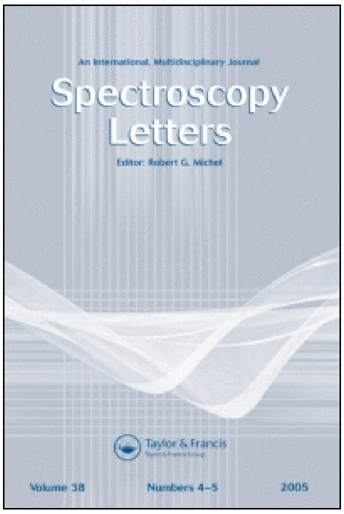

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Variation of Dipole Moment Function of O-H Bond of t-Butanol with the Nature of Solvent and Its Temperature

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VARIATION OF DIPOLE MOMENT FUNCTION OF O-H BOND OF t-BUTANOL WITH THE NATURE OF SOLVENT AND ITS TEMPERATURE

KEY WORDS: IR intensities, Molecular interactions, Dipole moment derivatives, Dipole moment function, Electrical anharmonicity, O-H bond

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Abstract

The intermolecular influence on dipole moment function is evaluated for O-H bond of t-butanol in different nonpolar solvents at temperatures ranging from 10° to $60^{\circ}C$ employing IR band intensities of fundamental

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and first overtone bands. Two sets of dipole moment derivatives have been calculated corresponding to -- and +- combinations of the transition moment matrix elements R_{10} and R_{20}, the values for ++ and -+ combinations are equal in magnitude to those for -- and +- combinations, respectively and opposite in signs. In general the dipole moment derivatives increase on lowering the temperature as well as with increasing molecular interactions with the solvent molecules. Dipole moment plots with dimensionless coordinate ξ [$=(r-r_e)/r_e$, where r and r_e are internuclear distances during vibration and at equilibrium, respectively] are reported for various systems considered. It is found that for +- combination the dipole moment maximum shifts to higher internuclear distances when polarisation of the solute molecules is increased by lowering of temperature or increase in molecular interactions between solute and solvent molecules. A reverse trend is observed for -- combination.- The OH band of t-butanol vapor has been measured.

1 INTRODUCTION

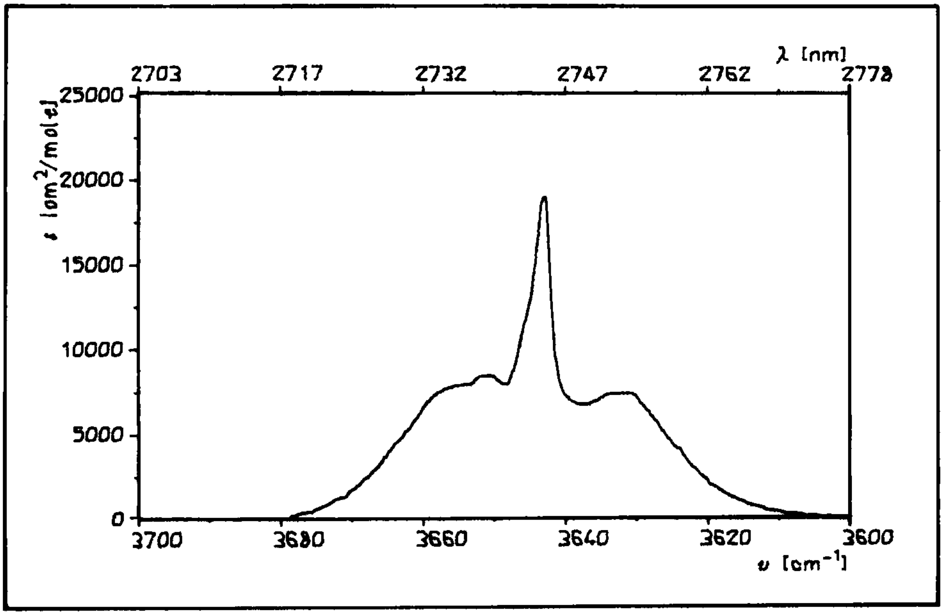
Dipole moment for diatomic molecules is known (1) to have a nonlinear dependence on its internuclear distance. This concept has been used in the literature to explain the observation of overtone bands in the vibrational spectra of diatomic molecules even under mechanical harmonic oscillator approximation. For polyatomic molecules the dipole moment depends on normal coordinates. Using diatomic oscillator approximation for X-H bonds (X = C,N,O) in polyatomic molecules and employing infrared band intensities of fundamentals and overtones various authors (2-6) have evaluated dipole functions. The first and second dipole moment derivatives are evaluated by solving two equations for transition moments obtained from IR band intensities of fundamental and overtone of X-H oscillator. The dipole moment at equilibrium is evaluated by assuming (2) the total dipole moment to be zero at zero internuclear distance. On comparison of expressions of varying complexity for transition moment matrix elements reported by different authors (7-25), we have proposed (6,26-29) optimum expressions suitable for calculation of dipole moment derivatives using IR intensities for diatomic oscillators.

