Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

Probing the Electronic Structure and Dipole-Bound State of the 7-Azaindolide Anion

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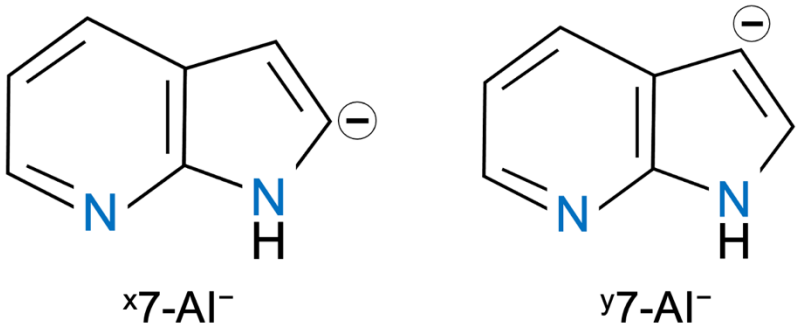

^{x}7-Al^{-} ^{y}7-Al^{-}

Fig. S1 The structures for the two isomers of 7-Al^{-}. (a) ^{x}7-Al^{-} (deprotonation at the α-carbon) and (b) ^{y}7-Al^{-} (deprotonation at the β-carbon).

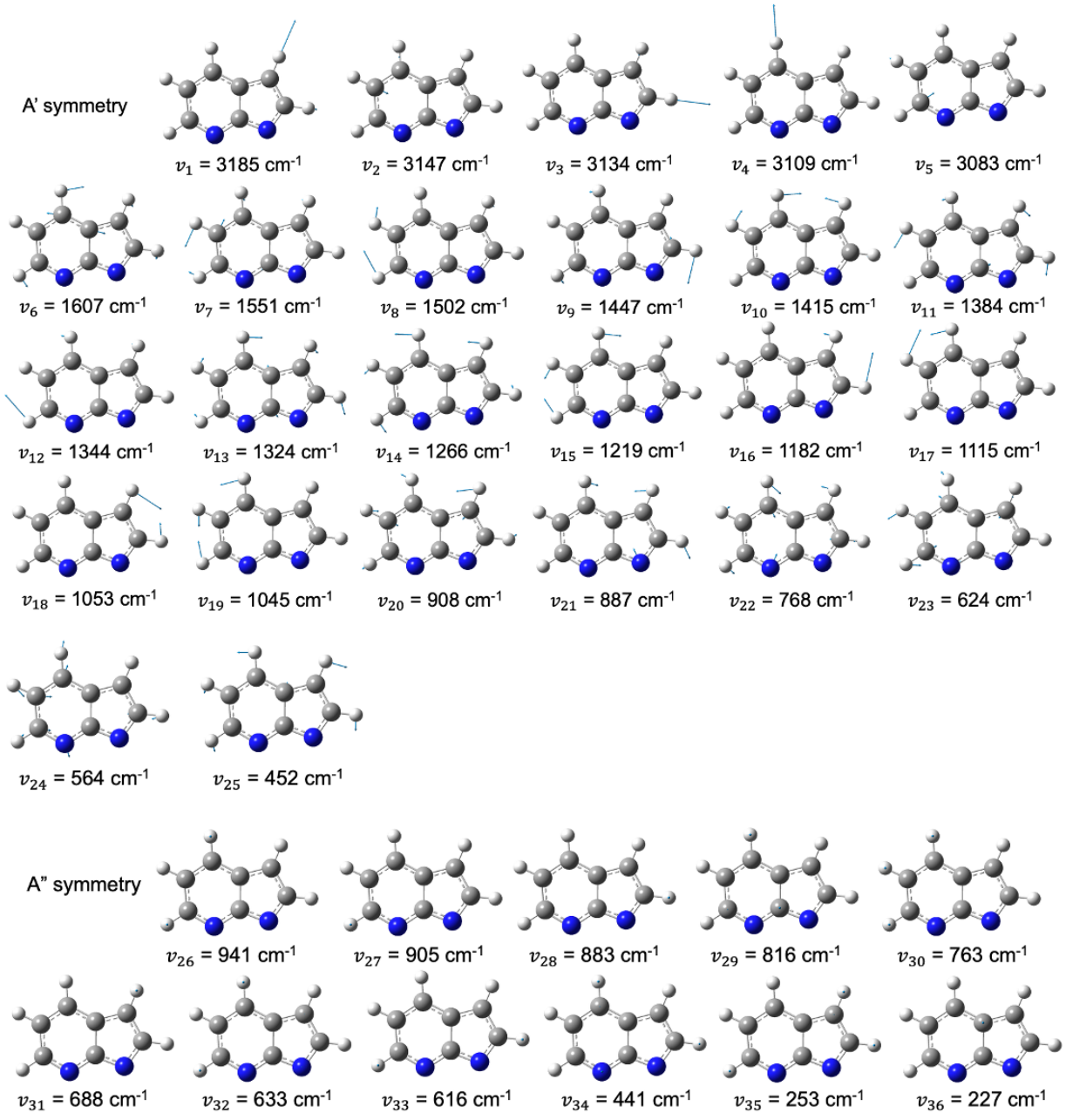

Fig. S2 The displacement vectors of the vibrational normal modes for the 7-Al$^-$ anion and their calculated harmonic frequencies, which are also given in Table S5.

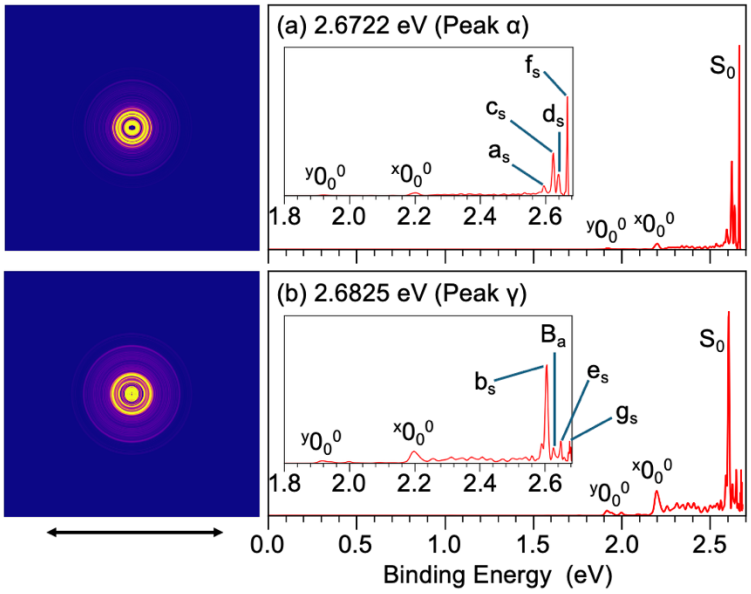

Fig. S3 PE images and spectra taken at peaks α and γ in the PDS. The insets show a magnified view of the 1.80–2.68 eV region.

