Electronic Supplementary Material

Microsolvation of the pyrrole cation (Py^+) with nonpolar and polar ligands: Infrared spectra of Py^+-L_n with L=Ar, N_2, and H_2O ($n \leq 3$)

Markus Schütz,[a] Yoshiteru Matsumoto,[b] Aude Bouchet,[a] Murat Öztürk,[a] and Otto Dopfer[a]*

[a] Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, 10623 Berlin, Germany.

[b] Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Suruga, Shizuoka, 422-8529, Japan.

* corresponding author: dopfer@physik.tu-berlin.de, tel. +49 30 314 23017

Figure S1. Mass spectrum of the electron impact ion source obtained by an expansion of Py vapor (T=50°C) seeded in Ar (6 bar). It is dominated by Ar_n^+ and Py_n^+ clusters as well as fragments of Py^+ produced by electron and/or chemical ionization. The H_2O impurity in the gas inlet system leads to the formation of $(H_2O)_n^+$, $(H_2O)_nH^+$, Py_m^+-$(H_2O)_n$, and PyH^+-$(H_2O)_n$ clusters. Part of the spectrum is vertically expanded by a factor of ten to show weak peaks. At *m*/*z* 107, the weak signal of Py^+-Ar is observed. In general, the abundance of Py^+-Ar_n clusters rapidly decreases with *n*, consistent with the formation of weakly bound clusters by sequential addition of Ar ligands to Py^+.

Figure S2. Mass spectra obtained by mass-selecting Py^+-Ar_n clusters with *n*=5 and 6 using the first quadrupole and scanning the second quadrupole for laser off (MD, metastable decay) and laser on (LID, laser-induced dissociation). The IR laser frequency is tuned to the NH stretch vibration at 3414 cm^{-1} (*n*=5, 6). LID of $n \leq 5$ produces Py^+-Ar_m fragment with *m*=0, while LID of *n*=6 produces mostly *m*=1.

Figure S3. The three highest occupied π molecular orbitals (HOMO, HOMO-1, HOMO-2) and the lowest unoccupied π molecular orbital (LUMO) of neutral Py calculated at the B3LYP-D3/aug-cc-pVTZ level.

Figure S4. Potential energy diagram for the π↔H isomerization of Py^+-L with L=Ar and N_2 calculated at the B3LYP-D3/aug-cc-pVTZ level. Distances, relative (E_0, E_e), and binding (D_0, D_e) energies are given in Å and kJ mol^{-1}.

Figure S5. Local minimum structures of Py^+-Ar_n clusters (*n*=1 and 2) obtained at the B3LYP-D3/aug-cc-pVTZ level (Table S2). Intermolecular bond lengths (in Å) and total binding energies (D_0) are indicated.

Figure S6. Minimum structures of neutral π-bonded and H-bonded Py-L dimers with L=Ar, N_2, and H_2O obtained at the B3LYP-D3/aug-cc-pVTZ level (Table S3). Intermolecular bond lengths (in Å), bond angle (in degree), and total binding energies (D_0) are indicated.

Figure S7. Local minimum structures of Py^+-$(N_2)_n$ clusters (*n*=1 and 2) obtained at the B3LYP-D3/aug-cc-pVTZ level (Table S2). Intermolecular bond lengths (in Å) and total binding energies (D_0) are indicated.

Figure S8. Local minimum structures of Py^+-H_2O dimers obtained at the B3LYP-D3/aug-cc-pVTZ level (Table S4). Intermolecular bond lengths (in Å) and total binding energies (D_0) are indicated.

