Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Rotational spectra of van der Waals complexes: pyrrole–Ne and pyrrole–Ne_2

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Supplementary Information

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Table S1. Rotational constants (in MHz) for the Pyr−Ne complex at different levels of theory. Experimental rotational constants are provided for comparison.

	A	***B***	***C***
EXPERIMENTAL	4654.5380	2101.6705	2099.3956
B3LYP/6−311++G(d,p)	5114.1	1751.7	1683.3
B3LYP/6−311++G(2d,p)	5423.2	1634.8	1549.3
B3LYP/cc−pVTZ	4694.4	2198.6	2176.5
B3LYP/aug−cc−pVTZ	4659.7	1701.3	1692.0
B3LYP/def2−TZVPP	4680.2	1848.3	1835.0
B3LYP−D3BJ/6−311++G(d,p)	4681.9	2287.0	2259.8
B3LYP−D3BJ/6−311++G(2d,p)	4637.9	2342.9	2329.4
B3LYP−D3BJ /cc−pVTZ	4626.6	2407.5	2398.9
B3LYP−D3BJ /aug−cc−pVTZ	4614.7	2273.7	2268.0
B3LYP−D3BJ /def2−TZVPP	4691.4	2269.3	2246.1
M06−2X/6−311++G(d,p)	4600.7	2596.2	2594.7
M06−2X/6−311++G(2d,p)	4609.5	2600.8	2600.3
M06−2X/cc−pVTZ	4613.0	2600.3	2598.7
M06−2X/aug−cc−pVTZ	4607.0	2541.8	2593.1
M06−2X/ def2−TZVPP	4604.5	2495.3	2491.3
MP2/6−311++G(d,p)	4613.3	2193.4	2181.9
MP2/6−311++G(2d,p)	4671.8	2198.5	2177.7
MP2/ cc−pVTZ	4626.7	2269.1	2263.3
MP2/aug−cc−pVTZ	4585.7	2355.8	2353.3
MP2/def2−TZVPP	4579.5	2347.8	2343.2
B97D/6−311++G(d,p)	4624.6	2140.5	2120.4
B97D/6−311++G(2d,p)	4660.3	2161.4	2136.7
B97D/ cc−pVTZ	4584.7	2315.0	2308.1
B97D/aug−cc−pVTZ	4567.4	2078.6	2075.9
B97D/def2−TZVPP	4647.9	2142.8	2123.3
wB97XD/6−311++G(d,p)	4634.0	2039.8	2033.6
wB97XD/6−311++G(2d,p)	4640.2	2055.4	2050.9
wB97XD/ cc−pVTZ	4645.9	2198.7	2194.4
wB97XD/aug−cc−pVTZ	4640.2	2077.8	2074.6
wB97XD/def2−TZVPP	4639.5	2049.0	2046.4
CCSD/6−311++G(d,p)	4650.4	2154.7	2132.7
CCSD/6−311++G(2d,p)	4681.8	2191.6	2167.4
CCSD/cc−pVTZ	4653.2	2215.1	2202.0
CCSD/aug−cc−pVTZ	4606.2	2303.0	2298.9
CCSD/def2−TZVPP	4638.1	2117.3	2108.7

Table S2. Rotational constants (in MHz) for the Pyr−Ne_2 complex at different levels of theory. Experimental rotational constants are provided for comparison.