Recently Luck and Zheng (30) have reported that the intensity of the O-H fundamental of monomeric t-butanol increases with decreasing temperature when the spectra is recorded in dilute solutions using nonpolar solvents. If frequency shift of the monomeric O-H band in solutions with respect to its position in vapor phase is taken as a measure of the interaction field of the solvent molecules, the intensity of the fundamental band was found to increase with increasing interactions of alcohol with solvent molecules through van der Waals forces. Similar observations were made earlier for IR intensities of O-H bond in hydrogen bonding systems (31). In both the cases of van der Waals as well as hydrogen bonding interactions the energy is found to be related to the frequency shift $\Delta\nu_{OH}$ which in turn is linearly related to the increase in intensity of the fundamental O-H band. The intensity of the O-H overtone band does not show much change in different solvents as well as at different temperatures.

We report here the dipole moment functions of the O-H oscillator obtained from the data on IR intensities (30) of O-H bands of t-butanol in several nonpolar solvents at temperatures ranging from 10^{o} to 60^{o}C. The data on solutions in perfluorohexane is not included because of higher possibility of self association because of low solubility, at lower temperature in this case, which in turn will show lowering of monomer band intensity. This effect is found to decrease the intensity by not more than 1 to 3% while varying the temperature from 60^{o} to 10^{o}C in the solvents considered. Spectral results for vapor phase are also included for comparison.

2 RESULTS AND DISCUSSION

The O-H stretching bands for fundamental and first overtone for t-butanol in vapor phase are shown in Fig.1. IR spectral data for its O-H stretching fundamental and first overtone bands in different solvents are summa-



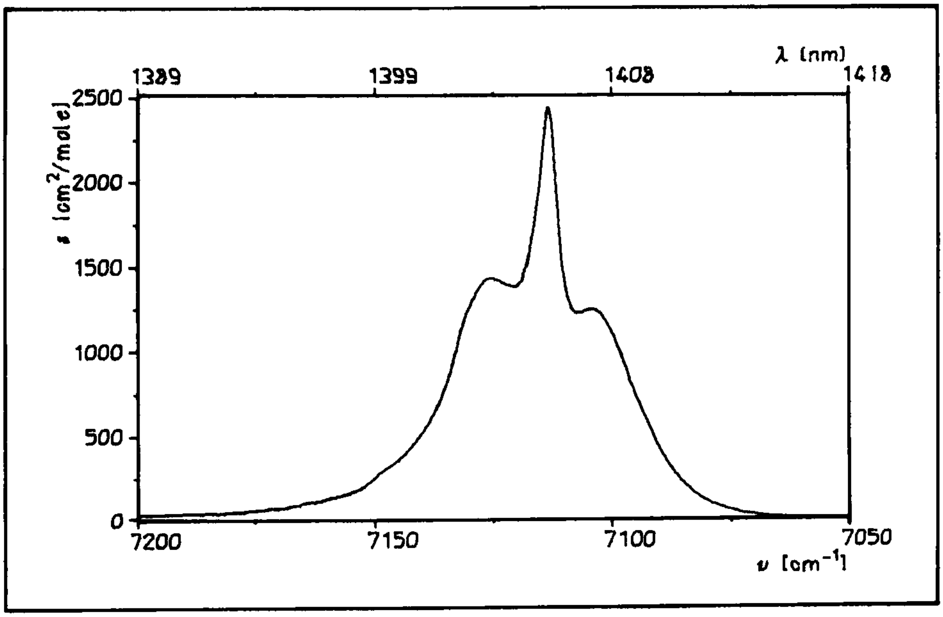


FIG.1 Vapor phase IR spectra of t-butanol in the O-H stretching fundamental and first overtone regions at 35°C.

