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Theoretical Study of the Anisotropy Spectra of the Valine Zwitterion and Glyceraldehyde

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Abstract

The absorption, electric circular dichroism, and anisotropy spectra of the L-valine zwitterion and D-glyceraldehyde are calculated by time-dependent density functional theory with the M06-2X and B3LYP functionals. It is found that the absorption and ECD spectra from TDDFT/M06-2X agree well with the experimental result measured from the L-valine amorphous film. Moreover, the theoretical calculation reproduces all three major peaks observed on the experimental anisotropy spectra. For D-glyceraldehyde, the TDDFT/M06-2X calculation indicates the excitation wavelengths of the first excited state of 32 stable conformers distribute from 288 to 320 nm, giving rise to two ECD peaks centered at 288 nm and 335 nm with the opposite sign. Both the anisotropy spectra of the L-valine zwitterion and D-glyceraldehyde exhibit a high negative peak in the ultraviolet (UV) region, which may lead to enantioenrichment of them by exposing the racemic films to the circular polarized light.

1 Introduction

The basic units of biochemical macromolecules of a given class, such as nucleic acids and proteins, are molecules with identical stereo-chemical L- or D-configurations, when chiral. For example, all chiral amino acids found in natural, ribosomally synthesized oligopeptides and proteins have a left-handed configuration, while nucleic acids possess a backbone composed exclusively of D-sugars. It is still unclear why life on Earth demonstrates such an intriguing asymmetry at the molecular level. A promising hypothesis is that photochemical processes in extraterrestrial space induced synthesis and enantioenrichment of the chiral organic molecules,^{1,2} which were delivered to the early Earth by meteorites or comets.³ Experiments that simulate the photochemical evolution of interstellar ice analogs have synthesized several amino acids.^{4,5} Other studies have identified the formation of DNA and RNA related molecules such as aldehydes, ribose, and related sugars in ultra-violet irradiated interstellar ice analogs.^{6,7} Furthermore, enantiomeric excesses (*ee*) of amino acids were obtained in

experiments where circularly polarized (CP) light, known to exist in astrophysical environments, was introduced.⁸⁻¹⁰ All these experimental evidence support an astrochemical origin of chiral, building block molecules for life on Earth.

The enantioselection of the chiral molecules exposed to CP light arises from the different absorption capacity of the enantiomers. That is, both left-hand and right-hand enantiomers absorb CP light, however, one has a slightly smaller absorption coefficient than the other, hence it will be photo-destroyed less rapidly and an initial racemic mixture will be enantioenriched. The reaction rate of photo-induced *ee* is mainly determined by the anisotropy factor g ,¹¹

$$g = 2 \frac{\varepsilon_R - \varepsilon_S}{\varepsilon_R + \varepsilon_S}$$

in which ε_R and ε_S are the molar absorption coefficients of the right-hand and left-hand enantiomers, respectively.

The anisotropy spectra $g(\lambda)$ can be derived from the absorption and electronic circular dichroism (ECD) spectra. Experiments using synchrotron radiation have extended the ECD spectra deep into the vacuum ultraviolet (VUV) region,¹²⁻¹⁶ reporting the anisotropy spectra of several amino acids.¹⁷ However, the derivation of the anisotropy spectra from experimental absorption and ECD spectra usually depends upon the segmentation of the latter into slices of somewhat arbitrary finite sizes to compute their ratio. In contrast, a theoretical anisotropy factor can be calculated simply as $g = \frac{4R}{D}$, where R is the rotational strength and D is the dipole strength of a chiral molecule, as discussed by Schellman more than forty years ago.¹⁸ Surprisingly, comparing with the experimental progresses, theoretical works which evaluate $g(\lambda)$, remain scarce with the exceptions of Refs. 10, 19.

This is arguably because it is a challenging task to obtain a theoretical anisotropy spectrum that agrees well with an experimental one. Firstly, experimental anisotropy spectra of amino acids have been evaluated so far by measuring absorption and ECD spectra of

amorphous films on an MgF_2 window. Theoretical calculations are usually carried out for isolated molecules, sometimes for molecules in solution but even in this case, comparison with experiments may be difficult, because there are strong differences between the ECD spectra recorded in amorphous solid state and in solution.¹⁹ Secondly, chiral molecules are floppy with many stable geometries distributed in a small energy window. Experimental spectra are the result of the Boltzmann statistical average of all energetically favoured structures, which, if some internal rotations are hindered, as it seems to be the case in alanine amorphous film for example,²⁰ can be a subset only of all low energy nuclear geometries. Nevertheless, to simulate such spectra, theoretical calculations should sample a large conformational space and locate all relevant structures corresponding to local minima of the energy. Finally, amino acids and sugars have plenty of bright states in the ultraviolet (UV), including in the VUV region, while it is not easy to calculate precisely, lots of high-lying excited states at the same time.

A popular workhorse to calculate the molecular excited states and ECD spectra is time-dependent density functional theory (TDDFT).^{21–24} Although TDDFT does not provide multi-excited states and the fact that predicted, mono-excited energy levels may vary depending on the selected exchange-correlation (XC) functional, fairly satisfactory ECD spectra have been obtained in previous studies.^{25,26} In this article, the anisotropy spectra $g(\lambda)$ of two chiral molecules, namely valine and glyceraldehyde, will be investigated. A previous theoretical work on the ECD spectra of the valine zwitterion has produced a theoretical spectra in reasonably good agreement with experiment, with the help of an artificial blue-shift of the energy levels.^{14,16} We will show that TDDFT can produce reasonable anisotropy spectra for valine amorphous film without blue-shift, provided that the right functional is used. Regarding glyceraldehyde, whose experimental anisotropy spectra has not been published yet, we will present the first theoretical calculation with the same functional validated for valine. Recalling that glyceraldehyde formation has been detected in interstellar ice analog experiments,⁶ this anisotropy spectra might shed light on the origin of sugar homochirality

in nucleic acids.

