

## COMMUNICATIONS

## The hydrogen-bonding topologies of indole-(water)<sub>n</sub> clusters from resonant ion-dip infrared spectroscopy

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A combination of resonant two-photon ionization, infrared-ultraviolet hole burning, and resonant ion-dip infrared spectroscopies are used to assign and selectively probe the hydrogen bonding topologies of indole-(water)<sub>n</sub> clusters with  $n=1,2$ . The indole-(water)<sub>1</sub> complex is confirmed to possess the N-H···OH<sub>2</sub> structure surmised from previous studies. However, the bands in the ultraviolet previously assigned to a  $\pi$  H-bound indole-water complex are shown to be due instead to the indole-(water)<sub>2</sub> cluster in which the water dimer forms a H-bonded bridge between the N-H and aromatic  $\pi$  clouds of indole. The implications of this reassignment for our understanding of the influence of H-bonding solvents on indole's fluorescence properties are discussed. © 1998 American Institute of Physics. [S0021-9606(98)02909-2]

Indole is the ultraviolet chromophore of the aromatic amino acid tryptophan, which has long served as a fluorescent probe of local structures and dynamics of proteins.<sup>1</sup> Recent studies of gas-phase indole-(solvent)<sub>n</sub> clusters have sought to understand the solvent-dependent photophysics of indole through characterizing the spectroscopy and photophysics of clusters of known composition and indole-solvent binding.<sup>2-7</sup> In the absence of solvent, the <sup>1</sup>L<sub>b</sub> origin of indole is known<sup>8</sup> to lie below <sup>1</sup>L<sub>a</sub> by about 1400 cm<sup>-1</sup>. However, polar solvents interacting with the  $\pi$  cloud are thought to selectively stabilize <sup>1</sup>L<sub>a</sub> while interaction with the N-H group shows no such preference.<sup>2,8-15</sup> Accompanying the stabilization of <sup>1</sup>L<sub>a</sub> in the excited state is a redshift and broadening of the fluorescence, while unshifted emission is attributed to <sup>1</sup>L<sub>b</sub>.<sup>8,12,13</sup>

Studies of indole-(water)<sub>n</sub> clusters (hereafter shortened to Ind-W<sub>n</sub>) have played a prominent role in these studies due to the unrivaled importance of water as nature's solvent. This prominence was heightened by the intriguing identification of two structural isomers of the Ind-W<sub>1</sub> isomer. Using resonant two-photon ionization (R2PI) spectroscopy, Wallace and co-workers<sup>16</sup> first identified transitions due to two distinct species in the Ind-W<sub>1</sub><sup>+</sup> mass channel. One species, with the S<sub>1</sub>←S<sub>0</sub> origin located 132 cm<sup>-1</sup> to the red of the indole monomer origin, has a strong origin and relatively little intermolecular Franck-Condon activity, indicating little change in the geometry following electronic excitation. A second, weaker origin is located at -452 cm<sup>-1</sup>. It possesses long Franck-Condon progressions in intermolecular modes, indicative of a large structural change upon electronic excitation.

Previous work has reasoned for the structure of these two species by comparing their spectral features to those of

previously assigned species in which indole acts either as H-bond donor (through the N-H group) or acceptor (through the  $\pi$  cloud).<sup>2,13,16</sup> On this basis, the -132 cm<sup>-1</sup> origin was assigned as the N-H···OH<sub>2</sub> isomer of Ind-W<sub>1</sub> while the far redshifted species was assigned to a second Ind-W<sub>1</sub> structure in which the water molecule is  $\pi$ -hydrogen bound to the indole  $\pi$  cloud.<sup>13</sup> The two conformers of Ind-W<sub>1</sub> provide an opportunity to study the photophysical properties of the two binding sites for water free of interference from one another. Several ensuing studies did precisely that.<sup>2,3,12,13</sup>

The present study returns to the fundamental issue of the assignment of the two conformational isomers of Ind-W<sub>1</sub>. The technique of resonant ion-dip infrared spectroscopy (RIDIRS) is used to record IR spectra of the two species in the hydride stretch region free of interference from one another. The frequencies and intensities of the NH and OH stretch fundamentals provide a sensitive probe of the cluster composition and hydrogen-bonding topology of the clusters.

