

## OPTICAL DISPERSION AND MOLAR REFRACTIVITIES OF ALKALI HALIDE CRYSTALS AND AQUEOUS SOLUTIONS

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The dispersion of refractive indices and molar refractivities of crystals and aqueous solutions of LiCl, CsCl, KF, and KI is determined with a single-oscillator dispersion formula. The dependence of the phase-matching angle of a four-wave mixing process on optical dispersion is applied in the calculations. The refractivities are decomposed into intrinsic and interaction parts. Their dependence on the structure of the ionic solutions is discussed.

### 1. Introduction

Dispersion data of refractive indices  $n$  and molar refractivities  $R$  of aqueous electrolytes are scarce. The optical refraction measurements were mostly limited to the wavelength of the sodium D line ( $\lambda_D = 589.3$  nm) [1]. Dispersion data are necessary for optical studies at different frequencies. In non-linear optical four-wave mixing experiments [2] (for a recent review, see ref. [3]) the refractive indices at the involved frequencies are needed for the calculation of the phase-matching angle. The molar refractivities contain information on the structure of the substances. A comparison of the refractivities of aqueous electrolyte solutions with solid- and gas-state data allows to interpret the interaction of electrolytes with water [1].

In this letter the phase-matching angles  $\varphi$  of the four-wave mixing process  $\omega_p + \omega_p - \omega_L \rightarrow \omega_S$  are measured and the dispersion of the molar refractivities is calculated over a wide frequency range. Literature values of molar refractivities  $R_D$  together with the phase-matching angles  $\varphi$  are used in the calculations. A single-oscillator dispersion formula is applied. The four-photon interaction process generates a new picosecond pulse at frequency  $\omega_S$  by mixing of two input picosecond laser pulses at frequencies  $\omega_p$  and  $\omega_L$  ( $\tilde{\nu}_p = \omega_p/2\pi c = 18957$  cm<sup>-1</sup>,  $\tilde{\nu}_L = 9479$  cm<sup>-1</sup>). Crystals and aqueous solutions of LiCl, CsCl, KF, and KI

are investigated. The electrolyte concentration is varied between 0.5 mol/l and saturation. The measurements are carried out at  $T = 25^\circ\text{C}$ . The results on the non-linear susceptibilities  $\chi^{(3)}(-\omega_S; \omega_p, \omega_p, -\omega_L)$  responsible for the four-photon frequency mixing are given elsewhere [2].

A measurement of the refractive indices  $n_L$ ,  $n_p$  and  $n_S$  at the frequencies  $\omega_L$ ,  $\omega_p$  and  $\omega_S$  by conventional techniques [4] (e.g. hollow prism spectrometer with spectral lamps) would be difficult since  $\omega_L$  is in the near infrared and  $\omega_S$  in the near ultraviolet spectral region. The technique used here measures the phase-matching angles needed for efficient non-collinear four-photon frequency mixing and the refractive indices are calculated from these values.

### 2. Method

The relation between refractive index  $n$  and molar refractivity  $R$  is given by the Clausius–Mosotti formula (Lorenz–Lorentz relation)

$$(n^2 - 1)/(n^2 + 2) = \beta R = \beta N_A \alpha / 3\epsilon_0. \quad (1)$$

$\beta = \rho/M = c/1000$  represents the molar density in mol/cm<sup>3</sup>.  $\rho$  is the density (g/cm<sup>3</sup>),  $M$  the molar mass (g/mol) and  $c$  the molarity (mol/l).  $N_A = 6.022045 \times 10^{23}$  mol<sup>-1</sup> is Avogadro's number and  $\alpha$  the molecular polarizability. Eq. (1) is valid for gases, liquids, amorphous and cubic solids.

For solutions the relation between refractive index  $n$  and molar refractivities  $R_1$  (solvent, index 1) and  $R_2$  (solute, index 2) reads

$$(n^2 - 1)/(n^2 + 2) = \beta_1 R_1 + \beta_2 R_2. \quad (2)$$

The molar density of the solvent may be expressed as  $\beta_1 = (\rho - \beta_2 M_2)/M_1$ , where  $\rho$  is the density of the solution.