The article is organized as follows, we present the details of our calculation in section 2. In section 3, we will first discuss the conformers, absorption and ECD spectra of the valine zwitterion and glyceraldehyde, obtained from different theoretical calculations. Then, the anisotropy spectra of the two species will be analysed. Section 4 will give a brief conclusion.

2 Computational methods

The experimental ECD spectra are the results of a statistical average of energetically allowed conformations. Therefore, a conformational search was performed for valine and glyceraldehyde. The valine molecule exists in the form of a zwitterion in the studied, amorphous films¹⁵ the proton from the carboxy group in the neutral form is transferred to the amino group. Direct optimization of the zwitterionic structure always results in the proton transferring back to the carboxy group. Therefore, the three N-H bond lengths of the amino group were constrained to 1.10 Å and only the other internal coordinates were relaxed in geometry optimizations. Three optimized structures labelled as *Trans/Gauche+*, *Gauche+/Gauche-* and *Gauche-/Trans*, drawn in Figures 1(a), 1(b), 1(c), respectively, were obtained for the L-valine zwitterion by density functional theory (DFT) with M06-2X functional²⁷ and cc-pVTZ basis set.²⁸ The Cartesian coordinates of the optimized geometries are presented in table S1 and S2 of supporting information (SI). For D-(+)-glyceraldehyde, that is (2R)-2,3-dihydroxypropanal, DFT with B3LYP functional²⁹ and cc-pVTZ basis, allowed us to locate 32 equilibrium structures by starting the optimization from different initial geometries obtained by rotating by intervals of 10 degrees the dihedral C1C2C3O1 and O5C1C2C3 angles (see Figure 1(d)). The geometries were reoptimized at M06-2X/cc-pVTZ level. Frequency analyses were performed for all these structures to check that there were no imaginary frequencies. All geometries are presented in table S3 to S10 in SI.

TDDFT calculations were carried out to calculate the absorption and ECD spectra of

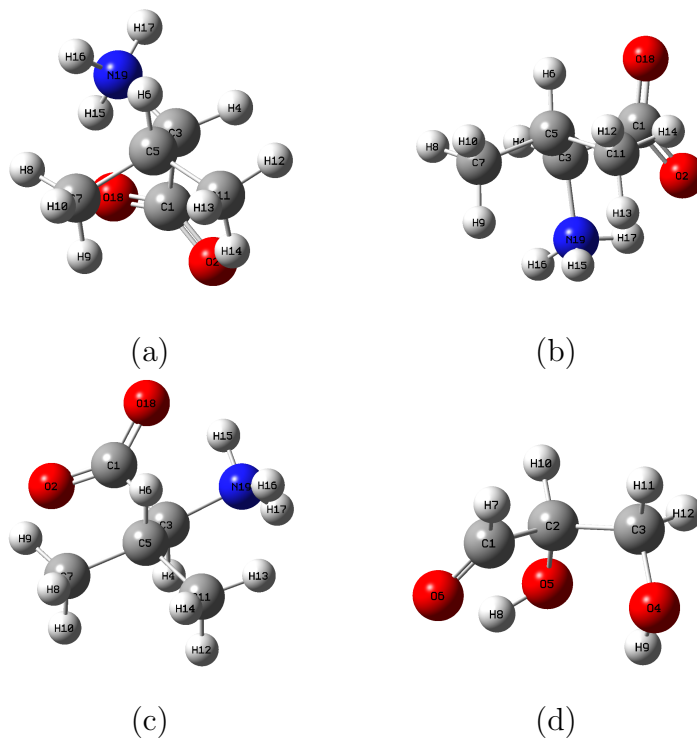


Figure 1: Three Optimized structures of the L-Valine zwitterion and the lowest energy geometry of D-glyceraldehyde. (a) *Trans/Gauche+*; (b) *Gauche+/Gauche-*; (c) *Gauche-/Trans*; (d) D-glyceraldehyde

the target species. For estimating the influence of basis sets on excitation energy, larger basis sets cc-pVQZ, aug-cc-pVTZ and aug-cc-pVQZ were used with TDDFT/B3LYP and TDDFT/M06-2X to calculate the first 30 excited states of glyceraldehyde at the lowest energy geometry obtained with the B3LYP functional. The excitation wavelengths and oscillator strengths are listed in table S10 and S11 in SI, respectively. As seen in these tables, the excitation energies of the first three excited states are not sensitive to the level of basis sets used, as indicated by the small red-shift of less than 2 nm between the cc-pVTZ and aug-cc-pvQZ results (except for the third energy level with the M06-2X functional, where it reaches 5 nm). However, the excitation wavelengths of other states are systematically reduced by more than 10 nm when diffusion functions are added, while extending basis sets from 3 to 4 sets of valence orbitals does not change significantly the energy differences. This is observed for both functionals. Therefore, aug-cc-pVTZ basis sets are adopted for glyceraldehyde to calculate the excitation energies. In contrast, we retain the cc-pVTZ rather than the aug-cc-pVTZ basis set for the valine zwitterion for reasons that will be explained in the next section.

For assessing the XC functional dependence of the excitation energies, five XC functionals B3LYP,²⁹ PBE0,³⁰ CAM-B3LYP,³¹ ω B97X-D,³² and M06-2X²⁷ ordered by increasing amount of the Hartree-Fock (HF) exchange, were used to calculate 30 excited states of glyceraldehyde at the lowest energy geometry optimized from B3LYP with cc-pVTZ basis sets. Excitation energies and oscillator strengths are presented in table S12 in SI. The absorption and ECD spectra of all five functionals are drawn in Fig. S2 of SI. The overall trend is that the excitation wavelengths are blue-shifted when adding more HF exchange with the exception of the first excited state. The M06-2X yields the longest excitation wavelength of 289 nm for the S1 state while the results of PBE0, CAM-B3LYP and ω B97X-D are close to 270 nm. It is noteworthy that a preliminary experimental study has recorded a weak absorption near 290 nm, with no other bump above 195 nm.³³ This is only compatible with the M06-2X result (which also gives a reasonable IR spectra for glyceraldehyde, as presented

in Fig. S1 of supporting information). However, we will also present B3LYP results for sake of comparison.

