Accuracy of Td-DFT in the Ultraviolet and Circular Dichroism Spectra of Deoxyguanosine and Uridine

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ABSTRACT: Accuracy of the time-dependent density functional theory (Td-DFT) was examined for the ultraviolet (UV) and circular dichroism (CD) spectra of deoxyguanosine (dG) and uridine, using 11 different DFT functionals and two different basis sets. The Td-DFT results of the UV and CD spectra were strongly dependent on the functionals used. The basis-set dependence was observed only for the CD spectral calculations. For the UV spectra, the B3LYP and PBE0 functionals gave relatively good results. For the CD spectra, the B3LYP and PBE0 with 6-311G(d,p) basis gave relatively permissible result only for dG. The results of other functionals were difficult to be used for the studies of the UV and CD



spectra, though the symmetry adapted cluster-configuration interaction (SAC-CI) method reproduced well the experimental spectra of these molecules. To obtain valuable information from the theoretical calculations of the UV and CD spectra, the theoretical tool must be able to reproduce correctly both of the intensities and peak positions of the UV and CD spectra. Then, we can analyze the reasons of the changes of the intensity and/or the peak position to clarify the chemistry involved. It is difficult to recommend Td-DFT as such tools of science, at least from the examinations using dG and uridine.

INTRODUCTION

Ultraviolet (UV) and circular dichroism (CD) spectra give valuable information on excited states of molecules. Their electronic structures are largely different from those of the ground state, and each excited state has a different character from other excited states. Though excited states are central in photochemistry, photobiology, and molecular design, it is difficult to elucidate their properties by experimental means alone. Therefore, an accurate and reliable excited-state theory is necessary not only for the understanding of experiments but also for the design of new photomaterials.

In 1978, the symmetry adapted cluster-configuration interaction (SAC-CI) theory¹⁻⁴ was proposed as a reliable theory for studying excited and ionized states of molecules. Since then, we have applied it to various phenomena of photochemistry and photobiology and clarified their natures, electronic origins and mechanisms.⁵⁻¹⁵ We have recently applied it to chiral molecules to investigate the natures behind the experimental CD spectra.¹⁵⁻²²

Around 1996, a treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory, now referred to commonly as TD-DFT, was published by Casida,²³ Bauernschmitt, and Ahlrichs,²⁴ which is different from the time-dependent version of the density-functional theory developed originally by Gross et al.²⁵ The Td-DFT was implemented into Gaussian by Stratmann, Scuseria, and Frisch.²⁶ It is widely used for excited-state calculations and for the spectroscopic studies of chiral molecules.^{27–34} Laurent and Jacquemin³⁵ reviewed Td-DFT benchmarks extensively.

Among many functionals, the B3LYP,^{36,37} PBE0³⁸ and M06³⁹ functionals could provide the peak positions within the deviations of about 0.25 eV for the valence excited states.³⁵ However, for charge transfer and Rydberg excitations for which the errors much increase,^{40,41} the CAM-B3LYP,⁴² wB97XD⁴³ and M06-2X³⁹ functionals were considered to be the best choices.³⁵ For oscillator strengths that are important for UV spectral simulations, the CAM-B3LYP and LC-wPBE^{44–46} functionals were considered to provide more accurate results than other functinals.⁴⁷ Furthermore, for the CD spectra, the B3LYP and PBE0 functionals were considered to give better agreement with experiments than other functionals:^{48,49} Goerigk and Grimme reported that B2PLYP can provide more accurate results than B3LYP.⁵⁰ Thus, many researchers' attempted to improve the accuracy of the Td-DFT. However, it is known that the Td-DFT results are strongly dependent on the functionals used,^{35,40,41,47–53} and therefore, the choice of the functional is critical to get reliable results.

In this article, we examine the accuracy and the reliability of the Td-DFT with 11 standard functionals by comparing the calculated results with the experiments and the SAC-CI results for the UV and CD spectra of deoxyguanosine (dG) and uridine shown in Figure 1. The functionals were selected from the hybrid and pure ones. Deoxyguanosine (dG) is an important element of DNA (DNA) and composed of guanine

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Figure 1. Geometries and interactions of anti conformers of deoxyguanosine (a) and uridine (b).

and deoxyribose (Figure 1a). Uridine is an important element of RNA (ribonucleic acid) and composed of uridine and ribose (Figure 1b). The single bonds between guanine and deoxyribose and between uridine and ribose can easily rotate. The geometries of both dG and uridine are known experimentally to be in an anti conformation and their UV and CD spectra were observed experimentally. Previously, we studied the UV and CD spectra of dG¹⁵ and uridine²⁰ for various conformations around these single bonds using the SAC-CI method. We confirmed that the anticonformers are most stable from their potential energy curves calculated for the ground state. It was found that the UV spectra are little dependent on the rotations around the single bonds between guanine and deoxyribose and between uridine and ribose but the CD spectra are strongly dependent on these rotations. Both UV and CD spectra of dG and uridine in their anticonformations calculated by the SAC-CI theory were in good agreement with the experimentally observed spectra, but the CD spectra of other conformations were much different from the observed ones, indicating that we can determine the conformational geometry of these compounds by the SAC-CI calculations of their CD spectra, likewise from the energy calculations and the X-ray experiments.

COMPUTATIONAL DETAILS

In this article, we calculate the UV and CD spectra of anti-dG and antiuridine by the Td-DFT²⁶ with seven hybrid functionals of B3LYP,^{36,37} PBE0,³⁸ CAM-B3LYP,⁴² LC-wPBE,⁴⁴⁻⁴⁶ M06-2X,³⁹ wB97XD,⁴³ and M06-HF^{54,55} and four pure functionals of OLYP,^{37,56} PBE,^{57,58} SVWN,^{59,60} and TPSS,⁶¹ from widely used functionals. The geometries of dG and uridine used in this calculation are shown in parts a and b of Figure 1, which are the anticonformers obtained in the previous studies.^{15,20} The basis sets employed were D95(d)⁶² and 6-311G(d,p).⁶³ For the SAC–CI calculations, the basis sets employed were D95(d) sets for the guanine and D95⁶² sets for the deoxyribose for dG and D95(d) sets for uridine. (See refs 15 and 20 for other computational conditions of the SAC–CI calculations.) All calculations were done using the Gaussian suite of programs.⁶⁴

with the SAC-CI and experimental spectra in Figures 2–5. The full width at half-maximum (fwhm) of the spectra was set to 0.6 eV that is the fwhm of the experimental UV and CD spectra of both dG and uridine. The lowest 20 excited states of the Td-DFT calculations using the D95(d) and 6-311G(d,p) basis sets are summarized in Tables 1–8 with the comparisons with the SAC-CI and experimental values. The peak positions and intensities of both UV and CD spectra of dG and uridine are shown for detailed examinations.

UV SPECTRA OF DEOXYGUANOSINE

As seen from Figure 2, the experimental UV spectrum of dG has the main peak at 4.96 eV (250 nm) with the shoulder peak at 4.49 eV (276 nm). This shoulder peak is very important for the identification of dG, because only dG has a shoulder peak among the four components of DNA.⁶⁵ The SAC–CI spectrum reproduced well both main and shoulder peaks of the experimental spectrum.

We note that the basis set dependence is very small for all the UV spectra calculated by Td-DFT with D95(d) and 6-311G(d,p) sets: two spectra are almost the same for all the 11 different functionals as shown in Figure 1 and Tables 1–4. However, the dependence on the different DFT functionals is very large as discussed below.

For the B3LYP calculations (Figure 2A,a), the main peak agrees with the experimental value but the shoulder peak does not appear in the TD-DFT spectrum, because the excitation energy of the main peak is calculated close to that of the shoulder peak. Though if we use the fwhm of 0.35, we can obtain a shoulder peak, 0.35 is much smaller than the fwhm of 0.6 of the experimental spectra.

