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THE RAMAN SCATTERING TENSOR COMPONENTS OF SOLUTIONS OF *D*-CHLOROFORM AND *D*-CHLOROFORM-DIMETHYLSULPHOXIDE COMPLEXES*

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The influence of dimethylsulphoxide (DMSO) on Raman scattering tensor components of four vibrations of *D*-chloroform $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_3(a_1)$ and $\nu_6(e)$ is studied. The measured intensities of the bands relative to the intensity of the 219 cm^{-1} band of CCl_4 (internal standard) and the ratios of depolarization ϱ enabled the calculation of their scattering activities and the components of the Raman scattering tensors. It is shown that the anisotropy and not the trace is varied when hydrogen bond is formed. The dependence of the depolarization ratio ϱ on the ratio x of the tensor components is divided into three parts. It is shown that one of them accounts for the totally symmetric vibrations only, the other to the totally symmetric deformation vibrations as well, the third part has no physical meaning.

1. Introduction

The variation of the depolarization ratio ϱ of Raman bands provoked by hydrogen bonding was recently observed in several cases [1–3]. On this basis conclusions were drawn concerning the changes of the ratio x of the values of principal axes of derived polarizability ellipsoids for symmetric top molecules. To calculate the Raman scattering tensor invariants: the trace b_i' and the anisotropy γ_i' of this tensor and the scattering activity SA_i of the i-th band besides its depolarization ratio ϱ_i should be known. The SA_i and ϱ_i values are related to the $\bar{\alpha}_i'$ and γ_i' values by relations

$$\mathrm{SA}_i = g_i(45\bar{\alpha}_i'^2+7\gamma_i'^2), \tag{1}$$

$$\varrho_i = \frac{3\gamma_i'^2}{45\bar{\alpha}_i'^2+4\gamma_i'^2}, \tag{2}$$

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where g_i is the vibrational degeneracy and $\bar{\alpha}_i' = \frac{1}{3}b_i'$ is the averaged value of the diagonal components of the Raman scattering tensor.

The scattering activity SA_i can be calculated from the scattering cross sections for gases $\left(\frac{d\sigma_i}{d\Omega}\right)_{\mathrm{gas}}$ [4]

$$\mathrm{SA}_i = \left(\frac{d\sigma_i}{d\Omega}\right)_{\mathrm{gas}} \frac{45cv_i}{2\pi^2 h} \frac{1-\exp(-hcv_i/kT)}{(v_0-v_i)^4}, \tag{3}$$

where v_0 and v_i are the exciting and vibrational frequencies respectively, c is speed of light and h — the Planck constant. The values for scattering cross sections for liquids are obviously more elevated than those for gases. Several correction functions were proposed to calculate the ratio of these cross sections. The values nearest the experimental values give the expression derived by Eckhardt and Wagner [5]. However, as it was shown by Schrötter and Klöckner [6], for some Raman bands of halomethanes the experimental values Λ,

$$\Lambda = \frac{(d\sigma/d\Omega)_{\mathrm{liquid}}}{(d\sigma/d\Omega)_{\mathrm{gas}}}, \tag{4}$$

differ from the Eckhardt–Wagner values by a factor of 0.88 to 1.48.

The scattering cross section for the liquid can be calculated from the measured integrated intensity I by the equation [7]

$$(d\sigma/d\Omega)_{\mathrm{liquid}} = In^2F/N, \tag{5}$$

where n is the refractive index of the liquid (the geometrical correction factor), F is the empirical instrument response factor and N is the number of molecules in a unit volume of the liquid.

The scattering activities and scattering cross sections are often measured in ratio to some standard Raman band (noticed by the subscript s) of a standard substance. This standard substance can be used as an internal or an external standard. In the former case the geometrical correction factors are of the same value for both the studied and the standard bands. Assuming that the factor F is independent of the wave length in the studied spectral range, one receives from equations (3), (4) and (5) an expression for the relative scattering activity of the i-th band

$$(\mathrm{SA}_i)_{\mathrm{rel}} = \frac{\mathrm{SA}_i}{\mathrm{SA}_s} = \frac{I_i}{I_s} \frac{N_s}{N_i} \frac{v_i}{v_s} \frac{(v_0-v_s)^4}{(v_0-v_i)^4} \frac{1-\exp(-hcv_i/kT)}{1-\exp(-hcv_s/kT)} \frac{\Lambda_s}{\Lambda_i}. \tag{6}$$

