Non-coincidence effect of aromatic ring vibrations*

A Morresi, M Paolantoni, P Sassi, R S Cataliotti and G Paliani

Dipartimento di Chimica, Laboratorio di Chimica Fisica, Università di Perugia, V. Elce di Sotto 8, 06100 Perugia, Italy

E-mail: morresi@unipg.it

Abstract. The non-coincidence of the maxima of the isotropic and the anisotropic profiles in Raman spectra has always been considered an efficacious probe of the structure and dynamics of polar liquids. An anomalous, negative non-coincidence effect has been observed in ring breathing modes of aromatic molecules, without dipole moment (*p*-xylene, mesitylene) or with a weak permanent dipole (toluene, *o*-xylene, *m*-xylene). Temperature effects and isotopic dilution have also been performed in toluene and *o*-xylene, confirming the presence of a resonant coupling mechanism. Previous analogous results of other aromatic non-polar liquids (benzene, hexafluorobenzene) have been confirmed. It has been hypothesized that quadrupolar intermolecular forces and steric repulsive interactions balance each other giving final negative values of non-coincidence effect.

1. Introduction

Conventional vibrational spectroscopy experiments are well suited to investigate the structure and dynamic processes in the liquid phase: it is possible to get information about the intermolecular potential in the chosen molecular system according to the shape and position of spectral bands at different temperature, density and molar fraction values [1].

For each totally symmetric vibration of a Raman spectrum, depending on the geometry of the scattering experiment, it is always possible to define two distinct band profiles, isotropic and anisotropic. The non-coincidence of the position of the maximum of these two profiles (non-coincidence effect, NCE, $\delta\nu$) is defined as:

$$\delta\nu = \nu_{aniso} - \nu_{iso}. \tag{1}$$

It is the result of a process of resonant energy transfer between two identical active oscillators. This phenomenon has been extensively observed in both Raman and IR strongly active bands, such as C=O, SO and CN stretchings [2–9]. In these systems the isotropic profile usually lies at lower wavenumbers than the anisotropic profile, so that the quantity in equation (1) has a positive value and we can speak about a positive NCE.

A number of theoretical models have been proposed to interpret this effect: Wang and McHale [10], Mirone [11], Döge [12], with the most detailed and complete by Logan [13]. All of them have suggested the presence of a certain degree of orientational order in the liquid.

A negative NCE value has been observed in some molecular liquids. For the C–O stretching of methanol [14], and ethanol [15] the negative NCE was attributed to the effect of the hydrogen bonding on the transition dipole–transition dipole mechanism.

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Recent molecular dynamics calculations and *ab initio* molecular orbital studies have been applied to the OH and CO stretching band of neat liquids $(CH_3)_2CO$, CH_3OH [16], and solutions $(CH_3)_2CO–CCl_4$ [17], CH_3OH, $CH_3OH–LiCl$ [18], which have substantially confirmed the Logan picture of the phenomenon and demonstrate that the magnitude and the sign of the splitting of equation (1) depend on the liquid structure and on the relative orientation of neighbouring molecules.

Negative NCE values have also been measured for ring vibrations of aromatic and aliphatic compounds [20]; up to now this fact has not been exhaustively explained. The present article is a continuation of the study of the negative NCE in ring breathing modes of aromatic compounds. The positions and the shapes of isotropic and anisotropic profiles have been examined in light (h_8) and heavy (d_8) toluene and light (h_{10}) and deuterated (d_{10}) *o*-xylene, varying both temperature and molar fraction in opportune isotopic solutions. The existence of an NCE effect in pure *m*-, *p*-xylene and mesitylene has also been observed.

For the first time, to our knowledge, density number effects and trends of single particle and collective orientational times were invoked to associate the phenomenon of NCE to orientational processes of the examined liquids, demonstrating that the study of the vibrational bandshapes can give important information about the structure and the dynamics of the liquid phase.

2. Experimental details

2.1. Materials

All samples were commercial products and were used as received. Toluene RS spectrograde ($>99.5\%$) was purchased from Carlo Erba Reagenti; *o*-xylene-d_{10} (98%) was a Cambridge Isotope Laboratory product, while toluene d_8 ($>99.5\%$) and *o*-xylene ($>99\%$) were purchased from Fluka Chemical.

