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Calculations of hyper-Raman tensor components of alkali halides

W Kucharczyk[†] and F L Castillo Alvarado[‡]

[†] Institute of Physics, Technical University of Łódź, Wólczajska 219, 93-005 Łódź, Poland

[‡] Escuela Superior de Fisica y Matematicas, Instituto Politecnico Nacional, Edificio 6 UPLAM, Delegado G A Madero, 07738 Mexico District Federal, Mexico

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Abstract. Calculations of hyper-Raman scattering by the zone-centre optical phonons in NaCl, KCl and KBr crystals based on the bond polarizability approach are presented. The results obtained for the hyper-Raman tensor components are in agreement with experimental data reported previously in literature. A weak cubic anisotropy of the hyper-Raman tensor is found. For the LO mode our results predict the lattice and electro-optic contributions to hyper-Raman scattering to be of the same order of magnitude.

1. Introduction

Second-harmonic generation (SHG), as described within the electronic dipole approximation by the third-rank polar tensor, is vetoed by symmetry in alkali halides. However, when phonons locally break the inversion symmetry a scattering in the vicinity of the second harmonic of the incident light can be observed. This effect is known as hyper-Raman (HR) scattering.

Previously, the bond-polarizability model has been applied to HR scattering in SrTiO₃ and KTaO₃ (Vogt 1988), where nonlinear bond polarizabilities and their derivatives with respect to the bond length were deduced from experimental HR data. A useful interpretation of the model which allows us to predict nonlinear optical phenomena starting with the bond parameters is based on the Penn (1962) model and the Phillips–Van Vechten theory (see, e.g., Phillips 1970). This method has been employed to calculate nonlinear susceptibilities responsible for second- (Levine 1973) and third-harmonic (Chemla *et al* 1974) generation, electric-field-induced second-harmonic generation (Fujii and Sakudo 1976), linear (Shih and Yariv 1982) and quadratic (Kucharczyk 1987) electro-optic coefficients and the strain derivatives of electronic dielectric constants (Kucharczyk 1994). The approach is not necessarily limited to covalent compounds. In the Penn model the optical susceptibility stems from transitions from the valence band to the conduction band or to an exciton state. In alkali halides the highest valence band is formed from the p electrons of the anions and the lowest conduction band from the s electrons of the cations.

The aim of this work is to apply the Phillips–Van Vechten approach to calculate components of the HR tensor measured, previously, in NaCl, KCl and KBr by Vogt and Presting (1985).

2. Method

Following Levine (1973) the electronic second-order susceptibility $\chi_{ijk}^{(2)}$ responsible for SHG can be expressed as

$$\chi_{ijk}^{(2)} = \frac{1}{V} \sum_n \frac{\beta_n^L f_{e,n}^L}{R_n} \alpha_{ni} \alpha_{nj} \alpha_{nk}. \quad (1)$$

In this the summation is taken over all n bonds in the volume V , β_n^L is the longitudinal component of the axially symmetric bond polarizability tensor, R_n is the bond length, α_{ni} is the relevant direction cosine and $f_{e,n}^L = (R_n/\beta_n^L)(\partial\beta_n^L/\partial E)_R$ is the purely electronic part of the second-order bond polarizability which describes the changes in β_n^L induced by the electric field with the lattice fixed. Because of strong anisotropy of the second-order bond polarizability (see, e.g., Chemla *et al* 1974) its transverse component is here neglected. Taking into account the rock-salt structure of the crystals, the results obtained by Levine (1973) and Shih and Yariv (1982) may be rewritten for SHG in the form

$$f_{e,n}^L = \frac{\beta_n^L}{q_{eff,n}} [23.24(1 - f_{i,n})\rho_n - 1.333f_{i,n}]. \quad (2)$$

Here $q_{eff,n}$ is an effective bond charge, $f_{i,n}$ is the Phillips–Van Vechten ionicity parameter and $\rho_n = (r_{\alpha,n} - r_{\beta,n})/R_n$, in which r_α and r_β are the cation and anion radii, respectively. Equations (1) and (2) show that in alkali halides SHG is allowed on the bond level. However, when the local changes in the symmetry due to the lattice vibrations are neglected, contributions of all bonds in the unit cell cancel themselves and the macroscopic SHG vanishes.

