Heterogeneous Proton-Bound Dimers with a High Dipole Moment Monomer: How Could We Experimentally Observe These Anomalous Ionic Hydrogen Bonds?

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Electronic structure calculations (CBS-QB3 and G3MP2) have been used to predict a suitable method to experimentally observe the anomalous structure which is predicted to exist in a proton-bound dimer with a high dipole moment monomer. The enthalpy associated with forming the proton-bound dimer from its protonated and neutral monomers is shown to be linearly related to the difference in proton affinities which has been observed experimentally. However, unlike previous experimental studies, the linear correlation is not predicted to depend strongly, if at all, on whether the basic sites are C=O, C=N, or O(H) n-donor bases. Thermochemical measurements, then, are probably not the best method to distinguish between the structures of heterogeneous proton-bound dimers. It has been shown that a suitable method to experimentally observe the anomalous structure of proton-bound dimers containing a high dipole moment monomer (or very polar monomer) is by spectroscopic measurement. The O–H⁺–O asymmetric stretch is probably not the best infrared band to try to correlate with structure. The best band to observe is one which is in a region of the spectrum not masked by other absorptions and is also sensitive to the proximity of the binding proton. For example, it is shown that the methanol-free O–H stretch is very sensitive to the O–H⁺ bond distance for a series of heterogeneous proton-bound dimers containing methanol. It is predicted that the free O–H stretch of the methanol/acetonitrile proton-bound dimer is more closely related to the O–H stretch in protonated methanol than the O–H stretch in neutral methanol. Observations of these bands should confirm that the proton is closer to methanol in the methanol/acetonitrile proton-bound dimer despite acetonitrile having a higher proton affinity.

1. Introduction

The bridging proton of a proton-bound dimer forms a very strong hydrogen bond between the two monomers typically known as an ionic hydrogen bond.[1] They are essentially stabilized intermediates of a proton-transfer reaction.[2] Simple proton-bound dimers can be used as a prototype to understand proton transfer in aqueous solutions. Understanding these strong hydrogen bonds is important since they are integral to many chemical and biochemical processes. Many physical and chemical properties of biomolecules are dependent on not only the formation and breaking of intermolecular and intramolecular hydrogen bonds but also ionic hydrogen bonds.[3] Furthermore, this strong ionic hydrogen bond between basic functional groups in peptides is essential for enzymatic activity in proteins, which is often accompanied by a proton release to a proton-bound substrate.[3,4] Developing methods to determine and predict the structures of proton-bound dimers, therefore, is of obvious importance.

It is expected that, in a heterogeneous proton-bound dimer, the binding proton would make a shorter bond with the basic site of the monomer with the higher proton affinity. This is in fact what is predicted for normal proton-bound dimers such as the methanol–water and ethanol–methanol proton-bound dimers (Figure 1). Experimental thermochemical values agree with the thermochemistry predicted for these structures,[5,6] and the binding energies of mixed proton-bound dimers have been found to be related to the difference in proton affinity.[6–9]
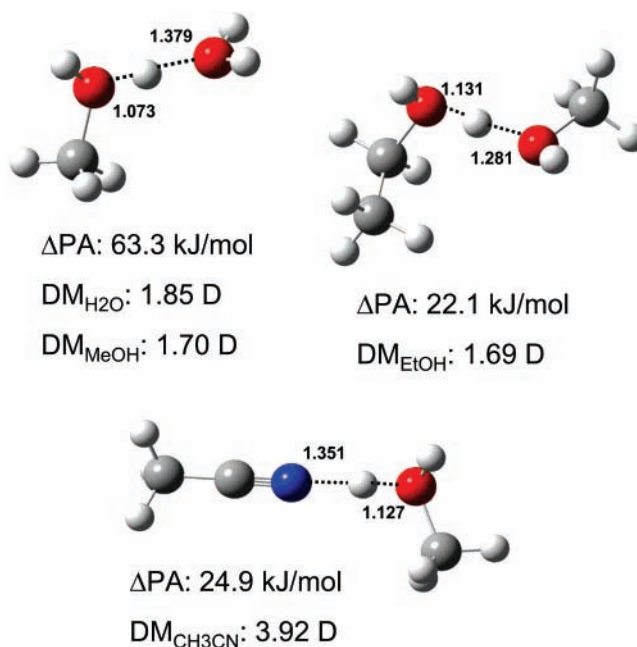

Figure 1. B3LYP/6-31+G** calculated structures of methanol-containing heterogeneous proton-bound dimers. Reproduced with permission from ref 15. Copyright 2006 American Chemical Society.