rised in Table 1 at six temperatures. As may be noticed, the intensities of the fundamental increases with decrease in temperature and increase in the extent of interaction of solute molecules with solvent, the overtone band does not show much variations. It is observed that the ratio of the intensities of fundamental and overtone bands for vapor is approximately 5 and it increases with molecular interactions with solvent molecules, being approximately 14 for solution in Hexane and 26 in trichlorethane. In strong hydrogen bonding solvents this ratio is found to be ~200 for CH_3OH (6).

The experimental absorption intensity integrated over the band, expressed in cm $mole^{-1}$ is given as

$$A = \frac{1000}{C \cdot \ell} \int \ell n \frac{I_o}{I} d\nu \qquad (1)$$

where C is the concentration in mole lit^{-1}, ℓ the path length in cm and ν the frequency in cm^{-1}. This intensity, A is related to the transition moment integral $R_{v'v''}$ as follows:

$$A_{v'v''} = \frac{8\pi^3 N}{3hc} \nu_{v'v''} |R_{v'v''}|^2 \qquad (2)$$

where $\nu_{v'v''}$ is the frequency, in cm^{-1}, of radiation at which maximum occurs for transition $v'' \rightarrow v'$ and N is Avogadro Number. The above two expressions may be used to determine the value of $R_{v'v''}$ from experimental intensi-

TABLE 1

Spectral data for O-H stretching vibration for t-butanol in various nonpolar solvents at different temperatures.

Solvent	Temp, ^{o}C	$\bar{\nu}_{01}$, cm^{-1}	A_{01}, cm mol^{-1} × 10^{-6}	$\bar{\nu}_{02}$, cm^{-1}	A_{02}, cm mol^{-1} × 10^{-5}
Vapor	35	3643.0	0.84	7114.0	1.64
Hexane	10	3622.4	3.02	7074.6	2.29
	20	3623.1	2.29	7075.6	2.28
	30	3623.5	2.90	7076.1	2.25
	40	3624.0	2.83	7076.6	2.18
	50	3624.5	2.74	7077.1	2.15
	60	3625.0	2.65	7078.6	2.13
Cyclohexane	10	3620.3	3.29	7064.5	2.07
	20	3621.0	3.20	7065.9	2.01
	30	3621.5	3.09	7066.9	1.94
	40	3622.0	3.02	7067.4	1.91
	50	3622.4	2.92	7068.0	1.91
	60	3623.0	2.74	7069.2	1.91
Carbontetrachloride	10	3616.4	4.24	7059.8	2.10
	20	3616.8	4.12	7060.8	2.10
	30	3617.2	4.10	7062.1	2.08
	40	3617.6	3.98	7063.3	2.06
	50	3618.4	3.91	7064.6	2.03
	60	3619.2	3.82	7065.7	2.03
Trichlorethane	10	3611.0	5.62	7051.6	2.05
	20	3611.7	5.50	7053.7	2.05
	30	3612.5	5.41	7055.2	2.06
	40	3613.2	5.37	7056.2	2.04
	50	3614.0	5.27	7057.7	2.01
	60	3614.7	5.20	7058.8	2.02

ties, its sign can, however, not be determined. The transition moment integrals, in terms of dipole moment derivatives are given as follows (6,26,27):

$$R_{10} = \frac{\Theta}{\sqrt{2}} p_1 - \frac{5}{2\sqrt{2}} a_1 \Theta^3 p_2 \qquad (3)$$

$$R_{20} = \frac{a_1\Theta^2}{2\sqrt{2}} p_1 + \frac{\Theta^2}{\sqrt{2}} p_2 \qquad (4)$$

