

Near infrared spectral studies on interactions of CH₃ groups with halide ions

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Abstract. Near infrared (NIR) spectra in the CH₃ stretching first-overtone region for methyl iodide, acetonitrile, nitromethane and dimethyl sulphoxide are discussed in terms of normal mode and local mode descriptions. NIR spectra in this region for solutions of several alkali metal halides and tetraalkyl ammonium halides in these solvents are also reported. It is found that the relative intensity of the cooperative excitation band with respect to the pure overtone excitation band reduces considerably on increase in the concentration of the electrolytes in solution. The results are discussed in terms of the formation of anion-molecular complexes as well as intermode coupling due to kinetic energy and anharmonicity effects.

Keywords. Anion-molecular interactions; overtone spectra; local modes; methyl iodide; acetonitrile; nitromethane; dimethyl sulphoxide.

1. Introduction

Molecular interactions through methyl groups of organic molecules have been reported earlier (e.g. Mitchell and Lippert 1978, Sastry and Singh 1986). It is suggested (Mitchell and Lippert 1978) that the effect of axial interactions on the CH₃ group on acetonitrile (AN) may be observed with respect to its symmetric stretching mode whereas the perpendicular interactions can be studied with respect to the antisymmetric stretching mode. A change in the intensity of the antisymmetric CH₃ stretching fundamental band was observed with variation in solvent and temperature (De Maine 1960; Mahnke 1971; Mitchell and Lippert 1978; E Knoezinger, private communication), and by means of the equilibrium model an association enthalpy of 6 kJmol⁻¹ was calculated for solutions of acetonitrile in carbon tetrachloride (Mahnke 1971).

Studies on the interactions of the CH₃ group of AN with halide ions employing IR and Raman spectroscopy have been reported (Roche and Huong 1979; Mitchell and Lippert 1978; Sastry and Singh 1986; Venkata Ramana and Singh 1988, 1989a) in the C–H (D) stretching region. It was observed (E Knoezinger, private communication) that the peak heights of the fundamental bands for the CH₃ antisymmetric and symmetric stretching modes of pure AN are comparable in its IR spectrum, and as the concentration of AN in its solution in carbon tetrachloride decreases, the relative intensity of the antisymmetric band with respect to the symmetric

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band gets reduced. In IR spectra of solutions of alkali metal halides in AN (Roche and Huong 1970) it is observed that both the bands show splittings because of the existence of an equilibrium between the bulk and associated AN, and on further increase in concentration of salts the bulk AN bands almost disappear. The antisymmetric CH_3 stretching band of associated AN has lower intensity than the symmetric CH_3 band, even though the overall intensities of both the bands are found to be much higher for associated AN than those of pure AN. The above observations seem to indicate that the ratio of the intensities of antisymmetric to symmetric CH_3 bands in the fundamental stretching region is less than unity for free AN as well as for AN associated with halide ion, whereas it is close to unity for liquid AN. The CH_3 symmetric stretching band of AN (Venkata Ramana and Singh 1988) and CH_3 symmetric as well as antisymmetric stretching bands of dimethyl sulphoxide [DMSO] in Raman spectra also show (Venkata Ramana and Singh 1989b) splittings in the presence of halide ions, thus indicating the involvement of the CH_3 group in AN and DMSO on interactions with halide ions.

As an extension to our work on the studies of the interaction of CH_3 groups with halide ions we now report near infrared (NIR) spectral studies of solutions of alkali metal- and tetraalkyl ammonium halides in methyl iodide (MI), acetonitrile (AN), nitromethane (NM) and dimethyl sulphoxide (DMSO).

2. Experimental

MI (Sisco), AN (Fluka), NM (Farek) and DMSO (Koch-light) were used after drying over 4 Å molecular sieves. Lithium halides (Fluka-AG), potassium halides (Merck), tetrabutyl ammonium bromide (Sigma), tetrabutyl ammonium iodide (Sigma), tetraethyl ammonium bromide (Sigma) and tetraheptyl ammonium bromide (Fluka AG) were used without further purification. IR spectra were recorded on a Varian 2390 spectrometer with a scan rate of 0.2 nm/s, response time of 10 s and spectral band width of 2 nm.

