Calculations of Mode-Specific Tunneling of Double-Hydrogen Transfer in Porphycene Agree with and Illuminate Experiment

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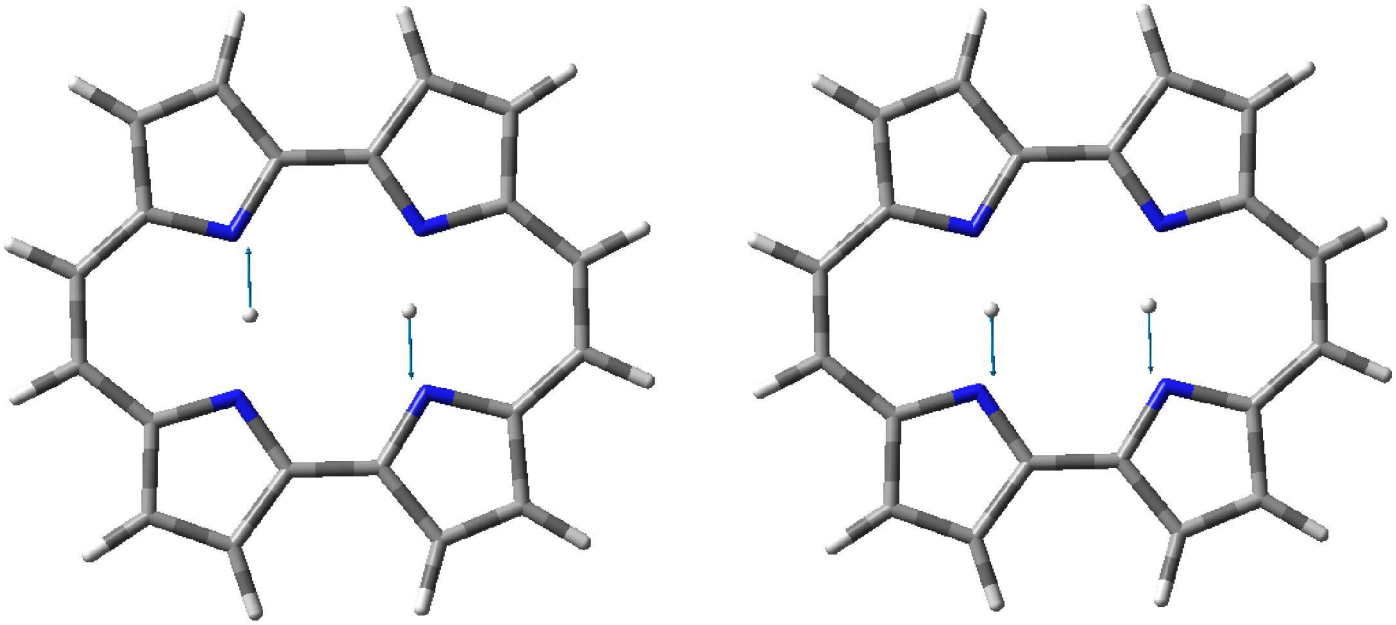
Supporting Information

Content



ν_1 (b_{3g})
i1206

ν_2 (b_{2u})
i1066

Figure S1: Presentation of imaginary frequency normal modes of SP. ν_1 is the imaginary-frequency that is responsible for double-H transfer of *trans*-PHC. ν_2 describes relevant motion of double-H transfer of *cis*-PHC.

