

A Tug-of-War between Electrostatics and Dispersion in Intermolecular Interactions

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[Abstract] The red-shifts in the X–H stretching vibration of X–H···Y hydrogen bonded complexes are correlated with the electrostatic component of the stabilization energy, while the dispersion modulates the stabilization energy. In the case of π -stacked complexes, marginal red shifts indicate the minimally perturbation relative to monomers. The observed red shift in the homo-dimers suggests that the antiparallel π -stacked structures contribute predominantly based on a simple coupled dipole model. While dispersion plays a pivotal role in π -stacking electrostatics contributes through the effect of dipole moment which enhances the ability to form π -stacked structures. Further, it is demonstrated that switching of electrostatic dominated regime to dispersion dominated regime leads to folding and unfolding of squaramide based foldamers.

[Introduction] Intermolecular interactions such as hydrogen bonding is primarily considered as an electrostatic interaction between the permanent multipoles located at the donor and acceptor molecules. However, the interaction energy calculated using higher level quantum mechanical calculations shows that various components such as electrostatics, polarization, dispersion, charge transfer and exchange-repulsion, contribute to the overall stabilization energy [1]. In a recent article Hoja et al. [2] raised a simple, yet fundamental, question “is electrostatics sufficient to describe hydrogen-bonding interaction?” and concluded that “electrostatics alone are a poor predictor of the hydrogen-bond stability trends and in fact, dispersion interactions predict these trends better.” On the other hand infrared spectroscopy has been primary choice of experimental method to investigate hydrogen bonding and other intermolecular interactions. The question that we seek to address is what part of the intermolecular interaction does infrared spectroscopy probe? Further taking cues from the gas-phase experiments, new squaramide based foldamers were designed and their structures were elucidated in solution and in the solid state.

[Methods] Experiments were carried out in the gas-phase with resonant multi photon ionization (REMPI) method and monitoring the mass ion using a two-stage Wiley-McLaren time-of-flight mass spectrometer. IR-UV double resonance spectroscopic method was used to record the infrared spectra using ion detection method [3]. The experimental results were supplemented with ab initio / DFT calculations to interpret the spectra. Further, squaramide based foldamers were synthesized and their structure were characterized using single crystal x-ray crystallography and two-dimensional NMR in solution.

[Results and Discussion] The infrared spectra of several linear X–H···Y (X = C, N, O; Y = O, N) hydrogen-bonded complexes of phenylacetylene, indole and phenol were analyzed using ab-initio calculations. The stabilization energies are in the order phenol > indole > phenylacetylene, which can be attributed to the stronger hydrogen donor ability of the O–H bond in phenol over N–H bond in indole and C–H bond in phenylacetylene. The SAPT2/cc-pVTZ energy decomposition analysis shows that for all the three sets of complexes observed red-shifts in the X–H stretching frequencies are linearly correlated with the

electrostatic component of stabilization energy [4]. Further, the ratio of dispersion for all the three sets of complexes the electrostatic components depends predominantly of the nature of the acceptor with very limited contribution for the donor. The shifts in X–H stretching frequencies were inversely correlated to the dipole moments of the acceptor, whereas X–H stretching frequencies against the calculated polarizability of the acceptors show a linear correlation for the X–H···O and X–H···N hydrogen-bonded complexes separately.

Comparison of IR spectra of the homo-dimers of phenylacetylene and single fluorine substituted phenylacetylenes with the corresponding monomers reveals marginal perturbation of the acetylenic C–H group with red-shifts of the order of 3-5 cm^{-1} . Such small shifts rule out the possibility of formation of structures involving C–H··· π interaction. On the basis of minimal perturbation of the acetylenic C–H groups it was inferred that all the homo-dimers form π -stacked structures, which was amply supported by electronic structure calculations. Further, the observed red shift in the acetylenic C–H stretching vibration were analyzed using coupled dipoles model which suggest the formation of antiparallel π -stacked structures. Partitioning of the interaction energy using SAPT0 scheme reveals that π -stacking in the dimers is dispersion-dominated with reasonable contribution from electrostatics. The stability trends indicate that the dipole moment enhances the ability to form π -stacked structures [5].

