

SOLVENT EFFECTS ON THE INFRARED INTENSITIES OF THE ν_2 , ν_4 , AND ν_9 BANDS OF 1,1-DICHLOROETHYLENE

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Received January 27th, 1986

The infrared intensities of the ν_2 , ν_4 , and ν_9 stretching bands of 1,1-dichloroethylene have been measured in eighteen solvents of different polarity. After correcting for the local field effect, the partial derivatives of the electric dipole moment and electric polarizability with respect to normal coordinates were calculated using the dipole-dipole interaction model. A good or a poor statistical correlation of the calculated and observed intensities then indicates whether this model is adequate or other phenomena are involved in the interaction.

Infrared band intensities of solutes often experience marked changes when passing from nonpolar to more polar solvents. These changes are due to two major factors, *viz.* variations in intermolecular interactions and the effect of local field¹. Thus, corrections of the intensities for the local field effect must be made² if the intermolecular interactions are to be studied.

The corrected observed intensity Γ_c is related to the transition dipole moment $(\partial m/\partial Q)$ of the vibrational transition as

$$\Gamma_c = (8\pi^3/3hc) N_A (\partial m/\partial Q)^2, \quad (1)$$

where h is the Planck constant, c is the velocity of light and N_A is the Avogadro constant. Kakimoto and Fujiyama^{1,3} have worked out a method which can be used for the description of the solvent-induced intensity changes assuming the sole occurrence of dipole-dipole interactions. The first step in this treatment is a calculation of the average molecular fields $\langle F_p \rangle_{av}$ as a function of the dipole moment, molecular weight, density and concentration of solute and solvents, according to Eq. (9) in ref.³ for a concentration series. $\langle F_p \rangle_{av}$ is the electric field produced by an average configuration of the solvent molecules with a permanent dipole moment. The average molecular fields provide, along with the corresponding dipole moments *via* linear regression, the partial derivatives of the electric dipole moment μ and the electric polarizability α with respect to the normal coordinate Q :

$$(\partial m/\partial Q) = (\partial \mu/\partial Q) + (\partial \alpha/\partial Q) \langle F_p \rangle_{av}. \quad (2)$$

It has been shown that the obtained derivatives, which are the slope and the intercept of the regression straight line, can not be compared with the derivatives obtained from Raman scattering measurements.

In the present paper we attempt to use the Kakimoto–Fujiyama method for the interpretation of the intensity changes for bands of several stretching vibration modes of a solute in a series of solvents. After correcting the intensities for the local field effect, the derivatives $(\partial\mu/\partial Q)$ and $(\partial\alpha/\partial Q)$ are calculated and used to obtain new calculated intensities Γ_{cal} ; these should correlate closely with the observed intensities Γ_c if the assumption of the sole occurrence of dipole–dipole interactions is correct. The fit is characterized by the correlation coefficient r .

The test compound is 1,1-dichloroethylene. The bands examined are ν_2 ($\tilde{\nu}_{\text{hexane}} = 1\,614.4\text{ cm}^{-1}$, $\Delta\tilde{\nu}_{1/2} = 10\text{ cm}^{-1}$), ν_4 ($\tilde{\nu}_{\text{hexane}} = 600.5\text{ cm}^{-1}$, $\Delta\tilde{\nu}_{1/2} = 12\text{ cm}^{-1}$), and ν_9 ($\tilde{\nu}_{\text{hexane}} = 3\,127.4\text{ cm}^{-1}$, $\Delta\tilde{\nu}_{1/2} = 12\text{ cm}^{-1}$). ν_2 corresponds basically to the C=C stretching vibration and only the solvent effect on its intensity is pronounced; ν_4 and ν_9 correspond basically to the symmetric CCl_2 stretching and antisymmetric CH_2 stretching vibrations, respectively, and changes in the solvent polarity induce marked changes not only in the band intensities but also in the band positions and half band widths⁴.

