Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for 'Vibrational Energy Redistribution in Catechol during Ultraviolet Photolysis'

Graeme A. King,[a] Thomas A.A. Oliver,[b] Richard N. Dixon and Michael N.R. Ashfold

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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Author for correspondence:
Prof. M.N.R. Ashfold
(address as above)
Tel: +44(0)117-9288312/3
Fax: +44(0)117-9250612
e-mail: mike.ashfold@bris.ac.uk

[a] Present address: Department of Physics and Astronomy, VU University - Faculty of Sciences, De Boelelaan 1081, NL-1081 HV Amsterdam, The Netherlands

[b] Present address: Department of Chemistry, University of California, Berkeley, California, 94720, U.S.A.

TD-DFT to Predict the Electronic Structure of Catechol

Electronic structure calculations were performed initially using the HCTH functional with a 6-311++G** basis set, since this level of theory could qualitatively predict the vertical excitation energies of many monohydroxybenzenes (phenols).[1-3] However, as shown in Table SI, this level of theory failed to reproduce the expected electronic state ordering in catechol: it underestimates the excitation energy of the $1^1\pi\pi^*$ state and predicts the $1^1\pi\sigma^*$ state to be the lowest singlet excited electronic state in the vertical Franck-Condon region. This is inconsistent with the UV absorption spectrum and far from expected given previous studies of phenols.[2] Duncan *et al.*[4] reported that the PW91PW91 exchange-correlation functional with TD-DFT could reproduce adequately the major features in the UV absorption spectrum of catechol. Using a 6-31G** basis set, the authors predicted that the lowest optically active (*i.e.* $^1\pi\pi^*$) states lie at ~260 nm and ~220 nm, respectively. Fig. 3(a) in the paper shows that the latter value is in good agreement with experiment. However, the excitation energy of the $1^1\pi\pi^*$ state is still overestimated. We repeated this calculation, obtaining similar results. This level of theory also predicts excitation to the $1^1\pi\sigma^*$ state at ~231 nm: a more satisfactory result than that obtained using the HCTH/6-311++G** level of theory.

Further TD-DFT calculations were performed using the PW91PW91 exchange-correlation functional, and with different basis sets. As summarised in Table SI, the excitation energies of the $1^1\pi\pi^*$ and $2^1\pi\pi^*$ states are relatively insensitive to the basis set used with this functional. In contrast, the excitation energies of the $1^1\pi\sigma^*$ and $2^1\pi\sigma^*$ states vary greatly with basis set. Most notably, it appears that the use of diffuse (+) functionals in the basis set improves slightly the calculated excitation energy of the $1^1\pi\pi^*$ state, but underestimates the excitation energies of the $^1\pi\sigma^*$ states significantly. Our preferred basis set for the PW91PW91 functional is thus 6-311G**. For completeness, the excitation energies were also calculated using this same basis set with the HCTH and B3LYP functionals. However, these offered no improvement on the PW91PW91 functional. It should be noted that for all TD-DFT calculations reported in Table SI, the excitation energy of the $1^1\pi\pi^*$ state (which corresponds to excitation wavelengths ~260 nm) is overestimated. This is consistent with the fact that catechol is non-planar in its $1^1\pi\pi^*$ state, but planar in its S_0 state.

Table SI

Comparison of the vertical excitation energies (ΔE, in eV / with the corresponding wavelength, in nm) of the two lowest $^1\pi\pi^*$ and $^1\pi\sigma^*$ states of catechol, calculated using TD-DFT (following a ground state geometry optimisation) with a variety of exchange-correlation functionals and basis sets.

Level of Theory	Parameter (in eV / nm)			
	$\Delta E(1^1\pi\pi^*\leftarrow S_0)$	$\Delta E(1^1\pi\sigma^*\leftarrow S_0)$	$\Delta E(2^1\pi\pi^*\leftarrow S_0)$	$\Delta E(2^1\pi\sigma^*\leftarrow S_0)$
HCTH/6-311++G**	4.70 / 264	4.43 / 286	5.00 / 248	5.09 / 244
PW91PW91/6-31G	4.78 / 259	5.36 / 231	5.58 / 222	6.27 / 198
PW91PW91/6-311G	4.74 / 261	4.75 / 261	5.57 / 223	5.55 / 223
PW91PW91/6-311G**	4.72 / 263	4.85 / 256	5.50 / 226	5.64 / 220
PW91PW91/6-311+G**	4.64 / 267	4.28 / 290	5.40 / 230	5.03 / 247
PW91PW91/6-311++G	4.68 / 265	4.13 / 300	5.48 / 226	4.89 / 254
HCTH/6-311G**	4.80 / 258	4.94 / 251	5.58 / 222	5.73 / 216
B3LYP/6-311G**	5.04 / 246	5.41 / 229	5.79 / 214	6.29 / 197