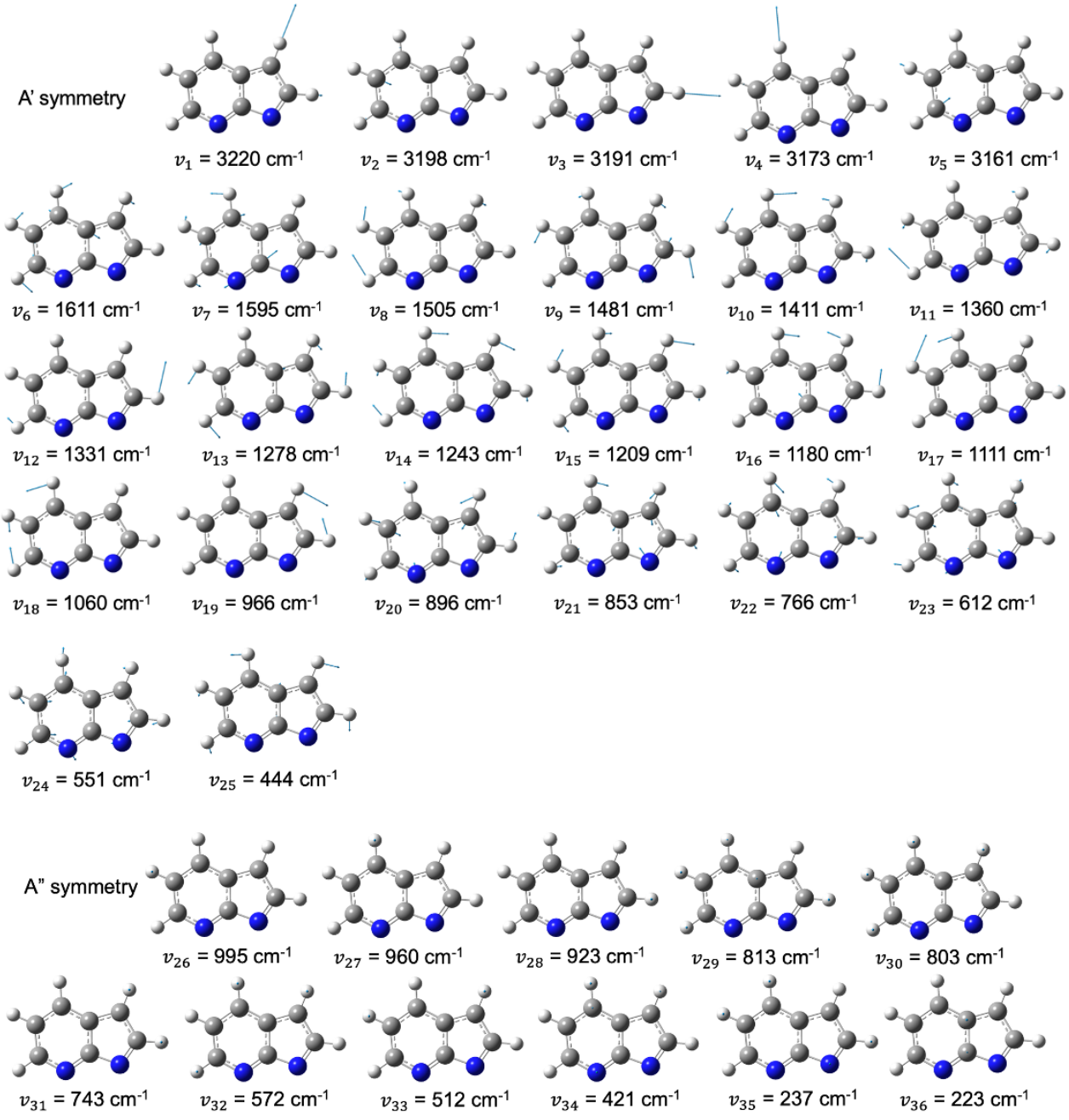

Fig. S4 The displacement vectors of the vibrational normal modes for the 7-AI radical and their calculated harmonic frequencies, which are also given in Table S8.

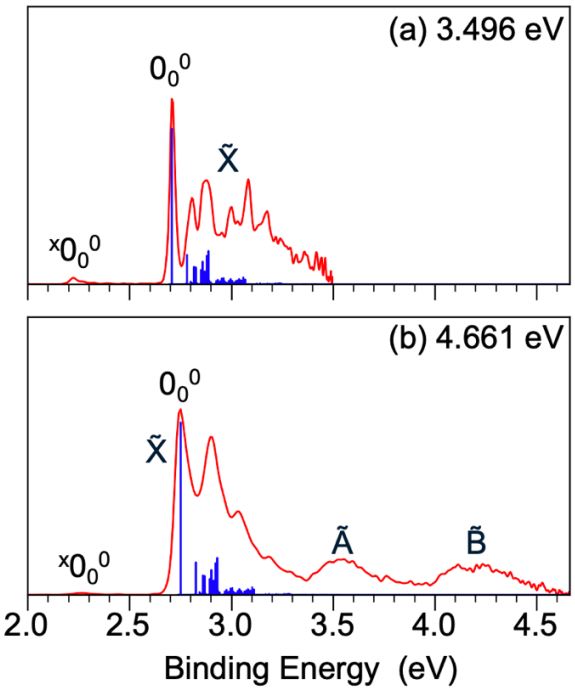

Fig. S5 The computed FC factors for the ground state detachment transition of 7-Al^-, compared with (a) the 3.496 eV and (b) the 4.661 eV