The PBE0 spectra (Figure 2B,b) are very similar to those of the B3LYP, but the excitation energy is slightly higher (lower in wavelength) than those of the B3LYP: B3LYP gives slightly better agreement with experiment.

For the CAM-B3LYP calculations (Figure 2C,c), the excitation energies of the main and shoulder peaks lie higher in energy than the experiments: the shoulder peak is hidden in the spectrum, though the unsymmetrical intensity of the calculated peak suggests the existence, as in the B3LYP case.

The LC-wPBE UV spectra (Figure 2D,d) have a shoulder peak, but the excitation energies are much higher than the experimental one and those of the B3LYP and CAM-B3LYP calculations.

The M06-2X UV spectra (Figure 2E,e) have a main peak at higher energy than the experimental one and also have no shoulder peak.

The wB97XD UV spectra (Figure 2F,f) are similar to the M06-2X UV spectra but different from the experimental spectra.

The M06-HF UV spectra (Figure 2G,g) are calculated in a higher energy but have a shoulder peak due to a large energy gap between the main and shoulder peaks. Both are different from the experimental spectrum.

With the OLYP functional (Figure 2H,h), the excitation energies are lower than the experimental values: the main peak was calculated at the region of the shoulder peak of the experiment. Further, many excited states with small oscillator strengths were calculated in the range of 200–340 nm as seen from Table 2. This is much different from the calculated spectra of the above seven functionals.

The PBE spectra are similar to the OLYP ones (Figure 2 I,i), but a small peak was calculated at 230 nm. But, this peak



Figure 2. Td-DFT UV spectra (red lines) of dG using B3LYP (A, a), PBE0 (B, b), CAM-B3LYP (C, c), LC-wPBE (D, d), M06-2X (E, e), wB97XD (F, f), M06-HF (G, g), OLYP (H, h), PBE (I, i), SVWN (J, j), TPSS (K, k), and all (L, l) functionals with 6-311G(d,p) (A–L) and D95(d) (a–l) basis sets, compared with the experimental (black line) and SAC–CI (blue line) UV spectra.¹⁵

corresponds to the 200 nm shoulder peak of the 187 nm strong peak of the experimental spectrum.⁶⁵ Anyway, the calculated PBE spectra are far different from the experimental spectrum.

main peak at 250 nm: the intensities of the main and shoulder peaks are opposite here.

With the TPSS functional (Figure 2 K,k), the main peak is also calculated at lower energy than the experimental one. This result is similar to the one obtained with PBE.

With the SVWN functional (Figure 2 J,j), the shoulder peak of the strong peak at about 187 nm is calculated to be at the

th 6-311G(d,p) Basis Sets, Compared with SAC–CI and Experimental	BE M06-2X SAC-CI ^a exptl ^a	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5.681 5.167 0.181 14.822 4.464 0.186 4.525 4.49	1.159 5.293 0.000 1.618 5.082 0.062 -76.314 4.96	-14.803 5.609 0.337 -32.456 5.096 0.259 68.201 4.96	12.115 5.924 0.008 11.042 5.909 0.002 17.315 5.79	-1.288 6.214 0.004 13.015 5.970 0.031 -2.248 5.79	-4.712 6.491 0.002 -1.027 6.082 0.005 -2.151 5.79	14.677 6.586 0.026 4.862 6.615 0.503 –7.815	42.293 7.019 0.001 -4.055	-29.404 7.051 0.003 -4.864	14.832 7.143 0.518 91.254	22.940 7.189 0.076 -43.019	-38.327 7.236 0.026 0.301	2.759 7.260 0.003 -7.258	10.098 7.352 0.042 13.038	2.835 7.399 0.003 -24.195	21.976 7.441 0.015 1.503	3.878 7.541 0.018 -9.639	2.181 7.701 0.134 10.511	-9.681 7.722 0.001 -0.297	-15.180 7.781 0.004 20.647	++
of both UV and CD Spectra	PBE0	V_{V}^{b} osc ^c rot ^d EE ^b V_{V} (au) (10 ⁻⁴⁰ cgs) (eV)	49 0.167 14.274 5.095	95 0.212 9.570 5.455	05 0.009 -33.352 5.556	63 0.013 7.944 5.878	09 0.000 1.727 6.270	69 0.003 9.793 6.398	21 0.005 -4.142 6.525	36 0.000 -1.819 6.882	80 0.005 6.710 6.986	60 0.003 -2.307 7.067	29 0.096 7.503 7.093	26 0.106 -15.743 7.101	64 0.222 22.989 7.262	73 0.000 -2.266 7.287	03 0.000 -2.005 7.292	27 0.088 10.460 7.390	64 0.032 16.894 7.396	25 0.055 -11.707 7.537	75 0.022 -0.206 7.627	93 0.013 13.786 7.665	the ancitations buncitation anoun
. Peak Positions and Intensitie	B3LYP	$\begin{array}{c c} EE^{b} & \operatorname{osc}^{c} & \operatorname{rot}^{d} & EI \\ (eV) & (au) & (10^{-40} \operatorname{cgs}) & (e^{b}) \end{array}$	4.802 0.149 21.978 4.9	5.096 0.024 -39.907 5.2	5.167 0.194 5.456 5.3	5.215 0.002 11.592 5.4	5.668 0.000 0.794 5.9	5.693 0.000 -0.832 6.0	5.881 0.000 -3.590 6.1	5.909 0.002 10.021 6.1	5.962 0.008 4.721 6.1	6.076 0.003 -1.302 6.4	6.256 0.013 -10.673 6.5	6.285 0.090 22.206 6.6	6.320 0.011 -2.450 6.6	6.419 0.009 5.510 6.7	6.460 0.230 -8.753 6.8	6.685 0.087 5.753 6.9	6.753 0.002 3.278 7.0	6.790 0.005 4.389 7.1	6.841 0.026 -13.322 7.1	6.853 0.040 42.846 7.1	16 in montion low about the mature of
Table 1 Results		excited state	1A	2A	3A	4A	SA	6A	7 A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A	19A	20A	a Coo rof

