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Computational and photoelectron spectroscopic study of the dipole-bound anions, indole(H$_2$O)$_{1,2}^-$

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We report our joint computational and anion photoelectron spectroscopic study of indole-water cluster anions, indole(H$_2$O)$_{1,2}^-$. The photoelectron spectra of both cluster anions show the characteristics of dipole-bound anions, and this is confirmed by our theoretical computations. The experimentally determined vertical electron detachment (VDE) energies for indole(H$_2$O)$_1^-$ and indole(H$_2$O)$_2^-$ are 144 meV and 251 meV, respectively. The corresponding theoretically determined VDE values for indole(H$_2$O)$_1^-$ and indole(H$_2$O)$_2^-$ are 124 meV and 255 meV, respectively. The vibrational features in the photoelectron spectra of these cluster anions are assigned as the vibrations of the water molecule. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4954937]

INTRODUCTION

The organic molecule-water interaction is of fundamental interest in chemistry. In previous papers, we reported our work on naphthalene-water, pyrimidine-water, and pyridine-water systems.[1,2] The cluster anions in the above three organic molecule-(H$_2$O)$_n^-$ systems were characterized as covalent anions. All the spectra are relatively broad (with a full-width-half-maxima of about 250 meV), which is typical for covalent cluster anions. Likewise, the spectral shift between adjacent-sized hydrated cluster anions, i.e., between n and n − 1, is relatively large (∼300 meV) compared to sequential shifts typically seen in non-hydrated systems. In each of these cases, the excess electron was bound to the organic molecule as evidenced by the fact that the cluster anion's photoelectron spectrum exhibited the vibrational frequencies of their respective organic molecules. This solvation process of organic molecules has been experimentally investigated by several groups. Kondow and co-workers studied pyridine-water cluster anions using mass spectrometry;[3] Desfrancois and Schermann *et al.*,[4] used Rydberg electron transfer; and both Weinkauf and co-workers[5] and Bowen and co-workers[6] investigated the hydration of uracil anions using anion photoelectron spectroscopy.

In addition to forming covalent anions, molecules or complexes with dipole moments larger than 2.5 D can attract an excess electron, creating what is known as a dipole bound anion.[7–11] The photoelectron spectrum of a dipole-bound anion usually exhibits a sharp peak at a rather low electron binding energy, with a few low intensity features due to molecular vibrations in the system. Many dipole-bound anions have been studied, including those by us, e.g., (H$_2$O)$_2^-$, (HF)$_2^-$,[12] uracil$^-$, thymine$^-$,[13] and glycine(H$_2$O)$_6^-$.[14] Also both, Desfrancois and Schermann[15] and Hammer and Compton[16] have studied dipole-bound, via Rydberg electron transfer. Gutowski[17] and Adamowicz[18–23] both performed theoretical calculations on various systems.

Indole is the ultraviolet chromophore of tryptophan, one of the essential amino acids. The interaction of indole with water is crucial for understanding the behavior of such molecules in aqueous environment. The vertical attachment energy (a.k.a. vertical electron affinity) of indole was measured to be −0.9 eV by electron transmission spectroscopy[24] and the dipole moment of indole is 2.1 D.[25] Clary *et al.* performed *ab initio* calculations on indole(H$_2$O)$_{1,2}$ neutral clusters.[26] Domcke *et al.* studied the photoinduced charge separation in indole-H$_2$O clusters using *ab initio* calculations.[27] Experimentally, Zwier and co-workers utilized resonant ion-dip infrared spectroscopy to investigate the hydrogen-bonding topologies of indole-H$_2$O clusters.[28,29] Schermann *et al.* also employed Rydberg electron transfer spectroscopy (RET) to study indole(H$_2$O)$_{0-3}^-$.[25] In the present contribution, we explore the structure and stability of multi-molecular dipole bound anion states of indole(H$_2$O)$_{1,2}^-$. The excess electron's role in binding to two and three polar molecules is studied both experimentally and theoretically which provides fresh insight into complex electron polar molecule interactions.

