Raman noncoincidence effect: A spectroscopic manifestation of the intermolecular vibrational coupling in dipolar molecular liquids*

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Abstract: This lecture addresses the analysis of the noncoincidence effect (NCE), a spectroscopic manifestation of the intermolecular coupling in molecular liquids. The vibrational bandshapes of molecular groups like C=O (strongly active in the IR spectrum) in dipolar liquids exhibit this phenomenon at a rather large extent. It will be shown that the vibrational exciton approach, developed under the assumption of the transition dipole coupling (TDC) mechanism, predicts how the orientational structure of the molecular liquid determines the magnitude and sign of the NCE. Specifically, it predicts that in simple molecular liquids, solely structured by dipolar forces, the NCE is large and positive, whereas when liquid structures are dominated by non-dipolar forces (as those present in H-bonded liquids), this scenario dramatically changes and IR-active modes may give rise to negative NCEs.

This lecture is intended to offer a general overview of NCEs observed in dipolar (simple and structured) liquids in different thermodynamic conditions and of the theoretical and simulation results that assisted in their interpretation.

INTRODUCTION

Intermolecular interactions in molecular liquids lead to a large variety of structural and dynamical processes. The extended phenomenology manifested in the vibrational spectra of molecular liquids witnesses, directly or indirectly, the existence and the peculiarities of these processes, thus allowing a characterization of the intermolecular interactions in dense phases.

This lecture addresses the analysis of the specific spectroscopic manifestation of the intermolecular coupling in molecular liquids that is conventionally referred to as the Raman noncoincidence effect (NCE). It consists of a splitting (Δ_α) between the anisotropic and isotropic components of a Raman band associated with a total-symmetric vibrational intramolecular normal mode α ($\Delta_\alpha = v_{\text{aniso},\alpha} - v_{\text{iso},\alpha}$). An observed Raman profile can, in fact, be regarded as a superposition of two independent spectra, the isotropic and the anisotropic Raman spectrum produced by the corresponding parts of the transition polarizability $\boldsymbol{\alpha}$ (the relevant property of any Raman spectroscopic experiment). From its first observation [1] to the NCE in dipolar liquids was given a quantum mechanical interpretation based on the vibrational exciton approach [2]. According to this theory, when intramolecular vibrations of pairs of adjacent molecules are coupled via an appropriate interaction (such as the transition dipole–transition dipole interaction, TDC), a splitting of the excited vibrational states can occur. In these cases, the magnitude and sign of this splitting are dictated by the orientational structure of the molecular liquid. Consequently, dipolar molecular groups like C=O (present in ketones, aldehydes, amides, esters…)

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having a strongly IR-active stretching vibration represent, as will be widely illustrated in this lecture, the best candidates for the observation of large and positive NCEs in simple molecular liquids, solely structured by dipolar forces [3,4]. Liquid structures dominated by non-dipolar forces (as those present in H-bonded liquids) dramatically change this scenario and IR-active modes (as, e.g., the C–O stretching in methanol) may give rise to negative NCEs, as experimentally observed in the v(C–O) stretching vibration in methanol [5,6,9] and calculated by computer simulation methods [7,8].

NCE is not a peculiarity of dipolar or H-bonded liquids. A few Raman investigations performed on nonpolar liquids (such as benzene) have revealed that slight, often negative, NCEs occur in IR-inactive (ring-breathing) modes. Since this topic is outside of the scope of this lecture, we limit ourselves to say that they were interpreted as the manifestation of a dominant repulsive coupling [10]. When present in IR-active modes of nonpolar liquids, the negative NCEs were interpreted, invoking the point of view stating that the orientational short order is not a necessary condition for the appearance of the NCE [11].

The thermodynamic state dependence of NCE was first investigated through studies of its concentration dependence and the results analyzed by an empirical equation in which the effect of the liquid structure was modeled through a macroscopic property, the dielectric constant of the mixtures [3]. The theoretical results obtained in the 1980s by Logan [12] offered an advanced tool for the interpretation of the thermodynamic state dependence (T, x_A, ρ) of NCE in dipolar liquids at the molecular level, with the introduction of the concept of liquid structure factor. The limit of this theory, represented by the approximate formulation (mean spherical approximation, MSA) of the latter quantity, encouraged the application of simulation methods (MC and MD) for the determination of the thermodynamic behavior of NCE [7,8]. Recourse to these approaches is mandatory for the interpretation of NCE in structured liquids [7,13] since these are outside the basic premises of the Logan theory.
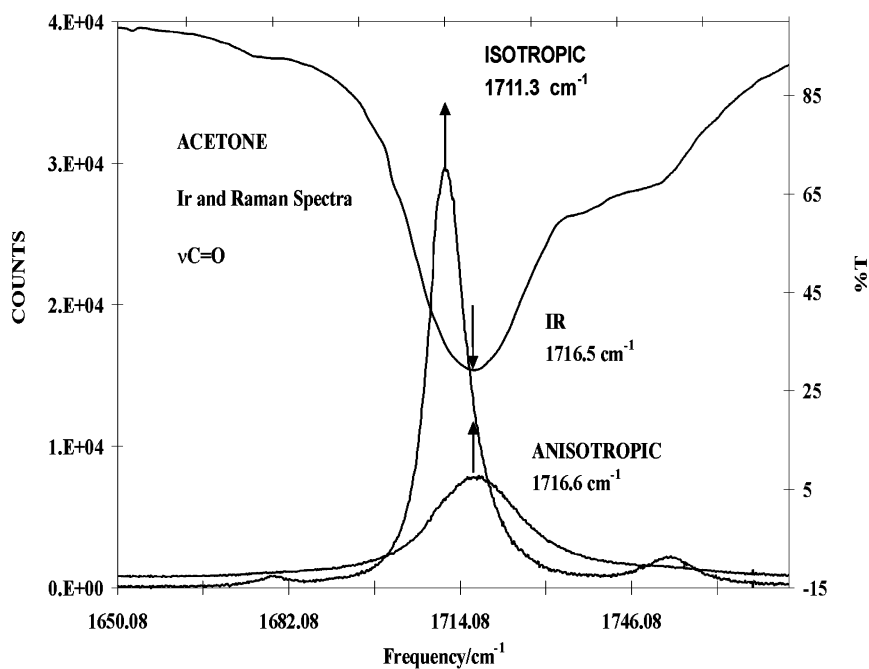
The aims of this lecture are as follows:

