

The structure and vibrational dynamics of the pyrrole dimer.

Supplementary information

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The empirical potential energy function used to fit the CCSD(T) data of the pyrrole dimer (see **Table A**)

$$V(R, \rho, \sigma) = \sum_{k,l,m} C(k, l, m) \{\exp[-a_R(R - R_r)]\}^k \times \{\cos \rho\}^l \times \{\cos \sigma\}^m \quad (1)$$

Table A The potential energy function parameters (in cm^{-1}) of the pyrrole dimer obtained by fitting to the *ab initio* data^a

<i>k l m</i>	$C(k, l, m)$	<i>k l m</i>	$C(k, l, m)$	<i>k l m</i>	$C(k, l, m)$	<i>k l m</i>	$C(k, l, m)$
0 0 0	12289.69	1 1 2	592345.40	0 0 5	-1326199.73	0 6 6	1949003.68
1 0 0	4993.59	2 2 2	747929.00	0 1 5	-7224232.27	0 0 7	-636903.25
0 1 0	50480.92	0 4 2	605065.85	2 0 5	-4866265.11	1 0 7	799506.60
1 1 0	69057.95	0 5 2	1484085.94	1 1 5	15690616.63	0 1 7	-3372205.80
3 0 0	7986.37	0 0 3	825698.23	0 2 5	-1290591.33	2 0 7	-10987971.29
1 2 0	162943.11	1 0 3	-875925.66	3 0 5	1100547.46	1 1 7	7662544.15
0 3 0	-217816.14	0 1 3	2443584.43	2 1 5	-11576215.67	3 0 7	3688554.03
4 0 0	-3851.78	1 1 3	-3643434.73	1 2 5	11208909.33	2 1 7	-12444885.50
2 2 0	-96117.39	2 1 3	1091245.69	0 6 5	-2987477.78	1 2 7	6366540.62
0 4 0	-259699.90	1 2 3	-1698130.98	0 0 6	1793968.45	0 3 7	562382.21
2 3 0	-129815.13	0 3 3	-841312.22	1 0 6	-1697147.20	2 0 8	3442001.13
1 4 0	-142687.29	0 5 3	-1054781.11	0 1 6	9038947.41	3 0 8	-1329901.46
4 2 0	4643.21	0 0 4	-385018.43	2 0 6	12306129.56	4 0 8	-112268.29
3 3 0	12124.38	1 0 4	1766004.31	1 1 6	-20441503.12	3 1 8	-32108.54
0 6 0	90375.26	3 1 4	20548.17	0 2 6	1638718.80	2 2 8	-3231984.54
0 1 1	-71538.90	2 2 4	-1564985.32	3 0 6	-3470561.97	4 1 8	4709.52
2 0 1	109045.36	1 3 4	1951170.84	2 1 6	21434997.39	0 2 9	-390097.03
1 1 1	79959.88	0 4 4	-1802285.46	1 2 6	-15969898.40	2 1 9	1495482.80
0 3 1	747739.39	2 3 4	154560.25	0 3 6	-327490.66	4 0 9	74121.78
2 2 1	-303149.89	1 4 4	662241.97	4 0 6	43162.10	2 2 9	1561790.89
1 3 1	-258873.94	0 5 4	-976410.49	2 2 6	2846299.86	1 3 9	1445650.56
0 4 1	742741.86	2 4 4	26921.21	1 3 6	-2320447.25	0 4 9	731422.14
0 0 2	-281331.71	1 5 4	-49314.82	2 3 6	-55901.08	0 5 9	655702.66
0 1 2	-863936.59	0 6 4	1006095.40	1 4 6	-574310.59	1 3 10	-751368.23

^a See Eq.(1) ($a_R=0.838144 \text{ \AA}^{-1}$, $R_r=4.2260 \text{ \AA}$).

