Optical Properties and van der Waals-London Dispersion Interactions in Inorganic and Biomolecular Assemblies

Daniel M. Dryden1*, Yingfang Ma1, Jacob Schimelman1, Diana Acosta1, Lijia Liu1, Ozan Akkus2, Mousa Younesi2, Islam Anowarul2, Linda K. Denoyer3, Wai-Yim Ching4, Rudolf Podgornik5, V. Adrian Parsegian5, Nicole F. Steinmetz6, Roger H. French1

1Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, U.S.A.
2Department of Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, OH 44106, U.S.A.
3Spectrum Square Associates Inc, Ithaca, NY 14850, U.S.A.
4Department of Physics and Astronomy, University of Missouri-Kansas City, Kansas City, MO 64110, U.S.A.
5Department of Physics, University of Massachusetts, Amherst, MA 01003, U.S.A.
6Department of Biomedical Engineering, Case Western Reserve University, Cleveland, OH 44106, U.S.A.
*corresponding author, daniel.dryden@case.edu

ABSTRACT

The optical properties and electronic structure of AlPO4, SiO2, Type I collagen, and DNA were examined to gain insight into the van der Waals-London dispersion behavior of these materials. Interband optical properties of AlPO4 and SiO2 were derived from vacuum ultraviolet spectroscopy and spectroscopic ellipsometry, and showed a strong dependence on the crystals’ constituent tetrahedral units, with strong implications for the role of phosphate groups in biological materials. The UV-Vis decadic molar absorption of four DNA oligonucleotides was measured, and showed a strong dependence on composition and stacking sequence. A film of Type I collagen was studied using spectroscopic ellipsometry, and showed a characteristic shoulder in the fundamental absorption edge at 6.05 eV. Ab initio calculations based on density functional theory corroborated the experimental results and provided further insights into the electronic structures, interband transitions and vdW-Ld interaction potentials for these materials.

INTRODUCTION

Mesoscale self-assembly has been identified as a promising area for technological development for energy applications [1]. Understanding and modeling the processes involved in self-assembly on scales above the atomic bond length requires a detailed knowledge of long-range interactions, including polar, electrostatic, and van der Waals-London dispersion (vdW-Ld) interactions [2]. Of these interactions, only vdW-Ld are therefore universally present. Understanding how these forces arise from the electronic structure of a material is paramount to the design of mesoscale systems. The vdW-Ld interactions in a material are directly linked to the interband optical properties of that material according to Lifshitz theory [3-5], with individual features having a large, nonlocal effect on the resulting vdW-Ld interactions [6]. Optical property measurements and calculation of subsequent vdW-Ld interaction strengths, as quantified by the
Hamaker coefficient $A_{121}$, have been well established in the fields of ceramics [2, 7-11], and we now turn our interest towards biological materials. Collagen is an important structural molecule [14,15] that, because of its rigidity and optical anisotropy, is expected to exhibit vdW-Ld torques like those seen in carbon nanotubes [16]. Double-stranded DNA oligonucleotides are well-studied systems that exhibit a wide range of long-range interactions, and their sequences may be varied to study the dependence of the vdW-Ld forces and optical properties on composition, stacking sequence, and conformation. Understanding these interactions is key to a range of applications in energy and medicine [1].

**EXPERIMENT**

**Ceramic sample preparation and measurement**

Quartz SiO$_2$, suprasil amorphous SiO$_2$ (a-SiO$_2$), and berlinite AlPO$_4$ were all studied using a vacuum ultraviolet variable angle spectroscopic ellipsometer (VUV-VASE) from J.A. Woollam Co., and a vacuum ultraviolet-laser plasma light source (VUV-LPLS) reflectometer; details of the sample preparation and measurement are described in detail elsewhere [9-13]. From the reflectance spectrum the reflected phase may be calculated according to the Kramers-Kronig Transform [17]

$$\theta(E) = -\frac{2E}{\pi} P \int_0^\infty \frac{\ln \rho(E')}{E'^2 - E^2} dE'$$  \hspace{1cm} (1)

where $\theta(E)$ is the reflected phase and $\rho(E)$ is the reflected amplitude.

