Effects of the Wire Length on H-Atom Transfer in 7-Hydroxyquinoline·(NH$_3$)$_n$: n = 2 and 3

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Abstract: Previously we have employed the 7-hydroxyquinoline·(NH$_3$)$_n$ ammonia-wire clusters to study excited state H-atom transfer along a sequence of hydrogen bonds. H-atom transfer experimentally occurs for n = 4 excited to its vibrationless S$_1$ state, for n = 3 with additional excitation of ammonia-wire vibrations (~200 cm^{-1}). However, for the n = 2 cluster, no reaction is observed, even with additional excitation energy of 900 cm^{-1}. CIS calculations have been performed on the n = 2 and n = 3 clusters to understand the effect of the wire length on the energy profile of the reaction. The *enol → keto* reaction is always exoergic, and the barrier for H transfer to the proximal ammonia controls the reaction kinetics.

Keywords: Ammonia wire · CIS calculations · Excited state · Hydrogen atom transfer/Proton transfer · Molecular beam

Introduction

Modeling and understanding proton and hydrogen transfer are among the most important challenges in biology. Proton transport through membrane ion channels ('proton wires') is of special interest: Many transmembrane proteins create, control, or utilize proton gradients across biological membranes, like the so-called 'proton pump' in the photosynthetic reaction center of *Rhodobacter sphaeroides* [1]. In contrast channel proteins like aquaporins provide a path for water molecules but prevent protons from crossing the cell membrane [2]. Direct experimental observation of the motion of protons along a wire would help in understanding factors favoring proton conduction, but is difficult, because of the short times, microscopic length scales, and solvent fluctuations involved.

We have focused on simple model systems in order to understand the basic aspects of proton and/or H-atom conduction along solvent wires, using the aromatic molecule 7-hydroxyquinoline (7HQ) as a scaffold for a hydrogen-bonded wire of NH$_3$ molecules [3–7]: 7HQ provides an –O-H donor and an H acceptor group to connect the ammonia wire and to determine the direction of the proton transfer reaction [3][4] as shown in Fig. 1. Another way to consider this reaction is as the *enol→keto* tautomerization of 7-hydroxyquinoline mediated by the ammonia wire [5][6].

Fig. 1 shows the optimized minimum energy structures of the 7-hydroxyquinoline·(NH$_3$)$_n$ clusters for 1 ≤n ≤ 4 at the CIS level of theory with a diffuse basis set 6-31(+)G(d,p), where (+) indicates diffuse *s* and *p* functions on the H atoms involved in the hydrogen bonds [3][4]. The n = 1 cluster obviously cannot connect to the quinolinic N group of the scaffold molecule. For n = 1–3, we have experimentally observed only one isomer in the molecular beam, *i.e.* the ammonia-wire form for n = 2, 3. For n = 4, other isomers are predicted with stability comparable to the solvent-wire form shown in Fig. 1 [5]. We expect to observe several isomers in the molecular beam under our experimental conditions. Here, we only discuss the wire form in order not to consider the isomer solvation effects but rather wire length.

When increasing the wire length from n = 1 to 4, CIS calculations predict a lengthening of the intramolecular O-H bond (from 0.961 to 1.077 Å) and a contraction of the intermolecular hydrogen bonds; *e.g.* the O···N distance between the heavy atoms decreases by 0.434 Å. The geometrical changes when increasing the wire size are intuitively expected to favor the proton transfer from the 7HQ -O-H group to the proximal ammonia molecule.

Experimental Results

Fig. 2 shows the S$_1$←S$_0$ 2C-R2PI spectra of 7HQ·(NH$_3$)$_n$ for 1 ≤ n ≤ 4. Up to n = 3, the spectra show discrete and narrow bands with widths of 1–2 cm^{-1}. The n = 1 spectrum presents sharp bands from 29900 to 30700 cm^{-1} at least (over 800 cm^{-1}) and the n = 2 spectrum from 29100 to 30000 cm^{-1} (900 cm^{-1}) [7], whereas the n = 3 spectrum abruptly falls off ~200 cm^{-1} above the electronic origin (Fig. 2c). In a previous study [3], we have shown that the loss of the excited state *enol* 7HQ*·(NH$_3$)$_3$ cluster population is due to the onset of a fast process at ~200 cm^{-1} excess energy in the S$_1$ state, *i.e.* the *enol→keto* tautomerization. *Ab initio* theory predicts that this reaction is an H-atom translocation along the ammonia wire to the quinolinic N atom with a Grotthuss type mechanism [8]. The first barrier of the reaction originates from a crossing of the optically excited ππ* state and a diffuse Rydberg-type πσ* state, indicating change of the excited state character.

