

## C=O STRETCHING VIBRATIONS IN RAMAN AND INFRARED SPECTRA OF SIMPLE ESTERS

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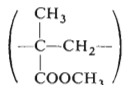
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Infrared and Raman spectra of methyl acetate, tert-butyl acetate, methyl pivalate and tert-butyl pivalate were measured in the liquid and crystalline states and solutions of different dielectric constants. In these molecules, the bands of the C=O str. vibrations are not affected by conformational structure. The shape and position of the band of the C=O str. vibration in methyl acetate are primarily determined by intermolecular order created by interactions of the permanent dipoles of the molecules. In methyl pivalate and in tert-butyl acetate, the shape of the carbonyl band is mainly determined by Fermi resonance.

The band of the C=O str. vibration often exhibits a complicated shape. The position and shape of the carbonyl band change considerably in solutions, and this band exhibits different positions<sup>1,2</sup> in spectra of isotropic and anisotropic Raman scattering. All these effects can be observed also on the bands of the carbonyl str. vibration of esters.

The shape of the carbonyl band in infrared and Raman spectra of liquids is mostly determined by vibrational and reorientational relaxation of molecules<sup>3,4</sup>, but it may also be affected by conformational structure and by the resonance interaction of the carbonyl vibration with other vibrational modes of the same molecule. The difference in the positions of the isotropic and anisotropic components of the carbonyl band in the Raman spectrum has been explained by resonance interaction between the transition dipoles of different molecules, connected with the local ordering of molecules in the liquid state in consequence of strong interaction between the permanent dipoles of the molecules<sup>5</sup>. Wang and McHale<sup>6</sup> have shown that  $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$  may be nonzero even in systems without any local order, and that an angular dependence of the interaction potential is sufficient for the appearance of a frequency difference. In view of the great sensitivity of the band of the C=O str. vibration to intermolecular interactions, the character of such interactions and molecular order in the liquid state can be investigated by studies of the position and shape of this band.

Polymers with ester groups in side chains, as *e.g.* poly (methyl methacrylate)



form associated structures in solutions which affect the properties of these polymers. So far it is not quite clear which interactions cause the formation of these associates. The results of some studies indicate that the associates are formed by interaction of ester groups<sup>7-11</sup>. In order to find out if such interactions between ester groups really exist, we have followed IR and Raman spectra of a series of simple esters, methyl acetate, tert-butyl acetate, methyl pivalate and tert-butyl pivalate.

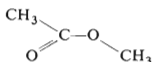
### EXPERIMENTAL

The samples were prepared by standard procedures and their purity was controlled by IR and NMR spectroscopy and by gas chromatography. IR spectra were measured on the spectrometer Perkin-Elmer 580B connected on-line with the data analyzer TN 4000 Tracor-Northern; Raman spectra were measured on the spectrometer Coderg LRDH-800 with an argon ion laser COHERENT CR-3. The line 514.5 nm was used for excitation. The spectrometer is connected on-line to the computer PDP-11 in the Tracor system. The spectra were measured in 90° arrangement; Harney-Miller cells were used for low-temperature measurements.

The anisotropic component of Raman scattering was obtained as  $I_{HV}$ , the isotropic component from the relation  $I_{iso} = I_{VV} - 4/3I_{HV}^2$ . At low ester concentrations the difference between  $I_{iso}$  and  $I_{VV}$  is negligible, in consequence of the coalescence of the maxima  $I_{VV}$  and  $I_{HV}$  and of the large polarization of the carbonyl band. Raman spectra were digitalized with the interval  $1 \text{ cm}^{-1}$  and IR spectra with  $0.25 \text{ cm}^{-1}$ . We have assumed that the asymmetric bands can be represented by the function  $I(\nu + \nu_0) = A/(1 + a\nu^2 + b\nu^3 + c\nu^4)$ . Band positions and widths were determined by fitting this function to experimentally measured bands.

### RESULTS AND DISCUSSION

*Methyl acetate:* The conformational structure of methyl acetate has been studied in detail by various methods and it was found that a single conformer is present both in the liquid and in the crystalline state: it has a planar structure with a *trans* orientation of the methyl groups<sup>12</sup>.