3. Results and discussion

In figure 1 are given NIR spectra of MI, AN, NM and DMSO in the first overtone region of the CH_3 stretching mode. For molecules having XY_3 functional groups the three X–Y bonds can be combined to give the symmetry coordinates A_1 and E corresponding to the three normal modes of vibration of the parent molecule. If the wavefunctions in terms of normal modes consisting of the XY_3 stretching vibrations with A_1 and E symmetries are given in terms of vibrational quantum numbers n_s and n_a as $|n_s, n_a\rangle$ then for the first overtone ($n_s + n_a = 2$) for XY_3 stretching vibrations, the three wavefunctions can be depicted as $|2, 0\rangle$, $|0, 2\rangle$ and $|1, 1\rangle$. The $|2, 0\rangle$ wavefunction belongs to symmetry A_1 whereas the $|0, 2\rangle$ wavefunction, because of degeneracy of the asymmetric mode, splits into two wavefunctions $|0, 2\rangle_{A_1}$ and $|0, 2\rangle_E$. The combination wavefunction $|1, 1\rangle$ belongs to the E symmetry species.

Recently, NIR spectra of molecules with CH_3 groups have been reported in terms of local mode theory (Halonen and Child 1983; Henry *et al* 1983; Ahmed and Henry 1987, 1988). It is found that, in general, molecules containing CH_3 groups tend to

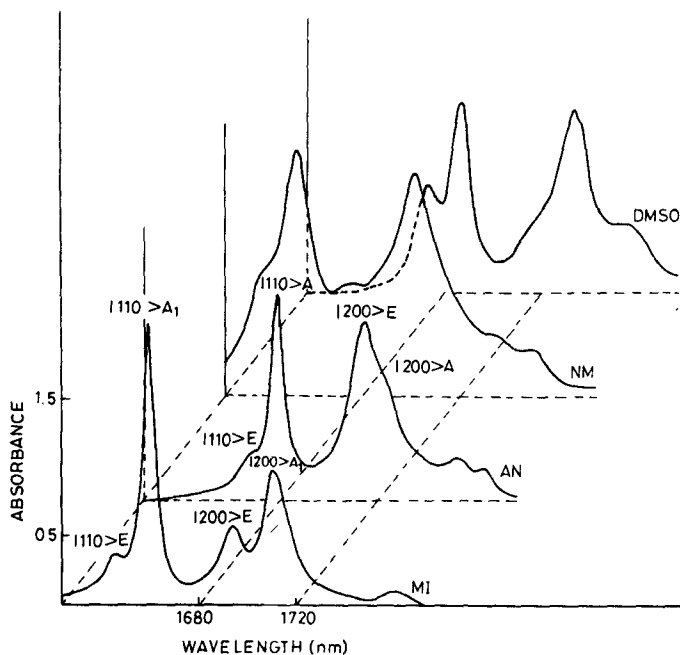


Figure 1. NIR spectra of methyl iodide (MI), acetonitrile (AN), nitromethane (NM) and dimethyl sulphoxide (DMSO) in first overtone region of the CH_3 stretching mode.

have similar band structures in various C–H stretching overtone regions with varying relative intensities of component bands within the region of the specific overtone of interest. Various components are assigned to pure overtones, local mode combinations (or cooperative excitations) and intermode combinations of local mode excitations with skeletal excitations. Definite correlations have been worked out (Sage and Jortner 1981; Child and Halonen 1984; Mills and Robiette 1985) between local mode and normal mode models for observed transitions. Ahmed and Henry (1987, 1988) discussed the assignments for NIR spectra of AN and AN (d_3) along with methyl halides in the overtone region and have proposed assignments for various bands on the basis of local mode theory.

If the vibrational quantum numbers for three X–Y oscillators are designated by l_1 , l_2 and l_3 , various wavefunctions $|l_1, l_2, l_3\rangle$ for the first overtone level ($l_1 + l_2 + l_3 = 2$) can be designated as $|2, 0, 0\rangle$, $|0, 2, 0\rangle$, $|0, 0, 2\rangle$, $|1, 1, 0\rangle$, $|1, 0, 1\rangle$ and $|0, 1, 1\rangle$. The first three wavefunctions with one of the local modes having a vibrational quantum number $l_i = 2$ are pure overtone levels and the remaining three with two local modes having one vibrational quantum number each are called cooperative excitation levels. Both these groups of wavefunctions have three equivalent functions which on projection operation give rise to two symmetry-adapted linear combinations (A_1 and E) each designated as $|2, 0, 0\rangle A_1$, $|2, 0, 0\rangle E$, $|1, 1, 0\rangle A_1$ and $|1, 1, 0\rangle E$, respectively. The two sets of wavefunctions under local and normal mode models with designated symmetries are correlated (Halonen and Child 1983; Child and Halonen 1984) as shown in figure 2. The transition from ground state to high energy state with wavefunctions in terms of local mode for MI and AN are shown in figure 1. The assignments for