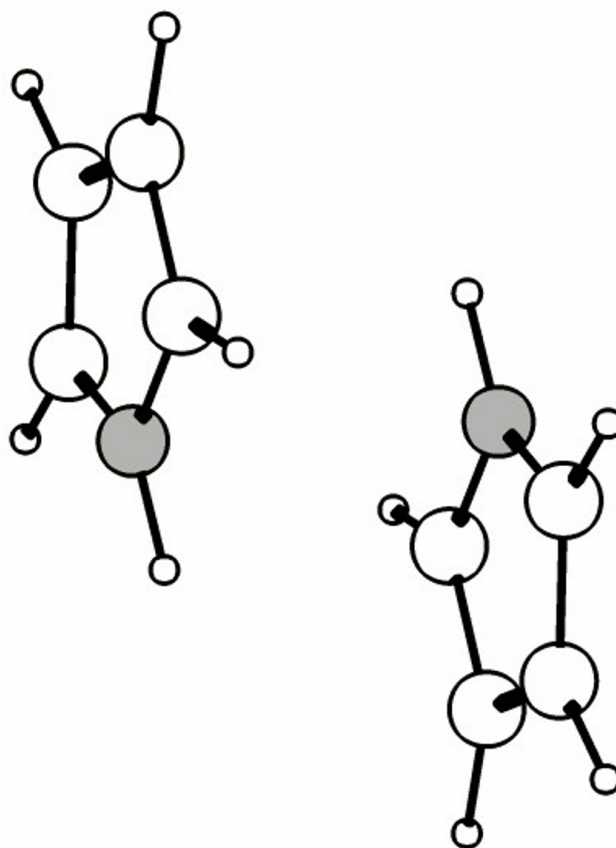
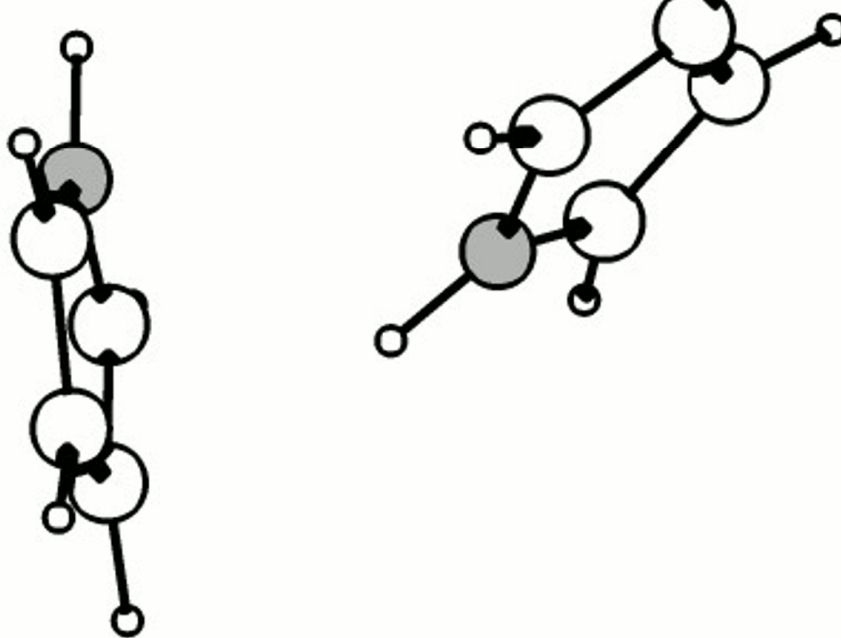


FIG. 1: The equilibrium (*T-shaped*) and transient (*parallel-displaced*) structures of the pyrrole dimer.