Foldamers incorporating squaramide rings fold due dispersion dominated π -stacking between two squaramide rings and are energetically favorable over unfolded structure. The variation of relative energies with respect to dihedral angle strain for these foldamers reveal that the two rings behave differently when it comes to secondary structure formation and there is asymmetry in the folding potential even in the absence of chiral elements. However, in the solid state these foldamers adapt unfolded structure due to extensive hydrogen bonding network, which is dominated by electrostatics.

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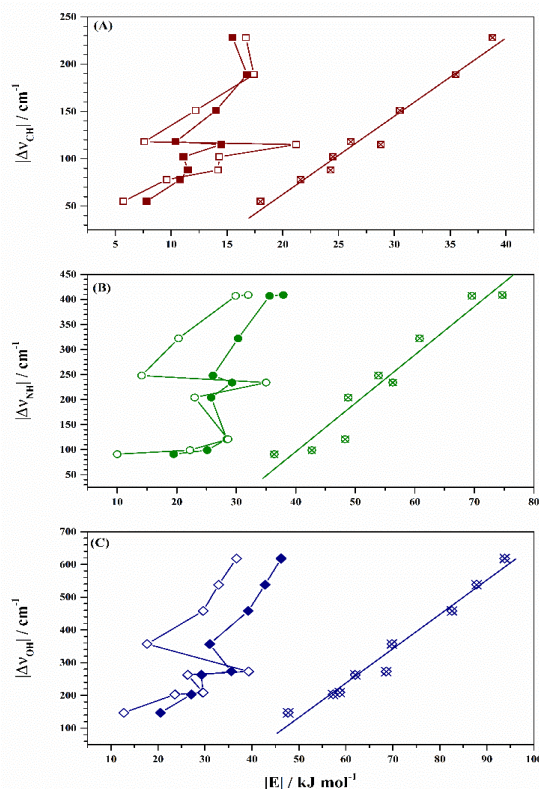


Fig. 1. Plot of shifts in the donor stretching frequency of (A) phenylacetylene (squares), (B) indole (circles) and (C) phenol (diamonds) in their hydrogen-bonded complexes against the corresponding ZPE corrected SAPT2 interaction energies (solid), electrostatic component (crossed) and dispersion component (open). The straight lines are the linear fits to the shifts vs electrostatic component

Supramolecular Chemistry Investigated by Cold, Gas-Phase Spectroscopy

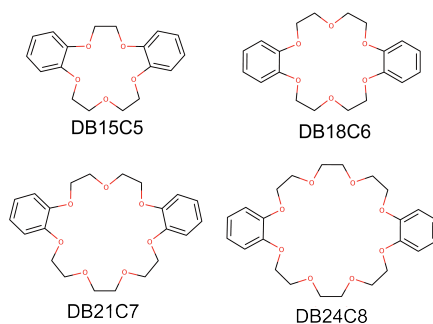
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【Abstract】 We examine the geometric and electronic structures of dibenzo-crown ether (CE) complexes with alkali metal ions by UV photodissociation (UVPD), UV-UV hole-burning, and IR-UV double resonance spectroscopy under cold gas-phase conditions. UV spectral features are strongly dependent on the ring size, or relative position of the benzene chromophores in the dibenzo-CEs. Results of gas-phase spectroscopy, quantum chemical calculations, and fluorescence spectroscopy in solution indicate that dibenzo-24-crown-8 (DB24C8) complex with K^+ ion ($K^+ \cdot DB24C8$) forms “intramolecular” excimer upon UV excitation. DB24C8 can emit strong “intramolecular” excimer fluorescence only with K^+ among alkali metal ions, suggesting that DB24C8 can be used as a sensitive, background-free, selective probe for K^+ in solution.

【Introduction】 Cooling of large functional molecules in the gas phase can suppress congestion in their spectra, which enables ones to explore their intrinsic natures in detail and sometimes to discover new functions that have never been known in condensed-phase studies. We have been investigating host-guest complexes of crown ethers (CEs), calixarenes, and other host molecules by cold, gas-phase spectroscopy. In this talk, we present our recent results on dibenzo-CE complexes with alkali metal ions, in particular with K^+ ion.