A detailed description of the experimental apparatus and the methods used in these studies, including R2PI, RIDIR, and hole-burning spectra, is available elsewhere.<sup>17,18</sup> Figure 1 presents one-color, mass-selected R2PI spectra in the Ind<sup>+</sup> [Fig. 1(a)] and Ind-W<sub>1</sub><sup>+</sup> [Fig. 1(b)] mass channels. The indole monomer possesses an S<sub>1</sub>←S<sub>0</sub> origin at 35 241 cm<sup>-1</sup>, with several weaker vibronic transitions built off this origin beginning about 250 cm<sup>-1</sup> above the origin. In the Ind-W<sub>1</sub><sup>+</sup> mass channel [Fig. 1(b)], the strong origin at 35 109 cm<sup>-1</sup> (corresponding to a -132 cm<sup>-1</sup> frequency shift) is that previously assigned to the N-H···OH<sub>2</sub>, Ind-W<sub>1</sub> complex. In keeping with previous work,<sup>2,12,13,16</sup> a second origin with a much larger redshift (-452 cm<sup>-1</sup>) also appears in this mass channel, containing two long, intermingled progressions in an intermolecular mode of 34 cm<sup>-1</sup>.

RIDIR spectra have been recorded for the indole monomer [Fig. 2(a)] and the two species present in the Ind-W<sub>1</sub><sup>+</sup> mass channel [Figs. 2(b) and 2(c)]. Table I summarizes the

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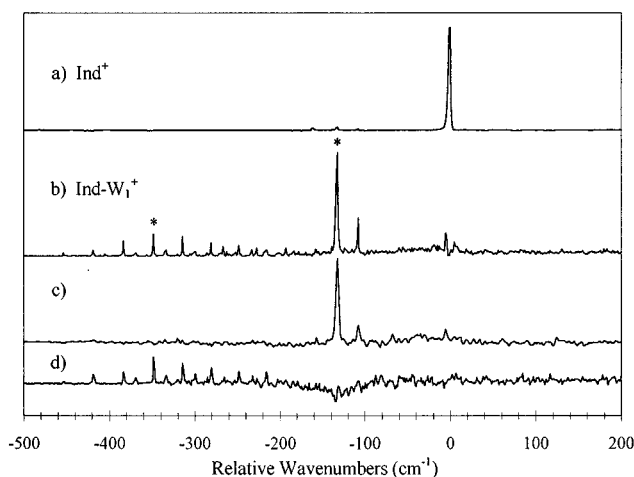


FIG. 1. One-color resonant two-photon ionization scans in the  $S_1 \leftarrow S_0$  origin region of indole, monitoring the  $\text{Ind}^+$  (a) and  $\text{Ind-W}_1^+$  (b) mass channels. The zero of the relative frequency scale is the origin of the indole monomer at  $35\,241\text{ cm}^{-1}$ . (c) and (d) IR-UV hole-burning spectra with the IR hole-burning laser tuned to  $3439\text{ cm}^{-1}$  transition of Fig. 2(b) and the  $3488\text{ cm}^{-1}$  transition of Fig. 2(c), respectively. In IR-UV hole burning, the IR source is fixed to a particular IR absorption of a given species and the UV is scanned. All UV transitions from this species will show a difference in ion intensity with and without the IR laser present.

results. The indole monomer RIDIR spectrum possesses a single strong transition at  $3524\text{ cm}^{-1}$  due to the N-H stretch fundamental which serves as a reference for the indole- $\text{W}_n$  cluster transitions. Weak transitions of the C-H stretch fundamentals are also observed near  $3070\text{ cm}^{-1}$ .