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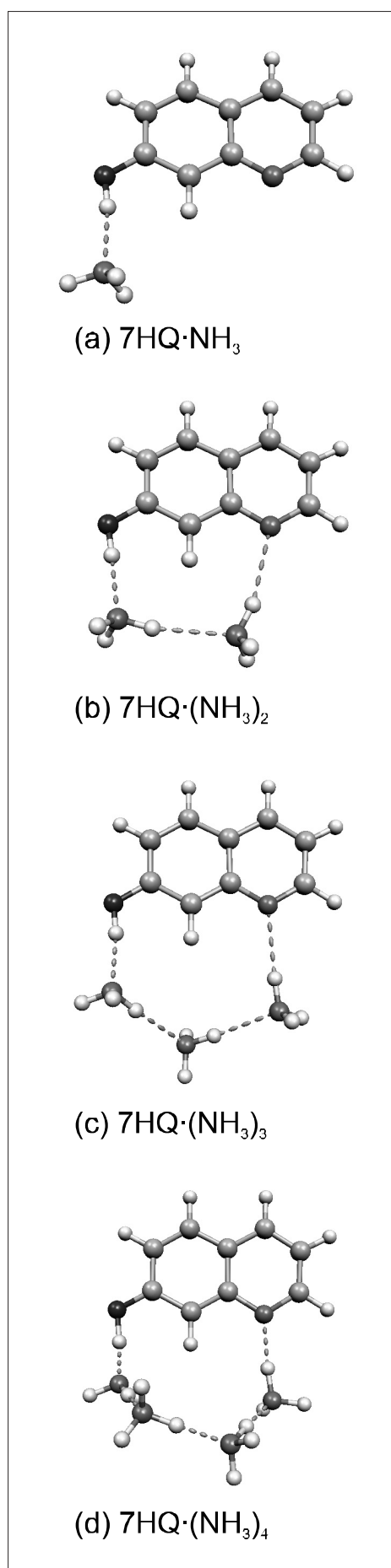Fax: +41 31 631 39 94
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(a) 7HQ·NH₃

(b) 7HQ·(NH₃)₂

(c) 7HQ·(NH₃)₃

(d) 7HQ·(NH₃)₄

Fig. 1. Calculated minimum energy structures in the S₁ excited state of the *enol* form of the 7-hydroxyquinoline 7HQ·(NH₃)ₙ clusters for 1 ≤ n ≤ 4
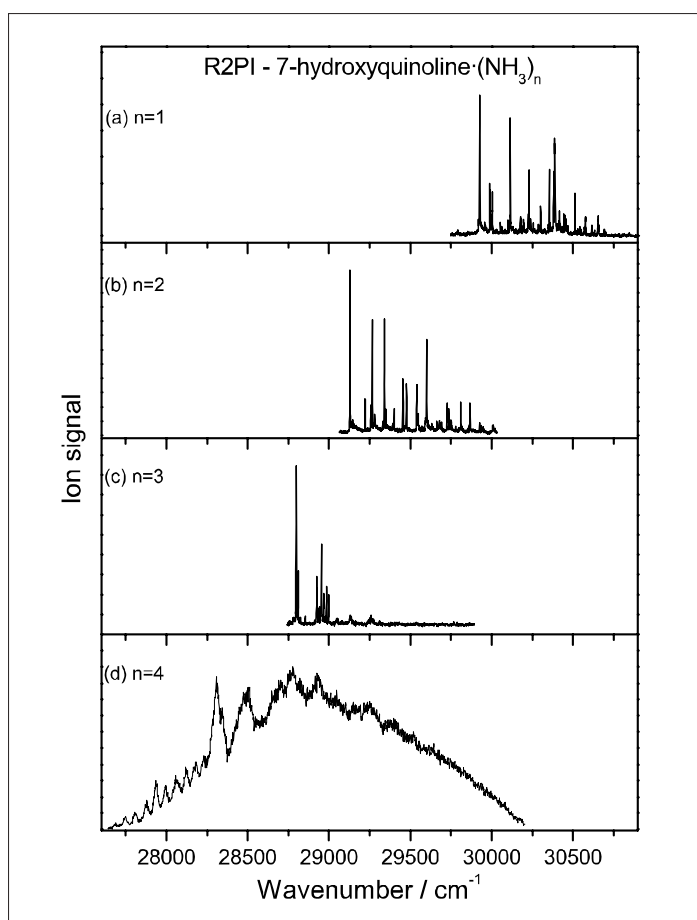

Fig 2. Two-color resonant two photon ionization spectra of 7HQ·(NH₃)ₙ, 1 ≤ n ≤ 4

A transfer of an electron from the 7HQ moiety to the proximal ammonia molecule occurs simultaneously with the proton transfer and the change of the excited state character: the reaction is a coupled proton/electron or H-atom transfer.