METHODS

Experimental

Indole-(H$_2$O)$_{1,2}^-$ was generated in a nozzle-ion source. Our negative ion photoelectron spectrometer has been described elsewhere.[30] Anions were formed in our supersonic expansion source. There, the mixture of indole and water was heated to approximately 70 °C and expanded together with argon gas through a 20 μm nozzle. Low energy electrons from a biased filament were injected into an expanding jet in the presence of a weak magnetic field. Once the anions

were mass-selected, photodetachment was accomplished with 2.54 eV (488 nm) photons from an intra-cavity argon ion laser. Photodetached electrons were analyzed with hemispherical electron energy analyzer with a typical resolution of about 25 meV. The well-known photoelectron spectra of O^- and NO^- were used for calibration.

Computational

All calculations were performed using the Gaussian 09 program package.[31] The search for stable structures of the neutral indole-$(H_2O)_1$ complex was performed with geometry optimization at the MP2/aug-cc-pVDZ level of theory. The standard aug-cc-pVDZ Gaussian basis set used in the calculations for the neutral system was augmented with additional diffuse orbitals in order to describe a dipole-bound state of an excess electron in the molecular ion. These additional orbitals include five diffuse sp shells with exponents equal to α, 3α, 9α, 27α, and 81α, and two additional d shells with exponents 3α and 27α, where α is an adjustable scaling parameter. This parameter was optimized by the minimization of the energy of the lowest unoccupied molecular orbital (LUMO) of the neutral system, which according to Koopmans' theorem approximates the system's vertical electron affinity. The standard aug-cc-pVDZ basis set augmented with the additional diffuse functions is herein referred to as aug-cc-pVDZ+X(α). In the first step the MP2/aug-cc-pVDZ+X(α) level of theory was employed to describe the electronic structure of the dipole-bound anion of the indole-water cluster and to perform its geometry optimization. The equilibrium geometry of the neutral complex was used as the initial geometry in the optimization of the dipole-bound anion of the complex, as the dipole-bound electron attachment is expected to have only a small effect on the geometry of the system.[21–23]

The calculations performed in this work of tiny electron bonding energies are challenging and require very careful attention to the convergence at all levels of theory used. When necessary the convergence criteria have been tightened to achieve the desired precision of the results. Also the calculations require unconventional basis sets that include very diffuse orbitals which are carefully optimized to describe the states of loosely bound electrons. As mentioned above, such an optimization is performed in this work.

For the indole-$(H_2O)_2^-$ anion complex, the search for stable structures involved more than one possible geometrical arrangements of the three molecules forming the complex. As all three molecules of indole-$(H_2O)_2$ have permanent dipole moments, the approach used to determine stable geometries of the dipole-bound indole-$(H_2O)_2^-$ anion involved taking equilibrium geometries of the dipole-bond anion formed by two of the three molecules and adding the third molecule to stabilize the anion. The two-molecule dipole-bound anions used in the procedure were the water-dimer anion and the indole-water dimer anion. To these two anions the third molecule being either a water molecule or an indole molecule was attached to form an indole-$(H_2O)_2^-$ anion. The third molecule was attached to the dipole-bound dimer anion either at the same side of the dipole-bound electron as the dimer or at

the opposite side. After the calculations of the indole-$(H_2O)_2^-$ anions were completed the structure of the anions were used as the initial geometries for the structure optimizations of the neutral complex. All structures converge, indicating that it is likely the global minimum on the indole-$(H_2O)_2$ potential energy surface.

The vertical electron detachment energies (VDEs) are direct observables in experimental anion photoelectron spectroscopy. VDE is defined as the energy of the neutral system minus the energy of the anion both determined at the equilibrium geometry of the anion. The adiabatic electron affinity (AEAs) is defined as the difference between the energies of the anion and the neutral system calculated at their respective equilibrium geometries. The vertical attachment energy (VAEs) is the difference between the energies of the anion and the neutral system calculated at the equilibrium geometry of the neutral. In this work the VDE, AEA, and VAE were calculated for both indole-$(H_2O)_1$ and indole-$(H_2O)_2$ complexes and their anions using the aug-cc-pVDZ+X(α) basis set and the HF, MP2, and CCSD levels of theory. Additionally, the somewhat smaller 6-31++G** basis set augmented with the extra X(α) diffuse functions was used to perform CCSD(T) level calculations and to estimate the contributions of the triple excitations to the VDE, AEA, and VEA. The triples contribution is calculated as a difference between the CCSD(T) and CCSD energies. Such an approach should be regarded as very approximate which in some cases may give unreliable results. Even in cases when the answer obtained with calculating the triple contribution with a smaller basis set looks physically correct, it may carry some significant error. When the CCSD(T) method is mentioned in the text, it refers to calculating the CCSD contribution with the aug-cc-pVDZ+X(α) basis set and the contribution of the triple excitations with the 6-31++G**+X(α) basis set.

