SOLVENT EFFECT ON RAMAN INTENSITY

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The observed Raman intensity in the liquid phase depends on several factors due to the arrangement of the apparatus as well as on the geometrical refractive index effect g, the internal field effect f, and the effect L due to the intermolecular field. The observed intensity I is related to the intensity in the gas phase I_0 (considering only these factors) as

$$I \propto \frac{1}{n} g f L I_0 \tag{1}$$

where $\frac{1}{n}$ is the correction applied by Polo and Wilson[1] which arises because the Poynting vector must remain invariant. Under ideal conditions of illumination[2,3]:

$$g = \frac{1}{n} \tag{2}$$

The effective field strength at a polarizable cavity of radius a depends on the refractive index of the medium n, so that[4]:

$$f = \left(\frac{3n^2}{2n^2 + 1}\right)^2 \left(\frac{1}{1 - \frac{2n^2 - 2}{2n^2 + 1} \times \frac{\alpha}{a^3}}\right)^4 \tag{3}$$

The intermolecular field acts essentially to change the values of the polarizability and anistropy derivatives α' and β' respectively, and we may denote L by:

$$L = \frac{45\alpha'^2 + 13\beta'^2}{45\alpha_0'^2 + 13\beta_0'^2} \tag{4}$$

where α_0' and β_0' are the values of these derivatives in the gas phase.

Experimentally, it is convenient to eliminate errors due to lack of rectilinearity in irradiation set-up by using illumination polarized in a direction perpendicular to the axis of the Raman tube. In this case we use $7\beta'^2$ and $7\beta_0'^2$ in equation (4) in place of $13\beta'^2$.

If one makes the reasonable assumption (for non-polar molecules) that the polarizability in the presence of an intermolecular field E is related to the gas value α_0 by:

$$\alpha = \alpha_0 + bE^2$$

it turns out that the factor L for a band of species A in solution with B molecules is given approximately by

$$L_{\mathrm{A}} = 1 + \frac{C_{\mathrm{A}}}{\sqrt{I_{\mathrm{A}}}} E_{\mathrm{A}}^2 \tag{5}$$

Here C_{A} is a constant dependent on the Raman band considered, and I_{A} is the intensity per molecule of this band.

The data of Pivovarov[4] and Rea[5] can be correlated very nicely by means of equation (5), so that it is possible to find the solvent effect by means of equation (5) on various Raman bands of the same molecule in solution.

In a solution of A and B molecules of volume fraction:

$$\varphi = \frac{V_{\mathrm{A}}}{V}, \left(\varphi_{\mathrm{B}} = 1 - \varphi = \frac{V_{\mathrm{B}}}{V}\right),$$

$$I_{\mathrm{A}}^{\varphi} \propto \varphi_{\mathrm{A}} \frac{g_{\mathrm{A}}^{\varphi}}{n_{\varphi}} f_{\mathrm{A}}^{\varphi} L_{\mathrm{A}}^{\varphi} I_{\mathrm{A}}^{0} \tag{6}$$

where V_{A} is the volume of A in the constant volume V and n_{φ} is the refractive index of the solution.

In practice:

$$n_{\varphi} = n_{\mathrm{B}} + (n_{\mathrm{A}} - n_{\mathrm{B}})\,\varphi \quad \text{with} \quad \frac{n_{\mathrm{A}} - n_{\mathrm{B}}}{n_{\mathrm{B}}} \ll 1$$

$\dfrac{g_{\mathrm{A}}^{\varphi}\, f_{\mathrm{A}}^{\varphi}}{n_{\mathrm{A}}^{\varphi}}$ is very nearly linear in φ. Also:

$$L_{\mathrm{A}}^{\varphi} \sim \varphi\, L_{\mathrm{A}}^{\mathrm{A}} + (1 - \varphi)\, L_{\mathrm{A}}^{\mathrm{B}}$$

where $L_{\mathrm{A}}^{\mathrm{A}}$ is the L value for an A line in liquid A, and $L_{\mathrm{A}}^{\mathrm{B}}$ is the L value for an A line at infinite dilution in B. Hence $\dfrac{I_{\mathrm{A}}^{\varphi}}{\varphi_{\mathrm{A}}}$ is expected to be very nearly a linear function of φ, as borne out by the data[4,5].

When the Raman intensity in solution is desired, one may refer all intensities of A to the liquid intensity, in which case one can form the ratio $r \sim$ given by:

$$r_{\mathrm{A}}^{\varphi} = \frac{I_{\mathrm{A}}^{\varphi}}{I_{\mathrm{A}}^{\mathrm{A}}} \times \frac{1}{\varphi} = \frac{g_{\mathrm{A}}^{\varphi} f_{\mathrm{A}}^{\varphi} L_{\mathrm{A}}^{\varphi}}{g_{\mathrm{A}}^{\mathrm{A}} f_{\mathrm{A}}^{\mathrm{A}} L_{\mathrm{A}}^{\mathrm{A}}} \times \frac{n_{\mathrm{A}}}{n_{\varphi}}$$

and correspondingly for a solvent line:

$$r_{\mathrm{B}}^{\varphi} = \frac{I_{\mathrm{B}}^{\varphi}}{I_{\mathrm{B}}^{\mathrm{B}}} \times \frac{1}{1 - \varphi} = \frac{g_{\mathrm{B}}^{\varphi} f_{\mathrm{B}}^{\varphi} L_{\mathrm{B}}^{\varphi}}{g_{\mathrm{B}}^{\mathrm{B}} f_{\mathrm{B}}^{\mathrm{B}} L_{\mathrm{B}}^{\mathrm{B}}} \times \frac{n_{\mathrm{B}}}{n_{\varphi}}$$

