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PAPER

Photon induced isomerization in the first excited state of the 7-azaindole–(H₂O)₃ cluster

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A picosecond pump and probe experiment has been applied to study the excited state dynamics of 7-azaindole–water 1 : 2 and 1 : 3 clusters [7AI(H₂O)_{2,3}] in the gas phase. The vibrational-mode selective Excited-State-Triple-Proton Transfer (ESTPT) in 7AI(H₂O)₂ proposed from the frequency-resolved study has been confirmed by picosecond decays. The decay times for the vibronic states involving the ESTPT promoting mode $\sigma(1)$ (850–1000 ps) are much shorter than those for the other vibronic states (2100–4600 ps). In the (1 + 1) REMPI spectrum of 7AI(H₂O)₃ measured by nanosecond laser pulses, the vibronic bands with an energy higher than 200 cm⁻¹ above the origin of the S₁ state become very weak. In contrast, the vibronic bands in the same region emerge in the (1 + 1') REMPI spectrum of 7AI(H₂O)₃ with picosecond pulses. The decay times drastically decrease when increasing the vibrational energy above 200 cm⁻¹. *Ab initio* calculations show that a second stable “cyclic-nonplanar isomer” exists in addition to a “bridged-planar isomer”, and that an isomerization from a bridged-planar isomer to a cyclic-nonplanar isomer is most probably responsible for the short lifetimes of the vibronic states of 7AI(H₂O)₃.

1. Introduction

Hydrogen-bonded networks play an important role in biomolecular systems. For example, hydration water is bound to the surface of the peptides, and the size of water networks becomes larger with the increasing hydration level (ratio of weight of water and weight of protein). The fluctuations of water networks in hydration water induce the fluctuations of peptides, which are important in their function.¹ Spectroscopic studies of hydrogen-bonded networks in molecular clusters prepared in the gas phase give detailed information on the structures and the dynamics, which provides insights into the dynamics of the hydrogen-bonded networks in the condensed phase.

Recently, excited state multiple-proton transfer reactions (ESPT) along the hydrogen-bonded networks in molecular clusters

such as 7-hydroxyquinoline(NH₃)_n(H₂O)_m ($n + m = 3$)^{2–4} and 7-azaindole(Solvent)_n [7AI(Solvent)_n] ($n = 1–3$; Solvent = H₂O/CH₃OH/C₂H₅OH/NH₃)^{5–9} have been extensively studied in the gas phase. A series of studies on the 7AI(Solvent)_n clusters demonstrated that the multiple-proton/hydrogen transfer is solvent and cluster-size selective. The ESPT is not evidenced in the ammonia cluster⁹ and for 7AI(H₂O/CH₃OH/C₂H₅OH)_n ($n = 1–3$) only the 1 : 2 clusters exhibit the excited-state triple-proton transfer reaction (ESTPT),^{5–8} whereas no clear evidence for the occurrence of excited-state double-proton transfer (ESDPT) in the 1 : 1 clusters and excited-state quadruple-proton transfer (ESQPT) in the 1 : 3 clusters has been obtained.

Another important feature of the multiple-proton transfer is vibrational-mode selectivity. It has been found that the symmetric intermolecular stretching vibrational mode ($\sigma(1)$) that involves the cooperative motion of the hydrogen-bonded network promotes the ESTPT reaction. Very recently, a clear evidence for ESTPT was obtained for 7AI(H₂O)₂ by measuring the dispersed fluorescence spectrum.⁸ The reason for the non-observation of ESQPT has been explained by quantum chemistry calculation on the potential curves along the proton-transfer coordinate for a bridged-planar structure of 7AI(H₂O)₃, where three water molecules form a hydrogen-bonded bridged-planar structure linking the NH and N groups of 7AI.⁸ The potential barrier for the ESQPT in 7AI(H₂O)₃ is significantly higher than that for the ESTPT in 7AI(H₂O)₂, which decreases the probability of the former process.

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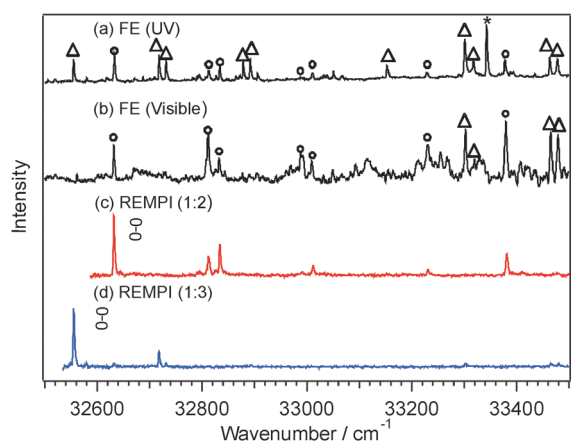


Fig. 1 FE spectra measured by detecting (a) UV and (b) visible fluorescence, and REMPI spectra of (c) $7\text{Al}(\text{H}_2\text{O})_2$ and (d) $7\text{Al}(\text{H}_2\text{O})_3$, respectively. The circles and triangles indicate the vibronic bands of $7\text{Al}(\text{H}_2\text{O})_2$ and $7\text{Al}(\text{H}_2\text{O})_3$, respectively. The band with asterisk indicates the origin band of $7\text{Al}(\text{H}_2\text{O})_1$.