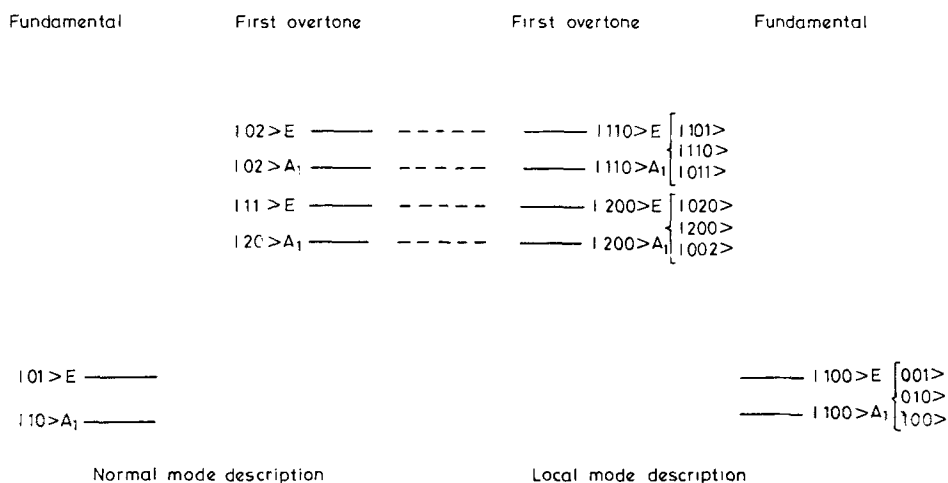


Figure 2. Normal mode to local mode correlation diagrams of the CH₃ group.

NM and DMSO are not available in the literature and therefore tentative assignments are assumed in the following section by comparison with MI and AN.

3.1 NIR spectra of solutions of halide ions

NIR spectra of solutions of alkali metal halides as well as tetraalkyl ammonium salts in MI, AN, NM and DMSO at various concentrations were recorded. A stack diagram showing the changes in band contour of the first overtone of the CH₃ stretching mode of MI in solutions of tetraheptyl ammonium bromide in MI is shown in figure 3. As can be noticed, with an increase in concentration of salt, the relative intensity of the $|1, 1, 0\rangle A_1$ band seems to reduce with respect to both $|2, 0, 0\rangle A_1$ and $|2, 0, 0\rangle E$ bands. The results of band fit analysis for this contour for various tetraalkyl ammonium salts dissolved in methyl iodide are given in table 1. The relative intensities in terms of $|2, 0, 0\rangle / |1, 1, 0\rangle$ shown in the last two columns indicate changes in the intensity pattern brought about by the interaction of halide ions with CH₃ groups of MI. Since $|2, 0, 0\rangle A_1$ band is found to be overlapped by $|2, 0, 0\rangle E$ band in AN and other solvents, further studies on effect of interactions on the relative intensities were confined to $|2, 0, 0\rangle E / |1, 1, 0\rangle A_1$ bands only.

In table 2 are shown the results of the analysis of band fitting on C-H first overtone band profiles of various systems of electrolytes and organic solvents exhibiting X⁻...H₃C interactions. In figure 1 the band assignments have been shown for MI and AN. On comparison of band contours of four solvents it is assumed that the corresponding bands for $|2, 0, 0\rangle E$ and $|1, 1, 0\rangle A_1$ for NM and DMSO have frequencies 1702.0, 1651.3 nm and 1687.6, 1657.7 nm, respectively. On the basis of these assignments the relative intensities of $|2, 0, 0\rangle E$ and $|1, 1, 0\rangle A_1$ bands show similar trends for solutions of electrolytes in NM and DMSO as found for the solutions of the corresponding electrolytes in MI and AN. The two bands for $|2, 0, 0\rangle E$, $|1, 1, 0\rangle A_1$ in local mode description are correlated to $|1, 1\rangle E$ and $|0, 2\rangle A_1$ under normal mode description.