Table 2. Results	Peak P	ositions	and Inten	sities of	both U	V and CD	Spectra	of dG C	alculated 1	by Td-L	OFT with	6-311G(c	l,p) Basi	s Sets, 1	Compared	with SA	VC-CI a	ınd Experii	nental
		wB97XI	0		M06-H	F		OLYP			PBE			SVWN			TPSS		exptla
excited state	EE ^b (eV)	osc ^c (au)	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)	osc ^c (au)	rot^d $(10^{-40}cgs)$	EE ^b (eV)	osc ^c (au)	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)	osc ^c (au)	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)	osc ^c (au)	$\underset{\left(10^{-40}\text{cgs}\right)}{\text{rot}^{d}}$	EE ^b (eV)	osc ^c (au)	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)
1A	5.115	0.168	7.241	4.861	0.000	2.141	4.191	0.026	14.371	4.415	0.088	23.047	4.467	0.096	30.222	4.563	0.125	17.175	4.49
2A	5.463	0.000	2.952	5.339	0.198	14.780	4.524	0.012	0.378	4.517	0.002	-3.452	4.477	0.029	-16.248	4.748	0.002	-2.548	4.96
3A	5.565	0.315	-15.124	5.930	0.493	-80.218	4.547	0.001	0.938	4.653	0.048	-17.004	4.688	0.095	-5.397	4.831	0.110	-8.781	4.96
4A	6.260	0.003	9.958	6.077	0.007	43.937	4.603	0.104	-16.084	4.708	0.098	-10.413	4.730	0.002	4.384	4.865	0.022	-11.176	5.79
5A	6.365	0.003	6.563	6.344	0.010	29.720	4.726	0.095	-9.257	4.773	0.001	6.819	4.777	0.008	-12.400	4.948	0.001	3.289	5.79
6A	6.366	0.001	-4.229	6.851	0.002	3.384	4.828	0.001	8.221	4.833	0.002	-1.324	4.829	0.005	-7.063	5.081	0.001	-0.873	5.79
7A	6.580	0.019	1.715	6.983	0.047	3.244	4.964	0.009	2.661	4.927	0.003	-4.779	4.968	0.002	-1.514	5.181	0.002	-3.239	
8A	6.845	0.000	2.162	7.297	0.011	21.413	4.982	0.007	-3.520	5.151	0.003	14.611	5.039	0.003	15.250	5.387	0.002	9.315	
9A	7.072	0.394	-5.209	7.343	0.011	25.441	5.119	0.002	1.180	5.177	0.023	0.699	5.122	0.033	17.438	S.447	0.042	21.812	
10A	7.097	0.171	9.200	7.505	0.004	-7.292	5.161	0.000	0.001	5.209	0.022	15.299	5.233	0.039	-19.307	5.488	0.005	7.196	
11A	7.288	0.124	15.321	7.568	0.513	6.164	5.226	0.009	-18.988	5.233	0.003	3.527	5.275	0.008	7.224	5.524	0.016	-3.198	
12A	7.436	0.025	15.492	7.636	0.009	-34.589	5.251	0.023	41.928	5.330	0.029	-15.294	5.301	0.012	0.657	5.554	0.022	-9.355	
13A	7.549	0.082	-5.787	7.768	0.028	8.844	5.348	0.007	-1.069	5.404	0.001	0.312	5.341	0.025	1.225	5.596	0.022	-9.110	
14A	7.590	0.003	-6.933	7.784	0.187	9.701	5.373	0.001	1.178	5.417	0.003	-0.463	5.422	0.002	-2.322	5.659	0.044	1.566	
15A	7.630	0.031	9.482	8.004	0.012	6.793	5.395	0.006	-4.470	5.422	0.042	-0.138	5.476	0.016	-0.936	5.748	0.001	-0.004	
16A	7.678	0.006	6.152	8.024	0.206	21.971	5.431	0.009	-4.776	5.561	0.005	-3.012	5.478	0.002	0.148	5.793	0.015	0.240	
17A	7.777	0.019	9.868	8.219	0.007	-0.909	5.455	0.037	-7.008	5.570	0.015	2.265	5.610	0.000	-2.003	5.893	0.001	-1.105	
18A	7.802	0.007	-14.502	8.305	0.001	-4.501	5.549	0.010	1.351	5.624	0.001	0.846	5.616	0.001	-1.667	5.927	0.000	0.302	
19A	7.896	0.027	3.727	8.536	0.007	11.597	5.557	0.016	7.216	5.669	0.000	0.507	5.646	0.005	2.584	5.950	0.005	1.035	
20A	7.914	0.033	7.474	8.561	0.009	10.335	5.608	0.001	-0.037	5.713	0.001	-2.330	5.728	0.000	0.173	5.979	0.001	-2.141	
^a See ref 1	5 in part	icular abc	out the natu	re of the	excitatior	is. ^b Excitation	n energy.	^c Oscillat	or strength.	^d Rotator	y strength	Ŀ.							

104

Results	exptl ^a	EE^b (eV)	4.49	4.96	4.96	5.79	5.79	5.79															
erimental I	[<i>a</i>	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	4.525	-76.314	68.201	17.315	-2.248	-2.151	-7.815														
and Exp	SAC-C	osc ^e (au)	0.186	0.062	0.259	0.002	0.031	0.005	0.503														
C-CI		EE ^b (eV)	4.464	5.082	5.096	5.909	5.970	6.082	6.615														
red with SA	X	$\inf_{(10^{-40} \text{cgs})}^{4}$	2.570	-0.128	-7.831	13.201	-0.646	1.770	10.992	44.834	-21.316	-5.902	3.927	2.794	-6.484	-1.348	3.952	42.143	-1.098	-35.766	4.707	-23.728	
Compa	M06-23	osc ^e (au)	0.184	0.000	0.350	0.004	0.001	0.026	0.369	0.174	0.059	0.026	0.047	0.150	0.077	0.022	0.023	0.016	0.001	0.058	0.003	0.011	
is Sets,		EE ^b (eV)	5.184	5.334	5.624	6.247	6.503	6.596	7.141	7.164	7.208	7.288	7.371	7.655	7.833	7.920	7.980	8.052	8.084	8.163	8.299	8.306	
D95(d) Bas	н	$\frac{\operatorname{rot}^{d}}{(10^{-40}\operatorname{cgs})}$	0.178	0.537	-5.482	13.092	-1.541	1.494	34.129	-28.846	20.890	5.695	2.137	-1.751	0.806	3.090	23.933	-47.640	12.563	-2.542	-4.719	4.558	Ŀ.
T with I	LC-wPB	osc ^e (au)	0.180	0.000	0.391	0.003	0.003	0.066	0.477	0.022	0.179	0.090	0.197	0.004	0.027	0.016	0.019	0.049	0.009	0.002	0.008	0.069	y strengtl
Td-DF		EE ^b (eV)	5.274	5.526	5.880	6.511	6.645	6.933	7.431	7.532	7.648	7.700	7.906	8.076	8.130	8.327	8.418	8.453	8.676	8.797	8.963	9.115	^d Rotator
ulculated by	"ХР	$\inf_{(10^{-40} \mathrm{cgs})}^{d}$	1.176	2.518	-6.815	11.862	-1.151	0.056	5.511	-5.985	21.980	2.140	4.966	6.023	-26.429	16.801	38.489	-8.031	-11.471	-1.659	-0.559	-28.278	tor strength.
f dG Ca	CAM-B3I	osc ^e (au)	0.175	0.000	0.312	0.003	0.002	0.022	0.001	0.009	0.488	0.089	0.093	0.127	0.064	0.049	0.022	0.036	0.026	0.002	0.012	0.019	^c Oscilla
pectra o		EE ^b (eV)	5.102	5.465	5.563	6.286	6.388	6.526	6.903	6.981	7.052	7.097	7.296	7.545	7.735	7.760	7.930	7.992	8.032	8.056	8.098	8.155	n energy.
and CD S		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	1.148	-10.422	7.256	1.272	11.401	1.919	-2.802	5.081	1.405	2.949	12.395	3.682	8.087	2.443	-4.598	-10.636	15.175	-23.424	-11.787	9.043	is. ^b Excitation
oth UV	PBE0	osc ^e (au)	0.172	0.230	0.001	0.000	0.003	0.000	0.009	0.003	0.092	0.314	060.0	0.023	0.034	0.004	0.038	0.072	0.022	0.098	0.014	0.021	excitation
ties of l		EE ^b (eV)	4.976	5.318	5.322	5.924	6.076	6.147	6.163	6.515	6.538	6.648	6.922	6.957	7.090	7.146	7.176	7.184	7.335	7.394	7.434	7.496	e of the
and Intensi		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	1.821	-2.639	-0.200	0.933	0.104	12.490	-3.130	-1.013	8.405	0.712	-0.115	15.715	-0.505	-7.255	7.424	-0.822	13.641	-32.891	-10.191	5.932	out the natur
sitions	B3LYP	osc ^c (au)	0.167	0.200	0.000	0.000	0.000	0.002	0.006	0.001	0.075	0.260	0.002	0.124	0.001	0.029	0.026	0.076	0.013	0.024	0.076	0.015	icular abc
Peak Pc		EE ^b (eV)	4.850	5.175	5.227	5.694	5.888	5.913	5.962	6.142	6.293	6.429	6.525	6.679	6.751	6.858	6.888	6.960	7.015	7.118	7.146	7.194	5 in parti
Table 3.		excited state	IA	2A	3A	4A	SA	6A	7 A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A	19A	20A	^a See ref 1