On the other hand, an unusual behavior has been observed in the electronic spectra of $7\text{Al}(\text{H}_2\text{O})_3$. In the REMPI spectrum measured with nanosecond pulses (Fig. 1(d)), the vibronic bands located higher than 200 cm^{-1} above the S_1 state origin get very weak but the corresponding vibronic bands appear in the hole-burning spectrum and in the fluorescence excitation (FE) spectrum obtained by recording the emission in the UV region.⁸ This behavior has not been observed in the electronic spectra of $7\text{Al}(\text{CH}_3\text{OH})_3$ and $7\text{Al}(\text{C}_2\text{H}_5\text{OH})_3$.^{6,7}

These results stimulated us to apply picosecond spectroscopy to investigate the unusual behavior of $7\text{Al}(\text{H}_2\text{O})_3$. The new results show that the vibronic bands that disappeared with nanosecond laser pulses gain intensity in the REMPI spectrum with picosecond laser pulses. It has been found that the decay times of the vibronic states and their internal energy dependence are remarkably different between $7\text{Al}(\text{H}_2\text{O})_3$ and $7\text{Al}(\text{H}_2\text{O})_2$. The combination of the spectroscopic study with quantum chemistry calculations shows that an isomerization due to the rearrangement of the water network of $7\text{Al}(\text{H}_2\text{O})_3$ occurs by exciting the vibronic bands higher than $+200\text{ cm}^{-1}$ above the 0–0 transition. A discussion on the structures of the isomers, the transition energies and the excited-state dynamics will be also presented.

2. Experimental

The experimental set-up has been previously described.¹⁰ Briefly, $7\text{Al}(\text{H}_2\text{O})_{2,3}$ clusters were generated by co-expanding a mixture of He seeded with H_2O . 7Al was purchased from Sigma-Aldrich (France) and used without further purification. The carrier gas (He) at a backing pressure of 1 bar was passed through two reservoirs, the first one containing water at room temperature and the second one containing 7Al heated at 363 K. The gas mixture was expanded into a vacuum chamber through a $300\text{ }\mu\text{m}$ diameter pulsed nozzle (Solenoid General Valve, Series 9). Under these conditions, no large clusters were observed and structured vibronic REMPI ($1 + 1'$) spectra were obtained.

The skimmed free jet was crossed at right angle by the co-propagated excitation and ionization laser beams, 10 cm downstream from the nozzle. The interaction region was the center of the extraction zone of a linear time-of-flight (TOF) mass spectrometer. The produced ions were accelerated perpendicularly to the jet axis toward a microchannel plate detector located at the end of a 1.5 m field-free flight tube.

The third harmonic (355 nm) output of a mode-locked picosecond Nd:YAG laser (EKSPLA-SL300) was split into two parts to pump two OPA and SHG systems (EKSPLA-PG411) to obtain tunable UV light. One of the systems was used as the excitation laser (ν_1) and the other OPA–SHG system was tuned to 310 nm and used as the ionization laser (ν_2), keeping its energy to approximately $120\text{ }\mu\text{J pulse}^{-1}$ while the energy of the ν_1 laser was attenuated to preclude one-color two-photon ionization. The temporal shapes of both pulses were determined in the fitting procedure as Gaussian functions of 15 ps FWHM, while the spectral linewidth was 5 cm^{-1} . Both laser pulses were optically delayed between -350 and 1350 ps by a motorized stage.

The experimental techniques used for the fluorescence, REMPI and hole-burning spectroscopy with nanosecond pulses were essentially the same as those described previously.^{5–8}

3. Theoretical calculation

Ab initio and DFT (density functional theory) calculations were performed with the TURBOMOLE[®] program package,¹¹ making use of the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals.¹² The equilibrium geometry of the clusters in their ground electronic state (S_0) was determined at both the MP2 and DFT levels using the B3LYP hybrid functional. Excitation energy and equilibrium geometry of the lowest excited singlet state (S_1) were determined at both RI-CC2¹³ and TD-DFT levels. In order to get meaningful information on the energetic, and to take into account the π bonding interaction of the water molecules, the dispersion was included in the DFT calculation as implemented in TURBOMOLE[®]. Calculations were performed with the correlation-consistent polarized valence double-zeta basis set (cc-pVDZ).¹⁴