If the standard values are known, one can calculate

$$S = \mathrm{SA}_s \frac{(v_0-v_s)^4}{v_s} \frac{\Lambda_s}{1-\exp(-hcv_s/kT)}, \tag{7}$$

and for the absolute value of the scattering activity SA_i of the i-th band one receives the expression

$$SA_i = S \frac{I_i}{I_s} \frac{N_s}{N_i} \frac{\nu_i}{(\nu_0-\nu_i)^4} \frac{1-\exp(-hc\nu_i/kT)}{\Lambda_i}. \tag{8}$$

The depolarization ratio ϱ_i is measured as the ratio of the two perpendicular components of the scattered light

$$\varrho_i = \frac{I_i[X(Y, X)Z]}{I_i[X(Y, Y)Z]}. \tag{9}$$

$\bar{\alpha}'_{i2}$ and $\gamma_i'^2$ can thus be calculated from equations (1) and (2)

$$\bar{\alpha}_i'^2 = \frac{SA_i(3-4\varrho_i)}{g_i 135(1+\varrho_i)}, \quad \gamma_i'^2 = \frac{SA_i}{g_i} \frac{\varrho_i}{3(1+\varrho_i)}. \tag{10}$$

For a symmetric top molecule the scattering tensor can be represented as a diagonal tensor with the components $\alpha'_{xx} = \alpha'_{yy} = \alpha'_{\perp}$ and $\alpha'_{zz} = \alpha'_{\parallel}$. Thus the trace b'_i and the anisotropy γ'_i can be expressed as

$$b'_i = 3\bar{\alpha}'_i = \pm(\alpha'_{\parallel}+2\alpha'_{\perp})_i, \quad \gamma'_i = \pm(\alpha'_{\parallel}-\alpha'_{\perp})_i. \tag{11}$$

(Equation (10) allows one to calculate the squares of $\bar{\alpha}'$ and γ' only, but the sign of these values cannot be determined by the experiment.)

Assuming that $\bar{\alpha}'$ is always positive one receives two sets of equations by transformation of equation (11) for positive and negative γ'_i (equations a or b):

$$(\alpha'_{\parallel})_a = \bar{\alpha}'+\tfrac{2}{3}\gamma', \quad (\alpha'_{\perp})_a = \bar{\alpha}'-\tfrac{1}{3}\gamma', \tag{12a}$$

$$(\alpha'_{\parallel})_b = \bar{\alpha}'-\tfrac{2}{3}\gamma', \quad (\alpha'_{\perp})_b = \bar{\alpha}'+\tfrac{1}{3}\gamma'. \tag{12b}$$

The Raman scattering tensors of the derived polarizabilities α can be represented by the ellipsoids or hyperboloids [8], the principal axes of which are the functions of the components of the diagonal tensor. The ratio $x = \alpha'_{\parallel}/\alpha'_{\perp}$ can be calculated from the values obtained by means of the equations (12a and b) or immediately from the values of $\bar{\alpha}'$ and γ'

$$x_a = \frac{\dfrac{\bar{\alpha}'}{\gamma'}+\tfrac{2}{3}}{\dfrac{\bar{\alpha}'}{\gamma'}-\tfrac{1}{3}}, \quad x_b = \frac{\dfrac{\bar{\alpha}'}{\gamma'}-\tfrac{2}{3}}{\dfrac{\bar{\alpha}'}{\gamma'}+\tfrac{1}{3}}. \tag{13a, b}$$

The x values form a measure of the elongation of the figures representing the tensors.

In the present study the depolarization ratio and the integrated intensities of four bands of d-chloroform: $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_3(a_1)$ and $\nu_6(e)$ were measured in two solutions in carbon tetrachloride; one of them also contained dimethylsulphoxide (DMSO). (The molar ratio DMSO:$CDCl_3$ was 1.83. The $\nu_2(e)$ band of CCl_4 ($\nu = 219\ cm^{-1}$) was used as the internal standard for intensity measurements. It is known that the intensity of this band does not change its value in the presence of electron donor reagents [9]. For this band, the S value was accepted as the average of two values calculated from data given in Ref. [4] $S = 1.01 \cdot 10^8$ cm g^{-1} mole^{-1}. The A values for the studied bands were taken from Ref. [6].

2. *Experimental part*

The spectra were recorded by means of a Cary 82 Raman laser spectrometer with the 514.5 μm argon ion laser line as the exciting line.

Commercially pure *D*-chloroform produced by Chemipan, Warszawa was used. Carbon tetrachloride produced by POCh, Gliwice was dehydrated by shaking with ethanol and dried over P_2O_5. DMSO of analytical purity was dried over MgO and CaO.

3. *Results and discussion*

The results of measurements and calculations are gathered in Tables I and II. The standard deviations for the measurements of the relative intensities I_i/I_s and of the depolarization ratios based on five measurements are given in per cent.