	A	***B***	***C***
EXPERIMENTAL	4408.6361	965.0390	954.7953
B3LYP/6−311++G(d,p)	3039.1	917.9	833.5
B3LYP/6−311++G(2d,p)	4256.9	876.6	863.8
B3LYP/cc−pVTZ	4191.4	1015.1	993.9
B3LYP/aug−cc−pVTZ	4447.5	1115.2	1113.3
B3LYP/def2−TZVPP	3604.9	860.5	818.3
B3LYP−D3BJ/6−311++G(d,p)	4286.8	1081.9	1065.3
B3LYP−D3BJ/6−311++G(2d,p)	4311.3	1090.4	1074.1
B3LYP−D3BJ /cc−pVTZ	4328.1	1129.3	1112.4
B3LYP−D3BJ /aug−cc−pVTZ	4317.8	1036.1	1021.5
B3LYP−D3BJ /def2−TZVPP	4322.4	1064.1	1048.8
M06−2X/6−311++G(d,p)	4274.3	1033.5	1017.9
M06−2X/6−311++G(2d,p)	4283.2	1065.9	1048.9
M06−2X/cc−pVTZ	4354.4	1054.9	1041.3
M06−2X/aug−cc−pVTZ	4525.6	1185.7	1179.6
M06−2X/ def2−TZVPP	4542.0	1158.7	1153.8
MP2/6−311++G(d,p)	4476.9	1227.3	1218.6
MP2/6−311++G(2d,p)	4283.2	1065.9	1048.9
MP2/ cc−pVTZ	4345.4	1054.9	1041.3
MP2/aug−cc−pVTZ	4443.9	1091.2	1082.4
MP2/def2−TZVPP	4365.0	933.7	922.6
B97D/6−311++G(d,p)	4035.1	1014.7	987.4
B97D/6−311++G(2d,p)	4144.2	1016.2	994.6
B97D/ cc−pVTZ	4281.8	1072.3	1056.2
B97D/aug−cc−pVTZ	4270.8	961.1	947.7
B97D/def2−TZVPP	4239.7	995.4	979.3
wB97XD/6−311++G(d,p)	4343.4	933.1	922.0
wB97XD/6−311++G(2d,p)	4358.2	933.8	922.6
wB97XD/ cc−pVTZ	4350.5	1035.2	1020.7
wB97XD/aug−cc−pVTZ	4364.7	938.6	927.7
wB97XD/def2−TZVPP	4365.9	933.7	922.7
CCSD/6−311++G(d,p)	4296.3	1019.6	1006.3
CCSD/6−311++G(2d,p)	4337.2	1053.6	1040.7
CCSD/cc−pVTZ	4292.7	1030.1	1013.8
CCSD/aug−cc−pVTZ	4409.3	1065.8	1055.3
CCSD/def2−TZVPP	4322.7	973.9	961.0

Table S3. Rotational constants (in MHz) for the Py−Ne complex at different levels of theory. The experimental values for this species (ref. 12) are also shown for comparison.

	A	***B***	***C***
EXPERIMENTAL	3011.463	1876.4048	1858.0647
B3LYP/6−311++G(d,p)	3555.4	1397.1	1306.5
B3LYP/cc−pVTZ	2994.9	1931.2	1905.0
B3LYP−D3BJ/def2−TZVPP	2989.4	2028.3	2005.7
B97D/aug−cc−pVTZ	2979.7	1860.9	1849.5
B97D/def2−TZVPP	2955.9	1960.1	1936.9
wB97XD/aug−cc−pVTZ	3032.0	1890.3	1880.9
wB97XD/def2−TZVPP	3006.0	1838.7	1820.4
MP2/6−311++G(d,p)	2975.4	1921.8	1907.8
MP2/6−311++G(2d,p)	2994.4	1958.2	1946.8
MP2/cc−pVTZ	2979.0	2027.8	2002.7
CCSD/6−311++G(d,p)	2982.3	1882.3	1869.9
CCSD/def2−TZVPP	2991.9	1876.6	1859.9

Table S4. Rotational constants (in MHz) for the Pyr−Ar complex at different levels of theory. The experimental values for this species (ref. 20) are also shown for comparison.

	A	***B***	***C***
EXPERIMENTAL	4601.423	1355.701	1355.070
B3LYP/6−311++G(d,p)	4711.7	424.4	423.3
B3LYP/cc−pVTZ	6838.9	2029.4	2000.5
B3LYP−D3BJ/def2−TZVPP	4600.8	1402.8	1402.1
B97D/aug−cc−pVTZ	4542.0	1297.2	1296.1
B97D/def2−TZVPP	4565.5	1306.0	1305.4
wB97XD/aug−cc−pVTZ	4632.8	1310.2	1309.7
wB97XD/def2−TZVPP	4637.8	1330.6	1329.1
MP2/6−311++G(d,p)	4565.9	1419.8	1419.6
MP2/6−311++G(2d,p)	4562.8	1424.7	1422.8
MP2/cc−pVTZ	4585.6	1437.0	1435.3
CCSD/6−311++G(d,p)	4580.1	1359.2	1365.6
CCSD/def2−TZVPP	4604.1	1333.5	1332.9

Table S5. Optimized geometry (xyz format, in Angstrom) at the CCSD/def2−TZVPP level of theory for the Pyr−Ne complex.