$R_1$  and  $R_2$  depend on the solute concentration since the polarizability is influenced by the solvent-solvent, solute-solute, and solvent-solute interactions (see later). In the experiments only  $n$  is determined and no separate values of  $R_1$  and  $R_2$  are obtained. For this reason it is customary to set  $R_1$  equal to the molar refractivity of the neat solvent  $R_0$  ( $R_0 = (M_0/\rho_0)(n_0^2 - 1)/(n_0^2 + 2)$ ). Deviation of  $R_1$  from  $R_0$  is included in the apparent molar refractivity  $R'_2$  of the solute. Eq. (2) transforms to

$$(n^2 - 1)/(n^2 + 2) = [(\rho - \beta_2 M_2)/\rho_0](n_0^2 - 1)/(n_0^2 + 2) + \beta_2 R'_2. \quad (3)$$

The data of neat water at  $T = 25^\circ\text{C}$  are taken from the literature ( $\rho_0 = 0.997047 \text{ g/cm}^3$  [5],  $n_{0D} = 1.33252$ ,  $n_{0L} = 1.3247$ ,  $n_{0P} = 1.33468$ ,  $n_{0S} = 1.34815$  [6]).

The dependence of  $R'_2$  on wavenumber  $\tilde{\nu}$  is approximated by a single-oscillator model

$$R'_2(\beta_2, \tilde{\nu}) = C(\beta_2)/[\tilde{\nu}_0^2(\beta_2) - \tilde{\nu}^2]. \quad (4)$$

This model assumes that the refraction is caused by a single transition from the ground state to an excited state with transition frequency  $\nu_0$  and transition strength  $C$ . It is applicable to the dispersion of alkali halides in the visible and near infrared region, since they are transparent from the middle infrared to the vacuum ultraviolet.

The two unknown parameters  $C(\beta_2)$  and  $\tilde{\nu}_0(\beta_2)$  are determined by (i) the apparent molar refraction  $R'_2(\beta_2, \tilde{\nu}_D)$  at the frequency of the sodium D line ( $\lambda_D = 589.3 \text{ nm}$ ) and (ii) the non-collinear phase-matching angle  $\varphi$  of the four-photon mixing process  $\omega_P + \omega_P - \omega_L \rightarrow \omega_S$ .

A more accurate dispersion model of strong electrolyte solutions should use separate oscillators for the cations and the anions since they are separated in solution. Such a model has four unknown parameters which cannot be determined by the described technique.

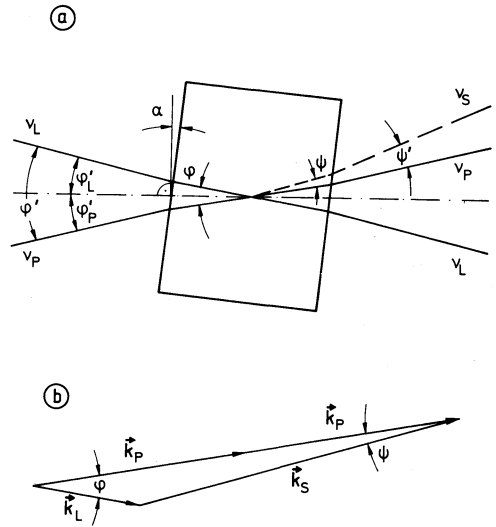


Fig. 1. (a) Geometry of interacting light pulses in sample; (b) phase-matching triangle of wave vectors.

Fig. 1a shows the geometrical arrangement of the interacting light beams in the four-photon mixing experiment [2, 7] and fig. 1b depicts the corresponding phase-matching triangle. Applying the cosine law one finds

$$\cos \varphi = [(2k_P)^2 + k_L^2 - k_S^2]/4k_P k_L, \quad (5)$$

where  $k_i = n_i \omega_i/c = 2\pi\nu_i n_i/c = 2\pi\tilde{\nu}_i n_i$  ( $i = P, L, S$ ).

In the experiments the external angles  $\varphi'_L$ ,  $\varphi'_P$  and  $\alpha$  are measured and the internal phase-matching angle  $\varphi = \varphi_L + \varphi_P$  is given by

$$\varphi = \arcsin[(n_L^A/n_L) \sin(\varphi'_L - \alpha)] + \arcsin[(n_P^A/n_P) \sin(\varphi'_P + \alpha)]. \quad (6)$$

$n_L^A = 1.0003155$  and  $n_P^A = 1.0003204$  are the refractive indices of air at frequencies  $\nu_L$  and  $\nu_P$ , respectively [5].

The dispersion of the refractive indices of the alkali halide crystals is determined in the same manner [ $R = C/(\tilde{\nu}_0 - \tilde{\nu}^2)$  in eq. (1)].

### 3. Experimental

The non-collinear phase-matched four-photon frequency mixing experiments are described elsewhere [2, 7]. The pump pulses are generated by a mode-locked

Nd-glass laser (fundamental frequency  $\tilde{\nu}_L = 9479 \text{ cm}^{-1}$  and second harmonic  $\tilde{\nu}_P = 18957 \text{ cm}^{-1}$ ).