Figure 2(b) shows a RIDIR scan taken with the R2PI laser fixed at the  $\text{Ind-W}_1$  origin  $132\text{ cm}^{-1}$  red of the indole monomer origin. Three hydride stretch fundamentals are evi-

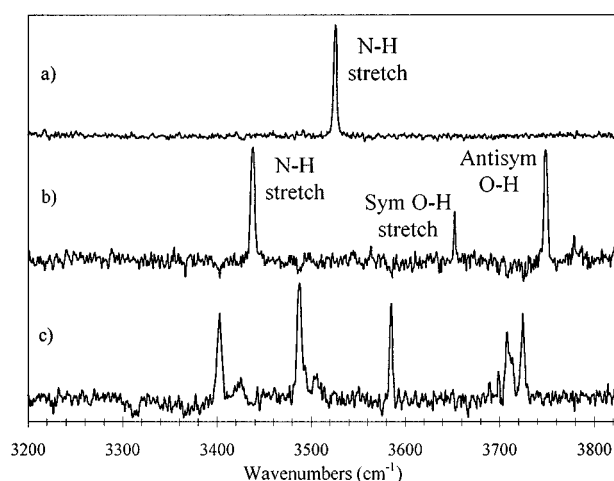


FIG. 2. Resonant ion-dip infrared spectra monitoring (a) the  $\text{Ind}^+$  mass channel with the R2PI laser tuned to the indole monomer origin in Fig. 1(a). (b) and (c) Corresponding RIDIR spectra monitoring the transitions marked by asterisks at  $-132$  and  $-346\text{ cm}^{-1}$  in the  $\text{Ind-W}_1^+$  mass channel of Fig. 1(b), respectively. In resonant ion-dip infrared spectroscopy (RIDIRS) the IR spectrum of a specific species is recorded by fixing the R2PI laser to a particular UV transition in a given mass channel, and the IR spectrum is recorded as ion depletions induced by the  $\text{LiNbO}_3$  optical parametric oscillator ( $1.5\text{ cm}^{-1}$  resolution), here using active baseline subtraction.

dent at  $3750$ ,  $3654$ , and  $3439\text{ cm}^{-1}$ . The spectrum bears all the expected signatures of a 1:1 complex in which indole's N-H group acts as H-bond donor to the water molecule. As H-bond acceptor, the water molecule's O-H stretch fundamentals at  $3750$  and  $3654\text{ cm}^{-1}$  appear close to the corresponding transitions of the free water monomer ( $3756$  and  $3657\text{ cm}^{-1}$ ). The relative intensities also mimic those in the water monomer. Due to the involvement of the N-H group

TABLE I. Comparison of experimental and calculated vibrational frequencies and frequency shifts in wave numbers of indole monomer and indole-(water) $_n$  clusters with  $n=1,2$ .

Species	Vibrational frequency <sup>a</sup>		Freq. shift <sup>b</sup>		Freq. shift <sup>c</sup>		Assignment
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	
Indole	3526	3668.4	-180	-121	0 N-H	0 N-H	N-H stretch
Indole- $\text{W}_1$	3750	3851.3	+44	+62	-6 O-H AS	0 O-H AS	Acceptor water antisym. stretch
	3654	3733.8	-53	-56	-3 O-H SS	+7 O-H SS	Acceptor water sym. stretch
Ind- $\text{W}_2$ (A)	3439	3558.4	-267	-231	-87 N-H	-110 N-H	N-H stretch
	3725	3824.2	+19	+35			Free O-H stretch
	3709	3810.0	+2	+21	-48 O-H AS	-41 O-H AS	$\pi$ bound water antisym. stretch
	3585	3656.7	-121	-133	-73 O-H SS	-70 O-H SS	$\pi$ bound water sym. stretch
Ind- $\text{W}_2$ (B)	3488	3526.4	-218	-273			H-bonded O-H/N-H
	3402	3492.7	-304	-297	-124 N-H	-176 N-H	H-bonded N-H/O-H
		3820.6		+31			Free OH stretch
		3815.6		+26		-36 O-H AS	$\pi$ bound water AS
	3671.7		-118		-55 O-H SS	$\pi$ bound water SS	
	3528.9		-261				H-bonded O-H/N-H
	3476.7		-313			-192 N-H	H-bonded N-H/O-H

<sup>a</sup>Calculated using DFT Becke3LYP 6-31+G\*(5d).

