Electronic Supplementary Material for PCCP

Vibronic Absorbtion and Emission Spectra of Psoralen: a Quantum Chemical Investigation (Electronic Supplementary Information)

Jörg Tatchen and Christel M. Marian

Insitute of Theoretical and Computational Chemistry, Heinrich-Heine-University, Universitätsstr. 1, D-40225 Düsseldorf, Germany, Tel.: +49-211-81-13209; Fax: +49-211-81-13466[*]

(Dated: February 24, 2006)

[*]Electronic address: Christel.Marian@uni-duesseldorf.de

I. CARTESIAN COORDINATES FOR OPTIMIZED GEOMETRIES OF THE GROUND AND LOW-LYING EXCITED STATES

TABLE I: Electronic ground state S_0 (planar, minimum according to B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.64639030542405	1.85763697196667	0.00000000000000
C	-5.71367717702227	0.66503404197151	0.00000000000000
O	-3.44142493376733	2.00748061419886	0.00000000000000
C	-5.48856395405689	-2.07707244300556	0.00000000000000
C	-3.21976431979261	-3.23037572860361	0.00000000000000
C	-0.90706301456734	-1.80154739354941	0.00000000000000
C	-1.12656844660222	0.86684506856927	0.00000000000000
C	0.96970830335816	2.44604837079944	0.00000000000000
C	1.48869835185168	-2.92483296601334	0.00000000000000
C	3.61888039246275	-1.39121824776394	0.00000000000000
C	3.29185235118840	1.25427746998339	0.00000000000000
O	5.58354850572023	2.43019380977270	0.00000000000000
C	6.31827538075786	-1.78417275054998	0.00000000000000
C	7.37225688572037	0.53611002000985	0.00000000000000
H	-7.25065719796082	-3.10971038758187	0.00000000000000
H	-3.10148829943337	-5.27704074293226	0.00000000000000
H	1.64703831901247	-4.96639159453573	0.00000000000000
H	0.75950033037576	4.47772060255002	0.00000000000000
H	7.31645150301005	-3.55932810001923	0.00000000000000
H	9.30293844213617	1.17708941463553	0.00000000000000

TABLE II: ($\pi \rightarrow \pi^*$) excited S_1 state (planar, saddle point according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.66441434977344	1.99311998958396	0.00000000000000
C	-5.91044166726740	0.56912331505024	0.00000000000000
O	-3.31963770374265	2.05815630973501	0.00000000000000
C	-5.60821028894090	-2.05567717683697	0.00000000000000
C	-3.27102471310462	-3.27262709941061	0.00000000000000
C	-0.95842226190077	-1.83215520224650	0.00000000000000
C	-1.12695855259129	0.88240264941041	0.00000000000000
C	1.05897597446325	2.45122859416576	0.00000000000000
C	1.42127473205986	-2.91521566564939	0.00000000000000
C	3.63640011338635	-1.37228548549526	0.00000000000000
C	3.36011829123982	1.25354376816689	0.00000000000000
O	5.72843087079299	2.39325257332417	0.00000000000000
C	6.26233373072756	-1.84035226427105	0.00000000000000
C	7.42040916704923	0.51112994116760	0.00000000000000
H	-7.35055698643200	-3.12322476988720	0.00000000000000
H	-3.16751797924916	-5.31139071247503	0.00000000000000
H	1.60706221093191	-4.95465025687071	0.00000000000000
H	0.83625657218294	4.48268563400686	0.00000000000000
H	7.22878515487968	-3.63422179721025	0.00000000000000
H	9.38120479600493	1.05930258201915	0.00000000000000

