Computational Modeling of the Polarizability of Liquid Crystals

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Abstract

Using the molecular modeling packages *Maestro and NWChem*, several liquid crystals (LCs) commonly used in laser systems were modeled using Density Functional Theory (DFT) to determine their dielectric anisotropy ($\Delta \epsilon$) values computationally. The difference in polarizability ($\Delta \alpha$) between the parallel and perpendicular axes of an LC molecule was calculated by DFT and used as input to calculate $\Delta \epsilon$ for each compound. The calculated $\Delta \epsilon$ values were compared to existing experimental data for two materials to determine the validity of the model. The calculated values from the Maier-Meier equation and the experimental values from the literature for the LC materials PCH5 and 5CB agreed to 8% and 29%, respectively, with the best agreement between calculated and experimental values obtained for the material with smaller molecular polarizability. This model can be used for future design efforts to develop LC materials with large $\Delta \epsilon$, fast response, and high laser damage resistance for current and future applications in OMEGA, OMEGA EP and other laser systems.

1. Introduction

A liquid crystal (LC) is a substance that exhibits properties of both solid crystals and liquids. The molecules in a LC are more organized than those in liquids but are not rigidly ordered like those in solids. LCs are characterized by the order parameter (S), which measures the degree of organization between molecules. The value of S ranges from 0 for an isotropic liquid to 1 for a solid crystal and generally decreases as the temperature increases (Fig. 1). Most LC molecules have a long, parallel axis and a short, perpendicular axis. The general direction that the long axes of the LC molecules follow is called the director (n). The greater the deviation of individual LC molecules from the director, the smaller the value of S will be.



Fig 1: Comparison of the ordering in liquid crystals as a function of temperature.

LC's also exhibit various phases, each with their own molecular packing and orientation variations that affect their physical properties. For the nematic phase, the value of S ranges typically between 0.5 and 0.8. Nematic phase LC molecules are arranged in relatively random positions with their long molecular axes facing a similar direction. This unique behavior allows nematic LCs to exhibit anisotropy in their physical and optical properties. Optical anisotropy, or birefringence (Δn) is defined as the difference between the refractive index when the electric field is parallel (n_e) and perpendicular (n_o) to the molecular axis (Equation 1) while dielectric anisotropy ($\Delta \epsilon$) is defined as the difference in electric field permittivity (how much the electron distribution is affected when an electric field is applied) when the electric field is either parallel (ϵ_{\parallel}) to the long molecular axis (Equation 2).

$$\Delta n = n_e - n_o \tag{1}$$

$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \tag{2}$$

Birefringence and dielectric anisotropy are both related to the degree of electron density delocalization and polarizability (how easily the electrons of a material are affected by an electric field) of the LC molecular structure. In general, the larger the degree of electron delocalization

and polarizability, the larger the values of both Δn and $\Delta \varepsilon$ will be. *Unsaturated* LC materials [containing carbon ring structures with alternating single (σ) and double (π) bonds, shown in Fig. 2(a)], will be highly polarizable due to their high degree of electron delocalization, and as a result will exhibit both high Δn and $\Delta \varepsilon$. Ideally, this class of LC material would be preferred for both passive and electrically driven applications in high power lasers due to the smaller path length requirements and faster response times, but the large electron delocalization due to the overlapping π -bonds also results in significantly reduced laser damage thresholds ^[1].



Fig. 2: (a) Delocalized electron distribution in an unsaturated material; (b) saturated materials are composed primarily or exclusively of σ -bonded atoms.

Saturated LC materials [those that are composed primarily of σ -bonded atoms, as diagrammed in Fig. 2(b)] show significantly higher laser damage thresholds, but both the resultant Δn and $\Delta \varepsilon$ values will be smaller, as both are intrinsically linked to the degree of molecular electron delocalization and polarizability. Consequently, thicker path lengths and higher drive voltages will be required for existing LC devices to meet present and future requirements for passive or electrically driven applications in high power laser systems. Using computational chemistry design tools, an analysis of the effect of molecular structure on the polarizability of unsaturated or fully saturated LC materials was undertaken as the first step in designing materials that combine fast electro-optical switching potential with high laser damage resistance for high power laser applications.

2. Materials and Computational Methods

Modeling of the $\Delta \varepsilon$ of LC materials was accomplished using two computational chemistry modeling packages to generate the physical properties of the materials based on molecular structure. Two-dimensional molecular structures were drawn using *Maestro*, a software module of Schrodinger's *Material Science Suite*^[2,3], using its 2D ligand interaction function.