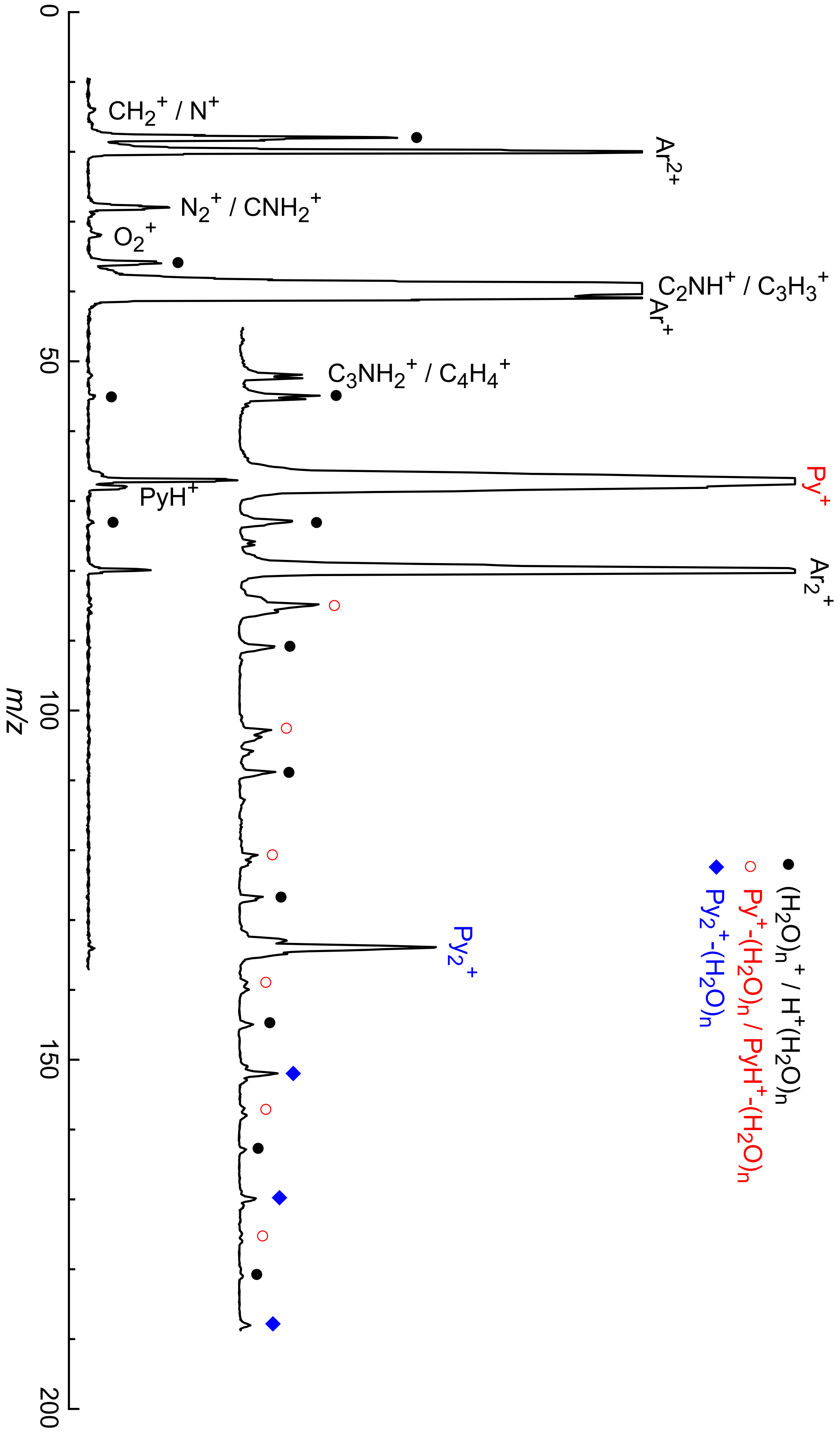

0
50
100
150
200
m/z
CH_2^+ / N^+
Ar^{2+}
N_2^+ / CNH_2^+
O_2^+
C_2NH^+ / $C_3H_3^+$
Ar^+
$C_3NH_2^+$ / $C_4H_4^+$
Py^+
PyH^+
Ar_2^+
Py_2^+
● $(H_2O)_n^+$ / $H^+(H_2O)_n$
○ Py^+-$(H_2O)_n$ / PyH^+-$(H_2O)_n$
◆ Py_2^+-$(H_2O)_n$