TABLE III: ($\pi \rightarrow \pi^*$) excited S_1 state (non-planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.66127954023667	1.99541234345628	-0.07946812053673
C	-5.91067845448293	0.56879800748849	-0.01743988096023
O	-3.31889425145244	2.05624837361495	0.11153793699293
C	-5.60779010787823	-2.05571251833691	-0.03067490136732
C	-3.27138677012114	-3.27255111813919	0.01803326027455
C	-0.95847615102943	-1.83236520505464	0.01855493904295
C	-1.12694652175309	0.88201028007393	0.04385798717204
C	1.05793691496532	2.45113670762022	-0.00220634115278
C	1.42093276155874	-2.91561844639579	0.01518639170896
C	3.63543697755002	-1.37233343367687	-0.00440388733708
C	3.35968385505675	1.25398609885090	-0.00341531199690
O	5.72796495278227	2.39385065238286	-0.02150998833403
C	6.26170793976936	-1.84053322181714	-0.01512885136245
C	7.41977137539692	0.51112519799018	-0.02752653239397
H	-7.34987766705837	-3.12285284314402	-0.07968495191998
H	-3.16753834026368	-5.31132961635020	0.01429413269719
H	1.60578433668967	-4.95508633719314	0.01674572797346
H	0.83487556259233	4.48172831719937	0.00134320694201
H	7.22801474638555	-3.63447489090043	-0.01731949477475
H	9.38060652632851	1.05889896328417	-0.04146888621331

TABLE IV: ($n \rightarrow \pi^*$) excited S_2 state (planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.59927061896794	2.02428100722377	0.00000000000000
C	-5.57678716455958	0.55260411831437	0.00000000000000
O	-3.48396056594409	1.96424203289848	0.00000000000000
C	-5.56597172914751	-2.02456407292954	0.00000000000000
C	-3.20210518029374	-3.28138114634197	0.00000000000000
C	-0.93481746105472	-1.88666807455006	0.00000000000000
C	-1.11411007716775	0.80513994668505	0.00000000000000
C	0.92728556417593	2.41712567106525	0.00000000000000
C	1.51475616761931	-2.95687108734932	0.00000000000000
C	3.61980975895823	-1.37930262756101	0.00000000000000
C	3.28205640371473	1.25547060625977	0.00000000000000
O	5.56279424491631	2.46234950646500	0.00000000000000
C	6.32354469988418	-1.74444741106665	0.00000000000000
C	7.36283796888469	0.58758548367592	0.00000000000000
H	-7.33825420600093	-3.03103874918508	0.00000000000000
H	-3.14357281515969	-5.32299674925331	0.00000000000000
H	1.71304700740241	-4.99323464464356	0.00000000000000
H	0.68602696849625	4.44531642352436	0.00000000000000
H	7.33701144068333	-3.51113656923826	0.00000000000000
H	9.28934349977274	1.24110064082126	0.00000000000000

TABLE V: ($\pi \rightarrow \pi^*$) excited S_3 state (planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.69119291643605	1.89412094953444	0.00000000000000
C	-5.78212472157810	0.61469185441705	0.00000000000000
O	-3.44285500088326	2.02121514508165	0.00000000000000
C	-5.52737636474048	-2.05428628922443	0.00000000000000
C	-3.18012966289829	-3.29770698874433	0.00000000000000
C	-0.93140242855296	-1.84495673904479	0.00000000000000
C	-1.16668183910744	0.86521153858751	0.00000000000000
C	0.94058121318728	2.42776522385047	0.00000000000000
C	1.56783709016781	-2.94307685476446	0.00000000000000
C	3.66453547137202	-1.39934082938818	0.00000000000000
C	3.30738401124273	1.25223968595178	0.00000000000000
O	5.55810900085979	2.44725716225549	0.00000000000000
C	6.38299961994037	-1.74626682655330	0.00000000000000
C	7.41072614319725	0.58986287405316	0.00000000000000
H	-7.27769329178167	-3.10871672615960	0.00000000000000
H	-3.08370636064155	-5.33889461119429	0.00000000000000
H	1.73567280376832	-4.98313608205696	0.00000000000000
H	0.72868477164537	4.45995220582728	0.00000000000000
H	7.40655760972442	-3.50701324439210	0.00000000000000
H	9.32104681249948	1.28373575014217	0.00000000000000