The Franck–Condon simulations were performed using the Pgopher software.¹⁵

4. Results

4.1 Fluorescence excitation spectra with nanosecond pulses

Fig. 1(a) and (b) show the FE spectra measured by monitoring UV and visible fluorescence, respectively, while Fig. 1(c) and (d) show the nanosecond REMPI spectra of $7\text{Al}(\text{H}_2\text{O})_2$ and $7\text{Al}(\text{H}_2\text{O})_3$, respectively, in the region $32\,500\text{--}33\,500\text{ cm}^{-1}$. We note that the vibronic bands observed in the FE spectrum of $7\text{Al}(\text{H}_2\text{O})_3$ in Fig. 1(a) disappear above the 200 cm^{-1} region of the REMPI spectrum in Fig. 1(d). The spectrum presents a larger energy scale than that reported in ref. 8 and surprisingly, at higher energy ($> +650\text{ cm}^{-1}$) the vibronic bands of $7\text{Al}(\text{H}_2\text{O})_3$ are detected in the FE spectrum measured by probing the visible fluorescence ($> 570\text{ nm}$) (Fig. 1(b)).

The picosecond experiments provide results complementary to the nanosecond experiments, which are described in Section 4.2.

4.2 Picosecond experiments

Fig. 2 shows the $(1+1')$ REMPI spectra of $7\text{Al}(\text{H}_2\text{O})_{2,3}$ recorded with picosecond pulses with no delay between the two laser pulses. The appearance of the spectrum of $7\text{Al}(\text{H}_2\text{O})_2$ is very similar to that recorded with nanosecond pulses in Fig. 1(a). However, the spectrum of $7\text{Al}(\text{H}_2\text{O})_3$ shows more vibronic transitions than the one recorded with nanosecond pulses (Fig. 1(d)). These new transitions also appeared in the UV–UV hole burning spectrum and in the FE spectrum obtained by recording the UV fluorescence⁸ (Fig. 1(a)).

To get more insight into the dynamics of these systems, the excited-state lifetimes of $7\text{Al}(\text{H}_2\text{O})_2$ and $7\text{Al}(\text{H}_2\text{O})_3$ were determined upon excitation of several vibronic states up to $+800\text{ cm}^{-1}$ above the origin of their $S_1 \leftarrow S_0$ transitions. The results are shown in Table 1 and plotted in Fig. 3(a) and (b) as a function of the vibrational energy in the S_1 state.

The excited-state lifetime determined for the 0_0^0 transition of $7\text{Al}(\text{H}_2\text{O})_2$ is $(4.6 \pm 0.7)\text{ ns}$, in good agreement with the value $(6.6 \pm 1)\text{ ns}$ reported by Sulkes and coworkers¹⁶ and the value 10 ns reported by Vu *et al.*¹⁷ based on the linewidth of this transition. This cluster also shows clear vibrational mode specificity on the excited-state lifetime. The excited-state lifetime becomes shorter when the symmetric intermolecular stretching has one or two quanta, $1\sigma(1)$ or $2\sigma(1)$, respectively, consistent with the concerted ESTPT mechanism suggested by Sakota *et al.*, as the main non-radiative process in the S_1 state of $7\text{Al}(\text{H}_2\text{O})_2$.⁸

On the other hand, the excited-state lifetime measured for the 0_0^0 transition of $7\text{Al}(\text{H}_2\text{O})_3$ is very long and cannot be determined with our experimental set-up, but it was estimated to be longer than 10 ns in agreement with the value, reported by Vu *et al.*,¹⁷ on the basis of the transition linewidth. It is worthwhile to note the lack of vibrational mode specificity on the excited state lifetime of $7\text{Al}(\text{H}_2\text{O})_3$ (Fig. 3(b)), as compared to $7\text{Al}(\text{H}_2\text{O})_2$. This suggests that ESQPT does not

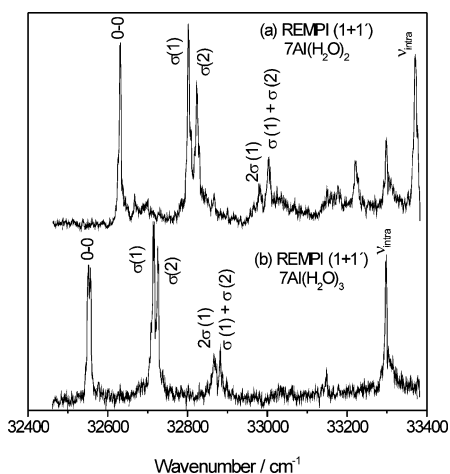


Fig. 2 $(1+1')$ REMPI spectra of (a) $7\text{Al}(\text{H}_2\text{O})_2$ and (b) $7\text{Al}(\text{H}_2\text{O})_3$ recorded with picosecond pulses with no delay between both laser pulses. The probe laser wavelength was 310 nm .