2.2. Measurements and treatment of data

The experimental setup has been extensively described elsewhere [21]. The detailed experimental procedure followed to obtain reproducible values of the position of the maxima of the spectra is reported in a previous paper [20]. This procedure allowed us to estimate the relative positions of the isotropic and anisotropic profiles within an accuracy of ± 0.1 cm^{-1}. In the present work, the recorded spectra were corrected for instrumental drifts using the 5460.7 Å line of a Hg calibration lamp. Some of the experimental profiles are perturbed by secondary structures or satellite bands; in all the cases, the weak asymmetries in the spectral profiles are not intrinsic properties of the examined bands, therefore these have been eliminated with a standard fitting procedure, assuming Voigt shapes for the principal profile and mixed Gaussian–Lorentzian forms for the secondary bands. All these manipulations were performed with GRAMS/32, a software package from Galactic Industries.

3. Results and discussion

The experimental results are reported in tables 1–3, together with a comparison with analogous data from the literature.

In spite of the small values of the measured NCE, the results shown in tables 1–3 are highly reproducible, even those that are of the same order of magnitude of experimental accuracy (for example, *p*-xylene, with a NCE $= -0.2$ cm^{-1}). In fact, the same final experimental results are obtained:

Table 1. Temperature and dilution effects on the ν_1 of toluene h_8 and toluene d_8.

	Toluene h_8		Toluene h_8 in toluene d_8			Toluene d_8
T (K)	NCE[a] (cm^{-1})	ν_{iso}^{b} (cm^{-1})	NCE[a] (cm^{-1})	$\nu_{iso}h_8^{b}$ (cm^{-1})	$\nu_{iso}d_8^{b}$ (cm^{-1})	ν_{iso}^{b} (cm^{-1})
282.1	−0.5	786.8	−0.2	785.9	717.7	719.0
349.6	−0.5	786.8	−0.1	785.8	718.8	719.3

[a] See text.
[b] Wavenumber of the maximum of the isotropic profile.

Table 2. Temperature and dilution effects on the ν_1 of *o*-xylene h_{10} and *o*-xylene d_{10}.

	o-xylene h_{10}		*o*-xylene h_{10} in *o*-xylene d_{10}, $X = 0.5$				*o*-xylene d_{10}	
T (K)	NCE[a] (cm^{-1})	ν_{iso}^{b} (cm^{-1})	NCE[a] (cm^{-1})	$\nu_{iso} h_{10}^{b}$ (cm^{-1})	NCE[a] (cm^{-1})	$\nu_{iso} d_{10}^{b}$ (cm^{-1})	NCE[a] (cm^{-1})	ν_{iso}^{b} (cm^{-1})
282.9	−0.6	735.9	−0.3	734.4	−0.1	669.5	−0.3	669.5
359.2	−0.5	733.6	−0.3	734.0	+0.2	668.1	0.0	669.1

[a] See text.
[b] Wavenumber of the maximum of the isotropic profile.

Table 3. NCE, density (ρ), density number (ρ_n), vibrational relaxation time (τ_V), orientational relaxation times: collective, from light scattering measurements (τ_{LS}), single particle, from Raman and/or NMR data (τ_S). Room temperature.

Substance	$\tilde{\nu}_{iso}$ (cm^{-1})	NCE (cm^{-1})	ρ (g cm^{-3})	ρ_n (cm^{-3}) $\times 10^{-3}$	τ_V (ps)	τ_{LS} (ps)	τ_S (ps)
Benzene h_6	991	−0.24[a]	0.879	11.253	3.5[b]	3.0[c]	2.7[c]
Benzene d_6	943	−0.50[a]	0.950	11.288	4.4[b]		
Hexafluorobenzene	560	−1.27[a]	1.612	8.664	2.1[d]	14.0[c]	5.5[c]
Toluene h_8	787	−0.4	0.867	9.409	3.3[e]	5.5[g]	2.3[f]
Toluene d_8	720	$\approx$ −1.0	0.944	9.422	3.3[e]		5.0[f]
o-xylene h_{10}	734	−0.6	0.881	8.298	3.9[e]	10.9[g]	4.6[f]
o-xylene d_{10}	670	−0.3	0.953	8.198	3.5[e]		6.1[f]
m-xylene	726	−0.4	0.864	8.138	5.4[e]		3.4[f]
p-xylene	829	−0.2	0.861	8.107	2.0[e]		2.7[f]
Mesitylene	578	−1.0	0.865	7.196	3.1[e]	11.3[h]	7.2[f]

[a] [19].
[b] $\tau_V = \pi c \text{FWHH}_{iso})^{-1}$, where the full width at half height of isotropic profile is taken from [30].
[c] τ_V is calculated as in b from [31].
[d] τ_V is calculated as in b from [32].
[e] Present work, from Kubo treatment of isotropic profile.
[f] Present work, from Raman bandwidth: $\tau_S = [\pi c (\text{FWHH}_{aniso} - \text{FWHH}_{iso})]^{-1}$.
[g] [33].
[h] [34].