• to show how this phenomenon (NCE) manifests itself in different molecular liquids,
• to show how NCE is affected by the change of thermodynamic conditions,
• to recognize the role played by the orientational structure of the liquid,
• to show how NCE may be theoretically predicted and computationally evaluated, and
• to show that NCE may be regarded as a manifestation of a resonant vibrational energy transfer.

MEASUREMENTS OF NCE

NCE is conventionally defined as the separation between the aniso- and isotropic profiles of a Raman band (see Figs. 1 and 2) associated with a total-symmetric normal mode, α. A Raman spectrum can be considered as the superposition of these two profiles determined by the corresponding rotational invariants a^α (isotropy) and β^α (anisotropy) of the transition polarizability tensor: $\alpha^\alpha = (1/3)a^\alpha + \beta^\alpha$. The isotropic and anisotropic contributions to a Raman band I^α_R can be extracted from its polarized (VV and VH) spectra: $I_{iso} = I_{VV} - (4/3)I_{VH}$, $I_{ani} = I_{VH}$, since according to [14]:

$$I^\alpha_{VV} = A(v_0 - v_\alpha)^4 \left(\frac{45(a^\alpha)^2 + 4(\beta^\alpha)^2}{45} \right) Q^2_\alpha$$

$$(1)$$

$$I^\alpha_{VH} = A(v_0 - v_\alpha)^4 \left(\frac{(\beta^\alpha)^2}{15} \right) Q^2_\alpha$$

Fig. 1 The peak frequencies of IR, isotropic, and anisotropic Raman profiles of the ν(C=O) mode of liquid acetone do not coincide. The isotropic profile has a peak frequency lower than the anisotropic one, and the latter approximately coincides with that of the IR profile.
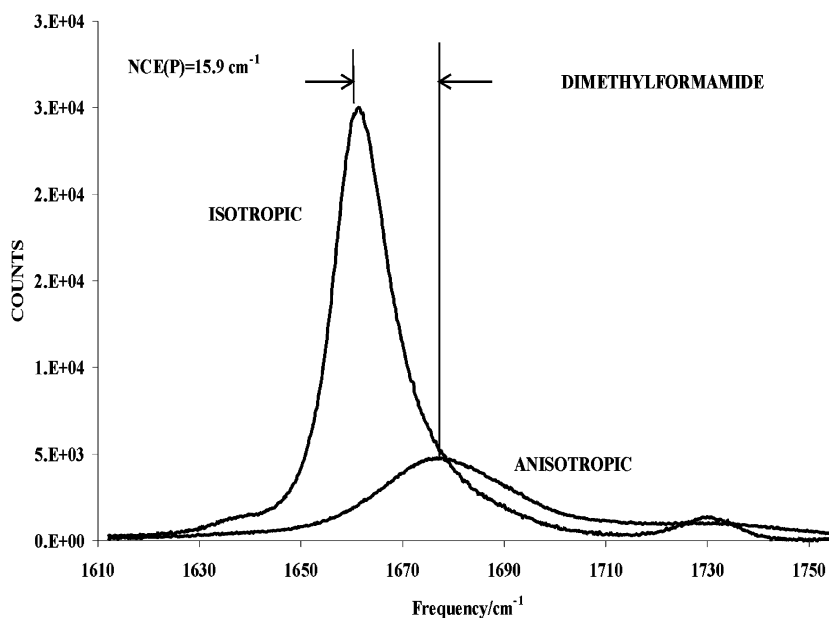
Fig. 2 The noncoincidence effect in the ν(C=O) mode in liquid dimethylformamide (DMFA).

A more direct contact with the theoretical predictions can be achieved by measuring NCE as the difference of the spectral isotropic and anisotropic first moments: $\Delta_\alpha(M1) = M(1)^\alpha_{ani} - M(1)^\alpha_{iso}$. The two definitions of NCE, $\Delta_\alpha(M1)$ and $\Delta_\alpha(peak)$, may give rather different results since, as theoretically predicted and experimentally observed, the isotropic spectral distribution of a Raman band may be asymmetric as a consequence of the same process (intermolecular vibrational coupling) that gives rise to NCE [15].

The measurements of the quantities I_{VV} and I_{VH} are obtained with rather conventional polarized Raman experiments. Briefly: The vertically polarized light of a laser source (free from any parasitic perpendicular component) excites the liquid sample; the scattered light, observed with a 90° geometry, is analyzed to alternatively select the vertically and horizontally polarized components; these, after depolarization (to avoid the different grating efficiencies for the two polarizations of light), are spectrally dispersed and then revealed through a single (PMT) or multiple (CCD) channel detectors. The raw spectral profiles, after frequency and detector sensitivity calibration, are numerically treated to get the spectral first moments or peak frequencies.

OBSERVATION AND INTERPRETATION OF NCE

Dipolar liquids: Standard thermodynamic conditions

Observations

In Table 1, we report the measured isotropic, anisotropic (and their separation Δ_v^α) and IR peak frequencies for a series of dipolar molecular liquids. It is evident that

- the anisotropic peak frequencies are always higher than the isotropic ones;
- the IR peak frequencies are approximately coincident with the anisotropic ones;
- the dipole moment is not a condition sufficient to justify the onset of NCE; and
- oscillators with high-transition dipole moments (high IR intensity), such as $v(C=O)$, have correspondingly high NCE; oscillators with low-transition dipole moment, such as $v(CN)$, have low NCE (see text).