Conversely, for 7HQ·(NH₃)₄, much broader bands with widths of 25–70 cm⁻¹ can be observed from 27700 to 28500 cm⁻¹. These bands are superimposed on a continuous background. Bach *et al.* [6] have concluded that the loss of well-resolved vibrational patterns and the appearance of broad bands arising at longer wavelengths as the number of solvent molecules increases indicate that H-atom transfer occurs. Summarizing the 2C-R2PI measurements for the n = 2–4 clusters: The reaction occurs for n = 4 when exciting the vibrationless S₁ state, for n = 3 additional excitation of the ammonia wire vibrations is needed to induce the reaction with a threshold of ~200 cm⁻¹, whereas for n = 2 additional excitation up to 900 cm⁻¹ above the electronic origin does not induce the reaction.

Theoretical Calculations

To understand the effect of the wire length, the present study will focus on n = 2 and n = 3 clusters. In the S₁ state, the *keto* form is predicted more stable than the *enol* form, independent of the cluster size: For n

= 2, the difference is –44.6 kJ mol⁻¹ and for n = 3, –46.1 kJ mol⁻¹. We do not believe that the slightly larger exoergicity for the n = 3 cluster will help the reaction to occur for n = 3 and not for n = 2, but we show below that the reaction is a barrier-controlled process.

For the n = 3 cluster, the CIS calculated height of the transition state TS$_{e/HT1}$ (Fig. 3a) is +44.5 kJ mol⁻¹, which is probably an overestimate, as will be detailed below. The *enol → HT1* step is predicted to be exoergic by about –31.1 kJ mol⁻¹, which provides the driving force of the reaction, HT1 being the intermediate with the H-atom transferred to the first ammonia (see Fig. 3a). As the intermediates HT1, HT2, HT3 [3][4] and the *keto* forms lie close in energy, the two subsequent barriers are surmounted once the system passes through the first barrier. We therefore focus on the first step of the reaction between the *enol* and the HT1 form. Calculations have been performed for n = 2 and n = 3 clusters increasing the OH distance of the 7HQ hydroxyl group, allowing the other parameters to relax. Such calculations are exploratory because the reaction path is constrained; a complete IRC calculation would provide a better description of the system. Nevertheless, these calculations give a qualitative overview of the reaction.