【Experimental and Computational Methods】 In UV photodissociation (UVPD) spectroscopy, ion complexes are produced by electrospraying methanol solutions of metal salts and CEs (Scheme 1). Ions are cooled in a cold (~ 4 K) Paul-type quadrupole ion trap and irradiated by a UV laser. Resulting fragment ions are mass-analyzed and detected with a home-made time-of-flight mass spectrometer. UVPD spectra are obtained by plotting yields of the fragment ions against the UV wavenumber. We employ UV-UV hole-burning and IR-UV double-resonance spectroscopy to identify vibronic bands of a single isomer and to obtain conformer-specific IR spectra. We also perform quantum chemical calculations of the complexes by using the CONFLEX, GAUSSIAN 09, and TURBOMOLE program packages to explain the experimental results and determine the geometric and electronic structures of the complexes.



Scheme 1. CEs used in this study.

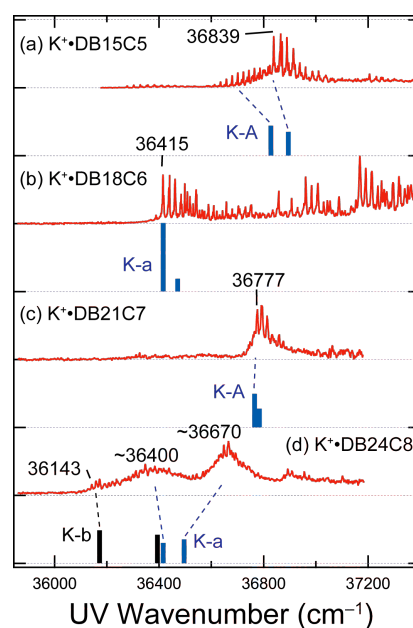


Fig. 1. UVPD spectra.

【Results and Discussion】 Figure 1 displays the UVPD spectra of the DB15C5, DB18C6, DB21C8, and DB24C8 complexes with K^+ ion. Thanks to the cooling of the complexes, the UVPD spectra of the K^+ •DB15C5, K^+ •DB18C6, and K^+ •DB21C8 complexes show sharp vibronic bands; results of UV-UV, IR-UV, and quantum chemical calculations suggest that these complexes each have a single isomer [1, 2]. In contrast, the K^+ •DB24C8 complex shows broad spectral features with maxima around 36400 and 36670 cm^{-1} , accompanied by weak but sharp bands around $\sim 36143\text{ cm}^{-1}$. Figure 2 shows the HOMO and HOMO-1 of the stable isomers. The crown cavity of DB15C5 is too small to fully encapsulate K^+ ion, giving a C_1 structure. The MOs and the electronic transitions of the K^+ •DB15C5 complex are almost localized in one of the two benzene chromophores. In the K^+ •DB18C6 complex, the crown opens the cavity the most, and the K^+ ion is located at the center of the cavity, providing a boat-type, C_{2v} form; the MOs are delocalized over the two benzene rings due to high symmetry, but the interaction is not so strong, providing an exciton splitting of $\sim 2.7\text{ cm}^{-1}$ in the UVPD spectrum [1]. For the K^+ •DB21C7 complex, the MOs are localized, similar to those of the K^+ •DB15C5 complex. In the case of the K^+ •DB24C8 complex, the most stable isomer (K-a, Fig. 2d) has a highly folded conformation for the encapsulation of K^+ ion with C_2 symmetry. As a result, the distance between the benzene rings is very short ($< 4\text{ \AA}$) [3]. This unique structure reminds us of “intramolecular” excimer formation, which should be related to broad features in the UVPD spectrum. In order to demonstrate the excimer formation after the UV excitation of the K^+ •DB24C8 complex, we observe fluorescence spectra of the K^+ •DB24C8 complex in solution [4]. As seen in Fig. 3b, the K^+ •DB24C8 complex shows strong, red-shifted fluorescence around 350 nm. This can be assigned to the fluorescence of “intramolecular” excimer, induced by the encapsulation of K^+ ion. One interesting finding in fluorescence spectroscopy in solution is that this excimer fluorescence is observed only with K^+ ion among alkali ions (Figs. 3b–e), which suggests that DB24C8 can be used as a sensitive, background-free, selective probe for K^+ ion in solution [3].