TABLE VI: ($\pi \rightarrow \pi^*$) excited T_1 state (planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.67937651227137	1.87501765306301	0.00000000000000
C	-5.72026984106634	0.66235977205489	0.00000000000000
O	-3.47688511839133	2.02672044979784	0.00000000000000
C	-5.56806514111758	-2.02118740396314	0.00000000000000
C	-3.10785534917419	-3.33232720905362	0.00000000000000
C	-0.93073658463632	-1.89448884500140	0.00000000000000
C	-1.14627162859192	0.85104415041634	0.00000000000000
C	0.91866945316523	2.41412529937020	0.00000000000000
C	1.57109193844281	-2.96841512349333	0.00000000000000
C	3.65749196387091	-1.38940944857480	0.00000000000000
C	3.29437505276719	1.24879453747881	0.00000000000000
O	5.55853850239112	2.47106112648404	0.00000000000000
C	6.36777439127174	-1.73005315294034	0.00000000000000
C	7.38329246496825	0.60859118905490	0.00000000000000
H	-7.33695224082739	-3.03954964860884	0.00000000000000
H	-3.03903182129634	-5.37307921001478	0.00000000000000
H	1.76351134574632	-5.00492510008661	0.00000000000000
H	0.69452226326120	4.44465629830114	0.00000000000000
H	7.39729498128717	-3.48731273566288	0.00000000000000
H	9.30199657448507	1.28410803127299	0.00000000000000

TABLE VII: ($\pi \rightarrow \pi^*$) excited T_2 state (planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.67544858213310	2.03273424162981	0.00000000000000
C	-5.96488767233300	0.56187853620827	0.00000000000000
O	-3.28809771053263	2.00416128327529	0.00000000000000
C	-5.62130222277653	-2.04177233150726	0.00000000000000
C	-3.26544624444034	-3.22138576493365	0.00000000000000
C	-0.95732765166087	-1.87312678776494	0.00000000000000
C	-1.12393102525388	0.86050186125108	0.00000000000000
C	1.06480306619347	2.45247517783294	0.00000000000000
C	1.45358420066816	-2.97586688890831	0.00000000000000
C	3.65794831148283	-1.38902349548266	0.00000000000000
C	3.36138907720445	1.25860056265157	0.00000000000000
O	5.69463637478820	2.42000845933844	0.00000000000000
C	6.27016378282320	-1.82224280979149	0.00000000000000
C	7.42381535518970	0.54801371377263	0.00000000000000
H	-7.34098605053620	-3.14553886437646	0.00000000000000
H	-3.19201268674009	-5.26562249385481	0.00000000000000
H	1.65265889843044	-5.01065209754600	0.00000000000000
H	0.83161778938821	4.48089455519679	0.00000000000000
H	7.24816151694321	-3.60971671355126	0.00000000000000
H	9.37567476689518	1.12370508771048	0.00000000000000

TABLE VIII: ($\pi \rightarrow \pi^*$) excited T_3 state (planar, minimum according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.65019281482665	1.90744709125749	0.00000000000000
C	-5.74591004222902	0.66185475850691	0.00000000000000
O	-3.43266740230905	2.05298267505637	0.00000000000000
C	-5.53931188542520	-2.04212228569431	0.00000000000000
C	-3.22173883843244	-3.28777817071764	0.00000000000000
C	-0.94479599171012	-1.85372105864414	0.00000000000000
C	-1.14191599667716	0.86534218039780	0.00000000000000
C	1.02774555221552	2.45598666158726	0.00000000000000
C	1.43458220693926	-2.94510248302264	0.00000000000000
C	3.63480039517900	-1.38947463461906	0.00000000000000
C	3.32132787019428	1.28150111528257	0.00000000000000
O	5.68154571919903	2.44190986397220	0.00000000000000
C	6.23867538246689	-1.84292417286702	0.00000000000000
C	7.41353364643307	0.52762501812088	0.00000000000000
H	-7.31181252233909	-3.05463265614536	0.00000000000000
H	-3.13037191083364	-5.33088171915007	0.00000000000000
H	1.61399803350435	-4.98510840227824	0.00000000000000
H	0.80939404616460	4.48791887703963	0.00000000000000
H	7.20404208868671	-3.63762419328563	0.00000000000000
H	9.36824404608617	1.08800019217856	0.00000000000000