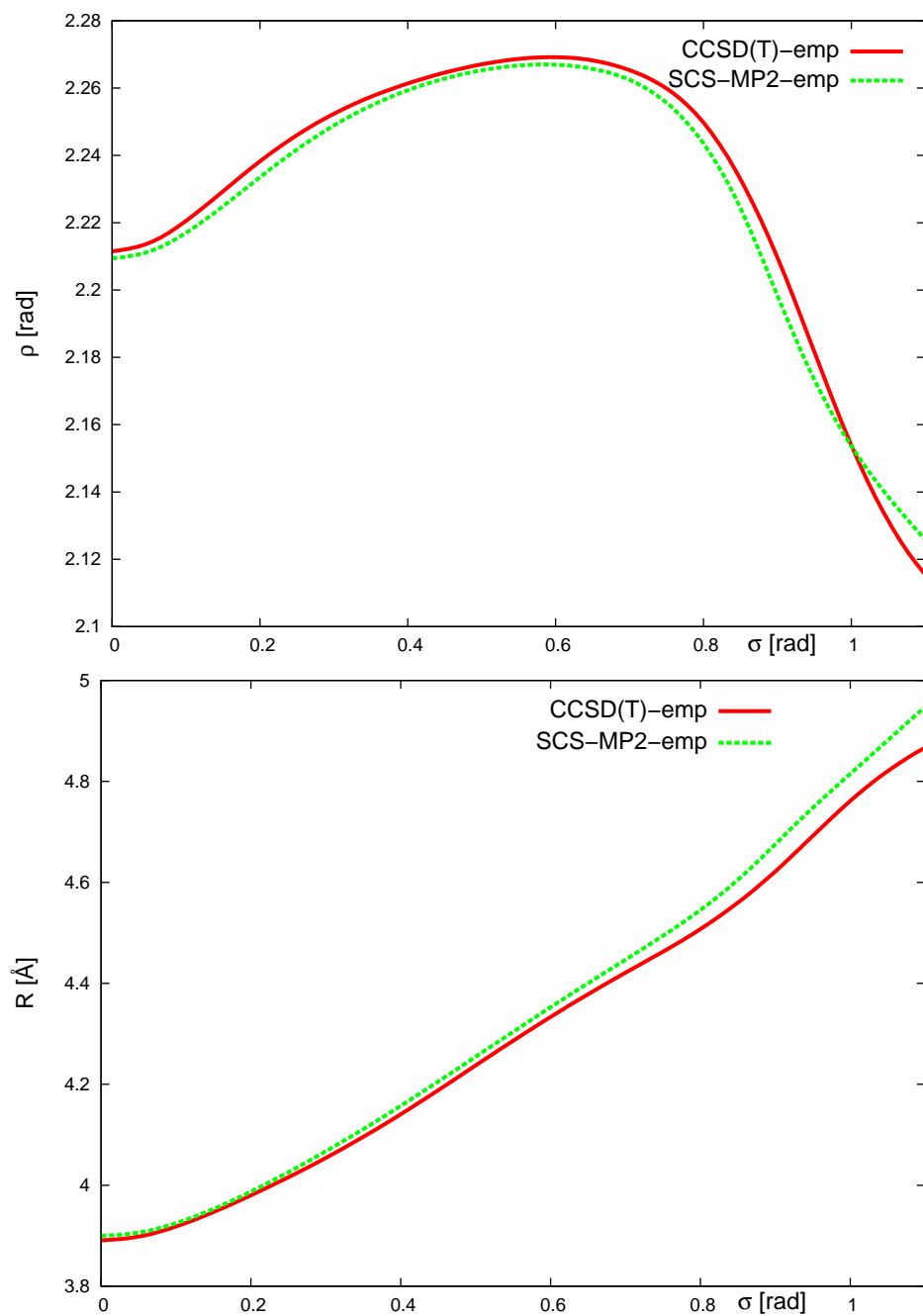


FIG. 2: The ‘energy minimum path’ values (calculated at the SCS-MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ level of theory) of the vibrational coordinates R and ρ .

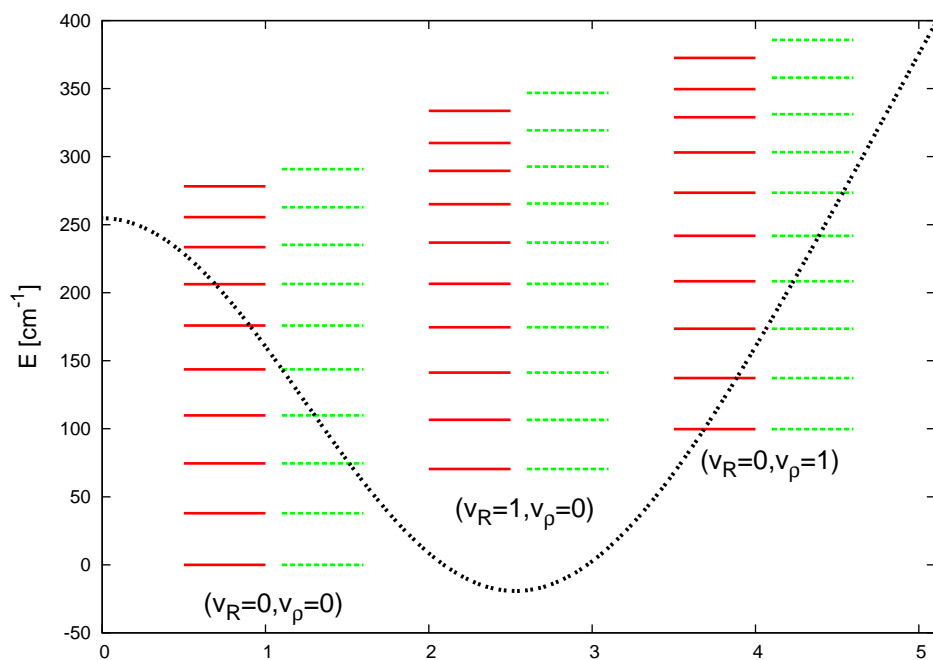


FIG. 3: The ‘interconverting’ energy patterns of the three lowest $[v_R, v_\rho]$ states (with the symmetric levels plotted in red and antisymmetric levels plotted in green) and the CCSD(T) ‘ground state’ $V_{v_R=0, v_\rho=0}(\sigma)$ adiabatic potential (which is plotted in black).