The shift of the carbonyl band in IR spectra caused by change of medium can be explained on the basis of the simple reaction field theory which yields a relation between the shift of the wavenumber of the vibration with respect to the wavenumber

in the vapour ( $\Delta\nu_v = \nu_v - \nu$ ) and the dielectric constant of the medium<sup>13</sup>:

$$\Delta\nu_v/\nu = C(\varepsilon - 1)/(2\varepsilon + 1). \quad (I)$$

Following this relation, in Fig. 1a the experimental values of the shift  $\Delta\nu_v$  for methyl acetate in various media are plotted *vs* dielectric constants, assuming that for a solution  $\varepsilon = \varepsilon_1\varphi_1 + \varepsilon_2\varphi_2$ , where  $\varphi_i$  are volume fractions of the components. Relation (I) describes the concentration dependence in most solvents, even if the effect of the refractive index on band position in polar media<sup>14</sup> is neglected. A quite anomalous behaviour is observed for the nonpolar solvents  $\text{CS}_2$  and  $\text{CCl}_4$ . The peculiar behaviour of these two solvents could be caused by the circumstance that the individual bonds C—Cl and C—S have a non-zero dipole moment, whereas the overall dipole moment of the molecule is zero in consequence of molecular symmetry.

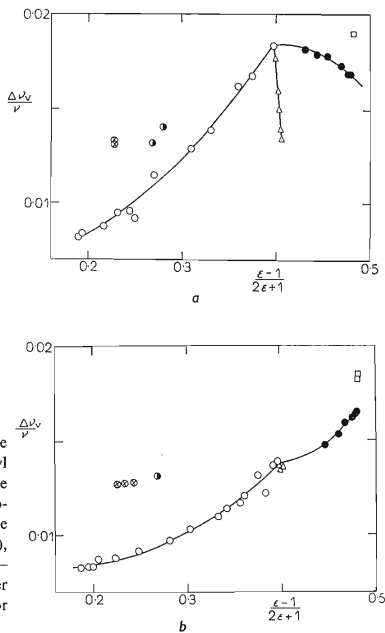


FIG. 1

Dependence of the relative shift  $\Delta\nu_v/\nu$  of the wavenumber of the carbonyl band of methyl acetate on the dielectric constant of the solution *a*) in IR spectra; *b*) in spectra of isotropic Raman scattering. Solvents: hexane (○),  $\text{CCl}_4$  (⊗),  $\text{CS}_2$  (●), tetrahydrofuran (Δ),  $\text{CH}_3\text{CN}$  (●), dimethylsulfoxide (□). — Curves fitted to experimental points under the assumption of a quadratic function for each solvent

With all solvents shown in Fig. 1, the positions and shapes of the carbonyl band were measured at several concentrations also in spectra of anisotropic Raman scattering. The positions of the carbonyl band in IR spectra and in the anisotropic Raman component differ by  $1.4 \text{ cm}^{-1}$  at most (in spectra of neat methyl acetate), and so the correlation between band shift and dielectric constant of the solution is roughly equal in both cases. Both in the IR spectra, and in anisotropic Raman scattering the carbonyl bands are symmetrical.

For neat methyl acetate, the difference  $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$  in the Raman spectrum is  $6.2 \text{ cm}^{-1}$ . Upon dilution in polar and non-polar solvents,  $\Delta\nu$  decreases and is zero beyond a certain limiting concentration. As seen from Fig. 1b,  $\nu_{\text{iso}}$  exhibits marked deviations from the relation (1) for the shift of the wavenumber with respect to the wavenumber in the vapour state, thus indicating that the difference  $\Delta\nu$  is caused by the shift of the isotropic component. This is very clearly manifested in tetrahydrofuran the dielectric constant of which ( $\epsilon = 7.39$ ) is very near to that of methyl acetate ( $\epsilon = 6.68$ ). For this solvent the position of the carbonyl band in the IR spectrum does not practically change in the measured concentration range: the shift  $\nu_{\text{aniso}}$  is  $2 \text{ cm}^{-1}$ , the shift  $\nu_{\text{iso}}$  is  $8 \text{ cm}^{-1}$  with respect to the band position in pure methyl acetate. The assumption that the difference is caused mainly by the shift of the wavenumber of the carbonyl band in the isotropic component of Raman scattering is also supported by the values of the wavenumbers of the carbonyl harmonic vibration  $2\nu_{\text{C=O}}$  which are shown in Table I. In IR spectra the wavenumber difference of  $2\nu_{\text{C=O}}$  and twice  $\nu_{\text{C=O}}$  is  $-19.6 \text{ cm}^{-1}$  for methyl acetate, and this value remains practically unchanged in solvents and also agrees with the corresponding difference