The angles  $\phi'_L$  and  $\phi'_P$  between the pump pulses and the tilting angle  $\alpha$  are varied and the generated signal light at frequency  $\nu_S$  is detected (fig. 1). At the phase-matching angle  $\varphi$  the energy conversion of laser light at frequency  $\nu_L$  to the signal at frequency  $\nu_S$  is maximal. The angles  $\phi'_L$ ,  $\phi'_P$  and  $\alpha$  are determined by measuring lengths of triangles. Angle  $\alpha$  is measured by observing the reflected alignment laser beams (He-Ne laser) from the entrance window of the sample. Variation of angle  $\alpha$  allows a fine tuning of the angle  $\varphi$ . The angles  $\phi'_L$  and  $\phi'_P$  are determined by removing the sample and the optical components behind the sample position. Only the wedge of the entrance window of the sample cell enters the relation between internal phase-matching angle  $\varphi$  and external angle  $\varphi' = \varphi'_P + \varphi'_L$ . In eq. (6) the entrance window was assumed to be plane-parallel ( $\gamma = 0$ ). A wedge  $\gamma$  would change the calculated angle  $\varphi$  ( $\gamma = 0$ ) to  $\varphi(\gamma) \approx \varphi(\gamma = 0) \pm \gamma(n_P^G/n_P - n_L^G/n_L)$ , where  $n_P^G$  and  $n_L^G$  are the refractive indices of the glass window at  $\nu_P$  and  $\nu_L$ , respectively. In the experiments plane windows with  $\gamma < 0.01^\circ$  were used ( $|\varphi(\gamma) - \varphi(\gamma = 0)| \lesssim 10^{-4}$ ). Their influence on the refractive index measurement is diminishing ( $|\Delta n| \lesssim 5 \times 10^{-7}$ ).

The angles  $\phi'_L$  and  $\phi'_P$  are measured to an accuracy of  $\pm 0.01^\circ$ . The corresponding error of the refractive indices is  $\Delta n \approx \pm 5 \times 10^{-5}$ . The effect of the non-linear refractive index  $n_2$  on the accuracy of the refractive index  $n$  is negligible. For typical experimental intensities of  $I \approx 2 \times 10^9 \text{ W/cm}^2$  and a non-linear refractive index of  $n_2 \approx 10^{-13} \text{ esu}$  one finds  $n(I) = n + \gamma I = n + n_2 \langle E^2 \rangle \approx n + 6 \times 10^{-7}$  ( $\gamma [\text{cm}^2/\text{W}] = n_2 [\text{SI}]/nc\epsilon_0 = n_2 [\text{esu}] 4\pi 10^7/nc$ ) [8].

#### 4. Results

Table 1 summarizes data on the investigated substances. The density values  $\rho$  and the optical refraction data  $R_D$  and  $n_D$  are taken from the literature. The angles  $\phi'_L$ ,  $\phi'_P$  and  $\alpha$  are measured and the constants  $\tilde{\nu}_0$  and  $C$  of the dispersion formula are calculated.

The dependence of the transition frequencies  $\tilde{\nu}_0$  and the transition strengths  $C$  on concentration is depicted in figs. 2 and 3, respectively. In case of KI,

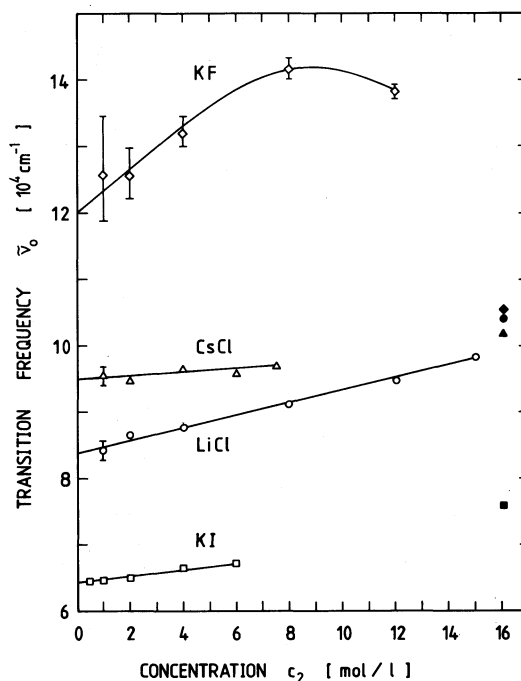


Fig. 2. Transition frequency  $\tilde{\nu}_0$  of single-oscillator dispersion formula versus concentration (0 mol/l-saturation). Temperature  $T = 25^\circ\text{C}$ . The crystal values are included at the right (full symbols).