It was noted previously, however, that in some proton-bound dimers, such as the acetonitrile–methanol[10–13] (Figure 1) and the cyanide–water[11,14] proton-bound dimers, the H⁺–O bond

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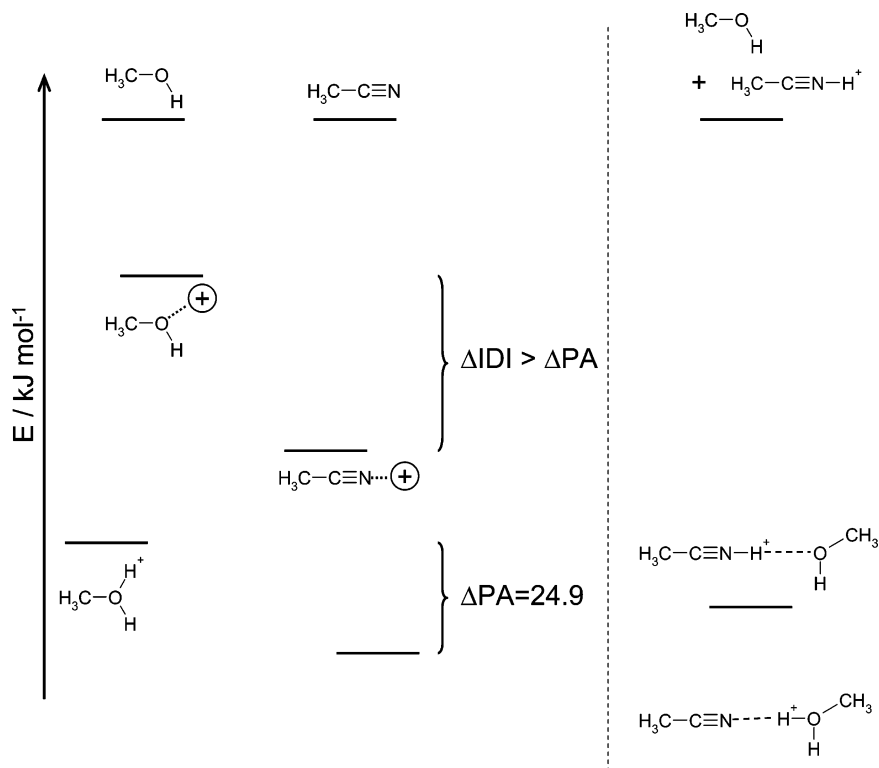*J. Phys. Chem. A, Vol. 111, No. 42, 2007* **10739**

Figure 2. Schematic energy level diagram to explain the geometry of mixed proton-bound dimers containing a high dipole moment monomer in terms of the stabilization of the monomers by protonation and electrostatic charge solvation.

is predicted to be shorter than the H^+-N bond. This is despite the fact that, in both cases, the nitrile has a significantly *greater* proton affinity. In a recent paper,[15] the structures of these proton-bound dimers where one of the monomers was a "high dipole moment monomer" was discussed with respect to a balance between covalent and electrostatic interactions surrounding the binding proton. In short, the stronger ion−dipole interaction (IDI) in the protonated methanol/acetonitrile structure more than offsets the weaker covalent bond between the proton and methanol than the proton and acetonitrile. This is summarized in Figure 2.

The present work constitutes a more detailed computational study of mixed proton-bound dimers than that previously published. It is an attempt to explore the binding energies and vibrational spectra of these species in order to advance which experimental methods might be best to probe the structures of heterogeneous proton-bound dimers with one very polar monomer.