where $a_1 = -[1 + \frac{\alpha_e\omega_e}{6B_e^2}]$, $\Theta = [\frac{2B_e}{\omega_e}]$, p_1 and p_2 are first and second dipole moment derivatives with respect to dimensionless coordinates ξ in the expansion $p = p_0 + p_1\xi + p_2\xi^2$, B_e and α_e are rotational constants and ω_e is harmonic frequency. In terms of anharmonicity constant b (= $k_3/\omega_e = a_1\Theta/2$), the above relations can be given (4,6) as follows:

$$R_{10} = \frac{\Theta}{\sqrt{2}} p_1 - \frac{5}{\sqrt{2}} b\Theta^2 p_2 \qquad (5)$$

$$R_{20} = \frac{b\Theta}{\sqrt{2}} p_1 + \frac{\Theta^2}{\sqrt{2}} p_2 \qquad (6)$$

k_3 the cubic force constant in cm^{-1}, in its first approximation is given by $[\frac{4\omega_e^2 x_e}{15}]$ where $\omega_e x_e$ is anharmonicity constant. The dipole moment derivatives p_1 and p_2 are determined using equations 5 and 6 for -- and +- combinations of R_{10} and R_{20} and are given in Table 2. For the sake of brevity values for only 10° and 60°C are shown.

As reported by Sverdlov et al.(32) the intensity in condensed media vary as a linear function of temperature

$$A = A_0 + \alpha\Delta T \qquad (7)$$

TABLE 2

Dipole moment expansion for O-H bond in t-butanol in vapor and nonpolar solvents

Solvent	Temp, ^{0}C	--			+-		
		p_0	p_1	p_2	p_0	p_1	p_2
Vapor	35	-1.29	0.37	1.66	1.48	0.47	-1.01
Hexane	10	-1.46	0.73	2.19	1.81	0.86	-0.95
	60	-1.40	0.69	2.09	1.74	0.80	-0.94
Cyclohexane	10	-1.38	0.77	2.15	1.73	0.89	-0.84
	60	-1.33	0.70	2.03	1.65	0.81	-0.84
Carbontetrachloride	10	-1.36	0.88	2.24	1.77	1.00	-0.77
	60	-1.34	0.84	2.18	1.73	0.95	-0.78
Trichlorethane	10	-1.29	1.03	2.32	1.78	1.14	-0.64
	60	-1.29	0.99	2.28	1.76	1.10	-0.66

where the temperature coefficient α is negative for liquids. In the zero approximation the probability of a vibrational transition is represented (33) as a product of two matrix elements of a transition dipole, the first corresponding to the free molecule and the second to the intermolecular interactions, the latter decreasing with increase in temperature and increase in intermolecular separation. Such a linear temperature dependence of IR intensities has been experimentally established by Luck and Zheng (30). Yao and Overrend (25) have, on the basis of a comprehensive treatment argued that temperature dependence of intensities in gas phase for high frequency oscillators is negligible at ordinary temperatures. They suggest that in condensed phase, however, there may be strong temperature dependence of the dipole function due to variation in polarisation as the average intermolecular separations change and this may lead to considerable temperature dependence of IR band intensities. The variation of p_1 and p_2 as a function of temperature and nature of solvent is in agreement with the conclusions drawn above.

Using the assumption suggested by Russel and Thompson (2) that dipole moment may be assumed to be zero at zero internuclear distance, the values of dipole moments at equlibrium bond distance, p_0 are evaluated as follows:

$$p = p_0 + p_1\xi + p_2\xi^2, \quad \xi = (r - r_e)/r_e$$

for $r = 0$, $\xi = -1$ and thus $p_0 = p_1 - p_2$.

The p_0 values thus calculated are also given in Table 2.

In Fig.2 are shown the dipole moment functions for O-H bond of t-butanol in various solvents at 10° and 60°C for -- and +- combinations of R_{10} and R_{20}. In many cases of diatomic oscillators it is found (26) that p_1 and p_2 have opposite signs. We feel, therefore, that values of p_1 and p_2 given under +- combination in Table 2 are better approximation to the correct dipole function. It is found that for this combination p_0, p_1 and p_2 in-