**Calculation of Hamaker coefficients**

Complex optical properties, including index of refraction, extinction coefficient, absorption coefficient, complex dielectric function, and London dispersion spectrum $\varepsilon(i\xi)$ [4,5] may be calculated from the complex pair of reflectance and reflected phase [17]. $\varepsilon(i\xi)$ is used in the calculation of Hamaker coefficients using the Gecko Hamaker software suite, a free-and-open-source software platform [18] which implements Lifshitz theory for a range of materials and geometries. Hamaker coefficients were calculated for a geometry of two semi-infinite halfspaces of material 1 separated by a 0.2 nm interlayer film of material 2, denoted $A_{121}$, or for a semi-infinite half-space of material 1, a 0.2 nm interlayer film of material 2, and vacuum, denoted $A_{123}$, according to the equation

$$A_{121} = -6\pi L^3 F_{LD}$$  \hspace{1cm} (2)

where $L$ is the interlayer spacing and $F_{LD}$ is the vdW-Ld interaction free energy.[10]

**Calculation of electronic properties of collagen and DNA**

The atomic model of Type I collagen was obtained from Vesentini et al [19]. The structure of this 7-2 triple helix collagen is from GenBank (No. NP000079), and consists of 1135 atoms and 3246 valence electrons placed in a box of 30 Å × 30 Å × 100 Å. H atoms were added to each end to pacify the dangling bonds. DNA models consisted of 10 base pairs with Na$^+$ counterions
in a unit cell of 30 Å × 30 Å × 33.8 Å, and were periodic in the z-direction. Calculations used the OLCAO-DFT method, which is described in detail elsewhere [20].

**VUV-VASE Measurements of Collagen**

Type I bovine Collagen from Advanced Biomatrix Co. was prepared via electrocompaction [21,22] on a quartz substrate, resulting in a 4 µm thick film. The polarization-dependent reflectance of the sample was measured in an air environment over an energy range of 0.8 eV to 6.5 eV, and the complex index \( n + ik \) was calculated point-by-point from the measured ellipsometric constants, assuming optical anisotropy in the film and substrate.

**Decadic Molar Absorptivity Measurements of DNA Oligonucleotides**

Four compositions of double-stranded DNA (ds-DNA) oligonucleotides were obtained from IDT Inc. Samples consisted of ten base pairs, either all C-G (denoted CG10), all A-T (AT10), alternating bases (CGAT5), or five of one then five of the other (CG5AT5). Seven concentrations of each oligonucleotide were prepared in TE buffer, and their absorption was measured using a Thermo Scientific NanoDrop 2000. Measurements were taken over an energy range of 1.47 eV to 6.5 eV and fitted to the Beer-Lambert law to derive the decadic molar absorption.

**DISCUSSION**

Interband absorption spectra for quartz SiO2, a-SiO2, and berline AlPO4 are shown in Figure 1. The exciton peak at 10.4 eV and higher energy interband transitions are nearly coincident for all three materials, and may therefore be indexed to particular interband transitions by comparing with previous studies of SiO2 [10,12]. While certain similarities may be explained by the isomorphic crystal symmetry of AlPO4 and quartz SiO2, and others by the chemical similarity of quartz SiO2 and a-SiO2, the coincidence in spectral features between all three indicates that the features arise from electronic transitions within individual tetrahedral units: SiO4 tetrahedra in the quartz and aSiO2, and PO4 tetrahedra in the berline AlPO4. These results have important implications for the role of phosphate complex anions on the interband optical properties and vdw-Ld forces in other biological systems such as apatites or DNA [23,24].
Hamaker coefficients for systems involving AlPO₄ are shown in Table 1. When two half-spaces are separated by a water interlayer reduces the optical contrast, resulting in a smaller value. In the case of a thin film on a substrate in vacuum, the Hamaker coefficient can model the vDW-Ld contribution to wetting, with a negative A₁₂₃ indicating good wetting. The two systems show that AlPO₄ will wet on an Al₂O₃ substrate, but not vice-versa.

