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Calculations of third-order electronic susceptibility of alkali halides

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ABSTRACT

Hyper-Raman scattering by the zone-centre optical phonons in some alkali halides is investigated. In our calculations we relate the electrooptic part of the hyper-Raman tensor to the third-order optical susceptibility and the electric field associated with the LO phonons. The results obtained for those alkali halides for which the third-order optical susceptibility has not been measured yet, show that the electrooptic and lattice contributions to the hyper-Raman scattering are comparable. In all crystals considered, we found the cubic anisotropy of the electrooptic part of the hyper-Raman tensor to be not strongly exhibited.

Keywords: Nonlinear susceptibilities, nonlinear refractive index, hyper-Raman scattering, electrooptic effects, alkali halides

1. INTRODUCTION

The bond polarizability model has been employed previously for various crystals, including alkali halides and crystals composed of different bonds, either to nonlinear effects of purely electronic origin or to phenomena due to nonlinear interactions of electric fields with the crystal lattice. For example, the method has been applied to second-¹⁻³ and third-harmonic generation⁴⁻⁶, and the linear^{7,8} and quadratic electrooptic coefficients.⁹ Recently, studies of hyper-Raman scattering in alkali halides by the zone-centre optical phonons¹⁰ and calculations of the nonlinear refractive of alkali halides have been presented as well.¹¹

The aim of this work is to present calculations of the electronic third-order nonlinear susceptibility of alkali halides and to discuss the contribution of the nonlinear susceptibility to the hyper-Raman scattering of the crystals.

2. METHOD

Our calculations utilize the approach based on the idea of interionic excitations. These are often described in terms of the one-gap Penn model.¹² In the model, the optical susceptibility can be related to the transition from the valence band to an exciton state or to the conduction band. One notes that the interionic description is not necessary limited to covalent compounds. 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.¹³

Within the Phillips-Van Vechten theory^{14,15}, the effective energy gap E_g of the Penn model can be decomposed into heteropolar C and homopolar E_h contributions. In the long-wavelength limit, the linear optical susceptibility $\chi(\infty)$ is given by

$$\chi(\infty) = \frac{(\hbar\omega_p)^2}{(C^2 + E_h^2)} \quad (1)$$

In this, ω_p is the plasma frequency of the free-valence electron gas defined as

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$$(\hbar\omega_p)^2 = \frac{N_e e^2 A D}{4 \pi m}, \quad (2)$$

where A and D are correction factors of order unity, N_e is the density of the valence electrons, and e and m are the electron charge and mass, respectively. The Phillips-Van Vechten theory introduces the so-called spectroscopic scale of ionicity^{14,15}, as measured by the parameter f_i

$$f_i = \frac{C^2}{C^2 + E_h^2}. \quad (3)$$

The heteropolar contribution is related to the ionic binding and in the $A^I B^{VII}$ compounds can be expressed by

$$C = b e^2 \left(\frac{1}{r_\alpha} - \frac{7}{r_\beta} \right) \exp \left(- \frac{k_s R}{2} \right), \quad (4)$$

where r_α and r_β are the cation and anion radii, respectively, $R = r_\alpha + r_\beta$ is the bond length, k_s is the Thomas-Fermi screening wave number and the parameter b accounts for the deficiency of the model in describing the screening by free electrons. Following Levine¹, we expressed E_h as

$$E_h = A_h R^{-s} \left(\frac{(R - 2r_c)^{2s}}{r_{\alpha c}^{2s} + r_{\beta c}^{2s}} \right)^{\frac{1}{2}}, \quad (5)$$

where A_h and s are constants, $r_{\alpha c} = r_\alpha - 0.175R$, $r_{\beta c} = r_\beta - 0.175R$ and $r_c = 0.175R$.

Although the approach describes the optical susceptibility in terms of the interionic excitations, Phillips and Van Vechten have introduced an additional coefficient D into the Eq. (2) to account for excitations of core electrons.^{14,15} Accordingly, Weber¹⁶ decomposed the linear susceptibility of alkali halides into two parts due to different microscopic phenomena

$$\chi_{ij} = \chi'_{ij} + \chi''_{ij}, \quad (6)$$

where the term χ'_{ij} describes that part of the optical susceptibility which is interionic and can be related to the bond polarizability. The contribution χ''_{ij} stems from excitations of the cation cores and represents the intraionic part of χ_{ij} . According to the bond polarizability approach (see, for example, in Refs 1,4), the macroscopic linear optical susceptibility χ'_{ij} can be expressed by

$$\chi'_{ij} = \frac{1}{V} \sum_n \beta_n^{L,T} \alpha_{ni} \alpha_{nj}. \quad (7)$$

Here, $\beta_n^{L,T}$ is the longitudinal or transverse component of the axially symmetric bond polarizability tensor, defined in a way which includes local field effects, α_{ni} is the relevant direction cosine, and the summation is taken over all bonds in the volume V. The bond polarizability model provides a simple link between the crystal structure and magnitude of nonlinear optical susceptibilities. In terms of the bond polarizability model these are described by higher-order bond polarizabilities. Dispersion in the linear and second-order bond polarizabilities of alkali halides has been discussed in Ref. 17.

