Reply to "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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In their Comment Catalan and de Paz (CP)[1] raised methodological and philosophical objections to the results of a recent study[2] that disagrees with their previous reports[3,4] but is in full agreement with the experimental findings from five groups.[5−9] They claimed that the used theoretical method (CIS/6-31G**) is inappropriate for studying excited state proton-transfer reaction, and therefore the conclusion on the proton-transfer (PT) reaction scheme is not correct. They still believe that the selected molecule (1-hydroxy-2-acetonaphthone, HAN) does not undergo any PT motion, according to their reports.[3,4] We wish to address few points about the method and compare the obtained result with the experimental observation. Our main aim is to clarify our position and show how and why it diverges from that of CP. This may avoid the confusion made by these authors in their Comment based on the lack of evidence and in their previous reports on PT reactions using fixed geometry at the excited state, as they recognize in their reports.[10] This reply is organized as follows. In the first section, we briefly comment on the theoretical methods. In the second section, we summarize and assess experimental arguments in favor of our theoretical results but in disagreement with the interpretation of CP.

Electronic Calculations of the Excited Electronic States. Let us first comment on the theoretical methods used to analyze the excited states. The computational study of hydrogen and proton transfers in the ground electronic state has been extensively considered so that the errors incurred by any particular method are well-known and documented. In this way it is widely recognized that Hartree−Fock (HF) leads to overestimated energy barriers that are greatly reduced upon inclusion of electron correlation. It is also accepted that the MP2 lowering of the barriers is exaggerated.[11] Proton transfers in the excited states, on the other hand, have been studied far less extensively so that there is no consensus yet as to which methods are most appropriate and accurate. Scheiner, who has devoted a great effort to theoretically study intramolecular proton-transfer reactions in excited states, concludes in a recent review that the trends observed for the proton transfer in the ground state are not necessarily maintained in the excited state.[11] To be more specific, let us concentrate on the CIS method, as this is the subject of the Comment. The CIS method has been known for decades[12] though only recently has it been developed as an efficient algorithm to deal with excited states.[13] Taking into account the Brillouin's theorem, the CIS method is formally equivalent for excited states to ground state HF calculations.[13] After saying that, it is also important to remark that the CIS method does not rely on the accuracy of the HF method, as it is an entirely new calculation. As CP said, the total energy comes as a sum of two terms: the HF ground state energy and the excitation energy. From a computational point of view the main (and wrong) point in the Comment by CP is that overall the CIS error is concentrated in the HF part whereas the excitation energy can be considered as virtually correct. *This assumption is in clear contradiction with previous reports by the authors of the CIS method*,[14] who have performed test calculations of vertical excitation energies to different electronic states of small molecules and obtained errors between 0.5 and 1.0 eV or more. These authors also conclude that CIS as a whole can be considered a zeroth-order method to analyze the potential energy surface of the excited state as, in terms of relative energy, the systematic errors of the CIS calculation will mostly cancel out.[14]

Optimization of Geometries. Another important point that has to be taken into account when discussing the best method to deal with excited states is the impossibility of more sophisticated (i.e., correlated) methods to optimize geometries. Up to now only CIS and CASSCF methodologies have analytic derivatives so that they can customarily be used to localize minima and transition states in the excited state. A usual strategy is to optimize at the CIS (or CASSCF) levels and then recalculate the energy with the use of a correlated method such as MP2 or CASPT2. This strategy can be qualitatively correct when the energy barrier is high enough but may lead to wrong conclusions with modest energy barriers.[15] This is an important point that invalidates most of the conclusions of previous theoretical works by CP, as they are based on geometries that are meaningless given that they have been optimized in the ground electronic state.[10]

Just to illustrate this point, Figure 1 schematically shows an idealized energy profile at two levels of calculation. In both of them there are two minima separated by a barrier. However, when the geometries of the low level are not reoptimized in the higher level, the obtained energies are not "seeing" the double-well profile and the nonexistence of such a barrier would be the (wrong) conclusion of such a limited calculation. The electronic calculations for a large system such as HAN at the excited electronic states are still in their infancy. Certainly, one may ask about the accuracy of calculations when dealing with large molecules at the excited state level. A widely recognized reference to validate or not theoretical findings is the comparison with the experimental results. In this sense, as our results[2] are in accordance with a great deal of experimental data coming from different groups (see below),[5−9] there is no reason to discard them. In the future, better methods will surface that will be able to theoretically answer this and other questions with less ambiguity. Until now we believe that our calculations for HAN have provided the more precise and unambiguous data that can be obtained in the present from state of the art