EXPERIMENTAL

The solvents were purified and dried by standard methods⁵. The physico-chemical constants of the solvents were taken from ref.⁶. All solutions of 1,1-dichloroethylene were prepared in concentrations of 0.1 or 0.5 mol l⁻¹ after purification of the chemicals. Liquid cell pathlengths of 0.2 and 1.0 mm were used. The measurements were carried out at room temperature (20°C). The spectra were run on a Perkin–Elmer 621 infrared spectrometer with an accuracy of 0.5 cm⁻¹ at a resolution of 2.0 cm⁻¹. The intensities were obtained by direct integration over a range spanning five times the half band width on either side of the band maximum. The error in the intensities is estimated to be below 2%. The correction for the local field effect and the calculation of $\langle F_p \rangle_{\text{av}}$ were accomplished following ref.³. All calculations were run on a Perkin–Elmer 3600 data station.

RESULTS AND DISCUSSION

The corrected observed intensities Γ_c , transition dipole moments $(\partial m/\partial Q)$ for the three vibrations and the average molecular fields $\langle F_p \rangle_{\text{av}}$ are given in Table I. The results can be summarized as follows:

a) the solvent effect on the intensities of the ν_2 and ν_4 bands makes up to 25% (relative to cyclohexane), whereas the intensity of the ν_9 band increases more than by a factor of 10;

b) the intensity of the ν_2 band decreases whereas the intensities of the ν_4 and ν_9 bands increase with increasing solvent polarity;

TABLE I
Observed intensities, transition dipole moments, and average molecular fields

No	Solvent	ν_2^a		ν_4^b		ν_9^b		c^d	$\langle F_p \rangle_{av} \cdot 10^{23}$ D cm ⁻³
		Γ_c cm ² mol ⁻¹	$(\partial m/\partial Q)$ D ^c	Γ_c cm ² mol ⁻¹	$(\partial m/\partial Q)$ D	Γ_c cm ² mol ⁻¹	$(\partial m/\partial Q)$ D		
1	n-Hexane	5 455.3	0.1475	3 648.6	0.1206	—	—	0.00027	0.00136
2	n-Heptane	5 375.3	0.1464	3 649.9	0.1206	—	—	0.00027	0.00136
3	Cyclohexane	5 411.5	0.1469	3 694.2	0.1214	51.5	0.0143	0.00027	0.00136
4	Carbon tetrachloride	—	—	—	—	41.6	0.0129	0.00027	0.00136
5	Decaline	5 501.9	0.1481	—	—	50.6	0.0142	0.00027	0.00136
6	Benzene	4 818.3	0.1386	3 975.7	0.1259	—	—	0.00027	0.00136
7	Carbon disulfide	—	—	—	—	52.2	0.0144	0.00027	0.00136
8	Di-n-Butylether	5 445.2	0.1474	3 982.4	0.1260	—	—	0.01122	0.01195
9	Di-i-Propylether	5 570.6	0.1490	4 003.8	0.1264	191.2	0.0276	0.01244	0.01314
10	Diethylether	5 496.2	0.1480	4 103.2	0.1279	—	—	0.02340	0.02374
11	Tetrahydrofuran	—	—	4 237.8	0.1300	283.2	0.0336	0.07573	0.07438
12	1-Chlorobutane	5 437.8	0.1473	—	—	106.0	0.0206	0.07188	0.07065
13	Dichloromethane	5 401.1	0.1468	3 829.4	0.1236	102.5	0.0202	0.08528	0.08362
14	Bromoethane	5 252.9	0.1447	—	—	102.4	0.0202	0.10605	0.10372
15	Cyclohexanone	—	—	—	—	352.5	0.0378	0.15574	0.15180
16	Methyl ethyl ketone	5 139.6	0.1432	—	—	301.4	0.0347	0.14749	0.14382
17	Acetone	5 056.8	0.1420	4 531.1	0.1344	—	—	0.22962	0.22330
18	Dimethylsulfoxide	4 762.0	0.1378	—	—	627.4	0.0500	0.44079	0.42765

^a $c = 0.1 \text{ mol l}^{-1}$, ^b $c = 0.5 \text{ mol l}^{-1}$, ^c $1 \text{ D} = 0.33356 \cdot 10^{-29} \text{ Cm}$.

c) the general trends of the intensity changes are not followed in the case of aliphatic ethers;

d) there is a marked intensity lowering for the ν_2 band in benzene, which has been reported before⁷ and which can be explained by a strong resonance of the π -orbital systems of solute and solvent; the corresponding value is therefore omitted from the treatment.

