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# Detection and Structural Characterization of Clusters with Ultrashort-Lived Electronically Excited States: IR Absorption Detected by Femtosecond Multiphoton Ionization

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The progress in chemical kinetics makes it clear that the so-called "elementary" reactions, such as proton or electron transfer, are, in fact, multidimensional processes, involving not only intramolecular degrees of freedom but also those of the environment. Elucidating the intricacies of such phenomena requires techniques of high spectral, temporal, and structural resolution. These conditions can be simultaneously fulfilled by isolating the reactants in supersonic beams. Recent examples of successful applications of this methodology for proton transferring systems include studies of the cooperativity in excited state double proton transfer (ESDPT) in 7-azaindole dimers[1] or detection of *cis* and *trans* tautomeric species in alkylated porphycenes and the determination of tunneling splittings for both forms in the ground and lowest singlet electronic states.[2]

The investigation of gas phase molecular clusters formed in supersonic beams at ultralow temperature is a very active research field since it allows studying the structure of microsolvated molecules by vibrational spectroscopy in combination with density functional theory (DFT). The selection of species out of a distribution of clusters differing in size and structure is feasible by IR/UV double resonance spectroscopy combining IR predissociation with UV resonant two-photon ionization and mass spectrometric detection.[3] This ultrasensitive IR/R2PI ion depletion method meanwhile finds widespread applications in the characterization of small biomolecules and their aggregates due to its size and isomer specificity.

We have chosen the 1-H-pyrrolo[3,2-*h*]quinoline (PQ)/methanol system since it constitutes an important model system for understanding the mechanism and dynamics of intermolecular ESDPT, which leads to tautomerization, a key reaction for chemical mutagenesis of DNA. PQ belongs to the group of bifunctional (H-bond donor/acceptor) heteroazaaromatics that have recently been studied in the condensed phase.[4−7] This group exhibits dual fluorescence, although, in the case of PQ, with very low quantum yield. The dual fluorescence is attributed to an ESDPT process mediated by a cyclic 1:1 complex with the alcohol solvent. The time scale of the ESDPT process in solution is in the subpicosecond to picosecond range.[6] In the gas phase, we have recently found different photophysical properties of PQ upon stepwise solvation by methanol. Namely, the laser-induced fluorescence (LIF) of the jet-cooled 1:1 cluster was not observed, while that of the 1:2 and larger complexes was quite strong upon $S_1 \leftarrow S_0$ excitation. This difference in fluorescence was indicative of a fast relaxation channel. Our goal was to investigate in detail the structure and dynamics of such photoreactive complexes and unveil their excited state reaction mechanism. For this purpose, their IR spectra in the NH, OH stretch region should be recorded using an extension of the double resonant IR depletion technique (IR/R2PI).

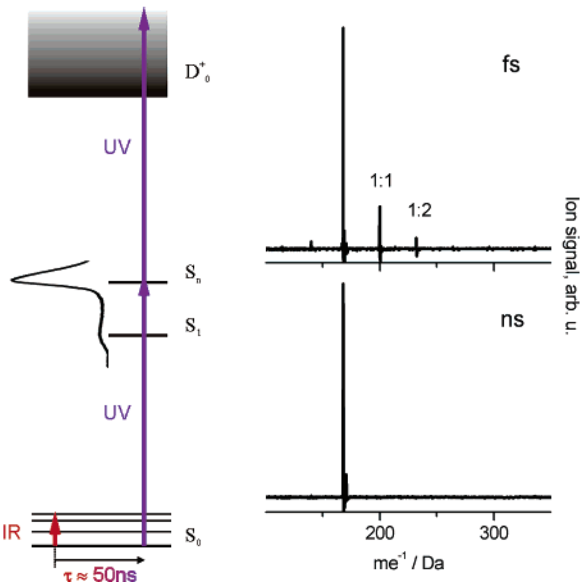

***Figure 1.*** One-color (266 nm) two-photon ionization scheme of PQ solvated by alcohol and mass spectra of jet-cooled PQ/methanol gas mixture obtained with the femtosecond and nanosecond laser pulses under otherwise identical conditions. The UV absorption spectrum of the PQ/alcohol solution is inserted. The timing of the IR/fsMPI experiment is also indicated.

The essential condition for the "classical" IR/R2PI depletion method is the existence of an electronically excited state of the cluster, halfway to the ionization potential, which can be excited resonantly and lives long enough to be able to ionize the species by nonresonant absorption of a second photon of the same energy. However, if this intermediate state is short-lived ($\ll$1 ns) due to fast proton or electron transfer or internal conversion, the ion yield observed with nanosecond lasers goes to zero.

An instructive example is given in Figure 1, where mass spectra of the same supersonic expansion of PQ with methanol were recorded for comparison, first with a nanosecond laser and second with a femtosecond laser. The excitation is performed via a higher lying electronic band, which can be attributed to electronically excited states $S_4$ or/and $S_5$ of $\pi\pi^*$ character (cf. scheme in Figure 1). Here, the third harmonic of a femtosecond Ti:sapphire laser (266 nm, 300 fs) is used. It is obvious that in the former spectrum the molecular aggregates of PQ with methanol are missing, probably due to their short excited state lifetime. From the displayed mass