Based on the UV absorption spectrum (Fig. 3(a)), TD-DFT / RI-CC2 calculations (Table SI and Table I of the main paper) and previous studies,[2] the lowest excited singlet electronic state of catechol ($1^1\pi\pi^*$) arises from electron promotion from the highest occupied molecular orbital (HOMO, π) to the lowest unoccupied molecular orbital (LUMO, π*). The second ($1^1\pi\sigma^*$) and third ($2^1\pi\pi^*$) excited singlet electronic states arise from $3s/\sigma^*\leftarrow\pi$(HOMO) and $\pi^*\leftarrow\pi$(HOMO) electron transitions, respectively. TD-DFT calculations at the PW91PW91/6-311G** level of theory predict that a second $^1\pi\sigma^*$ state associated with the $3s/\sigma^*\leftarrow\pi$(HOMO-1) transition lies at ~5.64eV / 220 nm.

Table SII

Assignments of peaks highlighted in Fig. 3(d), detailing the identity and vibrational energies (E_{vib}) of the $1^1\pi\pi^*$ state levels of catechol that enhance the 1+1 REMPI probability in the displayed wavelength range. Assignments come principally from refs. 5 and 6 and in some cases are supported by our own HRA-PTS studies.

Label in Fig. 3(d)	λ_{phot} / nm	$\tilde{\nu}_{\mathrm{phot}}$ / cm^{-1}	$1^1\pi\pi^*\leftarrow S_0$ transition	E_{vib} / cm^{-1}
[1]	280.523	35647	0^0_0	0
[2]	279.625	35762	$\tau_2{}^{1+}_0$	115
[3]	278.525	35903	$\tau_2{}^{2+}_0$	256
-	276.86	36119	$6b^1_0$	472
-	276.577	36156	$6a^1_0$	509
-	274.918	36374	$10b^1_0\,16a^1_0$	727
-	274.776	36393	12^1_0	746
-	274.035	36491	$1^1_0\,\tau_2{}^{1+}_0$	844
-	273.264	36594	$18b^1_0$	947

DFT to Calculate Normal Mode Vibrations of Catechol and Catechoxyl Species

Given our initial difficulties in predicting the UV absorption spectrum of catechol using TD-DFT, we must take particular care to test the predictive reliability of any normal mode frequency calculations. Unfortunately, there are no reported experimental vibrational frequencies for the catechoxyl radical. However, the experimental wavenumbers for the catechol molecule are known[9] and can thus be compared with calculations. Table SIII lists the harmonic normal mode wavenumbers of the molecule, calculated using four different levels of theory: B3LYP/6-311++G** (method 1), B3LYP/6-311+G** (method 2), B3LYP/6-311++G2df,2dp (method 3) and PW91PW91/6-311G** (method 4), along with the experimental wavenumbers. As in the previous spectroscopic studies of catechol,[7] we use the Varsányi vibrational mode labelling scheme for *ortho*-di-light benzenes.[8] As discussed in Refs. 1-3, method 2 has generally proved reliable for obtaining harmonic and anharmonic vibrational wavenumbers for a number of phenols. However, method 4 has been shown here to be most suitable for calculating vertical excitation energies of the catechol molecule (Table SI).

Table SIII reveals that there is relatively little difference between these four levels of theory when it comes to calculating the vibrational wavenumbers of catechol. While the calculated modes do not include any anharmonic corrections, they agree reasonably well with the experimental values for all but a couple of vibrations (*i.e.* modes 15 and 8*b*, which are slightly underestimated and overestimated, respectively). Given the success of calculating the vibrational modes of catechol, some of these methods were then used to derive the normal mode vibrations of the catechoxyl radical. The results of these calculations are listed in Table SIV. Once again, there is little difference in the magnitude of the values when comparing the various levels of theory.

Anharmonic corrections are generally required in order to assign TKER spectra correctly. Certain levels of theory calculate large and unphysical anharmonic corrections. Method 3 in Table SIV was found to be most suited for calculating anharmonic vibrational wavenumbers of both catechol and the catechoxyl radical; the latter are listed in Table SIV. Based on the above findings, the structure evident in TKER spectra recorded following UV excitation of catechol are most securely assigned using DFT at the B3LYP/6-311+G** level of theory.