RESULTS

Experimental

Figure 1 shows the anion photoelectron spectra of indole-$(H_2O)_1^-$ and indole-$(H_2O)_2^-$. Both spectra consist of a major, sharp peak at a quite low electron binding energy, and two small vibrational features at higher binding energies. Data extracted from our spectra are listed in Table I.

Peak **A** lies at 144 meV, with a full-width-half-maximum of about 40 meV. Peak **B** is at 251 meV, with a full-width-half-maximum of about 70 meV. We assign these two peaks as the origin of the transitions between the anions and their corresponding neutrals. Therefore, the vertical electron detachment energies the for indole$(H_2O)_1^-$ and indole$(H_2O)_2^-$ anions are 144 meV and 251 meV, respectively. The two small features (**a1** and **a2**, or **b1** and **b2**) in each spectrum are due to the vibrations of a water molecule. The two observable vibrational modes of water are H–O–H bending, with a frequency of 1595 cm^{-1}, and O–H stretching, with a frequency of 3652 cm^{-1}. Peak **a1** and **b1** belong to the H–O–H bending mode of water, while Peak **a2** and **b2** are due to the O–H stretching. In general, the vibrational features that appear in the photoelectron spectrum of a cluster dipole-bound anion
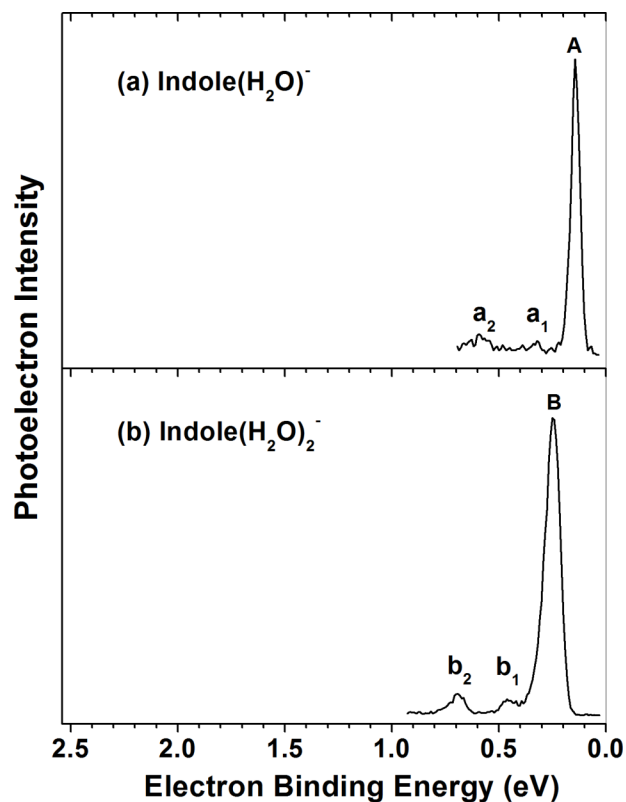
FIG. 1. Anion photoelectron spectra of (a) indole(H$_2$O)$_1^-$ and (b) indole(H$_2$O)$_2^-$, measured with 2.540 eV photons. Capital letters, "A" and "B," denote photodetachment transitions from the ground states of their respective cluster anions to the ground states of their corresponding neutral clusters, i.e., their origin transitions. The lower case letters, a$_1$, a$_2$, b$_1$, and b$_2$ are due to vibrational excitations (bends and stretches) of molecular water in both spectra.

are due to the vibrational modes of the sub-molecule in the cluster that is positioned closest to the excess dipole-bound electron.

