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Introduction

The non-linear optical properties of molecular crystals depend upon the hyperpolarizabilities of the molecules they contain. Consider an electric field with components E_j , $j = 1, 2, 3$, measured in a Cartesian system of coordinates. The i -th component, m_i , of the electric dipole induced in this molecule by the field is given by

$$m_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots \quad (1)$$

where on the right hand side, the double occurrence of a subscript implies a summation over all values (1, 2, and 3) which the index may take on. The second rank tensor coefficient, α_{ij} , is called the ordinary dipole polarizability, while the third rank tensor coefficient, β_{ijk} , is called the first dipole hyperpolarizability.

If the applied electric field oscillates at frequency, ω , the induced dipole moment, m_i , oscillates at frequency ω and also at frequency 2ω . The oscillation at 2ω is the origin of the non-linear optical phenomenon known as frequency doubling. Using the time dependent perturbation theory of quantum mechanics, the part of β_{ijk} associated with frequency doubling is

$$\beta_{ijk}(2\omega) = \frac{2\pi^2}{h^2} \sum_{n, l} \left[\mu_{0n}^i (\mu_{nl}^j \mu_{l0}^k + \mu_{nl}^k \mu_{l0}^j) \frac{\omega_n \omega_l + 2\omega^2}{(\omega_n^2 - 4\omega^2)(\omega_l^2 - \omega^2)} + \mu_{0n}^k \mu_{nl}^i \mu_{l0}^j \frac{\omega_n \omega_l - \omega^2}{(\omega_n^2 - \omega^2)(\omega_l^2 - \omega^2)} \right] \quad (2)$$

where the ω_n are resonance frequencies for excitation of the molecule from the ground electronic state to the n-th excited state.¹ The μ_{pq}^l are electric dipole transition moments connecting the p-th and q-th electronic states of the molecule and are given by

$$\mu_{pq}^l = \int \phi_p^*(\mathbf{r}) \mu^l \phi_q(\mathbf{r}) d^3r \quad (3)$$

where \mathbf{r} represents all of the electronic coordinates, $\phi_p(\mathbf{r})$ is the molecular orbital for the p-th state, and μ^l is the electric dipole moment operator. The subscript, zero, in Eq. (2) refers to the ground state. It is clear from Eq. (3) that, if a molecule is to have a non-zero value for $\beta_{ijk}(2\omega)$, it cannot have a center of symmetry.

In the laboratory, $\beta_{ijk}(2\omega)$ may be determined by laser frequency doubling experiments or indirectly by combining measurements of absorption spectral line strengths with the difference in the absorption frequency and the fluorescence frequency found for the molecule.²

This structure contains 3 carbon atoms, 5 hydrogen atoms, one carbonyl oxygen (=O), and one OH. By Landolt's Rule, the molar refraction of propionic acid is given by a linear combination of atoms and bond refractions with coefficients specified by the stoichiometry. Using the table, we write

$$R = 3(2.591) + 5(1.028) + 2.122 + 2.553 = 17.588 \quad (7)$$

The molecular weight and density of propionic acid are $M = 74.08$ gm/mole and $d = 1.0030$ gm/cm³, respectively. Solving Eq. (5) for n and substituting the molecular weight, density, and the value of R given by Eq. (7), we obtain a predicted value for the refractive index,

$$n = \left[\frac{1 + 2(d/M)R}{1 - (d/M)R} \right]^{\frac{1}{2}} = 1.3877 \quad (8)$$

This is to be compared with the measured value $n = 1.3869$ reported in the Handbook of Chemistry and Physics.

The Additivity Property for Absorbing Compounds

According to Eq. (2), the hyperpolarizability is a function of frequency. This is called dispersion. Because of the Kramers-Kronig relations, we can expect that a material which is dispersing light is also absorbing it.⁷ Where there is dispersion and absorption, the molecular polarizabilities are complex functions of the frequency. This has led us to consider atomic additivity in both the real and imaginary parts of the ordinary and hyperpolarizabilities. This effort is desirable not only from a theoretical point of view, but also because of the existence of a large body of complex refractive index data, which may be used to test additivity principle with the complex valued ordinary dipole polarizability.

To date, we have shown using Maxwell's equations, that if the wavelength of the light is long compared with the molecular size, the Lorentz-Lorenz equation becomes

$$\frac{\tilde{n}^2 - 1}{\tilde{n}^2 + 2} = \left[\begin{array}{c} d \\ - \\ M \end{array} \right] \tilde{R} \quad (9)$$

where the complex refractive index, \tilde{n} , has real and imaginary parts n and k , respectively, and where the complex valued molar refraction, \tilde{R} , has real and imaginary parts, R' , and R'' . Eq. (9) may be used to test the additivity concept on the case of dispersion/absorption.