H	-0.003486	-2.120706	-0.345434
N	-0.001857	-1.142982	-0.556452
C	1.119586	-0.373770	-0.720707
H	2.103256	-0.797922	-0.630723
C	0.714580	0.908333	-0.995403
H	1.362826	1.747566	-1.175695
C	-1.120732	-0.370131	-0.721145
H	-2.105810	-0.791086	-0.631546
C	-0.711456	0.910649	-0.995682
H	-1.356902	1.751984	-1.176227
Ne	0.000120	0.165867	2.649898

Table S6. Optimized geometry (xyz format, in Angstrom) at the CCSD/def2−TZVPP level of theory for the [1,1] isomer of Pyr−Ne_2 complex.

H	0.006371	-1.932099	-0.000003
N	0.003394	-0.931864	-0.000003
C	1.121137	-0.140212	-0.000003
H	2.106825	-0.569206	-0.000009
C	0.710138	1.169075	0.000002
H	1.354408	2.030455	0.000003
C	-1.119040	-0.146879	0.000004
H	-2.102157	-0.581732	0.000005
C	-0.715842	1.164831	0.000007
H	-1.365227	2.022361	0.000012
Ne	-0.000110	-0.312374	3.406266
Ne	-0.000113	-0.312371	-3.406271

Table S7. Optimized geometry (xyz format, in Angstrom) at the CCSD/def2−TZVPP level theory for the [2,0] isomer of Pyr−Ne_2 complex.

C	-0.678364	0.947185	0.757935
C	-1.715581	0.115741	1.084509
C	-2.198258	-0.451614	-0.122912
C	-1.438273	0.054125	-1.142974
N	-0.519309	0.902650	-0.596796
H	0.172905	1.410660	-1.111587
H	-0.044737	1.560446	1.374588
H	-2.087585	-0.066065	2.078440
H	-3.010137	-1.150764	-0.229688
H	-1.476323	-0.119982	-2.204193
Ne	2.985293	0.937664	-0.005610
Ne	1.323033	-2.051695	0.082212

Table S8. Observed transition frequencies of the Pyr–^{20}Ne complex (parent species).

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Frequency/ MHz	Obs.−calc./ MHz
4	1	4	3	4	0	4	3	2540.051	0.033
4	1	4	5	4	0	4	5	2540.081	0.031
3	1	3	4	3	0	3	4	2545.617	−0.036
3	1	3	2	3	0	3	2	2545.617	0.035
3	1	3	3	3	0	3	3	2545.843	−0.013
2	1	2	2	2	0	2	1	2548.988	0.006
2	1	2	2	2	0	2	3	2549.433	0.005
2	1	2	1	2	0	2	1	2549.604	−0.012
2	1	2	3	2	0	2	3	2549.836	0.000
2	1	2	2	2	0	2	2	2550.238	0.007
2	1	2	3	2	0	2	2	2550.637	−0.002
2	1	2	1	2	0	2	2	2550.863	−0.002
1	1	1	1	1	0	1	0	2551.797	−0.002
1	1	1	2	1	0	1	2	2552.549	−0.004
1	1	1	0	1	0	1	1	2552.731	−0.017
1	1	1	1	1	0	1	2	2552.928	0.006
1	1	1	2	1	0	1	1	2553.297	−0.005
1	1	1	1	1	0	1	1	2553.674	0.002
1	0	1	1	0	0	0	1	4200.316	0.005
1	0	1	2	0	0	0	1	4201.072	0.011
1	0	1	0	0	0	0	1	4202.200	0.016
2	0	2	2	1	1	0	1	5845.136	0.007
2	0	2	2	1	1	0	2	5845.505	−0.004
2	0	2	3	1	1	0	2	5846.317	0.005
2	0	2	1	1	1	0	0	5847.319	−0.009
1	1	0	0	0	0	0	1	6755.311	−0.005
1	1	0	2	0	0	0	1	6755.875	−0.011
1	1	0	1	0	0	0	1	6756.250	−0.016
4	2	3	3	4	1	3	3	7644.467	0.009
4	2	3	5	4	1	3	5	7644.547	−0.008
4	2	3	4	4	1	3	4	7644.893	−0.039
3	2	2	3	3	1	2	2	7652.084	0.000
3	2	2	2	3	1	2	2	7652.084	0.000
3	2	2	3	3	1	2	2	7652.084	0.000
3	2	2	2	3	1	2	2	7652.084	0.000
3	2	2	3	3	1	2	4	7652.294	−0.008
3	2	2	4	3	1	2	4	7652.294	−0.008
3	2	2	2	3	1	2	3	7652.917	−0.003
2	2	1	1	2	1	1	1	7657.373	−0.001