Table 1 Vibrational (IR, Raman isotropic and anisotropic) frequencies of some groups in molecular liquids.

$v(C=O)$	$\mu\ 10^{30}$/Cm	v_{ani}/cm^{-1}	v_{iso}/cm^{-1}	Δ/cm^{-1}	v_{IR}/cm^{-1}
DMFA	12.7	1674	1660	14	1675
Cyclobutanone	10	1781	1775	6	1782
Cyclohexanone	9.3	1714	1707	7	1714
Acetone	9.4	1714	1709	5	1715
γ-Butyrolactone	13.7	1770	1761	9	1772
Benzaldehide	9.2	1703	1698	5	1703
$v(S=O)$					
Sulfolane	15.09	1109	1106	3	1108
$v(NO_2)$					
Nitromethane	10.34	1403	1400	3	1404
p-Nitrobenzene	14.67	1344.5	1342.5	2	1344.2
$v(CN)$					
Acetonitrile	11.34	2251	2250	1	2251

Theoretical considerations

Intermolecular interactions

In dipolar liquids, the most relevant intermolecular perturbation V_{ij} is that between dipoles:

$$V_{ij} = \frac{(\boldsymbol{\mu}_i) \cdot (\boldsymbol{\mu}_j) - 3(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{n}_{ij})}{R_{ij}^3} \tag{2}$$

After performing scalar products:

$$V_{ij} = \frac{\mu_i \mu_j}{R_{ij}^3} K \tag{3}$$

where $K = [-2\cos(\theta_i)\cos(\theta_j) + \sin(\theta_i)\sin(\theta_j)\cos(\phi_i - \phi_j)]$ is a geometrical parameter describing the mutual orientation (θ,φ) of the two dipoles, $\boldsymbol{n}_{ij}$ is a unit vector in the direction of the intermolecular axis, R_{ij} is the magnitude of their separation.

Molecules vibrate: Q describes the normal coordinate of interest. From the expansion of the dipole moment (to second order) in the normal coordinate the TDC term arises as ($\partial\mu$ is a shorthand for $\partial\mu/\partial Q$):

$$V_{ij} = \frac{(\partial\mu_i)(\partial\mu_j)}{R_{ij}^3} K \tag{4}$$

Splitting of vibrational bands: The exciton theory

The idea that states in condensed matter could be coupled by a transition dipole mechanism was first proposed by Davidov [16] and then applied by Craig [17] to explain the splittings observed in the electronic spectra of molecular crystals. An extension of this approach to vibrational bands is due to Hexter [2], who contextually proposed the method of isotopic dilution in order to monitor the intermolecular coupling. All these approaches are termed "exciton theory", electronic or vibrational, depending on the state of matter considered. The central point of this theory is that of adopting a transition dipole–transition dipole interaction V_{ij} as a perturbation between the electronic or vibrational energies of distinct molecules (4). The band splitting by TDC mechanism in many-particle systems can be sketched using the perturbation scheme reported in Fig. 3a for the simple case of

- a pair of identical molecules i and j,
- with only one degree of freedom (normal coordinate Q^α and frequency $v_0{}^\alpha$), and
- perturbed by a potential V^α (taken to be static for simplicity).

The perturbations of the single particle coefficients $V^\alpha{}_k$ and $V^\alpha{}_{kk}$ ($k = i,j$) of the intermolecular potential V^α (reported here as a Q^α expansion for a many-particle system):

$$V^\alpha = \sum_{k=i,j} V_k^\alpha Q^\alpha + \frac{1}{2}\sum_{k=i,j} V_{kk}^\alpha Q_k^\alpha Q_k^\alpha + \frac{1}{2}\sum_{i<j} V_{ij}^\alpha Q_i^\alpha Q_j^\alpha \tag{5}$$

determined on the fundamental and on the (twofold degenerate, Ψ_{01} and Ψ_{10}) excited level are responsible for the frequency shift $[\omega - \omega_0 = (D_1 - D_0)/\hbar]$ observed in the gas–liquid phase transition whereas the intermolecular potential vibrational coupling term $V^\alpha{}_{ij}$ (dimensionally a force constant) (4) is responsible for the removal of the degeneracy of the excited level and then for the frequency splitting:

$$\Delta_\alpha = \frac{(\partial\mu_i^\alpha)(\partial\mu_j^\alpha)(\hbar/2m\,\omega_0^\alpha)}{R_{ij}^3} K \tag{6}$$

From this very elementary treatment some expectation can be formulated on NCE: in addition to being correlated with the IR intensity of the mode α through the transition dipole moment $\partial\mu^{\alpha}$, it depends on the orientational structure of the liquid through K; thus, NCE is expected to decrease with temperature, at constant density, as a consequence of thermal averaging ($<K>_{\text{or}} \propto 1/kT$). It depends on the separation R_{ij}, thus, it is expected to increase with external pressure and decrease with dilution in isotopic and chemical mixtures, but in different ways that the results of the Logan theory (in the next section) will clarify.

The simple considerations developed up to now allow the interpretation of NCE observations in nonstructured polar liquids and liquid mixtures. Its dependence on the transition dipole moment is evident by comparison of Figs. 1 and 2. At the same thermodynamic condition (T and P), the NCE of v(C=O) in DMFA is larger than that in acetone as a consequence of its larger transition dipole moment $(\partial\mu_{\text{DMFA}}{}^2/m) = 10.0 \times 10^{-12} C^2\ kg^{-1}$ and $(\partial\mu_{\text{acetone}}{}^2/m) = 2.7 \times 10^{-12} C^2\ kg^{-1}$ [18,19].