Off resonance, the HR tensor $R_{\alpha\delta\beta\gamma}$ of the zone-centre TO and LO phonons is given by derivatives of the susceptibility $\chi_{\alpha\beta\gamma}^{(2)}$ with respect to the relative displacement u of the alkali metal and halogen sublattices and the electric field E associated with the LO phonon (Vogt 1990)

$$\begin{aligned} R_{\alpha\delta\beta\gamma}^{TO} &= \frac{\partial\chi_{\alpha\beta\gamma}^{(2)}}{\partial u_\delta} \\ R_{\alpha\delta\beta\gamma}^{LO} &= \frac{\partial\chi_{\alpha\beta\gamma}^{(2)}}{\partial u_\delta} - \frac{4\pi e_s(\epsilon(\infty) + 2)N}{3\epsilon(\infty)} \frac{\partial\chi_{\alpha\beta\gamma}^{(2)}}{\partial E_\delta} \end{aligned} \quad (3)$$

where e_s is the Sziget effective charge, N is the density of ion pairs and $\epsilon(\infty)$ is the long-wave value of the electronic dielectric constant. The second term in the expression for $R_{\alpha\delta\beta\gamma}^{LO}$, where $\partial\chi_{\alpha\beta\gamma}^{(2)}/\partial E_\delta = 3\chi_{\alpha\delta\beta\gamma}^{(3)}$ with $\chi_{\alpha\delta\beta\gamma}^{(3)}$ being the third-harmonic generation susceptibility, is related to the so-called electro-optic contribution to HR scattering by the LO mode. Within the Kleinmann symmetry approximation, the zone-centre HR tensor of the crystals possesses 12 non-zero and two independent components. These independent components of the TO or LO phonons have been denoted as $R_{1111}^{TO,LO} = a^{TO,LO}$ and $R_{1122}^{TO,LO} = b^{TO,LO}$ (Vogt and Presting 1985, Vogt 1990). In the model, the components a^{TO} and b^{TO} may be calculated as derivatives of $\chi_{111}^{(2)}$ and $\chi_{122}^{(2)}$ given by equation (1) with respect to the relative displacement u_1 of the sublattices. This displacement can change both the lengths and directions of the bonds. We obtained the derivative $(\partial\beta_n^L/\partial R_n)$ as $(\partial\beta_n^L/\partial R_n) = f_{l,n}^L(\beta_n^L/R_n)$, where $f_{l,n}^L$ is the lattice contribution to the second-order bond polarizability which may be deduced from the elasto-optic effect. The derivative $(\partial f_{e,n}^L/\partial u_\delta)$ is calculated by assuming in equation (2) the ratio $r_{\alpha,n}/r_{\beta,n}$ to remain constant with changes in R_n , i.e. $(\partial\rho_n/\partial R_n) = 0$ and by employing the identity $(\partial q_{eff,n}/\partial R_n) = (\partial q_{eff,n}/\partial f_{i,n})(\partial f_{i,n}/\partial R_n)$. The derivatives of the direction cosines with respect to u_1 may be evaluated following the method shown by Shih and Yariv (1982).

According to the rock-salt symmetry of the crystals under consideration, the rotation of bonds due to u_1 does not contribute to a^{TO} . This component originates exclusively from stretching of the bonds parallel to the x direction. On the other hand, the component b^{TO} stems only from changes in directions of the bonds parallel to the y direction, for which $(\partial\alpha_1/\partial u_1) = 1/R$, without any contribution of the bond stretching.

3. Results

From equations (1)–(3) we have

$$a^{TO} = \frac{\beta^L f_e^L}{R^5} \left[2f_l^L - 1 - R \left(\frac{\partial f_i}{\partial R} \right) \left(\frac{1.333 + 23.24\rho}{23.24(1 - f_i)\rho - 1.334f_i} + \frac{1}{q_{eff}} \left(\frac{\partial q_{eff}}{\partial f_i} \right) \right) \right] \quad (4)$$

and

$$b^{TO} = \frac{\beta^L f_e^L}{R^5}. \quad (5)$$

Here, β^L and all other parameters correspond to the nondistorted centrosymmetric structure.

Numerical values of the parameters employed in our calculations are listed in table 1. The ionic radii correspond to the minimum of electron density between cation and anion as determined in x-ray scattering experiments. The values of β^L and f_l^L have been derived from interionic part of the linear optical susceptibility from elasto-optic data by Weber (1986). The dependence $(\partial f_i/\partial R)$ has been calculated previously in terms of the Phillips–Van Vechten theory and applied to evaluate the volume dependence of the Szigeti effective charge in alkali halides (Kucharczyk 1991). In our calculations we used q_{eff} derived from experimental values of $\chi_{1111}^{(3)}$ and took into consideration a correlation between q_{eff} and f_i observed for alkali halides (Kucharczyk 1995). The plot of q_{eff} against f_i shows for alkali halides with either the same cation or the same anion a linear decrease of q_{eff}/e with f_i . The values $(\partial q_{eff}/\partial f_i)$ are obtained as average slopes of these cation and anion dependencies.