The values of parallel and perpendicular tensor components $\alpha'_{||}$ and $\alpha'_{\perp}$ were calculated by means of equations (12a) and (12b). Only positive square roots of $\bar{\alpha}'^2$ were considered, whereas both the positive and negative values of γ' were taken into account. It was shown in [8] that when one of the Raman tensor components is negative, all components must change their signs simultaneously. Thus there is no need to consider the cases with negative $\bar{\alpha}'$ separately. The cases (a) and (b) give different values for the ratio x of the two tensor components. The x and ϱ values are interdependent [1] and Desbat and Huong have given explicit expression for the relation $\varrho = f(x)$ and its diagram as well [2]. On this diagram three sections a, b, and c can be distinguished (Fig. 1). According to considerations of Volkenshtein, Elyashevich and Stepanov [10] the range of the ϱ values of the bands of totally symmetric valence vibrations is between 0 and 1/3. This corresponds to section a and partly b of the diagram. For totally symmetric deformation vibrations the range ϱ of values between 0 and 3/4 is allowed. It corresponds to section b. Section c has no physical meaning. The comparison of the values $\alpha'_{||}$, $\alpha'_{\perp}$ and x calculated by means of equations (12) and (13) for the four studied bands (Table II) shows that the $\nu_1(a_1)$ and $\nu_2(a_1)$ valence vibration bands correspond to section a, and $\nu_3(a_1)$ deformation band and $\nu_6(e)$ degenerate vibration band correspond to section b. The negative α' value means that the polarizability diminishes when the value of the normal coordinate increases. In such a case the Raman scattering tensor should be illustrated by a hyperboloid [8]. As is seen from Table II this concerns the ν_6 vibration of chloroform.

The influence of the addition of DMSO to the solution of *D*-chloroform in carbon tetrachloride is analysed in Table III. For ν_6 vibration the values of α' and x are negative and an increase of their moduli is observed. It is seen from Table III that the changes for

TABLE I

The calculation of the Raman tensor invariants for $CDCl_3$ and $CDCl_3$-DMSO complexes in carbon tetrachloride solution

Solution	Quantity	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_6(e)$
$CDCl_3$	ν/cm^{-1}	2254	652	362	260
	I/I_s	0.264 ±1.5%	0.345 ±2.3%	0.244 ±2.1%	0.235 ±3.4%
	A[a]	5.1	3.3	3.26	3.58
	SA · 10^8/cm^4 g^{-1} mole^{-1}	60.26 ±3%	21.07 ±4%	6.81 ±7%	3.64 ±5%
	ϱ	0.180 ±2.8%	0.015 ±4.0%	0.089 ±5.6%	0.685 ±2.8%
	$\bar{\alpha}' \cdot 10^5$/cm^2	9.29	6.72	3.5	0.45
	$\gamma' \cdot 10^5$/cm^2	17.50	3.29	4.31	4.97
$CDCl_3$-DMSO complex	ν/cm^{-1}	2229	645	365	260
	I/I_s	0.298 ±1.7%	0.329 ±3.5	0.296 ±2.0%	0.240 ±5.0%
	A[a]	5.1	3.3	3.26	3.58
	SA · 10^8/cm^4 g^{-1} mole^{-1}	62.67 ±3%	20.82 ±5%	8.79 ±4%	3.91 ±3%
	ϱ	0.230 ±1.8%	0.026 ±3.5%	0.125 ±7.2%	0.739 ±2.8
	$\bar{\alpha}' \cdot 10^5$/cm^2	8.86	6.59	3.80	0.19
	$\gamma' \cdot 10^5$/cm^2	19.97	4.23	5.71	5.26

For $CDCl_3$ solution $N_s/N = 3.9678$; for $CDCl_3$-DMSO solution $N_s/N = 4.1702$.

[a] According to H. W. Schrötter and H. W. Klöckner [6].

TABLE II

The components of the Raman scattering tensor for $CDCl_3$ and $CDCl_3$-DMSO complexes in carbon tetrachloride solution