Theoretical

Indole(H$_2$O)$_1^-$

The optimized geometry for the neutral indole-water complex was identified with a sufficient dipole moment to bind an excess electron (Figure 2, Table II). The dipole moment obtained at the MP2 level is equal to 4.314 D which significantly exceeds the theoretically determined threshold of 1.625 D[7,10,11] for the formation of a stable dipole-bound anion with a point dipole, as well as the practical threshold of

TABLE I. Experimentally determined electron affinities (AEA's), binding energies of the vibrational features, their corresponding frequencies, and assignments for indole(H$_2$O)$_1^-$ and indole(H$_2$O)$_2^-$.

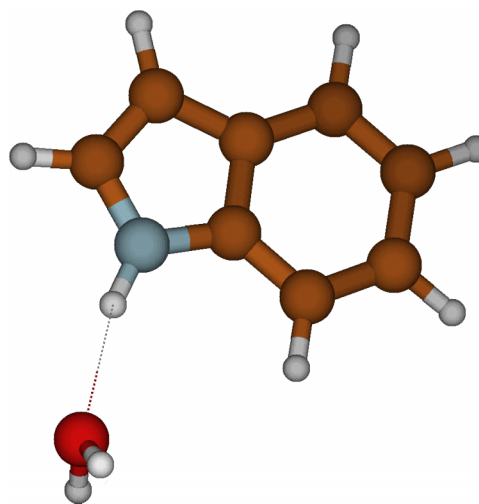| Anions	AEA (meV)	Peak position (meV)	Vibrations frequency (cm^{-1})	Assignment
Indole(H$_2$O)$_1^-$	144 (**A**)	331 (**a1**)	1508	H–O–H bending
		593 (**a2**)	3621	H–O stretching
Indole(H$_2$O)$_2^-$	251 (**B**)	462 (**b1**)	1702	H–O–H bending
		699 (**b2**)	3613	H–O stretching

FIG. 2. Neutral indole-water complex.

about 2.5 D[7] for the formation of a stable dipole-bound anion with a molecular dipole.

The calculations performed for the indole-(H$_2$O) complex and its anion resulted in the energies shown in Table II. The equilibrium geometry of the neutral indole-(H$_2$O) complex is shown in Figure 2. The equilibrium geometry of the indole-(H$_2$O)$^-$ anion is very similar to the geometry of the neutral complex and it is shown in Figure 3 along with the orbital occupied by the excess dipole-bound electron obtained at the HF/aug-cc-pVDZ+X(α) level of theory. The structure of the neutral complex was a good starting point for the optimization of the indole-water anion, as the excess dipole-bound electron only weakly interacts with the cluster and only marginally alters its structure. The HF/aug-cc-pVDZ+X(α) calculation of the anion at the geometry of the neutral complex was the first step in the geometry optimization of the anion and was used as a guess for the HOMO of the anion. The use of this basis set augmented with diffuse orbitals produced a negative value of the neutral's LUMO energy. As the calculation for the anion progressed the energy of the HOMO occupied by the excess electron became lower than the negative energy of the LUMO of the neutral complex. This lowering trend continued as the geometry of the anion was optimized. This happened due to two effects. The first was the relaxation of the electronic structure of the other electrons of the cluster in the presence of the excess electron and the stabilization of the state of the excess electron due to self-consistent interaction with the other electrons brought about in the HF procedure. The second effect is due to the relaxation of the geometrical structure of the anion, which contributed to further stabilization of the state of the excess electron. As a result, the HOMO energy of the anion at the optimized structure (equal to −0.002 125 a.u.) became noticeably lower than the energy of the corresponding LUMO of the neutral complex.

Calculations of the energies of the anion and neutral complexes yielded information on the following quantities: (1) the vertical detachment energy (VDE), the energy difference between the anion and neutral complex with both energies determined at the equilibrium geometry of the anion, (2) the adiabatic electron affinity (AEA), the energy difference

TABLE II. Energies of the neutral and anion indole-water complexes in a.u. The calculations are performed with the aug-cc-pVDZ+X(α) basis set. The notation "Anion//Anion," etc. denotes that the anion energy is calculated at the equilibrium geometry of the anion. The contribution from the triple excitations obtained as a difference between the CCSD(T) and CCSD energies are calculated with the 6-31++G**+X(α) basis set.