As reported earlier (Roche and Huong 1970), in complexes of AN with alkali metal

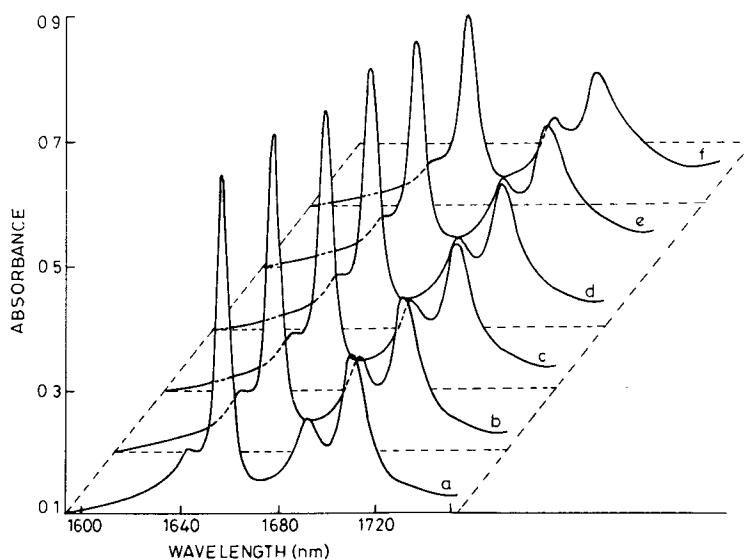


Figure 3. NIR spectra of solutions of THAB in MI in the first overtone region of CH_3 stretching mode. Concentration of THAB (a) pure, (b) 0.01 M, (c) 0.02 M, (d) 0.03 M, (e) 0.04 M, and (f) saturated.

Table 1. Spectral parameters for CH_3 stretching bands in first-overtone region for solutions of tetraalkyl ammonium salts in methyl iodide.

Electrolyte	Concentration of electrolyte (mol/l)	Frequency (nm)			$\frac{I_{ 200\rangle A_1}}{I_{ 110\rangle A_1}}$	$\frac{I_{ 200\rangle E}}{I_{ 110\rangle A_1}}$
		$ 200\rangle A_1$	$ 200\rangle E$	$ 110\rangle A_1$		
TBAB	0.22	1710.8	1693.8	1657.9	0.47	0.30
	0.43	1709.3	1692.3	1656.7	0.59	0.41
TBAI	0.09	1709.2	1694.2	1655.9	0.61	0.44
	0.33	1709.3	1694.7	1655.3	0.56	0.35
THAB	0.23	1710.0	1695.3	1656.1	0.60	0.38
	0.46	1713.1	1695.6	1660.4	0.55	0.35
		1711.2	1693.5	1658.3	0.64	0.41

THAB – tetrabutyl ammonium bromide; TBAI – tetrabutyl ammonium iodide; THAB – tetraheptyl ammonium bromide.

halides the relative intensity of the antisymmetric stretching fundamental to the symmetric stretching fundamental is less than unity whereas for pure AN the ratio is approximately unity. In the present studies, on formation of complexes between organic molecules and halide ions through interaction with CH_3 groups, the $|0, 2\rangle A_1$ band is found to decrease in intensity on increasing the concentration of salt with respect to the $|1, 1\rangle E$ band. Since no splitting of the original band is observed on dissolving halide ions in organic solvents, it can be surmised that CH_3 bands due to both the free as well as associated organic solvent molecules appear at similar positions in the NIR spectra. The change in the relative intensity therefore can be qualitatively

explained on the basis of change on complexation in the extinction coefficients of CH_3 -stretching NIR bands. A variation in the extent of change in the relative intensities of the two CH_3 bands for systems with similar compositions of salt solutions can be explained on the basis of the varying extinction coefficients of ion-molecular complexes with the varying nature of halide ions as well as solvent molecules. Alternatively, if one assumes the extinction coefficients of anion-solvent complexes to be similar, variation in the relative intensities can be employed to quantitatively predict the strength and extent of molecular interactions. Since we do not know the extinction coefficients of anion-molecular complexes, we have not made any attempt to derive quantitative trends regarding the strength of anion-molecular complexes

Table 2. Spectral parameters for CH_3 stretching bands in first overtone region for solutions of metal halides and tetraalkyl ammonium halides in AN, NM and DMSO.

