

THE SHAPE OF DIFFERENT POLARIZED COMPONENTS OF 1710 cm⁻¹ RAMAN BAND FOR METHYL ETHYL KETONE (2-BUTANONE) AND ITS SOLUTIONS

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Frequencies of maxima of the vibrational component and the component with perpendicular polarization of methyl ethyl ketone (MEK) in C=O vibration band are different by $\Delta\nu = 6.7 \text{ cm}^{-1}$. In mixtures with heptane, pyridine, and dimethylsulfoxide (DMSO), there is a decrease in this frequency difference with changing a concentration. However, a feature of the decrease in $\Delta\nu$ is different: in mixtures with heptane, both bands are displaced to the high-frequency side, and the vibrational component is displaced faster; in mixtures with pyridine, the components are displaced to the opposite directions. In mixtures with DMSO, the perpendicular component is displaced to the direction of the vibrational component. The peculiarity of the concentration dependence of $\Delta\nu$ behavior in mixtures of MEK with chloroform can be explained by possible intermolecular aggregations.

Introduction

For some molecular liquids certain vibrational bands, in Raman spectra have an asymmetry. Frequency maxima of parallel $I_{\parallel}(\nu)$ and perpendicular $I_{\perp}(\nu)$ polarized components are often non-coincident. A difference in frequency maxima is rather small - from $1.5 \cdot 10^2$ to $6 \cdot 10^7 \text{ cm}^{-1}$.

There are some theories [1 - 4], explaining the effect of non-coincidence (ENC) to be a result of available resonant transfer of the energy of vibrations (RTE) between molecules. Such a non-coincidence of frequency maxima of the bands in Raman spectra was discovered in ketones [1, 5, 6], amides [7 - 9], and some other compounds [4, 10, 11]. However, until the present time, there is no total accordance between the theory and experimental results, and further investigations connected with that problem are of a certain interest. In this paper, we present the results of study of the ENC in Raman spectra of MEK for the $\nu = 1710 \text{ cm}^{-1}$ band [13]. This band belongs to C=O vibrations of MEK.

Resonant transfer of the energy of vibrations, in accordance with the theory, causes not only the effect of non-coincidence, but it also leads to a broadening of vibrational bands [8, 12] in a rather complicated manner: only RTE is able to broaden a band, but the interaction of this effect with others (reorientation

of molecules, etc.) can lead to its narrowing [8, 12]. The experiments reveal that the dilution of a compound in different solvents leads to a decrease in the ENC, and the influence of RTE on broadening the band is also decreased. That is why we also studied the width of the 1710 cm^{-1} band of MEK in mixtures with polar and non-polar solvents (heptane, chloroform, pyridine, and dimethylsulfoxide).

Experimental Method

Raman spectra were recorded with the help of a spectrometer. As a source of exciting light, we used an argon laser with the wavelength $\lambda = 488 \text{ nm}$ and output of 1W. All spectra were recorded at the 90° scattering geometry and a linear polarization of exciting light. The polarized components of the band were separated by a polarizing prism. Polarizing effects of the experimental apparatus were eliminated by a depolarizing wedge. All chemicals used in the experiment were chemically pure compounds subjected to additional vacuum distillation. For all spectra, the width of a spectral split was 1.8 cm^{-1} . All spectra were obtained at 20°C . An error in determination of a relative position of bands' maxima was $\pm 0.2 \text{ cm}^{-1}$, and that for the half-width of the band was $\pm 0.3 \text{ cm}^{-1}$.

Results and Discussion

From our experiments, the polarizationally non-decomposed band of C=O vibrations for liquid MEK has its maximum at $\nu = 1711 \text{ cm}^{-1}$. The high-frequency side of the band is asymmetric. Both the parallel polarized $I_{\parallel}(\nu)$ and vibrational $I_{\text{vib}}(\nu) = I_{\parallel}(\nu) - 4 \cdot I_{\perp}(\nu)/3$ components also have asymmetric high-frequency sides with their maxima at 1711.5 and 1710.7 cm^{-1} , consequently. The component of the band with perpendicular polarization $I_{\perp}(\nu)$ has its maximum at $\nu = 1717.4 \text{ cm}^{-1}$. This component is also asymmetric, but the asymmetry is observed in the low-frequency region of the band

