Keto–Enol Tautomerization

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Catalytic Action of a Single Water Molecule in a Proton-Migration Reaction**

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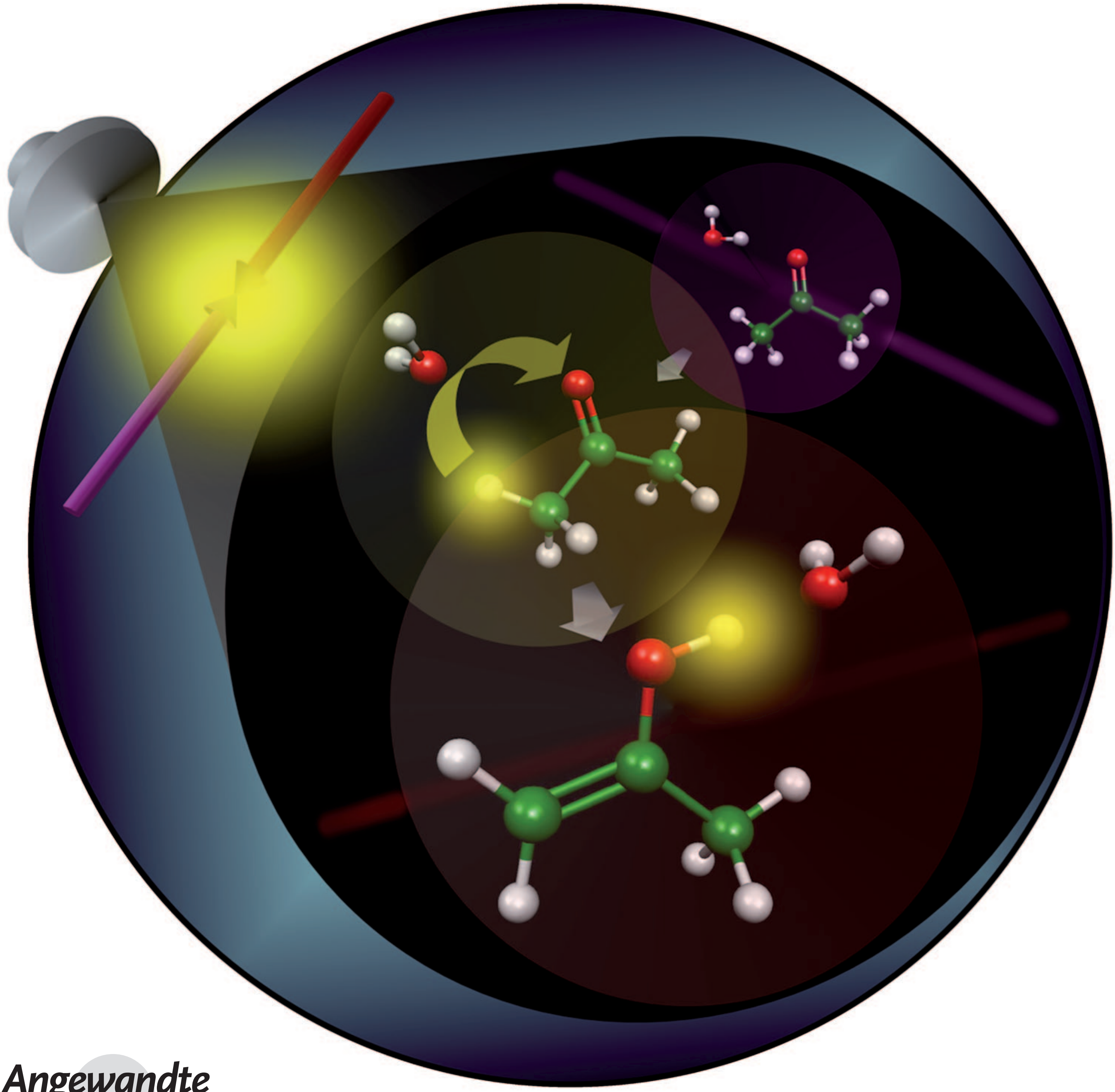

Water, the most ubiquitous and fundamental solvent on earth, is a critical component in many physical and chemical processes in chemistry, biology, and geochemistry.[1,2] In aqueous chemical reactions, for example, the process of hydration has a marked effect on the stabilities of products in chemical reactions. Moreover, the catalytic action of water is implied in many reactions of fundamental importance such as acid–base reactions and prototropic tautomerization, and in basic biological function that involve proton transfer.[2–6] In bulk systems, however, it is difficult to trace the detailed steps of proton migration and to clarify the microscopic role of water in the reaction. Only averaged data is experimentally available in the bulk because of its complexity and inhomogeneity.

