Ab Initio Study of the Electronic Spectrum of 7-Hydroxyquinoline

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The electronic spectrum of 7-hydroxyquinoline has been studied by using ab initio Multi-State Multi-Reference Møller-Plesset Second-Order Perturbation Theory (MSMRMP2). The energy range up to 6.5 eV is taken into consideration. The lowest π–π^* transition is calculated to have an energy of 3.65 eV in good agreement with experimental data. Several other π–π^* transitions are predicted to have excitation energies of 4.93, 5.20, 5.47, and 6.08 eV. Excitations out of the highest occupied σ orbital into the lowest unoccupied π^* orbitals are computed to occur at 5.28 and 6.44 eV. The π–σ^* transition is predicted at 5.87 eV. The σ^* orbital involved is identified as the Rydberg 3s orbital having antibonding character along the OH bond.

Hydroxyquinolines are known for their ability to perform proton-transfer reactions after photoexcitation.[1–3] In the excited state, the hydroxy group acts as a proton donor and the nitrogen atom acts as a proton acceptor. In 7-hydroxyquinoline (7HQ), the distance between donor and acceptor groups is too large to allow intramolecular proton transfer without being assisted by a bridge of solvent molecules.[4]

In the last decade, the proton transfer of 7HQ has been explored in diverse media such as water,[5] polymer matrices,[2] and the gas phase with different solvent clusters.[6–8] Fang has presented ab initio studies of the excited-state proton transfer in 7HQ(MeOH)$_n$ ($n = 1$–3) complexes by using the configuration interaction with single excitations (CIS) method and the complete active space self-consistent field (CASSCF) method.[7]

Recently, Tanner et al. investigated the reaction mechanism of photoinduced proton transfer in 7HQ(NH$_3$)$_3$ clusters with molecular-beam experiments and ab initio calculations using the CIS and the CASSCF methods.[8] They have proposed that the system is initially excited into a $\pi\pi^*$ state. A conical intersection with a $\pi\sigma^*$ charge-transfer state induces several coupled electron-proton transfers along the ammonia wire. A reverse crossing brings the system into the excited $\pi\pi^*$ state of the ketonic tautomer. The latter one can be detected by monitoring fluorescence. Sobolewski and Domcke have reported similar mechanisms for the coupled electron–proton transfer reactions from aromatic chromophores to solvent molecules.[9,10]

The experimental investigation of the reaction mechanism is complicated by the fact that only the $\pi\pi^*$ states are visible in the spectrum. The $\pi\sigma^*$ charge-transfer states are difficult to detect in the spectrum because of their small oscillator strengths and, therefore, ab initio calculations are in need. Theoretical and experimental investigations so far have concentrated on the first-excited singlet state. Although the $\pi\sigma^*$ state was mentioned in the ab initio works of Fang[7] and of Tanner et al.,[8] an estimate of its energetic position has not been given yet.

The purpose of this letter is to give a more complete picture of the electronically excited states up to 6.5 eV. Special attention is put on the characterization of the $\pi\sigma^*$ state and the σ^*-type orbital involved. Here, we focus only on the solvent-free 7HQ molecule having the hydroxy group in cis orientation.

The geometry has been optimized with the TURBOMOLE program package[11] using the B3LYP density-functional and the cc-pVTZ basis-set. The calculation of the electronically excited states has been performed with the DIESEL program package[12] using the Multi-State Multi-Reference Møller-Plesset Second-Order Perturbation Theory (MSMRMP2)[13] and the triple-ζ TZVP basis-set of Schäfer et al.,[14] augmented by two diffuse s-type Gaussian-functions ($\alpha_{3s} = 0.028$ and $\alpha_{4s} = 0.0066$) located in the molecular center of mass.[15]

The excitation energy into the lowest $\pi\pi^*$ state is calculated to be 3.65 eV. This is underestimated by 0.17 eV, compared with the experimental value of Lahmani et al. from molecular beam experiments on the solvent-free molecules. We assume that the errors might be somewhat larger in the higher excited states, possibly in the range of 0.3–0.5 eV. The oscillator strength is calculated to be 0.07. The next higher transitions are also $\pi\pi^*$ excitations, which come at 4.93 and 5.20 eV. They also have large oscillator strengths of 0.06 and 0.13, respectively. Further excited $\pi\pi^*$ states are calculated to locate at 5.47 and 6.08 eV with oscillator strengths of 0.03 and 0.1, respectively. The $\pi\pi^*$ states are dominated by linear combinations of configurations arising from excitations out of the two highest occupied π orbitals into the three lowest unoccupied π^* orbitals. The lowest $\sigma\pi^*$ states are calculated to have excitation energies of 5.28 and 6.44 eV with oscillator strengths of 0.006 and 0.0002, respectively. The lowest $\pi\sigma^*$ state is computed to have an excitation energy of 5.87 eV with an oscillator strength of 0.006.