Table 1 Excited state lifetimes of $7\text{Al}(\text{H}_2\text{O})_2$ and $7\text{Al}(\text{H}_2\text{O})_3$ recorded by exciting at different vibronic states. The reported lifetimes are the average of several measurements while the corresponding errors are the standard deviation of all the measurements

$7\text{Al}(\text{H}_2\text{O})_2$		
Vibrational assignment	Vibrational energy/ cm^{-1}	Lifetime/ps
0_0^0	0	4600 ± 700
$1\sigma(1)$	175	1000 ± 70
$1\sigma(2)$	196	2200 ± 100
$2\sigma(1)$	349	850 ± 80
$1\sigma(1) + 1\sigma(2)$	369	2100 ± 100
ν_{intra}	741	967 ± 30
$7\text{Al}(\text{H}_2\text{O})_3$		
Vibrational assignment	Vibrational energy/ cm^{-1}	Lifetime/ps
0_0^0	0	> 10000
$1\sigma(1)$	161	900 ± 50
$1\sigma(2)$	175	420 ± 30
$2\sigma(1)$	316	27 ± 10
$1\sigma(1) + 1\sigma(2)$	329	40 ± 10
ν_{intra}	744	15 ± 10^a

^a A double exponential decay has been observed upon excitation of the $+744\text{ cm}^{-1}$ band of $7\text{Al}(\text{H}_2\text{O})_3$ and the value listed corresponds to the shorter decay component.

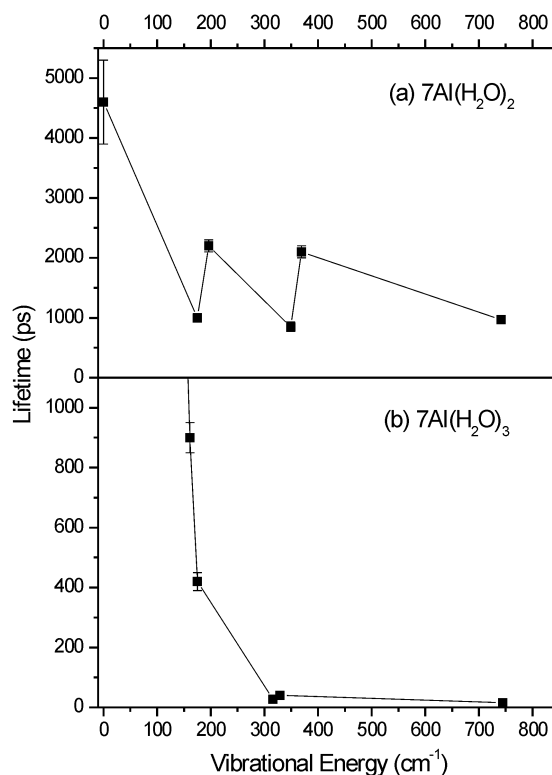


Fig. 3 Excited-state lifetimes of (a) $7\text{Al}(\text{H}_2\text{O})_2$ and (b) $7\text{Al}(\text{H}_2\text{O})_3$ as a function of the vibrational energy in the S_1 state.

take place in $7\text{Al}(\text{H}_2\text{O})_3$ in the region of low internal energy in agreement with previous results.⁸ Therefore, the excited-state lifetime of this cluster is governed by a different process in a more statistical fashion.

Fig. 4(a) depicts the time dependent signal recorded on the mass $7\text{Al}(\text{H}_2\text{O})_3^+$ upon excitation of the $+744\text{ cm}^{-1}$ (33298 cm^{-1})

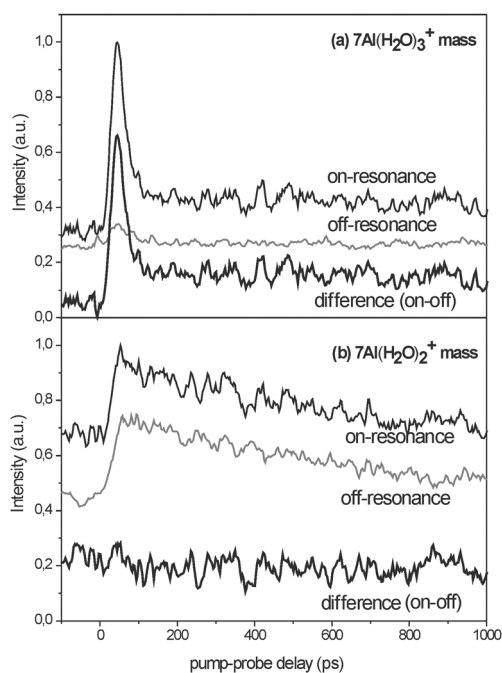


Fig. 4 Pump-probe signals obtained by exciting the $+744\text{ cm}^{-1}$ intramolecular vibrational band of $7\text{AI}(\text{H}_2\text{O})_3$ (on-resonance top trace), just at the bottom of the band (off-resonance middle trace) and the difference between them (bottom trace), recorded on the masses (a) $7\text{AI}(\text{H}_2\text{O})_3^+$ and (b) $7\text{AI}(\text{H}_2\text{O})_2^+$.