An alternative approach is to prepare jet-cooled clusters in the gas phase. These clusters can be subjected to size- and state-specific spectroscopic investigations without thermal effects and perturbations from the environment.[7] Such gas-phase clusters are ideal for investigating reaction mechanisms at the molecular level, and they enable us to elucidate molecular motion in individual steps of the reaction. The recent development of vibrational spectroscopic techniques based on vacuum-ultraviolet (VUV) photoionization enables us to observe the infrared (IR) spectra of simple and fundamental molecular clusters in both the neutral and cationic states; these can be regarded as precursors and products, respectively, in VUV one-photon ionization processes.[8]

Herein, we report on the proton transfer in the photoionization-induced keto–enol tautomerization of hydrated acetone. IR spectra of the neutral and cationic acetone–water clusters were measured by the VUV photoionization detection scheme.[8] Structure analysis of the clusters based on the IR spectra reveals the exact pathway of the migration of the methyl proton in the tautomerization process by means of the "catch-and-release" catalytic action of a single water molecule.

The observed and calculated IR spectra of the neutral acetone–water cluster are shown in Figure 1. The calculated spectrum is based on the most stable structure of the cluster at the MP2/6-31++G** level, and the vibrational frequencies are scaled by 0.94.[9] The good correspondence between the observed and calculated spectra indicates that the acetone–water cluster forms the most stable structure, which is depicted in Figure 1.[10] Figure 2a shows the observed IR spectrum of the acetone–water cluster cation, which is produced directly by the VUV (118 nm) one-photon ionization of the neutral cluster of the corresponding size. For the cluster cation, the symmetric OH stretching band (ν_1) and the antisymmetric OH stretching band (ν_3) of the water moiety are apparent, along with a broad and intense absorption from $3100\,\mathrm{cm}^{-1}$ to the lower-frequency region. The hydrogen-bonded (H-bonded) OH stretches of cluster cations generally show large low-frequency shifts from the free OH stretching region and have broad bandwidths. Thus, the broad absorption is clearly assigned to the H-bonded OH stretch band, which partly overlaps with the CH stretches of the acetone moiety. The representative optimized structures of the acetone–water cation at the MP2/6-31++G** level and their calculated vibrational spectra are shown in Figures 2b–f. All the isomeric structures found in computations and their vibrational simulations are given in the Supporting Information.

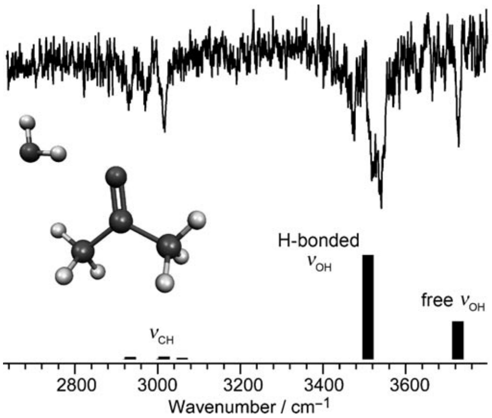

Figure 1. Observed IR spectrum of neutral acetone–H_2O and the calculated spectrum based on the optimized cluster structure shown (MP2/6-31++G** level). The calculated frequencies are scaled by 0.940.

Structures I and II are the most stable conformers among all the isomers. They have the H-bonded forms consisting of an enol–acetone cation and neutral water molecule. The simulations for structures I and II show good agreement with all the observed spectral features. In contrast, the calculated spectra for the other isomers fail to reproduce the observed intense H-bonded OH stretch. Therefore, we can determine that the acetone–water cation forms the same structures as those of structures I and II. Structure I is 0.6–$0.8\,\mathrm{kcal\,mol}^{-1}$ lower in energy than structure II at various calculational levels: MP2/6-31++G**, MPW1K/6-311+G(2d,2p), and PBE1PBE/6-311+G(2d,2p).