Solution	Quantity	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_6(e)$
$CDCl_3$	$(\alpha'_{\parallel})_a \cdot 10^5/cm^2$	$\underline{20.96}$	$\underline{8.92}$	6.37	3.77
	$(\alpha'_{\parallel})_b \cdot 10^5/cm^2$	−2.38	4.53	$\underline{0.63}$	$\underline{-2.86}$
	$(\alpha'_{\perp})_a \cdot 10^5/cm^2$	$\underline{3.45}$	$\underline{5.62}$	2.06	−1.20
	$(\alpha'_{\perp})_b \cdot 10^5/cm^2$	15.12	7.82	$\underline{4.94}$	$\underline{2.12}$
	$\left(\frac{\alpha'_{\parallel}}{\alpha'_{\perp}}\right)_a$	$\underline{6.07}$	$\underline{1.59}$	3.09	−3.14
	$\left(\frac{\alpha'_{\parallel}}{\alpha'_{\perp}}\right)_b$	−0.16	0.58	$\underline{0.13}$	$\underline{-1.35}$
$CDCl_3$ -DMSO complex	$(\alpha'_{\parallel})_a \cdot 10^5/cm^2$	$\underline{22.04}$	$\underline{9.41}$	7.61	3.67
	$(\alpha'_{\parallel})_b \cdot 10^5/cm^2$	−4.32	3.78	$\underline{0.00}$	$\underline{-3.32}$
	$(\alpha'_{\perp})_a \cdot 10^5/cm^2$	$\underline{2.27}$	$\underline{5.19}$	1.90	−1.56
	$(\alpha'_{\perp})_b \cdot 10^5/cm^2$	15.49	8.00	$\underline{5.71}$	$\underline{1.95}$
	$\left(\frac{\alpha'_{\parallel}}{\alpha'_{\perp}}\right)_a$	$\underline{9.70}$	$\underline{1.82}$	4.00	−2.37
	$\left(\frac{\alpha'_{\parallel}}{\alpha'_{\perp}}\right)_b$	−0.28	0.47	$\underline{0.00}$	$\underline{-1.71}$

The quantities with subscripts a nad b are calculated by means of equations (12a) or (12b) and (13a) or (13b) respectively. The underlined values should be considered as correct.

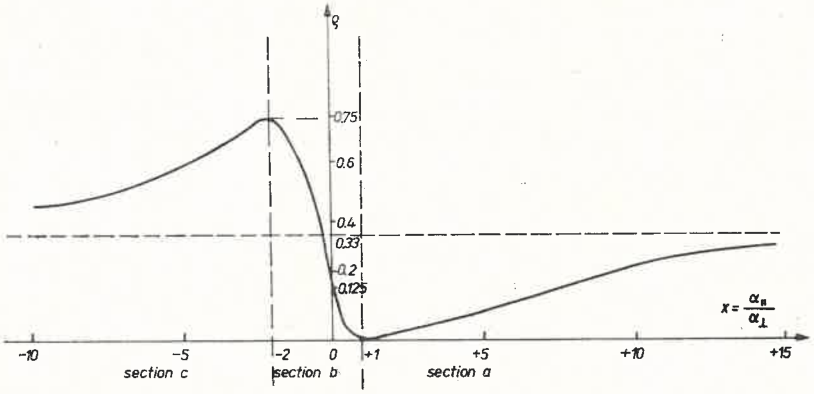

Fig. 1. The depolarization ratio ϱ as a function of the ratio x of the Raman tensor components $\alpha'_{\parallel}/\alpha'_{\perp}$ for symmetric top molecules. The meaning of sections a, b, and c are explained in the text

the valence vibrations ν_1 and ν_2 are similar. The frequency shift, SA, $\alpha'_{\parallel}$ and $\alpha'_{\perp}$ are different for ν_3 deformation vibration than for valence vibrations. The degenerate ν_6 vibration is, of course, influenced in a peculiar way.

TABLE III

The variations of the Raman band of the Raman scattering tensor parameters of *D* chloroform after the addition of DMSO

	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_6(e)$
ν	decr	decr	incr	unch
SA	unch	unch	incr	incr
ϱ	incr	incr	incr	incr
$\bar{\alpha}'$	unch	unch	unch	decr
γ'	incr	incr	incr	incr
$\alpha'_{\parallel}$	unch	unch	decr	incr mod
$\alpha'_{\perp}$	decr	decr	incr	unch
$x = \frac{\alpha'_{\parallel}}{\alpha'_{\perp}}$	incr	incr	unch	incr mod

incr — increase, decr — decrease, unch — unchanged within error limits, incr mod — increase of the modulus of negative value.

The increase of the depolarization ratio of the complex with respect to the free chloroform molecule is observed for all studied bands. The trace of the Raman scattering tensor is not influenced for a_1 vibrations and is diminished for the e vibration. The increase in the value of x means the elongation of the figures that are the loci of the induced dipole moment vectors at constant energy or at constant electric field [8]. The discussed variations should be considered as the result of the increase of the anisotropy of the scattering tensors. Thus, the increase of the anisotropy of the scattering tensors, observed for all four studied bands of chloroform, is the most general influence of dimethylsulphoxide on chloroform in carbon tetrachloride solution.

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