Method	Anion//anion	Anion//neutral	Neutral//anion	Neutral//neutral
HF	−437.553 650 0	−437.554 643 2	−437.551 972 2	−437.553 703 6
MP2	−439.038 725 8	−439.037 929 3	−439.035 450 6	−439.035 776 9
CCSD	−439.080 409 5	−439.080 072 8	−439.076 264 4	−439.076 962 4
CCSD(T)	−439.144 469 4	−439.143 919 9	−439.139 904 4	−439.140 435 7

between the anion and neutral complexes with both energies determined at their respective equilibrium geometries, and (3) the vertical electron attachment energy (VEA), the energy difference between the anion and neutral complexes with both energies determined at the equilibrium geometry of the neutral complex. The results of the calculations are shown in Table III. In addition the AEA was also determined with the inclusion of the zero-point vibrational correction. The calculations were done at the MP2 level of theory and the result was 62 meV.

Indole(H$_2$O)$_2^-$

The geometry optimization of the neutral indole-(H$_2$O)$_2$ complex resulted in the structure shown in Figure 4. As the dipole calculated for this structure was only 0.598 D (insufficient to form a bound state with an excess electron) a different approach than that used for the indole-(H$_2$O)$^-$ anion had to be applied to calculate the anions of the indole-(H$_2$O)$_2$ complex. As mentioned earlier, the calculations for the anions of the indole-(H$_2$O)$_2$ complex were initiated with the indole-water and water-water anionic complexes, before adding the third molecule to stabilize the anion (i.e., a water molecule was added to stabilize the indole-water anion and an indole molecule was added to stabilize the water dimer anion). The calculations resulted in three equilibrium structures of the
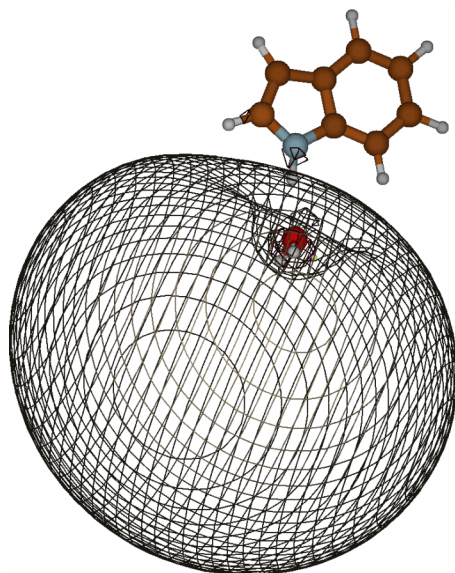
TABLE III. Adiabatic and vertical electron affinities (AEA and VEA) and the vertical detachment energy (VDE) for the indole-water complex in meV's calculated at different levels of theory with the aug-cc-pVDZ+X(α) basis set. The contribution from the triple excitations obtained as a difference between the CCSD(T) and CCSD energies are calculated with the 6-31++G**+X(α) basis set.

Method	VDE	AEA	VEA
HF	46	−1	26
MP2	89	80	59
CCSD	113	94	85
CCSD(T)	124	110	95

anion of the indole-(H$_2$O)$_2$ complex shown in Figure 5. In the figure, for each structure, the orbital occupied by the excess electron is also depicted with the 0.02 contour value. Structure A is formed by solvating the excess electron of the dipole-bound indole-water anionic complex by an additional water molecule. Structures B and C result from the solvation of the dipole-bound water-dimer anion by an indole molecule. The indole molecule either attaches to the water molecule of the water dimer (structure B) or to the water dimer anion's excess electron cloud (structure C). Structure B of the indole-(H$_2$O)$_2^-$ anion is the lowest-energy system. At the CCSD(T) level of theory it is by 7.69 kJ/mol lower in energy than structure C anion and by 5.08 kJ/mol lower than anion A (see Table IV).

