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COMMENTS

Comment on "Photoinduced Proton Transfer and Rotational Motion of 1-Hydroxy-2-acetonaphthone in the S_1 State: A Theoretical Insight into Its Photophysics" (*J. Phys. Chem. A* 2000, *104*, 8424)

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Douhal et al.[1] recently revisited the intramolecular proton-transfer (IPT) of 1-hydroxy-2-acetonaphthone (HAN) in its first singlet state, S_1, using the ab initio electronic-structure method at the CIS/6-31G** level. They concluded that, in this S_1 electronic state, the IPT process is controlled by a potential energy surface (PES) with a barrier of 5.49 kcal/mol between the enol form E* (E, the most stable structure in the ground state) and its keto tautomer K*, which results from the IPT reaction. According to these authors, the presence of this PES barrier is quite consistent with the PES diagram for the IPT previously proposed by Douhal, Lahmani, and Zewail (DLZ)[2] to account for the photophysics of HAN (see Figure 1) and, as repeatedly stated in their paper,[1] rather inconsistent with evidence for this compound reported by our group.[3−5]

It is an essential element for DLZ interpretation a PES of IPT that exhibits a double minimum, both in the S_0 state, which involves the E and K forms, and in the S_1 state, which involves the E* and K* forms. In fact, the absence of a double minimum for either electronic state (S_1 or S_0) would expose a wrong assignation of the photophysics of HAN by DLZ.

Our MP2/6-31G** and B3LYP/6-31G** results for the S_0 state[5] led us to conclude that the PES for the IPT in HAN possesses a single minimum and that it corresponds to its stable form, E. Our conclusion that the K form exhibits no energy minimum in the S_0 state was rechecked by Douhal et al.,[6] using the same computational method as we employed in 1997.[5] Douhal's et al. results[6] conform to our conclusion, and surprisingly, they do not transfer it to their DLZ diagram.

Let us comment on the origin of the energy barrier reported by Douhal et al.[1] in relation to the double minimum observed in the IPT process in the S_1 state. Accurately describing an intramolecular hydrogen bond energy is known to require considering electron correlation, as the proton transfer process involves the formation and cleavage of bonds; this causes HF methods to fail and distort the structure of the hydrogen bond. The energy of a molecular structure in an excited electronic state as calculated with the CIS method can be split into two individual contributions corresponding to the ground state, which is appraised at the HF level, and the electronic transition between the two states, which incorporates the effect of electron correlation. The combination of both contributions, which represents the energy for the excited electronic state, is optimized to obtain the structure corresponding to the singular points in the PES. It should be noted that the transition energy decreases monotonically as the O−H bond is stretched out, so it cannot be the origin of the energy barrier between the enol and keto forms as predicted by the CIS method. On the other hand, the HF energy of the ground state as calculated on each CIS optimized geometry increases abruptly in the beginning and more gradually at the O−H distances, corresponding to the transferred form. Let us compare the HF potential energy curve with the corresponding B3LYP/6-31G** curve (see Figure 2 in ref 5), which includes the effect of electron correlation in the ground state. Curve a in Figure 2 shows the difference between both curves as normalized at the energies of the corresponding minima; as can be seen, the resulting curve exhibits two minima (one for the enol form and the other for the keto form) separated by an energy barrier that occurs at distances similar to those in the CIS curve (curve b in Figure 2). We can thus conclude that the contribution of the ground state, at the HF level, is the origin of the energy barrier obtained by using the CIS method to optimize the proton transfer in HAN.

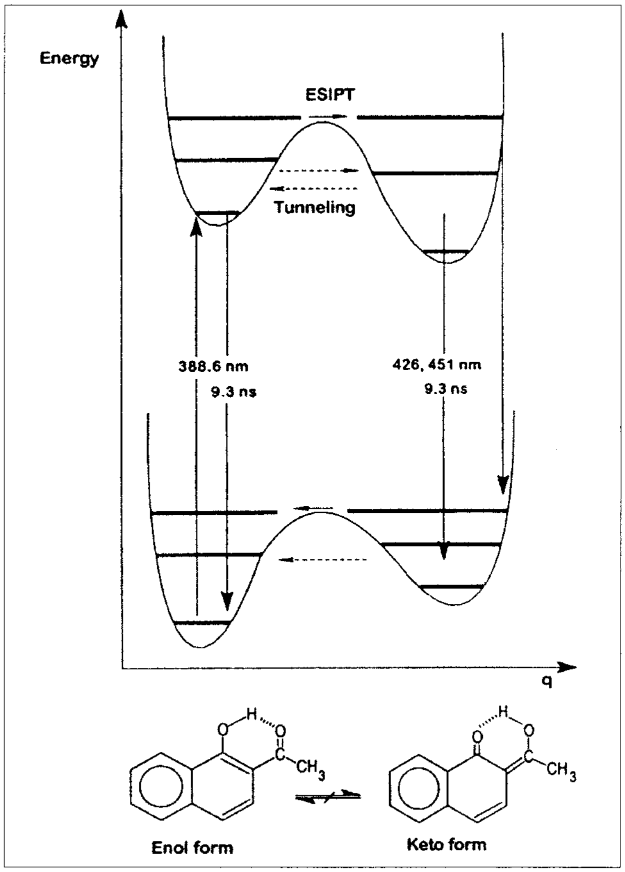

Figure 1. Double-well potentials of the H atom transfer in HAN in both ground and excited states. This figure corresponds to the Scheme 5 of the ref 2 (reprinted with permission from Elsevier Publishing, copyright 1996).