These spectroscopic results demonstrate that the keto–enol tautomerization occurs in the acetone–water cluster upon photoionization (118 nm), and that the methyl proton finally migrates to the carbonyl oxygen. The barrier height of the direct transfer of the methyl proton in the keto form to the carbonyl oxygen of the acetone cation has been estimated at 1.56 eV at the G3 level.[11] The adiabatic ionization energy of

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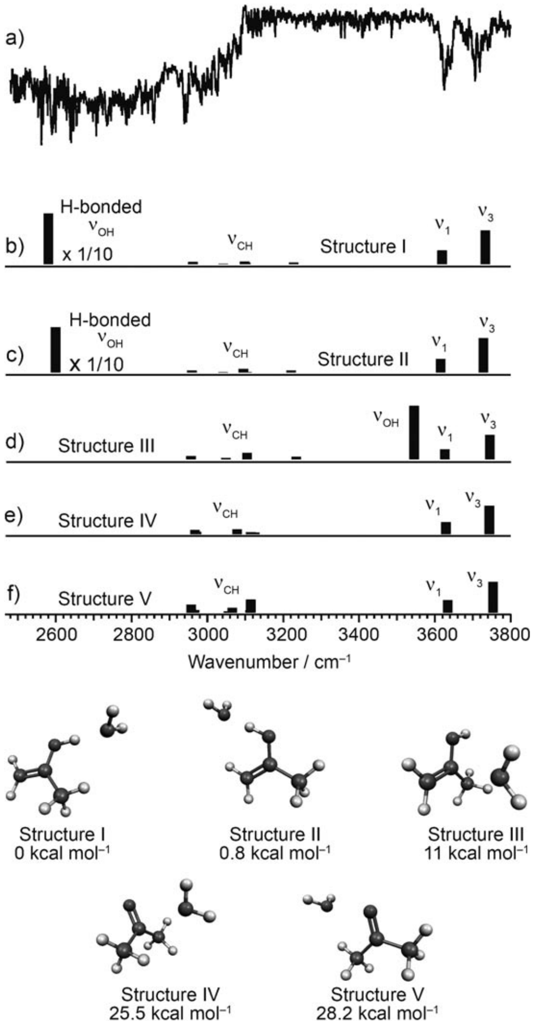

Figure 2. a) Observed IR spectrum of acetone–H_2O cation, and b–f) calculated spectra based on the optimized structures shown (MP2/6-31++G** level). All the calculated frequencies are scaled by 0.948.

the neutral acetone–water cluster to structure IV of the cation is estimated at 9.52 eV at the MP2/6-31++G** level. Structure IV is the most stable structure in which the keto form of the acetone cation is maintained. Because the photon energy at 118 nm is 10.48 eV, this result indicates that the direct transfer of the methyl proton is unlikely. Instead, the water molecule is likely to assist in the proton transfer, and two probable mechanisms are considered as the routes to structures I and II. One is the "proton-relay" mechanism, in which the water molecule abstracts the methyl proton and transfers its own hydroxy proton to the carbonyl oxygen. The other is the "catch-and-release" mechanism, in which the water abstracts the methyl proton and transfers it to the carbonyl oxygen.

To identify which mechanism is at play, IR spectra of the neutral and cationic acetone–D_2O cluster were acquired for the 118 nm photoionization. In the IR spectrum of neutral acetone–D_2O (Figure 3 a), CH stretch bands and a single free OD stretch band are observed, whereas the free and H-bonded OH stretch bands are missing. The H-bonded OD stretch band is also missing, because it should be out of the observed frequency range. This spectrum indicates that the contribution of the partially deuterated acetone–water (acetone–HOD) cluster is completely eliminated under the experimental conditions. Moreover, these spectral features demonstrate that the acetone–D_2O cluster forms the same intermolecular structure as the acetone–H_2O cluster.

The IR spectrum of the acetone–D_2O cation is shown in Figure 3 b. No free OH stretch band for HOD is observed in the expected region of 3650–3750 cm^{-1}, although the HOD moiety would be formed in the proton-relay mechanism. Instead, a broad band spreading from 3100 cm^{-1} to the lower-frequency region is observed in the spectrum. This band is reasonably assigned to the H-bonded OH stretch of the enol acetone cation moiety. Thus, the water moiety of the acetone–D_2O cation keeps its original two deuterium atoms upon the photoionization. This result demonstrates that the methyl proton itself is transferred to the carbonyl group by the catch-and-release mechanism. Although the proton-relay mechanism has been found for several intracluster proton-transfer reactions with ammonia and methanol,[12] this is the first time, to our knowledge, that the catch-and-release mechanism has been experimentally confirmed. In the keto–enol tautomerization of the acetone cation, the single water molecule acts as catalyst to lower the potential of the proton-transfer route.

