

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

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## ABSTRACT

The optical properties and electronic structure of  $\text{AlPO}_4$ ,  $\text{SiO}_2$ , 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  $\text{AlPO}_4$  and  $\text{SiO}_2$  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  $\text{SiO}_2$ , suprasil amorphous  $\text{SiO}_2$  (a- $\text{SiO}_2$ ), and berlinite  $\text{AlPO}_4$  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]

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

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  $\epsilon(i\xi)$  [4,5] may be calculated from the complex pair of reflectance and reflected phase [17].  $\epsilon(i\xi)$  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

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

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  $30 \text{ \AA} \times 30 \text{ \AA} \times 100 \text{ \AA}$ . H atoms were added to each end to pacify the dangling bonds. DNA models consisted of 10 base pairs with  $\text{Na}^+$  counterions

in a unit cell of  $30 \text{ \AA} \times 30 \text{ \AA} \times 33.8 \text{ \AA}$ , 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  $4 \text{ \mu m}$  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  $CG_{10}$ ), all A-T ( $AT_{10}$ ), alternating bases ( $CGAT_5$ ), or five of one then five of the other ( $CG_5AT_5$ ). 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  $SiO_2$ , a- $SiO_2$ , and berlinite  $AlPO_4$  are shown in Figure 1. The exciton peak at 10.4 eV and higher energy interband transitions are nearly

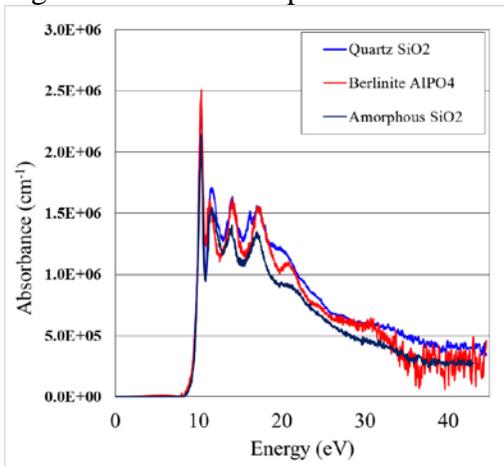


Table 1: Hamaker Coefficients

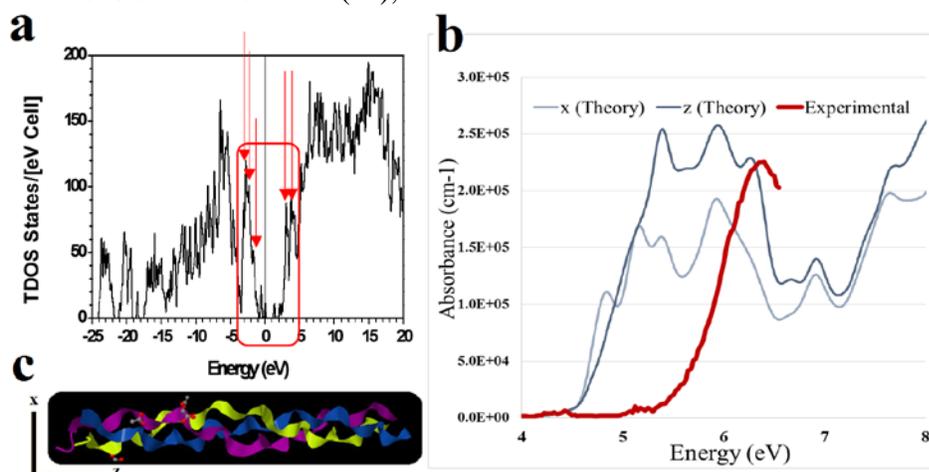
Physical Geometry	$A_{121}$
$(AlPO_4 - Vacuum - AlPO_4)$	87.5 zJ
$(AlPO_4 - water - AlPO_4)$	14.59 zJ
Physical Geometry	$A_{123}$
$(AlPO_4 - Al_2O_3 - Vacuum)$	50.55 zJ
$(Al_2O_3 - AlPO_4 - Vacuum)$	-36.41 zJ