photoelectron spectra. The computed vibrational frequencies used are scaled by a factor of 0.98).

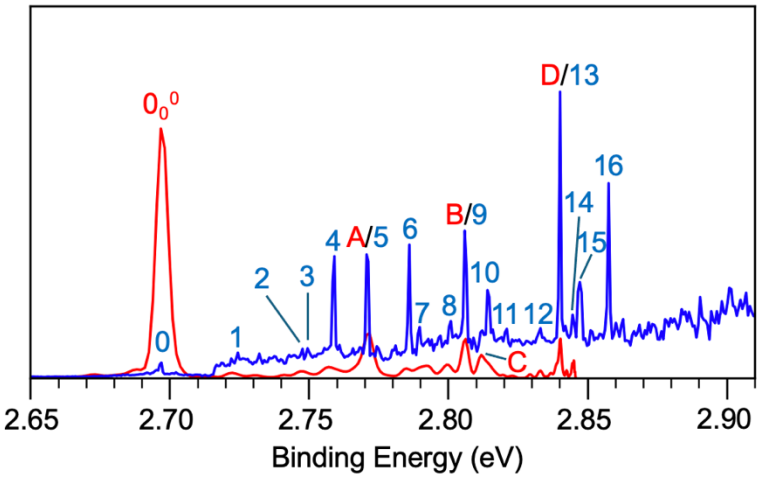

Fig. S6 Comparison of the photodetachment spectrum (blue) with the non-resonant PE spectrum taken at 2.8458 eV (red). The photodetachment spectrum is blue-shifted by 0.0193 eV (156 cm^{-1}) to align peak 0 with peak 0_0^0 of the PE spectrum.