105



Figure 3. Td-DFT CD spectra (red lines) of dG using B3LYP (A, a), PBE0 (B, b), CAM-B3LYP (C, c), LC-wPBE (D, d), M06-2X (E, e), wB97XD (F, f), M06-HF (G, g), OLYP (H, h), PBE (I, i), SVWN (J, j), TPSS (K, k), and all (L, l) functionals with 6-311G(d,p) (A–L) and D95(d) (a–l) basis sets, compared with the experimental (black line) and SAC–CI (blue line) CD spectra.¹⁵

In summary, we have shown all Td-DFT UV spectra in comparison with the experiment and SAC-CI at the righthand-side bottom of Figure 2, Figure 2 L,l. It shows strong functional dependences. The Td-DFT spectra spread over almost all the region of the spectra and it is difficult to find some regularity from the figure. With the B3LYP and PBE0, the position of the main peak agrees with the experimental one, but since the interval between the main and shoulder peaks is too narrow, the shoulder peak did not appear on the calculated spectra, though the asymmetry of the peak indicates the

ıd Experimental Results	TPSS exptl ^a		0.147 0.404 4.49	0.000 -0.526 4.96	0.108 -2.569 4.96	0.000 2.289 5.79	0.002 -2.804 5.79	0.002 8.487 5.79	0.037 22.639	0.003 1.584	0.038 -20.091	0.053 0.899	0.016 1.345	0.001 0.058	0.000 -0.975	0.000 -0.460	0.001 -1.241	0.000 0.017	0.002 1.632	0.034 3.797	0.212 6.758	0.013 -0.465	
C-CI aı		EE ^b (eV)	4.626	4.770	4.851	4.959	5.181	5.374	5.432	5.507	5.536	5.620	5.737	5.821	5.864	5.892	5.949	6.063	6.118	6.161	6.367	6.396	
ed with SA		$\frac{\operatorname{rot}^{d}}{(10^{-40}\operatorname{cgs})}$	-1.394	1.116	-2.449	5.465	-7.807	13.159	21.840	-22.043	1.414	1.028	1.845	-1.058	-1.397	-1.034	-0.524	0.149	1.422	1.862	-11.169	-1.086	
Compar	NWVS	osc ^c (au)	0.000	0.137	0.087	0.001	0.006	0.003	0.035	0.028	0.038	0.004	0.019	0.000	0.001	0.001	0.001	0.000	0.002	0.014	0.004	0.006	
is Sets, (EE ^b (eV)	4.494	4.507	4.697	4.745	4.827	5.018	5.085	5.187	5.281	5.303	5.398	5.550	5.561	5.566	5.641	5.669	5.796	5.927	6.010	6.101	
995(d) Bas		$\frac{\operatorname{rot}^{d}}{(10^{-40} \operatorname{cgs})}$	2.555	-2.047	-2.591	3.470	-4.668	6.579	27.078	-19.336	-1.099	0.629	0.156	1.041	-1.617	-0.363	-1.059	0.154	1.464	2.485	4.299	-21.161	
T with I	PBE	osc ^e (au)	0.139	0.000	0.093	0.000	0.004	0.002	0.035	0.022	0.010	0.043	0.015	0.003	0.000	0.001	0.001	0.000	0.002	0.023	0.006	0.009	y strength
Td-DF		EE ^b (eV)	4.520	4.549	4.732	4.791	4.934	5.135	5.184	5.292	5.330	5.375	5.497	5.539	5.612	5.642	5.676	5.790	5.830	5.975	6.115	6.119	^d Rotator
ilculated by		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	2.439	-1.496	-2.520	2.855	-4.051	3.270	28.382	0.718	-19.784	-2.504	0.927	2.153	0.626	-1.532	-1.348	1.712	0.018	2.682	-0.557	-3.954	tor strength.
of dG Ca	OLYP	osc ^c (au)	0.141	0.000	0.097	0.000	0.003	0.002	0.033	0.005	0.020	0.048	0.004	0.019	0.002	0.000	0.001	0.002	0.000	0.029	0.007	0.003	. ^c Oscilla
pectra o		EE ^b (eV)	4.546	4.617	4.780	4.858	5.025	5.231	5.273	5.347	5.386	5.457	5.482	5.587	5.639	5.691	5.777	5.890	5.900	6.033	6.108	6.164	n energy.
' and CD S	F	$\underset{\left(10^{-40}\text{cgs}\right)}{\text{rot}^{4}}$	1.740	1.309	-37.380	39.675	5.332	1.283	31.740	41.463	-47.339	58.332	-94.480	47.256	0.026	10.865	-1.513	0.433	6.765	-0.831	-1.137	-24.472	ns. ^b Excitatio
both UV	H-90M	osc ^e (au)	0.000	0.204	0.501	0.006	0.003	0.055	0.030	0.511	0.019	0.164	0.040	0.212	0.016	0.004	0.005	0.028	0.013	0.001	0.003	0.001	excitation
ities of l		EE ^b (eV)	4.908	5.350	5.959	6.131	6.898	6.992	7.531	7.572	7.696	7.818	7.936	8.031	8.214	8.254	8.358	8.648	8.684	8.845	8.874	8.947	re of the
and Intens	D	$\underset{\left(10^{-40}\text{cgs}\right)}{\text{rot}^{4}}$	0.634	1.737	-5.661	10.865	-0.105	0.390	3.894	-1.957	8.652	24.791	-5.986	4.330	-17.515	11.365	18.162	-9.186	-10.030	2.518	-15.124	1.148	out the natu
ositions	wB97XJ	osc ^c (au)	0.173	0.000	0.314	0.002	0.002	0.020	0.001	0.420	0.149	0.124	0.003	0.125	060.0	0.038	0.078	0.031	0.011	0.012	0.009	0.003	icular abc
Peak Po		EE ^b (eV)	5.121	5.472	5.572	6.274	6.357	6.576	6.858	7.056	7.101	7.283	7.397	7.549	7.743	7.772	8.012	8.124	8.203	8.347	8.388	8.438	S in part
Table 4.		excited state	IA	2A	3A	4A	SA	6A	7 A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A	19A	20A	^a See ref 1

existence of a small peak on the right-hand-side of the peak. The shoulder peak appears in the LC-wPBE and M06-HF UV spectra but the excitation energies are much higher than the experimental values. For the CAM-B3LYP, M06-2X, and wB97XD functionals, the main peak is higher than the experimental value and the shoulder peak was not displayed. For the OLYP, PBE, SVWN, and TPSS functionals, the main peak was calculated in lower energy than the experiment.

The calculated UV spectra were almost the same between the D95(d) (Tables 3 and 4) and 6-311G(d,p) calculations (Tables 1 and 2). The improvement in the basis set could not necessarily improve the calculated Td-DFT spectra.