TABLE IX: ($n \rightarrow \pi^*$) excited T_4 state (planar, saddle point according to TD-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-7.62935290616653	1.99378544628485	0.00000000000000
C	-5.56871234998162	0.55400915315851	0.00000000000000
O	-3.47590575649602	1.98969300334532	0.00000000000000
C	-5.55359076772776	-2.02196517746352	0.00000000000000
C	-3.21593366250461	-3.28339886133551	0.00000000000000
C	-0.93301804603114	-1.86972675355120	0.00000000000000
C	-1.11232222940260	0.81800706743763	0.00000000000000
C	0.93761868196784	2.42066986771771	0.00000000000000
C	1.49917515533151	-2.94459163445390	0.00000000000000
C	3.62002247744879	-1.37794298831867	0.00000000000000
C	3.28993012208925	1.25271444928632	0.00000000000000
O	5.57341150180890	2.45280799599174	0.00000000000000
C	6.32030223867240	-1.75539366255078	0.00000000000000
C	7.36918218267630	0.57295610353377	0.00000000000000
H	-7.33029357555858	-3.02498905954583	0.00000000000000
H	-3.15399646117057	-5.32376940447171	0.00000000000000
H	1.68886460427215	-4.98221395540141	0.00000000000000
H	0.70343548538217	4.44972458492987	0.00000000000000
H	7.32679550084321	-3.52614287211427	0.00000000000000
H	9.29740546938042	1.22090139299277	0.00000000000000

TABLE X: Furan side dissociative excited triplet state $T(\pi \rightarrow \sigma^*)_{fu}$ (planar, minimum according to U-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-8.06670842383100	1.64529114993191	0.00000000000000
C	-6.07719421112000	0.56280007842349	0.00000000000000
O	-3.87162387291277	2.04580198050268	0.00000000000000
C	-5.68445651424036	-2.16170364263799	0.00000000000000
C	-3.35285278202892	-3.17801857230642	0.00000000000000
C	-1.13270911854421	-1.60210960695944	0.00000000000000
C	-1.51718313170003	1.04276243409842	0.00000000000000
C	0.53742987496998	2.72194037744970	0.00000000000000
C	1.32405113294409	-2.54760993230010	0.00000000000000
C	3.45100400496322	-0.91990070739060	0.00000000000000
C	2.88231475088297	1.67365278621130	0.00000000000000
O	8.06655766119698	2.06123171457540	0.00000000000000
C	5.95085847073463	-1.86609807082510	0.00000000000000
C	8.14199795690860	-0.25712396770194	0.00000000000000
H	-7.38279766541248	-3.29616653877462	0.00000000000000
H	-3.10976848924177	-5.21298857366825	0.00000000000000
H	1.61161249205805	-4.57787253393235	0.00000000000000
H	0.20231362103188	4.74168382236813	0.00000000000000
H	6.24875344461341	-3.89341561673080	0.00000000000000
H	9.98617452703940	-1.23784703525034	0.00000000000000

TABLE XI: Pyrone side dissociative excited triplet state $T(\pi \rightarrow \sigma^*)_{py}$ (planar, saddle point according to U-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-9.29936956866615	0.70095281647962	0.00000000000000
C	-7.06905871982390	0.40011820493340	0.00000000000000
O	-2.60807872416317	3.02706619533443	0.00000000000000
C	-5.77925849692458	-2.05122504796379	0.00000000000000
C	-3.28297821433441	-2.59795678657245	0.00000000000000
C	-0.93004913194617	-1.17698454968519	0.00000000000000
C	-0.72992148730556	1.63489244288611	0.00000000000000
C	1.78365024148455	2.76866364601049	0.00000000000000
C	1.26519002786075	-2.60861577127444	0.00000000000000
C	3.65737018842059	-1.46020611666112	0.00000000000000
C	3.82493292581326	1.21534100666064	0.00000000000000
O	6.32474826871975	1.92806788584115	0.00000000000000
C	6.19751184358060	-2.35390161650760	0.00000000000000
C	7.69119984793523	-0.26053677228412	0.00000000000000
H	-7.06587585082639	-3.66172183847200	0.00000000000000
H	-2.91246910403713	-4.61975443748872	0.00000000000000
H	1.13694857449863	-4.65317592302084	0.00000000000000
H	1.91008935195138	4.80779379850061	0.00000000000000
H	6.84414356818255	-4.28544744209095	0.00000000000000
H	9.71331671974099	-0.02525906330675	0.00000000000000

