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IR−IR−UV Hole-Burning: Conformation Specific IR Spectra in the Face of UV Spectral Overlap

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A new technique, IR−IR−UV hole-burning, is reported for obtaining conformation specific IR spectra when the electronic spectra are too closely overlapped to obtain clean spectra free from interference from other conformations via standard ion dip or fluorescence dip methods. The 4′-aminobenzo-15-crown-5 ether−(HDO) complex is used as an example, on which the method was applied to prove the presence of two conformations having overlapped electronic spectra and to assign IR transitions belonging to the same conformation.

Introduction

Spectroscopists are often faced with the challenge of resolving the contributions to a highly congested spectrum from the components of the mixture under study. In the gas phase, supersonic expansion cooling reduces the effects of hot bands and narrows individual transitions to the point where spectral contributions due to individual components of the mixture can often be resolved.[1] Resonance-enhanced multiphoton ionization[2] provides mass-resolved spectra, thereby separating the contributions to the spectrum from components of different mass. Despite these powerful tools, the push to study larger molecules and molecular clusters brings with it the increasing potential for overlapped spectra.

When the molecules themselves have conformational flexibility, the observed spectra are a weighted sum of spectra due to the individual conformational isomers, even when mass resolved.[3,4] Similarly, as the complexity of the molecular components of a molecular cluster increases, the possibility for forming structural isomers grows. In both circumstances, an important goal is to determine the infrared and ultraviolet spectral signatures of each conformational or structural isomer free from interference from the others present in the sample.[3−9]

To accomplish this goal, UV−UV[10] and IR−UV[11,12] double resonance methods have been employed. In the former case, a high-powered UV hole-burn laser is used to modulate the ground state zero-point level population of a single conformational isomer. A second UV probe laser, delayed from the first, is then tuned through the spectrum while the difference in signal between successive shots from the probe laser is detected. All UV transitions that share the same ground state level as that involved in the hole-burn transition appear in the UV−UV hole-burning spectrum, thereby providing a single-conformation UV spectrum. In the IR−UV analog (sometimes called resonant ion-dip infrared spectroscopy, RIDIRS)[12] the UV probe laser is fixed on a particular transition due to a single conformational isomer, and the IR laser, preceding the UV probe, is tuned through the infrared region of interest. When IR transitions occur that arise from the same ground state zero-point level detected by the probe laser, population is removed from that level, partially depleting the signal from the probe laser. The single-conformation infrared spectrum is then recorded as a difference signal between successive probe laser pulses with and without the IR laser present. Alternatively, if the IR laser is fixed and the UV laser is tuned, the resulting IR−UV hole-burning spectrum can provide the single-conformation UV spectrum if the IR transition is due to a single conformation.

A necessary prerequisite for these methods is that the UV probe laser must selectively monitor the signal from a single conformational isomer. This condition is increasingly hard to achieve as the size and complexity of the molecule grows. If conformational differences are far from the UV chromophore used for detection, the electronic spectra of the conformers may be strongly overlapped with one another. Alternatively, the ultraviolet transitions due to one or more of the contributing conformational or structural isomers may be inherently broad, making it impossible to selectively probe a single one. In molecular clusters, fragmentation following photoionization can bring signal from higher clusters into the mass channel of interest, bringing contributions to the ion signal at any given UV wavelength from more than one sized cluster. In any of these circumstances, it then becomes difficult to take full advantage of the infrared spectra obtained via IR−UV double resonance, because there remains uncertainty in both the number of conformations or cluster contributions and which IR transitions belong together.

In this Letter, we present a triple resonance method, IR−IR−UV hole-burning, which provides conformation-specific IR spectra even when electronic spectra are too closely overlapped to cleanly resolve IR spectra via double resonance methods. The impetus for developing this method was the observation of more than the expected number of OH and OD stretch transitions in single H_2O and HDO complexes with a crown ether, 4′-aminobenzo-15-crown-5 (ABC). The implementation