In short, the UV spectra of dG calculated with Td-DFT did not reproduce both of the positions and the intensities of the experimental UV spectrum. Therefore, it is difficult to further investigate the nature and the chemistry of dG using Td-DFT. On the contrary, as the SAC–CI theory reproduced well the experimental spectra, we could study the chemistry of dG analyzing the information provided by the SAC–CI calculations as reported previously.¹⁵

CD SPECTRA OF DEOXYGUANOSINE

It is well-known that the calculations of the chiral properties like CD spectra are sensitive to the quality of the theory used: coupled-cluster level of theory is usually necessary for reliable investigation of the CD spectra.^{66,67} The SAC theory is equivalent to the CCSD theory. Thus, the CD spectra give more sensitive test on the reliability of the Td-DFT than the UV spectra. The experimental CD spectrum has a very weak peak (first band) at 4.49 eV (276 nm), a negative peak (second band) at 4.96 eV (250 nm) and a positive peak (third band) at 5.79 eV (214 nm). The SAC-CI CD spectrum is in good agreement with the experimental spectrum, though the positive intensity of the first band at about 276 nm is stronger than that observed. This first band is almost pure $\pi - \pi^*$ excitation. The second band is composed of the $\pi - \pi^*$ (3A) and $n - \pi^*$ (2A) excitations and both states have strong rotatory strength. However, the negative rotatory strength of the n- π^* excitation exceeds the positive intensity of the $\pi - \pi^*$ excitation, and therefore the negative second band results.¹⁵

Figure 3 shows the examination of TD-DFT with 11 different functionals. First we note that the Td-DFT CD spectra are largely dependent on the basis set used, in contrast to the case of the UV spectra shown in Figure 2. The Td-DFT CD spectra with the D95(d) basis is generally weak for both first and second bands, compared with that of the third band (Figure 3a-1). However, with the 6-311G(d,p) basis (Figure 3A-L), the intensities of the first and second bands become stronger: the intensity is improved with the use of a larger basis set. This larger basis set dependence, in contrast to the case of the UV spectra, shows that the CD spectrum is a more sensitive property than the UV spectrum on the quality of the wave function used. Below we examine the result of each functional.

With the B3LYP functional (Figure 3A,a), since the excitation energies are close to the experimental values, the B3LYP CD spectrum with the 6-311G(d,p) basis is in good agreement with the experimental spectrum for the second negative and third strong positive bands. However, the intensity of the first positive band is too strong. The result of the D95(d) basis is poorer than the one with the 6-311G(d,p) basis, as noted above.

The PBE0 CD spectra (Figure 3B,b) are very similar to the B3LYP spectra: this is like the UV case.

For the CAM-B3LYP CD spectra (Figure 3C,c), the excitation energies are calculated to be higher in energy than the experimental values as already seen for its UV spectra. Though the CAM-B3LYP CD spectra look opposite to the experimental one, it is actually shifted to higher energy.

The LC-wPBE gives the CD spectra in a higher energy region as the CAM-B3LYP functional (Figure 3D,d). So, the calculated CD spectra look very different from the experimental one.

Both M06-2X (Figure 3E,e) and wB97XD (Figure 3F,f) functionals give the similar results to the CAM-B3LYP and LC-wPBE ones. Their CD spectra are similar but different from the experimental one.

From B3LYP to wB97XD except for PBE0, the orders and the natures of the excitations are the same as those of the SAC-CI results. For the PBE0, the order of the 2 and 3 excited states is opposite.

The M06-HF CD spectra (Figure 3G,g) with 6-311G(d,p) basis set has a similar shape to that of the M06-2X. However, as shown in Table 2, the first strong peak is due to the 2A excited state of the M06-HF functional instead of the 1A excited state of the M06-2X functional. Since the excitation energies are higher than those of the M06-2X, the M06-HF functional gave worse results than the M06-2X functional.

The OLYP CD spectra (Figure 3H,h) with 6-311G(d,p) is calculated to be lower in energy than the experimental values, though their intensities are close to the B3LYP results. However, the intensity with the D95(d) basis set is much different from those with 6-311G(d,p) basis set. For the 6-311G(d,p) result, the first positive peak is due to the 1A excited state, the second negative peak is due to the 4 and 5A excited states, and the third positive peak is due to the 12A excited state, as seen from Table 2. For the D95(d) result, the positive peak at around 240 nm is calculated due to the 7A excited state with a strong positive oscillator strength, but the first and second peaks are not calculated because the oscillator strength is very weak for the states less than the 7A excited state, as seen from Table 4. Thus, the basis set dependence is very large.

With the PBE functionals (Figure 3I,i), the CD spectra are similar to the OLYP ones.

The shapes of the SVWN spectra (Figure 3J,j) are also similar to those of OLYP and PBE functionals, though the excitation energy and intensity are slightly different.

The excitation energies of the TPSS functional (Figure 3K,k) are higher than those of the OLYP, PBE and SVWN functionals. Then, the TPSS CD spectrum with the 6-311G(d,p) looks close to the experimental one. However, since its UV spectra are much different from the experimental one, this similarity would be just accidental.

For the Td-DFT calculations with the 6-311G(d,p) basis, the first band was the 1A excited state (the 2A excited state for only the M06-HF), which is the same as the SAC-CI result. However, the second band is composed of three excited states with B3LYP and PBE0, two excited states with CAM-B3LYP, wB97XD and M06-HF, and one excited state with LC-wPBE and M06-2X, 4–6 excited states with OLYP, PBE, SVWN and TPSS. The 2A excited state is assigned to the second band for the CAM-B3LYP and wB97XD but is calculated to be between the first and second bands for the LC-wPBE and M06-2X. Thus, the nature of the CD spectra is dependent on the functional used. So, it is difficult to analyze the CD spectra and to study the chemistry of chiral molecules by the Td-DFT.

Article



Figure 4. Td-DFT UV spectra (red lines) of uridine using B3LYP (A, a), PBE0 (B, b), CAM-B3LYP (C, c), LC-wPBE (D, d), M06-2X (E, e), wB97XD (F, f), M06-HF (G, g), OLYP (H, h), PBE (I, i), SVWN (J, j), TPSS (K, k), and all (L, l) functionals with 6-311G(d,p) (A–L) and D95(d) (a–l) basis sets, compared with the experimental (black line) and SAC–CI (blue line) UV spectra.⁶⁸

Thus, the CD spectra of dG calculated with Td-DFT are strongly dependent not only on the DFT functional, but also on the basis set used. At the right-hand-side bottom of Figure 3, Figure 3L, we showed the behaviors of all 11 Td-DFT results. They cover almost all the spectral regions and no regularity is seen. This is particularly so when we use the 6-311G(d,p) basis. With the D95(d) basis, the calculated CD spectra were much different from the experimental one, because the intensities of the first and second bands were much weaker than that of their third band. The B3LYP and PBE0 CD spectra were the closest



Figure 5. Td-DFT CD spectra (red lines) of uridine using B3LYP (A, a), PBE0 (B, b), CAM-B3LYP (C, c), LC-wPBE (D, d), M06-2X (E, e), wB97XD (F, f), M06-HF (G, g), OLYP (H, h), PBE (I, i), SVWN (J, j), TPSS (K, k), and all (L, l) functionals with 6-311G(d,p) (A–L) and D95(d) (a–l) basis sets, compared with the experimental (black line) and SAC–CI (blue line) CD spectra.⁶⁹

to the experimental one when 6-311G(d,p) basis was used. However, the intensity of the first band was too strong. Therefore, we recommend SAC-CI more than Td-DFT as a tool for analyzing the chemistry involved in the CD spectra. Though it takes larger computational time, the reliability is something more important for theoretical tools.

