SuppInfo for: On the multiphoton ionization photoelectron spectra of phenol

Diptesh Dey, Joanne L. Woodhouse, Marcus P. Taylor, Helen H. Fielding, and Graham A. Worth

November 15, 2023

1 Ground state normal mode frequencies

SI-Table 1 Calculated frequencies of vibrational modes, in cm^{-1} and electron volts, for the $\tilde{X}^1A_1$ state of phenol calculated at the MP2/aug-cc-pVDZ level of theory. The C_{2v} symmetries are obtained by ignoring the O-H hydrogen atom.

| Mode | Frequency | | Symmetry | | Description |
	cm^{-1}	eV	C_s	C_{2v}	
ν_1	223	0.028	a''	b_1	Out of plane C-O bend + ring torsion
ν_2	332	0.041	a''	b_1	Out of plane O-H bend
ν_3	397	0.049	a'	b_2	In plane C-O-H bend
ν_4	406	0.050	a''	a_2	C-C twist
ν_5	496	0.062	a''	b_1	Out of plane C-O bend + ring torsion
ν_6	520	0.065	a'	a_1	Ring deformation + C-O stretch
ν_7	612	0.076	a'	b_2	Ring deformation
ν_8	613	0.076	a''	b_1	Ring deformation
ν_9	742	0.092	a''	b_1	C-H bend out of plane
ν_{10}	812	0.101	a'	a_1	Ring deformation + C-O stretch
ν_{11}	817	0.101	a''	a_2	C-H bend
ν_{12}	864	0.107	a''	b_1	C-H bend out of plane
ν_{13}	910	0.113	a''	a_2	C-H bend out of plane
ν_{14}	926	0.115	a''	b_1	C-H bend out of plane
ν_{15}	998	0.124	a'	a_1	Breathing mode
ν_{16}	1035	0.128	a'	a_1	C-H bend in plane
ν_{17}	1083	0.134	a'	b_2	C-H bend in plane
ν_{18}	1161	0.144	a'	b_2	C-H bend in plane
ν_{19}	1176	0.146	a'	a_1	C-H bend
ν_{20}	1194	0.148	a'	a_1	OH bend
ν_{21}	1267	0.157	a'	a_1	C-O stretch + C-C stretch
ν_{22}	1332	0.165	a'	b_2	C-H bend
ν_{23}	1471	0.182	a'	b_2	C-C ring stretch
ν_{24}	1482	0.184	a'	b_2	C-C ring stretch
ν_{25}	1501	0.186	a'	a_1	C-C ring stretch
ν_{26}	1635	0.203	a'	b_2	C-C ring stretch
ν_{27}	1646	0.204	a'	a_1	C-C ring stretch
ν_{28}	3192	0.396	a'	a_1	C-H stretch
ν_{29}	3207	0.398	a'	b_2	C-H stretch
ν_{30}	3217	0.399	a'	b_2	C-H stretch
ν_{31}	3230	0.400	a'	b_2	C-H stretch
ν_{32}	3236	0.401	a'	a_1	C-H stretch
ν_{33}	3806	0.472	a'	a_1	O-H stretch

2 Vibronic Coupling Model Parameters

In the following tables, state numbering has the ground-state as 1. States 2,3, are the neutral $S_1(^1B_2)$ and $S_2(^1B_1)$ states, while states 4,5 are the cation states $D_0(^2B_1)$ and $D_1^2A_2$.

SI-Table 2 On-diagonal linear coupling constants $\kappa_k^{(i)}$ obtained by fitting the vibronic coupling model Hamiltonian to the adiabatic potentials and the vibrational normal mode frequencies ω_k. All values are in eV.

Mode	ω_k	$\kappa_k^{(i)}$			
		(2)	(3)	(4)	(5)
ν_3	0.04922				
ν_4	0.05034				
ν_6	0.06452	-0.10616	-0.02400	-0.11791	0.05073
ν_7	0.07588				
ν_{10}	0.10067	-0.09016	0.08000	-0.00800	-0.02000
ν_{11}	0.10129				
ν_{13}	0.11300				
ν_{15}	0.12376	0.00972	0.08400	0.00118	-0.01128
ν_{16}	0.12836	0.01075	0.10100	0.01229	0.01687
ν_{19}	0.14577	-0.06900	-0.00600	-0.04600	0.02000
ν_{20}	0.14803	-0.18100	-0.07600	-0.12622	-0.12171
ν_{21}	0.15707	-0.14964	-0.02000	-0.01000	-0.10000
ν_{25}	0.18608	-0.11589	-0.00464	-0.04496	-0.08291
ν_{27}	0.20406	0.13900	- 0.01305	0.20000	-0.07014
ν_{28}	0.39576	0.46400	- 0.45500	0.00300	-0.01200
ν_{32}	0.40100	0.14000	- 0.12200	0.00800	-0.03400

SI-Table 3 Off-diagonal linear coupling constants $\lambda_k^{(i,j)}$ (in eV) obtained by fitting the vibronic coupling model Hamiltonian to the adiabatic potentials. Only values larger than 0.001 eV are listed.