CsCl and LiCl,  $\tilde{\nu}_0$  is smaller for the solution than for the neat solid, while for KF  $\tilde{\nu}_0$  is larger for the solution than for the crystal. The transition frequencies  $\tilde{\nu}_0$  of KI and CsCl only slightly depend on concentration. LiCl shows an increase of  $\tilde{\nu}_0$  with concentration. In KF solutions  $\tilde{\nu}_0$  rises to a maximum at  $\approx 8 \text{ mol/l}$  and then slightly decreases. The transition strengths  $C$  of the aqueous solutions show the same concentration dependence as the transition frequencies  $\tilde{\nu}_0$ .

The calculated apparent molar refractivities  $R'_S$ ,  $R'_P$ , and  $R'_L$  are plotted in fig. 4. For LiCl, CsCl and KI the refractivities (polarizabilities) decrease with concentration towards the crystal values (LiCl:  $R_S = 7.97$ ,  $R_P = 7.64$ ,  $R_L = 7.45$ ; CsCl:  $R_S = 16.03$ ,  $R_P = 15.31$ ,  $R_L = 14.91$ ; KI:  $R_S = 21.99$ ,  $R_P = 20.10$ ,  $R_L = 19.11 \text{ cm}^3/\text{mol}$ ). For KF the refractivities increase with concentration towards the crystal values ( $R_S = 5.32$ ,  $R_P = 5.19$ ,  $R_L = 5.11 \text{ cm}^3/\text{mol}$ ).

The accuracy of the single-oscillator model in the spectral range between 350 nm and 1050 nm was

Table 1  
Data for the calculation of the dispersion of refractivities ( $T = 25^\circ\text{C}$ )

	$c_2$ (mol/l)	$\rho$ (g/cm <sup>3</sup> )	$R'_{2,D}$ (cm <sup>3</sup> /mol)	$n_D$	$\varphi'_L$ (deg)	$\varphi'_P$ (deg)	$\alpha$ (deg)	$\tilde{\nu}_0$ (10 <sup>4</sup> cm <sup>-1</sup> )	$C$ (10 <sup>10</sup> cm/mol)
<b>LiCl</b>									
$M = 42.392$ g/mol	1	1.021 a)	8.75 a)	1.3414	7.25	7.61	5.6	8.43	5.97
	2	1.043 a)	8.73 a)	1.3495	7.50	7.86	5.2	8.66	6.30
	4	1.086 a)	8.685 a)	1.3652	8.00	8.36	6.6	8.76	6.41
	8	1.170 a)	8.595 a)	1.3954	8.75	9.11	1.2	9.13	6.91
	12	1.256 b)	8.505 a)	1.4256	9.40	9.76	9.9	9.50	7.43
	15	1.320 b)	8.44 a)	1.4477	9.70	10.06	4.7	9.85	7.94
	solid	2.068 b)	7.586	1.662 b)	13.87	14.26	9.9	10.48	8.12
<b>CsCl</b>									
$M = 168.358$ g/mol	1	1.125 b)	15.611 b)	1.3458	7.30	7.66	4.7	9.56	13.82
	2	1.248 b)	15.606 b)	1.3572	7.65	8.01	6.1	9.48	13.59
	4	1.494 b)	15.595 b)	1.3803	8.28	8.63	4.2	9.65	13.81
	5.5	1.677 b)	15.588 b)	1.3969	8.73	9.08	2.8	9.59	13.90
	7.5	1.925 b)	15.575 b)	1.4200	9.30	9.66	3.0	9.70	14.20
	solid	3.988 b)	15.203	1.63966 b)	13.87	14.26	3.8	10.19	15.28
<b>KF</b>									
$M = 58.1004$ g/mol	1	1.044 b)	4.871 b)	1.3371	7.00	7.36	5.2	12.58	7.57
	2	1.092 b)	4.887 b)	1.3416	7.09	7.44	10.3	12.57	7.59
	4	1.177 b)	4.915 b)	1.3480	7.13	7.48	9.9	13.22	8.45
	8	1.335 b)	4.975 b)	1.3567	7.09	7.44	5.6	14.19	9.86
	12	1.480 b)	5.005 b)	1.3618	7.09	7.44	9.4	13.85	9.46
	solid	2.50 b)	5.169	1.3629 b)	6.38	6.74	5.4	10.54	9.32
<b>KI d)</b>									
$M = 166.0064$ g/mol	0.5	1.056 b)	21.445 b)	1.3425	7.65	8.01	2.8	6.47	8.36
	1	1.117 b)	21.41 b)	1.3529	8.36	8.72	9.4	6.48	8.38
	2	1.234 b)	21.338 b)	1.3745	9.60	9.96	9.6	6.51	8.42
	4	1.467 b)	21.18 b)	1.4145	11.62	11.97	3.8	6.65	8.75
	6	1.700 b)	21.023 b)	1.4535	13.59	13.89	7.0	6.70	8.83
	solid	3.113 c)	19.834	1.6663 c)	21.447	21.497	4.6	7.46	10.47