(a) recording the spectra only in a region strictly around the frequency value of the maximum of each band and measuring the position of the maxima of the isotropic and anisotropic profiles;

(b) recording the whole profiles and measuring the position of the maxima of the isotropic and anisotropic profiles;

(c) recording the whole profiles and applying equation (1), employing the values of the first band moments of the two profiles, as reported in [8].

We verified the assignment of the symmetric ring breathing vibration of toluene, as proposed in [22], measuring the NCE in both the strong and highly polarized Raman bands at 785 and 1000 cm^{-1}; we found a negative NCE value for the ν_1 at 785 cm^{-1}, while no NCE was observed for the other band. This phenomenon has confirmed that this anomalous behaviour of the NCE is a property of those normal modes that are specifically ring breathing ones, while it does not appear for generic symmetric ring vibrations.

It was not possible to measure the NCE of toluene d$_8$ because of the overlapping of the anisotropic profile with a near band of comparable intensity; in this case only the effect of the temperature and the dilution on the position of the maximum of the VV profile have been determined. From tables 1 and 2 it can be seen that:

(a) the NCE values in all the molecules decrease with isotopic dilution, according to the Logan hypothesis of a resonant coupling interaction;

(b) both NCE values of light toluene and *o*-xylene are independent of temperature, within the experimental uncertainties, while the NCE of *o*-xylene d$_{10}$ vanishes with increasing temperature;

(c) in *o*-xylene h$_{10}$ there is a temperature effect on the frequency position of the maximum of the isotropic profile, as opposed to the trend of its NCE, in disagreement with the Logan model;

(d) assuming that the NCE value in toluene d$_8$ is comparable with the shift of the isotropic profile in isotopic dilution, the NCE of toluene h$_8$ seems lower (-0.5 cm^{-1}) than that of the deuterated isotopomer (≈ -1.0 cm^{-1}), in agreement with analogous results obtained for the C$_6$H$_6$/C$_6$D$_6$ system (see table 3). On the other hand, *o*-xylene d$_{10}$ has a lower value of NCE (-0.3 cm^{-1}) with respect to *o*-xylene h$_{10}$ (-0.6 cm^{-1}).

Table 3 shows that a negative NCE can also be observed in *m*-, *p*-xylene and mesitylene, and that the highest value is found for the tri-substituted benzene. In table 3 it can also be seen that the vibrational relaxation times, τ_V, obtained from the isotropic Raman profiles always have similar values to the single-particle orientational times (τ_S), with the exception of mesitylene.

The presence of a NCE and its general vanishing on isotopic dilution indicates the presence of a resonant coupling mechanism. The low dipole values of the molecules and the low IR intensity of their ring breathing modes show that the dipolar coupling suggested by Logan cannot be totally operative in the present case. In addition, it is clear that higher absolute NCE values are obtained for the molecules with higher steric effects. The negative sign of the splitting between isotropic and anisotropic profiles has been attributed to a balance of repulsive and attractive forces, for ring breathing of aromatic systems [20].

It is well known [23, 24] that quadrupolar interactions cause complexes in pure benzene, mesitylene and hexamethylbenzene, with a preferred relative mutually perpendicular orientation. In these three systems, this quadrupolar order is also confirmed by the available thermodynamic data. It is reasonable to hypothesize that the quadrupolar forces are responsible for the attractive potential of these liquids, and consequently for their orientational order. The toluene quadrupolar interactions are also substantial, at least in the first coordination shell [25]. It is possible to extend this description of the attractive part of the intermolecular potential to the *o*-, *m*-, *p*-xylene, considering that from *ab initio* calculations it can be seen that the value of the quadrupolar moment increases with the number of methyl substituents in the aromatic rings [23].