Figure S1

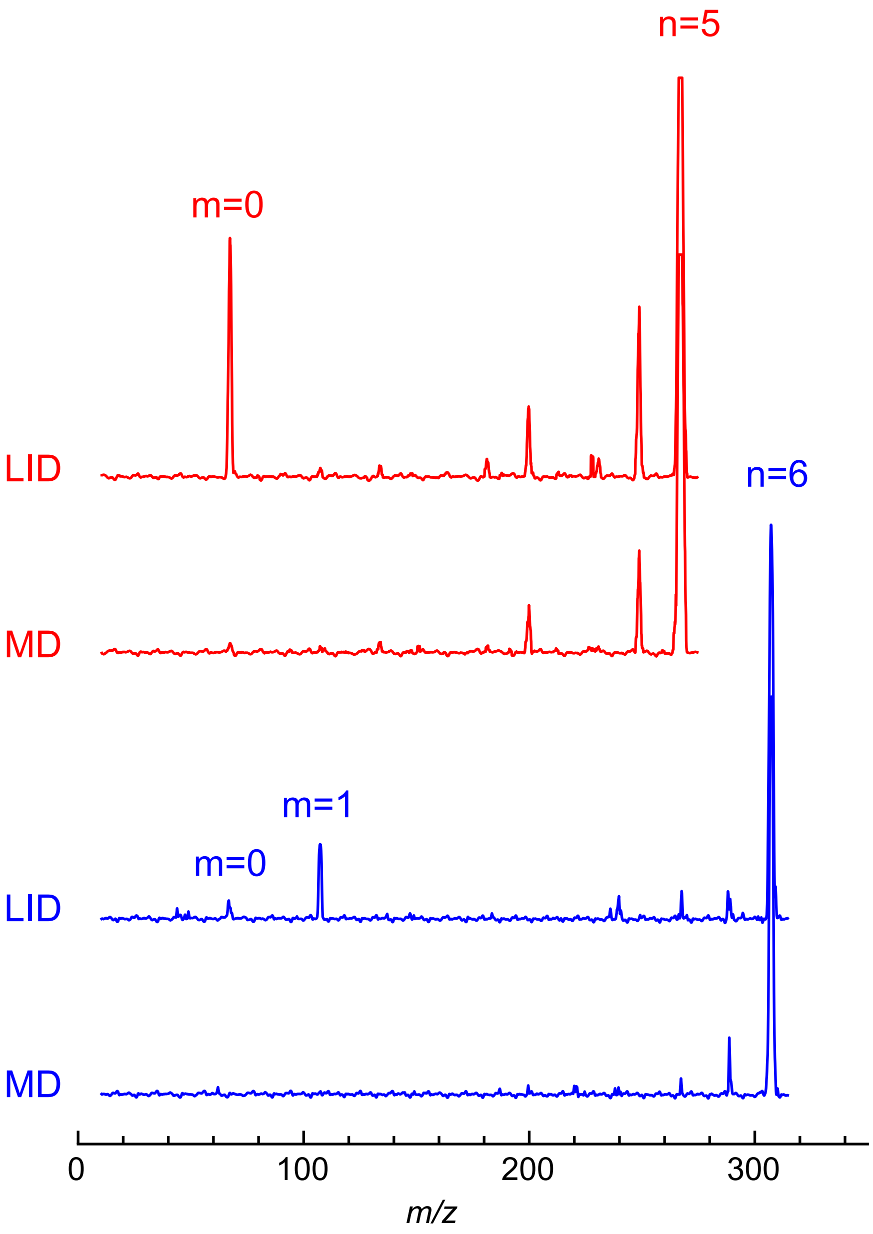