a) Ref. [10]. b) Ref. [9]. c) Ref. [5]. d)  $n$  and  $R$  data at  $\lambda = 587.6$  nm.

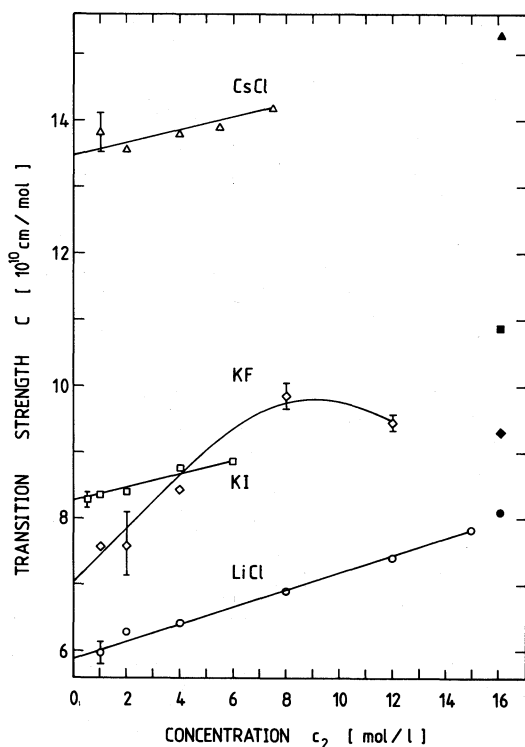


Fig. 3. Transition strength  $C$  of single-oscillator dispersion formula versus concentration (0 mol/l-saturation)  $T = 25^\circ\text{C}$ . Crystal values at the right (full symbols).

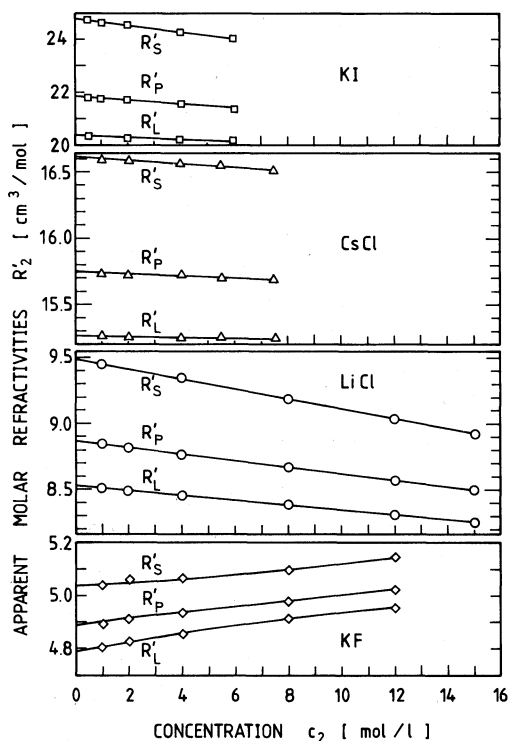


Fig. 4. Apparent molar refractivities  $R'_S$  ( $\tilde{\nu}_S = 28436\text{ cm}^{-1}$ ),  $R'_P$  ( $\tilde{\nu}_P = 18957\text{ cm}^{-1}$ ) and  $R'_L$  ( $\tilde{\nu}_L = 9479\text{ cm}^{-1}$ ) versus concentration.  $T = 25^\circ\text{C}$ .

tested by comparing calculated refractive indices with literature values. The refractive indices of CsCl crystals [9] agree within  $\Delta n = \pm 0.0005$ . For the aqueous electrolyte solutions dispersion data of refractive indices or refractivities are scarce. The few molar refractivity values for KF [9] and LiCl solutions [10] at  $\lambda = 656.3\text{ nm}$ ,  $486.1\text{ nm}$  and  $434.05\text{ nm}$  agree with our calculated values within  $\Delta R = \pm 0.02$  ( $\Delta n = \pm 0.001$ ).