【References】

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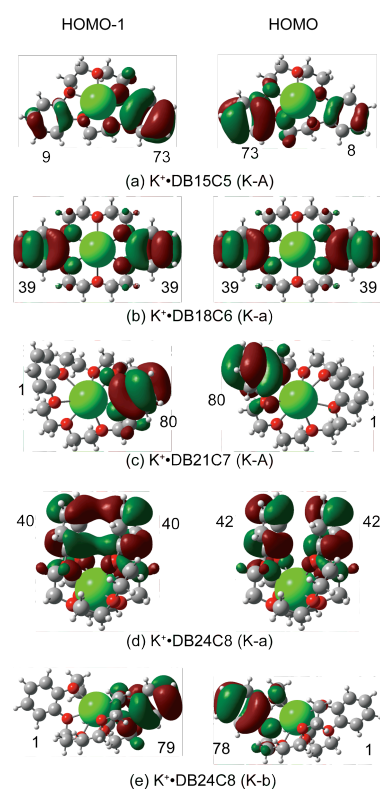


Fig. 2. HOMO and HOMO-1 of the complexes.

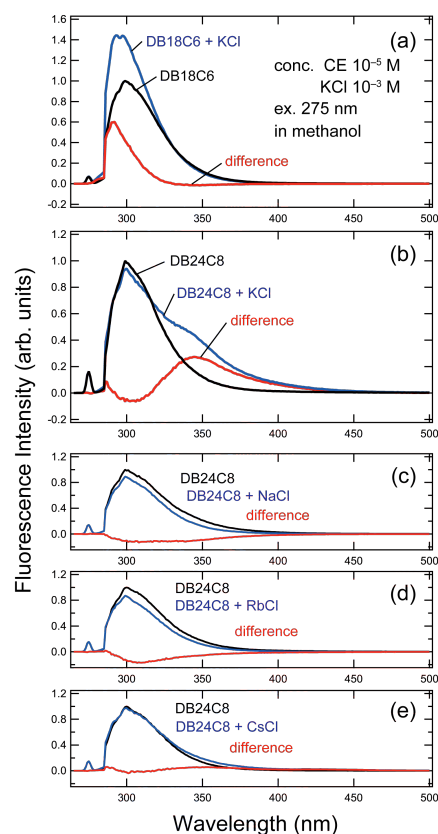


Fig. 3. Fluorescence spectra in methanol.

Understanding Vibrational Motions of H⁺ in Hydrogen Bonding via *Ab Initio* Anharmonic Approaches

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[Abstract] Understanding structures and properties of molecular systems bounded by hydrogen bonding has been an interesting and challenging task. The diverse range of interaction strength and intrinsic structural flexibility can be probed directly by vibrational spectroscopic methods. However, vibrational spectra of molecular systems containing proton is often far from trivial partially due to significant anharmonicity. In the last few years, we have been working to understand the vibrational motion of proton in various molecules using the computational algorithms to examine both types of proton (Zundel and Eigen) under different solvation environments. In this talk, we will use solvated H₃O⁺ as an example to demonstrate how we can combine both experimental spectra and *ab initio* anharmonic calculations to extract simpler and clearer pictures to understand the vibrational coupling in the protonated species.

[Introduction] Solvation of proton in hydrogen bond network has been an interesting and important problem in Physics, Chemistry and Biology. To gain a better understanding on the vibrational signatures of H₃O⁺, many previous studies using gas-phase Infra-Red Pre-Dissociation (IR-PD) spectroscopy and high-level *ab initio* calculations have been attempted. IR-PD of H₃O⁺ has been first demonstrated by Lee and coworkers with H₂ tags[1]. subsequently, spectra of H₃O⁺ with one to three Ar, N₂, or CH₄ tags have also been reported. In the frequency range above 3000 cm⁻¹, the main intensity carriers in IR spectra are the fundamental of O-H stretching modes, and their intensities and peak positions are very sensitive to the change in the solvation environments. Furthermore, different types of combinational and overtone modes has been observed depending on the solvation, but there is no clear indication on emergence of these dark states.

Theoretically, one can engage different level of theories to examine the vibrational coupling among different normal modes (NM) and the resulting spectra. Under the NM formalism, the kinetic energy terms are decoupled, and the potential energy component contains most of the anharmonic couplings. We have developed and implemented two *ab initio* anharmonic algorithms that can be applied to compute the vibrational spectra of protonated clusters. In this work, we will use solvated H₃O⁺ as an example to demonstrate how anharmonic algorithms can be applied to assist the assignment of experimentally observed spectra[2,3,4]. Moreover, we can analyze the vibrational coupling among different degrees of freedom to gain a better insight on how the dark (combinational and overtone states) can be activated.