Table SIII

Harmonic wavenumbers (in cm^{-1}) for the normal mode vibrations of catechol, calculated using DFT at various levels of theory: B3LYP/6-311++G** (method 1), B3LYP/6-311+G** (method 2), B3LYP/6-311++G2df,2dp (method 3) and PW91PW91/6-311+G** (method 4). Modes are quoted using the Varsányi labelling scheme[8] and ordered by symmetry. Experimental values come from gaseous phase IR measurements,[9] except those values marked with an asterisk, which are taken from IR and Raman studies of solid catechol.[10]

Catechol ($\tilde{X}$ $^1A'$)						
Mode	Symmetry	Method 1	Method 2	Method 3	Method 4	Expt.
OH stretch (2)	a'	3852	3853	3849	3746	3663
OH stretch (1)	a'	3793	3793	3797	3671	3605
2	a'	3198	3199	3203	3141	3069
20*a*	a'	3189	3190	3194	3131	3063
20*b*	a'	3175	3176	3181	3119	3060
7*b*	a'	3152	3152	3156	3092	3051
8*b*	a'	1651	1651	1652	1610	1616
8*a*	a'	1646	1646	1646	1607	1607
19*b*	a'	1540	1540	1546	1499	1504
19*a*	a'	1503	1503	1509	1463	1479
OH bend (1)	a'	1392	1391	1393	1385	1324
14	a'	1357	1357	1360	1326	1365
3	a'	1297	1297	1299	1271	1275
7*a*	a'	1264	1263	1268	1232	1251
13	a'	1204	1203	1206	1173	1195
9*a*	a'	1177	1177	1179	1144	1151*
OH bend (2)	a'	1165	1165	1168	1132	1187*
18*a*	a'	1107	1107	1110	1077	1092*
18*b*	a'	1050	1049	1052	1026	1035
12	a'	861	860	865	837	859
1	a'	779	779	781	762	768
6*a*	a'	590	590	592	572	581*
6*b*	a'	559	559	560	544	564*
9*b*	a'	449	448	449	443	449
15	a'	309	308	310	297	343
5	a''	958	969	975	924	963*
17*b*	a''	914	925	928	881	916*
17*a*	a''	837	841	856	803	850*
11	a''	746	749	751	717	741
4	a''	717	704	743	673	722*
16*a*	a''	568	568	574	550	555*
16*b*	a''	454	455	464	441	456*
OH torsion (τ_1)	a''	415	413	429	424	–
10*a*	a''	292	292	297	282	295
10*b*	a''	191	190	243	186	202*
OH torsion (τ_2)	a''	133	150	190	151	–

Table SIV

Harmonic wavenumbers (in cm^{-1}) for the normal mode vibrations of the catechoxyl radical, calculated using DFT at various levels of theory: B3LYP/6-311++G** (method 1), PW91PW91/6-311+G** (method 2) and B3LYP/6-311+G** (method 3). Method 3 is also used to compute anharmonic vibrational wavenumbers. Modes are quoted using the Varsányi labelling scheme[8] and ordered by symmetry.

Catechoxyl ($\tilde{X}$ $^2A''$)					
Mode	Symmetry	Method 1	Method 2	Method 3	Method 3 (anharmonic)
OH stretch (1)	*a*'	3560	3292	3562	3319
2	*a*'	3202	3142	3202	3053
20*a*	*a*'	3196	3137	3197	3072
20*b*	*a*'	3184	3126	3185	3058
7*b*	*a*'	3173	3114	3174	3043
8*b*	*a*'	1609	1574	1609	1572
8*a*	*a*'	1575	1545	1576	1534
19*b*	*a*'	1527	1498	1527	1505
19*a*	*a*'	1488	1468	1487	1446
OH bend (1)	*a*'	1438	1402	1437	1406
14	*a*'	1381	1355	1381	1326
3	*a*'	1334	1305	1334	1302
7*a*	*a*'	1262	1239	1261	1226
13	*a*'	1193	1168	1193	1177
9*a*	*a*'	1169	1137	1168	1152
18*a*	*a*'	1130	1102	1130	1108
18*b*	*a*'	1010	987	1109	990
12	*a*'	884	859	884	875
1	*a*'	755	742	755	742
6*a*	*a*'	578	562	578	572
6*b*	*a*'	566	552	566	558
9*b*	*a*'	451	436	450	451
15	*a*'	324	312	324	314
5	*a*"	967	941	982	976
17*b*	*a*"	941	910	950	936
17*a*	*a*"	848	820	851	856
11	*a*"	767	735	770	777
OH torsion (τ_1)	*a*"	721	781	723	727
4	*a*"	707	693	709	704
16*a*	*a*"	499	486	505	512
16*b*	*a*"	452	436	454	451
10*a*	*a*"	269	258	270	266
10*b*	*a*"	166	164	166	169

Notes and References

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[7] Note that Refs. 5, 6 and 10 generally use the Varsányi mode labelling scheme for *ortho*-di-light benzenes (Ref. 8), but for historical reasons swap (incorrectly) mode labels 17*a*, 17*b*, 9*a* and 18*a* with 10*b*, 10*a*, 15 and 9*b*, respectively. While this ensured self-consistency in the recent literature relating to this particular molecule, we choose to persist with the original Varsányi mode labelling scheme in order to aid cross-comparison between different phenols.

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