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Electronic Supplementary Information

Determination of the highest occupied molecular orbital and conformational structures of morpholine based on its conformer-specific photoionization dynamics

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Table S1 Relative energies (RE) and AIEs (in cm^{-1}) of Chair-Eq and Chair-Ax calculated with zero-point energy correction at various DFT and ab-initio calculation levels

Method	Basis set	RE (S_0)[a]		AIE_{cal}[b]	
		Eq	Ax	Eq	Ax
B3LYP	cc-pVDZ	0.0	177	61,903	61,726
	cc-pVTZ	0.0	246	62,915	62,670
	aug-cc-pVDZ	0.0	277	63,445	63,168
	aug-cc-pVTZ	0.0	255	63,448	63,193
CAM-B3LYP	cc-pVDZ	0.0	228	62,985	62,757
	cc-pVTZ	0.0	285	64,020	63,735
	aug-cc-pVDZ	0.0	305	64,505	64,201
	aug-cc-pVTZ	0.0	286	64,540	64,254
M062x	cc-pVDZ	0.0	223	63,661	63,438
	cc-pVTZ	0.0	280	64,837	64,557
	aug-cc-pVDZ	0.0	263	64,731	64,468
	aug-cc-pVTZ	0.0	259	65,240	64,981
wB97XD	cc-pVDZ	0.0	176	62,625	62,449
	cc-pVTZ	0.0	227	63,240	63,012
	aug-cc-pVDZ	0.0	233	63,818	63,586
	aug-cc-pVTZ	0.0	218	63,668	63,450
MP2	cc-pVDZ	0.0	267	64,635	64,368
	cc-pVTZ	0.0	315	67,010	66,695
	aug-cc-pVDZ	0.0	310	66,971	66,661
	aug-cc-pVTZ	0.0	308	67,903	67,595

[a] Calculated ionic transition energy for each conformer in neutral chair form to the axial-like NH conformer in cationic chair form. [b] Difference of the calculated adiabatic ionization energies (AIE_{cal} (Eq)-AIE_{cal}(Ax)) between the equatorial and the axial conformers equals the RE of axial NH conformer, of which the average difference for aug-cc-pVTZ basis set gives 265 cm^{-1}.

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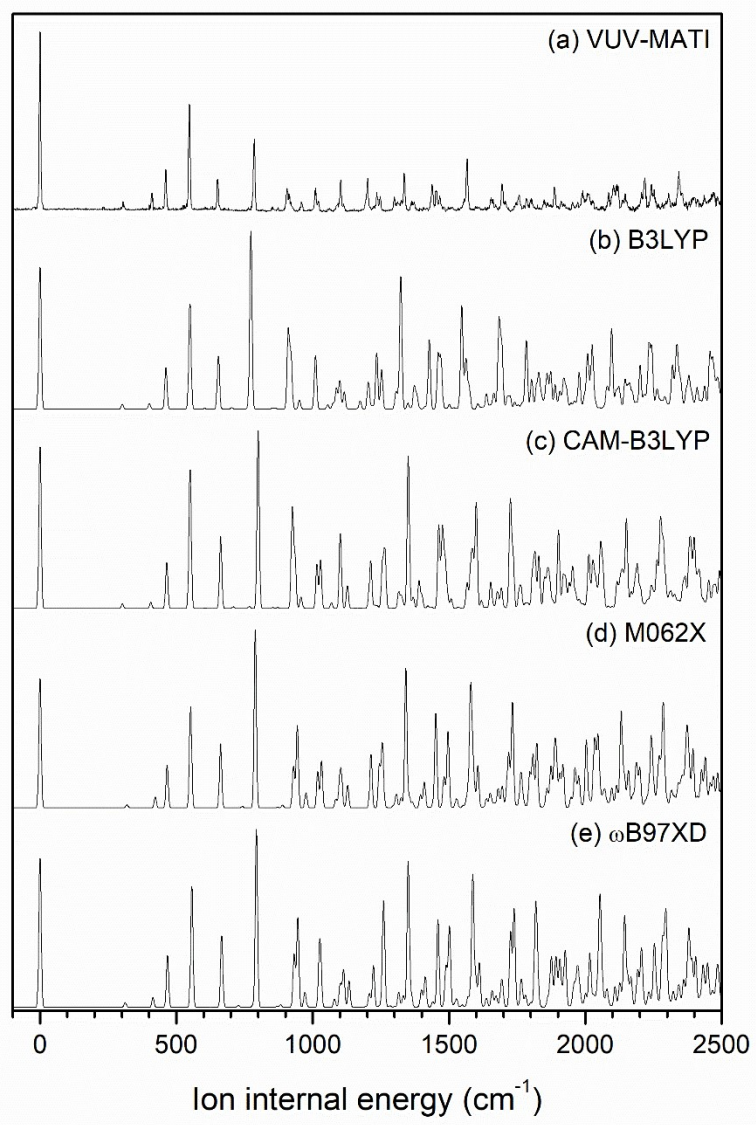