TABLE I

Anharmonicity of the overtone level of the C=O str. vibration for methyl acetate (I) and tert-butyl pivalate (II)

Ester	Solvent	Concentration w/w	Spectrum	$2\nu_{\text{C=O}}^a$	$\nu_{\text{C=O}}$	Anharmoni- city <sup>b</sup>
II	<sup>c</sup>	1.00	IR	3 435.1	1 727.4	-19.7
I	<sup>c</sup>	1.00	IR	3 474.2	1 746.9	-19.6
I	hexane	0.032	IR	3 493.8	1 756.4	-19.0
I	CH <sub>3</sub> CN	0.029	IR	3 466.2	1 742.4	-18.6
I	<sup>c</sup>	1.00	Ra <sub>iso</sub>	3 472.5	1 739.2	- 5.9

<sup>a</sup> Wavenumber of the overtone level of the C=O str. vibration. <sup>b</sup> Anharmonicity determined as difference between wavenumber of the overtone level  $2\nu_{\text{C=O}}$  and double wavenumber  $\nu_{\text{C=O}}$ .

<sup>c</sup> Neat compound.

for tert-butyl pivalate, whereas in spectra of isotropic Raman scattering it changes from  $-6 \text{ cm}^{-1}$  to  $-19 \text{ cm}^{-1}$  upon dilution.

According to an analysis by Wang<sup>6</sup>,  $\Delta\nu$  is non-zero also in systems without short-range order. Force constants of harmonic oscillators are modified by an interaction potential with angular dependence leading to an anisotropic frequency distribution. In isotropic Raman scattering an averaging of the frequency distribution takes place, but the anisotropy of frequency distribution can be detected by depolarized Raman scattering. In an isotropic system, the resonance transition dipole-transition dipole interaction leads to a high-frequency shift of  $\nu_{\text{aniso}}$ . In our measurements, however, a shift of the isotropic Raman component is observed for methyl acetate.

Döge<sup>15</sup> has shown that a band shift in isotropic Raman scattering may be caused by resonance interaction of transition dipoles only in those cases where some local order exists in the measured system. In the case of methyl acetate, such order could be generated also by strong interaction between the dipoles of individual molecules. For order generated by dipolar interactions to be effective, according to ref.<sup>15</sup>, the dipolar interaction energy must be larger than the thermal energy of molecular motion, *i.e.*  $\mu^2/R^3 > kT$ , where  $\mu$  is the dipole moment and  $R$  is the intermolecular distance. The molecule of methyl acetate is small and the dipoles can approach to a very small distance (about 0.51 nm) for which the above condition is fulfilled. Actually the magnitude of the interaction may be even larger than that which follows from the permanent dipole moment of the whole molecule, because the dipole moment of the methyl acetate molecule (1.72 D) is composed of two dipole moments with opposite orientation: the dipole moment of the C=O bond ( $\sim 2.9$  D) and the dipole moment of the group C—O—C ( $\sim 1.2$  D).

As in methyl acetate, no additional conformers are present, and as no effect of Fermi resonance upon carbonyl band shape could be detected, the asymmetry of this band which is manifested only in isotropic Raman scattering is evidently caused by a distribution of molecular order.

The existence of local molecular order generated in consequence of dipolar interactions in liquid methyl acetate is also indicated by the concentration dependence of  $\Delta\nu$  in solvents with different dielectric constants. The plot in Fig. 2 shows that for solvents with a dielectric constant larger than that of methyl acetate, the slope of the  $\Delta\nu$  plot increases with the increasing concentration of the ester, it decreases in the opposite case, and the plot is linear when the dielectric constant of both components is equal. Mirone and Fini<sup>5</sup> have shown that such an effect can be explained by an orientational correlation of molecules in consequence of static dipolar interactions.