The adiabatic electron affinities (AEAs) were calculated for the three indole-(H$_2$O)$_2$ structures and the results are also shown in Table IV. While AEA values are found to be negative for indole-(H$_2$O)$_2^-$ anions, A and C, indicating that the two anionic complexes are meta-stable systems, both positive (at the CCSD level of theory) and negative values (at the MP2 and CCSD(T) levels of theory) are found for
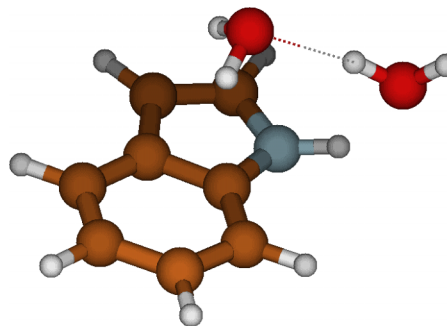

FIG. 3. HOMO of the indole-water anionic complex plotted with the contour value of 0.005.

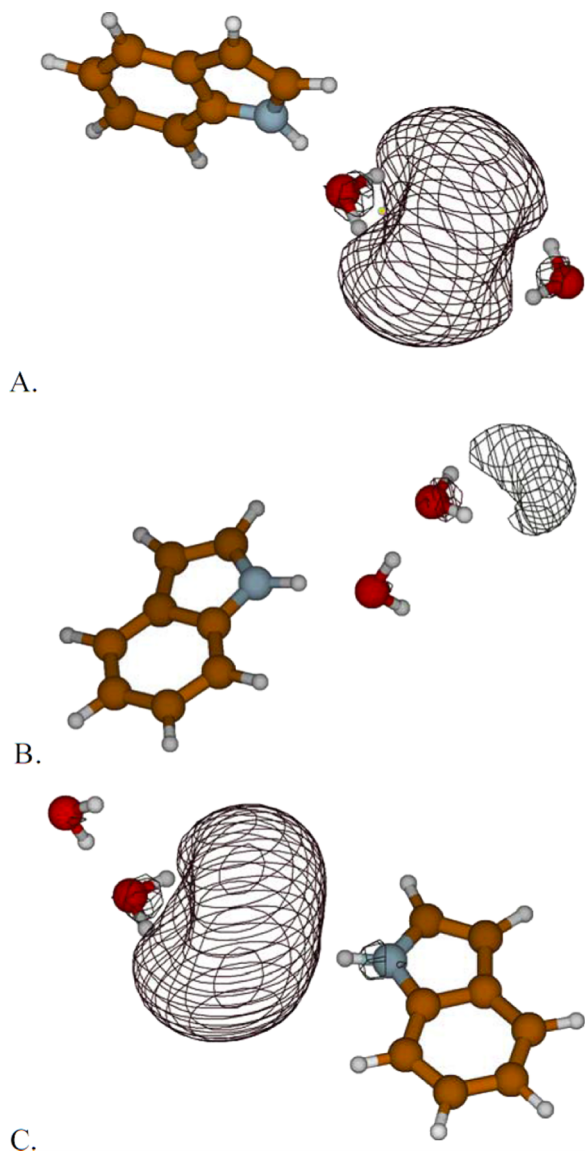FIG. 4. Neutral indole-(H$_2$O)$_2$ complex.

A.

B.

C.

FIG. 5. Structures A, B, and C of the anionic indole-$(H_2O)_2$ complexes. Electron density is plotted with the contour value of 0.02.

structure B, depending on the level of theory. Clearly the results are sensitive to the level of electron correlation effects in the calculation, but they also show that the excess electron is only marginally bound, if at all. As the triple correction in the CCSD(T) result was evaluated with the use of a smaller basis set (6-31++G^{**}+X(α)), it can be argued that the CCSD level of theory, without triples, provides a better AEA estimate and that the indole-$(H_2O)_2^-$ anion corresponding to structure B can be marginally adiabatically stable. Nevertheless, as the calculations show, anion B is definitely stable with respect to vertical electron detachment, since its VDE is determined to be 255 meV (Table IV) at the CCSD(T) level of theory.