### 5. Intrinsic and interaction refractivities

The polarizability  $\alpha$  of a particle in condensed phase is composed of an intrinsic part  $\alpha^{(g)}$  and an intermolecular contribution  $\alpha^{(i)}$ .  $\alpha^{(g)}$  is obtained from refractive index data of rarefied gases while  $\alpha^{(i)} = \alpha - \alpha^{(g)}$  is determined as difference between condensed phase and gaseous state polarizability.

For solutions (binary mixtures) the linear optical polarization may be written as (only pairwise interaction taken into account)

$$P = ELN_A [\beta_1(\alpha_1^{(g)} + X_1\alpha_{11}^{(i)}) + \beta_2(\alpha_2^{(g)} + X_2\alpha_{22}^{(i)}) + (\beta_1 + \beta_2)X_1X_2\alpha_{12}^{(i)}] \quad (7)$$

$L = (n^2 + 2)/3$  is the Lorentz local field correction factor.  $X_1 = N_1/(N_1 + N_2)$  and  $X_2 = N_2/(N_1 + N_2)$  are the mole fractions of solvent and solute, respectively.  $\alpha_1^{(g)}$  and  $\alpha_2^{(g)}$  are the intrinsic polarizabilities (rarefied solvent and solute).  $\alpha_{11}^{(i)}$  is the solvent-solvent,  $\alpha_{22}^{(i)}$  the solute-solute, and  $\alpha_{12}^{(i)}$  the solvent-solute interaction polarizability. The electrolytes are composed of cations (K) and anions (A). The polarizabilities of eq. (7) therefore consist of polarizability contributions of the ions according to  $\alpha_A^{(g)} = \alpha_A^{(g)}$  +  $\alpha_K^{(g)}$ ,  $\alpha_{AA}^{(i)} = \alpha_{AA}^{(i)} + \alpha_{KK}^{(i)} + \alpha_{KA}^{(i)}$  and  $\alpha_{12}^{(i)} = \alpha_{1A}^{(i)} + \alpha_{1K}^{(i)}$ .

Since  $P = \epsilon_0 \chi E = \epsilon_0 (n^2 - 1)E$  and  $R = (1/3\epsilon_0)N_A \alpha$ , eq. (7) may be rewritten as

$$(n^2 - 1)/(n^2 + 2) = \beta_1(R'_S + X_1R'_{11}) + \beta_2(R'_S + X_2R'_{22}) + (\beta_1 + \beta_2)X_1X_2R'_{12} \quad (8)$$

If the solvent-solvent, solute-solute and solvent-solute interactions are independent of concentration

then the interaction refractivities  $R_{11}^{(i)}$ ,  $R_{22}^{(i)}$ , and  $R_{12}^{(i)}$  are constants. In the following we assume  $R_{11}^{(i)}$  and  $R_{22}^{(i)}$  to be constant and accumulate concentration dependent effects in an apparent solvent-solute refractivity  $R'_{12}$ .

The relation between the apparent molar refractivity  $R'_2(\beta_2)$  and the intrinsic and interaction refractivities is found by comparing eqs. (3) and (8) ( $\beta_1/\beta_2 = X_1/X_2$ ,  $X_1 + X_2 = 1$ )

$$R'_2 = R_2^{(g)} + X_2 R_{22}^{(i)} + X_1 R'_{12} - X_1 R_{11}^{(i)} \quad (9)$$

$$= R_{2,n} + X_1 (R'_{12} - R_{22}^{(i)} - R_{11}^{(i)}) .$$

The refractivity of the neat solvent water is

$$R_0 = R_1^{(g)} + R_{11}^{(i)} , \quad (10)$$

$R_0$  is determined from the refractive index of liquid water ( $n_D = 1.33252$  [6],  $R_0 = 3.712 \text{ cm}^3/\text{mol}$ ).

$R_1^{(g)}$  is obtained from the refractive index of water vapor ( $n_D - 1 = 2.517 \times 10^{-4}$  [6],  $R_1^{(g)} = 3.76 \text{ cm}^3/\text{mol}$ ).  $R_{11}^{(i)}$  is calculated as difference of liquid and vapor data ( $R_{11}^{(i)} = -0.048 \text{ cm}^3/\text{mol}$ ).

The refractivity of neat solutes (alkali halide crystals) is

$$R_{2,n} = R_2^{(g)} + R_{22}^{(i)} . \quad (11)$$

$R_{2,n}$  data are listed in table 1.  $R_2^{(g)}$  values of alkali halides are taken from the literature [1]. They have been deduced indirectly from a comparison of apparent molar refractivities of alkali and halide ions with rare gases.

