Empirical electronic polarizabilities for use in refractive index measurements at 589.3 nm: Hydroxyl polarizabilities

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ABSTRACT

Refractive indices of minerals and inorganic compounds can be calculated from their chemical compositions using the additivity rule for electronic polarizabilities and converting the sum of polarizabilities α using the Anderson-Eggleton relationship:

$$\alpha_{AE} = \frac{\left(n_D^2 - 1\right)V_m}{4\pi + \left(\frac{4\pi}{3} - 2.26\right)\left(n_D^2 - 1\right)}$$

with the molar volume V_m solved for the mean refractive index n_D at 589.3 nm. Whereas the polarizability of cations is a single parameter, the polarizability of anions is described by a two-parameter term $\alpha_- = \alpha_-^{\circ} \cdot 10^{-N_o/V_{an}^{1.20}}$ with α_- = anion polarizability, V_{an} = anion molar volume, and the two least-squares parameters α_-° (corresponding to free-ion polarizability) and N_o. For hydroxyls, Shannon and Fischer (2016) introduced different parameter sets for non-H-bonded hydroxyls ($\alpha_-^{\circ} = 1.79$ Å^3, $N_o = 1.792$ Å$^{3.6}$) and moderately strong H-bonded hydroxyls ($\alpha_-^{\circ} = 1.73$ Å^3, $N_o = 2.042$ Å$^{3.6}$). In an effort to understand the lower polarizability of the H-bonded hydroxyl ions, we have evaluated observed and calculated polarizabilities, O-H, H···O, O···O distances, and O-H···O angles in 10 minerals with non-hydrogen-bonded hydroxyls (mean <O···O> distance 3.143 Å, mean <H···O> distance 2.352 Å), in seven minerals with H-bonded-hydroxyls (<O···O> = 2.739 Å, <H···O> = 1.856 Å), and in 10 minerals with very strongly H-bonded hydroxyls (<O···O> = 2.531 Å, <H···O> = 1.525 Å). On the basis of quantum chemical cluster calculations using atomic parameters of well determined crystal structures of hydroxyl containing compounds, we found that calculated intrinsic polarizabilities of OH are correlated with the hydrogen bond lengths H···O and O···O between donor and acceptor of the H-bond. This is demonstrated for LiOH, brucite [Mg(OH)$_2$], portlandite [Ca(OH)$_2$], clinometaborite (β-HBO$_2$), sassolite (H$_3$BO$_3$), archerite (KH$_2$PO$_4$), kalicinite (KHCO$_3$), metaborite (γ-HBO$_2$), and NaPO$_2$(OH)$_2$.

Thus, we find that these summed intrinsic polarizabilities for OH-bonds which are involved in H-bonding are significantly lower than the corresponding summed intrinsic polarizabilities for OH-bonds not involved in H-bonding. We attribute the reduction in polarizability of hydroxyl ions in clinometaborite, sassolite, archerite, kalicinite and metaborite, and the compound NaPO$_2$(OH)$_2$ to the presence of H-bonds and a reduction of Hirshfeld atomic charge on the O atom.

Keywords: Hydroxyl polarizabilities, refractive indices, electronic polarizabilities, intrinsic polarizabilities, hydrogen bonding