For both clusters, large geometry modifications occur during the first step of the
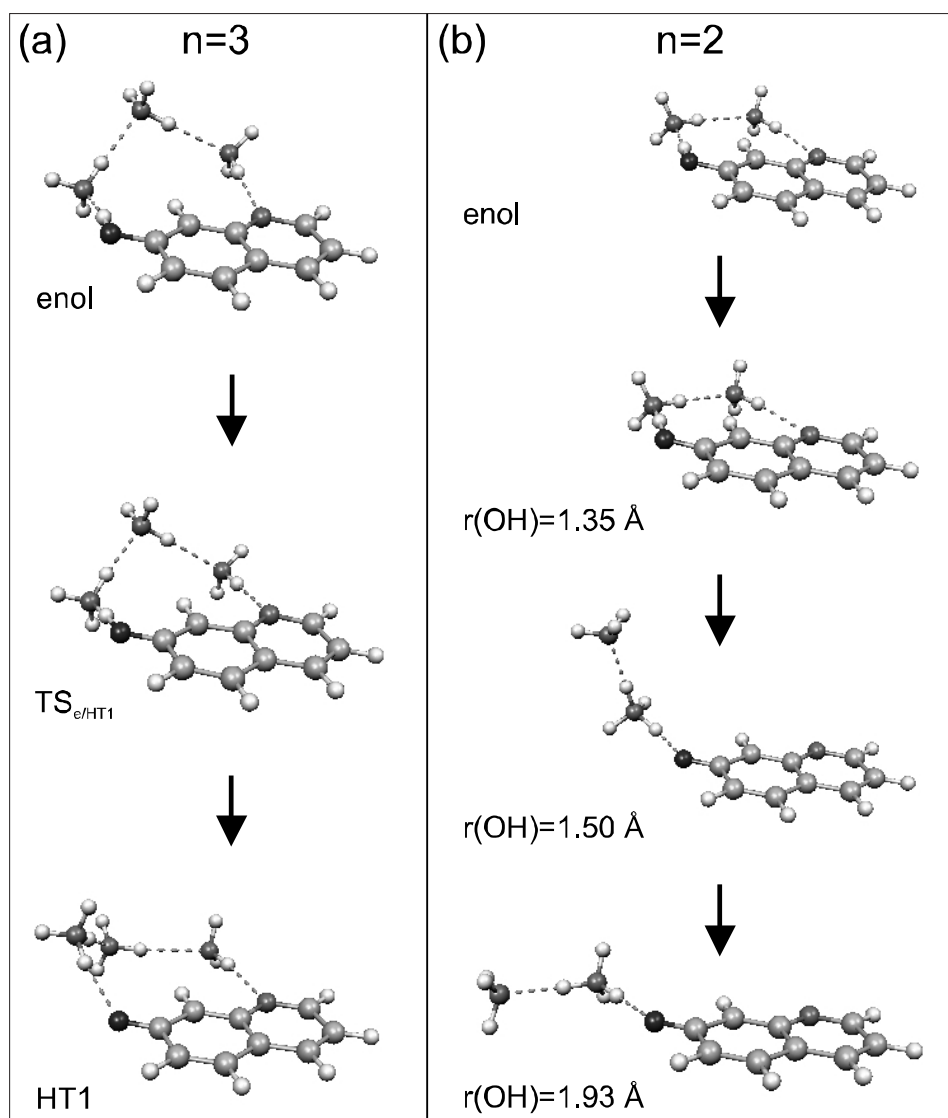
Fig 3. a) The calculated reactant, transition state and product structures for the S_1 state H-atom transfer reaction between the *enol* and the HT1 form of the n = 3 cluster; b) The calculated reactant, two points in the reaction path (r(OH) = 1.35 Å and r(OH) = 1.50 Å), and the HT1 form (r(OH) = 1.93 Å) of the n = 2 cluster.

reaction. The most striking change is the contraction of the O···N distance while increasing the O-H bond length until the H transfer to the ammonia occurs: for n = 2, the contraction is –0.345 Å and for n = 3 it is –0.388 Å. In the vicinity of the transition state $TS_{e/HT1}$, the unoccupied molecular orbital that contributes dominantly to the S_1 excited state wave function changes and becomes an antibonding σ^* orbital on the newly generated NH_4 moiety [3]. The large space occupancy of the σ^* orbital on the NH_4 moiety forces the O···N distance to lengthen, the H bond network of the n = 2 cluster becomes strained and the wire ruptures between the second ammonia and the quinolinic N. Fig. 3b shows structures of the *enol*, for OH bond lengths of 1.35 Å (before the transition state), 1.50 Å (after the transition state) and 1.93 Å (in the totally relaxed HT1 form). After breaking the N-H···N hydrogen bond, the ammonia wire rotates around the O···H-N axis, probably to reduce the steric repulsion between the N-H of the NH_4 moiety and the closest H atom of the 7HQ. In the enol form, this H···H distance is 2.28 Å only, while it is 2.78 Å in the

n = 3 cluster. The NH_4 radical is then in a torsional configuration close to that of NH_3 in the n = 1 cluster (Fig. 1a).

Discussion

Fig. 4 shows the S_1 state potential energy profile obtained by increasing the OH bond length in steps of 0.05 Å and optimizing the system geometry at every step; the *enol* minimum energy is taken as reference. The barrier height for n = 2 is around +5100 cm^{-1}, about 40% larger than that for n = 3 (+3700 cm^{-1}). The H-atom transfer reaction already occurs with additional excitation of ~200 cm^{-1} above the electronic origin for the n = 3 cluster, which implies that the H-atom tunnels through the barrier. This is in agreement with theories of solvent-controlled proton transfer predicting that the shortening of the tunneling distance (O···N in our case) should increase the tunneling rate through the transition state barrier by orders of magnitude [9]. A rough estimate of the relative areas leads to the conclusion that H-atom transfer tunnel-

