

Electronic Supplementary Information for: “The Conformer Resolved Ultraviolet Photodissociation of Morpholine”

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1. Experimental Setup

Morpholine ($\geq 99.0\%$, Sigma Aldrich) was used without further purification. The HRA-PTS experimental apparatus has been detailed previously.¹ Briefly, a sample of morpholine (room temperature vapour pressure, seeded in ~ 700 Torr of argon) was expanded into vacuum through a pulsed valve (General Valve Series 9) and skimmed to form a cold molecular beam. This molecular beam was intersected by a tunable nanosecond UV photolysis pulse generated by frequency doubling the output of a Nd-YAG pumped dye laser (Spectra Physics GCR-270 plus PDL-2, $250 \leq \lambda_{\text{phot}} \leq 210$ nm, ~ 0.5 - 2 mJ pulse⁻¹) or by use of an ArF excimer laser (Lambda-Physik OpteX, 193 nm, ~ 1 - 2 mJ pulse⁻¹). The precise wavelength of the former radiation was measured by directing a portion of the fundamental dye laser output into a wavemeter (Coherent Wavemaster). The UV radiation was focussed into the interaction region using an $f = 75$ cm lens. After a time delay $\delta t = 10$ ns, H atom photoproducts in the interaction region were tagged using a doubly-resonant two photon excitation scheme involving, first, Lyman- α (121.6 nm) excitation to the $2p$ state, followed by excitation at ~ 366 nm to a high n Rydberg state ($n \sim 80$). The requisite tagging photons were created using two separate dye lasers pumped by the second harmonic of a single Nd-YAG laser (Continuum Powerlite 9010). The Lyman- α radiation was produced by mixing the 554.8 nm output of one dye laser with residual 1064 nm radiation to produce light of wavelength 364.7 nm, which was then focused in a cell containing a phase matched Kr/Ar gas mixture. The resulting 121.6 nm radiation was then re-focussed into the interaction region (MgF₂ lens). Any prompt ions formed from unintentional vacuum UV or multiphoton induced ionisation processes are removed by biasing (20 V cm⁻¹) an extractor plate assembly that straddles the interaction region. Tagged H (Rydberg) atoms that recoil with velocities along the TOF axis travel to a Johnston multiplier detector (held at -4.2 kV) where they are field ionised and their arrival time recorded.

The length of the TOF axis used in these experiments, d (~ 37.1 cm), was frequently recalibrated by recording TOF spectra of H atoms resulting from H₂S photodissociation at $\lambda_{\text{phot}} < 240$ nm, and least squares fitting to well-characterised rotationally and spin-orbit resolved peaks associated with the H + SH (X, v, N) product channels, using the literature value for $D_0(\text{H-SH})$ ^{2,3} and the relevant diatomic term values.⁴ The electric polarisation vector, ϵ_{phot} , of the photolysis laser radiation was ordinarily aligned at an angle $\theta = 90^\circ$ to the TOF axis. When necessary, ϵ_{phot} could be rotated by inserting a double Fresnel rhomb (Optics for Research). As before,³ TOF (and thus kinetic energy) dependent recoil anisotropy parameters, β , were determined by recording spectra with ϵ_{phot} aligned at $\theta = 0^\circ, 54.7^\circ$ and 90° to the TOF axis.

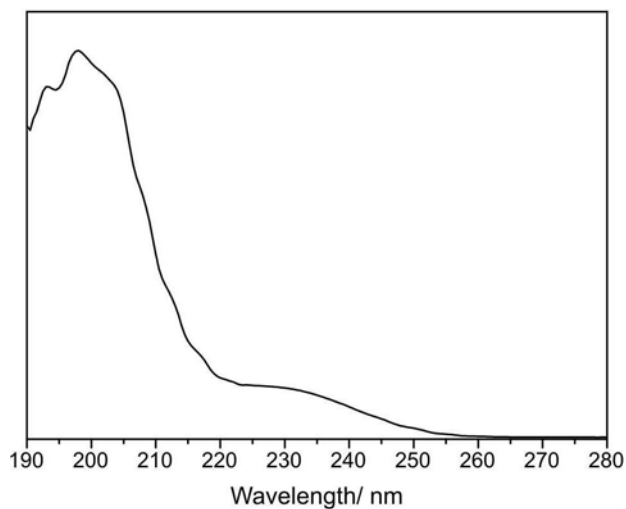
TOF-mass spectra (MS) of the morpholine sample were investigated by substituting a (removable) Wiley-McClaren TOF-mass spectrometer in place of the extractor plate.