Figure S1 (a) HR VUV-MATI spectrum of morpholine. Spectra simulated using FC factors and vibrational frequencies calculated at (b) B3LYP, (c) CAM-B3LYP, (d) M062X, and (e) ωB97XD levels with aug-cc-pVTZ basis set for adiabatic ionic transitions between Chair-Ax and Chair-Ax-like$^{+\bullet}$ conformers.

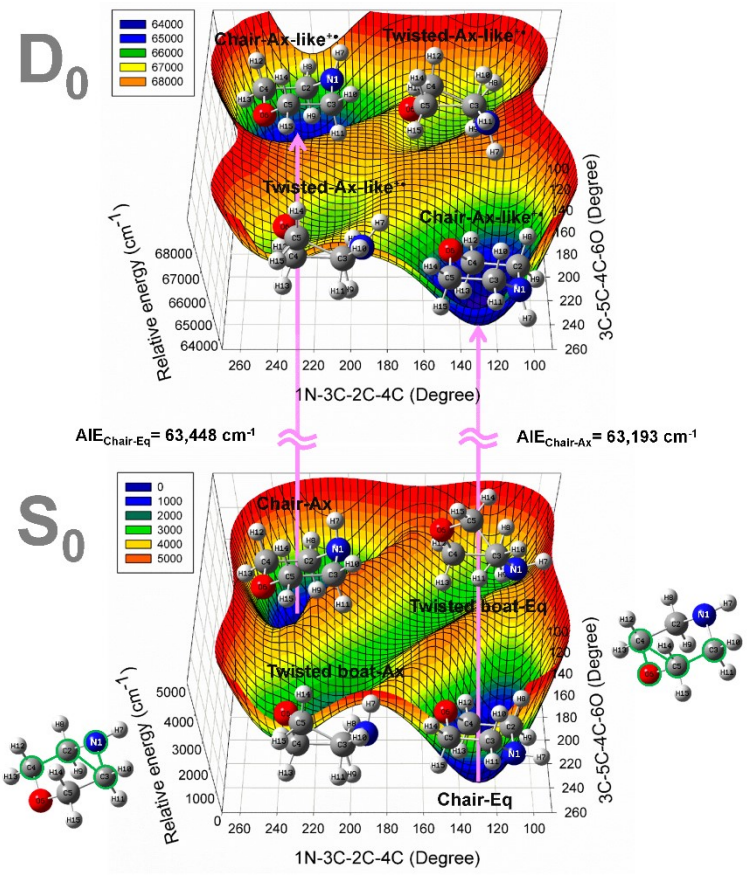

Figure S2 2D PESs of S_0 and D_0 states as functions of dihedral angles associated with two ring inversions, describing conformational interconversion between chair and twisted boat forms of morpholine as determined by optimizing remaining geometrical parameters. AIE_{cal} is adiabatic ionization energy calculated for each conformer with zero-point energy correction at B3LYP/aug-cc-pVTZ level.