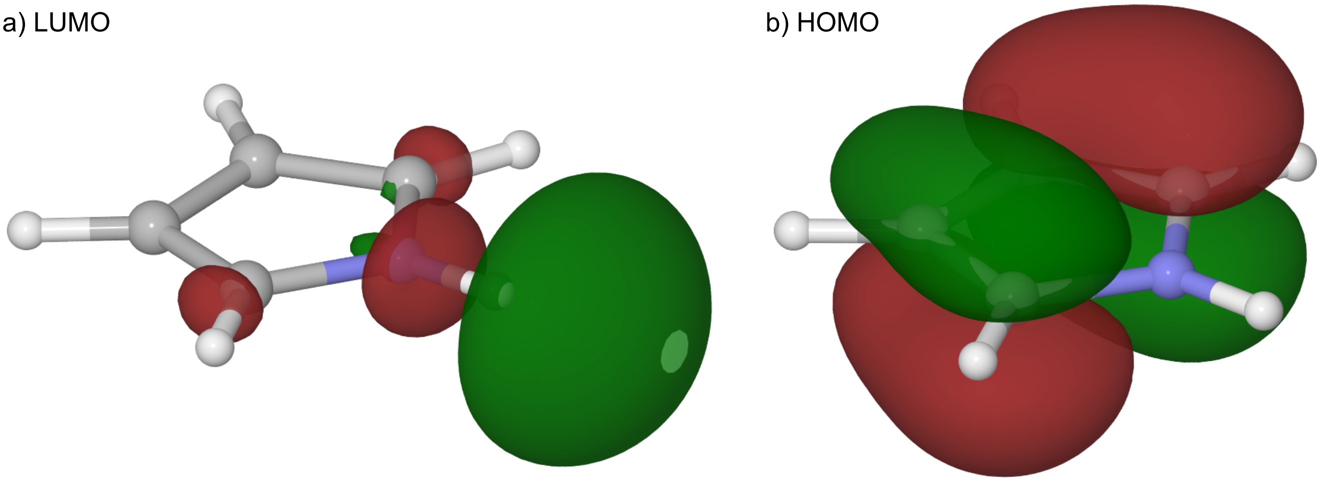
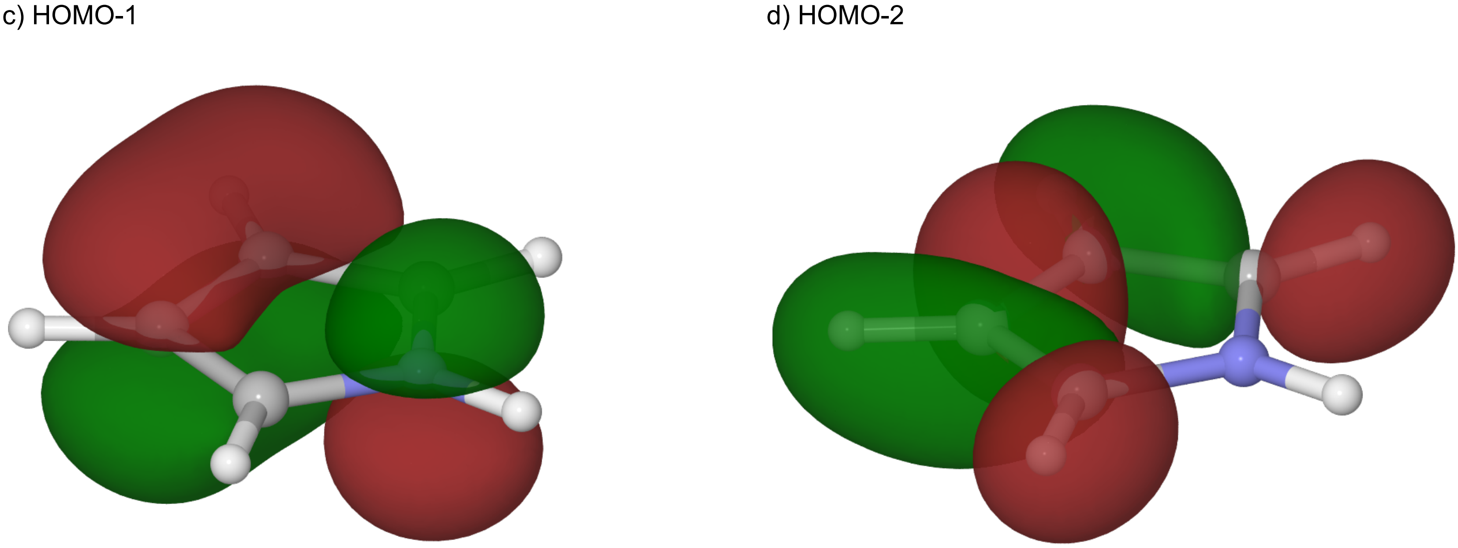