A system of two identical molecules (A,B) can be described through their unperturbed (nonstationary) states, φ_i(A) and φ_j(B). Under the influence of an intermolecular coupling the excited system evolves in time from one to the other excited configurations described in Fig. 3b with the consequence that the excitation present in molecule B in the left configuration is transferred to molecule A in the right configuration. In the language of quantum mechanics [20], the band splitting Δ reported in Fig. 3a represents the inverse of the time necessary for the transfer of the energy hv between the two identical molecules.
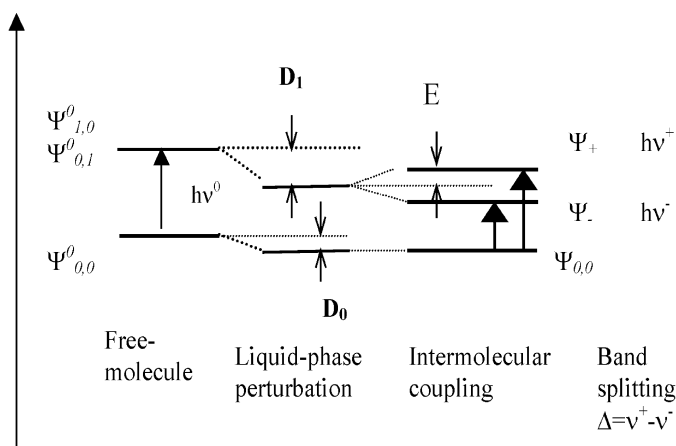
Fig. 3a Scheme illustrating the origin of the band shift and the band splitting in condensed phase in the exciton theory (for a pair of identical molecules). D_0–D_1 is the gas–liquid phase-transition frequency shift. Intermolecular coupling removes the degeneracy of the excited level.
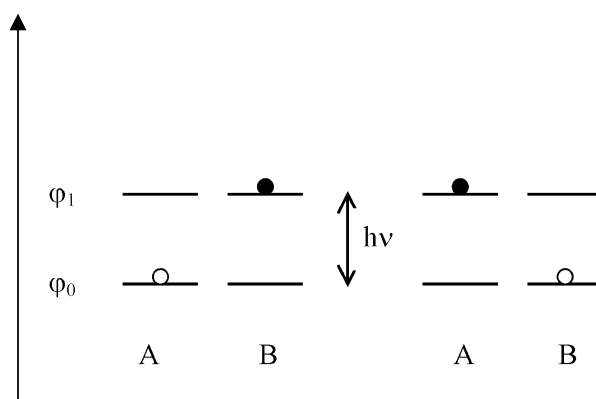
Fig. 3b Scheme illustrating the resonant transfer of energy between two molecules. In the left configuration, the excitation is confined to molecule B, in the right to molecule A. Coupled systems evolve from one configuration to the other, thus transferring energy resonantly.

Dipolar liquids in variable thermodynamic conditions (*X,T,P*)