Our theoretical b^{TO} are compared with the experimental one in table 2. The values of a^{TO} , a^{LO} and b^{LO} obtained in this work along with a^{TO} calculated by Vogt (1990) within an anharmonic shell model are also presented in table 2. Since the experimental $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}$ (Landolt–Börnstein 1984) and our theoretical a^{TO} and b^{TO} are of positive sign, the components a^{LO} and b^{LO} have the positive sign as well. The relative theoretical values of the HR elements a^{TO}/b^{TO} , a^{LO}/a^{TO} , b^{LO}/b^{TO} and a^{LO}/b^{LO} are compared with experimental results in table 3. Measurements performed by Vogt and Presting (1985) have not provided means to decide whether b^{LO} and b^{TO} have the same or opposite signs; consequently, in tables 2 and 3 two experimental values for $|b^{TO}|$ and $|a^{LO}/a^{TO}|$ are quoted. Moreover, Vogt and Presting (1985) have derived $|a^{LO}/a^{TO}|$ and $|b^{LO}/b^{TO}|$ using $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}$ of Burns and Bloembergen (1971). These relative HR components are also listed in table 3. The positive sign of a^{TO}/b^{TO} has been experimentally determined by further measurements in which the HR intensity was analysed as a function of the polarization of the incident light (Vogt 1990). Our positive signs of a^{LO}/a^{TO} and b^{LO}/b^{TO} are in agreement with that obtained within the anharmonic shell model with introduced fourth-order interionic coupling parameters (Vogt 1990).

In our opinion it is hard to judge whether discrepancies between our theoretical values and experimental data indicate a principal limitation of the model when applied to hyper-Raman scattering. The components b^{TO} reported by Vogt and Presting (1985) were determined by using their experimental values of the ratio $(b^{LO})^2/(b^{TO})^2$ and relating the electro-optic part of b^{LO} to $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}/\chi_{1111}^{(3)}$. The third-order nonlinear susceptibilities $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}$ of

Table 1. Values of input parameters used to calculate the HR components.

Parameter	NaCl	KCl	KBr
R (Å)	2.82 ^a	3.147 ^a	3.297 ^a
r_α (Å)	1.18 ^b	1.45 ^c	1.57 ^d
r_β (Å)	1.64 ^b	1.70 ^c	1.73 ^d
$\epsilon(\infty)$	2.33 ^e	2.17 ^e	2.36 ^e
e_S/e	0.77 ^e	0.81 ^e	0.78 ^e
β_L (10^{-24} cm ³)	10.4 ^f	12.8 ^f	17 ^f
f_i^L	1.4 ^f	0.3 ^f	0.4 ^f
f_i	0.937 ^g	0.961 ^g	0.957 ^g
$R(\partial f_i/\partial R)$	0.197 ^h	0.132 ^h	0.149 ^h
q_{eff}/e	0.88 ⁱ	0.64 ⁱ	0.82 ⁱ
$(1/q_{eff})(\partial q_{eff}/\partial f_i)$	-21 ⁱ	-40 ⁱ	-29 ⁱ
$\chi_{1111}^{(3)}$ (10^{-14} esu)	1.7 ^j	1.9 ^j	3.0 ^j
$\chi_{1122}^{(3)}/\chi_{1111}^{(3)}$	0.43 ^j	0.30 ^j	0.37 ^j

^a Landolt–Börnstein (1973).^b Schoknecht (1957).^c Patomäki and Linkoaho (1969).^d Meisalo and Inkinen (1967).^e Lowndes and Martin (1969).^f Weber (1986).^g Kucharczyk (1994).^h Kucharczyk (1991).ⁱ Kucharczyk (1995), see text.^j Maker and Terhune (1965).**Table 2.** Theoretical and experimental HR tensor elements (in esu); $a^{TO,LO}$ and $b^{TO,LO}$ stand for the hyper-Raman components $R_{1111}^{TO,LO}$ and $R_{1122}^{TO,LO}$, respectively.

Crystal	Theory					Experiment
	(This work)				(Vogt 1990)	(Vogt and Presting 1985)
	a^{TO}	b^{TO}	a^{LO}	b^{LO}	a^{TO}	$ b^{TO} $
NaCl	0.76	0.14	4.0	1.5	1.4	0.075; 0.056
KCl	0.73	0.15	3.6	1.0	0.33	0.11; 0.064
KBr	0.65	0.16	4.3	1.5	0.43	0.11; 0.070