Figure S2



a) LUMO

b) HOMO



c) HOMO-1

d) HOMO-2

Figure S3

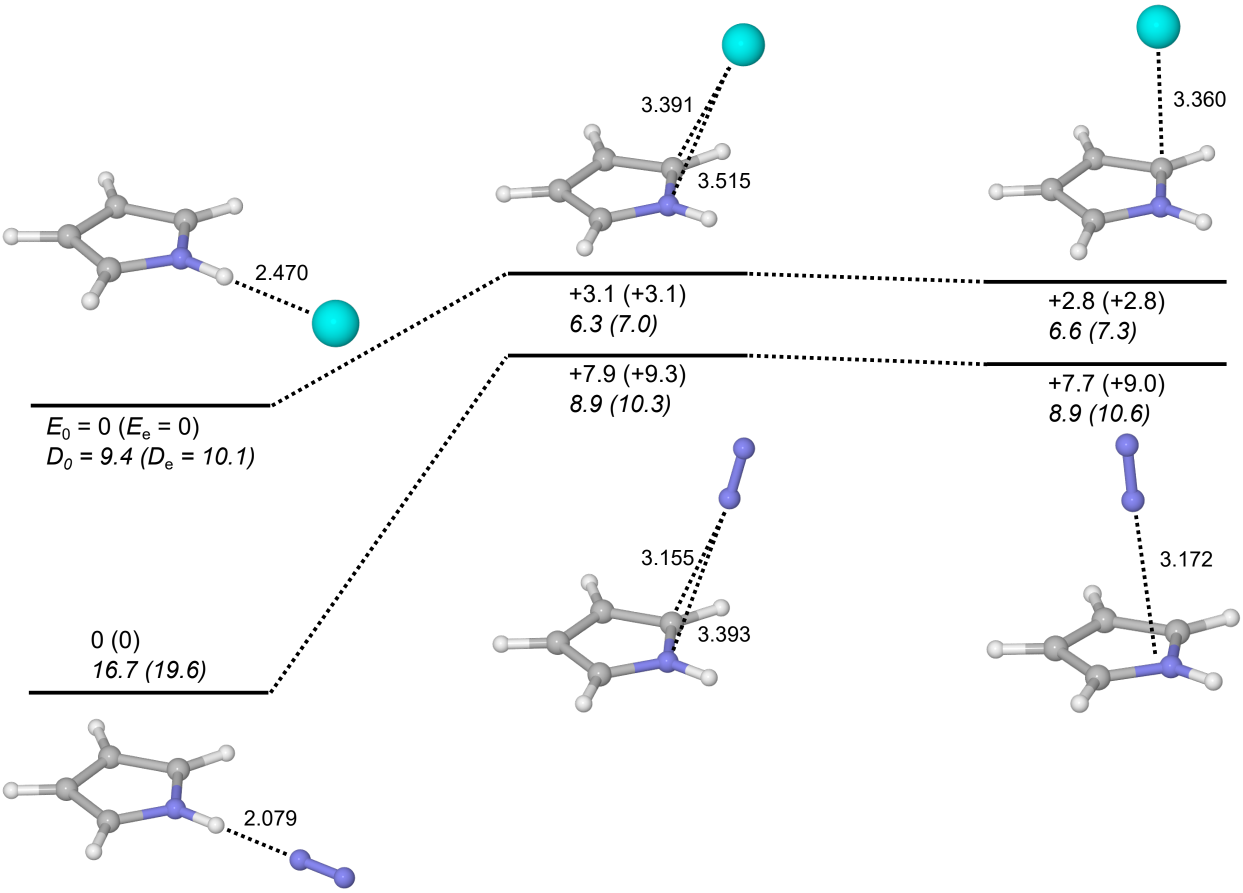
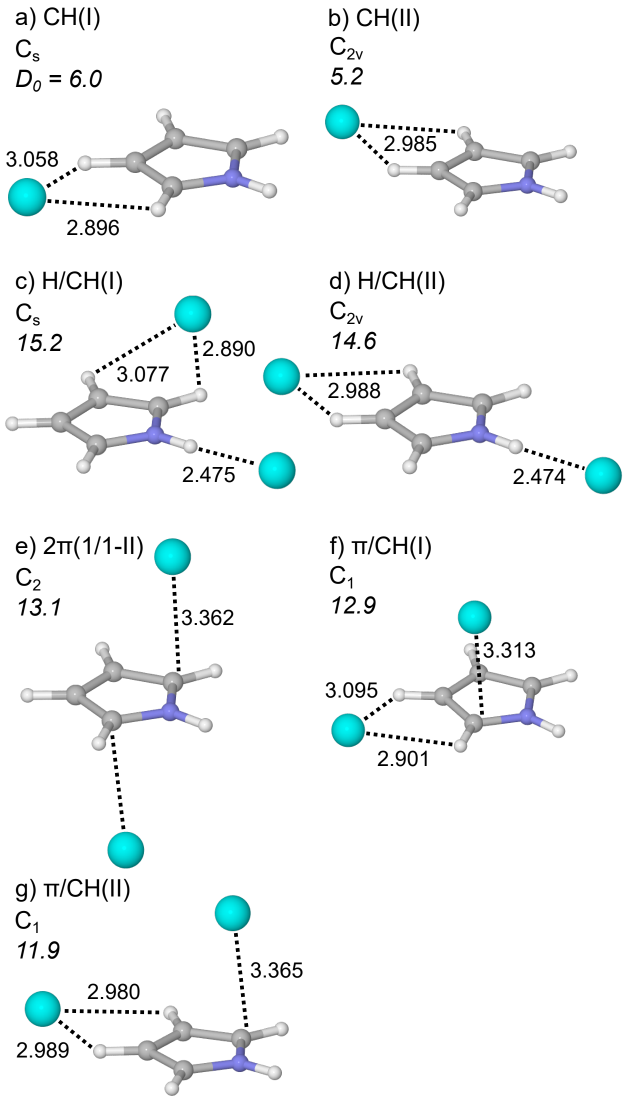