Observations

- NCE increases with pressure (in isothermal conditions) and decreases with temperature (in isochoric conditions), as described in Fig. 4.
- NCE decreases with dilution in a way different in isotopic (linear dependence, see Fig. 5) and chemical (nonlinear dependence, see Fig. 6) mixtures, and, in the latter case with a curvature determined by the relative dielectric constant, $\varepsilon_{solute}/\varepsilon_{solvent}$, or in molecular terms, by the relative dipole moments of the two mixture components (negative if $\varepsilon_{solute}/\varepsilon_{solvent}$ or $\mu_{solute}/\mu_{solvent} > 1$, positive in the opposite case). Considering the isotropic and anisotropic profiles, their peak frequencies (or $M1$) increase with chemical dilution in a different way and nonlinearly [3,18,19], whereas they increase linearly with isotopic dilution [21].
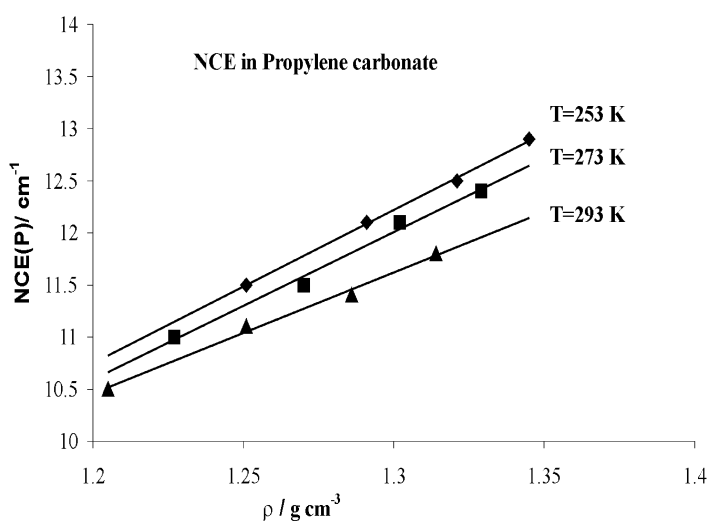
Fig. 4 The noncoincidence effect of the $\nu(C=O)$ mode in liquid propylene carbonate; it increases with density in isothermal conditions and decreases with temperature in isochoric conditions. (Redrawn from the data reported in ref. [25].)
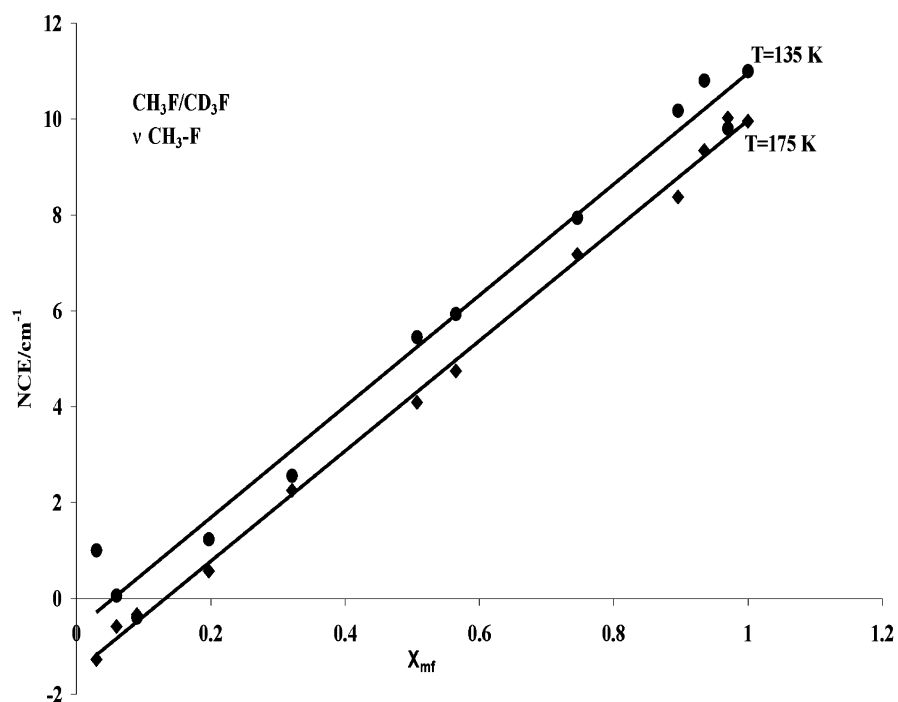
Fig. 5 The noncoincidence effect of $\nu(CH_3\text{-}F)$ in isotopic binary mixtures CH_3F/CD_3F at two temperatures: NCE decreases linearly with dilution. (Redrawn from the data reported in ref. [21].)
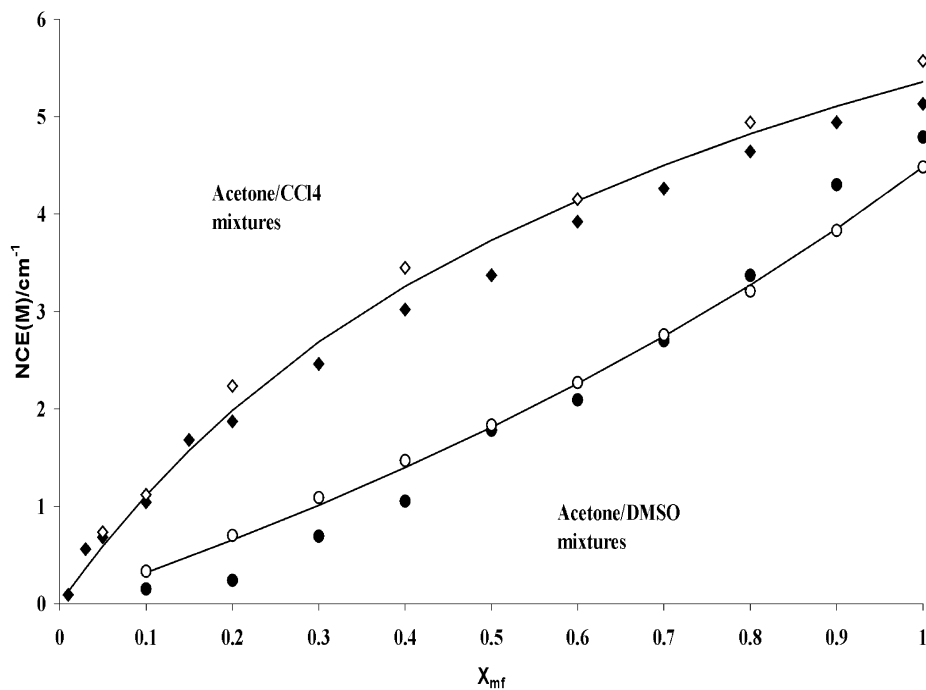
Fig. 6 The noncoincidence effect of the $\nu(C=O)$ mode of acetone in chemical mixtures acetone/CCl_4 (diamonds) and acetone/DMSO (circles) decreases nonlinearly with dilution with negative and positive curvature, respectively. Filled symbols: observed, open symbols simulated NCE [19,24].

Intermolecular vibrational coupling in addition to NCE promotes a rather evident blue asymmetry in the isotropic profile, rather common in polar liquids, that makes NCE(P), measured through peak frequencies, smaller than NCE(M), measured by first moments [19]. The progressive reduction of the blue asymmetry with dilution that eventually reverses to red at the highest dilutions, together with the subsequent observation of negative NCE(P) below a given concentration, led us to believe in the existence, later on disproved [4], of a threshold concentration for the onset of NCE [3]. In this context, the (nongenuine) observation of a threshold concentration for NCE was plausibly considered as the consequence of the premature switching off of the resonant transfer process caused by the competition with the energy relaxation process at high dilution.

Theoretical considerations

The first attempts to interpret the concentration dependence of the relative NCE (in the approach of the TDC mechanism) [3] were based on the idea of describing the effect of the medium on the intermolecular coupling, the screening factor S, through a macroscopic property, the dielectric constant, according to the Onsager–Frölich dielectric model.