2. Computational Methods

Calculations were done using both G3MP2 and CBS-QB3 theories to obtain the binding energies of nearly 90 different heterogeneous proton-bound dimers with respect to the lowest energy dissociation into a neutral and protonated monomer. The geometries reported were obtained using MP2/6-31G(d) and B3LYP/CBSB7 calculations. For the figures relating the geometries about the binding proton to the proton-affinity and dipole moment, the B3LYP/CBSB7 results are presented in this paper and the MP2/6-31G(d) versions can be seen in the Supporting Information provided. Similarly, the B3LYP/CBSB7 vibrational wavenumbers are reported for the OH^+O asymmetric stretch and compared to experimental values where they exist. For each proton-bound dimer, many possible conformations
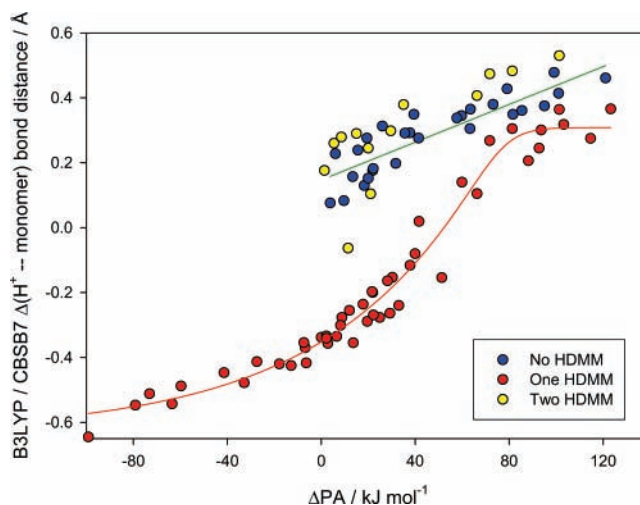

Figure 3. Difference in H^+-monomer bond distance plotted against the difference in proton affinity. Geometries are calculated using B3LYP/CBSB7.

were considered. All calculations were done using the Gaussian 03[16] suite of programs.

3. Results and Discussion

3.1. Geometries. The H^+-monomer bond distances are listed in Tables S1−S6 in the Supporting Information for both the MP2/6-31G(d) and B3LYP/CBSB7 calculations. In Figure 3 is a plot of the difference in H^+-monomer bond distance vs the difference in proton affinity. HDMM stands for high dipole moment monomer, which was defined previously as a monomer with a dipole moment higher than 2.9 D. The difference in proton affinity and the difference in H^+-monomer bond distance are in both cases taken such that the monomer with
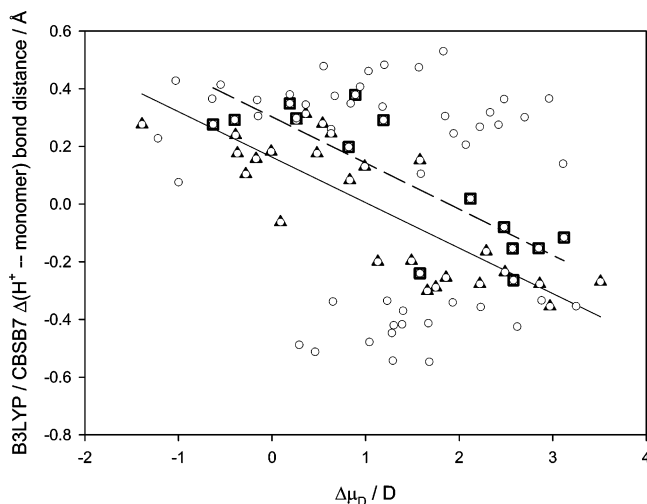
Figure 4. Difference in H$^+$−monomer bond distance plotted against the difference in dipole moment. See text for details. Geometries are calculated using B3LYP/CBSB7.

the highest proton affinity is the minuend for the cases when there are no or two HDMM. When there is only one HDMM (red circles), the monomer with the higher dipole moment is the minuend. In the previous study,[15] with a subset of the data that is provided here, there were two more or less linear relationships identified: one where there is one HDMM and another which was composed of proton-bound dimers where either both or neither monomer was a high dipole moment monomer.

With the added data it may be possible to divide the proton-bound dimers into the three groups based on how many HDMM's there are in the dimer: 0, 1, or 2. When the proton-bound dimer contains one high dipole moment monomer, the proton lies further from the HDMM than expected based on the proton-affinity difference and the trend observed when there is no HDMM or two HDMM. This trend levels off when the difference in proton affinity is very large since the structure of the proton-bound dimer approaches a protonated monomer which is solvated by a neutral, i.e., an ion−dipole complex rather than a proton-bound dimer. It also seems that when both monomers are HDMM, on average the difference in the H$^+$−monomer bond distance is slightly larger compared to when there are no high dipole moment monomers. This may also be due to a slightly larger degree of electrostatic interaction and therefore increased stability which accompanies an electrostatic interaction.