J'	K_a'	K_c'	*F'*	*J''*	K_a''	K_c''	*F''*	Frequency/ MHz	Obs.−calc./ MHz
2	2	1	3	2	1	1	3	7658.048	0.008
2	2	1	3	2	1	1	2	7658.449	0.013
2	2	1	2	2	1	1	1	7658.623	−0.001
2	2	1	2	2	1	1	3	7658.853	0.010
2	2	1	2	2	1	1	2	7659.251	0.012
2	2	0	1	2	1	2	1	7664.168	−0.023
2	2	0	1	2	1	2	2	7664.851	0.026
2	2	0	3	2	1	2	2	7665.245	−0.027
2	2	0	2	2	1	2	1	7665.430	−0.011
3	2	1	2	3	1	3	2	7665.734	0.000
3	2	1	4	3	1	3	4	7666.002	0.048
3	2	1	3	3	1	3	3	7666.588	0.003

Table S9. Observed transition frequencies of the Pyr–^{22}Ne isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Frequency/ MHz	Obs.−calc./ MHz
4	1	4	5	4	0	4	5	2652.219	0.006
4	1	4	4	4	0	4	4	2652.319	−0.021
4	1	4	5	4	0	4	4	2653.082	0.011
3	1	3	3	3	0	3	4	2656.107	0.007
3	1	3	2	3	0	3	2	2656.660	0.001
3	1	3	4	3	0	3	4	2656.720	−0.012
3	1	3	3	3	0	3	3	2656.940	0.000
2	1	2	2	2	0	2	1	2659.246	0.003
2	1	2	2	2	0	2	3	2659.699	0.006
2	1	2	1	2	0	2	1	2659.885	0.009
2	1	2	3	2	0	2	3	2660.109	0.009
2	1	2	2	2	0	2	2	2660.513	0.009
2	1	2	3	2	0	2	2	2660.908	−0.001
2	1	2	1	2	0	2	2	2661.137	0.001
1	1	1	1	1	0	1	0	2661.515	0.000
1	1	1	2	1	0	1	2	2662.272	0.000
1	1	1	0	1	0	1	1	2662.459	−0.005
1	1	1	1	1	0	1	2	2662.651	0.002
1	1	1	2	1	0	1	1	2663.028	0.000
1	1	1	1	1	0	1	1	2663.400	−0.004
1	0	1	1	0	0	0	1	3977.793	0.010
1	0	1	2	0	0	0	1	3978.543	0.004
1	0	1	0	0	0	0	1	3979.678	0.005
2	0	2	2	1	1	0	1	5290.948	0.011
2	0	2	2	1	1	0	2	5291.326	0.009
2	0	2	3	1	1	0	2	5292.135	0.009
2	0	2	1	1	1	0	1	5292.175	−0.022
2	0	2	1	1	1	0	0	5293.140	−0.006
1	1	0	0	0	0	0	1	6642.013	−0.004
1	1	0	2	0	0	0	1	6642.578	−0.008
1	1	0	1	0	0	0	1	6642.956	−0.008
4	2	3	5	4	1	3	5	7975.884	−0.040
4	2	3	4	4	1	3	4	7976.284	−0.025
3	2	2	3	3	1	2	2	7982.198	0.015
3	2	2	2	3	1	2	2	7982.198	0.015
3	2	2	3	3	1	2	4	7982.418	0.015
3	2	2	4	3	1	2	4	7982.418	0.015
3	2	2	2	3	1	2	3	7983.051	0.020
3	2	2	3	3	1	2	3	7983.051	0.020