For each equilibrium structure, the TDDFT dipole and rotational strength peaks were broadened by Gaussian convolution with the full width at half maximum (FWHM) 12 nm and 10 nm for absorption and ECD spectra, respectively. Then, to simulate the experimental conditions, in the absence of precise structural information for the molecules in amorphous films, all these spectra were averaged according to the Boltzmann weights of the corresponding structures,

$$w_i = \frac{e^{-\varepsilon_i/k_B T}}{\sum e^{-\varepsilon_i/k_B T}} \quad (1)$$

where ε_i is the energy difference of the i th geometry with the lowest one, k_B is the Boltzmann constant and T is temperature with the value of 300 Kelvin. Notice that we use total energy to calculate the Boltzmann weight rather than the Gibbs free energy, and that zero point energy corrections are neglected. All calculations have been performed with the Gaussian 09 package.³⁴

3 Results and discussion

3.1 Structures, absorption and ECD spectra of the L-valine zwitterion

Table 1 presents for different geometries of the valine zwitterion, the relative total energies, the excitation energy of the first excited states, three dihedral angles and their types according to the conformation classification of Ref. 35 (labelling that is based on the last two dihedral angles). The first three rows correspond to the optimized structures of Figure 1 (a)-(c). The structures of the 4th and 5th rows correspond to the geometries of the first and third rows, respectively, except for the dihedral angles which are those of the related X-ray structures.³⁵ The structures of the 6th and 7th rows are interpolated between the structures

1 and 4, while those of row 8 and 9 are interpolated between 3 and 5.

As seen in Figure 1a-1c and Table 1, the dihedrals N19C3C1O2 in all three optimized geometries are small due to the strong hydrogen bond between COO^- and NH_3^+ hindering rotation of COO^- . However, it is the inter-molecular hydrogen bond that stabilizes the valine zwitterion in the crystal. Therefore, the intra-molecular interaction between COO^- and NH_3^+ in the solid phase is weaker, giving rise to a larger dihedral angle N19C3C1O18 in the two geometries found in the crystal. The energies of the latter structures are only 6.72 and 7.82 KJ/mol higher than that of the optimized one, suggesting that thermal fluctuations can induce the distortion of three main dihedrals easily. To consider these possible geometrical fluctuations, linear interpolations of the three dihedral angles were performed between the optimized geometries and their counterparts in the valine crystal, giving the four structures (6th-9th rows) listed in Table 1. Then the absorption, ECD, and anisotropy spectra of the nine structures were averaged with Boltzmann weight according to Eq. (1).

Table 1: Relative total energy ΔE , excitation wavelength λ of the first excited state, three main dihedrals, and the structural type of 9 conformers of L-valine zwitterion.

<i>No.</i>	ΔE (KJ/mol)	λ (nm)	N19C3C1O18 (°)	N19C3C5C11 (°)	N19C3C5C7 (°)	Type
1	0.00	211	-5.6	-168.2	68.3	<i>Trans/Gauche+</i>
2	0.05	211	1.0	60.3	-66.1	<i>Gauche+/Gauche-</i>
3	10.48	212	-11.4	-61.8	175.7	<i>Gauche-/Trans</i>
4	6.72	214	-22.2	-154.4	81.1	<i>Trans/Gauche+</i>
5	18.30	221	-37.7	-52.4	-175.6	<i>Gauche-/Trans</i>
6	4.99	212	-11.1	-163.6	72.6	<i>Trans/Gauche+</i>
7	19.80	213	-16.7	-159.0	76.8	<i>Trans/Gauche+</i>
8	14.09	216	-20.2	-58.7	178.7	<i>Gauche-/Trans</i>
9	29.01	214	-28.9	-55.3	-178.7	<i>Gauche-/Trans</i>

The Boltzmann weighted absorption and ECD spectra of the L-valine zwitterion are drawn in Figure 2(a) and 2(b), respectively. The excitation wavelengths, oscillator strengths, and rotatory strengths of the first 20 excited states of the lowest-energy geometry are listed in Table 2 for both M06-2X and B3LYP functionals, for comparison.

Generally speaking, the absorption spectra from TDDFT/B3LYP has a noticeable red-shift compared to the M06-2X one, as seen in Figure 2(a). As can be seen in Table 2,

the first excited state from the TDDFT/M06-2X calculation locates at 211 nm with a small oscillator strength of 0.0016. The S2 state has an excitation wavelength of 197 nm and larger oscillator strength of 0.0081, indicating the stronger absorption than that of S1. However, the first two excited states from TDDFT/B3LYP locate at 257 nm and 225 nm, with the oscillator strengths 0.1770 and 0.0013, respectively. In the experimental spectra, the Valine film starts to absorb the UV light from 215 nm, and has a sharp rise at 195 nm, suggesting that the absorption of S1 is weaker than S2.^{14,17} Therefore, TDDFT/M06-2X produces more reasonable results than TDDFT/B3LYP taking into account the excitation energies, the oscillator strengths, and also the energy gap between S1 and S2.

