

799 C₇H₇NO

Mass-selective REMPI

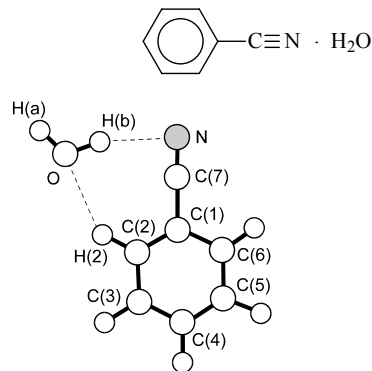
Benzonitrile – water

(weakly bound complex)

C_s(effective symmetry class)
(large-amplitude motion)

State	\tilde{X}^1A'	\tilde{A}^1A''
Energy [eV]	0.00	4.518
$r_0(\text{H}(2)\dots\text{O})$ [Å]	2.477(4)	2.457(2)
$r_0(\text{H}(b)\dots\text{N})$ [Å]	2.612(16)	2.631

The van der Waals complex was generated by passing a mixture of argon and water over heated fluid benzonitrile and expanding the mixture into a supersonic chamber. Excitation from the ground state to a selected rovibronic level of the \tilde{A} state was achieved by a single-frequency UV laser with a frequency width of 60 MHz. A counterpropagating ionization laser with lower power produced ions which were analyzed in a time-of-flight mass spectrometer. The spectra were found to consist of mixed *a*- and *b*- type transitions, hence the oxygen atom of the H₂O molecule must lie close to the benzonitrile plane. Rotational analysis of the spectra yielded rotational constants for the ground and excited states of the complex. The ground state constants were then refined by MW studies and these improved constants were used to refine the constants for the excited state. By assuming that the molecular geometries of the benzonitrile and water molecules are not changed by complex formation, the distances of the oxygen atom from an ortho hydrogen atom in the benzene ring and of one of the hydrogen atoms in the H₂O molecule from the N atom in CN group are determined in both the ground and excited states (see table).



Helm, R.M., Vogel, H.-P., Neusser H.J., Storm, V., Consalvo, D., Dreizler, H.: Z. Naturforsch. A **52** (1997) 655.

See also: Neusser, H.J., Siglow, K.: Chem. Rev. **100** (2000) 3921.

MW

r_0	Å	θ_0	deg
O...H(2)	2.484(3) ^{a)}	H(a)–O...H(2)	164.6(21) ^{a)}
H(b)...N	2.257(3) ^{b)}	O...H(2)–C(2)	144.0(6) ^{a)}
		H(b)...N–C(7)	89(1) ^{b)}
		O–H(b)...N	157(1) ^{b)}

A coupled analysis of the 0⁺ and 0[−] states observed for the normal species was performed and the experimental data were reproduced by a flexible model which allowed the determination of the barrier to internal rotation of water [$V_2 = 287(29) \text{ cm}^{-1}$] and the structural relaxation associated with the dynamic process.

^{a)} Uncertainties are increased, according to a comment of the authors, by a factor of three from those reported in the original paper.

^{b)} Derived from fitted parameters; uncertainties were not estimated in the original paper.

Melandri, S., Consalvo, D., Caminati, W., Favero, P.G.: J. Chem. Phys. **111** (1999) 3874.

See also: Storm, V., Dreizler, H., Consalvo, D.: Chem. Phys. **239** (1998) 109.