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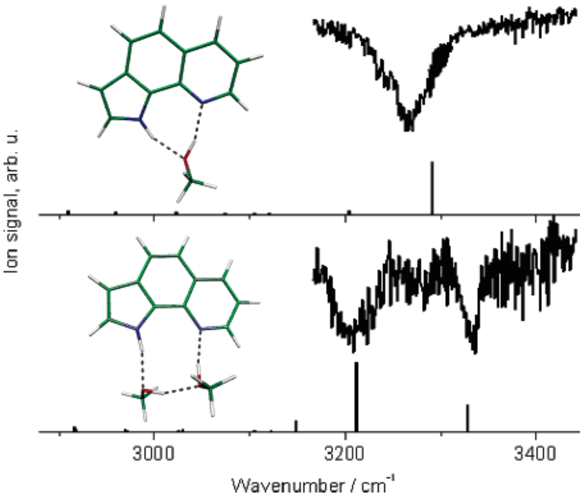

***Figure 2.*** IR/fsMPI spectra measured for PQ:methanol$_{n=1,2}$ mass channels. The calculated IR spectra are plotted with bars. Relevant cluster structures are inserted.

spectra, it is clear that if one is interested in an IR investigation of the PQ:methanol aggregates, this can only be achieved by femtosecond multiphoton ionization (fsMPI).

Our experimental setup consists of a narrow band nanosecond IR-OPO for vibrational excitation, a femtosecond chirped-pulse amplified Ti:Sa laser system for two-photon ionization of the cluster, and a vacuum apparatus equipped with a pulsed nozzle and a home-built time-of-flight mass spectrometer. All components have been described previously in separate publications.[8]

The resulting IR spectra in the region of 3150−3450 cm$^{-1}$ measured by IR/fsMPI for the PQ:methanol$_{n=1,2}$ ionic aggregates are depicted in Figure 2. Whereas for the 1:1 aggregate only one band at 3268 cm$^{-1}$ was found, the 1:2 complex exhibited two bands at 3332 and 3209 cm$^{-1}$. For assignment, these spectra are compared to the results of calculations obtained at the DFT level.[9] The calculated positions and intensities of the IR bands are plotted in Figure 2. They agree very well with the experimental spectra. The structures of the calculated aggregates are also depicted in Figure 2. In both clusters, the most stable geometries arise when the pyrrole donor and the pyridine acceptor of PQ are connected through H-bonds by a methanol OH bridge.

Thus, the strongest band of the 1:1 aggregate, calculated at 3291 cm$^{-1}$, is readily identified as the simultaneous anti-phase stretch of the OH group of methanol and the NH of the pyrrole unit of PQ. Due to the strong double H-bond interaction ($E_{\text{binding}} \approx 10$ kcal/mol[5]) in this cyclic complex, the local oscillator modes no longer exist. Similarly, for the 1:2 aggregate, the most intense mode calculated at 3212 cm$^{-1}$ is the anti-phase stretch of the pyrrole NH and pyridine-bound OH. The vibration predicted at 3328 cm$^{-1}$ is mainly the methanol dimer OH stretching, mixed, however, with elongations of the OH and NH bonds within the H-bond cycle.

The cyclic NH···OH···N bridge of the 1:1 aggregate was suggested as an intermediate for fast ESDPT in solution, which gives rise to the anomalous fluorescence and quenches the normal one.[4] After photoexcitation, the protons involved in the H-bonds undergo a concerted, albeit asynchronous, transfer. In principle, such a process is also possible in the 1:2 aggregate, but since there the "proton wire" is longer, a higher chance for dissipative side processes or of disturbances along the way is also conceivable. The different behavior of 1:1 and 1:2 PQ:methanol aggregates can be deduced from our recent IR nanosecond fluorescence depletion and R2PI[10] studies. As mentioned earlier, both failed to detect the 1:1 complex after excitation to the $S_1$ state, but the 1:2 and larger clusters appeared. Moreover, the spectra obtained by IR/LIF and IR/fsMPI depletion for the 1:2 species agree nicely, which supports the new method and the presented interpretation.

It should be emphasized that, under the employed experimental conditions (i.e., fixed femtosecond laser wavelength at 266 nm), no spectral selection of a specific cluster size by its UV fingerprints is possible. Therefore, one would expect that the obtained cluster mass spectra are dominated by fragmentation. However, conditions can be found where the parent ions $(1{:}1)^+$, $(1{:}2)^+$ can be measured nearly without contribution from larger clusters. For this purpose, a careful control of the expansion conditions is important, either by changing the vapor pressure of the solvent or by ionizing different segments of the gas pulse containing different cluster sizes.

Additionally, it should be pointed out that very similar results have been obtained for aggregates of PQ with water (spectra not shown here), where also the 1:1 cluster could not be investigated by LIF, but exclusively by the IR/fsMPI method.

In conclusion, we have presented a scheme for measuring the IR spectra of photoreactive molecular clusters, which is based on femtosecond multiphoton ionization probing (IR/fsMPI). We applied it successfully to PQ:methanol$_{n=1,2}$ clusters. One drawback of the method is that, in general, it does not provide size and isomer specificity. However, we could demonstrate that size-specific spectra for small complexes could be obtained if the supersonic expansion and excitation conditions are carefully controlled. In particular, PQ:methanol$_{n=1,2}$ aggregates could be identified and their structure analyzed. A time-resolved study of the ESDPT dynamics is underway. Thus, an important molecular model system for solvent-assisted photoinduced tautomerization reactions can be elucidated in full detail.

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**Supporting Information Available:** Experimental and calculation details as well as full authorship of ref 9a. This material is available free of charge via the Internet at http://pubs.acs.org.

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