(Fig.1). The depolarization ratio of the band at the maximum of $I_{\text{vib}}(\nu)$ is rather large, $\rho = 0.32$. In our opinion, the frequency difference between parallel and vibrational components is conditioned by this reason. Actually, although the vibrational component has a greater intensity and determines a location of the maximum in the parallel component, a rather high intensity in this polarization of anisotropic component, the maximum of which is displaced to the high-frequency side, 'shifts' the maximum of the whole $I_{\parallel}(\nu)$ band towards the high-frequency side. Superposition of the vibrational component and a part of the anisotropic component makes the half-widths of $I_{\parallel}(\nu)$ and $I_{\text{vib}}(\nu)$ bands different. In this connection, we speak here and after about the maxima and half-width of the vibrational component of the band, and the component of the band with perpendicular polarization. Thus, it follows from our results that the maximum of $I_{\perp}(\nu)$ is displaced with respect to the maximum of $I_{\text{vib}}(\nu)$ by 6.7 cm^{-1} . The width of the vibrational component of the band is different from that for the perpendicular component by 5.7 cm^{-1} . This difference becomes other one if we exclude the asymmetry of the bands by taking twice the value of a half of the low-frequency part of the $I_{\text{vib}}(\nu)$ half-width and by comparing the obtained value with twice the value of a half of the high-frequency $I_{\perp}(\nu)$ half-width. In this case, the difference in half-widths is 6.1 cm^{-1} . Both components of the band are wide. Their values, corrected for instrumental distortion, are 13.1 and 19.2 cm^{-1} , consequently. The large half-width of the perpendicular component is obviously caused by a contribution of rotational motion of molecules to a broadening of this component. The calculation of the orientational correlation relaxation time assuming the absence of any interaction between vibrational and orientation motions of molecules, gives the value 1.7 pc (after correction of the band for asymmetry). This value is different from that for the relaxation time of anisotropy, determined from the Rayleigh line wing, which is 4.3 pc .

Interesting changes in the frequencies of maxima and the shape of bands occur in solutions. Let us consider the solutions of MEK - heptane. Molecules of heptane are non-dipole ones, and that must weaken both the RTE effect and dipole-dipole interaction as a whole (as well as destroy possible aggregates ([14, 15]). As in other cases, the dilution of MEK in heptane leads to a decrease in the difference of the frequencies of maxima for $I_{\perp}(\nu)$ and $I_{\parallel}(\nu)$. Both bands are displaced with dilution towards the high-frequency region (Fig. 2); the vibrational component is displaced at a faster rate. Thus, at the 0.3 mole fraction of MEK, the difference in frequencies for these bands becomes equal to 1.6 cm^{-1} . As a change in band's shape occurs,

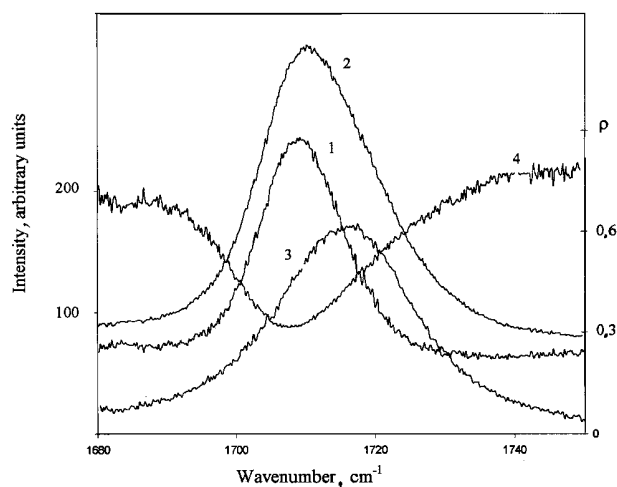


Fig. 1. Spectra of vibrational (1), parallel (2) and perpendicularly (3) polarized components of MEK C=O vibrations. Depolarization ratio ($\rho = I_{\perp}(\nu) / I_{\parallel}(\nu)$) within the band (4)