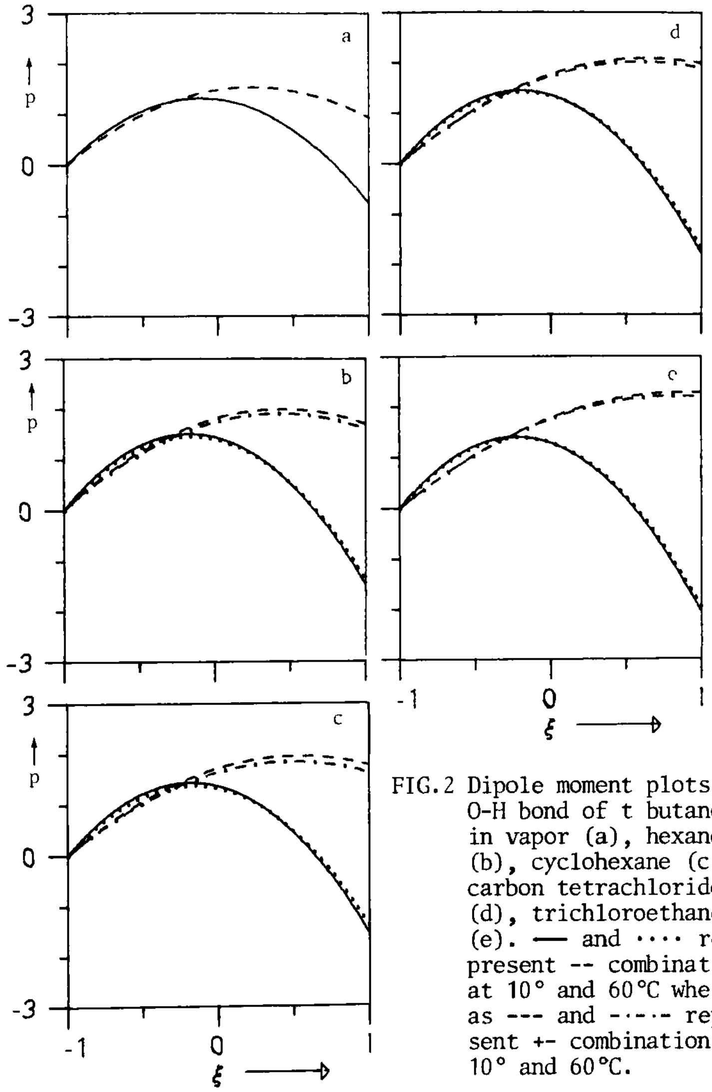


FIG.2 Dipole moment plots for O-H bond of t butanol in vapor (a), hexane (b), cyclohexane (c), carbon tetrachloride (d), trichloroethane (e). —— and ···· represent -- combination at 10° and 60°C whereas --- and -·-·- represent +- combination at 10° and 60°C.

crease with decrease in temperature and with increase in molecular interactions of the solvent molecules with alcohol.

In Fig.2 variations in dipole moment are shown for the region $-1 < \xi < 1$ corresponding to $0 < r < 2r_e$. However, since a limited dipole expansion is considered here, which is truncated at p_2 and higher derivative are not considered, we feel that the function may not be correct outside the region $-0.5 < \xi < 0.5$. We have also computed, ξ_{max}, the values of ξ for which dipole moment is maximum and they are given in Table 3 as internuclear distance, r_{max} in terms of r_e. It is found that in all the cases studied the r_{max} for -- combination is lower than equilibrium internuclear distance, r_e and for +- combination it is higher than r_e. Further, a definite trend in the r_{max} values is found, as a function of temperature and nature of solvent (Fig.3). For -- combination the r_{max} values decrease with decreasing temperature and with increasing extent of molecular interactions of solvent with the solute molecules (as measured by $\Delta\nu_{OH}$ of solute in various solvents) whereas for +- combination a reverse trend is observed; both for decreasing temperature and increasing extent of molecular interactions the r_{max} values increase. If the +- combination is the right choice as mentioned earlier, then the results show that the dipole moment function gets its maximum shifted to

TABLE 3

Values of r_{max}, internuclear distance at which dipole moment is maximum, in terms of r_e

Solvent	Temp, ^oC	$\Delta\nu_{OH}$	r_{max}	
			--	+-
Vapor	35	0	.889	1.234
Hexane	10 60	20.6 18.0	.832 .836	1.447 1.429
Cyclohexane	10 60	22.7 20.0	.821 .828	1.529 1.485
Carbontetrachloride	10 60	26.6 23.8	.803 .808	1.653 1.610
Trichlorethane	10 60	32.0 28.3	.779 .784	1.888 1.830

higher internuclear distances with increasing polarization of the solute molecules by solvent molecules and reduction in temperature.

