Structure and vibrations of a hydrogen-transferring ammonia wire cluster

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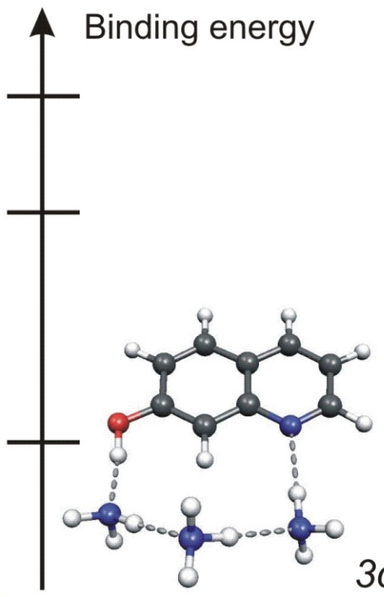
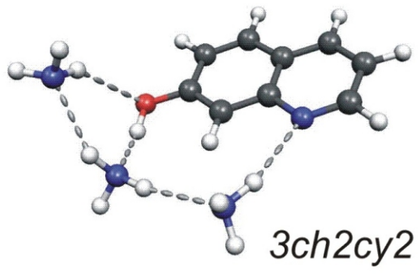
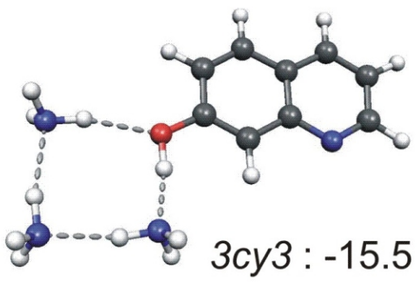
Isomers of the 7-hydroxyquinoline·$(NH_3)_3$ cluster





3ch2cy2 : -15.0 kcal·mol^{-1}

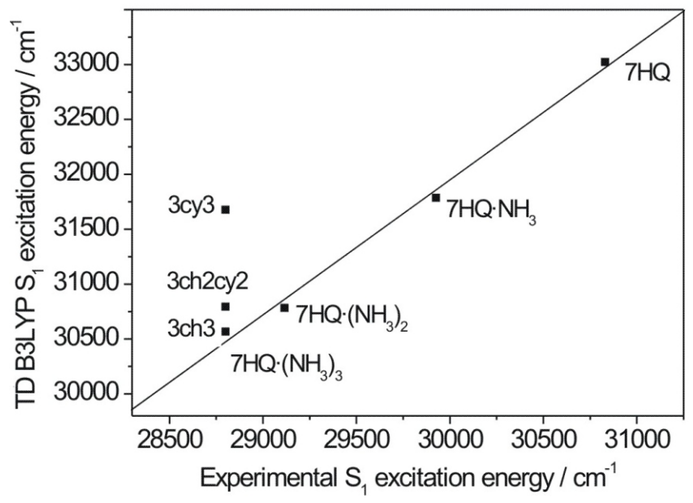


3cy3 : -15.5 kcal·mol^{-1}

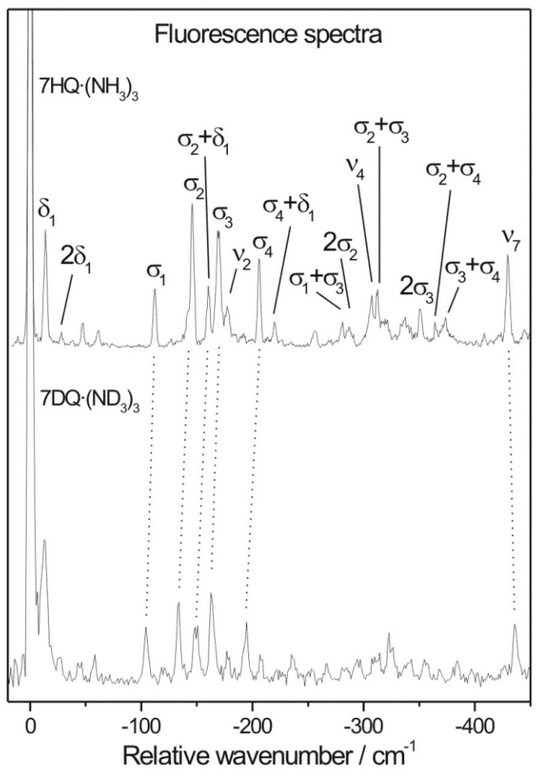
3ch3 : -16.8 kcal·mol^{-1}

B3LYP/6-311++G(d,p) calculations predict that ***3ch3*** is the **most stable** isomer.

Electronic excitation



3ch3 is **observed experimentally** in the molecular beam.



