

Non-coincidence of Isotropic and Anisotropic Raman Spectra of the ν_3 Mode of the $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ System

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It has been proved with the aid of $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ mixtures that the remarkably large non-coincidence effect in the Raman scattering spectrum of the ν_3 mode of liquid methyl fluoride is due to intermolecular vibrational coupling mediated mainly by transition dipole interaction. The amount of the effect and its temperature and mole fraction dependence are – at least qualitatively – in agreement with Logan's theoretical concept. The rather different behaviour of the isotopic species and the asymmetry and narrow width of the isotropic band, however, raise new questions which require further investigations.

Key words: Raman spectroscopy, Liquids, Intermolecular interactions, Isotopic dilution, Band shift.

The non-coincidence of the isotropic and anisotropic Raman scattering spectra of certain symmetrical modes of polar molecules in the liquid state, caused by resonant intermolecular vibrational coupling via transition dipoles, is an indication of orientational order in the liquid [1, 2] and therefore of importance for the research into the structure and dynamics of liquids. Compared with methyl iodide which has often been used as a model substance in this field, liquid methyl fluoride exhibits a very large non-coincidence effect of up to 13.4 cm^{-1} near the melting point.

The most recent contribution to the study of the non-coincidence effect of methyl fluoride has been made by Zyung and Wilde [3]. These authors measured the Raman spectrum of the ν_3 mode of liquid and solid methyl fluoride and attempted to prove by dilution in two solvents that the origin of the non-coincidence effect is due to resonant intermolecular vibrational coupling mediated by transition dipole–transition dipole interaction. The results of these investigations must, however, be regarded with some scepticism, as the authors themselves admit, since isotopic dilution was not applied.

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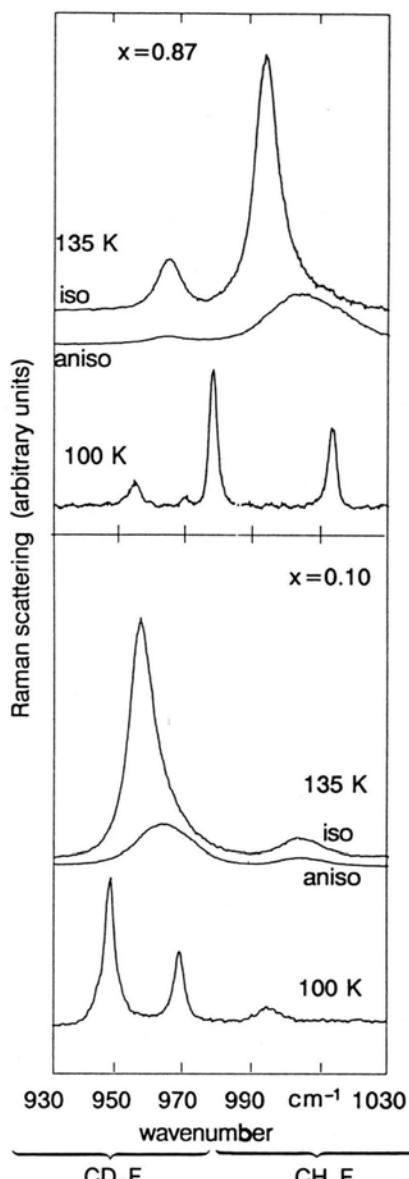


Fig. 1. Isotropic (iso) and anisotropic (aniso) Raman scattering spectra of the ν_3 modes of liquid $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ mixtures with x the mole fraction of CH_3F . In the solid mixtures (100 K) only the polarised scattering is shown, since the isotropic and anisotropic parts cannot be separated.

We have studied the $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ system over the entire composition range. Figure 1 shows the isotropic and anisotropic Raman spectra for the ν_3 mode of two $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ mixtures, in which CD_3F respectively CH_3F is diluted, in the liquid and solid states.

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The separation of the corresponding spectra of the isotopic species is large enough to observe the non-coincidence effect without appreciable disturbances.

A comparison of the isotropic and anisotropic spectra indicates that the non-coincidence effect is absent for the diluted isotopic species, thus confirming that its origin is due to resonant intermolecular vibrational coupling. Since the infrared absorption coefficients of the v_3 mode of methyl fluoride and its deuterated analogon are fairly high, transition dipole-transition dipole interaction is the most probably coupling mechanism.

In the solid mixtures the appearance of two widely separated lines at high concentration of an isotopic species and only one line at low concentration also points to the action of resonant intermolecular vibrational coupling. This cannot, however, be observed in the form of a non-coincidence effect since the isotropic and anisotropic scattering cannot be separated due to the scrambling effect of the polycrystalline system. The two lines at high concentration represent the factor group splitting due to the crystal field.

As has already been shown by Zyung and Wilde, the magnitude of the non-coincidence effect in liquid methyl fluoride agrees fairly well with the prediction of Logan's theoretical treatment [2] on the basis of the model of a liquid structure where the pair distribution function is evaluated using Wertheim's [4] mean spherical approximation. As a result of our dilution experiments the shift of the anisotropic first moment of both, CH_3F and CD_3F , is negligible compared with that of the isotropic first moment, thus confirming – at least qualitatively – the statement of Logan's theory that the former amounts to only 1/25 of the latter.

In addition, we have found a linear dependence of the isotropic first moments on the mole fraction, the slope of which increases with decreasing temperature, which is also in agreement with the above-mentioned theory.

Several questions remain, however, to be answered:

(i) The isotropic band profiles are asymmetrical and remarkably narrow compared to the isotropic-aniso-

tropic band splitting, and no significant further narrowing occurs upon dilution of the isotopic species. This behaviour indicates a high amount of orientational order [1], higher than that expected from dipolar interaction. Current theories cannot be applied in this case because they are based on the assumption that orientational order is merely due to this kind of interaction. A specific additional interaction associated with the fluorine atoms, for example a weak hydrogen bond-like interaction, would be a possible explanation. This assumption is supported by the exceptional thermodynamic behaviour of mixtures of alkane halides with alkanes if the halogen is fluorine, as described by Rowlinson and explained in terms of the great electronegativity of the fluorine atom [5].

(ii) The non-coincidence effect of CD_3F is much smaller than that of CH_3F , 5.7 cm^{-1} compared with 13.4 cm^{-1} at 135 K. Taking the frequencies of the anisotropic bands at 135 K, 966.2 cm^{-1} for CD_3F and 1006.0 cm^{-1} for CH_3F , as representative of the band positions of the v_3 modes of these two molecules in the liquid state, the isotropic-anisotropic band separation of CD_3F should amount to at least 90% of that of CH_3F , on account of the isotropic mass difference assuming equal intrinsic dipole moment derivatives. In fact, only 40% of the effect is observed. The assumption of an H bond-like interaction would probably provide an explanation to the extent that this kind of interaction is weaker with deuterium than with hydrogen.

(iii) Whereas the isotropic profile width of CD_3F slightly decreases with dilution, that of CH_3F increases. Together with the considerably different non-coincidence effect this manifests a remarkable difference in the behaviour of these two isotopic substances with regard to intermolecular interaction.

Additional research work, including infrared spectrometric investigations, are in progress in our laboratories with the aim of improving the understanding of the intermolecular interactions of this system.

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