intramolecular vibration of $7\text{AI}(\text{H}_2\text{O})_3$ (on-resonance signal, upper trace), the corresponding signal recorded with the pump laser set slightly to the red of the band at $+718\text{ cm}^{-1}$ ($33\,272\text{ cm}^{-1}$) that accounts for the dynamics of the evaporation of solvent molecules in larger clusters (off-resonance signal, middle trace), and the result of the subtraction of the off-resonance signal from the on-resonance signal (lower trace), which accounts for the dynamics of the $7\text{AI}(\text{H}_2\text{O})_3$. Note the latter signal shows a very fast decay before it reaches a plateau, indicative of a slow decay. The fast decay is fitted to 15 ps, which represents an upper limit since the decay time is the same as the laser pulse temporal width (15 ps).

The REMPI spectra in Fig. 2 clearly show the evaporation of one water molecule upon excitation of the $+744\text{ cm}^{-1}$ intramolecular vibration, but the dynamics observed on the $7\text{AI}(\text{H}_2\text{O})_2^+$ mass when exciting this band is very different from that observed on the parent ion mass, as shown in Fig. 4(b). In addition, the same behavior is observed when the laser is tuned on or off-resonance. The surprising result is shown on the lower trace of Fig. 4(b), obtained from the difference of on- and off-resonance signals, which turns out to be independent of the pump and probe delay, while the transition is clearly observed in the REMPI spectrum. The band at $+744\text{ cm}^{-1}$ in the REMPI spectrum of $7\text{AI}(\text{H}_2\text{O})_2$ is actually due to the evaporation of one water molecule from $7\text{AI}(\text{H}_2\text{O})_3$, but this process takes place only *via* the absorption of two photons of the pump laser, the one-color-two-photon energy being 8.26 eV. The absence of pump/probe signal implies that evaporation does not take place with the two-color-two-photon energy of 8.13 eV. This emphasizes the fact

that the observation of dynamics is strongly dependent on the probe photon energy.

4.3 Calculations

Let us first point out that the observed excitation spectrum for $7\text{AI}(\text{H}_2\text{O})_3$ is due to the bridged-planar structure (Fig. 5(a)), *i.e.* a structure similar to the bridged structure of the $7\text{AI}(\text{H}_2\text{O})_2$ complex obtained by addition of one water molecule in the water bridge.

The calculated $S_1 \leftarrow S_0$ transition energy of this bridged-planar isomer is very close to that of the $7\text{AI}(\text{H}_2\text{O})_2$ complex ($\Delta E = -80\text{ cm}^{-1}$ determined experimentally and $\Delta E = -230\text{ cm}^{-1}$ calculated at the TD-DFT level). Also, the vibrational structure obtained by the Franck–Condon (FC) calculation (*vide infra*) for the bridged-planar isomer compares satisfactorily with the experimental spectrum.

The experimental observations suggest that in the higher energy region ($> +200\text{ cm}^{-1}$) of the S_1 state, the $7\text{AI}(\text{H}_2\text{O})_3$ bridged-planar structure isomerizes to a more stable structure. In order to explain the experimental data, the most stable structure should have a higher ionization potential (IP) than that of the bridged-planar structure. This suggests that some interaction occurs between one of the H atoms of the water network and the π electrons of the indole ring.

We have explored many structures starting with one water on the top of the indole ring and the two others forming the bridged structure in the molecular plane. For most of the structures optimized in the excited state at the TD-DFT level, the optimization stops with an energy higher than the bridged-planar isomer. However, starting from a cyclic water trimer above the 7AI ring, the optimization process leads to a structure with energy well below that of the bridged-planar structure (-2400 cm^{-1} at the DFT level and -2590 cm^{-1} at the CC2 level) that will be called the cyclic-nonplanar structure (Fig. 5(b)).

Starting from this initial structure optimized in the excited state, the ground state has been optimized and we found that in this state the cyclic-nonplanar isomer is also more stable than the bridged-planar structure by 1017 cm^{-1} at the DFT level and 467 cm^{-1} at the CC2 level. The change of the geometry between the ground and excited states is rather important and in particular the hydrogen bonds substantially shorten in the excited state as shown in Fig. 6.

The Franck–Condon analysis, shown in Fig. 7, has been performed for the two structures discussed above at the TD-DFT level. The FC simulation of the bridged-planar structure is in good agreement with the observed spectrum.

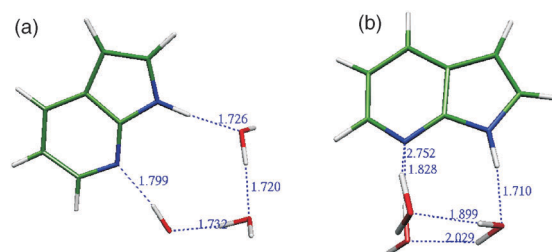


Fig. 5 Ground state calculated structures for the $7\text{AI}(\text{H}_2\text{O})_3$ complex; (a) bridged-planar isomer and (b) cyclic-nonplanar isomer.