J'	K_a'	K_c'	*F'*	*J''*	K_a''	K_c''	*F''*	Frequency/ MHz	Obs.−calc./ MHz
3	2	2	4	3	1	2	3	7983.051	0.020
2	2	1	1	2	1	1	1	7986.506	−0.011
2	2	1	3	2	1	1	3	7987.201	0.010
2	2	1	3	2	1	1	2	7987.591	−0.003
2	2	1	2	2	1	1	1	7987.755	−0.021
2	2	1	2	2	1	1	3	7987.990	−0.011
2	2	1	2	2	1	1	2	7988.403	0.000
2	2	0	1	2	1	2	1	7991.824	−0.015
2	2	0	3	2	1	2	3	7992.492	−0.024
3	2	1	3	3	1	3	2	7992.834	−0.001
3	2	1	4	3	1	3	4	7993.052	−0.004
3	2	1	4	3	1	3	3	7993.692	0.005
4	2	2	5	4	1	4	5	7993.692	0.007
3	2	1	3	3	1	3	3	7993.692	0.005
3	2	1	2	3	1	3	3	7993.692	0.005

Table S10. Observed transition frequencies of the Pyr–$^{20}Ne^{20}Ne$ complex (parent species).

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Frequency/ MHz	Obs.−calc./ MHz
1	1	0	1	1	0	1	0	3452.806	0.004
1	1	0	2	1	0	1	2	3453.600	−0.006
1	1	0	0	1	0	1	1	3453.827	−0.001
1	1	0	1	1	0	1	2	3453.980	−0.006
1	1	0	2	1	0	1	1	3454.397	0.002
1	1	0	1	1	0	1	1	3454.771	−0.003
2	1	1	2	2	0	2	1	3462.982	−0.007
2	1	1	2	2	0	2	3	3463.463	0.004
2	1	1	1	2	0	2	1	3463.672	−0.001
2	1	1	3	2	0	2	3	3463.895	−0.003
2	1	1	2	2	0	2	2	3464.310	0.005
2	1	1	3	2	0	2	2	3464.749	0.005
2	1	1	1	2	0	2	2	3464.990	0.002
3	1	2	4	3	0	3	4	3479.244	−0.018
3	1	2	3	3	0	3	3	3479.469	0.006
4	1	3	5	4	0	4	5	3499.802	0.009
4	1	3	3	4	0	4	3	3499.802	0.039
4	1	3	4	4	0	4	4	3499.902	−0.008
5	1	4	4	5	0	5	4	3525.550	−0.007
5	1	4	6	5	0	5	6	3525.550	−0.021
5	1	4	5	5	0	5	5	3525.650	0.006
4	0	4	4	3	1	3	3	4259.920	0.003
4	0	4	3	3	1	3	2	4260.175	−0.004
4	0	4	5	3	1	3	4	4260.175	0.002
1	1	1	0	0	0	0	1	5362.696	0.005
1	1	1	2	0	0	0	1	5363.305	−0.001
1	1	1	1	0	0	0	1	5363.709	−0.006
5	0	5	5	4	1	4	4	6198.934	−0.008
5	0	5	4	4	1	4	3	6199.108	0.007
5	0	5	6	4	1	4	5	6199.108	0.001
2	1	2	1	1	0	1	0	7271.760	0.001
2	1	2	2	1	0	1	2	7272.309	−0.002
2	1	2	3	1	0	1	2	7272.718	0.001
2	1	2	2	1	0	1	1	7273.100	0.001
2	1	2	1	1	0	1	1	7273.731	−0.001