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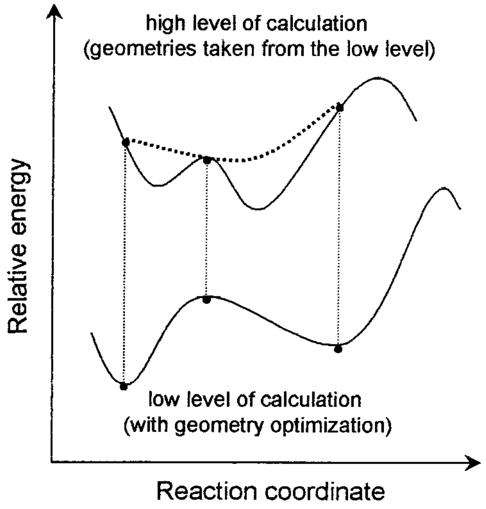

Figure 1. Idealized energy profile along a single reaction coordinate. The stationary points are located at the low level of calculation, and their energy is recalculated within the high level of calculation (solid line). As the geometries are not reoptimized at the high level of calculation, the obtained results (bold broken line) do not show the presence of a double-well energy profile. In this case the unrealistic potential indicated by the bold dashed curve would be obtained.

theoretical techniques, and account for the dual emission qualitatively correctly. The calculations also predict a twisting motion in the keto-type structure at both S_0 and S_1, in agreement with the experiment.[9,16]

Jet-Cooled Molecular Beam, Femtosecond to Microsecond Contributions: Proton Transfer, Energy Barrier, and Twisting Motion. From the point of view of experiment, under jet-cooled molecular-beam conditions, the excitation of HAN at 388.58 nm (0−0 transition) gives birth to a structured emission due to excited enol (E*) and to a two-band emission from the keto-type structures with maxima at 426 and 452 nm.[5,17] When E* is located beyond 300 $\mathrm{cm^{-1}}$ over the 0-vibrational level energy in S_1, the structured emission of E* disappears, providing *experimental* evidence of the existence of an energy barrier (∼300 $\mathrm{cm^{-1}}$, ∼0.9 kcal/mol) in the potential energy surface of S_1. The nanosecond-fluorescence lifetime of E* and of the produced phototautomers under isolated-cooled conditions are very similar, suggesting the establishment of an equilibrium between the involved structures in the photoreaction. OH/OD isotope exchange abnormally suppresses the emission of E* due to the enhancement of the forward rate of the photoreaction ($E^* \rightarrow K^*$) relative to the back ($K^* \rightarrow E^*$) and radiative emission rates of E*.[5] Femtosecond experiments in the gas phase performed by Cheng's group[7] found a time constant in the picosecond time scale (60−85 ps when excitation was performed at 385−410 nm) for shifting the proton within E* to rapidly equilibrate with the produced K*, in agreement with the gas-phase jet-cooled molecular-beam scheme.[5,17] Earlier, nanosecond−microsecond time-resolved experiments in solution and in rigid media carried out by Tobita et al.[6] interpreted the results in terms of PT in E* and showed a long-lived *ground* keto tautomer (KR* where the protonated acetyl group has rotated) after relaxation of K*. The twisting motion in the keto type (K*) has been also observed in a the proton-transfer cycle of 3′,4′-benzo-2′-hydroxychalcone, a derivative of HAN.[18] Recently, Stolow and co-workers found a 30 ps component in the femtosecond transient of excited (excess energy ∼2500 $\mathrm{cm^{-1}}$) HAN in a molecular beam, which was assigned to an internal conversion process enhanced by a close-lying n,π^* state.[8] Because of the large excess of energy of the pump, the experiment could not probe the small barrier (∼300 $\mathrm{cm^{-1}}$).[5,7,8]