[Methods] In the following, we will summarize our implementations of the two anharmonic schemes. In **Quartic potential (QP)**, all the cubic, and part of the quartic terms are included in the potential energy surface (PES) operator. The vibrational Hamiltonian can be cast into a matrix using direct products of the eigenstates of the harmonic oscillators. After that, the Hamiltonian matrix is diagonalized directly. This way of solving the vibrational problem is known as Vibrational Configuration Interaction (VCI). Furthermore, dipole moment surface (DMS) is approximated by keeping only the linear term, and infrared absorption intensities can be obtained by applying the Fermi's golden rule. Our implementation of QP+VCI has

been applied to study FR of the $(\text{NH}_3)_n$ and $(\text{CH}_3\text{NH}_2)_n$ clusters [5] with a satisfactory agreement with the experimental spectra. **Discrete Variable Representation (DVR)** is another powerful numerical methods to solve partial differential equations. In our DVR implementation, Gauss-Hermite functions were used as basis functions and the potential energy operator is discretized leading to a matrix on the DVR grid. Thus all the high-order terms are kept. In one of our previous works, we found that in $\text{H}_3\text{O}^+\dots\text{Ar}_3$, we can reach a convergence in the eigen-values of less than 2 cm^{-1} using five and seven grid points for the bending and stretching modes, respectively. To summarize, in our implements, the DVR approach includes both electronic and mechanical anharmonicity and QP only considers the latter (with the limitation to up to the 4th order in PES).

[Results and Discussion]

The results of our five-dimensional calculations (by QP and DVR) are compared against the experimental spectra in Figure 1. It is interesting to note that (1) QP+VCI has a better description on the peak position than DVR across all six spectra, and (2) QP+VCI introduces a symmetry breaking of the doubly degenerated state in $\text{H}_3\text{O}^+\dots\text{RG}_3$. The former is clear due to the cancellation of errors, and the cause of the latter will be investigated further by DVR.

Through extensive checking and comparisons[4], we found (1) DVR with 3MR gives a reasonable description of both the peak positions and intensity borrowing, but the truncation at 3MR is found to break the degeneracy of C_{3v} symmetry in $\text{H}_3\text{O}^+\dots\text{RG}_3$. (2) 4MR@DVR is sufficient for the convergence of PES (based on MP2/aDZ). (3) Mixed-Level (2MR based on high-level (CCSD/aTZ)) leads to quantitatively improved agreements.

Good agreements between our *ab initio* anharmonic calculations and experimentally measured spectra on both the Ne-tagged and Ar-tagged species confirm our previous finding [3] that coupling between overtones of bending and fundamental of stretching modes is indeed stronger in Ne-tagged than Ar-tagged H_3O^+ . The reason that overtone in Ne-tagged H_3O^+ is less visible is mainly attributed to the greater mis-matching in the frequency rather than a weak coupling strength. We believe the conclusions drawn from rare-gas tagged H_3O^+ can be generalized and applied to H_3O^+ solvated under other conditions.

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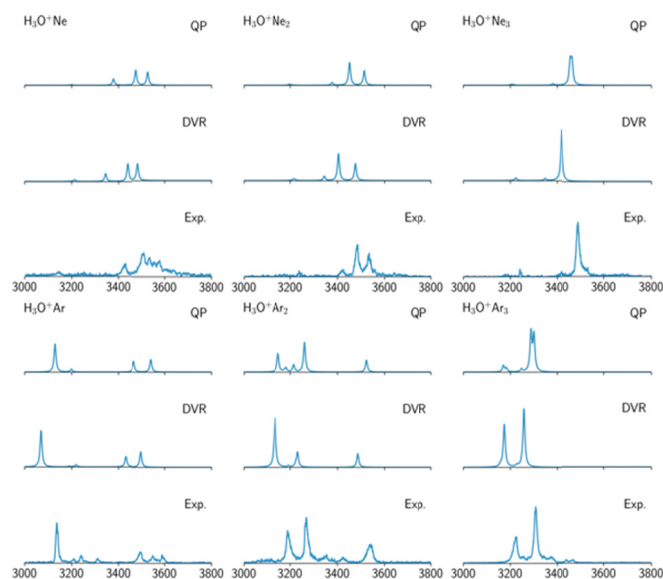


Fig. 1: Comparison of experimental IR-PD of $\text{H}_3\text{O}^+\dots\text{RG}_n$ and absorption spectra simulated with QP and DVR methods.