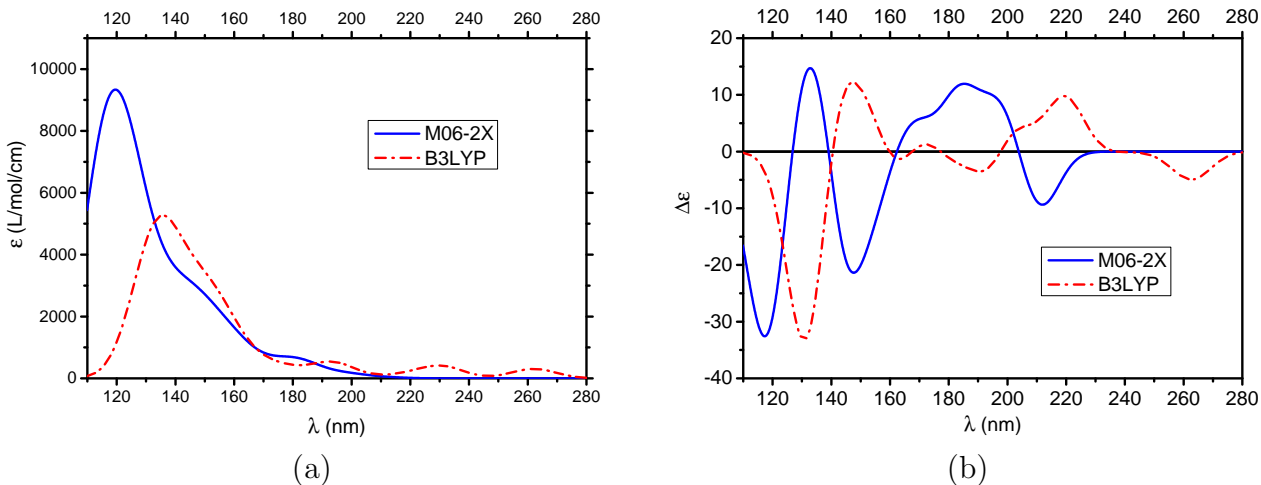


Figure 2: Absorption and ECD spectra of the L-valine zwitterion: (a) absorption spectra (b) ECD spectra.

Natural transition orbital (NTO) analysis from TDDFT/M06-2X (see in Figure 3) shows that the S1 state arises from a $n \rightarrow \pi^*$ transition, where n is a C1-C3 bonding orbital mixed with lone pair orbitals from two oxygen atoms, and the π^* orbital is an anti-bonding one between C and O in COO^- . The hole NTO of S2 is the same as that of S1 but the particle NTO mainly distributes on the NH_3^+ group. Interestingly, NTOs from TDDFT/B3LYP indicate that the S1 and S2 states are exchanged. TDDFT/M06-2X using aug-cc-pVTZ basis sets also give the inverse order for S1 and S2 states like TDDFT/B3LYP. Thus, we adopt the cc-pVTZ basis sets to calculate the valine zwitterion.

The absorption of the valine film has a sharp rise from 185 nm to 170 nm (see supporting information of Ref.¹⁷), giving rise to a shoulder structure on the experimental spectra. In agreement with this, we could identify a shoulder structure near 180 nm in the theoretical spectra that arises from the S3 and S4 states at 181 nm and 178 nm. These states have much larger oscillator strengths than those of the nearby states, as demonstrated in Table 2. Furthermore, we can locate another shoulder from 170 nm to 135 nm on the theoretical spectra, which should correspond to the shoulder from 170 to 155 nm in the experimental work. As can be seen in Table 2, several excited states, from S6 to S19, are distributed in this region. All of them have substantial oscillator strengths. Generally speaking, TDDFT/M06-2X produces an absorption spectra that agrees well with the experimental measurement.

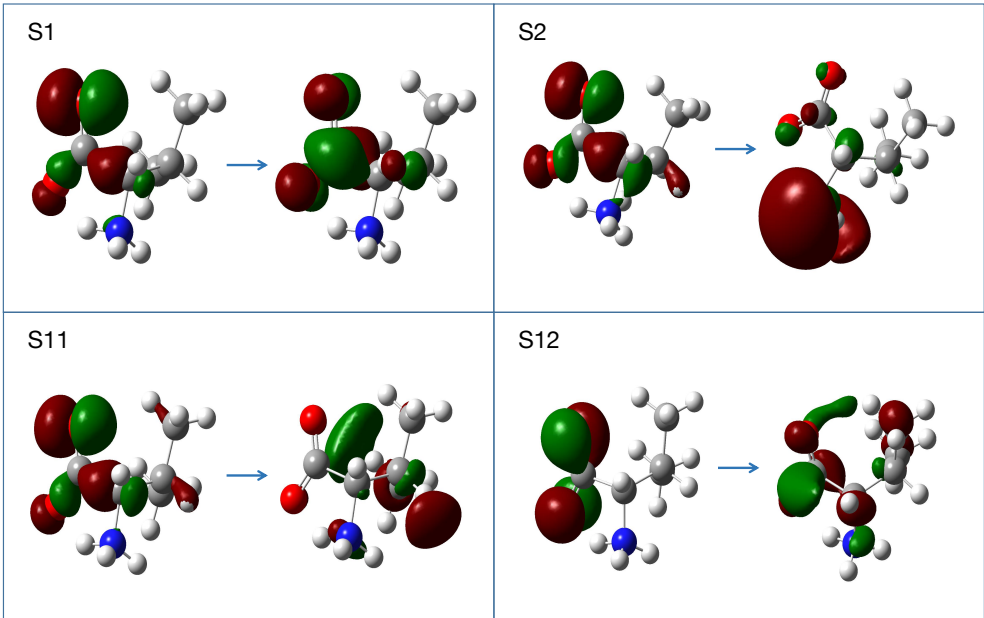


Figure 3: Natural transition orbitals (NTO) of the S1, S2, S11 and S12 states of the valine zwitterion from TDDFT/M06-2X. Left is the hole NTO.

