 leads to a narrowing of the bandwidth of the CN oscillator profile to FWHH = 6.4 cm^{-1} relative to its liquid-phase value of 8.6 cm^{-1} (see Fig.1), dissolution to 0.02 mol/l in polar $CHCl_3$ creates the opposite effect: FWHH = 9.2 cm^{-1} (not shown here). Yet, for both solution systems, the CN peak frequency is blue-shifted by $\sim$ 2 cm^{-1} (from the neat liquid) at the highest dilution (see also Fig.1).

Without knowing the correlation functions C(t) of the CN profile in these solutions, we can at present only isolate some likely scenarios that would, on the basis of the dynamics of the system, explain the behavior of 9-CB.

(i) Under the hypothesis that both solvents, nonpolar CCl_4 and polar $CHCl_3$, lead at high dilution of 9-CB to an essentially complete destruction of near-parallel (or other preferred)directions , the different behavior of CCl_4 and $CHCl_3$ is simply one "of type". By this we mean that the perturbative effects of the polar molecule on the CN oscillator energies lead to a different (larger) local disorder at the CN oscillator site than the corresponding effects ofthe nonpolar solvent; in either case, the vibrational dephasing process arises from interaction of an isolated solute molecule with many solvent molecules. That the CN oscillator is isolated from the modulation effects of its 9-CB neighbors in both solvents seems indicated by the (near-equal) blue-shift of its peak frequency (see above).

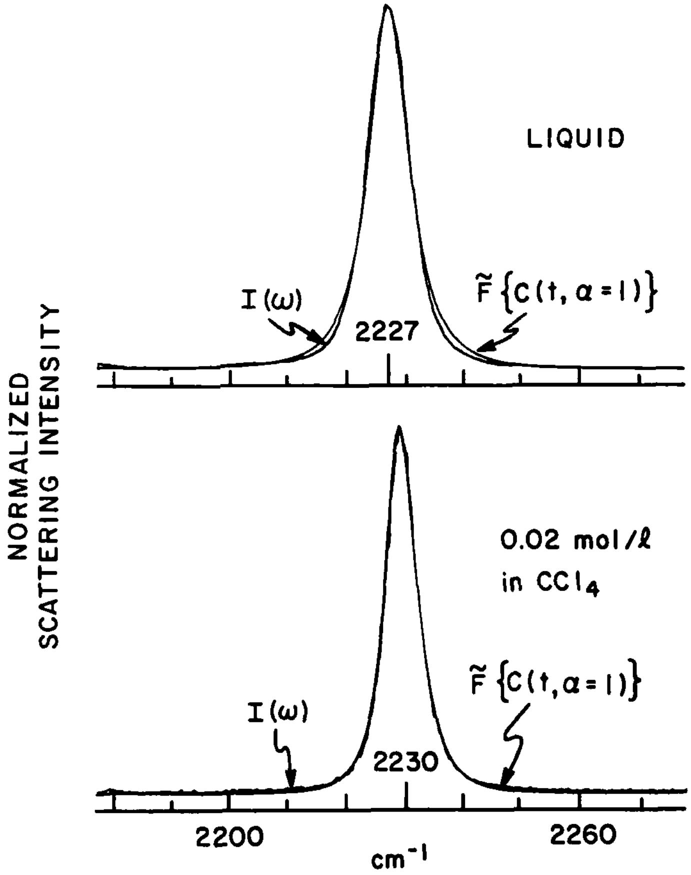

FIGURE 1. Band profile and fit by $\tilde{F}\{C(t);Eq.4\}$ with $\alpha = 1$ of the CN oscillator of neat (upper) 9-CB and diluted to 0.02 mol/l in CCl_4 (lower spectrum).

(ii) Under the hypothesis that, specifically, a nonpolar solvent solvates mainly the alkyl chain whereas the polar solvent preferentially solvates the CN group (and the phenyl ring),[4] a situation may arise where aggregation of a few 9-CB molecules, for instance via $CHCl_3$ molecules that "bridge" their more polarizable sections (CN groups, phenyl), persists into the solution regimes. That Eq.4, with $\alpha = 1$, fails to simulate the corresponding CN band profile, in other words, that the dynamics of the 9-CB/$CHCl_3$ system are still influenced by interactions between 9-CB molecules even in the dilute solution regime, lends support to this hypothesis.

Note that 8-OCB, a liquid crystal with as many flexible CH_2 groups as 9-CB (eight),[19] shows identical solution behavior: In the polar solvent $CHCl_3$ and CH_3SCN, the published correlation data[4] suggest a modulation mechanism with $\alpha < 1$, with apparently little change upon increasing dilution. On the contrary, for nonpolar solvents (CCl_4, C_6H_6), the bandwith of the CN profile decreases considerably with increasing dilution, hinting $\alpha \approx 1$ at the highest dilutions investigated (0.03-0.04 mol/l).[4] From this, it seems that the (additional) polar -O- group at the phenyl ring of 8-OCB bestows only the expected greater stability ranges[16c] to its mesophases relative to 9-CB (as can be seen from the higher transition point temperatures for 8-OCB)[4,14] but does not fundamentally influence the picosecond-range dynamics of these systems.

SUMMARY

We have shown here that the change of vibrational band profiles of convenient probe oscillators in liquid crystal systems can be used to infer the variations of local order and degree of association upon phase transitions, describes the general nature of fast dynamical processes in the medium, and leads to conclusions on types of molecular aggregations in solution environments upon dissolution of the compound in polar and nonpolar solvents.

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