ing is by far less efficient for the n = 2 cluster; the same tunneling efficiency as for n = 3 should only be reached when exciting the n = 2 cluster at ~2900 cm^{-1} above the electronic origin. Obviously this estimate has to be viewed with great caution, considering that the reaction path was forced in one direction and the *enol→HT1* reaction should be treated as a multidimensional process. Nevertheless, this provides a qualitative reaction profile and explains why no falloff of the 2C-R2PI spectrum is observed even 900 cm^{-1} above the electronic origin. It is also interesting to note that from r(OH) = 1.35 Å to 1.50 Å, the n = 2 cluster is stabilized by more than 6000 cm^{-1} although an H bond is broken. By rotating the ammonia wire out of the 7HQ plane, the repulsion between the C(8)-H group of 7HQ and the NH_4 moiety is lowered, which compensates the loss of the H bond. The geometries with r(OH) = 1.35 Å and 1.50 Å were calculated without the second ammonia: the same order of stabilization energy as for n = 2 was found, which confirms that the main part of the stabilization arises from the torsion of the NH_4.
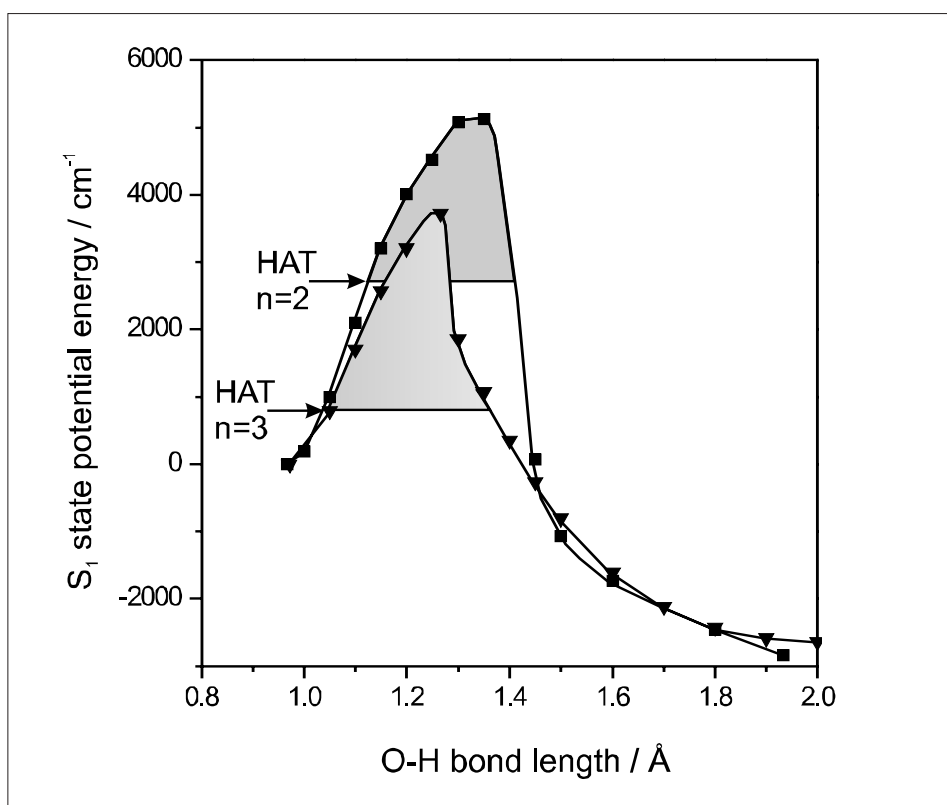
Fig 4. CIS/6-31(+)G(d,p) calculated S_1 state *enol → HT1* energy profiles of 7HQ·$(NH_3)_n$ for n = 2 (squares) and n = 3 (triangles). The O-H distance is increased in steps of 0.05 Å and the structure optimized at every step. The *enol* forms are taken as zero energy reference for both clusters. The light gray area for n = 3 corresponds to the area under the barrier for the ~200 cm^{-1} energy at which tunneling occurs. The dark gray area for n = 2 corresponds to the area estimated to yield the same tunneling efficiency.

Conclusion

We have shown that excited state H atom transfer along the ammonia wire in the 7-hydroxyquinoline·$(NH_3)_n$ system is strongly wire-length dependent: The reaction occurs for the n = 3 cluster in the S_1 state with an additional ~200 cm^{-1} excitation of ammonia wire vibrations, but does not occur for the n = 2 cluster with additional excitation up to 900 cm^{-1}. The *keto* form is always more stable than the *enol* form in the n = 1–4 cluster size range. The H-atom transfer reaction is controlled by the O-H···N transfer to the proximal ammonia molecule. Preliminary CIS calculations show that for the n = 2 cluster the barrier is 1.4 times larger than for the n = 3 cluster, preventing tunneling for n = 2 in the spectroscopic region we probed, contrary to the n = 3 cluster.

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