DISCUSSION

Anion photoelectron spectroscopy provides information about the energy required for detachment of an electron from the system. The calculated VDE provides the best estimate of the experimentally measured electron detachment energy. Comparing the experimental VDE values of indole-$(H_2O)_1^-$, and indole-$(H_2O)_2^-$ with the calculated VDE values, one notices good agreement (144 vs. 124 meV for indole-$(H_2O)_1^-$, and 251 vs. 255 meV for indole-$(H_2O)_2^-$ in structure B, which is the lowest energy structure). Also, the observation of molecular vibrational peaks in the experimental PES, which, as mentioned, were assigned to the vibrational modes of a water molecule, confirms, in agreement with the calculations, that the excess electron resides in both indole-$(H_2O)_1^-$, and indole-$(H_2O)_2^-$ anions states on the water molecule. The photoelectron spectra of indole-$(H_2O)_{1,2}^-$ indicate that these states are dipole-bound anionic states which is also corroborated by the calculations.

The covalent anions, indole-$(H_2O)_1^-$ or indole-$(H_2O)_2^-$, are thought to be very unlikely to be observed since just one or two water molecules will not stabilize the indole anion. Instead, four or five water molecules would probably be required to stabilize the otherwise unstable indole anion. That is to say, since the EA of indole is −0.9 eV, it would likely take

TABLE IV. Total energies (in a.u.), vertical electron detachment energies (VDE, in meV), and adiabatic electron affinities (AEA, in meV) determined for three structures (A, B, and C) of the indole-$(H_2O)_2$ anion found in the calculations at different levels of theory with the aug-cc-pVDZ+X(α) basis set. The contribution from the triple excitations obtained as a difference between the CCSD(T) and CCSD energies are calculated with the 6-31++G^{**}+X(α) basis set.

System	$\alpha/10^{-3}$	Method	Anion//anion	Neutral//anion	VDE	AEA
A	0.6	HF	−513.593 864 7	−513.588 403 3	149	−186
		MP2	−515.306 137 8	−515.294 442 9	318	−281
		CCSD	−515.354 795 2	−515.342 650 1	330	−208
		CCSD(T)	−515.354 795 2	−515.342 650 1	355	−273
B	0.9	HF	−513.602 580 7	−513.597 422 0	140	51
		MP2	−515.314 535 1	−515.306 709 7	213	−52
		CCSD	−515.362 895 6	−515.354 096 7	239	12
		CCSD(T)	−515.362 895 6	−515.354 096 7	255	−42
C	0.9	HF	−513.591 624 8	−513.588 829 9	76	−247
		MP2	−515.301 392 9	−515.291 861 7	259	−410
		CCSD	−515.350 647 7	−515.341 028 0	262	−321
		CCSD(T)	−515.350 647 7	−515.341 028 0	290	−392

TABLE V. Comparison of the PES (photoelectron spectroscopy) electron detachment energies of indole(H_2O)$_1^-$ and indole(H_2O)$_2^-$ with the vertical electron detachment energies (VDE) obtained at the CCSD(T) level of theory in the present work. The electron attachment energies obtained using the Rydberg electron transfer spectroscopy (RET) are also shown. All data are in meV.

Anion	Electron affinity/detachment energy		
	RET	PES	VDE CCSD(T)
Indole(H_2O)$_1^-$	68	144	124
Indole(H_2O)$_2^-$ (B)[a]	12	251	255
Indole(H_2O)$_2^-$ (A)[a]	…	…	355
Indole(H_2O)$_2^-$ (C)[a]	…	…	290

[a]Three isomers of indole(H_2O)$_2^-$, as described in Ref. 25.

FIG. 6. An isomeric structure of the indole-(H_2O)$_2$ complex obtained in the calculation performed at the MP2/6-31++G++ level of theory.

4.5 molecules of water, with stabilizations of 0.2 eV each, to stabilize the resulting indole(water)$_n^-$ cluster anion. However, from previous experimental results, theoretical work, and from our combined study presented here, we know that indole-(H_2O)$_{1,2}$ can also form complexes with large dipole moments.