The observed and calculated intensities of the ν_2 band are compared in Fig. 1. The correlation coefficient for thirteen data points is $r = 0.953$ ($r^{99\%} = 0.680$), which is indicative of a close correlation between Γ_c and Γ_{cal} . Thus the model used proves adequate to account for the intensity changes of the ν_2 band; in other words, the solvent effect can be attributed to the dipole-dipole interactions. Gribov⁸ suggested that the intensity of the C=C stretching vibrations of compounds of this kind is basically determined by the parameters of the neighbouring C—H bonds. This concept, however, does not seem to apply to our case in view of the different solvent effects of aliphatic ethers on the intensities of the ν_2 and ν_9 bands and also of the small contributions of the C—H symmetry coordinates to the potential energy distribution of the ν_2 band⁹. Cuncliffe-Jones⁷ has suggested that the solvent dipoles are aligned along the C=C bond without change in the normal coordinate. This assumption agrees with the small shift ($<2 \text{ cm}^{-1}$) of the ν_2 band to lower wavenumbers⁴. The alignment of the solvent dipoles along the C=C bond leads to a polarization of the π -orbital system causing a decrease in the transition dipole moment ($\partial m/\partial Q$), and also in the molecular dipole moment. This is the reason for the negative sign of the $(\partial\mu/\partial Q)(\partial\alpha/\partial Q)$ product, the high value of $(\partial\mu/\partial Q)$ (Table II), and also for the decrease in the ν_2 band intensity with increasing solvent polarity. The low solvent effect on the intensity of this band in the case of aliphatic ethers can be explained in terms of shielding of their oxygen atoms by the neighbouring aliphatic groups, making the alignment impossible.

TABLE II
Partial derivatives $(\partial\mu/\partial Q)$ and $(\partial\alpha/\partial Q)$

Band	$(\partial\mu/\partial Q)$ D	$(\partial\alpha/\partial Q)$ \AA^3	Sign ^a	N^b
ν_2	0.148(± 0.001)	0.234(± 0.078)	—	13
ν_4	0.124(± 0.001)	0.507(± 0.196)	+	10
ν_9	0.018(± 0.008)	0.845(± 0.534)	+	12

^a Sign of the product $(\partial\mu/\partial Q) \cdot (\partial\alpha/\partial Q)$; ^b number of data points.

The plot of Γ_c vs Γ_{cal} for the ν_4 band is shown in Fig. 2. The points of this plot depart from the regression line to a considerably greater extent than for the ν_2 band; the correlation coefficient is $r = 0.779$ ($r^{99\%} = 0.770$), indicating a poor correlative relationship. Thus the dipole-dipole interaction model used is unable to sufficiently account for the intensity changes of this band, and additional interactions have to be taken into consideration for some of the solvents. We suggest that these additional interactions are associated with the pairs of chlorine atoms, the potential energy distribution of the ν_4 vibration being contributed to by the

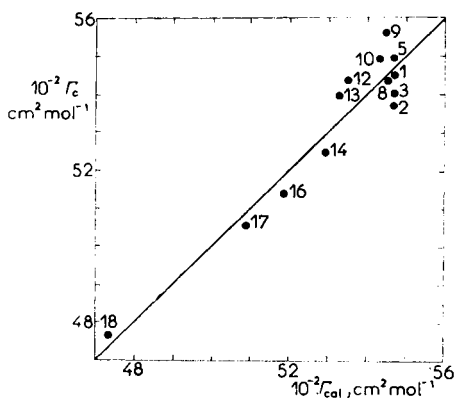


FIG. 1

Correlation of observed and calculated intensities of the ν_2 band. Solvent numbering as in Table I

