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Theoretical study of the X-ray natural circular dichroism of some crystalline amino acids

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ABSTRACT

X-ray natural circular dichroism (XNCD) spectra of alanine and serine were calculated at the C, N, and O *K*-edges within the framework of density functional theory. Basis set and gauge dependence of D-alanine were examined as a test case. XNCD spectra of crystalline D-alanine and L-serine were obtained using cluster models of increasing size. The absolute intensities of the XNCD spectra were found to be reduced in the solid phase compared to the gas phase monomers, suggesting that a monomer model is not necessarily a good representation of the solid phase.

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1. Introduction

Chirality [1] is an important chemical property in particular for organic molecules and biomolecular systems containing asymmetric carbon atoms [2]. The chirality results in a difference in absorption and emission of left and right circularly polarized light which is exploited in several spectroscopies, such as vibrational circular dichroism (VCD) for infrared (IR) [3,4] and electronic circular dichroism (ECD) for ultraviolet–visible (UV–Vis) light. These spectroscopic techniques are useful to determine the absolute configuration in a molecule and are also found to be sensitive to the conformation, especially in the liquid phase.

Core-level spectroscopy using soft X-rays has undergone a strong development over the last two decades. In particular, X-ray absorption spectroscopy (XAS) has become a standard tool for investigating local structure through measurements of the electronic structure in gas phase or condensed phase [5]. Similar to VCD and ECD, CD effects are expected also when using soft X-rays, called X-ray natural circular dichroism (XNCD). Early observations of XNCD have been reported by Stewart et al. in enantiomorphic crystals of $Na_3Nd(digly)_3 \cdot 2NaBF_4 \cdot 6H_2O$ [6] and $2[Co(en)_3Cl_3] \cdot NaCl \cdot 6H_2O$. [7] Following their studies, the range of systems was extended to chiral organic compounds [8]. Tanaka et al. have succeeded to observe the XNCD signal for some amino acids [9–11]. Very recently, Izumi et al. improved XNCD spectra at the oxygen *K*-edge of some amino acids by measuring under thin film condition [12]. Note that the samples in the above experiments were in the solid phase in order to improve the signal.

XNCD has been studied theoretically by several groups [13–17]. For amino acids, XNCD has been discussed by Plashkevych et al. [14], Kimberg et al. [15], and Villaume et al. [17] using *ab initio* quantum molecular theory. However only line spectra were shown which were furthermore produced using a single gas phase molecule. There is thus a gap between the solid state experimental conditions and theoretical models.

In the present study, we have computed theoretical XNCD spectra within the framework of density functional theory (DFT). As a test case, we apply our procedure to alanine and serine not only for a single molecule but also for cluster models of the crystal structure where several molecules of these amino acids are included in the unit cell with different orientations. Geometries of our target molecules are shown in Fig. 1. We find that intermolecular interactions in the condensed phase have significant effects on the computed XNCD spectra.

2. Basic theory

The basic theory of XNCD has been described elsewhere [13–17]. In brief, the probability of X-ray absorption by excitation of the core electron to an unoccupied state is given in terms of the oscillator strength, which can be obtained from electric dipole moment integrals between the ground and core-excited states. The oscillator strength can be defined as the norm of the dipole

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vectors in the length and velocity formulations depending on the different gauge forms,

$$f^L_{\rm ge} = \frac{2}{3}\omega_{\rm ge}|\langle\Psi_g|\boldsymbol{r}|\Psi_e\rangle|^2 \tag{1}$$

$$f^V_{\rm ge} = \frac{2}{3}\omega^{-1}_{\rm ge}|\langle\Psi_g|\boldsymbol{\nabla}|\Psi_e\rangle|^2 \tag{2}$$

where ω_{ge} is the excitation energy from the ground to core-excited state, and $\boldsymbol{r}$ and $\boldsymbol{\nabla}$ denote the position and the gradient vector operators for electron i and are to be interpreted as $\boldsymbol{r} = \sum_i \boldsymbol{r}_i$ and $\boldsymbol{\nabla}_i = \sum_i \boldsymbol{\nabla}_i$. Note that these two forms should give the same value at the basis set limit. Comparison of the oscillator and rotational strengths computed in the different forms is thus a useful check for consistency of the results in particular excitation channels.