When the Td-DFT CD spectra of dG are shifted to the lower energy (higher wavelength), they look closer to the

mental	exptl ^a	EE ^b (eV)	4.64 ^e	4.77 ^f	5.28	5.71 ^e	6.05																	f ref 68.
and Experi	Ia	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	50.759	-35.886		-6.342	0.849	10.465	15.437	3.411	-25.102	41.497	-10.028											/ spectrum a
AC-CI	SAC-C	osc ^e (au)	0.016	0.232		0.058	0.098	0.028	0.006	0.063	0.478	0.008	0.008											from UV
l with S [,]		EE ^b (eV)	4.740	4.886		6.200	6.311	6.517	7.140	7.246	7.556	8.067	8.882											Obtained
, Compared	X	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	7.704	4.876		-3.476	3.632	2.907	3.101	-0.104	-15.757	9.966	-3.927	-52.882	39.554	16.095	-10.878	-17.031	0.763	7.016	8.547	18.125	-5.311	n of ref 69. f
isis Sets,	M06-2.	osc ^e (au)	0.000	0.263		0.006	0.156	0.020	0.006	0.000	0.008	0.001	0.009	0.164	0.028	0.246	0.007	0.019	0.004	0.006	0.005	0.004	0.009	spectrur
(d,p) Ba		EE ^b (eV)	5.176	5.595		6.547	6.855	7.147	7.488	7.528	7.620	7.655	7.962	8.021	8.046	8.059	8.211	8.265	8.415	8.474	8.542	8.594	8.679	from CD
ith 6-311G	н	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	8.148	3.768		-5.557	2.993	3.984	-1.598	0.279	-0.277	9.623	-5.603	3.322	-6.981	-6.401	-1.371	18.627	-17.186	-18.325	-12.900	12.645	-3.647	. ^e Obtained
DFT wi	LC-wPB	osc ^e (au)	0.001	0.278		0.004	0.182	0.053	0.001	0.000	0.035	0.432	0.010	0.001	0.003	0.025	0.004	0.004	0.057	0.024	0.013	0.023	0.003	r strength
d by Td		EE ^b (eV)	5.437	5.741		6.818	7.172	7.555	7.872	7.911	8.222	8.257	8.411	8.524	8.679	8.811	8.856	8.982	9.204	9.303	9.338	9.386	9.440	⁴ Rotatory
e Calculate	"ХР	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	11.181	0.716		-7.500	3.085	3.289	-15.916	10.053	2.690	2.779	-5.404	-5.693	23.342	-24.040	-1.603	-11.414	2.333	-0.911	27.615	4.006	-5.834	or strength.
f Uridin	CAM-B3I	osc ^e (au)	0.001	0.247		0.011	0.141	0.021	0.005	0.007	0.001	0.004	0.004	0.001	0.082	0.030	0.330	0.018	0.005	0.005	0.004	0.006	0.013	^c Oscillat
pectra of		EE ^b (eV)	5.297	5.567		6.626	6.823	7.025	7.356	7.391	7.437	7.510	7.700	7.785	7.989	8.017	8.046	8.117	8.202	8.356	8.385	8.411	8.514	n energy.
and CD SJ		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	12.977	-3.154		9.565	-5.693	1.942	1.040	0.316	-23.737	5.581	-2.374	1.083	9.245	-15.602	-3.692	10.442	-1.332	-2.660	-9.048	-0.433	2.834	is. ^b Excitatio
oth UV	PBE0	osc ^e (au)	0.002	0.207		0.004	0.013	0.061	0.001	0.002	0.080	0.001	0.003	0.003	0.005	0.026	0.002	0.007	0.004	0.006	0.022	0.003	0.024	excitatior
ties of b		EE ^b (eV)	5.040	5.364		6.233	6.357	6.450	6.504	6.531	6.676	6.769	6.839	6.905	7.160	7.477	7.521	7.570	7.587	7.649	7.695	7.765	7.787	te of the
and Intensi		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	12.371	-3.165		11.006	-5.455	2.121	-9.293	9.313	-26.503	-14.138	20.126	-1.916	13.951	-13.437	-4.990	-1.098	8.295	1.358	-4.193	-0.589	-8.444	out the natu
sitions a	B3LYP	osc ^c (au)	0.002	0.189		0.003	0.003	0.001	0.020	0.037	0.050	0.017	0.027	0.001	0.007	0.014	0.001	0.001	0.002	0.004	0.004	0.003	0.008	icular, abo
Peak Po		EE ^b (eV)	4.918	5.249		6.022	6.112	6.185	6.229	6.256	6.476	6.504	6.521	6.550	6.967	7.173	7.198	7.242	7.269	7.286	7.300	7.400	7.463	0, in part
Table 5. Results		excited state	1A	2A		3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A	19A	20A	^a See ref 2

Table 6. Results	Peak Po	ositions	and Intens	ities of l	both UV	and CD Spo	ectra of	Uridine	Calculated	l by Td-	DFT wi	th 6-311G	(d,p) Ba	sis Sets,	Compared	with S/	AC-CI	und Experiu	nental
		wB97X	D		M06-F	H		OLYP			PBE			NWVS			TPSS		exptl ^a
excited state	EE ^b (eV)	osc ^c (au)	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)	osc ^c (au)	$\frac{\mathrm{rot}^{d}}{(10^{-40}\mathrm{cgs})}$	EE ^b (eV)	osc ^c (au)	$\frac{\operatorname{rot}^{d}}{(10^{-40}\operatorname{cgs})}$	EE ^b (eV)	osc ^c (au)	$\cot^{d}_{(10^{-40} \mathrm{cgs})}$	EE ^b (eV)	osc ^e (au)		EE ^b (eV)	osc ^e (au)	$\frac{\mathrm{rot}^d}{(10^{-40}\mathrm{cgs})}$	EE^b (eV)
1A	5.289	0.001	11.100	4.817	0.000	2.490	4.293	0.004	12.484	4.221	0.004	13.000	4.180	0.008	16.343	4.431	0.004	13.056	4.64 ^e
2A	5.561	0.243	0.406	5.751	0.332	12.071	4.490	0.041	-4.433	4.401	0.035	-4.483	4.302	0.027	-7.375	4.648	0.054	-4.749	4.77 ^f
																			5.28 ^e
3A	6.621	0.011	-6.672	6.330	0.001	4.070	4.746	0.011	-3.074	4.657	0.009	-2.553	4.560	0.009	-2.502	4.918	0.011	-2.838	5.71 ^e
4A	6.818	0.143	4.915	7.082	0.189	0.878	4.930	0.033	-7.221	4.836	0.031	-8.348	4.743	0.027	-8.826	5.075	0.041	-7.579	6.05
SA	6.985	0.022	2.817	7.634	0.001	-2.700	5.093	0.030	12.508	5.000	0.028	9.810	4.885	0.022	5.258	5.249	0.032	16.053	
6A	7.313	0.002	-10.394	7.821	0.023	37.769	5.188	0.016	-7.477	5.122	0.025	-7.138	5.072	0.034	-7.617	5.355	0.004	-10.562	
7 A	7.388	0.008	10.486	7.832	0.114	-23.572	5.342	0.002	11.914	5.266	0.003	19.929	5.196	0.008	32.880	5.483	0.003	13.058	
8A	7.716	0.001	1.178	8.175	0.362	12.388	5.370	0.001	3.257	5.353	0.000	0.471	5.331	0.038	-19.887	5.586	0.000	1.705	
9A	7.747	0.001	-11.121	8.225	0.001	-8.658	5.407	0.000	0.591	5.435	0.032	-12.608	5.336	0.000	0.376	5.643	0.030	-9.228	
10A	7.787	0.003	-6.522	8.494	0.005	-16.390	5.497	0.001	-0.571	5.601	0.018	0.691	5.541	0.009	-2.435	5.826	0.036	-2.540	
11A	7.914	0.007	6.938	8.646	0.007	14.294	5.513	0.028	-9.384	5.632	0.002	0.203	5.620	0.012	-0.058	5.925	0.001	0.140	
12A	8.042	0.439	4.691	8.694	0.001	1.864	5.679	0.028	-0.931	5.733	0.008	-3.547	5.737	0.000	0.695	5.998	0.010	-5.545	
13A	8.169	0.058	-7.328	8.864	0.004	35.666	5.830	0.011	-7.356	5.755	0.002	-1.852	5.785	0.013	-1.146	6.098	0.001	-0.226	
14A	8.288	0.002	-2.176	8.980	0.005	16.451	5.922	0.001	-2.255	5.897	0.016	-0.504	5.851	0.001	-5.098	6.136	0.019	2.632	
15A	8.319	0.005	-11.564	9.095	0.003	9.576	5.991	0.018	3.237	5.966	0.003	-8.872	5.877	0.001	-1.554	6.210	0.006	-11.989	
16A	8.364	0.001	2.202	9.152	0.005	-0.351	6.061	0.006	8.866	6.056	0.006	-2.286	5.910	0.003	-3.968	6.323	0.021	2.511	
17A	8.472	0.004	21.311	9.260	0.054	-54.070	6.064	0.003	-15.730	6.162	0.001	-4.456	6.145	0.066	-4.223	6.442	0.026	2.086	
18A	8.670	0.009	5.978	9.269	0.008	7.403	6.157	0.010	-0.968	6.211	0.054	8.317	6.238	0.003	5.602	6.533	0.001	1.261	
19A	8.726	0.006	-2.747	9.391	0.010	-42.920	6.267	0.033	0.794	6.301	0.007	3.794	6.383	0.006	4.202	699.9	0.007	4.450	
20A	8.774	0.004	-0.933	9.418	0.007	-18.184	6.307	0.004	-15.009	6.481	0.008	6.103	6.453	0.003	-6.096	6.692	0.002	-8.598	
^a See Table of ref 68.	e S and re	ef 20, in F	oarticular, ab	out the n	ature of t	he excitations.	^b Excitati	on energ	7. ^c Oscillator	strength.	. ^d Rotato	ry strength.'	Obtained	l from Cl) spectrum o	of ref 69. ^J	Obtained	l from UV sp	ectrum