The solvent-solute apparent molar interaction refractivities  $R'_{12}$  are calculated with the aid of eq. (9) [ $X_2 = c_2/(c_1 + c_2) = M_1 c_2 / (1000\rho - c_2 M_2 + c_2 M_1)$ ].

Table 2 lists the molar refractivities of the neat solutes  $R_{2,n}$ , the apparent refractivities of the solutes at zero concentration  $R'_{2,0}$  (extrapolated to  $\beta_2 = 0$  in

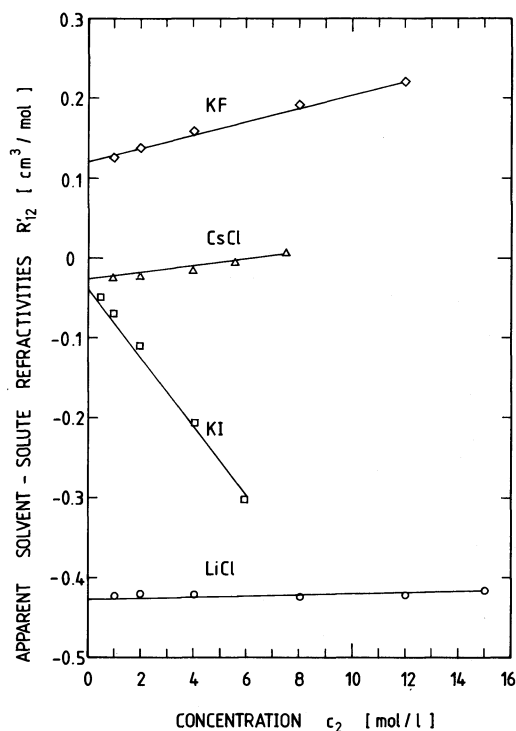


Fig. 5. Apparent solvent-solute interaction refractivities  $R'_{12}$  ( $\lambda_D = 589.3 \text{ nm}$ ) versus concentration. KI curve is calculated for  $\lambda = 587.6 \text{ nm}$ .

table 1) together with the intrinsic  $R_2^{(g)}$  and interaction refractivities  $R_{22}^{(i)}$  and  $R_{12,0}^{(i)}$  ( $\beta_2 = 0$ ) for  $\lambda_D = 589.3 \text{ nm}$  and  $T = 25^\circ \text{C}$  (KI data for  $\lambda = 587.6 \text{ nm}$ ).

The apparent molar solvent-solute interaction refractivities  $R'_{12}(\beta_2)$  are plotted in fig. 5.  $R'_{12}$  of KF is positive and increases with concentration. The  $R'_{12}$  numbers of CsCl are approximately zero. The LiCl values are negative and practically constant while the KI data are negative and decreases with concentration.

Table 2  
Molar refractivities in  $\text{cm}^3/\text{mol}$  at  $\lambda_D = 589.3 \text{ nm}$  and  $T = 25^\circ \text{C}$

Substance	$R_{2,n}$	$R'_{2,0}$	$R_2^{(g)}$	$R_{22}^{(i)}$	$R_{12,0}^{(i)}$
LiCl	7.586	8.76	9.145 a)	-1.559	-0.43
CsCl	15.203	15.62	15.595 a)	-0.392	-0.023
KF	5.169	4.86	4.69 a)	0.479	0.12
KI b)	19.834	21.465	21.46 a)	-1.626	-0.043

a) Ref. [1]. b) Values for  $\lambda = 587.6 \text{ nm}$ .

## 6. Structure effects on refractivities

The data of tables 1 and 2 and figs. 4 and 5 indicate the following structural dependences:

(i) The molar refractivities ( $R_{2,n}, R'_{2,0}, R_2^{(g)}$ ) and therefore the polarizability or deformability of the electron clouds of the ions increase with the atomic number of the cations ( $\text{Li}^+, \text{Cs}^+$ ) and the anions ( $\text{F}^-, \text{I}^-$ ). The refractivities are approximately proportional to the ionic volumes.

(ii) The condensation of water reduces weakly the refraction of water ( $R_{11}^{(i)} = -0.048 \text{ cm}^3/\text{mol}$ ). The dipole-dipole interaction of liquid water only slightly changes the electron cloud distribution of water molecules.