Maestro's molecular mechanics energy optimization routine was then applied to the structure to ensure that each atom was in its lowest energy conformation. The energy-minimized structures were then exported into the open source molecular modeling program *NWChem*^[4] for computation of polarizability, dipole offset (displacement of the separation between charges in a molecule away from the center of the molecule), and density using Density Functional Theory (DFT). For these computations the basis set 6-311++G** was used, as it was determined to be the best fit to these types of calculations based on the existing literature. One-hundred iterations were used for each simulation, with a total runtime for each calculation of ~1 hour on a Linux based supercomputing cluster with a total computational capacity of 7000 Xeon x86 CPUs and 200 TB of memory.

Figure 3 shows the molecular structures of the two LC molecules modeled in this study [4– cyano– 4'–pentylbiphenyl (5CB) and 4–*trans*–4–pentylcyclohexylbenzonitrile (PCH5)]. Both molecules are structurally similar in that they contain the same terminal functional groups (cyano and n-pentyl alkyl) and the molecular core is composed of two connected six-membered carbon rings, but for 5CB both rings are unsaturated (contain electron-rich π -bonds that are highly polarizable), whereas in PCH5 only one of the six-membered rings is fully saturated (contains only σ -bonds). The molecular polarizability is related to both the $\Delta \varepsilon$ and the birefringence (Δn), and thus the large polarizatility should also lead to a larger value of $\Delta \epsilon$ for 5CB. Concomitantly, the higher polarizability of 5CB reduces its resistance to laser damage ^[1].



Fig. 3: Molecular structures of unsaturated (5CB) and partially saturated (PCH5) LC materials modeled in this study.

The molecular polarizability output from NWChem calculated using DFT was used as input to the Maier-Meier equation (Equation 3) ^[5,6] to calculate the $\Delta \varepsilon$ for each LC material:

$$\Delta \varepsilon = \frac{NFh}{\varepsilon_0} \left[\Delta \alpha - F \frac{\mu^2}{2kT} \left(1 - 3\cos^2 \beta \right) \right] S$$
(3)

where $\Delta \epsilon$ is the dielectric anisotropy, N is the number of molecules per unit of density, h and F are the internal cavity field and reaction field factors for aspherical polarization, respectively, ϵ_0 is the permittivity of free space, $\Delta \alpha$ is the difference in polarizability between the long and short axes of the molecule (i.e., the polarization anisotropy), μ is the magnitude of the dipole moment, k is the Boltzmann constant, T is the temperature in degrees Kelvin, β is the angle between the dipole moment and the director (n), and S is the order parameter. For this series of calculations, the temperature was set to 293°K, S was 0.8 (a typical value for a nematic LC at room temperature), and μ was 5.95 Debye ^[7]. All calculations were conducted on a single molecule in the gas phase for simplicity to avoid the complexities and computational intensity required to take into account associative effects from neighboring molecules that occur in the condensed phase.

3. Results

Figure 4 compares the values of $\Delta \varepsilon$ for 5CB and PCH5 calculated from the Maier-Meier equation with experimental data for these two materials from the literature ^[8]. The agreement between calculated and experimental values of $\Delta \varepsilon$ was within 8% (PCH5) and 29% (5CB). The better agreement was for the material with smaller molecular polarizability (PCH5).



Comparison of calculated and experimental $\Delta\epsilon$ data for 5CB and PCH5

Fig. 4: Calculated and experimental values for $\Delta \varepsilon$ for the LC materials 5CB and PCH5. Better agreement between calculated and experimental values was observed for PCH5.

Maier-Meier calculations of this nature are susceptible to a range of errors that can be as large as 200% ^[9]. There are a number of factors that are responsible for these large deviations from experimental values. Because these calculations were performed on the basis of a single isolated molecule in the gas phase for simplicity, physical interactions between LC molecules in

the condensed phase (e.g., Van der Waal's forces and other electrostatic forces) that could have an effect on the molecular polarizability and $\Delta \varepsilon$ were neglected. Complex molecular dynamics calculations would have been required to account for these interactions, which was clearly beyond the scope and time frame of this project. The parameter assumptions for the values of S and T and the particular DFT basis set employed in the calculations (6-311++G**) all have an impact on the calculated value of $\Delta \varepsilon$. Future efforts should incorporate more accurate values for assumed parameters, other DFT basis sets, and molecular dynamics simulations to improve accuracy.

4. Conclusions

Overall, the calculated $\Delta\varepsilon$ for the LC materials 5CB and PCH5 are in relatively good agreement with previous experimentally determined values, which implies that DFT modeling using *NWChem* and the Maier-Meier equation is valid for qualitative estimation of the molecular polarizability of LC molecules whose molecular structures are similar and differ only by the number and distribution of π -bonds throughout the molecule. Although the model at this point is qualitative, incorporation of more advanced computational methods such as molecular dynamics simulations will allow more accurate prediction of $\Delta\varepsilon$ and other physical properties of LCs important for device applications in high-peak-power laser systems.

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