mental	exptl ^a	EE ^b (eV)	4.64 ^e	4.77 ^f	5.28	5.71 ^e	6.05																	f ref 68.
and Experi	Ia	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	50.759	-35.886		-6.342	0.849	10.465	15.437	3.411	-25.102	41.497	-10.028											∕ spectrum α
VC-CI	SAC-C	osc ^e (au)	0.016	0.232		0.058	0.098	0.028	0.006	0.063	0.478	0.008	0.008											from UV
with S ²		EE ^b (eV)	4.740	4.886		6.200	6.311	6.517	7.140	7.246	7.556	8.067	8.882											Dbtained
Compared	Х	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	8.247	3.183		-5.626	7.586	2.717	2.174	-2.632	-9.314	-39.992	57.521	-33.646	-0.015	-8.218	8.773	-2.806	-13.177	-9.262	3.139	32.482	8.819	m of ref69. f
is Sets,	M06-2.	osc ^e (au)	0.000	0.269		0.008	0.166	0.022	0.001	0.008	0.008	0.313	0.163	0.028	0.002	0.009	0.001	0.004	0.029	0.004	0.005	0.006	0.005) spectru
(d) Bas		EE ^b (eV)	5.229	5.605		6.579	6.837	7.181	7.542	7.629	7.964	8.040	8.075	8.228	8.363	8.482	8.594	8.791	8.856	8.909	9.041	9.066	9.154	from CI
[with D95	н	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	8.071	3.021		-5.776	4.217	3.622	1.037	-3.151	6.956	1.391	-9.920	-14.429	-8.727	-11.898	24.798	-9.440	-6.015	0.689	61.997	-40.836	24.594	ı. ^e Obtained
Td-DF1	LC-wPB	osc ^e (au)	0.000	0.280		0.005	0.193	090.0	0.001	0.032	0.455	0.001	0.005	0.024	0.010	0.065	0.005	0.003	0.003	0.018	0.027	0.040	0.010	v strengtl
ated by		EE ^b (eV)	5.454	5.747		6.803	7.140	7.553	7.871	8.198	8.230	8.512	8.709	8.796	9.057	9.196	9.371	9.396	9.415	9.524	9.597	9.651	9.769	^d Rotator,
line Calcul	XP	$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	12.443	-1.206		-8.967	6.765	3.359	-6.596	7.383	-4.620	-3.935	2.703	-15.398	2.321	8.156	-7.587	7.368	-22.131	-7.346	-5.886	50.560	2.747	tor strength.
of Urid	CAM-B3I	osc ^c (au)	0.001	0.247		0.015	0.148	0.023	0.009	0.001	0.004	0.001	0.026	0.486	0.015	0.001	0.004	0.006	0.031	0.010	0.003	0.014	0.002	^c Oscillat
Spectra		EE^b (eV)	5.325	5.560		6.621	6.793	7.025	7.335	7.366	7.668	7.775	7.940	8.030	8.097	8.366	8.402	8.514	8.695	8.733	8.884	8.992	9.013	n energy.
V and CD		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	14.157	-5.616		10.134	-7.313	0.200	2.554	1.522	-18.979	2.988	-0.209	9.873	-13.794	-6.637	-2.993	-0.033	-1.337	12.813	-0.160	-0.909	-6.593	is. ^b Excitatio
both U	PBE0	osc ^c (au)	0.002	0.208		0.004	0.019	0.068	0.001	0.002	0.080	0.001	0.003	0.005	0.027	0.010	0.006	0.015	0.008	0.453	0.005	0.001	0.005	excitatior
ities of		EE ^b (eV)	5.072	5.369		6.231	6.349	6.447	6.491	6.509	6.680	6.767	6.827	7.151	7.455	7.561	7.619	7.737	7.784	7.907	8.101	8.330	8.373	te of the
and Intens		$\operatorname{rot}^{d}_{(10^{-40} \mathrm{cgs})}$	14.105	-5.904		10.126	-4.144	1.717	-8.850	8.994	-34.857	17.752	-1.033	15.012	-13.144	-3.243	-5.388	-3.299	-0.856	0.602	16.728	-8.971	-2.703	out the natu
ositions	B3LYP	osc ^e (au)	0.002	0.188		0.003	0.003	0.000	0.020	0.049	0.069	0.021	0.001	0.008	0.015	0.004	0.004	0.008	0.001	0.163	0.298	0.012	0.002	icular, abo
Peak Pi		EE ^b (eV)	4.948	5.241		6.001	6.095	6.159	6.195	6.246	6.480	6.507	6.525	6.945	7.133	7.241	7.254	7.397	7.430	7.722	7.755	8.008	8.086	0, in part
Table 7. Results		excited state	1A	2A		3A	4A	5A	6A	7 A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A	19A	20A	^a See ref 2

experimental spectra, but the intensity is different. Though the frequently shifting is often done in the Td-DFT studies, it may cause contradictions in the assignment of the peaks.

UV SPECTRA OF URIDINE

Next, we use uridine molecule shown in Figure 1b to examine the TD-DFT calculations of the UV and CD spectra with the same set of 11 DFT functionals combined with the same two basis sets. The experimental UV spectrum of uridine has two strong peaks between 200 and 350 nm as shown in Figure 4. The first band is the peak at 4.77 eV (260 nm) and the second band is the peak at 6.05 eV (205 nm).⁶⁸ With the SAC–CI calculations (see Figures 4 and 5), the first and second bands were assigned to the π – π * of the 2 and 4A excited states, respectively, as seen from Table 5. The 1A and 3A excited states are n- π * states and weak. As reported previously, the SAC–CI result is in good agreement with the experiments.²⁰

Figure 4 shows the results of the Td-DFT calculations of the UV spectra of uridine with the 11 DFT functionals and the two basis sets. We notice immediately that the basis set dependence between the 6-311G(d,p) and D95(d) sets is very small for the UV spectra, as we have already seen for dG

The B3LYP UV spectra (Figure 4A,a) are higher by about 0.5 eV than the experimental one. Similarly, the PBE0 peak is higher by 0.6 eV (Figure 4B,b), CAM-B3LYP by 0.8 (Figure 4C,c), LC-wPBE by 1.0 (Figure 4D,d), M06-2X by 0.8 (Figure 4E,e), wB97XD by 0.8 (Figure 4F,f), and M06-HF by 1.0 (Figure 4G,g). The nature of the excited states is the same, the $\pi - \pi^*$ of the 2A excited state (see Tables 5 and 6). These results are similar to the UV spectra of dG shown in Figure 2, though there the excitation energy of the B3LYP result agreed well with the experimental value.