*Methyl pivalate:* The carbonyl band of methyl pivalate is a doublet, and the intensity ratio of the doublet components changes with temperature and also with concentration in solutions. In order to detect any connection of these changes with the

conformational structure of the molecule, we measured the Raman spectra in the liquid and crystalline states. Besides changes on the carbonyl band, the spectrum of liquid methyl pivalate exhibits only a very weak band at  $1\,355\text{ cm}^{-1}$  which disappears upon crystallization. The temperature dependence of this band indicates that the possible corresponding conformer is present in only a very small amount in liquid methyl pivalate at room temperature. The conformation of this minor component cannot be determined from vibrational spectra.

The appearance of the doublet on the carbonyl band cannot be explained by the presence of this minor conformer. The appearance of the doublet can be explained by Fermi resonance of the carbonyl vibration with the harmonic level of the symmetric  $\text{CH}_3\text{—O}$  str. vibration ( $863\text{ cm}^{-1}$ ), as follows from Table II. The assignment of the characteristic band  $863\text{ cm}^{-1}$  was based on the interpretation of the spectrum of methyl acetate<sup>16</sup>. Vibrational levels unperturbed by Fermi resonance were calculated<sup>17</sup> from positions and intensities of bands obtained by separation of the carbonyl band into two components by a least-squares method. In this separation, bands in the Raman spectrum were approximated by a Lorentz function and bands in the IR spectrum by a product of Lorentz and Gauss functions; this procedure resulted in good agreement of the measured and calculated carbonyl doublet.

The difference  $\Delta\nu$  calculated from unperturbed wavenumbers for neat methyl pivalate is  $2.9\text{ cm}^{-1}$ . For solutions of methyl pivalate the values of  $\Delta\nu$  cannot be determined as it lies within experimental error. The decrease of  $\Delta\nu$  as compared to methyl acetate is caused by the increase of the minimum separation of the molecular dipoles in the liquid state.

*Tert-butyl pivalate:* In IR and Raman spectra of tert-butyl pivalate, no band was found indicating the presence of several conformers in the liquid state. The carbonyl band is symmetrical in the spectrum of pure tert-butyl pivalate and in the spectra

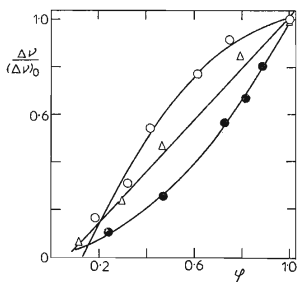


FIG. 2

Dependence  $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$  for the  $\text{C=O}$  str. vibration of methyl acetate on the volume fraction of methyl acetate in various solvents: hexane ( $\circ$ ), tetrahydrofuran ( $\Delta$ ),  $\text{CH}_3\text{CN}$  ( $\bullet$ ).  $(\Delta\nu)_0$  value of  $\Delta\nu$  for neat methyl acetate. — Curves fitted to experimental points under the assumption of a quadratic function

of its solutions. The wavenumber difference of the carbonyl band in the isotropic and anisotropic components of Raman scattering is  $1.2 \text{ cm}^{-1}$  for neat tert-butyl pivalate. A comparison of this value with the corresponding values of  $\Delta\nu$  for the other studied esters indicates a dominating effect of molecular volume on the magnitude of the transition dipole-transition dipole interaction.

*Tert-butyl acetate:* The C=O str. vibration band of tert-butyl acetate in IR and Raman spectra is asymmetrical and its shape is strongly affected by solvents. Óki<sup>18</sup> explained the asymmetry of this band in IR spectra by Fermi resonance of the carbonyl vibration with a combination level resulting from the antisymmetric C—O—C str. vibration ( $1\,240\text{--}1\,280 \text{ cm}^{-1}$ ) and an unassigned vibration causing absorption in the range  $430\text{--}470 \text{ cm}^{-1}$ . On the other hand, based on a correlation of the wavenumber shift of the carbonyl band in IR spectra with empirical relations, Morgan<sup>19</sup> assumes that conformer populations change with solvation so that in polar solvents the conformer with a *cis* orientation of the alkyl groups predominates. In order to determine the reason of the changes of position and shape of the carbonyl band, we have measured IR and Raman spectra of tert-butyl acetate in liquid and crystalline state and in polar and non-polar solvents.