Table V lists our experimental and theoretical results, as well as the results from the Rydberg electron transfer spectroscopy (RET) experiments.[25] The experimental RET results are significantly different from the PES results. In order to obtain a RET signal corresponding to a formation of an anion, the parent neutral system has to have a positive vertical electron affinity. Only then, can an energy-conserving transfer of a Rydberg electron from an excited noble gas atom to the studied system occur. In the case of indole-(H_2O)$_1$ the present calculation shows that the dipole moment of the system is sufficiently large to support a dipole-bound state of an excess electron (the VEA is predicted to be 95 meV). This is roughly consistent with the value of 68 meV, obtained from the RET experiment. However, the RET signal corresponding to the formation an anion of indole-(H_2O)$_2$ is puzzling because, as mentioned, the equilibrium structure of this system shown in Figure 4 has insufficient dipole-moment to form a bound state with an excess electron. Thus, we concluded, there must be a second isomeric structure of indole-(H_2O)$_2$ with a sufficient dipole moment to form a dipole-bound anion in the RET experiment. A series of calculations at the MP2/6-31++G** has been performed to find such a structure. It resulted in the structure shown in Figure 6. The subsequent calculation of the IR frequencies showed that the structure is a minimum on the indole-(H_2O)$_2$ potential energy surface and its MP2/6-31++G** dipole moment is 4.693 D. It is sufficient for the formation a dipole-bound anion with an excess electron. However, when the geometry optimization of the trimer structure depicted in Figure 6 is carried out at the MP2/aug-cc-pvdz level of theory the calculation converges to the global minimum for the trimer depicted in Figure 4. Thus the existence of such a structure is still an open question. If the structure exists, it would provide a possible explanation of the observation of an indole-(H_2O)$_2^-$ anion in the RET experiment.

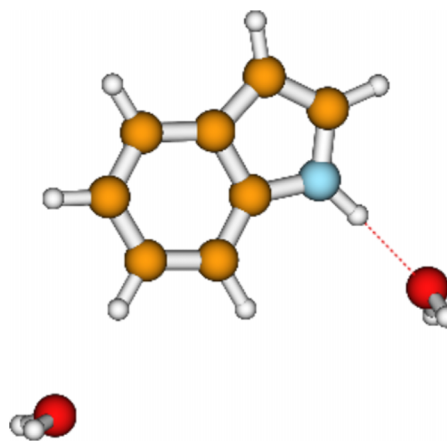While in order to see formation of a dipole bound anion in the RET experiment the parent neutral system has to

have a dipole moment, in the photoelectron experiment the formation of anions occurring through attachment of low-energy electrons in its ion source may involve more than one step. The structure of the anion can either correspond to the global minimum on the anion potential energy surface or to a local minimum, but in that case the anion should be a long-lived metastable species. As mentioned above, in the case of structure B of the indole-(H_2O)$_2^-$ anion, which corresponds to the global minimum on the anion potential energy surface, two steps are involved in its formation. The first step is the formation of the dipole-bound (H_2O)$_2^-$ anion, while the second step is the solvation of the water anion dimer by an indole molecule.

We did not produce indole anions in our beam probably because the dipole moment of indole is still slightly below the critical value to form a dipole-bound anion. It may only be marginally able to attract an excess electron, if at all. The RET experiment showed that the EA of indole is barely above zero, with a binding energy of 3 meV. This very low binding energy could have made any indole anion that was produced, subject to field detachment from numerous ion optical elements along the path of the ion beam from its source to the photodetachment region of the apparatus, thereby explaining why we did not see them. As already mentioned, our photoelectron experimental VDE value matches the computed VDE value of conformer B. The RET value[25] is perhaps due to the indole-(H_2O)$_2$ conformer depicted in Figure 6.

CONCLUSION

We produced dipole-bound cluster anions, indole(H_2O)$_1^-$ and indole(H_2O)$_2^-$, and studied them using anion photo-electron spectroscopy and theoretical calculations. Theory confirmed that both indole(H_2O)$_1^-$ and indole(H_2O)$_2^-$ are stable dipole-bound ions. The photoelectron spectra provided their vertical detachment energies. We also assigned the vibrational frequencies of water molecules in these complexes. The comparison of our photoelectron experiments with RET experiments suggests that there could be some basic differences in ion formation mechanisms in two

techniques, leading to the detection of different indole-$(H_2O)_2^-$ conformers.

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