Employing Eqs (1)-(7), two independent components of the third-order optical susceptibility tensor of the rock salt-structure crystals can be expressed as⁶

$$\chi_{1111} = \frac{(\chi')^3 R^4 (F_e^L + 2c^3 F_e^T)}{(4\pi)^2 q_{\text{eff}}^2 (1+2c)^3}, \quad (8)$$

and

$$\chi_{1122} = \frac{2(\chi')^3 R^4 c^3 F_e^T}{8\pi^2 q_{\text{eff}}^2 (1+2c)^3}, \quad (9)$$

where $c = \beta^T / \beta^L$ describes the anisotropy of the linear bond polarizability tensor, q_{eff} is the effective bond charge, and $F_e^{L,T}$ defined as

$$F_e^{L,T} = \frac{R^2}{2\beta^{L,T}} \left(\frac{\partial^2 \beta^{L,T}}{\partial (\Delta r_{\text{eff}}^{L,T})^2} \right)_R, \quad (10)$$

represents the electronic contribution to the longitudinal or transverse component of the third-order bond polarizability tensor.

Except for the effective bond charge, all parameters which appear in Eqs (8) and (9) can be easily obtained from experimental data. The way of deriving the numerical values of components β^L and β^T and, therefore, c from the interionic part of the linear optical susceptibility, has been proposed in Ref. 16. In our calculations, we employed the effective bond charge determined by taking into account the relationship between the charge and the ionicity of the crystals.^{18,19}

3. HYPER-RAMAN SCATTERING IN ALKALI HALIDES

In centrosymmetric crystals like alkali halides, the second-order nonlinear susceptibility $\chi_{ijk}^{(2)}$ is allowed on the bond level. 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 $\chi_{ijk}^{(2)}$ vanishes on the macroscopic level.¹⁰ However, when phonons locally brake the inversion symmetry, an observation of scattering of light in the vicinity of the second harmonic of the incident light, i.e. hyper-Raman scattering, is possible.^{20,21}

In the halite-type alkali halides, of-resonance, the HR tensor $R_{\alpha\beta\delta\gamma}$ of the zone-center TO and LO phonons is given by derivatives of the susceptibility $\chi_{ijk}^{(2)}$ with respect to the relative displacement u of the alkali metal and halogen sublattices and the macroscopic electric field E associated with the LO phonon^{20,21}

$$\begin{aligned} R_{\alpha\beta\gamma}^{TO} &= \frac{\partial \chi_{\alpha\beta\gamma}^{(2)}}{\partial u_{\delta}}, \\ R_{\alpha\beta\gamma}^{LO} &= \frac{\partial \chi_{\alpha\beta\gamma}^{(2)}}{\partial u_{\delta}} + R_{\alpha\beta\gamma}^{eo}. \end{aligned} \quad (11)$$

In this, the second term in the expression for $R_{\alpha\beta\gamma}^{LO}$ is related to the electro-optic contribution to HR scattering by the LO mode, namely

$$R_{\alpha\beta\gamma}^{eo} = -\frac{4\pi e_s N (\epsilon(\infty) + 2)}{3 \epsilon(\infty)} \left(\frac{\partial \chi_{\alpha\beta\gamma}^{(2)}}{\partial E_{\delta}} \right)_R, \quad (12)$$

where e_s is the Szigeti effective charge, $\epsilon(\infty)$ is the long-wave value of the electronic dielectric constant, N is the density of ion pairs and $\partial \chi_{\alpha\beta\gamma}^{(2)} / \partial E_{\delta} = 3 \chi_{\alpha\delta\beta\gamma}^{(3)}$, with $\chi_{\alpha\delta\beta\gamma}^{(3)}$ being the third harmonic generation susceptibility. Within the Kleinmann symmetry approximation, the zone-centre HR tensor of the crystals possess 12 non-zero and 2 independent components R_{xxxx} and R_{xxyy} for $\alpha=\delta=x$ and $\beta=\gamma=y$, and $\alpha=\delta=\beta=\gamma=x$, respectively.²¹

The hyper-Raman-spectra of some alkali halides have been measured by Vogt and Presting at room temperature. Two hyper-Raman lines corresponding to the transverse-optic (TO) and longitudinal-optic (LO) phonons at the center of the Brillouin zone were observed. Different configurations have been considered.²⁰ The first one was the configuration $x(yx)z$ where the scattering is due to the hyper-Raman tensor elements R_{xxyy}^{TO} and R_{xxyy}^{eo} . The spectral hyper-Raman efficiencies $S_{TO}(\Omega)$ and $S_{LO}(\Omega)$ can be given by²⁰

$$S_{TO}(\Omega) = \frac{h I_L}{4\pi \eta c N^2} [\Omega c]^4 [n(\omega) + 1] \frac{|R_{xxyy}^{TO}|^2}{Z^2} \text{Im}[\epsilon(\omega)], \quad (13)$$

$$S_{LO}(\Omega) = \frac{h I_L \epsilon(\omega)^2}{4\pi \eta c (ZN)^2} [\Omega c]^4 [n(\omega) + 1] \left| R_{xxyy}^{TO} + \frac{R_{xxyy}^{eo}}{N} \right|^2 \text{Im} \left[\frac{-1}{\epsilon(\omega)} \right]. \quad (14)$$