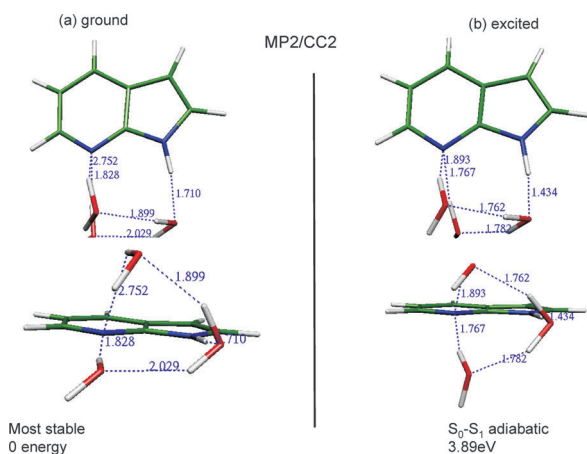


Fig. 6 (a) Ground and (b) first singlet excited state optimized structures for the $7\text{Al}(\text{H}_2\text{O})_3$ cyclic-nonplanar isomer.

The spectrum for the cyclic-nonplanar structure is very congested with many active low vibrational modes. Moreover, the FC factors for the cyclic-nonplanar structure are 2 orders of magnitude smaller than those for the bridged-planar structure making its observation very difficult.

The calculated Ionization Potential (IP) for the cyclic-nonplanar structure (8.10 eV at the TD-DFT level) is higher in energy than the IP for the bridged-planar structure (7.97 eV at the TD-DFT level). In addition, after isomerization the cyclic-nonplanar structure remains with an internal (vibrational) energy of at least 2400 cm^{-1} (the difference between the stability of both isomers), which has to be conserved upon ionization. Thus, the vertical IP of this hot cluster should be around 2400 cm^{-1} higher in energy than the IP of the colder bridged-planar structure. This hot cyclic-nonplanar structure will not be ionized as efficiently as the bridged-planar structure and thus the excited-state lifetime of the vertically excited bridged-planar isomer, determined by pump-probe ionization

experiments, reveals the isomerization rate, which increases monotonically with the internal energy of the complex.

5. Discussion

5.1 The $7\text{Al}(\text{H}_2\text{O})_2$ cluster

The comparison of the electronic spectra in Fig. 1 measured with nanosecond pulses with those in Fig. 2 obtained with picosecond pulses provides intriguing information. The picosecond REMPI spectrum of $7\text{Al}(\text{H}_2\text{O})_2$ in Fig. 2(a) is similar to the corresponding nanosecond REMPI spectrum in Fig. 1(c). The intensity distribution of the vibronic bands reflects the vibrational-mode specific ESTPT, which is well-correlated with vibronic state-dependent decay times in Fig. 3(a). The picosecond experimental data show a shorter lifetime for the excitation of the intermolecular band at $+175\text{ cm}^{-1}$ ($\sigma(1)$) than for the band at $+196\text{ cm}^{-1}$ ($\sigma(2)$). In the previous paper, from *ab initio* TD-DFT calculations (see the ESI of ref. 8) these two bands have been assigned to different in-plane breathing modes of the water chains.

The experimental observation of a faster reaction for the excitation of the $\sigma(1)$ vibration corresponding to the reaction coordinate is totally consistent with the proposed concerted reaction mechanism.

5.2 The $7\text{Al}(\text{H}_2\text{O})_3$ cluster

The REMPI spectrum of $7\text{Al}(\text{H}_2\text{O})_3$ in Fig. 2(b) is very different from that in Fig. 1(d). The vibronic pattern of the REMPI spectrum measured with picosecond pulses shows bands in the energy region higher than $+200\text{ cm}^{-1}$ above the transition origin and is more similar to the FE spectrum observed by probing the UV fluorescence (Fig. 1(a)). This result implies that the decay times measured by multiphoton ionization of vibronic bands above $+200\text{ cm}^{-1}$ are much shorter than those for the $0-0 + 161\text{ cm}^{-1}$ and $0-0 + 175\text{ cm}^{-1}$