It is more difficult to obtain a theoretical ECD spectrum of the valine film that matches well the experimental measurements. The experimental ECD spectra are characterized by five peaks at 213(-) nm, 188(+) nm, 165(-) nm, 149(+) nm and 137(-) nm, respectively.¹⁴⁻¹⁶ The peak at 213(-) nm should arise from the S1 state, as supported by the small negative peak centered at 211 nm in the theoretical calculation. The peak centered at 188(+) nm has

Table 2: Comparing the excitation wavelength λ , dipole oscillator strength f , and rotatory strength R of the first 20 excited states the L-valine zwitterion on its lowest-energy geometry calculated by TDDFT/M06-2X and TDDFT/B3LYP

State	M06-2X			B3LYP		
	$\lambda(\text{nm})$	f	R	$\lambda(\text{nm})$	f	R
1	211	0.0012	-12.2511	257	0.0177	-6.6521
2	197	0.0081	13.9018	225	0.0013	-1.4187
3	181	0.0130	18.4377	223	0.0120	4.1660
4	180	0.0016	3.0047	218	0.0070	25.8166
5	178	0.0113	-4.9941	209	0.0034	-3.3600
6	169	0.0146	3.6546	191	0.0037	-15.4107
7	161	0.0176	8.4576	189	0.0055	3.1835
8	157	0.0208	-7.1196	188	0.0034	-0.3084
9	154	0.0044	-13.9811	183	0.0053	-0.9284
10	151	0.0406	0.0706	178	0.0074	4.0803
11	147	0.0202	-16.1892	174	0.0051	-7.2763
12	143	0.0347	-30.342	166	0.0016	2.3315
13	141	0.0040	-0.7203	164	0.0069	6.3020
14	139	0.0047	-9.8122	160	0.0172	-5.8125
15	138	0.0165	27.8018	159	0.0078	8.6033
16	136	0.0051	6.4944	156	0.0012	7.1900
17	136	0.0115	-5.5526	153	0.0059	5.5724
18	136	0.0075	14.6826	152	0.0124	-8.9647
19	135	0.0143	12.1560	151	0.0046	1.8114
20	133	0.0119	-10.1010	150	0.0088	-3.0247

a smooth shape and spreads from 195 to 175 nm. The shape of the theoretical spectra from 205 to 162 nm is irregular, and three peaks at 197 nm, 185 nm and 165 nm with positive signs can be identified in this region. Moreover, the experimental spectra have a large negative peak at 165 nm. On the theoretical side, we assign the peak at 148 nm as the peak at 165(-) nm because this peak only appears on the experimental spectra of amino acid with the alkyl group in the side chain.¹⁶ As demonstrated in Table 2, the S11 and S12 states at 146 nm and 143 nm have a large rotatory strength that can produce a high negative peak. The hole NTOs of these two states largely spread on the CH₃ group (Figure 3), supporting speculations from experimental studies.¹⁶ The other two peaks at 149(-) nm and 137(+) nm also shift to the blue region at 133 and 118 nm in the theoretical calculation. Tanaka et al. had calculated the ECD spectra of the valine zwitterion by averaging two geometries from the crystal structure.¹⁶ Besides, the B3LYP functional and 6-31+G(d,p) basis sets were used in their work. Notice that their spectra had been blue-shifted by 0.6 eV to adjust the ECD peaks to the experimental measurement. In contrast, the ECD spectra in this work are obtained with no artificial shift, for a match to experiments by no means inferior to Tanaka’s results.

3.2 Structures, absorption and ECD spectra of glyceraldehyde

Table 3 lists the relative total energy, excitation wavelength, dipole oscillator strength, rotatory strength of the first excited state, and two dihedral angles of 32 optimized structures of D-glyceraldehyde calculated by TDDFT/M06-2X with aug-cc-pVTZ basis sets. The Boltzmann weighted absorption and ECD spectra of D-glyceraldehyde from TDDFT with M06-2X and B3LYP functionals are presented in Figure 4. The excitation wavelength λ , dipole oscillator strength f , rotatory strength R of the first 20 excited states of the lowest-energy geometry of D-glyceraldehyde calculated by TDDFT with two different functionals are presented in Table 4 for comparison.

Several authors have previously studied glyceraldehyde conformers both theoretically and

Table 3: Relative total energy ΔE , excitation wavelength λ of the first excited state, dipole oscillator strength f , rotatory strength R , and two main dihedrals of 32 conformers of D-glyceraldehyde.

<i>No.</i>	ΔE (KJ/mol)	λ (nm)	f	R	O6C1C2C3 ($^\circ$)	C1C2C3O4 ($^\circ$)
1	0	288	0.0001	-6.4499	-126.3	60.3
2	4.66	293	0.0003	-12.3435	-118.2	178.7
3	7.47	319	0.0003	11.9961	8.3	64.5
4	9.40	294	0.0001	-8.2137	-123	-62.9
5	10.70	294	0.0001	-10.3402	-124.4	-63.1
6	12.24	315	0.0000	-9.6257	48.6	70.4
7	13.46	287	0.0001	2.2599	-125.3	50.7
8	14.37	311	0.0001	-0.3631	44.1	178.3
9	15.98	309	0.0001	-0.3252	30.0	-68.9
10	15.70	313	0.0001	3.2308	59.9	174.5
11	17.71	320	0.0002	4.9252	16.9	-64.8
12	17.14	315	0.0006	-12.8125	-91.9	68.0
13	18.55	321	0.0001	6.8206	70.9	-180
14	18.92	318	0.0000	5.2564	78.9	61.8
15	19.82	309	0.0001	3.6866	61.3	63.6
16	19.21	292	0.0001	-6.5259	-124.7	-163.9
17	22.10	322	0.0002	3.0277	30.2	-175.7
18	21.06	294	0.0002	-12.1897	-123.9	-174.1
19	27.25	303	0.0001	-8.5460	-123.1	60.5
20	27.01	315	0.0002	7.7219	23.4	53.4
21	27.30	308	0.0001	-3.4812	-118.5	-177.9
22	29.65	310	0.0001	-5.4518	-115.6	177.8
23	29.98	320	0.0001	1.2921	135.0	-57.6
24	29.90	315	0.0000	3.7045	78.8	53.1
25	31.89	322	0.0002	5.4518	63.5	-170.8
26	35.41	313	0.0002	6.9185	97.4	-69.6
27	36.62	322	0.0001	7.9033	-20.9	-68.4
28	36.86	311	0.0001	-6.6276	-125.5	-66.3
29	37.18	317	0.0000	1.8084	112.2	-58.5
30	39.25	312	0.0001	-6.8418	-126.4	-62.9
31	39.86	313	0.0001	1.5423	9.2	-76.0
32	41.74	318	0.0001	6.1216	5.0	-75.2