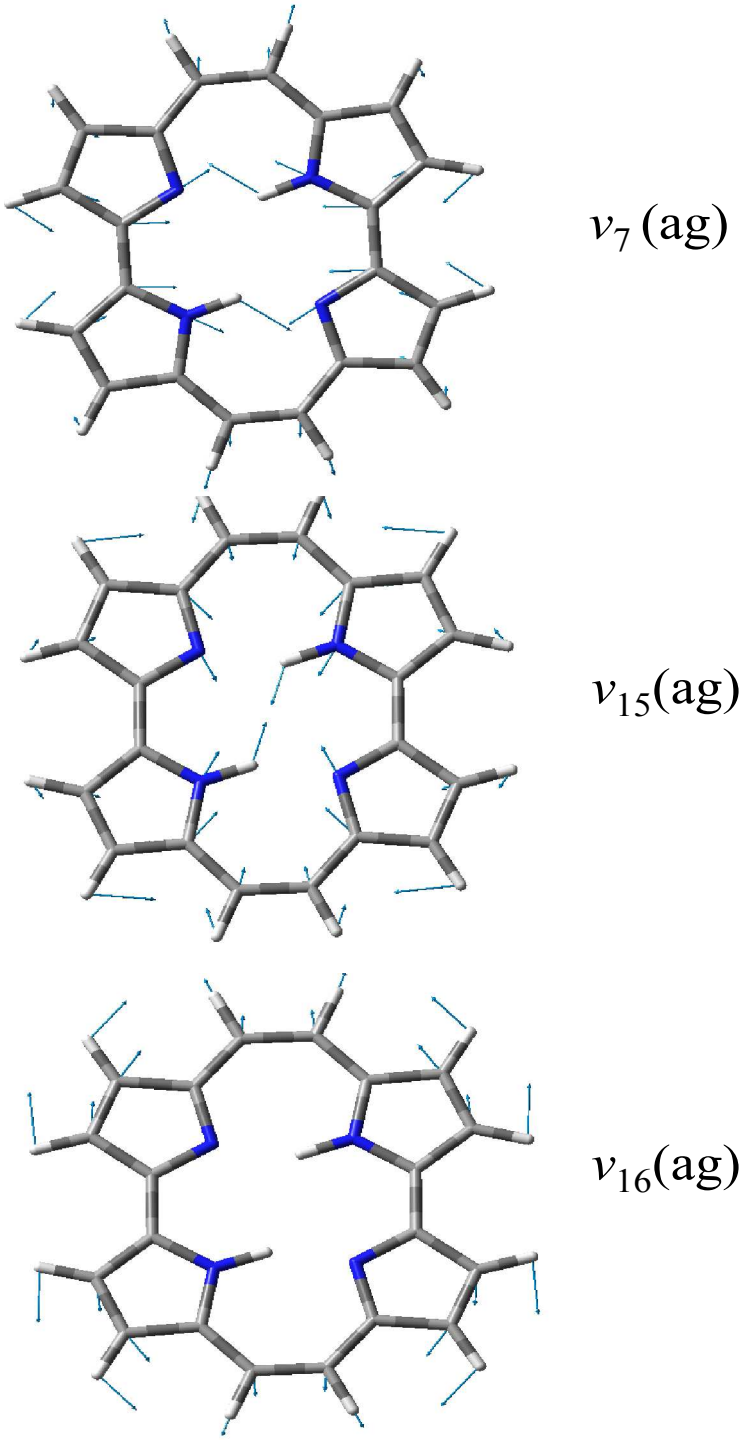


Figure S2: Presentation of three normal modes of *trans*-PH

Table S1:. *trans*-PHC harmonic frequencies and projection of normal modes onto imaginary-frequency of saddle point. Harmonic frequencies (cm^{-1}) are calculated at the B3LPY/6-31G(d,p) level of theory.