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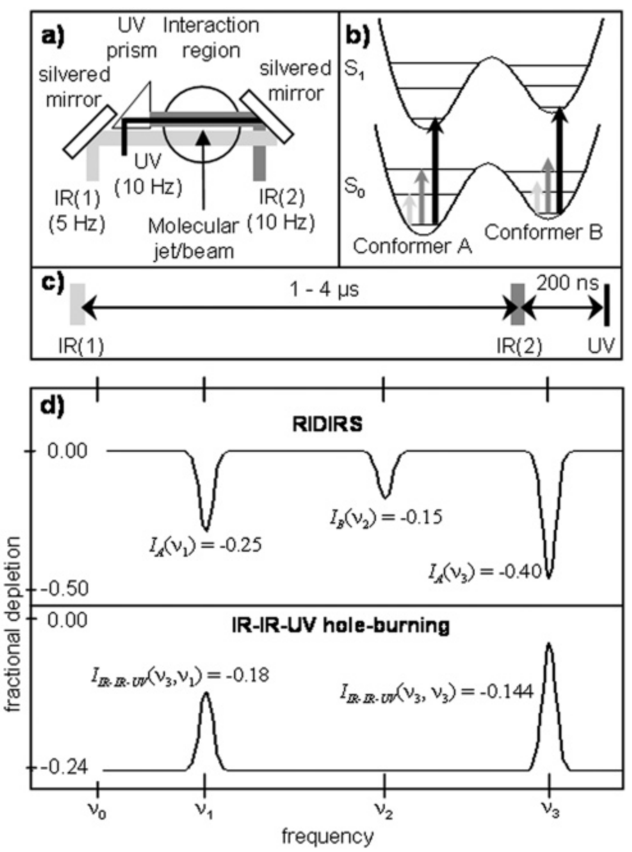

Figure 1. (a) Spatial arrangement of lasers. (b) Energy level diagram presenting the transition scheme of the experiment. (c) Temporal arrangement of lasers. (d) Example RIDIR and IR−IR−UV hole-burning spectra.

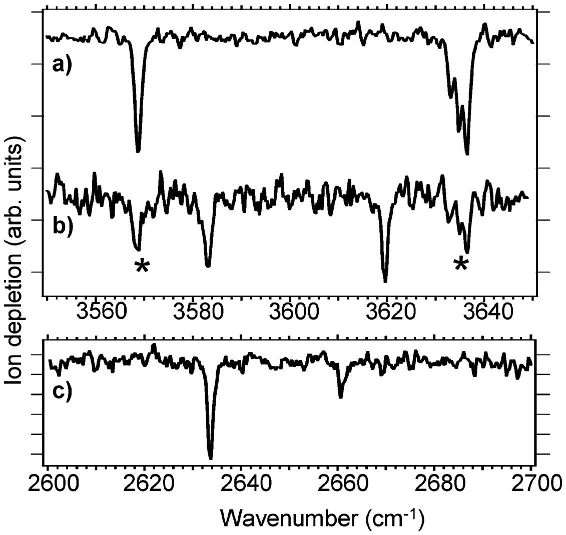

Figure 2. RIDIR spectra of (a) ABC−H_2O, (b) ABC−HDO in the OH stretch region, and (c) ABC−HDO in the OD stretch region.

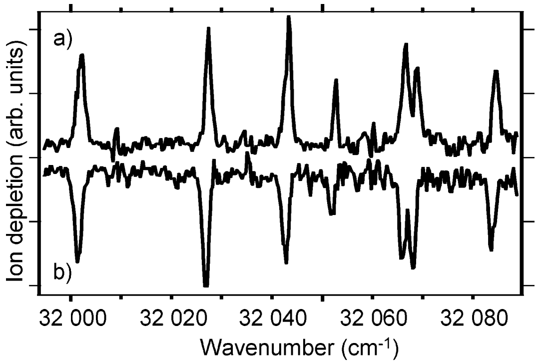

Figure 3. IR−UV hole-burning spectra of ABC−HDO with IR laser fixed at (a) 3620.0 cm^{-1} and (b) 3582.6 cm^{-1}. Spectra are presented as mirrors to demonstrate overlap of electronic spectra.

of this method allowed us not only to determine that two conformations exist for the ABC−HDO complex but also to exclude the possibility that a closely spaced triplet of transitions observed in ABC−H_2O arises from tunneling splitting.

Experimental Methods

ABC was used as supplied (Sigma Aldrich, 97% purity). The experimental apparatus has been previously described.[13] Briefly, the crown ether of interest was introduced into the chamber by passing the buffer gas, a 70% Ne/30% He mixture at a pressure of 2 bar, over the heated (145 °C) sample reservoir and through a pulsed valve (Parker General Valve Series 9, 0.4 mm orifice, 20 Hz). ABC−H_2O and ABC−HDO clusters were produced by splitting off 15% of the buffer gas flow and allowing it to flow through a room-temperature reservoir containing either pure H_2O or a 1:1 mixture of D_2O and H_2O before recombining with the main gas flow and passing through the heated sample reservoir.