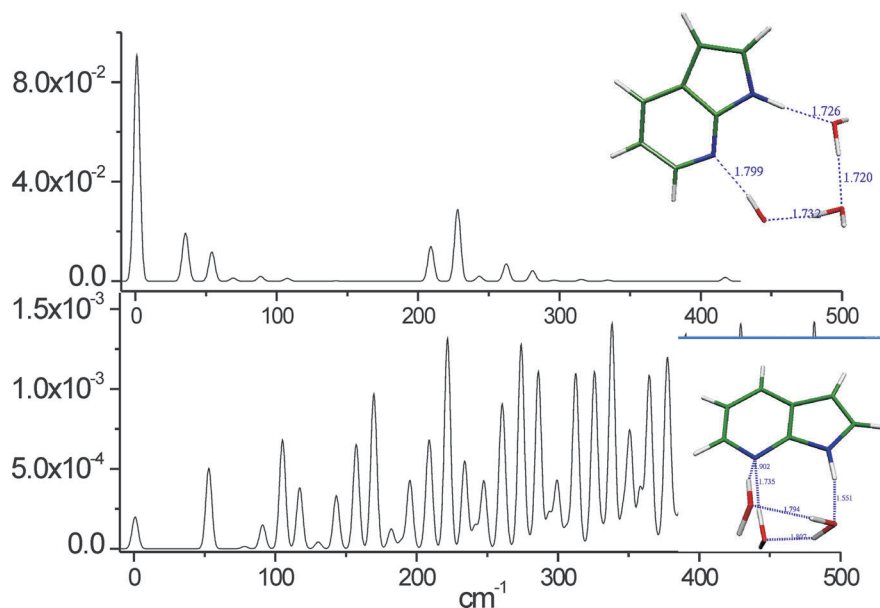


Fig. 7 Franck-Condon simulation of the electronic spectrum at the TD-DFT level for the bridged-planar and the cyclic-nonplanar isomer. Note that the vertical axis scales are quite different and that the band origins have been set to 0.

bands. However, the system does not undergo an efficient tautomerization or a non-radiative process since the UV fluorescence is still observed while the red-shifted fluorescence is absent.

The fact that the ionization efficiency of the $7\text{Al}(\text{H}_2\text{O})_3$ complex decreases drastically when ionizing with nanosecond pulses as compared with ionization with picosecond pulses is indicative of a fast non-radiative process that precludes the ionization at long delays.

This non-radiative process is not likely to be the excited-state concerted-proton-transfer as in the case of $7\text{Al}(\text{H}_2\text{O})_2$ (at least in the low energy region), because the signatures for this reaction are mode specificity on the excited-state lifetime and red-shifted (visible) fluorescence from the tautomeric form. In contrast, the excited-state lifetime of $7\text{Al}(\text{H}_2\text{O})_3$ decreases monotonically with the excitation energy and the cluster fluoresces efficiently in the UV region and not in the visible range. Therefore, although the new process precludes ionization, the system still remains in the excited state. The most likely process is then excited-state solvent isomerization. It does not change the nature of the chromophore that remains in the excited state, but the conformation of the solvent strongly changes the ionization potential of the complex.

The analysis of the dispersed fluorescence (DF) spectra of $7\text{Al}(\text{H}_2\text{O})_3$ measured by Hara *et al.*¹⁸ provides insights into the above idea of the excited-state solvent isomerization. We noted that unusually red-shifted (~ 30 nm) DF spectra were observed for the excitation of the vibronic bands at $+163$, $+176$, $+313$ and $+327$ cm^{-1} (these bands correspond to the $+161$, $+175$, $+316$ and $+329$ cm^{-1} bands in the picosecond REMPI spectrum). On the other hand, the decay time of the vibronic state decreased from >10 ns for the origin band to 900 ps for the $+161$ cm^{-1} band. Thus, the unusual red-shift of the DF spectrum well correlates with the drastic decrease in the decay time. These observations are consistently explained by the occurrence of isomerization from the planar-ring structure to the cyclic-nonplanar structure as suggested by *ab initio* calculations.

Besides, the isomerization hypothesis seems to be well confirmed by the calculations.

(a) It explains the absence of vibrational bands in the REMPI spectrum, and their presence in the FE spectrum.

(b) The DF spectra are red-shifted for the excitation at higher excess energy, *i.e.* above the isomerization threshold. This can be explained by the emission of the hot isomer emitting on a broad Franck–Condon envelope as suggested by the FC calculation of the absorption spectrum.

(c) The presence of this very stable structure in the excited state is sufficient to explain the experimental observation but we cannot ensure that it is the lowest excited state structure.

(d) We already have seen that, concerning the $S_1 \leftarrow S_0$ transition of the bridged-planar structure, the relative energy, the IP and the FC calculations are in good agreement with the experimental results.

(e) From Fig. 4, we notice the observation of a biexponential decay (picosecond decay and plateau) when exciting the $+744$ cm^{-1} intramolecular vibration of $7\text{Al}(\text{H}_2\text{O})_3$, but the corresponding plateau (slow decay) is absent upon excitation of the lower energy intermolecular modes. At excitation

energies close to the origin of the $S_1 \leftarrow S_0$ transition (32554 $\text{cm}^{-1} = 4.04$ eV), we can exclusively measure the excited-state lifetime of the bridged-planar isomer, associated with the isomerization rate, since it is the only isomer that can be ionized with the probe photon used in this measurement (4.00 eV). The calculated IP (8.10 eV) of the cyclic-nonplanar isomer at the S_1 optimized geometry is 0.06 eV above the total energy of the two photons (8.04 eV). However, upon excitation of the $+744$ cm^{-1} intramolecular vibration of the bridged-planar isomer, the total energy deposited in the system is 8.13 eV. This energy is above or near the IP of the cyclic-nonplanar isomer calculated at the S_1 geometry (8.10 eV). From an energetic point of view, at this excitation energy it is also possible to ionize the cyclic-nonplanar isomer through vibrational auto-ionization.