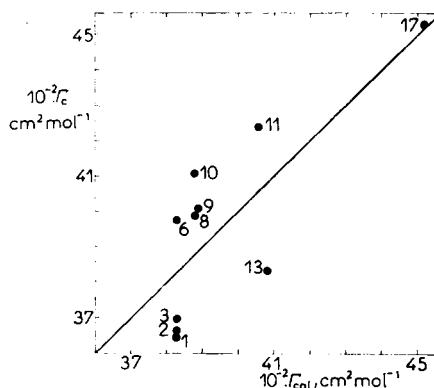


FIG. 2

Correlation of observed and calculated intensities of the ν_4 band. Solvent numbering as in Table I

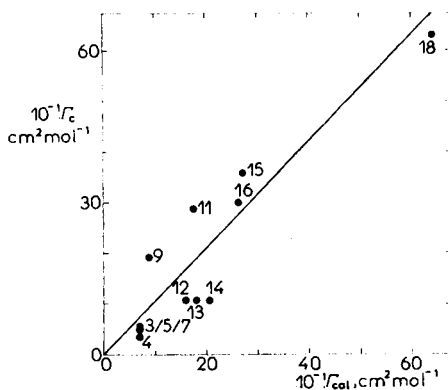


FIG. 3

Correlation of observed and calculated intensities of the ν_9 band. Solvent numbering as in Table I

symmetry coordinates of the CCl_2 grouping more than by 85% (ref.⁹). These additional interactions in some solvents evidently induce an additional dipole moment which has the same direction as the molecular dipole moment (because the sign of the $(\partial\mu/\partial Q)(\partial\alpha/\partial Q)$ product is positive). This is the reason why the intensity of the ν_4 band increases. The assumption of additional dipole-induced interactions is also supported by the significant correlations⁴ of the intensity changes with the empirically derived solvent polarity parameter π^* (ref.¹⁰) and also with the solvent polarizability term $(n^2 - 1)/(2n^2 + 1)$, where n is the refractive index of the solvent. The superimposing interactions lead to small changes in the normal coordinate and thus to a slight shift to lower wavenumbers as well as to an increase in the partial derivatives. Thus, the relatively high $(\partial\mu/\partial Q)$ and $(\partial\alpha/\partial Q)$ values (Table II) can be ascribed to changes in the normal coordinate of this vibration due to intermolecular interactions.

Fig. 3 shows that for the ν_9 vibration, which is associated with the symmetry coordinate of C—H bond length variations, there is a clear-cut correlation between Γ_c and Γ_{cal} ($r = 0.915$ as against the $r^{99\%} = 0.710$) for twelve data points. In this case, however, additional effects operate. Fermi resonance may be involved¹¹; also, it should be borne in mind that weak hydrogen bonds occur between the CH_2 group of 1,1-dichloroethylene and proton acceptor solvents^{7,12} such as dimethyl sulfoxide. This is corroborated by the perfect correlation⁴ of the intensity changes of this band with the empirically derived electron donicity parameter $\Delta\nu_D$ (ref.¹³) of the solvents. Assuming hydrogen bonding in some solvents, the relatively high value of $(\partial\alpha/\partial Q)$ can be explained in terms of a larger C—H bond lengthening, while the low value of $(\partial\mu/\partial Q)$ is due to the low C—H bond dipole moment. Thus, the high increase in the ν_9 band intensity is a consequence of the C—H bond lengthening caused by hydrogen bonding effects.

CONCLUSIONS

The intensities of the ν_2 , ν_4 , and ν_9 bands of 1,1-dichloroethylene experience different solvent effects. The Kakimoto–Fujiyama method, based on the dipole–dipole interaction model, suits well as a basis for the discussion of the solvent effects on the intensities of the three bands. Statistical evaluation indicates that the C=C bond is the centre of the dipole–dipole interactions with the solvent dipoles whereas for the CH_2 and CCl_2 groups, additional interactions such as hydrogen bonding and dipole-induced interactions have to be taken into account.

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