A plot of the difference in H$^+$−monomer bond length vs the difference in dipole moment is shown in Figure 4 for all the data (all symbols in plot) and resembles a shotgun blast which might indicate that there is not much dependence in the structure on the difference in dipole moment. However, a more likely interpretation could be that the dependence of the structure on the dipole moment is masked by the dependence on the difference in proton affinity. If we take a subset of the data, all proton-bound dimers where the difference in proton affinity is between 8 and 28 kJ mol^{-1} (darkened triangles and solid linear regression line) and between 30 and 50 kJ mol^{-1} (darkened squares and dashed linear regression line), we can see a trend peaking out indicating at least some dependence on the difference in dipole moment as might be expected. In Figure 5 three different views are presented of a three-dimensional plot relating the geometry about the central proton to both the difference in proton affinity and the difference in dipole moment (dipole moment differences given in Tables S1−S6 in the

Supporting Information). It appears that the proton-affinity and the dipole moment together might be sufficient to estimate the geometry about the central proton. The plane fitting this data is described by the following equation:

$$\Delta BL = 6.4 \times 10^{-4} + 6.0 \times 10^{-3} (\Delta PA) - 0.13 (\Delta DM)$$

The average error in using this equation to predict the difference in bond length for the complete set of data is 47%, but this translates into much less error in the overall bond length. This two-parameter fit is probably too simplistic since it does not take into account the detailed chemical interactions between the two monomers but it does serve to show that the difference in proton affinity alone is not sufficient to predict the position of the proton and one clearly needs to also consider the difference in dipole moment.

3.2. Bond Enthalpies. For the present purposes we define the bond energy as the enthalpy associated with the formation of the proton-bound dimer,

$$AH^+ + B \rightarrow AHB^+ \qquad \Delta_r H = \text{bond enthalpy}$$

where A has a proton affinity greater than that of B.

The bond enthalpies were calculated using both the G3MP2 and CBS-QB3 protocols. In Figure 6a the calculated bond enthalpies are compared to experimental values from NIST.[17] On the basis of the linear regressions, CBS-QB3 calculations overestimate the experimental values by an average of about 2% and the G3MP2 calculations underestimate them by about 6% on average. The scatter in the plots of experimental vs calculated bond enthalpies is only slightly troubling and is probably more a reflection on the measured values than the calculated values. In Figure 6b, CBS-QB3 and G3MP2 are compared and it can be seen that on average the CBS-QB3 values are 5% higher than the G3MP2 calculations.

In Figure 7, the CBS-QB3 calculated bond enthalpies are plotted against the proton-affinity difference of the monomers making up the proton-bound dimers for all three groups of proton-bound dimers (see Supporting Information for the similar G3MP2 plot). For the proton-bound dimers with a negative ΔPA, the absolute value was used and these are indicated with a dot in the center of the red symbol. The principle reason for calculating the bond enthalpies was to determine if the measured values could be used to distinguish these from the normal proton-bound dimers, where the proton "belongs" to the monomer with the higher proton affinity. The rationale for this reasoning is based on the model described above (Figure 2) which simply states that the reason the proton lies closer to the monomer with a lower proton affinity in the heterogeneous proton-bound dimers with a HDMM is that this structure is stabilized by forming a strong ion−dipole complex. Witt and Grützmacher[3] found a slight difference (<10 kJ mol^{-1}) in the free energy of binding a polar base (3−4 D) compared to the free-energy of binding a nonpolar base. Similarly, Meot-Ner[8] and Speller and Meot-Ner[9] found that OH$^+$−NCR proton-bound dimers are bound more strongly by roughly <20 kJ mol^{-1} compared with OH$^+$−O proton-bound dimers. These larger bond enthalpies for proton-bound dimers containing one polar monomer (or HDMM) were surmised to be due to an increase in electrostatic interaction.