In Eqs (13) and (14), $\Omega=2\omega_L-\omega$ is the frequency of the scattered light, N is the number of primitive cells per unit volume, I_L is the laser intensity, Z is the transverse effective ionic charge, $[n(\omega)+1]$ is the Bose occupation factor and η is the refractive index. From Eqs (13) and (14) one obtains²⁰

$$S_{TO}(\Omega) = \frac{\pi}{\eta c} \left[\frac{\Omega}{c} \right]^4 \frac{h}{2NM\omega_{TO}} [n(\omega) + 1] |R_{xxyy}^{TO}|^2 I_L, \quad (15)$$

where M is the reduced mass of the vibrating ions. Analogously, the expression for S_{LO} can be obtained by replacing ω_{TO} by ω_{LO} and the hyper-Raman tensor element R_{xxyy}^{TO} by R_{xxyy}^{eo} .²⁰ The values $|R_{xxxx}^{TO} / R_{xxyy}^{TO}|$ have been experimentally determined by switching between the scattering configurations $x(yy)z$ and $x(yx)z$. To obtain more information about the relative values of

the hyper-Raman components, in Ref. 20 the intensities of the LO-phonon lines in the scattering configurations $x(yy^*)z^*$ and $x(yx)z^*$, $y^*=[001]$ and $z^*=[011]$ were compared. The ratio of the corresponding hyper-Raman efficiencies

$$\frac{S_{LO}[x(yy^*)z^*]}{S_{LO}[x(yx)z^*]} = \frac{1}{4} \left[\frac{R_{xxxx}^{LO}}{R_{yyxx}^{LO}} - 1 \right]^2, \quad (16)$$

along with Eqs (13) and (14), allowed the experimental values of $|R_{xyxy}^{LO}/R_{xyxy}^{TO}|$, $|R_{xxxx}^{LO}/R_{xyxy}^{LO}|$, $|R_{xxxx}^{LO}/R_{xxxx}^{TO}|$ and next $|R_{xyxy}^{TO}|$ to be determined.²⁰ The values presented in Refs 10,20 show that the magnitude of the lattice contributions to R_{xxxx}^{TO} and R_{xyxy}^{TO} are of the order of magnitude of 10^{-14} esu.

4. RESULTS

The electrooptic contributions to the HR tensor of alkali halides derived in this work by employing Eqs (8) - (10) and (12) are listed in Table 1. The values obtained correspond to the long-wavelength limit, what is an intrinsic feature of the approach. In

Table 1. Calculated values of the electrooptic contribution to the HR tensor of alkali halides. Like previously published results^{10,19,20}, our values are given in 10^{-14} esu.

Crystal	R_{xxxx}^{eo}	R_{xyxy}^{eo}	$R_{xxxx}^{eo} / R_{xyxy}^{eo}$
LiCl	1.79	0.50	3.55
LiBr	2.46	0.73	3.35
LiI	2.90	1.45	2.90
NaI	2.23	0.93	2.40
KF	0.60	0.18	3.39
KI	1.32	0.52	2.56
RbF	1.12	0.38	2.95
RbCl	0.77	0.24	3.16
RbBr	0.86	0.27	3.25
RbI	1.17	0.41	2.84

our calculations we employed values of χ'_{ij} , χ''_{ij} , and f_i as listed in Ref. 22, along with the ionic radii corresponding to the minimum of electron density between cation and anion.²³ The long-wavelength values of the linear refractive index were taken from Refs 24,25. In our work we adopted calibration scale for the third-order optical susceptibility recommended in Ref. 26. This scale is roughly midway between the lowest²⁷ and the highest²⁸ proposed scales. To compare the values of the electrooptic contribution to the HR tensor calculated or measured at different frequencies, the dispersion in the third-order optical susceptibility should be taken into account. This can be done by using the generalized Miller rule or some others semi-empirical formulas (see, for example, Refs 11,29).

5. CONCLUSION

The ratio $R_{xxxx}^{eo} / R_{xyxy}^{eo}$ is close to 3, as it should be in isotropic materials. This proves that in the alkali halides the cubic anisotropy of the electrooptic contribution to the HR tensor is not strongly exhibited. When comparing our results with the previous experimental and theoretical results^{10,20,21} one observes that the lattice and electro-optic contribution to HR scattering are of comparable magnitudes.

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