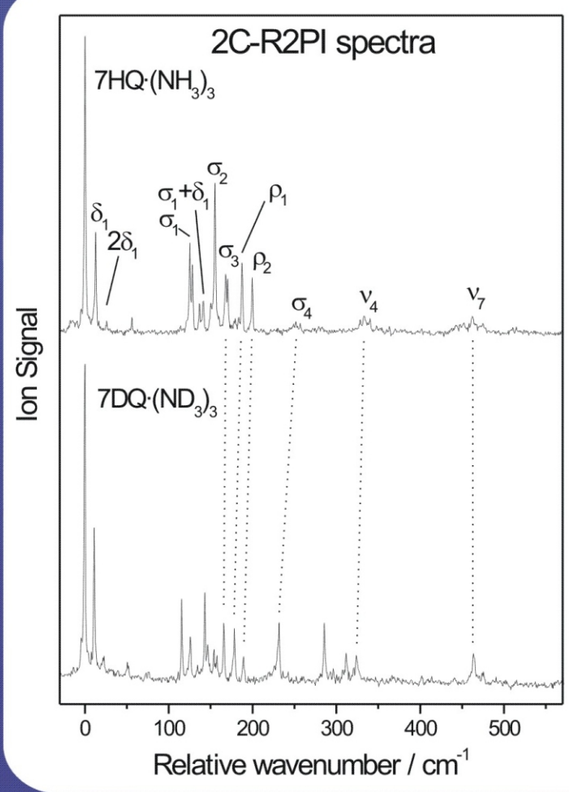
Ground State Vibrations

Intermolecular frequencies in cm^{-1}:

Mode	SCF 6-31G(d,p)	B3LYP 6-311++G(d,p)	Exp.
δ_1	**16.4**	**19.9**	**14**
σ_1	**99.0**	**115.8**	**112**
σ_2	**140.7**	**161.0**	**146**
σ_3	**187.3**	**187.1**	**169**
σ_4	**206.4**	**228.8**	**206**
ν_4	**338.4**	**332.7**	**307**
ν_7	**415.2**	**443.6**	**429**

The intermolecular stretches are strongly active.

The assignment is reinforced by the use of the deuterated cluster 7DQ·$(ND_3)_3$.



Excited State vibrations

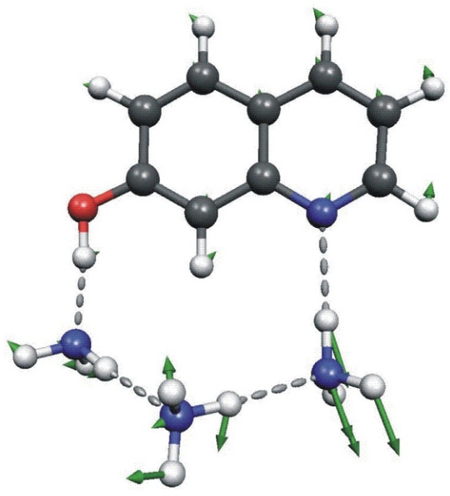
Mode	CIS 6-31G(d,p)	Exp.
δ_1	**16.9**	**13.0**
σ_1	**108.3**	**125.3**
σ_2	**149.6**	**155.4**
σ_3	**173.0**	**170.4**
σ_4	**222.4**	**256.1**

The increases in intermolecular stretch mode frequencies are in agreement with the intermolecular hydrogen bond contraction upon excitation predicted by calculations .

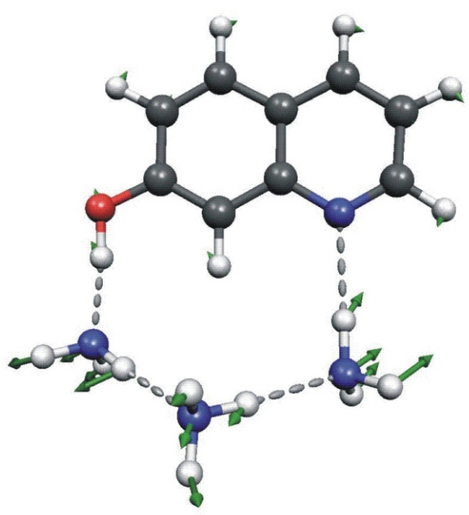
The falloff of the 2C-R2PI spectrum is due to the loss of 7HQ·$(NH_3)_3$ and the *enol* ➝ *keto tautomerization* in the S_1 state, the NH_3 wire acting as an H relay.