A unified approach for the thermodynamic state dependence (X_A, ρ, T) of IR, isotropic and anisotropic frequency shifts, and then of NCE, was given by Logan [12] as an extension to polyatomic molecules and binary mixtures of the theoretical treatments of band profiles worked out, in the time-correlation function approach, for zero- ($\lambda = 0$, isotropic), first- ($\lambda = 1$, IR) and second- ($\lambda = 2$, anisotropic) rank tensors [22,23]. The extension of the static pair-particle to dynamical, many-particle, systems requires performing averages over the bath coordinates and taking into account the time dependence of the potential $V(t)$ in the perturbation treatment so that the diagonal and off-diagonal elements of the perturbation matrix $\Omega(t)$ enter, by virtue of the stationarity of the ensemble average, as zero-time ensemble averages. Depending on the tensor rank (λ) of the spectroscopic property relevant to the experiment ($a^\alpha, \lambda = 0; \boldsymbol{\beta}^\alpha, \lambda = 2; \boldsymbol{\mu}^\alpha, \lambda = 1$) the first moments for the iso- ($\lambda = 0$), aniso- ($\lambda = 2$), and IR ($\lambda = 1$) profiles associated with the α normal mode result: $M(1)_\lambda = \omega^0 + <\Omega_{ii}(0)> + Nx_A<\Omega_{ij}(0)P_\lambda(\boldsymbol{n}_i\cdot\boldsymbol{n}_j)>$. Here, $\Omega_{ii}(0)$, $\Omega_{ij}(0)$ are the zero-time diagonal and off-diagonal elements of perturbation matrix corresponding to the environmentally induced and intermolecular coupling induced frequency shifts, respectively, described as $D_1 – D_0$ and E, respectively, in the scheme reported in Fig. 3a. X_A is the molar fraction of component A containing the intermolecularly coupled oscillator, α ($X_A = 1$ for neat liquids), ω^0 is its free molecule vibrational frequency. P_λ is the Legendre polynomial of rank λ; $\boldsymbol{n}_i$, $\boldsymbol{n}_j$ are unit vectors in the directions of the dipole (transition dipole) moments. Some conclusions can be drawn:

1. Both observables: $M(1)_{aniso} – M(1)_{iso} = Nx_A<\Omega_{ij}(0)[P_2(\boldsymbol{n}_i\cdot\boldsymbol{n}_j) – 1]>$ and $M(1)_{IR} – M(1)_{iso} = Nx_A<\Omega_{ij}(0)[P_1(\boldsymbol{n}_i\cdot\boldsymbol{n}_j) – 1]>$ are different spectroscopic manifestations of the intermolecular vibrational coupling and thus a measure of the NCE;
2. the intermolecular vibrational coupling has the largest effect on $M(1)_{iso}$ and no effect on $M(1)_{IR}$ since $25<\Omega_{ij}(0)P_2(\boldsymbol{n}_i\cdot\boldsymbol{n}_j)> = <\Omega_{ij}(0)P_0(\boldsymbol{n}_i\cdot\boldsymbol{n}_j)>$ and $<\Omega_{ij}(0)P_1(\boldsymbol{n}_i\cdot\boldsymbol{n}_j)> = 0$; and
3. the concentration dependence of the NCE in liquid mixtures has a twofold origin, from the factors x_A and $<\Omega_{ij}(0)[P_2(\boldsymbol{n}_i\cdot\boldsymbol{n}_j) – 1]>$, where the structural effects of dilution are embodied. The latter are, however, constant in isotopic mixtures and correspondingly the concentration dependence of NCE is linear in these systems, whereas it is nonlinear in chemical mixtures (see Figs. 5 and 6).

These points (mainly the first one) state unambiguously that NCE represents a probe of the average orientational structure in dipolar liquids. The Logan theory [12] has offered to Raman spectroscopists several possibilities for interpreting their experimental results on the thermodynamic state dependence of $M(1)$ and NCE. The quantitative prediction of these quantities entails the evaluation of the averages $<\Omega_{ij}(0)P_\lambda(\boldsymbol{n}_i\cdot\boldsymbol{n}_j)>$, $\lambda = 0,2$. They both come out always negative in systems dominated by dipolar forces since here the sign of the perturbation Ω_{ij} is negative (see eqs. 2–4). It can then be con-

cluded that, taking into account their different magnitudes (reported in point 2), TDC-induced NCE (point 1) must be always positive in dipolar systems. As anticipated, Logan formulates the averages (in point 1) in terms of the liquid structure factor $\xi_A(X_A,\rho,T)$, which is obtained exactly within the MSA.

$$M(1)_{\text{ani}} - M(1)_{\text{iso}} = \Delta_{\alpha,A}(X_A,\rho,T) = \frac{X_A \xi_A(X_A,\rho,T)}{cT_{\alpha,A}} \tag{7}$$

In $T_{\alpha,A}$ all molecular ($m_{\alpha,A}$ and σ, the hard sphere diameter) and spectroscopic ($\omega_{\alpha,A}$, $\gamma_{\alpha,A}$ proportional to the transition dipole moment) parameters are collected. It was used for the prediction of the NCE of several dipolar binary mixtures [4,5b,18,19,24]. Alternatively, NCE can be evaluated by a numerical calculation of the liquid structure factor through the integrated second component of the pair distribution function, $H_D(\infty)$, for the neat compound obtained in computer (MC or MD) simulations, according to [8,19]. The Logan theory fails in predicting the NCE in complex liquids since here the prevailing orientational organization between the permanent and transition dipoles is largely determined by steric (polymers, liquid crystals, [26]) or strongly directional intermolecular interactions (H bonds). The negative noncoincidence effect observed in the ν(C–O) mode and its thermodynamic state dependence cannot be interpreted within this theory.