2. Optimised Geometry Parameters

Method	Parameter	Structure		
		TS [‡]	AX	EQ
B3LYP	$\phi/^\circ$	-4.8	-53.0	50.8
	$\alpha/^\circ$	117.1	111.2	111.2
	$R_{N-H}/\text{\AA}$	1.001	1.016	1.013
BMK	$\phi/^\circ$	-4.3	-53.5	51.5
	$\alpha/^\circ$	116.7	110.8	110.7
	$R_{N-H}/\text{\AA}$	1.001	1.017	1.014
MPWB1K	$\phi/^\circ$	-5.1	-53.4	51.0
	$\alpha/^\circ$	116.6	110.5	110.5
	$R_{N-H}/\text{\AA}$	0.993	1.008	1.005
B972	$\phi/^\circ$	-4.8	-53.7	51.4
	$\alpha/^\circ$	117.1	110.9	111.0
	$R_{N-H}/\text{\AA}$	0.997	1.013	1.010
BB1K	$\phi/^\circ$	-5.1	-53.5	51.1
	$\alpha/^\circ$	116.7	110.5	110.5
	$R_{N-H}/\text{\AA}$	0.993	1.009	1.005
QCISD	$\phi/^\circ$	-5.6	-49.3	54.7
	$\alpha/^\circ$	116.8	110.2	110.0
	$R_{N-H}/\text{\AA}$	1.001	1.018	1.014
MP2	$\phi/^\circ$	-4.2	-53.0	53.7
	$\alpha/^\circ$	116.4	111.2	109.7
	$R_{N-H}/\text{\AA}$	1.002	1.016	1.016

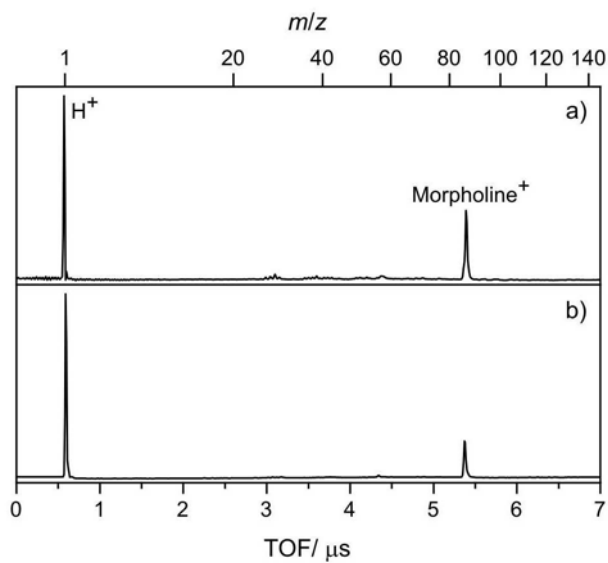
Optimised values of ϕ , α and R_{N-H} for the axial, equatorial and transition state conformations of morpholine calculated using a 6-311+G** basis set.

3. UV Spectrum



The room temperature UV absorption spectrum of morpholine has a bimodal appearance, with a long wavelength onset at ~255 nm and a secondary rise at ~220 nm. On the basis of the CASPT2 optimised excitation energies, we assign the longest wavelength onset to the $\sigma^* \leftarrow n$ transition and the more intense absorption at shorter wavelengths to $(3p \text{ and higher})\text{Rydberg} \leftarrow n$ transitions.

4. Photoionisation Mass Spectrometry



Ion TOF-mass spectra obtained following excitation of jet cooled morpholine at $\lambda_{phot} =$ (a) 250.0 nm and (b) 193.3 nm and subsequent introduction of Lyman- α radiation after $\delta t = 10$ ns.