Intermolecular Vibrational Modes

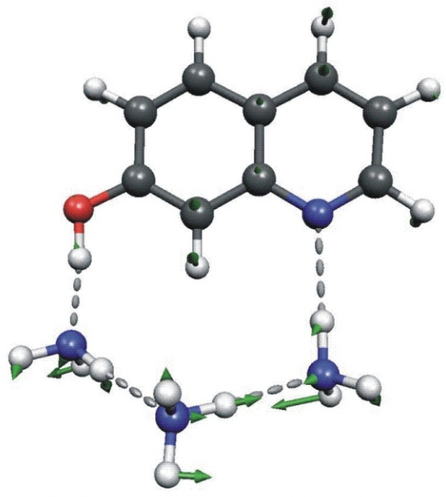
σ_1 N_Q · · · H-N stretch



σ_2 N-H · · · N sym. Stretch

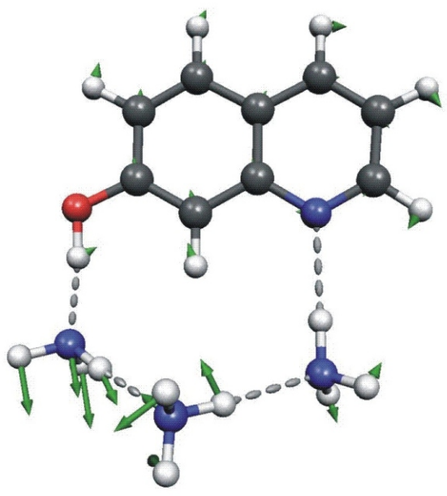


σ_3 N-H · · · N antisym. Stretch



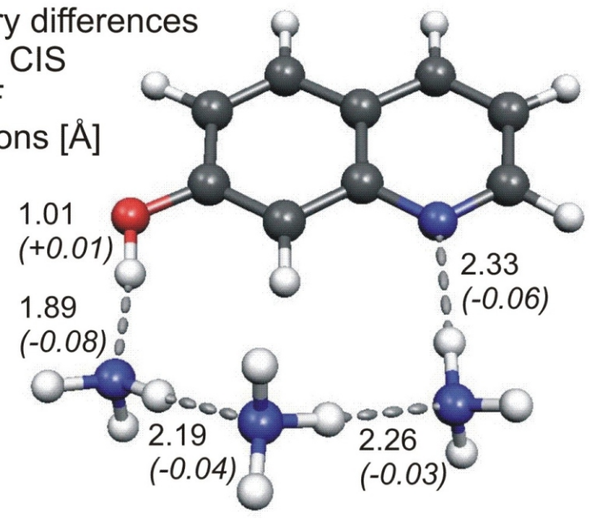
coupled with an oop 7HQ mode

σ_4 O-H · · · N Stretch



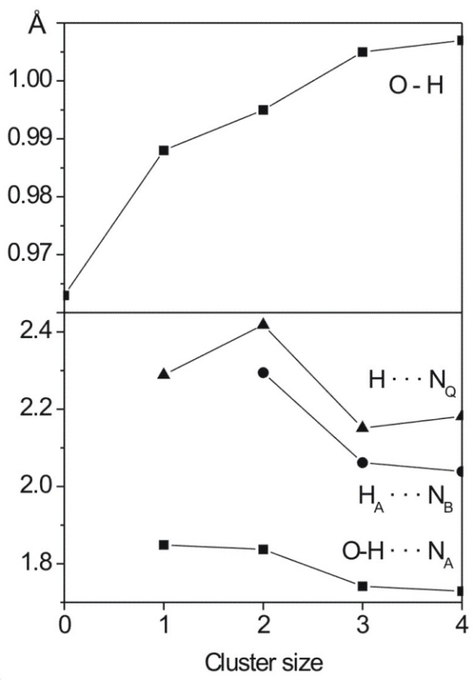
Changes upon excitation

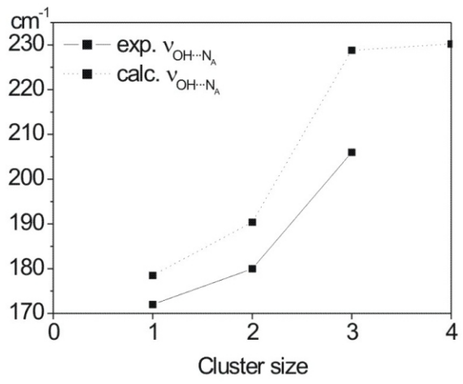
Geometry differences between CIS and SCF calculations [Å]



Electronic excitation leads to
- a contraction of the hydrogen bonds
- a lengthening of the O-H bond

Trends in structures and vibrational frequencies





The larger the cluster,
- the larger the O-H bond,
- the shorter the hydrogen bonds,
- the larger the OH···N stretch frequency.

n=3 clearly appears as a critical size: adding one NH_3 does not provide more favorable features to a H transfer reaction.

(a) A. Bach, S. Coussan, A. Müller and S. Leutwyler, *J. Chem. Phys.* **113** (2000), 9032
(b) M. Meuwly, A. Bach and S. Leutwyler, *J. Am. Chem. Soc.* **123** (2001), 11446
(c) S. Coussan, C. Manca, C. Tanner, A. Bach and S. Leutwyler, *J. Chem. Phys.* **119** (2003) 3774