Empirical electronic polarizabilities for use in refractive index measurements at 589.3 nm: Hydroxy 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 \( \alpha \) 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 \( \alpha_\text{an} = \alpha_\text{an}^{(-1)} + \alpha_\text{an}^{(+1)} \) with \( \alpha_\text{an} \) = anion polarizability, \( V_m \) = anion molar volume, and the two least-squares parameters \( \alpha_\text{an}^{(-1)} \) (corresponding to free-ion polarizability) and \( N_\text{an} \). For hydroxyls, Shannon and Fischer (2016) introduced different parameter sets for non-H-bonded hydroxyls \( (\alpha_\text{an} = 1.79 \text{ Å}^3, N_\text{an} = 1.792 \text{ Å}^6) \) and moderately strong H-bonded hydroxyls \( (\alpha_\text{an} = 1.73 \text{ Å}^3, N_\text{an} = 2.042 \text{ Å}^6) \). 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], clinometa borite (β-HBO₂), sasso litie (H₂BO₃), archerite (KH₂PO₄), kalicinite (KHCO₃), metaborite (γ-HBO₂), and NaPO₄(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 clinometa borite, sasso litie, archerite, kalicinite and metaborite, and the compound NaPO₄(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

Introduction

General

Shannon and Fischer (2016) evaluated the dynamic polarizabilities of 2600 minerals and 675 synthetic compounds using refractive indices determined at \( \lambda = 589.3 \text{ nm} \) (\( n_D \)) to yield a unique set of individual electronic polarizabilities of ions, which can be used for the interpretation of optical properties. Various definitions of polarizabilities have been proposed, but we use the Anderson-Eggleton relationship (Anderson 1975; Eggleton 1991) discussed in Shannon and Fischer (2016) and defined as:

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

where \( \alpha_{AE} \) = the total polarizability of a mineral or compound, \( n_D \) = the refractive index at \( \lambda = 589.3 \text{ nm} \), \( V_m \) = molar volume in Å³, and \( c = 2.26 \). For example, the total polarizability of albite (NaAlSi₃O₈) is calculated according to \( \alpha_{AE}(albite) = \alpha(Na^+) + \alpha(Al^{3+}) + 3\alpha(Si^{4+}) + 8\alpha(O^2-) \) using individual polarizabilities, \( \alpha \), given in Shannon and Fischer (2016). The calculated mean values of \( \langle \alpha_{AE}\rangle \) for 54 common minerals and 650 minerals and synthetic compounds differ by <3% from the observed values. Using dynamic polarizabilities, we observed systematic deviations in (1) \( M^2SO_4 \cdot nH₂O \), blödite [Na₂M³(SO₄)₂·4H₂O], and

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