Figure 1 VUV-LPLS absorption spectra for quartz  $SiO_2$ , amorphous  $SiO_2$ , and berlinite  $AlPO_4$ .

coincident for all three materials, and may therefore be indexed to particular interband transitions by comparing with previous studies of  $SiO_2$  [10,12]. While certain similarities may be explained by the isomorphous crystal symmetry of  $AlPO_4$  and quartz  $SiO_2$ , and others by the chemical similarity of quartz  $SiO_2$  and a- $SiO_2$ , the coincidence in spectral features between all three indicates that the features arise from electronic transitions within individual tetrahedral units:  $SiO_4$  tetrahedra in the quartz and a $SiO_2$ , and  $PO_4$  tetrahedra in the berlinite  $AlPO_4$ . 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  $\text{AlPO}_4$  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  $A_{123}$  indicating good wetting. The two systems show that  $\text{AlPO}_4$  will wet on an  $\text{Al}_2\text{O}_3$  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



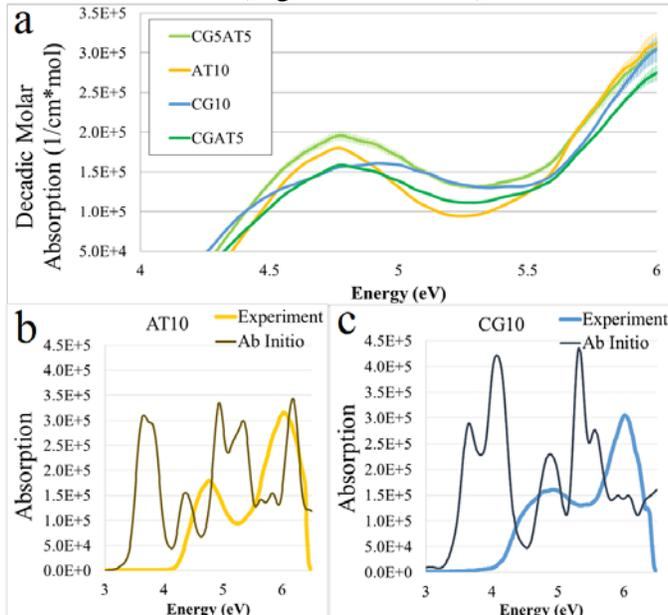
**Figure 2a) Density of states for type I collagen calculated by OLCAO-DFT b) Theoretical and experimental absorbance spectra of Type I collagen, and c) model Type I collagen's triple-helix structure**

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.  $\text{AT}_{10}$  shows a well-defined peak at 4.76 eV, as expected;  $\text{CG}_{10}$ , however, shows a broader peak with a maximum shifted up to 4.91 eV.  $\text{CG}_5\text{AT}_5$  shows a spectral line shape somewhere between  $\text{AT}_{10}$  and  $\text{CG}_{10}$ , but has a larger magnitude than either.  $\text{CGAT}_5$  has a line shape very similar to  $\text{CG}_5\text{AT}_5$ , 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



**Figure 3a)** decadic molar absorption coefficients for AT<sub>10</sub>, CG<sub>10</sub>, CG<sub>5</sub>AT<sub>5</sub>, and CGAT<sub>5</sub> ds-DNA oligonucleotides, **b)** theoretical and experimental absorption spectra for AT<sub>10</sub>, and **c)** theoretical and experimental absorption spectra for CG<sub>10</sub>.

CG<sub>10</sub> and AT<sub>10</sub>: the first absorption feature for AT<sub>10</sub> is narrow and well-defined, whereas CG<sub>10</sub> 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 CG<sub>5</sub>AT<sub>5</sub> and CGAT<sub>5</sub> 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 SiO<sub>2</sub> and AlPO<sub>4</sub> as case studies, while elucidating the role of the PO<sub>4</sub> 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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