(iii) The refractivity of alkali halide crystals is lower than the gas-state refractivity ( $R_{22}^{(i)} = R_{2,n} - R_2^{(g)} < 0$ , except KF), i.e. the distortion of the electron clouds by an acting local light field is smaller in the condensed phase than in the gas-state. The solute-solute interaction refractivity  $R_{22}^{(i)} = R_{AA}^{(i)} + R_{KK}^{(i)} + R_{AK}^{(i)}$  changes oppositely with increasing atomic number of the cations and anions.  $R_{22}^{(i)}$  rises to less negative values with increasing atomic number of the cation ( $R_{22}^{(i)}(\text{LiCl}) < R_{22}^{(i)}(\text{CsCl}) < 0$ ) while it decreases with growing atomic number of the anions [ $R_{22}^{(i)}(\text{KF}) > 0 > R_{22}^{(i)}(\text{KI})$ ].

(iv) Dissolving of alkali halides in water reduces the polarizability ( $R_{12,0}^{(i)} < 0$ , except KF). The interaction of the alkali and halide ions with the water dipoles reduces the deformation of the electron cloud in an applied light field with the exception of  $\text{F}^-$ . This stabilizing effect reduces with the atomic number of the cations ( $R_{12,0}^{(i)}(\text{LiCl}) < R_{12,0}^{(i)}(\text{CsCl}) < 0$ ) and increases with the atomic number of the anions ( $R_{12,0}^{(i)}(\text{KF}) > 0 > R_{12,0}^{(i)}(\text{KI})$ ; same behaviour as  $R_{22}^{(i)}$ ).

The cations and anions bind tightly water molecules in a primary co-sphere. In a secondary co-sphere the structural reordering of water molecules from the ordered state in the primary sphere to the bulk water structure takes place [11–13]. The number of bound water molecules in the primary hydration sheath (hydration number  $h$ ) decreases with ionic radius ( $h(\text{Li}^+) = 4.5$ ,  $h(\text{K}^+) = 3.8$ ,  $h(\text{Cs}^+) = 2.5$ ,  $h(\text{F}^-) = 4.0$ ,  $h(\text{Cl}^-) = 2.2$  and  $h(\text{I}^-) = 1.5$  [15]). The  $\text{H}_2\text{O}$  molecules arrange differently around the cations and the anions due to the positive charge of the H atoms and negative charge of the O atoms of water [13].

$\text{F}^-$  increases the polarizability in condensed phase ( $R_{22}^{(i)} > 0$  and  $R_{12}^{(i)} > 0$ ). It is known as a strong structure maker [11,12], i.e. the structural ordering of water molecules in the primary co-sphere outweighs the breaking of hydrogen bonding structure in the secondary co-sphere [11–13].

(v) The apparent solvent-solute refractivity  $R'_{12}(\beta_2)$  increases slightly with concentration for LiCl, CsCl and KF (strongest effect for KF). In case of KI,  $R'_{12}$  decreases with concentration. The variation of  $R'_{12}$  indicates changes of the solvent-solvent, solute-solute or solvent-solute interaction with concentration.

These changes are thought to be due to structural changes of the aqueous solutions with concentration. The ions  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{F}^-$  have smaller diameters than the voids in water.  $\text{Cs}^+$  fits well in the interstitial positions.  $\text{Cl}^-$  is slightly larger than the average voids. The  $\text{I}^-$  ion has a diameter larger than the voids in water [11–14] so that strong structural changes of the solution with concentration are expected.

$\text{I}^-$  is known as a strong structure breaker [11,12], i.e. the structural ordering of water in the primary co-sphere is small compared to the structure breaking in the secondary co-sphere.

It should be noted that at high concentration the primary co-spheres of the ions come in close contact and even overlap in case of KF and LiCl for  $c_2 \gtrsim 7 \text{ mol/l}$ .

## 7. Conclusions

The dispersion of refractive indices and molar refractivities of some alkali halide crystals and aqueous alkali halide solutions were measured since literature values are not available. The measurement of phase-matching angles of the non-collinear optical four-photon frequency mixing was involved in the determination of refractive indices. The single oscillator model gives rather accurate values for the refractive indices and molar refractivities since the transition frequencies are far from studied dispersion region.

The presented parameters allow the calculation of  $n$  and  $R$  values in the wavelength range between  $\approx 350$  and  $1000 \text{ nm}$  for LiCl, CsCl, KF and KI crystals and aqueous solution between infinite dilution and saturation. The group refractive indices  $n_g = n/[1 - (\tilde{\nu}/n)]$

$\times \partial n / \partial \tilde{\nu}$ ] are readily derived from the dispersion formula.

The splitting of the molar refractivities into intrinsic and interaction parts makes it possible to gain information on the structure of aqueous electrolyte solutions from refractivity measurements.

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