Table S1 Experimental binding energies (BEs) for the three PES bands observed in Figure 1, and the experimental and theoretical excitation energies for bands Ã and B̃. All energies are in eV

	BE	ΔE (exp.)	ΔE (theo.)[a]
X̃	2.6967[b]	0	0
Ã	~3.5	~0.8	1.32
B̃	~4.1	~1.4	1.57

[a]Calculated using TD-DFT at the B3LYP level of theory.
[b]From the PE spectrum in Figure 3. Uncertainty: ± 0.0008 eV.

Table S2 The binding energies (BEs) of the observed vibrational peaks in the PE spectra of 7-Al$^-$, shifts from the 0-0 transition, assignments and calculated shifts

Peak	BE (eV)[a]	BE (cm^{-1})[a]	Shift (cm^{-1})[b]	Assignment	Calc. Shift (cm^{-1})[c]
0_0^0	2.6967(8)	21,751(6)	0		
a	2.7228(11)	21,961(9)	210	36^1	219
b	2.7241(15)	21,972(12)	221	35^1	232
c	2.7470(12)	22,156(10)	405	34^1	413
d	2.7510(10)	22,188(8)	437	25^1	435
e	2.7589(8)	22,252(6)	501	33^1	502
f	2.7659(8)	22,301(6)	550	32^1	561
A	2.7717(10)	22,355(8)	604	23^1	600
g	2.7859(10)	22,468(8)	717	31^1	728
h	2.8040(10)	22,616(8)	865	25^2	870
B	2.8063(12)	22,635(10)	884	20^1	878
C	2.8119(15)	22,680(12)	929	19^1	947
i	2.8207(8)	22,751(6)	1000	33^2	1004
j	2.8322(8)	22,843(6)	1092	17^1	1089
D	2.8403(10)	22,909(8)	1158	16^1	1156

[a]The numbers in parentheses denote the uncertainty associated with the last digit.
[b]The shift is relative to peak 0_0^0.
[c]The calculated shift is scaled by a factor of 0.98.

Table S3 Observed DBS vibrational peaks from the PD spectrum of 7-Al$^-$, their corresponding photon energies, shifts relative to the ground vibrational level, calculated frequencies, and assignments

Peak	Photon Energy (eV)[a]	Photon Energy (cm^{-1})[a]	Shift (cm^{-1})[b]	Assignment	Calc. Frequencies (cm^{-1})[c]
0	2.6774	21,595	0	DBS Ground State	
1	2.7048	21,816	221	$35'^1$	232
2	2.7279	22,002	407	$34'^1/36'^2$	413/438
3	2.7298	22,018	423	$25'^1/35'^136'^1$	435/451
4	2.7395	22,096	501	$33'^1$	502
5	2.7510	22,188	593	$23'^1$	600
6	2.7665	22,314	719	$33'^136'^1$	720
7	2.7701	22,343	748	$22'^1/33'^135'^1$	751/734
8	2.7814	22,434	839	$21'^1$	836
9	2.7865	22,475	880	$20'^1/25'^2$	878/870
10	2.7944	22,539	944	$19'^1/31'^136'^1$	947/947
11	2.8015	22,596	1001	$31'^135'^1/23'^134'^1/33'^2$	960/1013/1004
12	2.8137	22,694	1099	$23'^133'^1$	1102
13	2.8206	22,750	1155	$16'^1/23'^132'^1/31'^134'^1$	1156/1161/1141
14	2.8251	22,786	1191	$23'^2/30'^134'^1$	1200/1200
15	2.8275	22,806	1211	$29'^134'^1/31'^133'^1/33'^236'^1$	1210/1230/1223
16	2.8381	22,891	1296	$12'^1/25'^3/17'^136'^1$	1304/1305/1308

[a]The uncertainty associated with the peak position is ± 0.0006 eV or ± 5 cm^{-1}.

[b]The shift is relative to the BE of peak 0.

[c]The calculated shift is scaled by a factor of 0.98.