2.470
E_0 = 0 (E_e = 0)
D_0 = 9.4 (D_e = 10.1)
0 (0)
16.7 (19.6)
2.079
3.391
3.515
+3.1 (+3.1)
6.3 (7.0)
+7.9 (+9.3)
8.9 (10.3)
3.155
3.393
3.360
+2.8 (+2.8)
6.6 (7.3)
+7.7 (+9.0)
8.9 (10.6)
3.172

Figure S4



a) CH(I)
C_s
D_0 = 6.0

b) CH(II)
C_{2v}
5.2

c) H/CH(I)
C_s
15.2

d) H/CH(II)
C_{2v}
14.6

e) 2π(1/1-II)
C_2
13.1

f) π/CH(I)
C_1
12.9

g) π/CH(II)
C_1
11.9

Figure S5

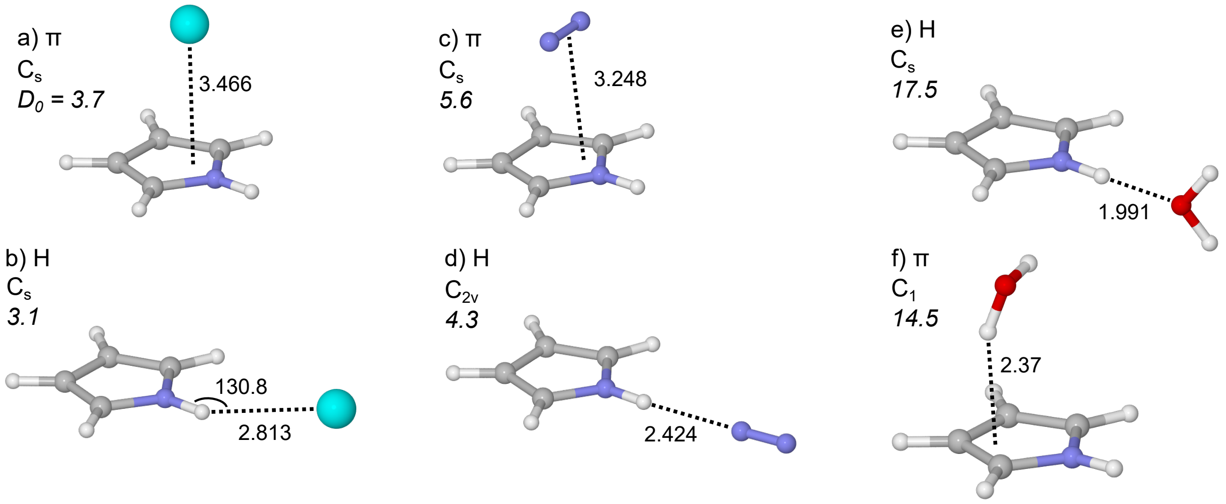
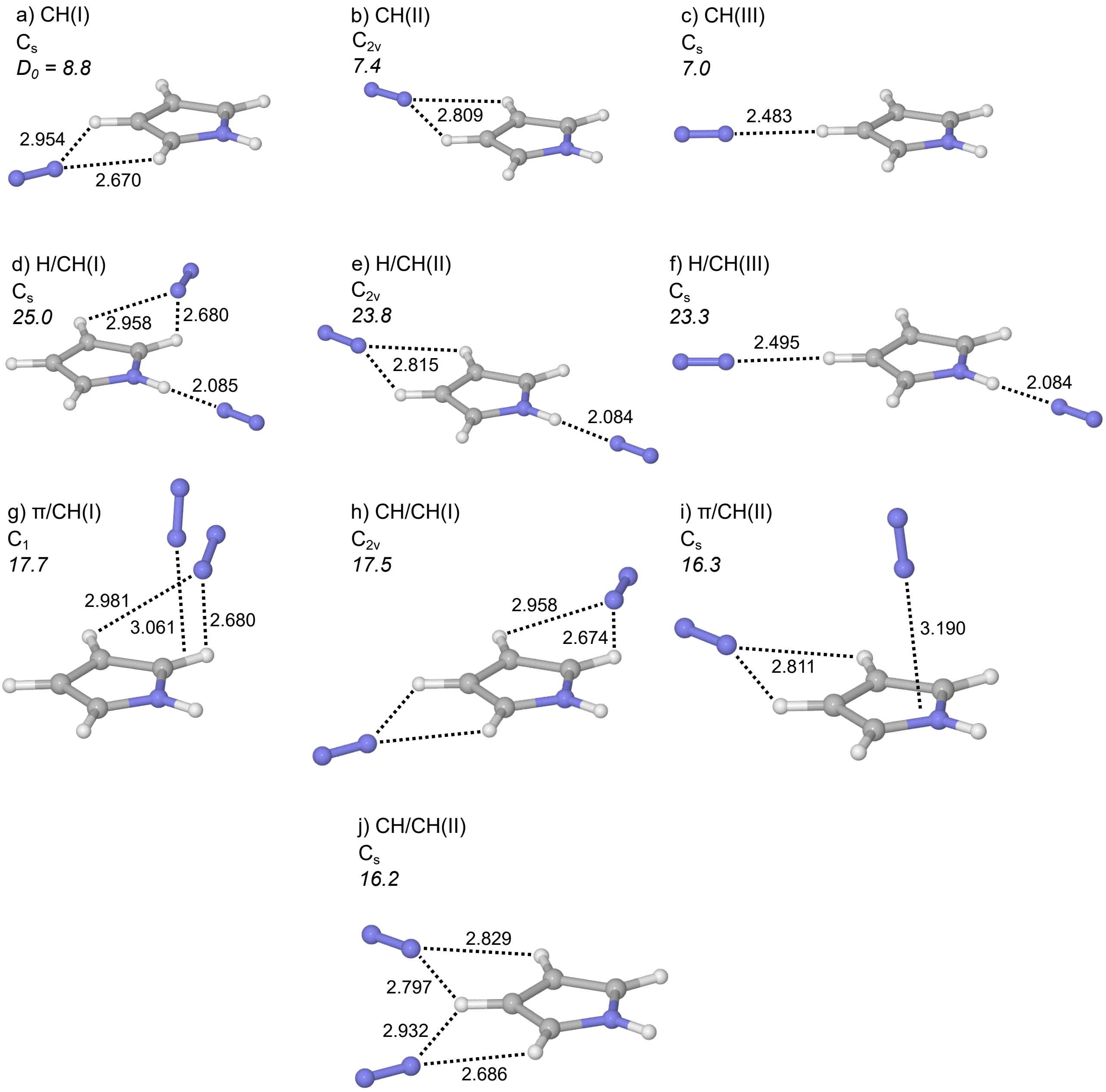

a) π
C_s
D_0 = 3.7
3.466
b) H
C_s
3.1
130.8
2.813
c) π
C_s
5.6
3.248
d) H
C_2v
4.3
2.424
e) H
C_s
17.5
1.991
f) π
C_1
14.5
2.37