Let us now examine the case of methyl salicylate (MS), a homologue of HAN. That the PES for MS in its first π,π^* excited electronic state poses no energy barrier to the proton transfer has been experimentally confirmed by Goodman and Brus[7] in a solid neon host at 4.2 K, by Nishima et al.[8] in Durene

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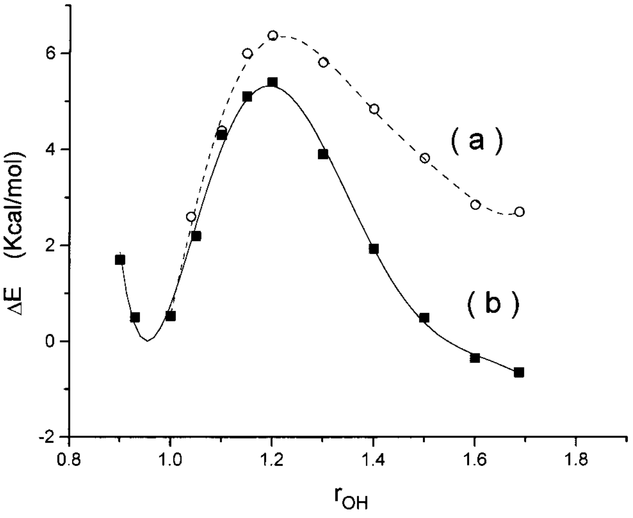

Figure 2. (a) Normalized difference for the ground state between the HF potential energy curve and the GSIPT B3LYP one, both using 6-31G** basis set for HAN (see text), as increasing the O−H distance in the proton transfer. (b) Corresponding potential energy curve of IPT calculated with CIS/6-31G** method for the S_1 state of HAN.

mixed crystals at 4.2 K and in supersonic helium jets, and by Zewail et al.[9] in their femtosecond depletion study of the dynamics of hydrogen atom transfer in the gas phase under collisionless conditions. Additional, theoretical support for this assumption has been provided by Catalán et al.[10] Figure 3 shows the CIS curves for the IPT of MS in its S_1 state and the curve obtained as the difference between the corresponding HF curve for S_0 in the CIS-optimized structures of MS and the curve calculated at the B3LYP/6-31G** level.[10] As can be seen, both curves exhibit two minima separated by a barrier at the same O−H distance.

These results reveal that computations of ab initio configuration interactions with singles (CIS) using full optimization of the molecular geometry provide inaccurate descriptions of a photoinduced proton transfer along an intramolecular hydrogen bond (IMHB), as they give rise to spurious energy barriers for the transfer. One case in point is methyl salicylate: the curve for the proton transfer from its first π,π^* excited electronic state has been experimentally found to exhibit a single minimum in the region corresponding to the keto form, whereas the above-mentioned computations predict a curve with one minimum each for the enol and keto forms, the two separated by an energy barrier of 5.1 kcal/mol.

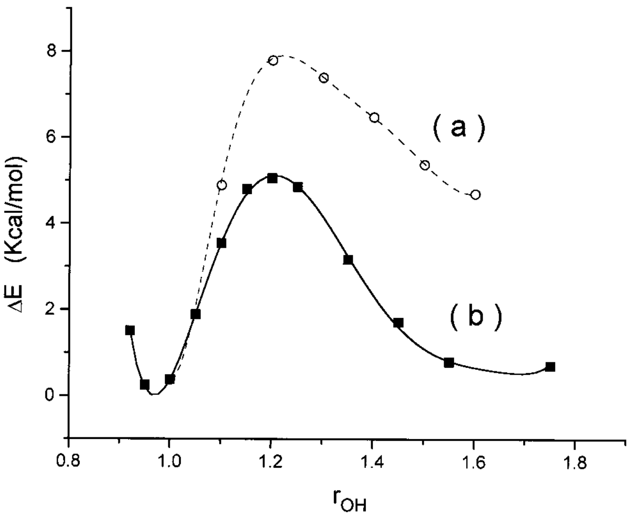

Figure 3. (a) Normalized difference for the ground state between the HF potential energy curve and the GSIPT B3LYP one, both using 6-31G** basis set for MS (see text), as increasing the O−H distance in the proton transfer. (b) Corresponding potential energy curve of IPT calculated with CIS/6-31G** method for the S_1 state of MS.

This evidence led us to reappraise the conclusions of previous work where the ab initio CIS method predicted the presence of an energy barrier in proton phototransfer processes, and also to request that, since the PES for the IPT in HAN exhibits no double minimum in the S_1 or S_0 state and the DLZ diagram cannot accurately explain the photophysics of this compound, the diagram should be discarded or modified.

References and Notes

(1) Organero, J. A.; Moreno, M.; Santos, L.; Lluch, J. M.; Douhal, A. *J. Phys. Chem. A* **2000**, *104*, 8424.

(2) Douhal, A.; Lahmani, F.; Zewail, A. H. *Chem. Phys.* **1996**, *207*, 477.

(3) Catalán, J.; del Valle, J. C. 14th Symposium on Photochemistry, K. U. Leuven, Belgium, 1992; p 163.

(4) Catalán, J.; del Valle, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4321.

(5) Catalán, J.; Palomar, J.; de Paz, J. L. G. *Chem. Phys. Lett.* **1997**, *269*, 151.

(6) Organero, J. A.; García-Ochoa, I.; Moreno, M.; Lluch, J. M.; Santos, L.; Douhal, A. *Chem. Phys. Lett.* **2000**, *328*, 83.

(7) Goodman, J.; Brus, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 7472.

(8) Nishima, T.; Yamauchi, S.; Horota, N.; Baba, M.; Hanazaki, I. *J. Phys. Chem.* **1986**, *90*, 5730.

(9) Herek, J. L.; Pedersen, S.; Bañares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 9046.

(10) Catalán, J.; Palomar, J.; de Paz, J. L. G. *J. Phys. Chem. A* **1997**, *101*, 7914.