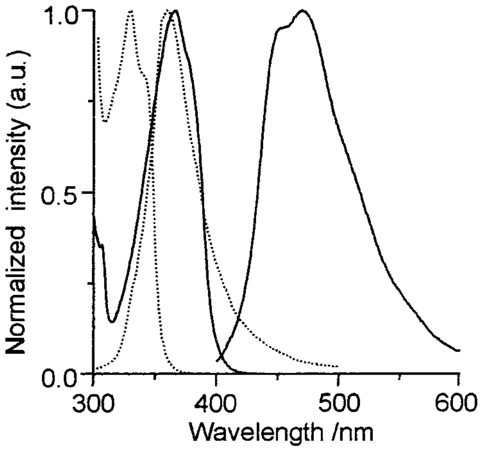

Figure 2. Steady state UV−visible absorption and emission (excitation at 380 nm) spectra of MAN (···) and HAN (−) in methylcyclohexane (MC) at 298 K.

Our calculations at the excited state[2] have shown that in-plane and out-of-plane vibrational motions of OH and $CO(CH_3)$ groups involved in the H-bonded chelate ring might be the origin of the energy barrier for the transfer in excited E. In addition to that, the high activity of the O−H out-of-plane motion (bending mode at 822 $\mathrm{cm^{-1}}$) in E* explains the suppression of the emission signal in the molecular beam beyond ∼900 $\mathrm{cm^{-1}}$.[5,17] Theoretical results also suggest the existence of a barrier to convert the phototautomer K* to its rotamer KR*, and a double potential energy surface where E and its rotamers and tautomers have their own minimum, in full agreement with the experiments. In our previous scheme based on molecular-beam data, we have already established the existence of a barrier to produce keto phototautomers and the existence of double potential energy surface at S_0. With the recent experimental and theoretical data, obviously the picture becomes more rich and complete.

Solution and Nanocavities Data Using Picosecond Spectroscopy: Direct Evidence of Proton and Twisting Motions. Figure 2 shows UV-visible absorption and emission spectra of 1-methoxy-2-acetonaphthone (MAN) and HAN in methylcyclohexane (MC, an inert solvent) at 298 K. While the emission of MAN does not show any abnormal behavior, that of HAN is broad and has a maximum at 480 and shoulder at 460 nm. We note that these data have been already reported[16] and are in agreement with previous studies.[5,6] We interpreted the emission of HAN in terms of proton transfer in E*, producing phototautomers emitting in this region. We note that CP's previous reports[3,4] and their Comment[1] did not recognize the occurrence of PT in excited HAN. While a low barrier for the proton-transfer reaction in solution may not be directly observed because of solvation, thermalization, intramolecular vibrational energy redistribution (IVR), and quantum tunneling (besides the need of a short time resolution technique),[17,19] the jet-cooled molecular-beam experiment has shown a barrier of ∼300 $\mathrm{cm^{-1}}$.[5] Obviously, this energy is too small to be easily detected in solution. Furthermore, to observe the barrier between E* and its phototautomers depends on the excess energy of excitation. Upon lowering the temperature to 77 K, the emission of HAN exhibits a structured band with clear maxima at 460 and 485 nm. In addition to these bands, blue (420 nm) and green (500 nm) shoulders appear at low temperatures. The structural difference between both spectra of HAN when lowering the