TABLE II

Effect of Fermi resonance on the carbonyl band of methyl pivalate

Solvent	Concentration w/w	Spectrum	$\nu_1^a$	$\nu_2^a$	$\frac{S_1^b}{S_2}$	$\nu_{\text{C=O}}^0^c$	$\nu_{\text{O-CH}_3}^0^c$	$\nu_{\text{O-CH}_3}^{\text{exp}}^c$
<sup>d</sup>	1.00	Ra <sub>iso</sub>	1 735.2	1 722.2	5.46	1 733.2	862.1	862.5
<sup>d</sup>	1.00	Ra <sub>aniso</sub>	1 738.3	1 724.5	5.09	1 736.1	863.4	863
<sup>d</sup>	1.00	IR	1 737.9	1 723.7	9.67	1 736.5	862.5	863
Cryst.	1.00	Ra	1 735.4	1 720.0	0.16	1 722.1	866.7	867
CH <sub>3</sub> CN	0.49	IR	1 734.3	1 723.1	2.74	1 731.3	863.1	864
CH <sub>3</sub> CN	0.12	Ra <sub>iso</sub>	1 732.9	1 723.1	0.84	1 728.5	863.8	<sup>e</sup>
CH <sub>3</sub> CN	0.12	Ra <sub>aniso</sub>	1 733.3	1 723.0	1.03	1 727.2	864.2	<sup>e</sup>
CH <sub>3</sub> CN	0.030	IR	1 733.1	1 723.0	0.95	1 727.9	864.1	864.5
(CH <sub>3</sub> ) <sub>2</sub> SO	0.017	IR	1 731.6	1 721.3	0.86	1 726.0	863.4	<sup>e</sup>
Tetrahydro- furane	0.018	IR	1 736.0	1 724.0	4.25	1 733.7	863.2	<sup>e</sup>
Hexane	0.057	Ra <sub>iso</sub>	1 742.5	1 722.2	18.5	1 741.4	861.6	<sup>e</sup>
Hexane	0.065	IR	1 742.9	1 722.9	16.1	1 742.7	862.5	<sup>e</sup>

<sup>a</sup> Wavenumbers of the two components obtained by separation of the measured carbonyl band.

<sup>b</sup> Ratio of the integrated intensities of the bands  $\nu_1$  and  $\nu_2$ . <sup>c</sup> Calculated wavenumbers of the vibrations unperturbed by Fermi resonance. <sup>d</sup> Neat compound. <sup>e</sup> Not measured.

In dependence on temperature and solvent, prominent changes are exhibited, besides the carbonyl band, also by the broad bands in the range  $1\ 140\text{--}1\ 280\text{ cm}^{-1}$ .

TABLE III  
Effect of Fermi resonance on the carbonyl band of tert-butyl acetate

Solvent	Concentration w/w	Spectrum	$\nu_1^a$	$\nu_2^a$	$\frac{S_1^b}{S_2}$	$\nu_{\text{C=O}}^0^c$
<sup>d</sup>	1.00	Ra <sub>iso</sub>	1 739.8	1 729.9	0.99	1 734.8
<sup>d</sup>	1.00	Ra <sub>aniso</sub>	1 740.3	1 730.3	1.91	1 736.9
<sup>d</sup>	1.00	IR	1 740.4	1 730.0	2.00	1 736.9
CH <sub>3</sub> CN	0.032	IR	1 736.8	1 726.6	0.19	1 728.2
(CH <sub>3</sub> ) <sub>2</sub> SO	0.018	IR	1 734.0	1 723.5	0.25	1 725.9
Hexane	0.055	Ra <sub>iso</sub>	1 744.0	1 734.8	4.90	1 742.5
Hexane	0.066	IR	1 744.5	1 735.7	7.76	1 743.4

<sup>a</sup> Wavenumbers of the two components obtained by separation of the measured carbonyl band.