To overcome the limitation imposed by the MSA and to interpret NCE in complex liquids, Torii and Tasumi [7] and Torii [8] proposed the MC(MD)/TDC simulation method. Basically, the liquid structures are evaluated by (NVT) MC(MD) simulations considering only one vibrational degree of freedom per molecule by extracting (400 or more) configurations (R_{ij},$\boldsymbol{n}_{ij}$ and $\boldsymbol{n}_i$,$\boldsymbol{n}_j$). The transition dipole moment $\partial\mu_i$ for the vibration under study are calculated by quantum mechanical methods (ab initio MO calculations); with these quantities the F matrix for the N-oscillators system can be built (eqs. 2 or 4):

$$F_{ij} = \frac{(\partial\boldsymbol{\mu}_i)\cdot(\partial\boldsymbol{\mu}_j) - 3(\partial\boldsymbol{\mu}_i\cdot\boldsymbol{n}_{ij})(\partial\boldsymbol{\mu}_j\cdot\boldsymbol{n}_{ij})}{R_{ij}^3} \tag{8}$$

Its diagonal elements (the same for all molecules) are chosen to reproduce the vibrational frequency, the off-diagonal elements are described on the basis of the transition dipole mechanism.

The solution of the eigenvalues problem for this F matrix (for each configuration) gives N normal frequencies and the corresponding eigenvectors; on the basis of these results and of the Raman tensors (chosen to reproduce the experimental depolarization ratio for the band under consideration), the isotropic and anisotropic profiles can eventually be evaluated. These methodologies (MC/TDC and MD/TDC) are described in detail in refs. [7–9,13,19] and have been applied to the determination of the NCE in dipolar and structured molecular liquids and under different thermodynamic conditions: at different pressures [7] (acetone and methanol), in binary mixtures (acetone in CCl_4 [19], acetone in DMSO [24], methanol in CCl_4 [9]), and electrolytic mixtures (LiCl in methanol solutions [13]). To be more specific: It may be worthwhile to mention, one for all, the results obtained from the interpretation of the NCE in methanol (structured as, broadly, parallel winding chains of H-bonded methanol molecules) and its concentration dependence [9]. The NCE results consisted of a positive contribution from inter-chain, prevalently antiparallel, ν(C–O) interactions and a negative contribution from intra-chain, prevalently parallel, ν(C–O) interactions. The negative NCE observed in neat methanol (see Fig. 7) is the consequence of the higher efficiency of the latter. With increasing pressure or increasing concentration in binary mixtures, the negative NCE decreases in magnitude compared to the increased efficiency of the inter-chain interactions (see Figs. 8 and 9). These investigations on methanol/CCl_4 have revealed that dilution modifies the local anisotropic structure around each molecule since intermolecular separations predominantly change in all directions except along the hydrogen-bond direction.
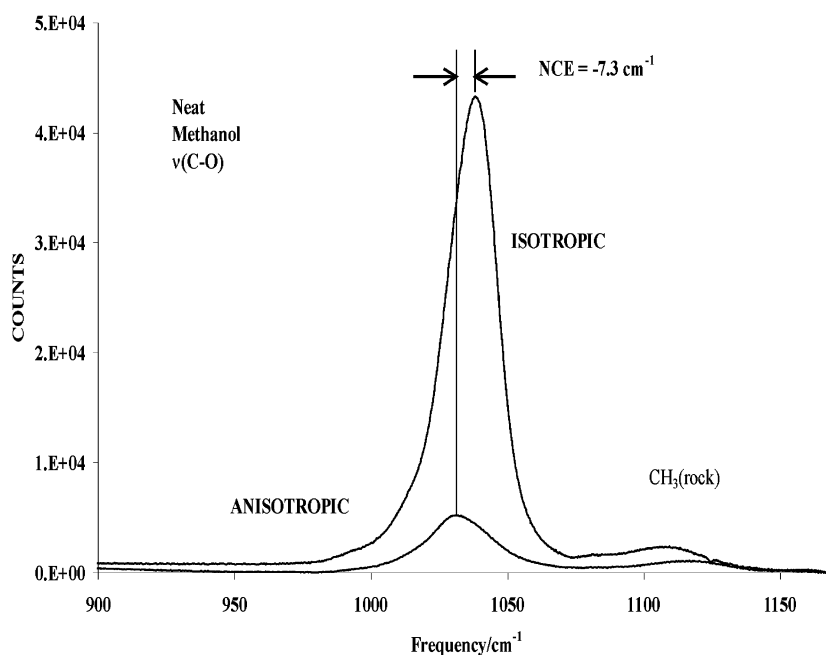
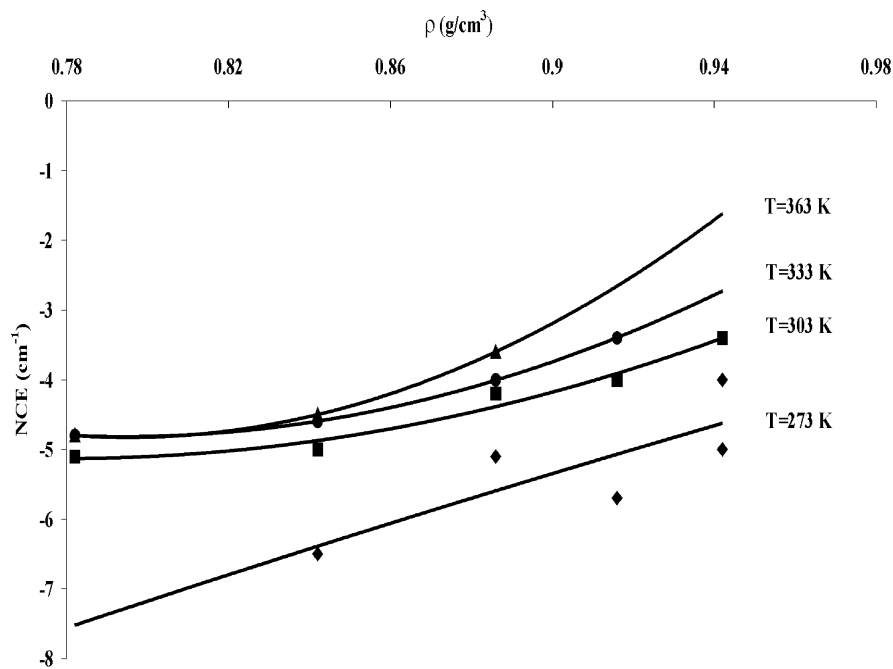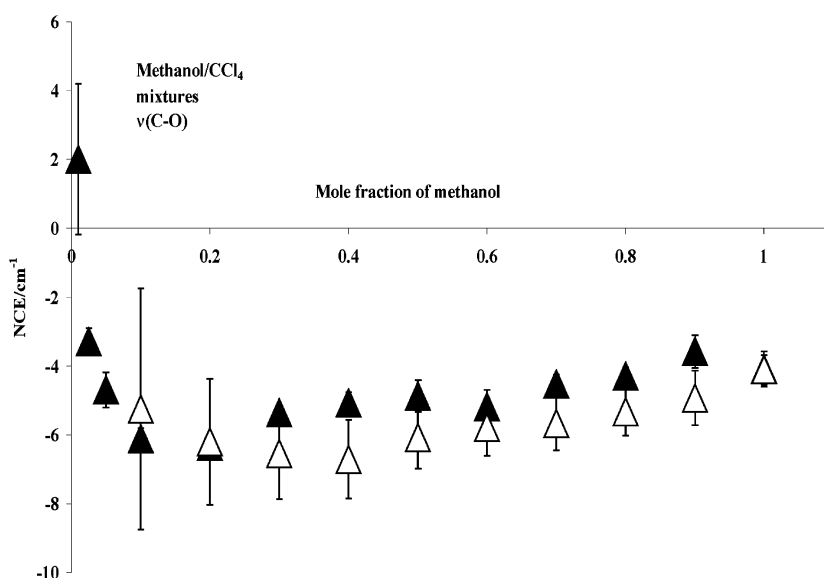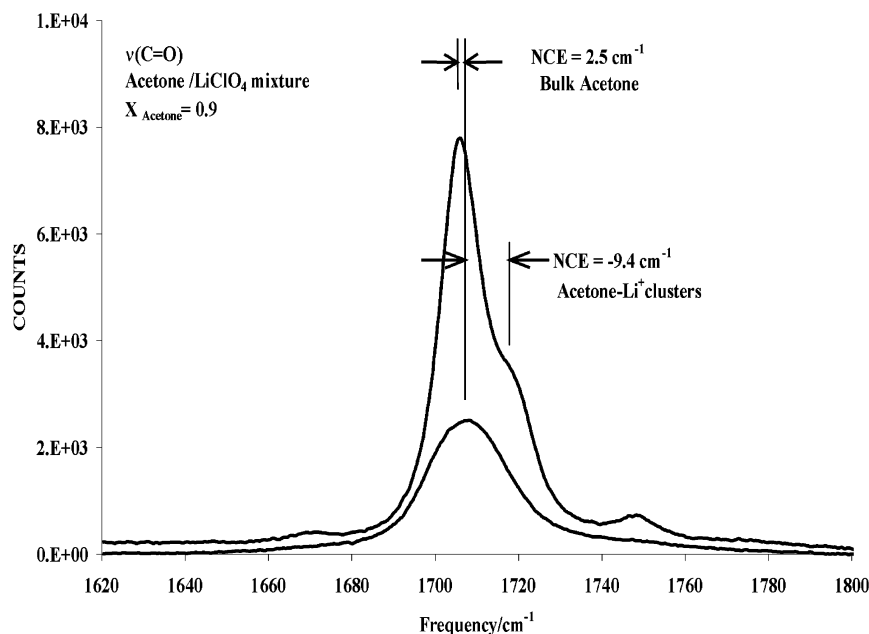**Fig. 7** The negative noncoincidence effect of v(C–O) mode in liquid methanol.