<sup>b</sup>Vibrational frequency shift relative to the mean of the symmetric and antisymmetric stretch fundamentals of water monomer ( $3706.5\text{ cm}^{-1}$  experimentally,  $3789.6\text{ cm}^{-1}$  from calculation).

<sup>c</sup>Vibrational frequency shift relative to the indicated mode: N-H=N-H stretch of indole monomer; O-H AS=the antisymmetric stretch of water monomer; O-H SS=the symmetric stretch of water monomer.

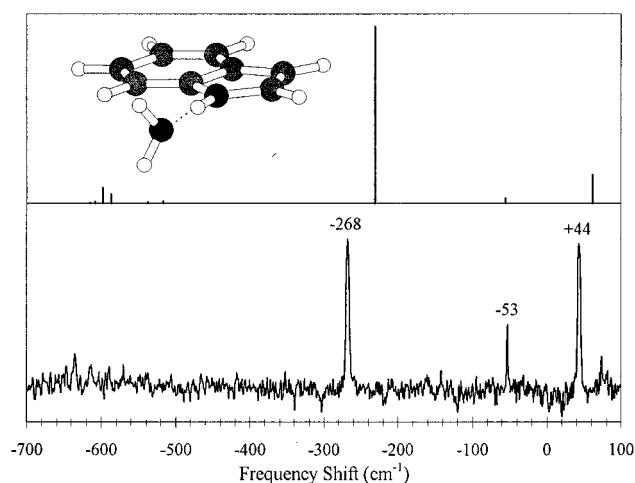


FIG. 3. Comparison of Ind- $W_1$  RIDIR spectrum with the calculated harmonic vibrational frequency shifts and infrared intensities calculated for the Ind- $W_1$  structure shown as an inset. This structure is the global minimum calculated for Ind- $W_1$ . The zero of the relative wave number scale is the average of the O-H stretches of the water monomer ( $3706\text{ cm}^{-1}$  for experiment and  $3789\text{ cm}^{-1}$  for the calculated spectrum).

in a H-bond with water, the N-H stretch fundamental is shifted  $85\text{ cm}^{-1}$  lower in frequency than the bare indole N-H stretch. This frequency shift is consistent with that found for other N-H $\cdots$ O hydrogen bonds.<sup>19</sup>

The spectrum presented in Fig. 2(c) is a RIDIR scan taken with the R2PI laser fixed to the peak in the long, red-shifted Franck-Condon progression with largest intensity ( $-346\text{ cm}^{-1}$ ). Five strong transitions appear in the RIDIR spectrum, consistent with an assignment as an Ind- $W_2$  cluster (one N-H, four O-H) rather than Ind- $W_1$  (one N-H, two O-H).

With the RIDIR spectra in hand, IR-UV hole-burning spectra were then recorded to determine if all UV transitions belong to one of these two species. As can be seen from Figs. 1(c) and 1(d), the R2PI spectrum cleanly divides into two constituent parts under IR hole burning at  $3439$  and  $3488\text{ cm}^{-1}$ , respectively. Thus there are only two species with significant population appearing in the Ind- $W_1^+$  mass channel.<sup>20</sup> The source of the broad ion gain signal centered on  $35109\text{ cm}^{-1}$  in Fig. 1(d) is probably due to larger Ind- $W_n$  clusters which fragment more efficiently into the Ind- $W_1^+$  mass channel after being vibrationally excited as neutrals.