5. Calculated normal mode wavenumbers for the equatorial and axial conformers of ground state morpholine and for the ground state of the morpholinyl radical

Morpholine(\tilde{X})						Morpholinyl(\tilde{X})			
Equatorial Conformer				Axial Conformer					
Mode	Symm.	Harmonic	Anharmonic	Harmonic	Anharmonic	Mode	Symm.	Harmonic	Anharmonic
v ₁	a'	3538	3372	3500	3340	Disappearing Mode			
v ₂	a'	3094	2952	3078	2936	v ₁	a'	3097	2953
v ₃	a'	3061	2922	3070	2923	v ₂	a'	3063	2914
v ₄	a'	2986	2867	3024	2904	v ₃	a'	2993	2849
v ₅	a'	2932	2779	2951	2791	v ₄	a'	2962	2779
v ₆	a'	1500	1460	1490	1464	v ₅	a'	1495	1465
v ₇	a'	1493	1459	1481	1436	v ₆	a'	1503	1471
v ₈	a'	1424	1461	1408	1377	v ₇	a'	1328	1305
v ₉	a'	1408	1376	1391	1363	v ₈	a'	1404	1375
v ₁₀	a'	1332	1293	1343	1299	v ₉	a'	1306	1264
v ₁₁	a'	1300	1269	1318	1288	v ₁₀	a'	1248	1208
v ₁₂	a'	1142	1110	1164	1137	v ₁₁	a'	1026	1006
v ₁₃	a'	1077	1052	1049	1032	v ₁₂	a'	1090	1070
v ₁₄	a'	1038	1012	1011	984	v ₁₃	a'	946	920
v ₁₅	a'	909	884	906	887	v ₁₄	a'	881	863
v ₁₆	a'	839	821	834	819	v ₁₅	a'	840	824
v ₁₇	a'	781	736	771	755	Disappearing Mode			
v ₁₈	a'	585	576	592	617	v ₁₆	a'	612	625
v ₁₉	a'	443	435	441	436	v ₁₇	a'	461	448
v ₂₀	a'	415	404	397	433	v ₁₈	a'	367	368
v ₂₁	a'	263	254	255	267	v ₁₉	a'	239	229
v ₂₂	a''	3092	2950	3077	2934	v ₂₀	a''	3096	2952
v ₂₃	a''	3060	2921	3069	2922	v ₂₁	a''	3062	2913
v ₂₄	a''	2981	2828	3021	2899	v ₂₂	a''	2990	2834
v ₂₅	a''	2928	2804	2942	2784	v ₂₃	a''	2952	2750
v ₂₆	a''	1490	1443	1492	1461	v ₂₄	a''	1478	1439
v ₂₇	a''	1485	1439	1477	1447	v ₂₅	a''	1490	1456
v ₂₈	a''	1482	1442	1472	1436	Disappearing Mode			
v ₂₉	a''	1377	1346	1377	1346	v ₂₆	a''	1364	1342
v ₃₀	a''	1347	1312	1351	1321	v ₂₇	a''	1317	1294
v ₃₁	a''	1250	1219	1272	1240	v ₂₈	a''	1272	1241
v ₃₂	a''	1226	1197	1215	1190	v ₂₉	a''	1212	1192
v ₃₃	a''	1156	1119	1145	1112	v ₃₀	a''	1167	1133
v ₃₄	a''	1112	1075	1123	1082	v ₃₁	a''	1084	1046
v ₃₅	a''	1087	1066	1043	1027	v ₃₂	a''	1055	1023
v ₃₆	a''	896	875	885	869	v ₃₃	a''	878	860
v ₃₇	a''	862	843	838	835	v ₃₄	a''	844	830
v ₃₈	a''	481	473	484	482	v ₃₅	a''	482	482
v ₃₉	a''	266	246	245	266	v ₃₆	a''	222	227

Harmonic and anharmonic corrected vibrational wavenumbers (in cm⁻¹) at the DFT/B3LYP/6-311+G** level for the equatorial and axial morpholine conformers, and for the morpholinyl radical. The parent equatorial conformer modes are labelled according to Herzberg notation,⁵ whereas the ordering of the morpholinyl radical modes have been adjusted so as to map through from those of the parent morpholine molecule.

References

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