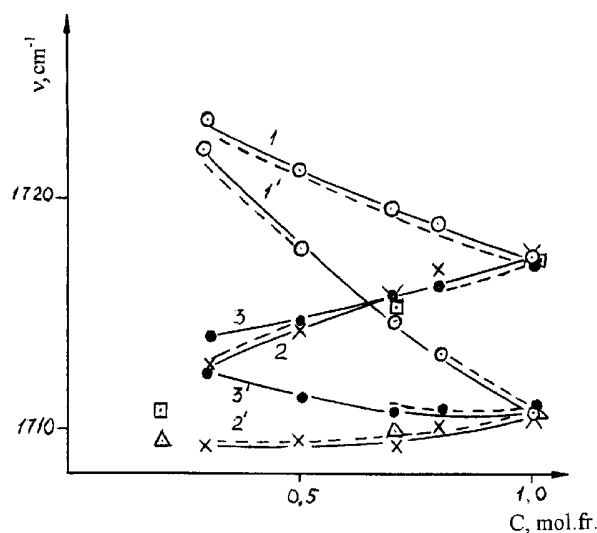


Fig. 2. Maximum frequencies for vibrational (1 - 4) and perpendicularly (1' - 4') polarized components of MEK C=O vibrational band in mixtures with heptane (1, 1'), chloroform (2, 2'), pyridine (3, 3'), and DMSO (4, 4'), at 20 °C. Dotted lines above or below curves correspond to asymmetry on the high- or low-frequency side of the band

first of all, parallel and vibrational components lose the high-frequency asymmetry, but with a further dilution, these components gain the low-frequency asymmetry. The component with perpendicular polarization in the studied range of concentrations conserves its low-frequency asymmetry. The half-width of the band's component with perpendicular polarization in a mixture with heptane does not reveal any significant change (Table). Only at the 0.3 mole fraction, we observed a significant decrease in the

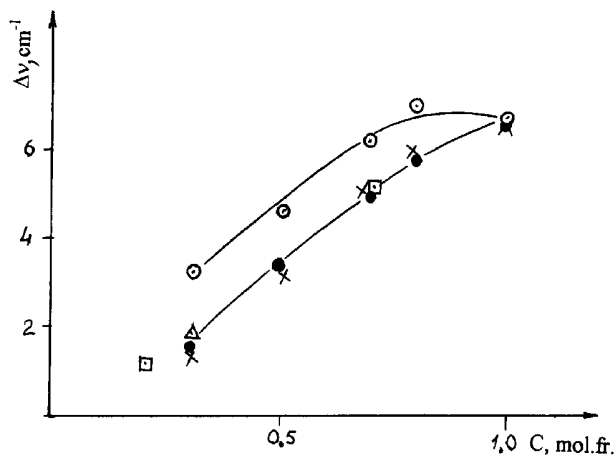


Fig. 3. Frequency difference ($\Delta \nu = \nu_m^\perp - \nu_m^{vib}$) of MEK $I_\perp(\nu)$ and $I_{vib}(\nu)$ C=O vibrational band maxima in mixtures at 20 °C. (White rounds - in chloroform; black rounds - in heptane; crosses - in pyridine; squares - in DMSO; triangles - in the equimolar mixture heptane - DMSO)

width of this band. For the vibrational component in the mixture with heptane, there occurs at first a slight increase in the half-width, then a decrease occurs, and at the 0.3 mole fraction, its width appears to be very nearly the same as for the perpendicular component. For simple bands of non-viscous liquids, such a situation is usually not observed.

Features of a change in the C=O vibrations spectra for MEK in a mixture with chloroform look somewhat different. A dipole moment of chloroform $\mu = 1.15$ D [16] is slightly less than that for MEK, $\mu = 2.8$ D (dipole moment of C=O bond). As in other cases, the difference in maximum's frequency of $I_\perp(\nu)$ and $I_{vib}(\nu)$ in the mixture decreases. However, in this case, in contrast to the above-described solvent, the frequency difference decreases due to a "tightening" of the component with perpendicular polarization towards the vibrational component. A location of the vibrational component in the mixture is practically not changed (Fig.2), and, for this component, the high-

frequency asymmetry of the band over the range of studied concentrations is preserved. The maximum of the component with perpendicular polarization is shifted towards the low-frequency region; this shifting is accompanied by a change in bands' asymmetry: the low-frequency asymmetry is followed by the high-frequency one. It seems to be that this band is composed by two different bands, and while diluting, the intensity of one band is turned into the intensity of other band. The half-width of this band passes through the maximum (Table). For the vibrational component, we observed only an insignificant increase in the band's width.