The OLYP UV spectra (Figure 4H,h) are much different from the experimental spectra and the above Td-DFT results. There are many excited states in the range of 200 nm (6.2 eV) to 300 nm (4.1 eV): the lowest 20 excited states are listed in Tables 6 and 8. Furthermore, their oscillator strengths are weaker by an order of magnitude than those of the above seven hybrid functionals. Therefore, the OLYP spectra are calculated not as two strong peaks but as one board peak, which are far from the experimental spectrum.

Similar results were obtained with the PBE, SVWN and TPSS functionals (Figure 4I,J,K,i,j,k).

For the second strong band at 205 nm, which is assigned to the 4A excited state by SAC-CI, the five hybrid functionals except for B3LYP and PBE0 gave a strong peak as seen from Tables 5 and 6. (Their peak positions were outside of Figure 4.) However, for the B3LYP, PBE0, OLYP, PBE, SVWN, and TPSS, the second strong band was composed of several excited states with the oscillator strengths smaller by 1 order of magnitude than those of the five hybrid functionals. The summary of all the Td-DFT spectra shows a large dependence of the Td-DFT UV spectra on the functionals used (Figure 4L,I).

Thus, all Td-DFT spectra look different from the experimental one. The excitation energies did not agree with the experimental values even with the B3LYP and PBE0 functionals that provided good results for dG. Among the theoretical spectra shown here, only the SAC–CI one reproduces well the experimental features and are worthy of further investigations of the experimental nature.

For the hybrid functionals, when the Td-DFT spectra are shifted to the lower energy (larger wavelength), they look

closer to the experimental spectra. Therefore, we may be able to use them for the assignment of the experimental spectra. However, with the pure functionals, their results are different much in the intensity. Therefore, this author cannot recommend the usage of pure functionals.

CD SPECTRA OF URIDINE

Figure 5 shows the comparisons of Td-DFT, SAC–CI and experiments. Tables 5–8 show the details. The experimental CD spectrum of uridine are composed of the three bands: the first band is a strong positive peak at 4.64 eV (267 nm), the second and third bands are weak negative peaks at 5.28 eV (235 nm) and 5.71 eV (217 nm).⁶⁹ The SAC–CI CD spectrum reproduced the signs and the intensities of these peaks, though the intensity was weak for the third band.²⁰

We notice first that the basis set dependence is very small for the CD spectra of uridine: the results of the 6-311G(d,p) and D95(d) basis sets are quite similar. This is different from the dG case where a large basis set dependence was observed for the CD spectra. We have some speculation on this fact. The anticonformer of uridine forms a hydrogen-bond between uracil and ribose as shown in Figure 1b. On the other hand, the anticonformer of dG may have a hydrogen-bond-like interaction between guanine and deoxyribose as shown in Figure 1a, but as expected from the O–H distance (2.52 Å vs 1.99 Å), it must be very small. Namely, the geometry is fixed with uridine but flexible and distorted with dG. This is also seen from the fact that the potential energy curve around the anti conformer was sharp for uridine but flat for dG in the previous studies.^{15,20} In particular, the CD spectra are sensitive to the geometrical changes. Therefore, the triple- ζ level basis set may be necessary to calculate the CD spectra of dG to describe the distortion by the small interaction. But, the double- ζ level basis set may be enough for the calculations of uridine. It would be necessary to investigate this speculation using other molecules and/or other basis sets.

The B3LYP CD spectra (Figure 5A,a) are much different from the experimental one. The positive peak at 4.918 eV (252 nm) may be assigned to the first band at 4.64 eV. However, the 2A excited state at 5.249 eV (236 nm) is negative but its intensity is very weak. The 3A excited state at 6.022 eV (205 nm) is positive. Therefore, The B3LYP spectra do not agree with the experimental one.

The PBE0 CD spectra (Figure 5B,b) are very similar to those of the B3LYP one: this is similar to the UV and dG cases.

The CAM-B3LYP functional (Figure 5C,c) gives only one positive peak at 5.297 eV (234 nm) at around the second band of the experiment. Even when the CAM-B3LYP spectra are shifted to the lower energy, two negative peaks are not found with this functional because the intensity is very weak for the 2A excited state and is positive for the 4A excited state (Table 5).

With the CAM-B3LYP, M06-2X, and wB97XD functionals (Figure 5D,E,F,d,e,f), we obtained similar results.

With the M06-HF functional (Figure 5G,g), the rotatory strengths of the lowest four excited states are positive and the intensity of the 1A excited state is weaker than those of 2A and 3A excited states (Table 6). Therefore, the CD spectra are much different from the experiment.

With the OLYP spectra (Figure 5H,h), there are many peaks in the 200-350 nm as noted above. The first band is the 1A excited state and positive, the second band is composed of the 2A, 3A, and 4A excited states and is negative, and the third

band is composed of the 5A and 7A excited states and is positive. Even when the OLYP CD spectra are shifted to the higher energy, the sign of the third band is opposite to that of the experiment.

The PBE, SVWN and TPSS functionals (Figure 5I,J,K,i,j,k) give similar CD spectra to OLYP above. The assignment of each peak is given in Tables 5–8. Like the OLYP case, the results are useless from the theoretical point of view.

The summary figure (Figure 5L.l) shows that the Td-DFT CD spectra are strongly dependent on the functionals used: this is similar to the UV and dG cases.

The first positive band originates from the 1A excited state with a positive sign. However, since the excitation energy is higher for the hybrid functinals and lower for the pure functionals than the experimental value, we have to shift the Td-DFT spectra to assign to the experiment.

The 2A excited state is positive with the LC-wPBE, M06-2X and M06-HF, negative with the B3LYP and PBE0, and very weak with the CAM-B3LYP and wB97XD. For the OLYP, PBE, SVWN and TPSS, the negative band was calculated from the 2, 3 and 4A excited states but the positive band was calculated from the 5A and 7A excited states. Therefore, two negative bands cannot be calculated by the Td-DFT.

Thus, the Td-DFT CD spectra of uridine are largely different from the SAC-CI and experimental spectra in both the excitation energy and the intensity. Even when the Td-DFT CD spectra are shifted toward the experimental one, the sign of the CD spectra does not agree with the experiment for either of the second or third bands.

CONCLUSION

In this article, we have examined the accuracy and the reliability of Td-DFT by calculating the UV and CD spectra of dG and uridine using 11 different functionals and two different basis sets and by comparing them with the experiments and the SAC-CI results.^{15,20} The Td-DFT results did not satisfactorily reproduce the experimental UV and CD spectra of dG and uridine: the excitation energies of the Td-DFT calculations were higher or lower than the experimental values and the intensities of UV and CD spectra were different from the experimental observations: in particular, the signs of the CD spectral peaks were different from those of the experiments. In addition, the Td-DFT spectra were strongly dependent on the functionals used. In actual calculations, we have no a priori knowledge on the choice of the functionals to be used for a special subject. To deduce valuable information from the UV and CD spectra, we have to use reliable excited-state theory that can reproduce correctly both of the intensities and peak positions of the UV and CD spectra. Then, we can analyze, from the theoretical point of view, why the intensity decreases or increases or why the peak position is shifted in some way, which leads us to clarify the nature and the origin of the chemistry involved. It is difficult to recommend Td-DFT as such tools of science, at least from the examinations using dG and uridine.

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Notes

The authors declare no competing financial interest.

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