mode		freq DFT	Freq[a] Exp	projection	mode		Freq[a] DFT	Freq[a] Exp	projection	mode		freq DFT	Freq[a] Exp	projection
ν_1	a_u	64		0.00	ν_{37}	b_g	788		0.00	ν_{73}	b_u	1326		0.00
ν_2	a_u	76		0.00	ν_{38}	a_u	796		0.00	ν_{74}	b_u	1334		0.00
ν_3	a_u	93		0.00	ν_{39}	b_g	831		0.00	ν_{75}	a_g	1367	1336	0.03
ν_4	b_g	121		0.00	ν_{40}	a_g	832		0.00	ν_{76}	a_g	1384		0.09
ν_5	b_g	140		0.00	ν_{41}	a_u	833		0.18	ν_{77}	b_u	1400		0.00
ν_6	a_g	151	147	0.03	ν_{42}	b_u	835		0.00	ν_{78}	b_u	1409		0.00
ν_7	a_g	186	178	0.13	ν_{43}	a_g	877		0.22	ν_{79}	a_g	1410		0.06
ν_8	b_g	203		0.00	ν_{44}	a_u	894		0.00	ν_{80}	a_g	1438	1403	0.03
ν_9	a_u	208		0.00	ν_{45}	b_u	895		0.00	ν_{81}	a_g	1445		0.03
ν_{10}	b_g	211		0.00	ν_{46}	b_g	895		0.00	ν_{82}	b_u	1455		0.00
ν_{11}	b_u	239		0.00	ν_{47}	b_g	903		0.00	ν_{83}	a_g	1484		0.17
ν_{12}	a_u	314		0.00	ν_{48}	a_u	904		0.00	ν_{84}	b_u	1505		0.00
ν_{13}	a_u	322		0.00	ν_{49}	b_g	928		0.00	ν_{85}	b_u	1509		0.00
ν_{14}	b_u	323		0.00	ν_{50}	b_u	946		0.00	ν_{86}	b_u	1527		0.15
ν_{15}	a_g	347	341	0.04	ν_{51}	a_u	956		0.00	ν_{87}	a_g	1527	1478	0.01
ν_{16}	a_g	370	364	0.02	ν_{52}	b_g	957		0.00	ν_{88}	a_g	1556	1506	0.13
ν_{17}	b_u	391		0.00	ν_{53}	b_u	963		0.00	ν_{89}	b_u	1564		0.00
ν_{18}	b_g	401		0.00	ν_{54}	a_g	987	966	0.05	ν_{90}	a_g	1587		0.05
ν_{19}	b_u	472		0.00	ν_{55}	a_g	992	990	0.17	ν_{91}	a_g	1607	1567	0.03
ν_{20}	a_g	491	481	0.00	ν_{56}	a_u	995		0.00	ν_{92}	b_u	1613		0.00
ν_{21}	b_g	494		0.00	ν_{57}	a_g	1014		0.16	ν_{93}	b_u	1627		0.00
ν_{22}	a_u	513		0.00	ν_{58}	b_u	1027		0.00	ν_{94}	a_g	1659	1615	0.16
ν_{23}	a_g	609		0.12	ν_{59}	b_u	1073		0.00	ν_{95}	a_g	2916		0.64
ν_{24}	b_u	625		0.00	ν_{60}	a_g	1081		0.07	ν_{96}	b_u	2916		0.50
ν_{25}	a_u	641		0.00	ν_{61}	b_u	1086		0.00	ν_{97}	b_u	3164		0.00
ν_{26}	b_g	645		0.00	ν_{62}	a_g	1091	1060	0.03	ν_{98}	a_g	3164		0.00
ν_{27}	b_u	672		0.00	ν_{63}	b_u	1120		0.00	ν_{99}	b_u	3183		0.00
ν_{28}	a_g	673	667	0.00	ν_{64}	a_g	1140		0.00	ν_{100}	a_g	3183		0.00
ν_{29}	b_g	674		0.00	ν_{65}	a_g	1190	1160	0.01	ν_{101}	a_g	3234		0.00
ν_{30}	a_u	675		0.07	ν_{66}	b_u	1207		0.00	ν_{102}	b_u	3234		0.00
ν_{31}	b_g	714		0.00	ν_{67}	b_u	1224		0.00	ν_{103}	b_u	3249		0.00
ν_{32}	a_u	714		0.00	ν_{68}	a_g	1238	1202	0.01	ν_{104}	a_g	3249		0.00
ν_{33}	b_g	719		0.00	ν_{69}	b_u	1267		0.00	ν_{105}	b_u	3255		0.00
ν_{34}	a_u	726		0.00	ν_{70}	b_u	1281		0.00	ν_{106}	a_g	3255		0.00
ν_{35}	a_u	765		0.00	ν_{71}	a_g	1290	1260	0.05	ν_{107}	b_u	3267		0.00
ν_{36}	b_g	775		0.00	ν_{72}	a_g	1309		0.22	ν_{108}	a_g	3267		0.00

[a] Vdovin, A.; Sepioł, J.; Urban´ ska, N.; Pietraszkiewicz, M.; Mordzin´ ski, A.; Waluk, J. *J. Am. Chem. Soc.* **2006**, 128, 2577-2586.