Figure S6



a) CH(I)
C_s
D_0 = *8.8*

b) CH(II)
C_{2v}
7.4

c) CH(III)
C_s
7.0

d) H/CH(I)
C_s
25.0

e) H/CH(II)
C_{2v}
23.8

f) H/CH(III)
C_s
23.3

g) π/CH(I)
C_1
17.7

h) CH/CH(I)
C_{2v}
17.5

i) π/CH(II)
C_s
16.3

j) CH/CH(II)
C_s
16.2

Figure S7

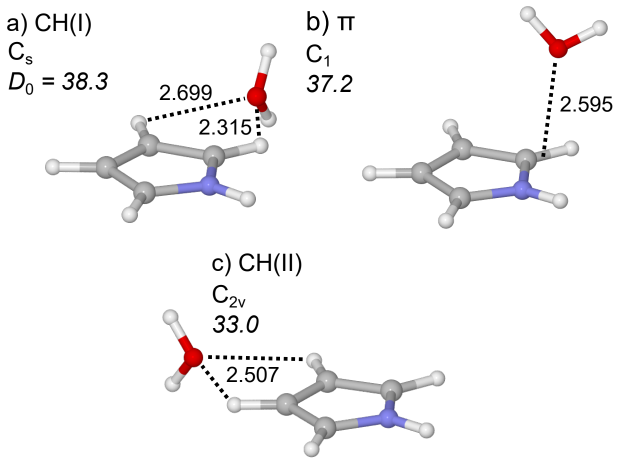


Figure S8

Table S1. Calculated harmonic and scaled vibrational frequencies of Py^+ compared to experimental frequencies (in cm^{-1}).

B3LYP-D3/aug-cc-pVTZ[a]	B3LYP-D3/aug-cc-pVTZ[b]	Symmetry	Experiment[c]	B3LYP/6-311++G(3df, 3pd)[a,c]
490	480	b_1		486
510	500	a_2	495	509
673	660	b_1	679	670
734	719	b_2	715	735
750	735	b_1	728	750
862	845	a_2	838	858
895	877	a_1	874	897
911	893	b_1	895	904
977	957	a_2	943	974
995	975	b_2	979	997
1026	1005	b_2	1003	1025
1075	1054	a_1	1060	1075
1097	1075	a_1	1078	1100
1177	1153	a_1	1150	1177
1288	1262	b_2		1286
1337	1310	b_2	1353	1336
1458	1429	a_1	1418	1459
1494	1464	b_2		1496
1550	1519	a_1	1508	1549
3238	3115	b_2		3247
3244	3120	a_1		3253
3251	3127	b_2		3259
3263	3139	a_1		3271
3596	3459	a_1	3447[d]	3602

[a] Unscaled. [b] Scaled by 0.98 (< 2000 cm^{-1}) and 0.9619 (> 2000 cm^{-1}). [c] Ref. 53. [d] This work.

Table S2. Selected geometrical parameters, vibrational frequencies, and intermolecular interaction energies of Py^+-L_n clusters (L=Ar and N_2, *n*=1 and 2) obtained at the B3LYP-D3/aug-cc-pVTZ level.

Cluster	Symmetry	R_{NH}/Å	R/Å	θ/°	ν_{NH}/cm$^{-1\ a}$	D_e/kJ mol^{-1}	D_0/kJ mol^{-1}
Py^+-Ar(CH(I))	C_s	1.0101	2.896/3.058^b	117.4/114.1^a	3460 (208)	6.7	6.0
Py^+-Ar(CH(II))	C_{2v}	1.0101	2.985^b	115.4^a	3460 (218)	6.0	5.2
Py^+-Ar_2(H/CH(I))	C_s	1.0124	2.475^b 2.890/3.077^b	177.5^a 117.9/113.7^d	3412 (517)	16.7	15.2
Py^+-Ar_2(H/CH(II))	C_{2v}	1.0125	2.474^b 2.988^b	180.0^a 115.5^d	3411 (539)	16.0	14.6
Py^+-Ar_2(π/CH(I))	C_1	1.0098	3.313^c 2.901/3.095^b	90.8^e 115.7/111.3^d	3463 (200)	4.5	12.9
Py^+-Ar_2(π/CH(II))	C_1	1.0098	3.365^c 2.989/2.980^b	85.3^e 115.2/115.6^d	3463 (209)	13.3	11.9
Py^+-Ar_2(2π,1/1-II)	C_2	1.0097	3.362^c	85.7^e	3464 (194)	14.5	13.1
Py^+-N_2(CH(I))	C_s	1.0100	2.670/2.954^b	118.2/110.4^a	3461 (207)	10.7	8.8
Py^+-N_2(CH(II))	C_{2v}	1.0100	2.809^b	113.8^a	3461 (218)	9.2	7.4
Py^+-N_2(CH(III))	C_s	1.0100	2.483^b	179.4^a	3461 (213)	8.8	7.0
Py^+-$(N_2)_2$(H/CH(I))	C_s	1.0160	2.085^b 2.680/2.958^b	179.9^a 118.2/110.5^d	3347 (782)	29.8	25.0
Py^+-$(N_2)_2$(H/CH(II))	C_{2v}	1.0161	2.084^b 2.815^b	180.0^a 113.9^d	3346 (816)	28.4	23.8
Py^+-$(N_2)_2$(H/CH(III))	C_s	1.0161	2.084^b 2.495^b	179.9^a 179.8^d	3346 (801)	28.0	23.3
Py^+-$(N_2)_2$(CH/CH(I))	C_{2v}	1.0095	2.674/2.958^b	118.2/110.4^a	3463 (203)	21.1	17.5
Py^+-$(N_2)_2$(CH/CH(II))	C_s	1.0098	2.686/2.932^b 2.797/2.829^b	117.2/110.6^a 114.2/113.1^d	3463 (213)	19.7	16.2
Py^+-$(N_2)_2$(π/CH(I))	C_1	1.0096	3.061^c 2.680/2.981^b	93.4^e 116.8/108.5^d	3465 (198)	21.2	17.7
Py^+-$(N_2)_2$(π/CH(II))	C_s	1.0096	3.190^c 2.811^b	102.1^f 113.8^d	3466 (209)	19.6	16.3