Electrolyte	Concentration of electrolyte (mol/l)	Frequency (nm)		$\frac{I_{ 200\rangle E}}{I_{ 110\rangle A_1}}$
		$ 200\rangle E$	$ 110\rangle A_1$	
<i>Acetonitrile</i>		1714.1	1678.5	0.77
TBAB	0.49	1716.6	1680.2	1.12
	1.28	1713.8	1680.2	1.71
TBAI	0.27	1715.9	1678.6	1.08
	0.61	1715.1	1679.2	1.40
THAB	0.29	1715.8	1680.0	1.04
	0.63	1715.3	1679.6	1.27
KI	0.07	1713.3	1678.7	0.97
	0.13	1713.0	1677.6	1.03
LiBr	0.25	1713.7	1677.4	0.90
	1.04	1713.7	1677.0	1.00
LiI	0.52	1714.5	1677.2	1.01
	1.57	1715.9	1678.2	1.19
<i>Nitromethane</i>		1702.0	1651.3	0.65
TBAB	0.20	1700.7	1652.0	0.86
	0.99	1701.0	1653.4	1.81
TBAI	0.33	1703.3	1650.9	1.01
	0.87	1701.7	1651.4	1.59
<i>DMSO</i>		1687.6	1657.7	0.38
TBAB	0.11	1684.4	1655.8	0.42
	0.48	1683.7	1655.9	0.53
TBAI	0.33	1687.0	1657.6	0.43
	0.52	1687.9	1657.9	0.48
THAB	0.05	1687.7	1657.3	0.41
	0.24	1686.3	1656.2	0.48
TEAB	0.17	1687.1	1656.8	0.39
	0.27	1686.3	1656.4	0.40
LiBr	0.10	1690.2	1659.5	0.43
	0.43	1688.8	1658.4	0.45
KI	0.21	1688.9	1658.8	0.41
	1.08	1689.4	1659.3	0.46

*DMSO – dimethylsulphoxide; TBAB – tetramethyl ammonium bromide; TBAI – tetrabutyl ammonium iodide; THAB – tetraheptyl ammonium bromide; TEAB – tetraethyl ammonium bromide

using the present data, even though some familiar trends in this direction are quite evident from the values given in table 2.

Burberry and co-workers (Burberry and Albrecht 1979; Burberry *et al* 1979) have reported the intensities of CH-stretching overtone spectra in terms of the local modes for a variety of hydrocarbons. It was found that for a given overtone all CH local modes contribute equally to the intensity. These results provide compelling evidence for the validity of local mode descriptions of overtone spectra. In addition to the pure overtone transition, combination bands corresponding to one-photon cooperative excitation of two bond modes are also observed which provide experimental evidence for the breakdown of the additivity concept in the excitation of CH bonds. An understanding of the nature of the cooperative excitation gives interesting information regarding intramolecular coupling between bond modes. It is observed, in general, that the relative intensity of cooperative excitation with respect to pure overtone transition decreases considerably with an increase in the order of overtone excitation along with a decrease in energy separation between the two bands. For CH oscillators of dihalomethanes (Sage and Jortner 1981), the relative intensity of cooperative excitation with respect to the conventional one mode-overtone excitation is given by

$$r_{v_1 v_2} = I_{00 \rightarrow v_1 v_2} / I_{0 \rightarrow v} \cong (4 \langle W \rangle / \Delta E)^2$$

where $\langle W \rangle$ represents, (i) the perturbation-containing kinetic and potential energy terms which couples the bond modes, as well as, (ii) the kinetic and potential energy coupling for bond and skeletal modes. The term $\Delta E = 2V_1 V_2 x$, where x is the anharmonicity and V_1, V_2 are the vibrational quantum numbers for local bond modes. Thus the relative intensity of cooperative excitation with respect to pure local mode excitation is a measure of intermode coupling due to kinetic energy and anharmonicity effects and a decrease in the relative intensity with increasing order of overtone excitation indicates a decrease in intermode coupling. A similar reasoning may also hold good for the variation in the intensity of the cooperative excitation with respect to pure overtone excitation on increasing the concentration of electrolytes in the solutions. This is being looked into quantitatively by analysing the mathematical terms involved in the above expression and the results of such a study will be reported in due course.

4. Conclusions

The CH₃ first-overtone band contour is found to change on increase in concentration of halide ions for their solutions in all the four solvents considered. The effect is larger for solutions of tetraalkyl ammonium salts than for metal halides. The variation in relative intensity of the pure overtone excitation band with respect to the cooperative excitation band shows familiar trends representative of the nature of the halide ion, the tetraalkyl ammonium groups as well as the solvents used. However, quantitative conclusions cannot be drawn because of the lack of information on the extinction coefficients of the anion-molecular complexes. The local mode description for explaining the changes in the relative intensities of the two bands under consideration, in terms of intermode coupling due to kinetic energy and anharmonicity effects, needs further exploration for better understanding of the intermode coupling in electrolyte solution.

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