The intensity of the electronic circular dichroism is, on the other hand, described by the rotational strength, which is evaluated as the scalar product of the dipole and angular momentum vectors in the length and velocity representations,

$$R^L_{\rm ge} = \frac{1}{2c}\langle\Psi_g|\boldsymbol{r}|\Psi_e\rangle\cdot\langle\Psi_g|\boldsymbol{r}\times\boldsymbol{\nabla}|\Psi_e\rangle \tag{3}$$

$$R^V_{\rm ge} = \frac{1}{2c}\omega^{-1}_{\rm ge}\langle\Psi_g|\boldsymbol{\nabla}|\Psi_e\rangle\cdot\langle\Psi_g|\boldsymbol{r}\times\boldsymbol{\nabla}|\Psi_e\rangle \tag{4}$$

where c is the speed of light, and $\boldsymbol{r}\times\boldsymbol{\nabla}$ is to be interpreted as $\boldsymbol{r} = \sum_i \boldsymbol{r}_i \times \boldsymbol{\nabla}_i$. Note that the oscillator strength does not depend on the selection of the origin, while the rotational strength does depend on it [18]. A detailed derivation was given in the Supplementary Material in Ref. [18]. For matrix elements of the electric-dipole transition moment in the length and velocity representations, one has

$$\langle\Psi_g|\boldsymbol{r}(\boldsymbol{O}+\boldsymbol{a})|\Psi_e\rangle = \langle\Psi_g|\boldsymbol{r}(\boldsymbol{O})|\Psi_e\rangle \tag{5}$$

$$\langle\Psi_g|\boldsymbol{\nabla}(\boldsymbol{O}+\boldsymbol{a})|\Psi_e\rangle = \langle\Psi_g|\boldsymbol{\nabla}(\boldsymbol{O})|\Psi_e\rangle \tag{6}$$

where $\boldsymbol{O}$ means the origin and $\boldsymbol{O}+\boldsymbol{a}$ corresponds to the origin shifted from $\boldsymbol{O}$ to $\boldsymbol{O}+\boldsymbol{a}$, i.e., these terms do not depend on the origin of the coordinate. However, for matrix elements of the angular momentum transition moment, we can derive

$$\begin{aligned}\langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O}+\boldsymbol{a})\times\boldsymbol{\nabla}]_x|\Psi_e\rangle &= \langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O})\times\boldsymbol{\nabla}]_x|\Psi_e\rangle \\ &\quad + a_y\langle\Psi_g|[\boldsymbol{\nabla}]_z|\Psi_e\rangle - a_z\langle\Psi_g|[\boldsymbol{\nabla}]_y|\Psi_e\rangle\end{aligned} \tag{7}$$

$$\begin{aligned}\langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O}+\boldsymbol{a})\times\boldsymbol{\nabla}]_y|\Psi_e\rangle &= \langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O})\times\boldsymbol{\nabla}]_y|\Psi_e\rangle \\ &\quad + a_z\langle\Psi_g|[\boldsymbol{\nabla}]_x|\Psi_e\rangle - a_x\langle\Psi_g|[\boldsymbol{\nabla}]_z|\Psi_e\rangle\end{aligned} \tag{8}$$

$$\begin{aligned}\langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O}+\boldsymbol{a})\times\boldsymbol{\nabla}]_z|\Psi_e\rangle &= \langle\Psi_g|[\boldsymbol{r}(\boldsymbol{O})\times\boldsymbol{\nabla}]_z|\Psi_e\rangle + a_x\langle\Psi_g|[\boldsymbol{\nabla}]_y|\Psi_e\rangle \\ &\quad - a_y\langle\Psi_g|[\boldsymbol{\nabla}]_z|\Psi_e\rangle\end{aligned} \tag{9}$$

where, e.g., $[\boldsymbol{f}]_x$ means the x component of the operator $\boldsymbol{f}$. Thus, in the present formulation the rotational strength, which includes the angular momentum transition moment, does depend on the selection of the origin. Using Eqs. (7)–(9), the matrix elements are corrected to refer to the core-excited atom as origin such that the spectra of different conformers and structures are directly comparable.