The $\pi\sigma^*$-type states in other organic chromophores have been identified to be responsible for excited-state proton or hydrogen transfer, because of the repulsive character of the σ^* orbital. The main electronic configuration is an excitation out

Table 1. Calculated electronic transition energies (ΔE) and oscillator strengths (f) of the *cis*-7HQ

State	ΔE/eV	f
$\pi\pi^*$	3.65	0.07
$\pi\pi^*$	4.93	0.06
$\pi\pi^*$	5.20	0.13
$\sigma\pi^*$	5.28	0.006
$\pi\pi^*$	5.47	0.03
$\pi\sigma^*$	5.87	0.006
$\pi\pi^*$	6.08	0.1
$\sigma\pi^*$	6.44	0.0002

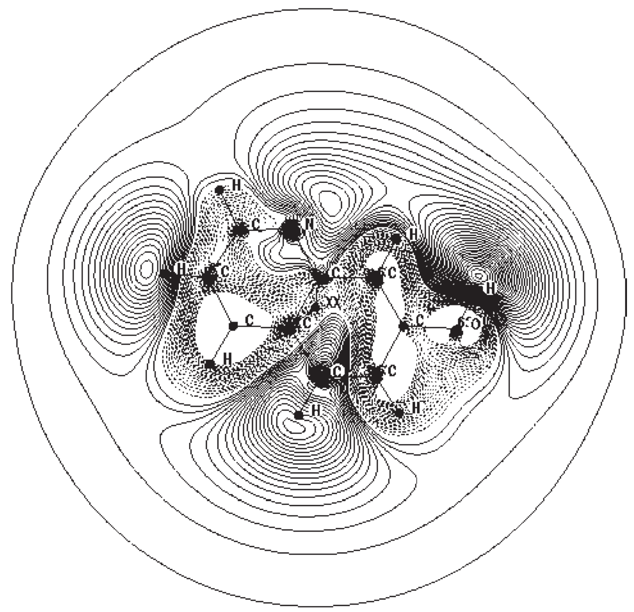

Figure 1. The contour plot of the σ^* orbital interpreted as a Rydberg 3s orbital with antibonding character along the OH bond.

of the highest occupied π orbital into the σ^* orbital. The latter one is shown in Figure 1. It can be interpreted as a Rydberg 3s orbital with some contribution of a σ^* orbital, which is strongly antibonding along the oxygen–hydrogen bond (OH bond). Some nodes are also found in the ring. The effect of photoexcitation into this state can only be discussed qualitatively here. The excitation will bring about the elongation or the breakage of the OH bond, and will induce some geometrical changes of the ring. In turn, the elongation of the bond will increase the antibonding character of the orbital. In intermediate OH bond separations, the orbital is expected to transform into an antibonding σ^* orbital. This will be converted into a purely hydrogenic 1s orbital, if dissociation proceeds. Similar observations have been made in detail for the photodissociation of NH_3 into NH_2 and H by Runau et al.,[17] and for systems like phenol, indole, and pyrrole by Sobolewski et al.[10] Additional effects will arise from the nodal structure in the ring, inducing intramolecular vibrational-energy redistribution. Such effects have been observed by Knochenmuss and Fisher in ammonia clusters of naphthol.[18]

The above discussion strengthens the picture that proton or hydrogen transfer can occur in the $\pi\sigma^*$ state. However, in the experimental studies, the molecule is initially excited into the lowest $\pi\pi^*$ state. The potential energy curves of both states involved should cross in order to allow the dissociation of the OH bond. If a crossing exists, then the crossing is expected to determine the reaction rate. It is difficult to give any estimate for the reaction rate from the vertical excitation energies alone. The calculated energy gap between both states is 2.22 eV. This is quite large compared with those of other organic chromophores such as phenol, where the gap between the lowest $\pi\pi^*$ and the lowest Rydberg 3s state is predicted to be 1.23 eV.[19] In our future study, the effects of solvation on the proton transfer of 7HQ will be investigated.

In summary, we have presented ab initio calculations for the electronically excited states of 7HQ having high energies up to 6.5 eV. The vertical excitation energy into the lowest $\pi\pi^*$ state is predicted to be 3.65 eV in good agreement with the experimental value of 3.82 eV. Further higher $\pi\pi^*$ states are predicted to have excitation energies of 4.93, 5.20, 5.47, and 6.08 eV. All of them have large oscillator strengths in the range of 0.03 and 0.13. Excitations out of the highest occupied σ orbital into the lowest unoccupied π^* orbitals are predicted to occur at 5.28 and 6.44 eV. The $\pi\sigma^*$ state is calculated to have an excitation energy of 5.87 eV. At the equilibrium geometry of the electronic ground state, the σ^* orbital involved is mostly identified as a Rydberg 3s orbital. The antibonding character along the OH bond is expected to induce proton or hydrogen transfer.

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15 The molecular orbitals have been generated with the effective exact-exchange Kohn–Sham density-functional method of Della Sala and Görling implemented in the TURBOMOLE program package.[16] The reference space consists of all configurations that can be generated by single and double excitation out of the highest 7 occupied molecular orbitals (MOs) into the lowest 9 unoccupied MOs from the ground state. In the MSMRMP2-calculation, for all configurations, that have an energetic contribution larger than the selection threshold $T_{sel} = 10^{-6}$ Hartree, the diagonal-projected form of the generalized Fock-operator has been chosen. The lowest 25 MOs of A′-symmetry have kept doubly occupied, and the highest 25 virtual MOs have been deleted. We have checked the influence of different Rydberg basis sets onto the electronic spectrum of benzene to find that our results obtained with the present basis set is reliably converged to other experimental and theoretical ones.
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