If there were no effects due to g, f, L, *etc.*, both r_{A}^{φ} and r_{B}^{φ} plotted against φ would be horizontal lines with the ordinate equal to one. In practice, these are very nearly linear with φ, and the value at infinite dilution gives:

$$r_{\mathrm{B}}^{0} = \frac{g_{\mathrm{A}}^{\mathrm{B}} f_{\mathrm{A}}^{\mathrm{B}} L_{\mathrm{A}}^{\mathrm{B}} n_{\mathrm{A}}}{g_{\mathrm{A}}^{\mathrm{A}} f_{\mathrm{A}}^{\mathrm{A}} L_{\mathrm{A}}^{\mathrm{A}} n_{\mathrm{B}}}$$

$$r_{\mathrm{B}}^{1} = \frac{g_{\mathrm{B}}^{\mathrm{A}} f_{\mathrm{B}}^{\mathrm{A}} L_{\mathrm{B}}^{\mathrm{A}} n_{\mathrm{B}}}{g_{\mathrm{B}}^{\mathrm{B}} f_{\mathrm{B}}^{\mathrm{B}} L_{\mathrm{B}}^{\mathrm{B}} n_{\mathrm{A}}}$$

If one measures the intensity of an A line relative to that of a B line, one can form the ratio R_{φ} given by:

$$R_{\varphi} = \frac{I_{\mathrm{A}}^{\varphi}}{I_{\mathrm{B}}^{\varphi}} \times \frac{1-\varphi}{\varphi} = \frac{f_{\mathrm{A}}{}^{\varphi} L_{\mathrm{A}}^{\varphi} I_{\mathrm{A}}^{0}}{f_{\mathrm{B}}{}^{\varphi} L_{\mathrm{B}}^{\varphi} I_{\mathrm{B}}^{0}}$$

Since $g_{\mathrm{A}}^{\varphi} = g_{\mathrm{B}}^{\varphi}$ for this internal intensity ratio.

Again, for no contributions from g, f, and L, a horizontal line is obtained for R_{φ} plotted against φ of ordinate $\frac{I_{\mathrm{A}}^{\varphi}}{I_{\mathrm{B}}^{0}}$ which equals the gas ratio, R_{gas}.

From equations (2) and (3), the value of $\frac{g_{\mathrm{A}}^{\varphi} f_{\mathrm{A}}^{\varphi}}{g_{\mathrm{B}}^{\varphi} f_{\mathrm{B}}^{\varphi}}$ can be shown to account for only a small per cent of the observed variation in R_{φ} with φ, and the conclusion is reached that most of the intensity enhancement due to solvent arises because of intermolecular interactions. If the experimental curve for R_{φ} *v.* φ is extrapolated to infinite dilution, the following two intercepts are obtained:

$$R_{0} = \frac{f_{\mathrm{A}}^{\mathrm{B}} L_{\mathrm{A}}^{\mathrm{B}}}{f_{\mathrm{B}}^{\mathrm{B}} L_{\mathrm{B}}^{\mathrm{B}}} R_{\mathrm{gas}}$$

$$R_{1} = \frac{f_{\mathrm{A}}^{\mathrm{A}} L_{\mathrm{A}}^{\mathrm{A}}}{f_{\mathrm{B}}^{\mathrm{A}} L_{\mathrm{B}}^{\mathrm{A}}} R_{\mathrm{gas}}$$

Values for r_{A}^{0}, r_{B}^{1}, R_{0}, and R_{1} as well as R_{gas} have been obtained experimentally for carbon tetrachloride in hexane, and carbon disulphide in benzene. The results and preliminary estimates of the L values are given in *Table 1.*

*Table 1**

A	B	R_{gas}	r_{A}^{0}	r_{B}^{1}	$\frac{R^{0}}{R_{\mathrm{gas}}}$	$\frac{R^{1}}{R_{\mathrm{gas}}}$	$\frac{L_{\mathrm{A}}^{\mathrm{A}}}{L_{\mathrm{B}}^{\mathrm{B}}}$	$\frac{L_{\mathrm{A}}^{\mathrm{B}}}{L_{\mathrm{B}}^{\mathrm{B}}}$	$\frac{L_{\mathrm{B}}^{\mathrm{A}}}{L_{\mathrm{B}}^{\mathrm{B}}}$
Carbon tetrachloride	Hexane	0·27	0·86	1·17	0·91	0·85	1·03	0·90	1·18
Carbon disulphide	Benzene	1·87	0·79	1·52	2·13	1·80	1·28	1·07	1·39

***In this table the value of R_{gas} is the observed value and has not been reduced to intensity per molecule.**

The magnitude of $L_{\mathrm{B}}^{\mathrm{B}}$ for the system carbon tetrachloride–hexane can be evaluated from a potential energy function using dispersion forces only. This agrees with the experimental values. For the system carbon disulphide–benzene, however, only a quarter to a third of the observed intensity enhancement can be accounted for by Van der Waals interaction. This suggests that unsaturated solutes and solvents experience changes in polarizability derivatives which are due to the π-electrons as well as conventional Van der Waals interaction. The detailed presentation of this work will be published elsewhere.

References

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