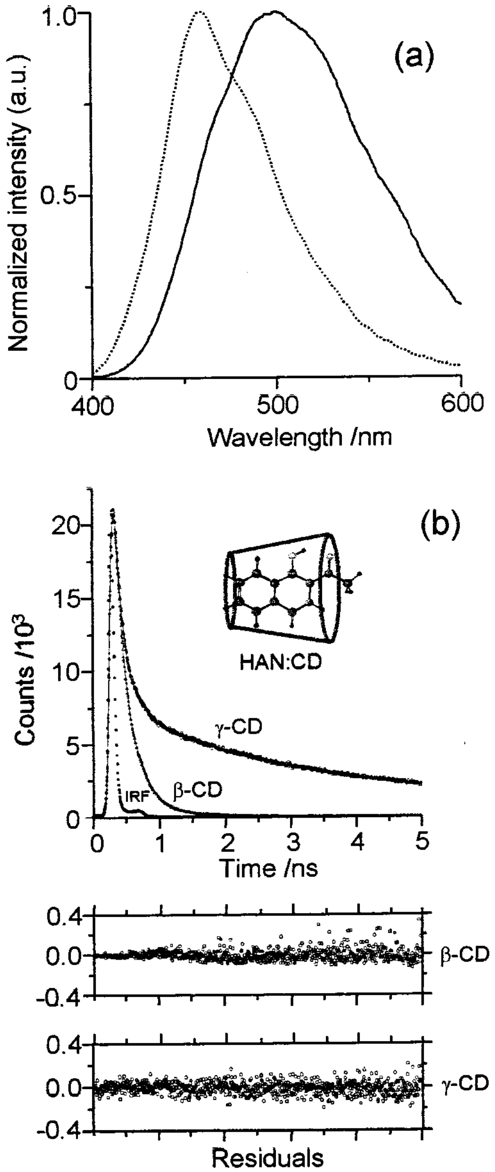

Figure 3. (a) Steady state emission (excitation at 380 nm) spectra of the 1:1 complex between HAN and β- (···) and γ-CD (−) in a neutral water solution at 298 K. (b) Emission decays of HAN plus 6 mM of β- and γ-CD in a neutral water solutions (−). The IRF is 65 ps and the inset shows the HAN:CD inclusion complex. When the emission is gated at 480 nm, the fitting parameters are for the HAN:β-CD complex, 134 ps (76%) and 310 ps (24%), $\chi^2 = 1.07$, and for the HAN:γ-CD complex, 120 ps (84%), 985 ps (7%), and 4.40 ns (9%), $\chi^2 = 1.10$.

temperature must be caused by an energy barrier separating two different keto type phototautomers (K* and twisted rotamers KR*). Accurate fitting of the emission decay in MC at 298 K needed two time constants (±10 ps) of 40 ps (22%) and 100 ps (78%).[20] The shortest time assigned to the decay of K* can be considered as a limiting time for the twisting motion in K* to produce KR* having the longest time constant. We could not resolve any rising component that might be attributed to the time constant of the proton-transfer reaction in E*. The time constant of this reaction is shorter than the time resolution of the used apparatus (~7 ps).[20] In other solvents, we found multiexponential decays of the tautomers emission with the shortest component being 20−60 ps.[9] To further demonstrate the involvement of twisting motion, we show the effect of the nanocavity size on the spectroscopy and dynamics of HAN. Figure 3 clearly demonstrates that the size of the encapsulating nanocavities (β- and γ-CD's with interior diameters of ~8 and 9.5 Å, respectively) affects the spatial and time domains of excited HAN when caged by the molecular chamber. In a larger cavity, the emission shifts to the red due to a larger relaxation of the phototautomers and the decay is longer with nanosecond components (lifetimes of ~1 and 4.4 ns) assigned to KR* structures formed within the molecular chamber after proton transfer in E* and a twisting motion in K*.

Therefore, our theoretical results are consistent with these *experimental* observations using nanocavities, and femtosecond to millisecond time-resolved spectroscopy armed with an array of techniques.[5−9,17] However, both theory and experiment do not agree with the interpretation of Catalan et al. stressing (i) the absence of proton-transfer reaction in S_1 and (ii) the existence of a single minimum in the PES at S_0 and S_1.[1,3,4] As a final remark on the CP Comment, we do not understand how relevant experimental reports on HAN using millisecond to femtosecond spectroscopy have been simply ignored by these authors, and how interpretations based on *experimental findings*[21−23] are treated by these authors as "*assumption*" while their theoretical data for the ground state[10a] are used as confirmation to direct observation of excited states events. A few years ago, calculations on salicylic acid and derivatives including methyl salicylate by Catalán and co-workers predicted two minima at the excited state PES.[24] The prediction resulted in a clear contradiction with other calculations[25,26] and experimental results.[21−23] We hope that these authors will be able to show in future convincing data for discussion taking into account the previous findings for the advancement of Science.

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(0.8 mW), and the emission was magic angle selected, spectrally resolved, and detected with a Hamamatsu microchannel plate photomultiplier. Details will be given elsewhere.

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