experimentally, see Refs.³⁶⁻⁴⁰ to quote a few. As can be seen in Table 3, the geometry with the highest total energy is only 41.74 KJ/mol above the lowest one, indicating that glyceraldehyde is very floppy. Notice that Vogt and co-workers have located 36 conformers with B3LYP/cc-pVTZ calculations by hunting them on a 5-dimensional section of the potential energy surface.⁴⁰ Among these conformers, 31 can be identified in our results. However, their B3LYP/cc-pVTZ energy ordering of the lowest 5 conformers differs from our M06-2X/aug-cc-pVTZ ordering, in that our third conformer is found only in fifth position. The B3LYP/cc-pVTZ ordering is the same as that found by Lovas et al. at MP2/6311++G** calculation level (but starting from B3LYP results).³⁹ In contrast, the M06-2X/aug-cc-pVTZ ordering of the first five conformers is the same as that of the MP2/cc-pVQZ calculations of Vogt et al. (see supporting information).⁴⁰ Note that in support to the latter ordering, a microwave study has identified our 3 first conformers but neither the 4th nor the 5th conformer that B3LYP/cc-pVTZ and MP2/6311++G** found lower in energy.

As seen in Table 3, the distribution of excitation wavelengths of the S1 state of 32 the tabulated geometries range from 288 to 322 nm. Interestingly, the oscillator strength of S1 at the lowest energy geometry is close to zero while some other geometries have larger oscillator strengths, indicating that internal rotation could be responsible for the absorption of glyceraldehyde in this region. These small oscillator strengths give rise to a tiny absorption peak centered at 318 nm as shown in Figure 4(a). The NTOs displayed in Fig.5 show that the hole NTO of the S1 state is a combination of an O6 lone pair with the C1-C2 σ -bonding orbital. The particle NTO is an anti-bonding π^* orbital of the C1=O6 double bond. This observation supports our hypothesis that the distortion of the O6C1C2O5 dihedral angle can promote the absorption of S1. Another interesting finding is that the rotatory strengths of S1 for different conformers can have opposite signs, leading to two moderate opposite peaks centered at 288 nm and 335 nm on the ECD spectra after statistical averaging. More precisely, the third conformer has a positive rotatory strength while the four other conformers in the five lowest ones have negative rotatory strengths. Therefore, ECD spectra may be

Table 4: Comparing the excitation wavelength λ , dipole oscillator strength f , rotatory strength R of the first 20 excited states of D-glyceraldehyde on its lowest-energy geometry calculated by TDDFT/M06-2X and TDDFT/B3LYP.

State	M06-2X			B3LYP		
	$\lambda(\text{nm})$	f	R	$\lambda(\text{nm})$	f	R
1	288	0.0001	-6.1035	275	0.0001	-7.9344
2	185	0.0270	-19.8234	230	0.0151	-0.7521
3	170	0.0133	3.3057	204	0.0062	-13.5072
4	167	0.0099	1.8848	169	0.0062	3.6294
5	165	0.0006	-7.2808	165	0.0023	12.7276
6	163	0.0085	-15.1908	163	0.0044	5.7125
7	157	0.0713	40.6152	160	0.0118	3.9061
8	155	0.0121	7.9807	159	0.0087	-26.8748
9	154	0.0089	16.3031	154	0.0880	22.8567
10	149	0.0247	-17.1176	149	0.0208	3.2984
11	148	0.0112	1.5426	144	0.0107	0.4992
12	147	0.0149	-13.4758	143	0.0381	4.9907
13	146	0.0112	19.3435	141	0.0455	13.9929
14	142	0.0052	4.3228	140	0.0244	-28.6825
15	141	0.0034	4.7636	139	0.0144	3.3023
16	140	0.0061	3.4244	138	0.0051	-4.6863
17	139	0.0054	-9.0742	135	0.0436	11.8780
18	139	0.0070	0.7750	134	0.0458	15.2718
19	137	0.0302	-8.5185	132	0.0357	4.8782
20	137	0.0106	2.3694	131	0.0033	-18.2336

used to detect if the 3rd conformer can exist under given experimental conditions as it was the case in a microwave study.³⁹ TDDFT/B3LYP gives a similar feature for the S1 state, but the two peaks are blue-shifted by about 15 nm compared to TDDFT/M06-2X. The small dipole strength and large rotatory strength of S1 will give rise to large anisotropic factors in the long wave length region.

The two XC functionals produce different TDDFT energy gaps between the S1 and S2 states. As seen in Table 4, with M06-2X, the S2 state is 103 nm away from S1, while the same gap with B3LYP is only of 35 nm. The S3 state has an excitation wavelength of 170 nm (TDDFT/M06-2X), which is blue-shifted by 15 nm from S2. Both the S2 and S3 states have much larger oscillator strength than that of S1, giving rise to two shoulders at 188 nm and 162 nm on the M06-2X absorption spectra. On the contrary, no clear shoulder structure can