TABLE XII: Pyrone side dissociative excited triplet state $T(\pi \rightarrow \sigma^*)_{py}$ (non-planar, minimum according to U-B3LYP)

atom	x [a.u.]	y [a.u.]	z [a.u.]
O	-8.37371862062672	1.28547662771427	-1.22071914040309
C	-6.40774475515927	0.21274753940812	-1.17609313710622
O	-2.82882839878535	2.67456290118766	1.21628560302034
C	-5.69366843507624	-2.08342674170445	0.19293626893468
C	-3.32604642534000	-2.79174001213170	0.79011323637660
C	-0.97617651409481	-1.38785762399544	0.51230391481333
C	-0.91051193071973	1.42093573584778	0.69909685354885
C	1.49995661234642	2.69102158809824	0.35951417002998
C	1.24335848679466	-2.72040150339611	0.19175744203489
C	3.55567564904200	-1.43911196706581	-0.09818697195669
C	3.58912986244894	1.24012593931188	-0.00363310757296
O	6.02393538612246	2.08974591487909	-0.32990127863430
C	6.10985469473617	-2.18917317331102	-0.49816331713339
C	7.48362914938150	-0.01782517942436	-0.62064803451239
H	-7.24742067270193	-3.37976613148699	0.56577701777372
H	-3.10487050590593	-4.67488192344729	1.57772392482559
H	1.20160204667455	-4.76742635586742	0.11422541546044
H	1.54380094161800	4.73079054008137	0.46552774972431
H	6.84364357801984	-4.08099688072308	-0.67705517927332
H	9.47028459814921	0.32897094690181	-0.89805233107877

II. INTENSITY BORROWING OF THE RADIATIVE SPIN-FORBIDDEN $S_0 \leftarrow T_1$ TRANSITION

TABLE XIII: Significant contributions to the transition dipole moment from singlet states (top) and triplet states (bottom). All values were obtained at the T_1 minimum geometry. Vertical energy differences $[cm^{-1}]$. $\langle T_1|\mathcal{H}_{\mathrm{SO}}|^1\Phi\rangle$ and $\langle^3\Phi|\mathcal{H}_{\mathrm{SO}}|S_0\rangle$: spin-orbit coupling matrix elements $[cm^{-1}]$. $\langle S_0|\mu|^1\Phi\rangle$ and $\langle T_1|\mu|^3\Phi\rangle$: electric dipole (transition) moments $[ea_0]$ of spin-allowed transitions. Cartesian components of the spin-orbit coupling and electric dipole operators are given in parantheses.

singlets $\|^1\Phi\rangle^\dagger$	@T_1	$E_{^1\Phi} - E_{T_1}$	$\langle^1\Phi\|\mathcal{H}_{\mathrm{SO}}\|T_1\rangle$	$\langle S_0\|\mu\|^1\Phi\rangle$
S_0	$X\,^1A'$	–17157.4	$-i\cdot 3.0\cdot 10^{-2}(z)$	2.095(x)/–1.677(y)
S_1	$2\,^1A'$	9811.3	$i\cdot 1.7\cdot 10^{-2}(z)$	–1.483(x)/–0.255(y)
S_2	$1\,^1A''$	12196.7	$i\cdot 28.585(x)/16.815(y)$	0.045(z)
S_3	$3\,^1A'$	13422.1	$i\cdot 1.8\cdot 10^{-2}(z)$	–1.898(x)/ 0.279(y)
	$4\,^1A'$	19551.8	$i\cdot 2.2\cdot 10^{-2}(z)$	–0.810(x)/ 0.648(y)
	$5\,^1A'$	20512.8	$i\cdot 3.9\cdot 10^{-2}(z)$	0.187(x)/ 0.036(y)
triplets $\|^3\Phi\rangle^\dagger$	@T_1	$E_{^3\Phi} - E_{S_0}$	$\langle^3\Phi\|\mathcal{H}_{\mathrm{SO}}\|S_0\rangle$	$\langle^3\Phi\|\mu\|T_1\rangle$
T_1	$1\,^3A'$	17157.4	$i\cdot 3.0\cdot 10^{-2}(z)$	1.522(x)/–1.489(y)
T_2	$2\,^3A'$	24921.7	$-i\cdot 1.5\cdot 10^{-2}(z)$	0.027(x)/–0.316(y)
T_3	$3\,^3A'$	29150.6	$-i\cdot 3.0\cdot 10^{-2}(z)$	0.140(x)/ 0.007(y)
T_4	$1\,^3A''$	28845.6	$-i\cdot 35.846(x)/25.846(y)$	–0.022(z)
	$4\,^3A'$	32549.5	$-i\cdot 2.3\cdot 10^{-2}(z)$	–0.369(x)/–0.185(y)
	$5\,^3A'$	34645.2	$i\cdot 1.3\cdot 10^{-2}(z)$	0.646(x)/–0.244(y)
	$6\,^3A'$	36850.0	$i\cdot 0.7\cdot 10^{-2}(z)$	–0.024(x)/–0.043(y)
	$7\,^3A'$	40680.1	$-i\cdot 7.6\cdot 10^{-2}(z)$	–0.771(x)/–0.188(y)