The presence of a static orientational pair correlation in these liquid systems is also confirmed by their light scattering values (τ_{LS}) and single particle (τ_S) orientational times, reported in table 3. It is well known from the theory [26] that when the ratio τ_{LS}/τ_S deviates from unity, static orientational pair correlations exist. All the available, experimental data
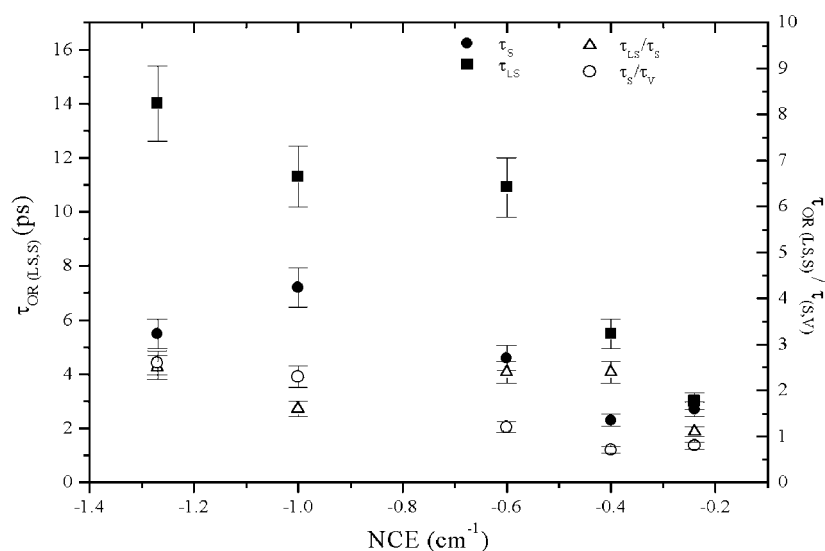
Figure 1. Reorientational light scattering (τ_{LS}), single particle (τ_S) relaxation times, ratios of reorientational (τ_{LS}/τ_S) and reorientational and dephasing relaxation times (τ_S/τ_V) of molecules with different values of NCE.

confirm the existence of strong pair correlations in the systems showing negative NCE values [27].

It is therefore possible to assume that the coupling mechanism responsible of the NCE effect must be associated with quadrupolar resonant coupling, analogously to that hypothesized for CS_2 [28].

An indication of a physically meaningful correlation between the values of the NCE and the relaxation times of table 3 is shown in figure 1. Here the initial evidence is that the light scattering reorientational time values (τ_{LS}) increase with the absolute value of the NCE, in the examined molecules; at the same time, it is possible to observe that the analogous increasing of the values of the reorientational times of the single particle (τ_S) shows a less pronounced trend. Considering that the light scattering relaxation times are related to both collective and single particle contributions [26], it is reasonable to deduce that the correlations between the molecules are strongly connected to the existence of the NCE. This fact is confirmed by the values of the ratios τ_{LS}/τ_S, always being bigger than unity; in addition, the ratio of the orientational and dephasing times τ_S/τ_V indicates that the two relaxation processes are not statistically independent, being roughly in the same temporal region. Surprisingly the τ_{LS}/τ_S and τ_S/τ_V ratios are nearly coincident in their numerical values; this could not be a simple coincidence, but also an indication of the fact that all the dynamical processes involved in the chosen molecules are strictly related to each other.

The presence of strong repulsive interactions has recently been reported in ring breathing modes of neat benzene, pyridine and toluene in experiments with varying pressures [29]; these have been evaluated with a hard-sphere model. The repulsive potential is probably due to a steric hindrance, which is higher due to the number and the position of the substituent in the aromatic ring. Following this philosophy and looking at the density number values in table 3 (ρ_n) it is also possible to explain the different trends of the *o*-xylene h_{10}/d_{10} system with respect to the other isotopomers. The deuterated *o*-xylene has a lower ρ_n value than the light molecule. There are fewer molecules per unit volume, so the steric hindrance and the repulsive

contribution to the intermolecular potential is less in the *o*-xylene d_{10} than in the *o*-xylene h_{10}; in agreement, the NCE value is 'less negative' in the deuterated (-0.3 cm^{-1}) than in the light molecule (-0.6 cm^{-1}). In all the other isotopomer couples there is the opposite trend; the density number is higher in the deuterated than in the hydrogenated molecule (which means more repulsions), and the NCE value is 'more negative' in the heavy molecule than in the light molecule.

4. Conclusions

The NCE has been shown to be an efficient probe of molecular structure and dynamics. The presence of a negative NCE can be ascribed to a coupling resonant process, even if it lacks the usual transition dipole–transition dipole mechanism, it is lowered in opportune isotopic dilution. The presence of an orientational order in association with a NCE is confirmed from *ab initio* calculations and experimental results. To our knowledge, this is the first time that the existence of the NCE has been quantitatively associated with orientational times. In addition, in the examined systems vibrational relaxation times and single-particle orientational times are of the same order of magnitude, which supports a unified picture of the vibrational and rotational dynamics. The repulsive contribution to the intermolecular potential can be considered responsible for the negative sign of the NCE. This could be due to steric effects; the experimental data on the density number is an indication of this.

Up to now, it has not been possible to satisfactorily explain the temperature behaviour.

Acknowledgments

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