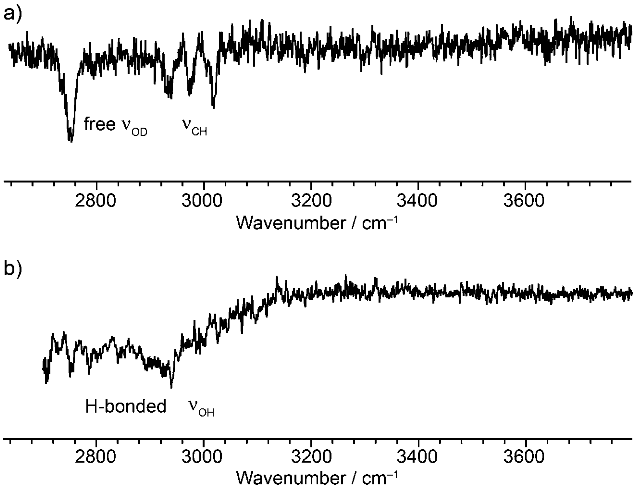

Figure 3. IR spectra of acetone–D_2O in a) neutral and b) cationic states.

To confirm this experimental evidence for the proton-transfer mechanism, we calculated the energy of the reaction path. Figure 4 shows the energy diagram calculated for the isomerization reaction of the acetone–water cluster upon photoionization (118 nm). The stable structures and the transition-state (TS) structures were initially searched by a global reaction route mapping (GRRM) program[13] at the UPBE1PBE/6-31+G* level. Then each of the structures was optimized using a higher basis set (6-311+G(2d,2p)). Within the 10.48 eV ionization energy, only one isomerization path exists from the Frank–Condon structure after the photoionization to the most stable structures I and II, as shown in

Figure 4. After one-photon ionization of the acetone–water cluster, the water molecule first changes its orientation to adopt structure V from the neutral form. The methyl proton is abstracted by the water via TS1 and is successively transferred to the carbonyl group. This proton-migration process catalyzed by the catch-and-release action of the water molecule leads to the formation of structure II. The 0.7 kcal mol^{-1} energy difference between structures I and II, and the 11.8 kcal mol^{-1} energy of TS2 is sufficient for the coexistence of structures I and II in equilibrium. This calculated reaction path agrees with the present experimental findings.

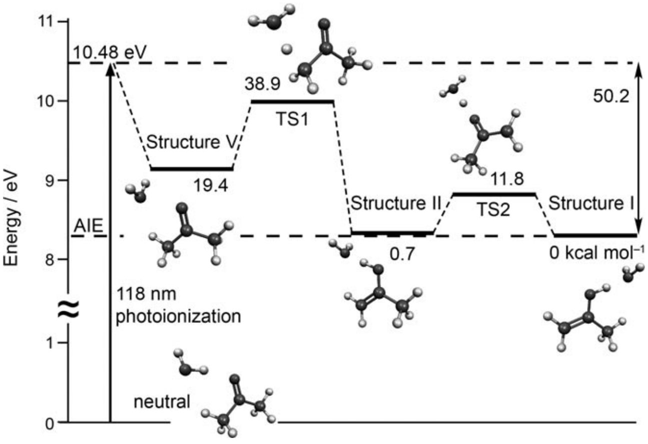

Figure 4. Energy diagram of the reaction path of acetone–H_2O cation in the VUV one-photon ionization from the neutral state. The intrinsic reaction coordinate (IRC) calculation for the vertically ionized state leads to the most accessible isomerization path to structure V. The reaction path beyond structure V was determined by the GRRM program at the UPBE1PBE/6-31+G* level. Relative energies [kcal mol^{-1}] are evaluated by geometry re-optimization of the stable structures at the UPBE1PBE/6-311+G(2d,2p) level and recalculation of the transition-state structures at the same level. The middle dotted line indicates the calculated adiabatic ionization energy (AIE).

In this study, the proton-transfer path in the keto–enol tautomerization of the acetone cation was investigated using IR spectroscopy and theoretical calculations, and the catch-and-release catalytic action of a single water molecule was identified as the relevant reaction path. In the reaction, the water molecule enables the proton to migrate approximately 3.5 Å from the methyl group to the carbonyl group of the acetone cation. Proton-transfer/migration phenomena are the most fundamental and essential reactions in chemistry, biology, and geochemistry. The present findings on the microscopic role of water catalysis will contribute to understand further details of the role of water in proton-transfer/migration phenomena.

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