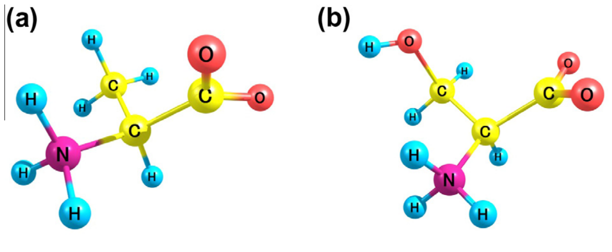

Fig. 1. Molecular geometries of (a) alanine and (b) serine.

3. Computational method

For the study of basis set and gauge dependence of XNCD spectra the geometry of molecular alanine in the gas phase was optimized using the GAUSSIAN 03 program [19] at the MP2/cc-pVTZ level of approximation. The crystal structures for the amino acids are well-known from X-ray diffraction and are obtained from the Cambridge Structural Database (CSD). In the present study, the geometry of the monomer is used for alanine [20] and serine [21] also when modeling the crystal.

The XA spectrum calculations were performed using the StoBe-deMon program [22] extended to compute the XNCD intensity; the detailed computational method for the XA spectroscopy has been described in previous reports [23–26]. In brief, the theoretical XA and XNCD spectra were generated by the transition potential (DFT-TP) method [23]. The gradient-corrected exchange (PD86) [27] and correlation functional (PD91) [28] established by Perdew and Wang was applied. The orbitals for the species in the excited states were determined using a half-occupied core orbital at the core-ionized site. The orbitals for the excited electron were then obtained by diagonalizing the Kohn–Sham matrix built from this density with the basis set extended by a large set of diffuse basis functions centered on the excited atom. The obtained orbital energies and computed transition moments provide the excitation energy and associated intensities in the theoretical absorption spectrum. The DFT-TP calculation of the spectrum corresponds to the static exchange approach [29] and, thus, the relaxation effect of the created ion core by adding the excited electron is neglected. This effect is the largest for valence-like excitations and, thus, these states were computed with fully-relaxed Kohn–Sham calculations [24]. For a more accurate estimate of the absolute excitation energy, relativistic and functional corrections were added to the excitation energy [30]. The relativistic corrections added to the ionization potential were 0.08 eV, 0.18 eV, and 0.33 eV for the C, N, and O *K*-edges, respectively. The non-core-excited atoms were described by effective core potentials [31]. Finally, the spectra were generated by a Gaussian convolution of the discrete lines by varying the broadenings.

4. Results and discussion

4.1. Basis set and gauge dependence

In Fig. 2, benchmark tests of the XNCD spectrum of D-alanine for C1 excitation are collected, where the C1 atom is the chirality-centered carbon atom. Spectra for other edges are collected in the Supplementary content. In Fig. 2(a), the basis set dependence is shown. Note that even carbon atoms which are not chirality-centered contribute to the total XNCD spectrum. We first focus on the selection of the basis set on the core-excited atom where it is well known that IGLO-III basis sets can reproduce relaxation effects in the core region well, allowing a reliable treatment upon creation of the core hole [23]. Kimberg et al. [15] also concluded that tight basis functions, as in IGLO-III, become important for description of relaxation effects involving the 1*s* core orbitals. From the figure we note that XNCD spectra computed with the IGLO-III basis set are comparable to those obtained with the very large cc-pV5Z basis set.

We also examined the gauge dependence of the XNCD spectra, i.e., comparing the length and velocity representations as shown in Fig. 2(b) and in the Supplementary Material for the other atoms.

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