An interesting change in band's composition takes place in a mixture of MEK with pyridine ($\mu = 2.25$ D [16]). As in other cases, the difference in the frequencies of $I_\perp(\nu)$ and $I_{vib}(\nu)$ maxima is decreased with dilution. However, this decrease is distinctive. In this case, in the process of dilution, the component with perpendicular polarization is displaced towards the low-frequency side, and the vibrational component is shifted towards the high-frequency side. The rates of displacement of these bands are very much the same. In this case, the low-frequency asymmetry of $I_\perp(\nu)$ disappears, and the high-frequency asymmetry of the vibrational band disappears, too. The half-width of $I_\perp(\nu)$ is practically not changed up to the 0.5 mole fraction, and it is slightly decreased only at the 0.3 mole fraction of MEK; the half-width of the $I_{vib}(\nu)$ component in the studied range of concentrations increases.

The summary data for the difference in the frequencies of $I_\perp(\nu)$ and $I_{vib}(\nu)$ maxima in mixtures are presented in Fig. 3. One can see that it is no matter whether the solvents (heptane, pyridine, DMSO) are polar or non-polar, what values of dipole moment of molecule are, and what values of static dielectric permeability are MEK-18, heptane-1.92, DMSO-48, pyridine-12.5 [16, 17]. The behavior of the $\Delta \nu$ curve in relation to the concentration is practically the same one. All experimental points for these solvents lie on a single curve. Only for a mixture of MEK with chloroform ($\epsilon = 5.1$; $\mu = 1.15$), the behavior of $\Delta \nu$ in relation to the concentration is

Half-width (cm^{-1}) of the vibrational component ($\Delta \nu_{1/2}^{vib}$) and the component with perpendicular polarization ($\Delta \nu_{1/2}^\perp$) for C=O band of MEK in mixtures (without correction for apparatus distortions)

Content of MEK (mol.fr.)	Heptane		Chloroform		Pyridine		DMSO	
	$\Delta \nu_{1/2}^{vib}$	$\Delta \nu_{1/2}^\perp$	$\Delta \nu_{1/2}^{vib}$	$\Delta \nu_{1/2}^\perp$	$\Delta \nu_{1/2}^{vib}$	$\Delta \nu_{1/2}^\perp$	$\Delta \nu_{1/2}^{vib}$	$\Delta \nu_{1/2}^\perp$
1.0	15.2	20.9	15.2	20.9	15.2	20.9	15.2	20.9
0.8	17.2	20.0	15.8	21.2	16.3	21.2	-	-
0.7	17.9	20.6	18.4	22.4	18.0	-	16.2	-
0.5	19.4	19.8	-	20.6	-	20.3	-	-
0.3	17.8	17.9	18.2	20.8	19.4	17.7	-	-
0.2	-	-	-	-	-	-	14.6	17.8

essentially different. A possible reason is a possibility of the formation of chloroform - MEK aggregations. An interesting conclusion can be made about the mechanism of a decrease of the difference in the frequencies of $I_{\perp}(\nu)$ and $I_{\text{vib}}(\nu)$ maxima in the studied solutions. In case of a non-polar solvent (heptane), the frequency difference with dilution of MEK decreases due to a 'tightening' of the vibrational component towards the component with perpendicular polarization; both components are displaced towards the high-frequency side. The situation is different in case of polar solvents. In this case, for molecules with an intermediate value of the dipole moment (pyridine), the maxima of $I_{\perp}(\nu)$ and $I_{\text{vib}}(\nu)$ are displaced towards each other: the vibrational component - towards the high-frequency side, and the component with perpendicular polarization - towards the low-frequency side. In case of a strongly polar solvent (DMSO) and a solvent whose molecules have a

relatively small dipole moment, but have a tendency to form H-bonds (chloroform), the perpendicular component is displaced towards the low-frequency side, and the position of the vibrational component is practically not changed. We emphasize that the dipole moment of MEK molecule is rather large (2.8 D), but it is not so large as that for DMSO (4.2 D) [17]. Thus, if the solvent exerts a weak influence on the difference in the frequencies of $I_{\perp}(\nu)$ and $I_{\text{vib}}(\nu)$ maxima of the band, then the mechanism of disappearance of this difference and the method of change in the shape of band's contour are determined only by the solvent.

The availability and the value of the dipole moment of solvent's molecules have an important significance. It is obvious that the dipole-dipole interactions between MEK molecules and those between MEK and solvent molecules determine the ENC and a change of the ENC in solutions to a certain extent.