Maker and Terhune (1965), employed by Vogt and Presting (1985) and in our calculations, are in agreement with some other sets of $\chi_{1111}^{(3)}$ (Levenson and Bloembergen 1974, Lynch *et al* 1974) and are also consistent with the calibration scale recommended in Landolt–Börnstein (1984). However, these values of $\chi_{1111}^{(3)}$ are roughly midway between the lowest (Adair *et al* 1989) and the highest (Smith *et al* 1975) proposed in the literature. If based on the experimental $\chi_{1111}^{(3)}$ of Adair *et al* (1989) or Smith *et al* (1975) the electro-optic contribution to b^{LO} should be multiplied or divided by a factor of about 2.3 (Kucharczyk 1995), respectively. Moreover, even within the same calibration scale, slightly different relative values of $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}$ for the alkali halides are reported by various authors. Since q_{eff} scales as $(\chi_{1111}^{(3)})^{-1/2}$ (Kucharczyk 1995) according to equations (2)–(5) the use of $\chi_{1111}^{(3)}$ and $\chi_{1122}^{(3)}$ other than those of Maker and Terhune (1965) in a different way affects the experimental and theoretical results listed in tables 2 and 3.

Table 3. Relative values of the HR tensor components.

Crystal	Theory (this work)			
	a^{TO}/b^{TO}	a^{LO}/b^{LO}	a^{LO}/a^{TO}	b^{LO}/b^{TO}
NaCl	5.6	2.6	5.3	11
KCl	4.9	3.6	4.9	6.8
KBr	4.1	2.9	6.6	9.5

Crystal	Experiment (Vogt and Presting 1985)				
	a^{TO}/b^{TO}	a^{LO}/b^{LO}	$ a^{LO}/a^{TO} ^a$	$ a^{LO}/a^{TO} ^b$	$ b^{LO}/b^{TO} ^b$
NaCl	4.5	2.3	2.0; 2.6	3.7	7.2
KCl	2.2	2.8	3.0; 2.7	5.5	4.3
KBr	2.7	2.8	2.9; 3.3	4.4	4.2

^a Obtained using $\chi^{(3)}$ of Maker and Terhune (1965).

^b Obtained using $\chi^{(3)}$ of Burns and Bloembergen (1971).

We found the ratios a^{TO}/b^{TO} and a^{LO}/b^{LO} to be close to 3, as they should be in isotropic materials (Nye 1979). This shows that in the crystals under consideration the cubic anisotropy of the HR tensor is not strongly exhibited. Our results predict the lattice and electro-optic contributions to HR scattering to be of the same order of magnitude.

References

- Adair R, Chase L L and Payne S A 1989 *Phys. Rev. B* **39** 3337
 Burns W K and Bloembergen N 1971 *Phys. Rev. B* **4** 3437
 Chemla D S, Begley R F and Byer R L 1974 *IEEE J. Quantum Electron.* **QE-10** 71
 Fujii Y and Sakudo T 1976 *Phys. Rev. B* **13** 1161
 Kucharczyk W 1987 *J. Phys. C: Solid State Phys.* **20** 1875
 ———1991 *Physica B* **172** 473
 ———1994 *J. Phys. Chem. Solids* **55** 237
 ———1995 *J. Phys. Chem. Solids* **56** 871
Landolt-Börnstein New Series 1973 Group III, vol 7, ed K-H Hellwege and A M Hellwege (Berlin: Springer)
 ———1984 Group III, vol 18, ed K-H Hellwege and A M Hellwege (Berlin: Springer)
 Levenson M D and Bloembergen N 1974 *Phys. Rev. B* **10** 4447
 Levine B F 1973 *Phys. Rev. B* **7** 2600
 Lowndes R P and Martin D H 1969 *Proc. R. Soc. A* **308** 473
 Lynch R T Jr, Levenson M D and Bloembergen N 1974 *Phys. Lett.* **50A** 61
 Maker P D and Terhune R W 1965 *Phys. Rev.* **137** A801
 Meisalo V and Inkinen O 1967 *Acta Crystallogr. A* **22** 58
 Nye J F 1979 *Physical Properties of Crystals* (Oxford: Clarendon)
 Patomäki L L and Linkoaho M V 1969 *Acta Crystallogr. A* **25** 304
 Penn D R 1962 *Phys. Rev.* **128** 2093
 Phillips J C 1970 *Rev. Mod. Phys.* **42** 317
 Schoknecht G 1957 *Z. Naturwiss. A* **12** 983
 Shih C and Yariv A 1982 *J. Phys. C: Solid State Phys.* **15** 825
 Smith W L, Bechtel J H and Bloembergen N 1975 *Phys. Rev. B* **12** 706
 Vogt H 1988 *Phys. Rev. B* **38** 5699
 ———1990 *J. Raman Spectrosc.* **21** 813
 Vogt H and Presting H 1985 *Phys. Rev. B* **31** 6731
 Weber H-J 1986 *Z. Kristallogr.* **177** 201