In the vacuum ultraviolet, both n and k have been measured for a number of compounds,⁸ among them being cyclohexane (no carbon-carbon double bonds), cyclohexene (one double bond), and cyclohexadiene (two double bonds).⁹ Substituting n and k , molecular weight, and density into Eq. (9), we have solved for \tilde{R} for each compound. Our hypothesis of additivity in the case of these three dispersing/absorbing compounds can be tested in the following way: We let \tilde{R}_0 , \tilde{R}_1 , and \tilde{R}_2 be the complex valued molar refractions of the compounds with none, one, and two double bonds. Letting \tilde{H} , \tilde{C}_1 , and \tilde{C}_2 be the complex valued refractions of the hydrogen atom, the carbon-carbon single bond, and the carbon-carbon double bond, we have assuming the additivity principle,

$$\tilde{R}_0 = 6\tilde{C}_1 + 12\tilde{H} \quad (10)$$

$$\tilde{R}_1 = 5\tilde{C}_1 + 10\tilde{H} + \tilde{C}_2 \quad (11)$$

$$\tilde{R}_2 = 4\tilde{C}_1 + 8\tilde{H} + 2\tilde{C}_2 \quad (12)$$

These three equations are not linearly independent, and we find

$$\tilde{R}_1 = (1/2)(\tilde{R}_0 + \tilde{R}_2) \quad (13)$$

which serves as a check on the additivity principle. We have found Eq. (13) to obeyed within experimental error throughout the entire wavelength region (775 to 1770 Angstroms) where complex refractive index data are available for the cyclic hexanes. This result gives us confidence that the additivity principle extends to dispersive systems in general.

The Quantum Theory of Additivity

A theoretical proof of the additivity idea, nevertheless, would be useful. For non-dispersive wavelengths (e.g., for most organic molecules at the Na D line), the electric field of the light wave may be assumed to be static. Since there are in this case no quantum transitions between states, the variation method of quantum mechanics is applicable and has been used with molecular orbital theory of the dipole moment to demonstrate that the additivity principle applies to the ordinary dipole polarizability in the limit of zero frequency.¹⁰

We are searching for a similar proof for dispersing systems. Using time dependent perturbation theory, we have found that the real part, $\alpha_{ij}'(\omega)$, and the imaginary part, $\alpha_{ij}''(\omega)$, of the ordinary dipole polarizability satisfy the equations,

$$\alpha_{ij}'(\omega) = \frac{2\pi}{h} \sum_l \mu^{i0l} \mu^{j l0} \left[\frac{(\omega_l - \omega)}{(\omega_l - \omega)^2 + \frac{1}{4}\gamma_l^2} + \frac{(\omega_l + \omega)}{(\omega_l + \omega)^2 + \frac{1}{4}\gamma_l^2} \right] \quad (14)$$

$$\alpha_{ij}''(\omega) = \frac{2\pi}{h} \sum_l \mu^{i0l} \mu^{j l0} \left[\frac{\frac{1}{2}\gamma_l}{(\omega_l + \omega)^2 + \frac{1}{4}\gamma_l^2} - \frac{\frac{1}{2}\gamma_l}{(\omega_l - \omega)^2 + \frac{1}{4}\gamma_l^2} \right] \quad (15)$$

The quantity, γ_l , is the rate of decay of the l -th(excited) state of the molecule due to the joint effect of collisions and spontaneous emission. In the

limit $\gamma_{\ell} \rightarrow 0$, $\alpha_{ij}''(\omega)$ becomes the difference of delta functions in accord with Fermi's Golden Rule.¹¹ We maintain γ_{ℓ} finite, in both Eq. (14) and (15) to avoid this singularity in the latter.

Eq. (2) is the real part of the first hyperpolarizability and is analogous to Eq. (14) with $\gamma_{\ell} = 0$. One notes that Eqs. (2), (14), and (15) all contain the same set of transition dipole matrix elements, so that if additivity applies to one, it should apply to all. We propose to demonstrate this by following closely the proof already available in the static case.

Applications

We envisage three important applications of the additivity principle as generalized to dispersing/absorbing systems:

1. We have already mentioned the concept of predicting molecular dipole hyperpolarizabilities from bond and atomic hyperpolarizabilities. Using the concepts demonstrated above for propionic acid and for the cyclic hexanes, we propose to construct a table of bond hyperpolarizability contributions found by solving appropriate linear systems of equations involving measured molecular hyperpolarizabilities. These tables will be used to predict the hyperpolarizabilities of molecules not yet synthesized.
2. The rate of energy loss of a fast charge particle (e.g. proton or alpha) moving through matter is determined by the optical properties of the material.¹² To understand this, one should note that the charge of the particle is the source of an electric field, and because the particle is moving, the field is time varying. However, by Fourier's theorem, a

time varying field may be decomposed into sinusoidal frequency components. Individually, these have the same effect on the material as light. By demonstrating the additivity principle, we shall show that fast charged particles lose energy in covalently bonded materials by depositing it in the individual chemical bonds. For a complex material such as a living cell, there are many types of molecules but a far fewer number of bond types. By showing that chemical bonds are the fundamental structure in energy loss, we will greatly simplify the study of the structure of ionization tracks, which is so important in radiation biology and chemistry.

3. In a dilute gas, $\alpha''(\omega)$ determines the intensities of spectral lines. In condensed matter, we have shown that both $\alpha'(\omega)$ and $\alpha''(\omega)$ are involved, combined in a non-linear way. By demonstrating the additivity principle, we shall show that the intensities of spectral lines are determined by the number and types of bonds in the molecules. This should permit us to examine regularities in spectra with new insight.

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