Table 11. Observed transition frequencies of the Pyr–^{20}Ne^{22}Ne isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Frequency/ MHz	Obs.−calc./ MHz
1	1	0	1	1	0	1	0	3487.167	0.000
1	1	0	2	1	0	1	2	3487.974	−0.002
1	1	0	0	1	0	1	1	3488.199	−0.005
1	1	0	1	1	0	1	2	3488.352	0.002
1	1	0	2	1	0	1	1	3488.767	0.002
1	1	0	1	1	0	1	1	3489.145	0.006
2	1	1	2	2	0	2	1	3496.749	0.007
2	1	1	2	2	0	2	3	3497.215	0.002
2	1	1	1	2	0	2	1	3497.415	−0.019
2	1	1	3	2	0	2	3	3497.657	0.000
2	1	1	2	2	0	2	2	3498.072	0.014
2	1	1	3	2	0	2	2	3498.507	0.006
2	1	1	1	2	0	2	2	3498.737	−0.012
3	1	2	3	3	0	3	2	3511.122	0.012
3	1	2	3	3	0	3	4	3511.389	−0.028
3	1	2	4	3	0	3	4	3512.092	−0.005
3	1	2	3	3	0	3	3	3512.314	0.021
3	1	2	4	3	0	3	3	3512.944	−0.029
3	1	2	2	3	0	3	3	3513.231	0.020
5	1	4	5	5	0	5	5	3555.629	−0.037
5	1	4	6	5	0	5	6	3555.629	0.031
5	1	4	4	5	0	5	4	3555.629	0.044
6	1	5	6	6	0	6	6	3584.814	−0.038
6	1	5	7	6	0	6	7	3584.814	0.004
6	1	5	5	6	0	6	5	3584.814	0.011
4	0	4	4	3	1	3	3	3908.540	0.010
4	0	4	5	3	1	3	4	3908.792	0.000
4	0	4	3	3	1	3	2	3908.792	−0.008
1	1	1	0	0	0	0	1	5318.925	0.004
1	1	1	2	0	0	0	1	5319.542	−0.001
1	1	1	1	0	0	0	1	5319.946	−0.011
5	0	5	5	4	1	4	4	5767.693	−0.007
5	0	5	6	4	1	4	5	5767.871	0.001
5	0	5	4	4	1	4	3	5767.871	0.005
2	1	2	1	1	0	1	0	7149.884	0.011
2	1	2	2	1	0	1	2	7150.417	−0.015
2	1	2	2	1	0	1	1	7151.221	0.000
2	1	2	1	1	0	1	1	7151.851	0.007

Table S12. Observed transition frequencies of the Pyr–^{22}Ne^{22}Ne isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	Frequency/ MHz	Obs.−calc./ MHz
1	1	0	1	1	0	1	0	3519.542	−0.005
1	1	0	2	1	0	1	2	3520.397	0.028
2	1	1	2	2	0	2	1	3528.444	0.007
2	1	1	2	2	0	2	3	3528.890	−0.028
2	1	1	1	2	0	2	1	3529.128	−0.010
2	1	1	3	2	0	2	3	3529.356	−0.011
2	1	1	2	2	0	2	2	3529.771	−0.009
2	1	1	3	2	0	2	2	3530.219	−0.011
2	1	1	1	2	0	2	2	3530.491	0.011
3	1	2	2	3	0	3	2	3542.707	0.003
3	1	2	3	3	0	3	3	3542.997	0.017
1	1	1	0	0	0	0	1	5276.642	0.015
1	1	1	2	0	0	0	1	5277.259	0.002
1	1	1	1	0	0	0	1	5277.676	−0.001
2	1	2	1	1	0	1	0	7033.057	−0.008
2	1	2	3	1	0	1	2	7034.055	0.013
2	1	2	2	1	0	1	1	7034.432	−0.003
2	1	2	1	1	0	1	1	7035.068	−0.010