[a] Values in parenthesis are IR intensities in km mol^{-1}. [b] NH…Ar/N_2 or CH…Ar/N_2 bond. [c] Distance between Ar/N_2 and aromatic ring plane. [d] NH…Ar/N_2 or CH…Ar/N_2 bond angle. [e] NCα…Ar/N_2 bond angle. [f] HN…N_2 bond angle.

Table S3. Selected geometrical parameters, vibrational frequencies, and intermolecular interaction energies of Py-L clusters (L=Ar, N_2, H_2O) obtained at the B3LYP-D3/aug-cc-pVTZ level.

Molecule/Cluster	Symmetry	R_{NH}/Å	R/Å	θ/°	ν_{NH}/cm^{-1} [a]	ν_{OH}/cm^{-1} [a]	D_e/kJ mol^{-1}	D_0/kJ mol^{-1}
Py	C_{2v}	1.0031			3531 (65)			
Py-Ar(H)	C_s	1.0030	2.813[b]	130.8[d]	3534 (83)		3.9	3.1
Py-Ar(π)	C_s	1.0030	3.466[c]	101.0[e]	3531 (64)		4.5	3.7
Py-N_2(H)	C_{2v}	1.0034	2.424[b]	180.0[d]	3528 (190)		6.3	4.3
Py-N_2(π)	C_s	1.0031	3.248[c]	102.9[e]	3531 (65)		7.8	5.6
Py-H_2O(H)	C_s	1.0095	1.991[b]	179.6[d]	3422 (517)	3658 (14) 3756 (85)	22.4	17.5
Py-H_2O(π)	C_1	1.0034	2.37[c]	167.3[f]	3528 (74)	3601 (157) 3729 (79)	19.7	14.5

[a] Values in parenthesis are IR intensities in km mol^{-1}. [b] NH…Ar/N_2 or NH…OH_2 bond. [c] Distance between Ar or center of mass of N_2 or the H atom of H_2O and the aromatic ring plane. [d] NH…Ar/N_2 or NH…OH_2 bond angle. [e] HN…Ar or HN…center of mass of N_2 bond angle. [f] OH…Cβ bond angle.

Table S4. Selected geometrical parameters, vibrational frequencies, and intermolecular interaction energies of Py^+-H_2O, Py^+-H_2O-Ar, and Py^+-H_2O-N_2 clusters obtained at the B3LYP-D3/aug-cc-pVTZ level.

Cluster	Symmetry	R_{NH}/Å	R_{OH}/Å	R/Å	θ/°	ν_{NH}/cm^{-1} [a]	ν_{OH}/cm^{-1} [a]	D_e/kJ mol^{-1}	D_0/kJ mol^{-1}
Py^+-$H_2O(\pi)$	C_1	1.0088	0.9642 0.9638	2.595[b]	91.4[d]	3474 (186)	3635 (60) 3723 (100)	42.6	37.2
Py^+-H_2O(CH,I)	C_s	1.0095	0.9635	2.315/2.699[c]	117.6[d] 106.4[d]	3466 (196)	3643 (34) 3727 (101)	44.2	38.3
Py^+-H_2O(CH,II)	C_{2v}	1.0094	0.9633	2.507[c]	111.5[d]	3467 (207)	3645 (28) 3731 (95)	38.7	33.0

[a] Values in parenthesis are IR intensities in km mol^{-1}. [b] Distance between O of H_2O and aromatic ring plane. [c] CH…O bond. [d] NCα…O or CH…O bond angle.