As an aid in the analysis and assignment of the RIDIR spectra, density functional theory (DFT) calculations have been carried out using the Becke-3LYP functional<sup>21,22</sup> with a  $6-31+G^*(5d)$ <sup>23,24</sup> basis set. The fully optimized structures, binding energies, and harmonic vibrational frequencies have been computed for indole, indole- $W_1$ , and two isomers of indole- $W_2$  (Table I).

A comparison is made in Fig. 3 between the experimental and calculated IR spectra of the Ind- $W_1$  complex in the C-H and O-H stretch regions. As anticipated, the lowest energy structure calculated for Ind- $W_1$  is that shown in the inset of Fig. 3, in which the N-H hydrogen bond donates to a lone pair of the water molecule, directing the two free

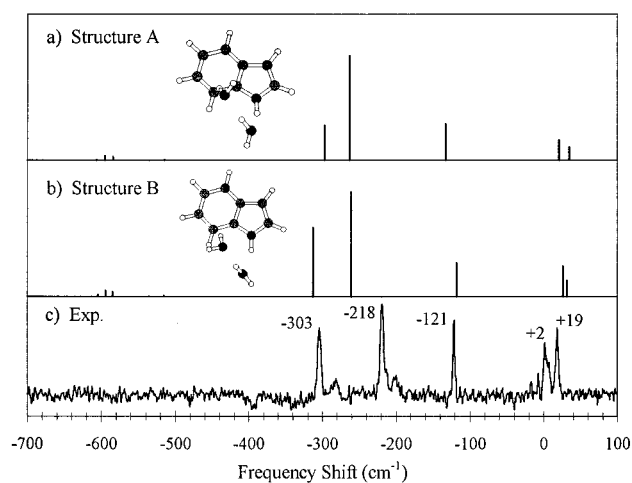


FIG. 4. Comparison of Ind- $W_2$  RIDIR spectrum (c) with the harmonic vibrational frequency shifts and infrared intensities calculated for the Ind- $W_2$  structures shown as insets. Structure A is calculated to be  $0.7\text{ kcal/mol}$  more strongly bound than structure B. The zero of the relative wave number scale is the average of the O-H stretches of the water monomer ( $3706\text{ cm}^{-1}$  for experiment and  $3789\text{ cm}^{-1}$  for the calculated spectrum).

hydrogens out-of-plane. The match-up between experiment and calculation is sufficiently good to confirm our assignment of the Ind- $W_1$  complex as a N-H $\cdots$ OH<sub>2</sub> structure.

The two lowest energy structures calculated for Ind- $W_2$  are shown as insets in Fig. 4. The global minimum is structure A, with structure B  $0.7\text{ kcal/mol}$  less strongly bound. Both structures incorporate the indole N-H group in a N-H $\cdots$ O hydrogen bond similar to that in indole- $W_1$ . The second water molecule accepts a H bond from the first, but also seeks to optimize its interaction with the indole  $\pi$  cloud. The water dimer thus forms a bridge between the indole N-H group and the  $\pi$  cloud on the phenyl ring of indole. The two structures differ in the lone pair of the first oxygen used to accept the N-H group from indole.

Figure 4 presents a comparison between the calculated harmonic vibrational frequency shifts for structures A and B [Figs. 4(a) and 4(b), respectively] and experiment [Fig. 4(c)]. The close one-for-one correspondence argues persuasively for the N-H $\cdots$ O-H $\cdots$ OH<sub>2</sub> $\cdots\pi$  structure. The RIDIR spectrum cannot distinguish between the two isomers, though the calculated preference for A over B would suggest it as the more likely possibility.