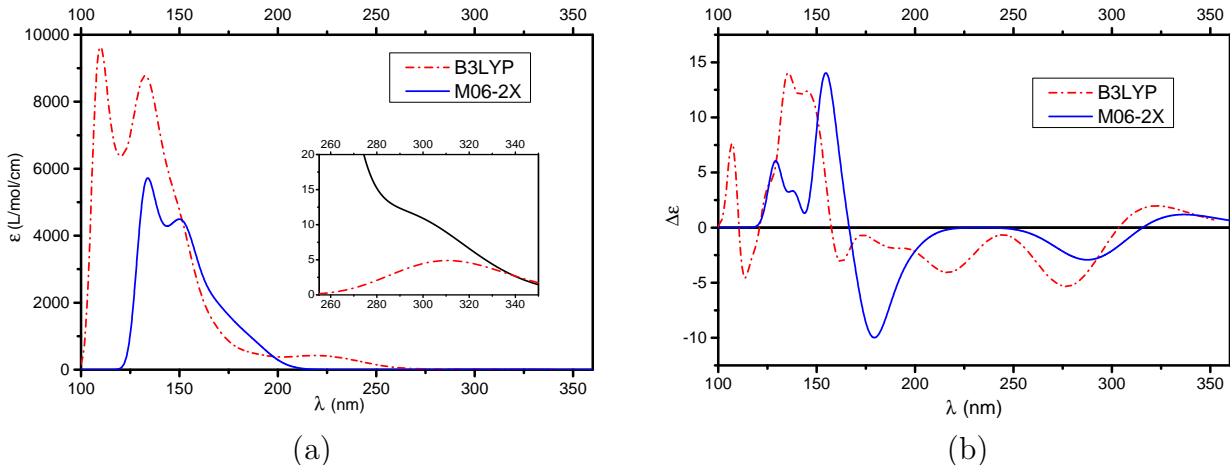


Figure 4: Absorption and ECD spectra of D-glyceraldehyde. (a) absorption spectra. (b) ECD spectra.

be observed on the absorption spectra from B3LYP. The two XC functionals also produce very distinct ECD features for S2 and S3. As seen in Figure 4(b), there are two high peaks with the opposite sign at 180 nm and 170 nm in the M06-2X result while TDDFT/B3LYP gives two small negative peaks at 220 nm and 188 nm. The hole NTO (Fig. 5) of S2 is a combination between the C2-C3 σ -bonding orbital and lone pair orbitals of the O4 and O5 atoms. The particle NTO (Fig. 5) is dominated by the C1=O6 anti-bonding π^* orbital. Therefore, the S2 state arises from an $n \rightarrow \pi^*$ transition. In contrast, the NTOs of the S3 state distribute on many atomic centers (Fig. S3 in SI), thus it is difficult to identify the type of excitation. The rest of the bright states above S3 is dense, producing a broad absorption feature in the short wavelength region. However, if our M06-2X theoretical ECD spectrum is qualitatively correct, it should be experimentally feasible to resolve the S2 and S3 ECD features. So, future experimental work could identify which XC functional, M06-2X or B3LYP, produce the best absorption and ECD spectra of D-glyceraldehyde.

3.3 Anisotropy spectra

The wavelength dependent anisotropy factor $g(\lambda)$ of L-valine and D-glyceraldehyde from TDDFT/M06-2X calculations are presented in Figure 6a and 6b, respectively.

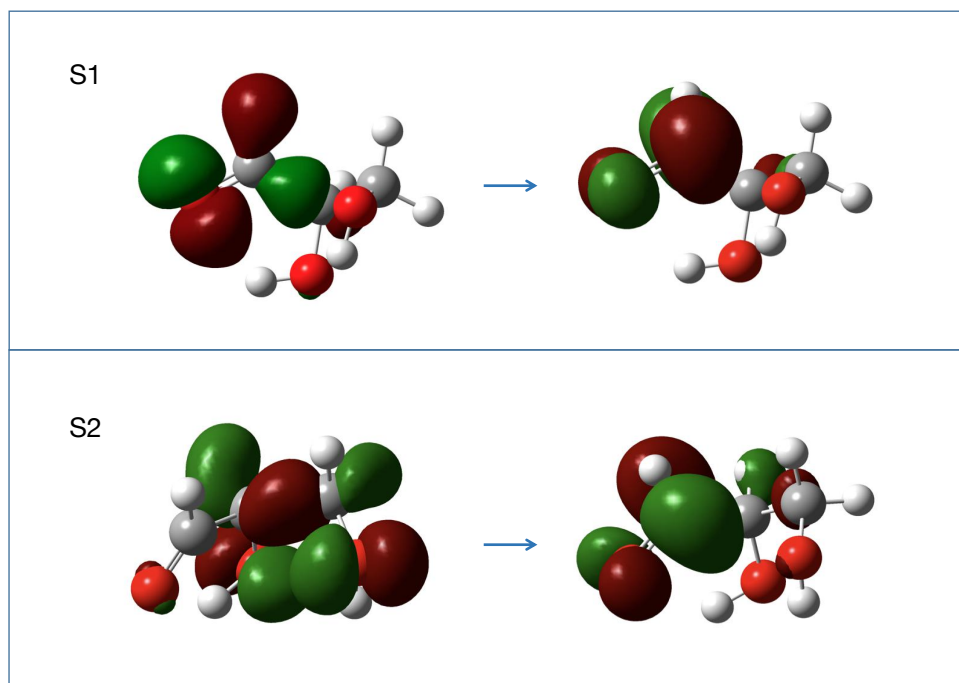


Figure 5: Natural transition orbitals (NTOs) of the S1 and S2 states of glyceraldehyde from TDDFT/M06-2X. Left are the hole NTOs, right the particle NTOs.