Mode	$\lambda_k^{(i,j)}$	
	(2,3)	(4,5)
ν_3		-0.100
ν_4	0.085	
ν_7		0.080
ν_{11}	0.140	
ν_{13}	0.099	

SI-Table 4 On-diagonal bilinear coupling constants $\gamma_{kk}^{(i)}$ (in eV) obtained by fitting the vibronic coupling model Hamiltonian to the adiabatic potentials.

| Mode | $\gamma_{kk}^{(i)}$ | | | |
	(2)	(3)	(4)	(5)
ν_3			0.02918	0.02305
ν_4	0.01000	-0.02800		
ν_6	0.00383	-0.00111	0.00617	0.01234
ν_7			-0.00310	0.02637
ν_{10}	0.00771	0.00878	0.00708	0.01448
ν_{11}	0.07000	0.00900		
ν_{13}	0.07200	0.01500		
ν_{15}	0.01640	0.01572	0.01825	0.01532
ν_{16}	0.01871	0.01041	0.01848	0.01466
ν_{19}	0.04400	0.04600	0.04463	0.04455
ν_{20}	0.01800	0.07200	0.04947	0.06664
ν_{21}	0.01120	0.03111	0.03020	0.04694
ν_{25}	0.02563	0.02926	0.04001	0.05935
ν_{27}	0.00024	0.02990	-0.01069	0.07536

SI-Table 5 On-diagonal bilinear coupling constants $\gamma_{km}^{(i)}$ (in eV) obtained by fitting the vibronic coupling model Hamiltonian to the adiabatic potentials.

Mode	$\gamma_{km}^{(i)}$			
	(2)	(3)	(4)	(5)
$\nu_{3,7}$			-0.01894	-0.05213
$\nu_{6,10}$			0.01907	0.06142
$\nu_{6,15}$			0.00368	0.00950
$\nu_{6,16}$			-0.00482	-0.00969
$\nu_{6,19}$			-0.01600	0.01900
$\nu_{6,20}$			-0.01000	0.00500
$\nu_{6,21}$			0.01335	0.02000
$\nu_{6,25}$				0.00402
$\nu_{6,27}$	-0.00014	0.00014	0.00476	-0.01000
$\nu_{10,15}$			-0.00286	-0.00688
$\nu_{10,16}$			0.00341	0.00699
$\nu_{10,19}$			0.01000	0.02400
$\nu_{10,20}$			-0.00800	0.06000
$\nu_{10,21}$			-0.00667	-0.01911
$\nu_{10,27}$		-0.00014	-0.01005	-0.03783
$\nu_{15,16}$			0.00032	0.00079
$\nu_{15,20}$			-0.00300	-0.01000
$\nu_{15,21}$	0.00031	0.00033	-0.00264	-0.00426
$\nu_{15,27}$		0.00011	-0.00331	-0.00781
$\nu_{16,20}$			0.00400	0.01000
$\nu_{16,21}$				0.00212
$\nu_{16,27}$	0.00013	-0.00016	0.00339	0.00605
$\nu_{19,20}$			0.01713	0.04461
$\nu_{19,21}$			0.00491	0.01399
$\nu_{19,27}$			0.00966	0.02745
$\nu_{20,21}$			-0.01427	-0.02000
$\nu_{20,27}$			-0.01609	-0.02000
$\nu_{21,25}$				-0.00132
$\nu_{21,27}$	-0.00043	-0.00023	-0.00981	-0.02263
$\nu_{25,27}$		-0.00019		-0.00361
$\nu_{28,32}$	-0.10210	-0.05320		

SI-Table 6 Numerical values of the parameters of the diabatic potentials for the r, θ coordinates of the cationic states, D_0 and D_1.

V_4	
$D_e^4 = 4.63139$ eV	$J_1 = 0.33$ eV
$r_4 = 0.982916$ Å	$J_2 = 0.29$ eV
$a_4 = 2.31572$ Å^{-1}	$J_3 = 0.044$ eV
$a_{40} = 8.608$ eV	
V_5	
$D_e^5 = 5.00107$ eV	$K_1 = 0.08155$ eV
$r_5 = 0.975598$ Å	$K_2 = 0.03136$ eV
$a_5 = 2.28858$ Å^{-1}	$K_3 = 0.04872$ eV
$a_{50} = 9.38$ eV	