<sup>b</sup> Ratio of the integrated intensities of the bands  $\nu_1$  and  $\nu_2$ . <sup>c</sup> Calculated wavenumbers of the vibrations unperturbed by Fermi resonance. <sup>d</sup> Neat compound.

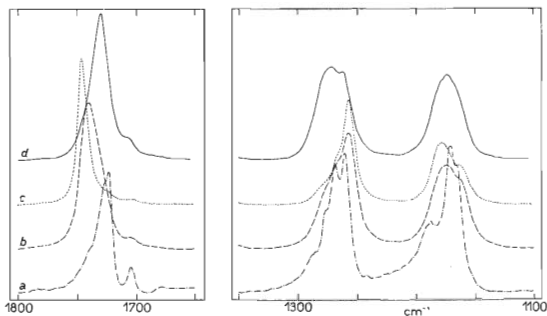


FIG. 3

Infrared spectrum of tert-butyl acetate in crystalline (a) and liquid (b) state and of solutions of tert-butyl acetate in hexane (c) and in CH<sub>3</sub>CN (d)



From Fig. 3 it can be seen that no bands in this range disappear upon crystallization of tert-butyl acetate, and therefore the changes in the spectra cannot be caused by changes of conformation. The changes in the range  $1\ 170\text{--}1\ 140\text{ cm}^{-1}$  are evidently caused by a relative shift of the three bands occurring in this range. Separation of the range  $1\ 280\text{--}1\ 250\text{ cm}^{-1}$  into three bands indicates that not only relative positions, but also the integrated intensities change appreciably in dependence on solvent. We assume that these bands are affected by Fermi resonance with the harmonic level of the vibration  $631\text{ cm}^{-1}$  which we assign to a skeletal deformation of type  $a'$ , in analogy to methyl acetate<sup>16</sup>. The carbonyl band behaves similarly as the bands in the range  $1\ 280\text{--}1\ 140\text{ cm}^{-1}$  — none of its components disappears upon crystallization. In Table III are shown the results of the separation of the carbonyl band into two components and the unperturbed values of the wavenumber of the carbonyl vibration, based on the assumption of Fermi resonance with one combination level. The agreement of the carbonyl band wavenumbers obtained in this way for neat compounds and solutions of tert-butyl acetate and methyl pivalate is evident, and parallels the agreement of the carbonyl band wavenumbers of methyl pivalate ( $1\ 756\text{ cm}^{-1}$ ) and tert-butyl acetate ( $1\ 756\text{ cm}^{-1}$ ) in the vapour phase.

The difference  $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$  is  $2.1\text{ cm}^{-1}$  for neat tert-butyl acetate, and is comparable for both esters. As the broad band in the range  $1\ 240\text{--}1\ 280\text{ cm}^{-1}$  causing Fermi resonance with the carbonyl vibration is probably composed of three components, the structure of the carbonyl band may be even more complicated.

## CONCLUSIONS

Analysis of vibrational spectra has shown that all the studied esters exist in solution in the form of essentially only a single conformer, and therefore the complicated form of the band of the C=O str. vibration cannot be interpreted as due to conformational structure. In all four esters the positions of the band of the C=O str. vibration are affected by transition dipole-transition dipole interactions, and this is manifested mainly by the non zero values of the difference  $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$ . This difference is largest for methyl acetate ( $6.2\text{ cm}^{-1}$ ) and it decreases with the increasing volume of the molecule and consequently increasing mean distance between carbonyl groups. For methyl pivalate and tert-butyl acetate,  $\Delta\nu$  reaches the value  $3\text{ cm}^{-1}$  and for tert-butyl pivalate it is only about  $1\text{ cm}^{-1}$ . The positions  $\nu_{\text{iso}}$  and  $\nu_{\text{aniso}}$  of the carbonyl band of methyl acetate as well as their concentration dependence indicate that both in the neat liquid and in solutions of methyl acetate, some intermolecular order, probably due to dipolar interactions, must exist. Because of the presence of Fermi resonance and of the small value of  $\Delta\nu$  the question about the existence of intermolecular order in the other studied esters cannot be clearly decided.

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