The UV laser source was the doubled output of an Nd:YAG (Continuum 7000 series) pumped dye laser (Lambda-Physik Scanmate). Mass-resolved, resonance-enhanced two-photon ionization (R2PI) was used as the detection scheme. Tunable infrared radiation from 2600 to 3750 cm^{-1} was produced by two seeded Nd:YAG pumped parametric converters (LaserVision), each with typical IR laser powers of 1−5 mJ/pulse. IR spectra were obtained via resonant ion dip infrared spectroscopy (RIDIRS).[11,12] The IR and probe UV lasers were counterpropagated, spatially overlapped, and temporally separated so that the IR laser preceded the probe by 200 ns. The UV probe laser wavelength was fixed on the S_0−S_1 origin of the ABC−water complex of interest, monitoring the requisite mass channel in the time-of-flight mass spectrum. IR transitions arising from the same ground state level(s) as the UV probe produce depletions in the ion signal of the probe laser. Active baseline subtraction was used to record the difference between IR laser "on" or "off".

IR−IR−UV Hole-Burning

Operationally, the experimental procedure can be viewed as a modification of resonant ion dip infrared (RIDIR) or fluorescence dip infrared (FDIR) spectroscopies.[11,12] The first IR laser, IR(1), is fixed on a transition observed in the IR spectrum, the second IR laser, IR(2), is scanned, and the UV laser is fixed on the overlapped S_0−S_1 origins.

The optical train, energy level scheme, and temporal laser arrangement implemented for IR−IR−UV hole-burning is presented in Figure 1a−c. The IR(2) and UV lasers were counterpropagated, spatially overlapped, temporally separated so that IR(2) precedes the UV by 200 ns, and operated at 10 Hz. IR(1) was copropagated with the UV laser but displaced to intersect the molecular beam 1−3 mm upstream from the UV laser. This arrangement resulted in a temporal separation of 1−4 μs between IR(1) and IR(2). IR(1) was operated at 5 Hz and IR−IR−UV hole-burning spectra were recorded by monitoring, via active baseline subtraction, the difference in ion signal from the IR(2)/UV probe laser combination with the IR(1) hole-burning laser "on" versus "off".

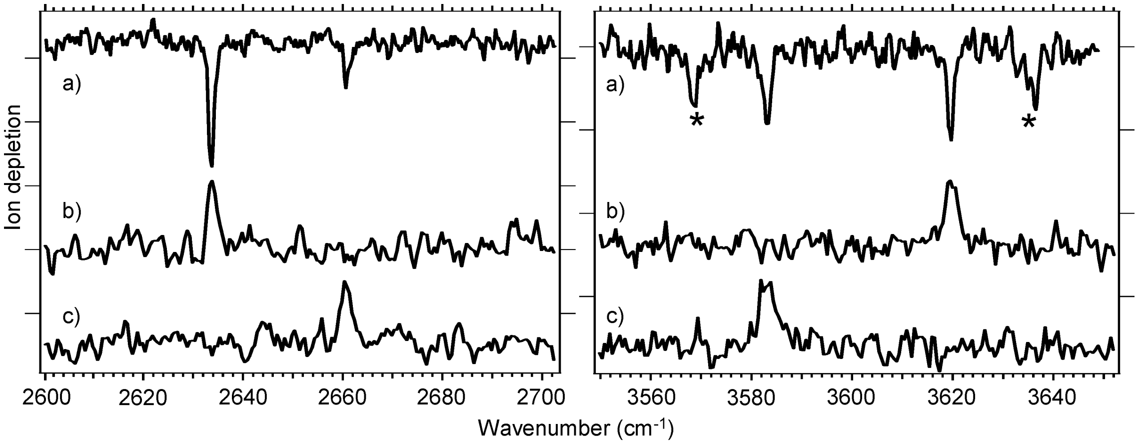

Figure 4. (a) RIDIR and (b, c) IR−IR−UV hole-burning spectra of ABC−HDO. The OD stretch bands were used as the IR hole-burning transitions, with 2633.7 and 2660.7 cm^{-1} used to obtain the spectra in (b) and (c), respectively. Transitions marked with asterisks are due to ABC−H_2O + 1 amu from either ^{13}C or NHD (see text).

When reported as a fractional depletion, the intensity of a transition in the IR−IR−UV hole-burning spectrum due to IR-(2) at frequency ν with IR(1) fixed on a transition at ν' is given by

$$I_{\mathrm{IR-IR-UV}}(\nu',\nu) = \sum_i f_i \cdot I_i^{(1)}(\nu') \cdot (I_i^{(2)}(\nu) + 1) \qquad (1)$$

where f_i is the fraction of the signal at the UV probe wavelength ascribable to species i. $I_i^{(1)}(\nu')$ and $I_i^{(2)}(\nu)$ are the fractional depletions of species i created when IR(1) and IR(2) have frequencies ν' and ν, respectively. In eq 1, the only nonzero terms that will contribute to the sum are those where $I_i^{(1)}(\nu') \neq 0$. Thus by fixing IR(1) on a transition, ν', exclusively due to species j, only transitions due to species j appear in the IR−IR−UV spectrum, simplifying eq 1 to eq 2

$$I_{\mathrm{IR-IR-UV}}(\nu',\nu) = f_j \cdot I_j^{(1)}(\nu') \cdot (I_j^{(2)}(\nu) + 1) \qquad (2)$$