Table S2*: trans*-PHC-d_1 harmonic frequencies and projection of normal modes onto imaginary-frequency of saddle point. Harmonic frequencies (cm^{-1}) are calculated at the B3LPY/6-31G(d,p) level of theory.

mode	freq	projection	mode	freq	projection	mode	freq	projection
ν_1	61	0.00	ν_{37}	780	0.00	ν_{73}	1323	0.16
ν_2	71	0.00	ν_{38}	791	0.00	ν_{74}	1328	0.01
ν_3	88	0.00	ν_{39}	796	0.00	ν_{75}	1368	0.02
ν_4	118	0.00	ν_{40}	826	0.11	ν_{76}	1373	0.04
ν_5	136	0.00	ν_{41}	832	0.00	ν_{77}	1395	0.05
ν_6	150	0.01	ν_{42}	834	0.00	ν_{78}	1407	0.05
ν_7	185	0.10	ν_{43}	835	0.12	ν_{79}	1412	0.05
ν_8	198	0.00	ν_{44}	873	0.15	ν_{80}	1420	0.05
ν_9	206	0.00	ν_{45}	894	0.00	ν_{81}	1445	0.01
ν_{10}	208	0.00	ν_{46}	894	0.10	ν_{82}	1452	0.00
ν_{11}	237	0.03	ν_{47}	896	0.00	ν_{83}	1463	0.06
ν_{12}	310	0.00	ν_{48}	903	0.00	ν_{84}	1502	0.13
ν_{13}	319	0.00	ν_{49}	904	0.00	ν_{85}	1509	0.01
ν_{14}	323	0.05	ν_{50}	930	0.16	ν_{86}	1521	0.01
ν_{15}	346	0.03	ν_{51}	954	0.07	ν_{87}	1531	0.14
ν_{16}	370	0.02	ν_{52}	956	0.00	ν_{88}	1557	0.08
ν_{17}	391	0.04	ν_{53}	956	0.00	ν_{89}	1570	0.09
ν_{18}	398	0.00	ν_{54}	973	0.00	ν_{90}	1592	0.01
ν_{19}	471	0.05	ν_{55}	979	0.15	ν_{91}	1602	0.09
ν_{20}	490	0.04	ν_{56}	988	0.11	ν_{92}	1613	0.08
ν_{21}	492	0.00	ν_{57}	1013	0.09	ν_{93}	1623	0.01
ν_{22}	511	0.00	ν_{58}	1023	0.09	ν_{94}	1653	0.14
ν_{23}	609	0.07	ν_{59}	1048	0.03	ν_{95}	2155	0.06
ν_{24}	625	0.03	ν_{60}	1076	0.05	ν_{96}	2890	0.82
ν_{25}	639	0.00	ν_{61}	1085	0.06	ν_{97}	3164	0.00
ν_{26}	644	0.00	ν_{62}	1089	0.00	ν_{98}	3165	0.00
ν_{27}	655	0.00	ν_{63}	1091	0.05	ν_{99}	3183	0.00
ν_{28}	665	0.02	ν_{64}	1135	0.06	ν_{100}	3184	0.00
ν_{29}	674	0.00	ν_{65}	1168	0.01	ν_{101}	3235	0.00
ν_{30}	674	0.09	ν_{66}	1198	0.01	ν_{102}	3235	0.00
ν_{31}	702	0.00	ν_{67}	1210	0.06	ν_{103}	3249	0.00
ν_{32}	713	0.00	ν_{68}	1228	0.01	ν_{104}	3249	0.00
ν_{33}	714	0.00	ν_{69}	1239	0.02	ν_{105}	3256	0.00
ν_{34}	719	0.00	ν_{70}	1279	0.12	ν_{106}	3256	0.00
ν_{35}	726	0.00	ν_{71}	1284	0.03	ν_{107}	3267	0.00
ν_{36}	767	0.00	ν_{72}	1298	0.05	ν_{108}	3267	0.00

Table S3*: trans*-PHC-d_2 harmonic frequencies and projection of normal modes onto imaginary-frequency of saddle point. Harmonic frequencies (cm^{-1}) are calculated at the B3LPY/6-31G(d,p) level of theory.