Therefore, the fast exponential decay is associated with the excited-state lifetime of the bridged-planar isomer determined by the isomerization rate, and the slow exponential decay (plateau) might be associated with the excited-state lifetime of the cyclic-nonplanar isomer.

(f) At $+744$ cm^{-1} excitation, the red (tautomeric) emission is observed. This means that the reaction barrier for ESPT in $7\text{Al}(\text{H}_2\text{O})_3$ is higher in energy than for ESTPT in $7\text{Al}(\text{H}_2\text{O})_2$. For $7\text{Al}(\text{H}_2\text{O})_2$ the tautomeric emission is observed when exciting the band origin, but the tautomerization is still a slow process since the excited-state lifetime is in the nanosecond range. This reaction has been ascribed to a concerted mechanism, *i.e.* all the hydrogen atoms involved in the reaction move simultaneously. In addition, it was shown that the barrier for this mechanism is much lower in energy than for a sequential (Grothuss type) mechanism.⁸

In many systems, like in phenol(NH_3)_{*n*} ($n = 1-3$),^{19,20} indole(NH_3)_{*n*} ($n = 3-5$),²¹ and *p*-cresol(NH_3)_{*n*} ($n = 1, 2$) clusters,^{22,23} the excited-state hydrogen transfer reaction rate increases as the cluster size increases, which has been interpreted as the lowering of the transition state energy with increasing cluster size due to better solvation. In a previous paper⁸ it has been calculated that the reaction barrier for the concerted mechanism in the bridged-planar isomer of $7\text{Al}(\text{H}_2\text{O})_3$ is slightly higher (~ 0.1 eV = 800 cm^{-1}) than for $7\text{Al}(\text{H}_2\text{O})_2$. The calculated barrier height seems to be in quite good agreement with the observed onset of the reaction. However, this might be a coincidence since the cluster isomerizes before the ESPT reaction takes place and the calculated pathway might be different than the concerted mechanism taking place in the bridged-planar type cluster. It would be very interesting to test the reaction paths with *ab initio* molecular dynamics calculations.

(g) The ground-state cyclic-nonplanar isomer is more stable than the bridged-planar isomer, according to our calculations at the MP2 and DFT level. However, it has not been yet detected and it will be very difficult to observe as long as the signal-to-noise ratio of the experiment is not better than 1/1000, which is not easy to achieve. Many experiments searching for the most stable ground state conformers obtained in a supersonic expansion have employed IR/UV techniques. The observation/non-observation of some isomers is often used as a signature of the stability of the ground-state structure or as a signature of the relative excited state lifetimes

of different structures²³ but the calculation of the FC factors for the $S_1 \leftarrow S_0$ transition is rarely made. The example presented here shows the absolute necessity of the FC factors calculation in order to discuss whether or not the non-observation of an isomer is linked to its stability in the ground state and/or its short excited state lifetime or just to unfavorable Franck–Condon factors.

6. Conclusions

Once more the study of 7AI clusters is presenting surprising results that the combination of many experimental and theoretical techniques allows to disentangle. We have seen the indirect evidence of an excited-state solvent isomerization, which is not so common to observe. An isomer that is difficult to detect but more stable than the experimentally observed one is then predicted. This leads us to point out the necessity of Franck–Condon analysis for the different isomers before concluding about the observation of an isomer as a signature of the ground-state stability by using IR/UV experiments.

The picosecond experiments have allowed rationalizing surprising results obtained by nanosecond experiments. The fast process observed in 7AI(H₂O)₃ is linked to the possibility for the water network to make the cyclic-nonplanar structure, which seems to be more stable than the bridged-planar structure. This is probably what is happening in larger clusters in which the nanosecond REMPI spectra are vanishing at higher vibrational excitation.¹⁶

For the 7AI(H₂O)₂ complex, we have experimentally evidenced that excitation of intermolecular vibrations along the concerted reaction path increases the reaction rate, and this may be considered as a very strong support to this reaction mechanism.

At last, in 7AI(H₂O)₃ the occurrence of the excited-state multiple proton transfer is evidenced at a high excess of energy, which is in agreement with previous calculations.⁸ The 7AI(H₂O)_n system is a peculiar case in which the reaction barrier does not decrease as the cluster size increases. This may be due to the reaction mechanism which involves a collective dynamics and this collective movement may be more difficult to achieve when more molecules are involved.

It seems that this work brings consistent support to the concerted ESPT mechanism, which is a totally different mechanism than the Grotthuss sequential proton transfer mechanism commonly accepted.

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