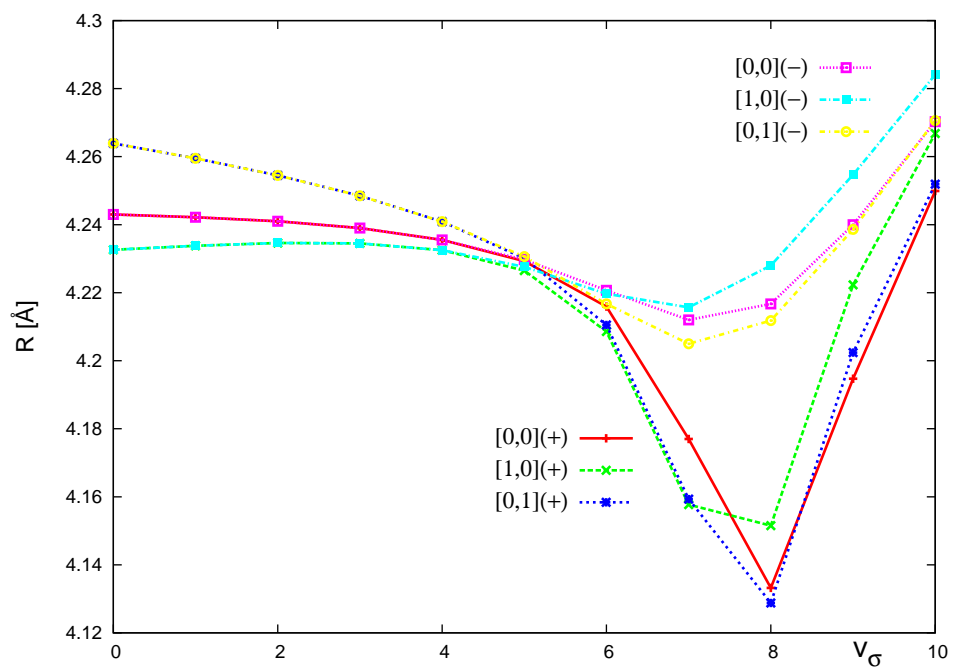


FIG. 4: The ‘interconverting’ average values of R for the three lowest vibrational states.

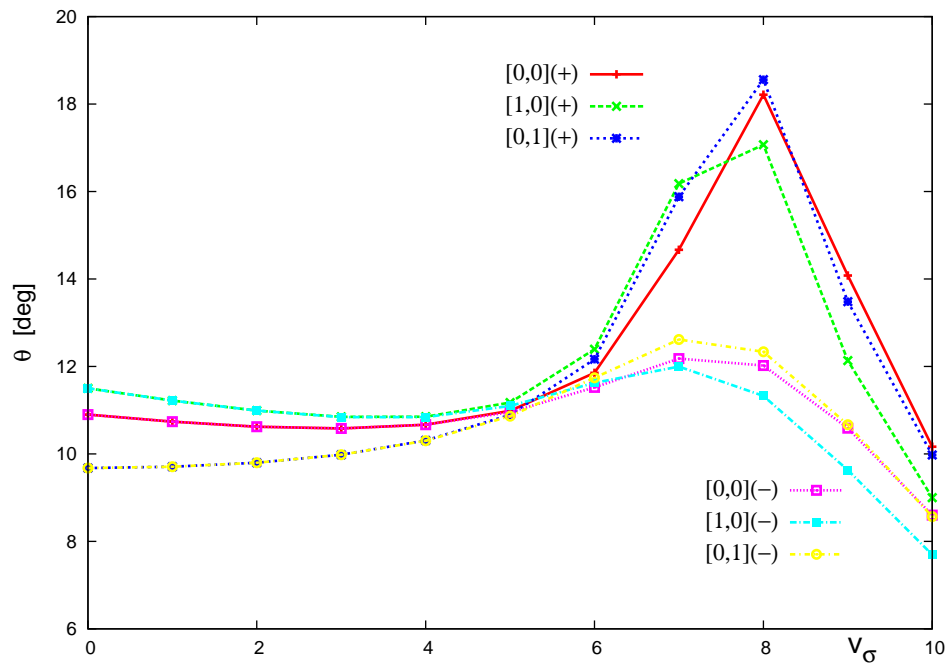


FIG. 5: The ‘interconverting’ average values of θ for the three lowest vibrational states.