mode		freq	Projection	Mode		freq	Projection	Mode		freq	Projection
ν_1	a_u	64	0.00	ν_{37}	b_g	777	0.00	ν_{73}	b_u	1296	0.07
ν_2	a_u	76	0.00	ν_{38}	a_u	780	0.00	ν_{74}	b_u	1323	0.00
ν_3	a_u	92	0.00	ν_{39}	b_g	792	0.00	ν_{75}	a_g	1351	0.02
ν_4	b_g	120	0.00	ν_{40}	a_g	797	0.00	ν_{76}	a_g	1368	0.04
ν_5	b_g	139	0.00	ν_{41}	a_u	823	0.32	ν_{77}	b_u	1383	0.00
ν_6	a_g	150	0.04	ν_{42}	b_u	830	0.00	ν_{78}	b_u	1397	0.04
ν_7	a_g	184	0.18	ν_{43}	a_g	835	0.00	ν_{79}	a_g	1405	0.00
ν_8	b_g	202	0.00	ν_{44}	a_u	836	0.00	ν_{80}	a_g	1413	0.02
ν_9	a_u	208	0.00	ν_{45}	b_u	870	0.27	ν_{81}	a_g	1429	0.00
ν_{10}	b_g	210	0.00	ν_{46}	b_g	890	0.00	ν_{82}	b_u	1442	0.01
ν_{11}	b_u	238	0.00	ν_{47}	b_g	894	0.00	ν_{83}	a_g	1452	0.11
ν_{12}	a_u	314	0.00	ν_{48}	a_u	895	0.00	ν_{84}	b_u	1466	0.00
ν_{13}	a_u	321	0.00	ν_{49}	b_g	903	0.00	ν_{85}	b_u	1502	0.00
ν_{14}	b_u	322	0.00	ν_{50}	b_u	904	0.00	ν_{86}	b_u	1511	0.05
ν_{15}	a_g	344	0.06	ν_{51}	a_u	919	0.00	ν_{87}	a_g	1514	0.00
ν_{16}	a_g	370	0.03	ν_{52}	b_g	946	0.00	ν_{88}	a_g	1544	0.01
ν_{17}	b_u	390	0.00	ν_{53}	b_u	956	0.00	ν_{89}	b_u	1561	0.00
ν_{18}	b_g	401	0.00	ν_{54}	a_g	956	0.25	ν_{90}	a_g	1586	0.03
ν_{19}	b_u	467	0.00	ν_{55}	a_g	957	0.00	ν_{91}	a_g	1588	0.00
ν_{20}	a_g	488	0.06	ν_{56}	a_u	980	0.16	ν_{92}	b_u	1603	0.02
ν_{21}	b_g	494	0.00	ν_{57}	a_g	1009	0.13	ν_{93}	b_u	1618	0.00
ν_{22}	a_u	513	0.00	ν_{58}	b_u	1011	0.00	ν_{94}	a_g	1627	0.02
ν_{23}	a_g	607	0.16	ν_{59}	b_u	1040	0.00	ν_{95}	a_g	2171	0.64
ν_{24}	b_u	624	0.00	ν_{60}	a_g	1054	0.15	ν_{96}	b_u	2172	0.39
ν_{25}	a_u	640	0.00	ν_{61}	b_u	1077	0.00	ν_{97}	b_u	3164	0.00
ν_{26}	b_g	640	0.00	ν_{62}	a_g	1087	0.00	ν_{98}	a_g	3164	0.01
ν_{27}	b_u	646	0.00	ν_{63}	b_u	1090	0.04	ν_{99}	b_u	3183	0.00
ν_{28}	a_g	662	0.00	ν_{64}	a_g	1097	0.03	ν_{100}	a_g	3183	0.00
ν_{29}	b_g	664	0.00	ν_{65}	a_g	1163	0.08	ν_{101}	a_g	3234	0.00
ν_{30}	a_u	665	0.13	ν_{66}	b_u	1172	0.00	ν_{102}	b_u	3234	0.00
ν_{31}	b_g	694	0.00	ν_{67}	b_u	1202	0.10	ν_{103}	b_u	3248	0.00
ν_{32}	a_u	709	0.00	ν_{68}	a_g	1206	0.00	ν_{104}	a_g	3248	0.00
ν_{33}	b_g	714	0.00	ν_{69}	b_u	1227	0.00	ν_{105}	b_u	3255	0.00
ν_{34}	a_u	719	0.00	ν_{70}	b_u	1238	0.10	ν_{106}	a_g	3255	0.00
ν_{35}	a_u	720	0.00	ν_{71}	a_g	1280	0.00	ν_{107}	b_u	3267	0.00
ν_{36}	b_g	728	0.00	ν_{72}	a_g	1293	0.00	ν_{108}	a_g	3267	0.00