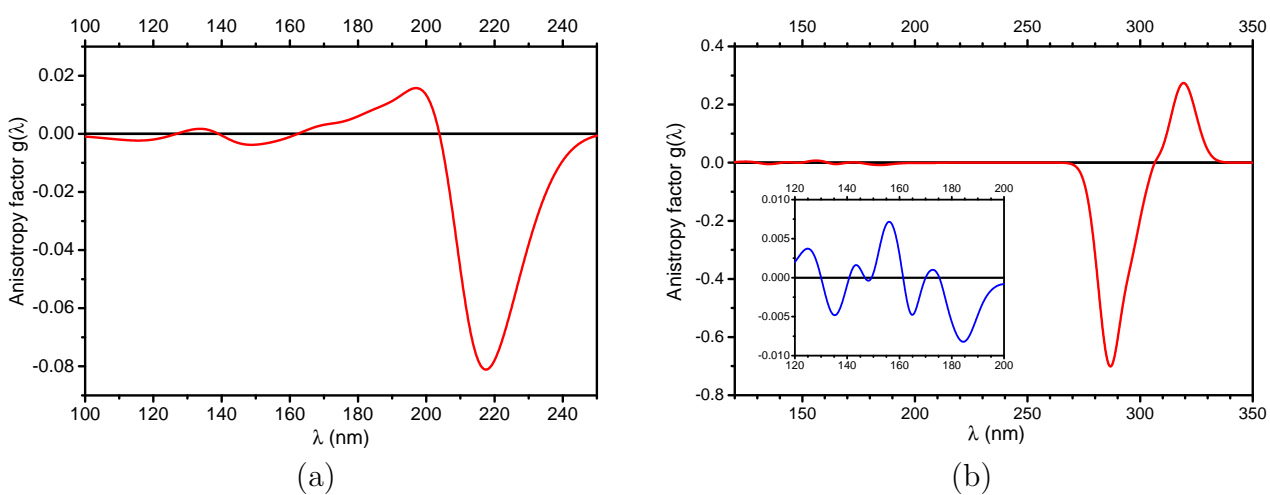


Figure 6: Anisotropy spectra (a) L-valine zwitterion (b) D-glyceraldehyde

The anisotropy spectra of the L-valine zwitterion (Fig. 6(a)) exhibits a high negative peak at 217 nm and a small positive peak at 197 nm, which are in good agreement with the experimental peaks¹⁷ at 206(−) nm and 188(+) nm, respectively. Besides, there is a negative peak centered at 171 nm in experimental anisotropy spectrum¹⁷ that should be related to the ECD peak at 167(−) nm. Recall, that we have assigned the theoretical ECD peak at 148 nm as the peak at 167(−) nm in experiments, and thus the negative peak at 148 nm on the theoretical anisotropy spectra should correspond to the peak at 171 nm. Comparing this small peak with the two peaks in the long-wavelength region, we found that their relative magnitudes are in good agreement with the experimental ones. However, the theoretical spectrum has two peaks situated at 133 nm and 117 nm, whereas we could not identify clearly such extra peaks in the experimental spectrum of L-valine (though the D-valine spectrum displays a small wavy feature).¹⁷ This maybe due to the fact that valine films have very strong and broadened absorption in the short-wavelength region, as indicated by both the theoretical and experimental studies. As a result, it is hard to obtain a highly precise anisotropy spectra in this region. In conclusion, the theoretical calculation reproduces the experimental anisotropy spectrum of L-Valine in a satisfactory manner, although the latter was measured in an amorphous film on an MgF2 window.

As seen from Fig. 6(b), the anisotropy spectrum of D-glyceraldehyde is characterized by two high peaks centred at 320 nm and 287 nm with magnitudes of 0.27 and −0.70, respectively, which are about one order larger than the two major peaks of the anisotropy spectrum of L-Valine (Fig. 6(a)). According to the absorption and ECD spectra, the two peaks arise from the first excited state of different conformers. Such large g factors are caused by the much weaker absorption of the S1 state of glyceraldehyde than that of the two lowest excited states of L-Valine. Moreover, a negative peak is located at 184 nm with a small g factor of −0.008. There are many more peaks between 120 and 180 nm, however their g factors are small, because the absorption of glyceraldehyde is strong in this region, posing a great challenge for their experimental measurement.

4 Conclusion

TDDFT calculations with the M06-2X and B3LYP functionals were performed to calculate the absorption, ECD, and anisotropy spectra of the L-valine zwitterion and D-glyceraldehyde. To simulate the experimental spectra, we first carried out conformer searches to hunt for possible low energy structures of the target molecules. The valine molecule exists in the zwitterionic form in the experimentally studied, amorphous film, whereas there is no stable zwitterionic structure in the gas phase. Therefore, the N-H bond length in the NH_3^+ group was fixed in the structure optimization. Then, the so-optimized conformations were completed with 2 others whose dihedral angles were taken from X-ray structures of valine crystals, and with four more geometries produced by linear interpolation between the optimized structures and the structures from valine crystals. For D-glyceraldehyde, we have located 32 structures with no frozen parameter, which were all real minima of the potential energy surface. For both systems, the spectra from all the so-obtained geometries were averaged with Boltzmann weight to calculate their absorption and ECD spectra.

The absorption and ECD TDDFT/M06-2X spectra agree much better with experimental results than the TDDFT/B3LYP ones. Moreover, this is achieved with no ad-hoc wavelength shifting. We observe also that the TDDFT/M06-2X anisotropy spectrum of L-valine reproduces the three main peaks of the experimental spectrum in a satisfactory fashion. For D-Glyceraldehyde, the excitation wavelengths of the first excited state of 32 conformers spread from 288 nm to 322 nm (TDDFT/M06-2X results), giving rise to two peaks with the opposite signs in the ECD spectrum. As a consequence of this and of the very weak absorption of the S1 state, the anisotropy spectra of D-glyceraldehyde exhibits two high peaks at 287 and 320 nm, which should be measurable experimentally. Both L-valine and D-glyceraldehyde have large anisotropy factors in the UV region, supporting the hypothesis that CP UV-light could induce the enantio-enrichment of these life-related chiral molecules.

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Supporting Information Available

- The optimized geometries of the valine zwitterion and glyceraldehyde are listed in Tables S1 to S12. Figure S1 gives the vibrational spectra of glyceraldehyde on its lowest energy geometry optimized by DFT/M06-2X. Figure S2 compares the absorption spectra of glyceraldehyde calculated via TDDFT with the five different XC functionals. Figure S3 presents the natural transition orbitals of the S3 state of glyceraldehyde from TDDFT/M06-2X.

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