When IR(2) is nonresonant, $I_j^{(2)}(\nu) = 0$, and $I_{IR-\mathrm{IR-UV}}(\nu',\nu)$ is a constant depletion of size $f_j I_j(\nu')$. When an infrared transition due to species j is encountered by IR(2), it reduces the UV signal due to species j on every UV pulse (because IR(2) is pulsed at the repetition rate of the UV laser), and thereby modulates the difference signal created by IR(1) by $(I_j^{(2)}(\nu) + 1)$. The net effect is to create a gain at ν built off the constant depletion due to IR(1). Figure 1d illustrates the observed spectrum for a model case in which the ion signal arises from overlap in the UV such that 60% of the UV-induced signal is from A and 40% from B, with equal IR laser powers.

Results and Discussion

Figure 2a presents the RIDIR spectrum of ABC−H_2O in the OH stretch region, with the ultraviolet laser fixed at 312.51 nm, the S_0−S_1 origin transition for the complex, while monitoring the ABC−H_2O^+ mass channel. In Figure 2b,c the corresponding spectra at the same ultraviolet wavelength are recorded in the (m + 1) mass channel, with a 50% H_2O/50% D_2O mixture in the expansion. The ABC−H_2O spectrum shows a single OH stretch transition at 3568.7 cm^{-1}, ascribable to the symmetric stretch of H_2O in the complex. However, in the antisymmetric stretch region, there is a triplet of transitions rather than the single transition anticipated. In ABC−HDO (Figure 2b,c), there are a total of two OD stretch and four OH stretch transitions, when the expectation is that the complex should possess only one of each. The OH stretch transitions marked by asterisks in Figure 2b are ascribable to an ABC−H_2O complex appearing in this mass channel due to overlap in the R2PI spectrum from an H_2O complex with a ^{13}C or NHD substitution, leaving two OH and two OD stretch transitions unaccounted for.

Figure 3 shows two IR−UV ABC−HDO hole-burning spectra recorded with the IR hole-burning laser fixed at 3620.0 cm^{-1} (Figure 3a) and 3582.6 cm^{-1} (Figure 3b), respectively, while the UV laser is tuned through the UV transitions due to ABC−HDO. The two UV spectra are nearly identical, indicating that if two distinct conformers are responsible for the two OD and two OH stretch transitions, they possess very similar UV spectra that are almost entirely overlapped with one another.

The IR−IR−UV hole-burning spectra presented in Figure 4b,c prove that the ABC−HDO transitions are due to two distinct conformations. Furthermore, the spectrum obtained with IR(1) fixed at 2633.7 cm^{-1} (Figure 4b) indicates that this transition, shifted further from the free OD stretch at 2727 cm^{-1},[14] is associated with the less shifted OH stretch (at 3620.0 cm^{-1}, compared to the free OH stretch at 3707 cm^{-1}).[14] In the other conformer, the less shifted OD stretch accompanies the more strongly H-bonded OH stretch at 3582.6 cm^{-1}. Although the focus of a future publication,[15] these results point toward conformations where the OH and OD H-bonds involve inequivalent acceptor sites, thereby forming H-bonds of slightly different strengths, as reflected in the OH/OD stretch frequencies. The essential difference between the two conformations, then, is the orientation of the HDO molecule in the complex.

Finally, analogous IR−IR−UV scans of the triplet of transitions in the antisymmetric OH stretch region of ABC−H_2O (not shown) reveal that all three transitions arise from the same lower level of the same complex. As a result, the triplet of transitions cannot arise from tunneling splittings due to different ground state tunneling levels.[15]

Conclusions

We have reported an experimental procedure for obtaining conformation-specific IR spectra that can be used successfully even in the face of extensive overlap in the ultraviolet spectrum. The results of this experiment unambiguously proved that in the case of the ABC−HDO complex, the observed OD and OH stretch transitions were due to two separate conformations, and proved which transition went with which. The method will be applicable in any circumstance where the ultraviolet spectrum has contributions from more than one species and can test the extent and importance of this interference. Furthermore, even within a single complex, the method can test whether observed infrared transitions arise from the same ground state level or not, serving as a diagnostic that discriminates between splittings occurring in the lower or upper state(s) associated with the observed transitions. Finally, one can envision circumstances where the UV detection step is inherently non conformation-specific, where the IR−IR−UV scheme could divide an IR spectrum into its conformation-specific contributions.

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