The close match-up between experiment and calculation provides some insight into the nature of the hydride stretch modes responsible for the observed absorptions. The highest frequency mode is calculated to be almost entirely localized on the free OH of the N-H bound water molecule. The bands at  $+2$  and  $-121\text{ cm}^{-1}$  are the OH stretches on the  $\pi$  bound water. Its weak interactions with the  $\pi$  cloud, especially in its constrained geometry, produces OH stretch modes which are still largely symmetric and antisymmetric stretches, as in the free water monomer. The frequency shifts relative to these modes in the monomer ( $3657$  and  $3756\text{ cm}^{-1}$ ) are  $-48$  and  $-73\text{ cm}^{-1}$ , respectively, similar in magnitude to the corresponding modes of the  $\pi$  bound water molecule in benzene-(water)<sub>2</sub>.<sup>25,26</sup> The transitions at  $-218$

and  $-304\text{ cm}^{-1}$  are mixtures of N-H and H-bonded O-H stretches involving the bonds which compose the H-bonded bridge.

The major result of this work is that the species previously assigned as a  $\pi$ -interacting, Ind- $W_1$  complex is actually an Ind- $W_2$  cluster in which the water dimer bridges between the N-H and  $\pi$  clouds of indole. The efficient loss of a single water molecule from Ind- $W_2$  upon photoionization is reminiscent of the similar behavior seen in benzene-(solvent) $_n$  clusters.<sup>17,27,28</sup> As there, the efficient fragmentation arises from a neutral solvent cluster geometry which is highly unfavorable for the ionized cluster. The Franck-Condon factors in the ion $\leftarrow S_1$  step are then poor to regions of the ionic cluster's potential energy surface below the fragmentation threshold, hindering two-color R2PI studies<sup>16</sup> which intend to suppress such fragmentation. What is particularly insidious about the present example is that the indole- $W_1$  cluster experiences little fragmentation, and appears primarily in the parent Ind- $W_1^+$  mass channel along with the transitions due to Ind- $W_2$ . This is because in Ind- $W_1$ , the N-H $\cdots$ OH $_2$  structure is not changed significantly upon photoionization.

The reassignment of the  $-452\text{ cm}^{-1} S_1\leftarrow S_0$  transitions to Ind- $W_2$  necessitates a reevaluation of the site-specific solvation effects of water on indole. First, the Ind- $W_1$  complex no longer provides a simple, clear example of the effects of the binding site of water on the spectral and photophysical effects of indole since only the N-H bound isomer has been observed experimentally. Second, the large redshift of the  $S_1\leftarrow S_0$  origin from  $-132\text{ cm}^{-1}$  in Ind- $W_1$  to  $-452\text{ cm}^{-1}$  in Ind- $W_2$  is probably due to a cooperative strengthening of the N-H $\cdots$ O H bond in the presence of the second water molecule rather than a solvent-dependent lowering of the  $^1L_a$  state. Third, the long intermolecular progressions which suggested a  $\pi$  H-binding site are probably still due to such binding by the strained H-bonded bridge formed in Ind- $W_2$ . Given the tenuous nature of this strained bridge, it is likely that  $\pi\text{-}\pi^*$  electronic excitation will change the interaction of the  $\pi$  bound water with the  $\pi$  cloud, resulting in long progressions in intermolecular vibrations which will reorient the water dimer bridge in the  $S_1$  state. Fourth, the computed structure for Ind- $W_2$  predicts that the water dimer interacts with the phenyl ring rather than the pyrrole ring of indole. It is the pyrrole ring that has been implicated as important for  $^1L_a$  lowering in tryptophan and its derivatives. Calculations on the  $\pi$  bound isomer of Ind- $W_1$  show that water preferentially binds to the pyrrole ring. In Ind- $W_2$  this site may not be accessible given the geometric constraints of the water dimer bridge. Finally, the formation of H-bonded water bridges between H-bonding sites on larger solute molecules may be a regular feature of large molecule-(water) $_n$  clusters. The role such bridges play in providing a conduit for proton or electron transfer, and the strength and dynamical coupling

along such bridges will be interesting subjects for future studies.

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