†: For the higher excited states it becomes exceedingly difficult to find a 1:1 correspondence between the CI root at the T_1 geometry and a state at the ground state minimum.

III. ANALYSIS OF THE VIBRONIC SPETRA: CONTRIBUTING VIBRATIONAL NORMAL MODES OF THE S_0, S_1, AND T_1 STATE

TABLE XIV: Totally symmetric harmonic vibrational modes of the S_1 state with large contributions to the vibronic structure of the absorption band. The frequencies $\bar{\nu}$ [cm^{-1}] have not been scaled. Δ denotes the shift in natural (dimensionless) oscillator coordinates with respect to the S_0 state. Only modes with $\Delta > 0.6$ are listed.

mode	$\bar{\nu}$	type	Δ
4	192	C_7-O_8 str., frame def. (pyrone)	0.618
7	320	frame def. (coumarin), C_6-C_7-O_8 bend, C_7-O_8 str.	0.755
9	382	frame def. (coumarin), C_6-C_7=O_{10} bend, O_{10}-C_7-O_8 bend	1.349
13	518	frame def. (pyrone)	0.844
15	544	C_7-O_8 str., frame def. (pyrone)	0.773
18	618	frame def. (coumarin), C_6-C_7-O_8 bend, C_7-O_8 str., C_6-C_7 str.	0.608
46	1564	C-C str., frame def. (psoralen), C-H bend	0.701
48	1863	C_7=O_{10} str., C_6-C_7 str.	0.696

TABLE XV: Totally symmetric harmonic vibrational modes of the S_0 state with large contributions to the vibronic structure of the fluorescence emission band. The frequencies $\bar{\nu}$ [cm^{-1}] have not been scaled. Δ denotes the shift in natural (dimensionless) oscillator coordinates with respect to the S_0 state. Only modes with $\Delta > 0.7$ are listed.

mode	$\bar{\nu}$	type	Δ
9	399	frame def. (coumarin), C_6-C_7-O_8 bend	1.429
18	740	frame def. (psoralen), C_7-O_8 str., C_6-C_7 str.	1.330
31	1090	C-H bend, C_6-C_7 str., C_7-O_8 str., C_6-C_7-O_8 bend	1.311
32	1119	C-H bend, O_8-C_{8a} str., frame def. (psoralen)	0.713
33	1154	C-H bend, C_2-C_3 str., frame def. (psoralen)	1.148
46	1658	C_5-C_6 str., C-C str., C-H bend, frame def. (psoralen)	0.779

TABLE XVI: Totally symmetric harmonic vibrational modes of the S_0 state with large contributions to the vibronic structure of the phosphorescence emission band. The frequencies $\bar{\nu}$ [cm^{-1}] have not been scaled. Δ denotes the shift in natural (dimensionless) oscillator coordinates with respect to the T_1 state. Only modes with $\Delta > 0.5$ are listed.

mode	$\bar{\nu}$	type	Δ
4	239	frame def. (psoralen)	0.579
15	616	frame def. (coumarin)	0.570
34	1184	C-H bend, C_5-C_6 str.	0.522
35	1196	C-H bend, C_7-O_8 str., O_1-C_{9a} str.	0.501
40	1392	C-C str., C-H bend, frame def. (psoralen)	0.529
45	1600	C_5-C_6 str., C-C str., C-H bend, frame def. (psoralen)	0.870
46	1658	C_5-C_6 str., C-C str., C-H bend, frame def. (psoralen)	0.964
47	1667	C_5-C_6 str., C-C str., C-H bend, frame def. (psoralen)	1.473