This methodology can be applied to biomaterials, and studies are underway to understand the optical properties of collagen and DNA. Figure 2a shows the total density of states (TDOS) for collagen, calculated by OLCAO-DFT; 2b shows the resulting anisotropically resolved theoretical absorbance (blue) and the isotropic absorbance calculated from VUV-VASE measurements (red). Spectral features at 4.86 eV 5.17 eV, 5.39 eV 5.95 eV, 6.27 eV, and 7.65 eV can be indexed according to prevalent features in the valence and conduction band states near the band gap, indicated by red arrows. Optical anisotropy is observed between the x and z directions of the molecule (2c), with

![Figure 2a) Density of states for type I collagen calculated by OLCAO-DFT b) Theoretical and experimental absorbance spectra of Type I collagen, and c) model Type I collagen's triple-helix structure](image)

features resulting from the projection of transition dipole vectors onto the optical axes. Work is ongoing to resolve these features according to the partial densities of states by individual residue.

Theoretical results provide insight on features observed in the experimental spectrum. The shift in energy between the theoretical and experimental spectra results from the well-documented [20] underestimation of the band gap in the LDA approximation of DFT. The shoulder seen in the experimental results at 6.05 eV may correspond to the first peak in the x spectrum at 4.86 eV; work is ongoing to measure the optical properties at higher energies in order to resolve other spectral features and to model the film anisotropically.

DNA can vary in composition, stacking sequence, chain length, and conformation, all of which affect its electronic structure and optical properties. UV-Vis absorbance spectroscopy is commonly used to determine the concentration of DNA in solution by measuring the magnitude of the 4.76 eV peak [25], but is also suitable for characterizing the electronic structure of the material. In Figure 3a, decadic molar absorption coefficients show major variations based on stacking sequence and composition. AT₁₀ shows a well-defined peak at 4.76 eV, as expected; CG₁₀, however, shows a broader peak with a maximum shifted up to 4.91 eV. CG₅AT₅ shows a spectral line shape somewhere between AT₁₀ and CG₁₀, but has a larger magnitude than either. CGAT₅ has a line shape very similar to CG₅AT₅, but exhibits significant hypochromicity. This results in a shift of the fundamental absorption edge to higher energies, an effect also observed in
copolymers when lengths of consecutive like monomers are eliminated [26]. Comparison to theoretical results (Figures 3b and 3c) elucidates certain observations for

![Decadic Molar Absorption Coefficients](image1)

**Figure 3a)** decadic molar absorption coefficients for AT10, CG10, CG5AT5, and CGAT5 ds-DNA oligonucleotides, **b)** theoretical and experimental absorption spectra for AT10, and **c)** theoretical and experimental absorption spectra for CG10.

CG10 and AT10: the first absorption feature for AT10 is narrow and well-defined, whereas CG10 shows a broader doublet at higher energies, corresponding to the differing feature shapes in experiment. Work is ongoing to extend these measurements to higher energies and to study oriented samples, as well as to run DFT calculations for CG5AT5 and CGAT5 oligonucleotides.

**CONCLUSIONS**

Understanding the electronic structure and optical properties materials is paramount to predicting their vdW-Ld behavior. We have demonstrated a methodology for measuring the optical properties of a material and calculating the behavior of the respective vdW-Ld interactions, using SiO2 and AlPO4 as case studies, while elucidating the role of the PO4 complex ion in the electronic structure and interband optical properties of phosphates, with implications for biological phosphates. Collagen exhibits a shoulder in its fundamental absorption edge that corresponds to a feature in *ab initio* spectra. DNA oligonucleotides also show substantial variation in their UV-Vis decadic molar absorption spectra, with dependence on both stacking sequence and composition; aspects of these results are corroborated by theoretical spectra. Work is ongoing to extend these experimental optical properties to higher energies, further index features with respect to the theoretical electronic structures and optical properties calculated, and calculate vdW-Ld forces and torques for these and other biomolecular systems.

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