Fig. 8 The negative noncoincidence effect of v(C–O) in liquid methanol gets smaller (in magnitude) with pressure in isothermal conditions at different temperatures. (Redrawn from the data of isotropic and anisotropic peak frequencies reported in Table I of ref. [5].)

Fig. 9 The negative noncoincidence effect of ν(C–O) in methanol gets slightly smaller (in magnitude) with concentration in CCl_4 (down to $X_{MeOH} = 0.1$). The concentration dependence of the noncoincidence effect parallels the density dependence reported in Fig. 8. (These results appear as a part of Fig. 7 in ref [9].)

Fig. 10 The negative noncoincidence effect of ν(C=O) of acetone in the electrolytic mixture $LiClO_4$/acetone (Xacetone = 0.9): the isotropic (1705.3 cm^{-1}) is lower than the anisotropic (1707.8 cm^{-1}) peak frequency in bulk acetone and higher (1717.2 cm^{-1}) in acetone/Li^+ clusters [27].

Experimental observations such as the NCE of liquids in confined geometries and the negative NCE of acetone in electrolytic mixtures [27] (see Fig. 10), first reported in ref. [28], are planned to be interpreted within these methodologies.

CONCLUSIONS

NCE is a rather easily accessible spectroscopic observable. An extended phenomenology indicates that it is a sensitive indicator of the liquid structure and of its changes with thermodynamic conditions. The interpretation of this phenomenology in dipolar liquids can take advantage of the applicability, even though with some minor restriction, of the results of the Logan theory. For all liquids, but particularly for structurally complex systems, MC(MD)/TDC simulation methodologies offer a unique tool to shed light onto the structural organization of liquids by fine-tuning the calculated to the observed thermodynamic behavior of the NCE.

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