Table S4 The binding energies in both eV and cm^{-1} of the vibrational peaks observed in the R2PD PE spectrum of 7-Al$^-$, their shifts relative to the 0_0^0 transition in the PE spectra in Fig. 3, and tentative assignments based on the computed anion vibrational frequencies

Peaks	BE (eV)[a]	BE (cm^{-1})[a]	Shift (cm^{-1})[b]	Assignment	Calc. Frequencies (cm^{-1})[c]
A_a	2.6011(22)	20,979(18)	772	ν_{22a}	753
B_a	2.6269(34)	21,188(27)	563	ν_{24a}	553
C_a	2.6435(14)	21,321(11)	430	ν_{34a}	432
D_a	2.6702(12)	21,537(10)	214	ν_{36a}	222

[a]The numbers in parentheses denote the uncertainty associated with the last digit.

[b]The shift is relative to peak 0_0^0 at 2.6967 eV in the PE spectra in Fig. 3.

[c]Scaled by a factor of 0.98.

Table S5 The harmonic frequencies of the 7-AI$^-$ anion computed at the B3LYP/aug-cc-pVTZ level of theory and scaled with a factor of 0.98

Mode	Symmetry	Frequency (cm^{-1})
ν_1	A’	3121
ν_2		3084
ν_3		3071
ν_4		3047
ν_5		3021
ν_6		1575
ν_7		1520
ν_8		1472
ν_9		1418
ν_{10}		1387
ν_{11}		1356
ν_{12}		1317
ν_{13}		1298
ν_{14}		1241
ν_{15}		1195
ν_{16}		1158
ν_{17}		1093
ν_{18}		1032
ν_{19}		1024
ν_{20}		890
ν_{21}		869
ν_{22}		753
ν_{23}		612
ν_{24}		553
ν_{25}		443
ν_{26}	A”	922
ν_{27}		887
ν_{28}		865
ν_{29}		800
ν_{30}		748
ν_{31}		674
ν_{32}		620
ν_{33}		604
ν_{34}		432
ν_{35}		248
ν_{36}		222

Table S6 The binding energies (BEs) of the resolved spectral peaks in both eV and cm^{-1} in the PE spectra shown in Fig. S3, taken at peaks α and γ from the PDS

Peaks	BE (eV)[a]	BE (cm^{-1})[a]
a_S	2.5939(30)	20,921(24)
b_S	2.6062(16)	21,021(13)
c_S	2.6234(16)	21,159(13)
d_S	2.6397(20)	21,291(16)
e_S	2.6486(19)	21,363(15)
f_S	2.6663(12)	21,505(10)
g_S	2.6759(16)	21,583(13)

[a]The numbers in parentheses denote the uncertainty associated with the last digit.

Table S7 The adiabatic detachment energy (ADE) of the ^{x}7-Al$^-$ and ^{y}7-Al$^-$ isomers (see Fig. S1) compared with the calculated values at the B3LYP level

	ADE (exp) (eV)	ADE (theo) (eV)
^{x}7-Al$^-$	2.200 ± 0.003	2.17
^{y}7-Al$^-$	1.918 ± 0.005	1.79

Table S8 The harmonic frequencies of the 7-AI neutral radical computed at the B3LYP/aug-cc-pVTZ level of theory and scaled with a factor of 0.98

Mode	Symmetry	Frequency (cm^{-1})
ν_1	A’	3156
ν_2		3134
ν_3		3127
ν_4		3110
ν_5		3098
ν_6		1579
ν_7		1563
ν_8		1475
ν_9		1451
ν_{10}		1383
ν_{11}		1333
ν_{12}		1304
ν_{13}		1252
ν_{14}		1218
ν_{15}		1185
ν_{16}		1156
ν_{17}		1089
ν_{18}		1039
ν_{19}		947
ν_{20}		878
ν_{21}		836
ν_{22}		751
ν_{23}		600
ν_{24}		540
ν_{25}		435
ν_{26}	A”	975
ν_{27}		941
ν_{28}		905
ν_{29}		797
ν_{30}		787
ν_{31}		728
ν_{32}		561
ν_{33}		502
ν_{34}		413
ν_{35}		232
ν_{36}		219

Table S9 The low-lying electronic excited states and the computed vertical excitation energies (ΔE) of 7-AI^- using TD-DFT at the B3LYP/aug-cc-pVTZ level of theory

	Spin State	ΔE (eV) (Theo.)	ΔE (cm^{-1}) (Theo.)
1st Excited State (S_1)	Singlet	2.8065	22,636
2nd Excited State (T_1)	Triplet	2.8125	22,685