The implications and correct interpretation of these observations on r_{max} may be made sometime later when more data is available on related systems. The present observations on dipole function seem to be interesting for further work in this direction.

3 EXPERIMENTAL

The spectra in the fundamental region were recorded on PE 325 IR spectrometer and in the overtone regions on Cary-17I spectrometer. The vapor phase spectrum in the fundamental region was recorded in a gas cell fitted

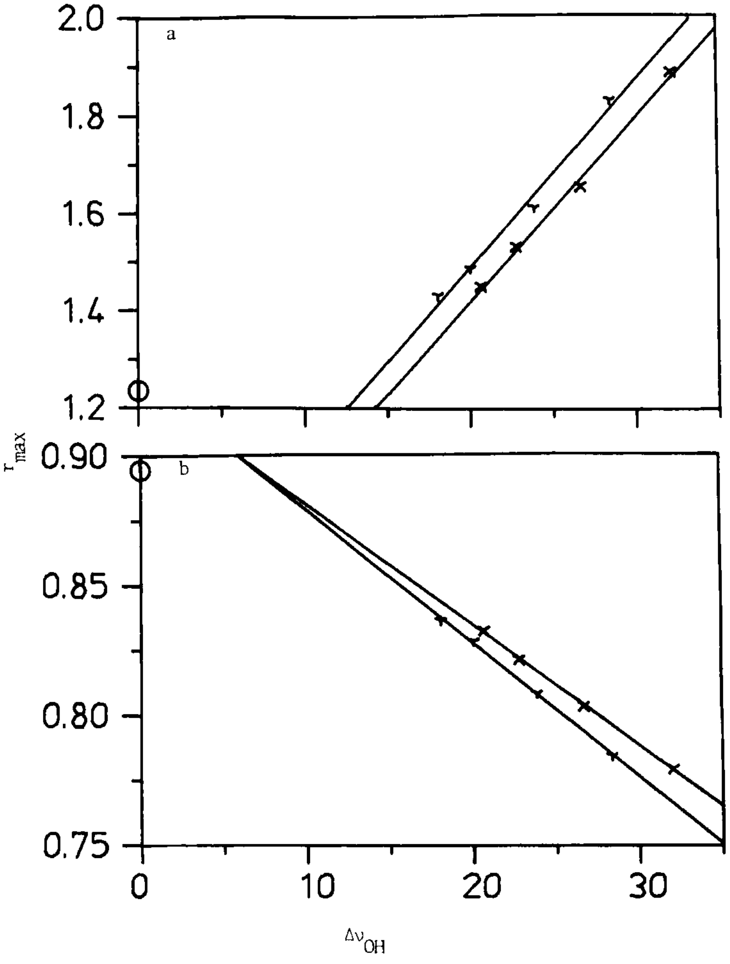


FIG.3 Plot of r_{max}(in terms of r_e)vs $\Delta\nu_{OH}$ for +-(a) and --(b) combinations at 10°C(X) and 60°C(Y). The vapor phase value is shown by O.

with KBr windows with a path length of 10 cm maintained at $35^{o}C$. After evacuation the cell was filled with vapors from a flask containing liquid t-butanol at $35^{o}C$. The spectra were recorded after the system attained an equilibrium for 1/2 hr. For the overtone spectrum multiple pass gas cell fitted with glass windows with an effective path length of 1 m was used. Since it was not possible to evacuate the cell, it was filled with dry air and then vapors of t-butanol were allowed in, while maintaining a constant temperature of $35^{o}C$ for the cell and $30^{o}C$ for the flask containing liquid alcohol. The IR spectra were recorded every-day for 14 days till the proper equilibrium was attained, which was ensured by constant intensity measurements on last four consecutive days. The vapor pressure for t-butanol at above temperature was taken from the literature (34) for calculation of the integrated intensities. The experimental details for spectra in solutions are given elsewhere (30).

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