**Table S1** Relative energies (RE) and adiabatic ionization energies (AIEs) in cm^{-1} of the equatorial NH (Eq) and the axial NH (Ax) conformers in chair form in the S_0 state calculated with zero-point energy correction at various DFT levels.

Method	Basis set	RE$_{cal}$(S_0)		AIE$_{cal}$[a]		ΔAIE$_{cal}$[b]
		Eq	Ax	Eq	Ax	
B3LYP	cc-pVDZ	0.0	167.0	61,885.7	61,718.7	167.0
	cc-pVTZ	0.0	227.6	62,637.4	62,409.8	227.6
	aug-cc-pVDZ	0.0	297.8	62,915.5	62,617.7	297.8
	aug-cc-pVTZ	0.0	262.1	62,959.2	62,697.1	262.1
CAM-B3LYP	cc-pVDZ	0.0	190.1	62,519.6	62,329.5	190.1
	cc-pVTZ	0.0	241.9	63,295.6	63,053.8	241.9
	aug-cc-pVDZ	0.0	297.8	63,528.1	63,230.2	297.8
	aug-cc-pVTZ	0.0	266.2	63,606.4	63,340.2	266.2
M062x	cc-pVDZ	0.0	165.0	63,428.6	63,263.6	165.0
	cc-pVTZ	0.0	202.8	64,267.7	64,064.9	202.8
	aug-cc-pVDZ	0.0	253.1	64,071.7	63,818.6	253.1
	aug-cc-pVTZ	0.0	235.5	64,498.1	64,262.6	235.5
wB97XD	cc-pVDZ	0.0	127.3	62,387.0	62,259.7	127.3
	cc-pVTZ	0.0	188.1	62,794.6	62,606.5	188.1
	aug-cc-pVDZ	0.0	217.1	63,116.8	62,899.7	217.1
	aug-cc-pVTZ	0.0	194.9	63,046.3	62,851.4	194.9
MP2	cc-pVDZ	0.0	204.3	63,503.7	63,299.4	204.3
	cc-pVTZ	0.0	274.8	65,725.7	65,450.9	274.8
	aug-cc-pVDZ	0.0	308.1	65,341.1	65,033.0	308.1
	aug-cc-pVTZ	0.0	300.5	66,430.0	66,129.5	300.5

[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 252 cm^{-1}.
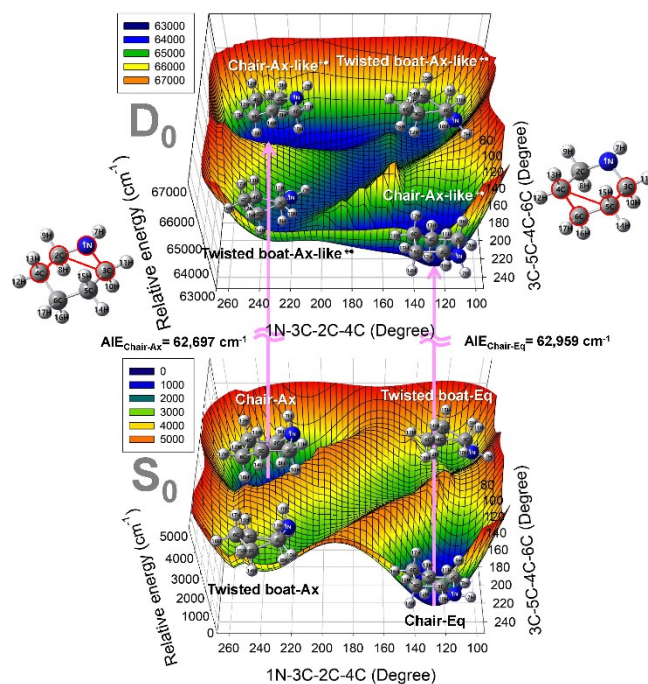
Figure S2 2D PESs of S_0 and D_0 states as functions of dihedral angles associated with two ring inversions, describing the conformational interconversion between the chair and the twisted boat forms in piperidine performed by optimizing the remaining geometrical parameters. AIE$_{cal}$ is the adiabatic ionization energy calculated for each conformer with zero-point energy correction at the B3LYP/aug-cc-pVTZ level.
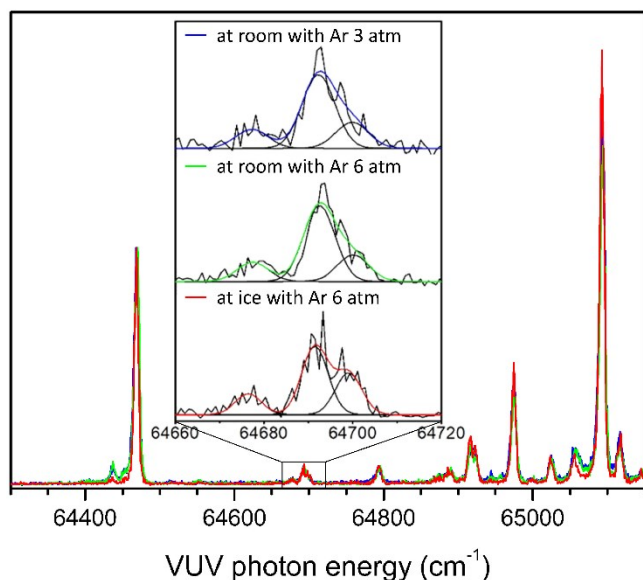
Figure S1 Conformer-specific VUV-MATI spectra in the 64,300-65,150 cm^{-1} region for piperidine measured under supersonic expansion conditions with Ar carrier gas at several backing pressures and sample reservoir temperatures. Insets show the three peaks at ca. 64,700 cm^{-1} measured under three molecular beam conditions, which were fitted with Gaussian profiles to estimate their relative intensities.