Proton-bound dimers of amino acids with aliphatic side chains were recently determined to have a nonclassical structure.[18,19] An N-protonated amino acid is bound to the carboxyl group of the other amino acid due to the very high dipole moment (∼5 D). The structures of these amino acid proton-bound dimers
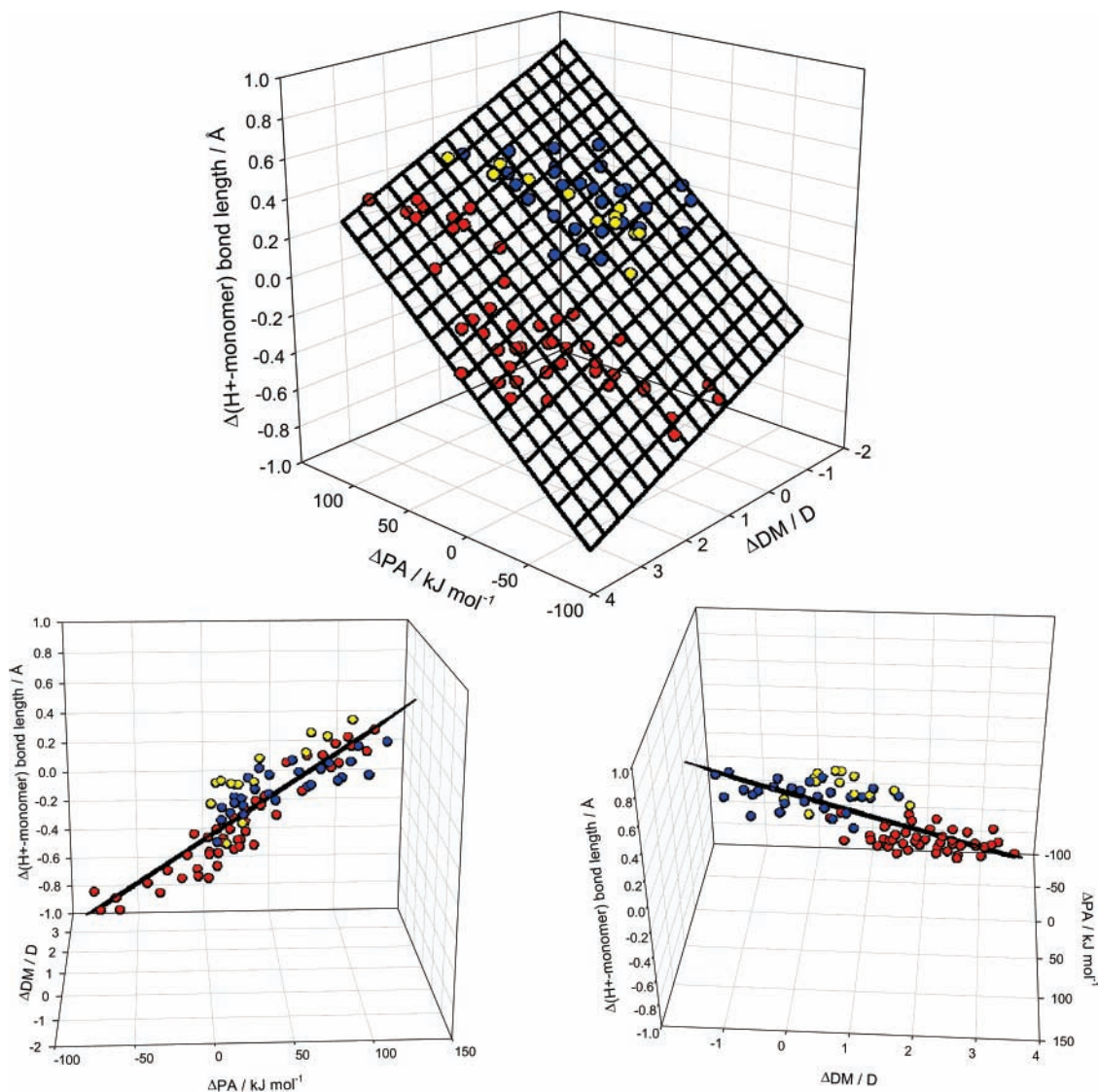
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Figure 5. Three different views of a 3-D plot relating the B3LYP/CBSB7 calculated difference in H⁺−monomer bond distance to the difference in proton affinities and the difference in dipole moments of the neutral monomers.

are best described as an ion−dipole complex rather than having strong ionic hydrogen bonding. Though this example is not exactly the same as the proton-bound dimers discussed here, it is one which shows that the propensity to form an ion−dipole complex can over strong hydrogen bonds if there is a very polar molecule involved.

From Figure 7 it can be clearly seen that the difference between the calculated bond enthalpies for proton-bound dimers with one HDMM and with no HDMM are at best only slightly different but really are not distinguishable. Furthermore, the calculated trend in bond energy with proton affinity does not follow that determined experimentally by Meot-Ner[8] (blue dashed line) for proton-bound dimers with no HDMM or by Speller and Meot-Ner[9] for proton-bound dimers with one HDMM. To be fair though, there are only a few proton-bound dimers which are common in this computational study and with those in the experimental studies. However, if we only use the nitrile data, one HDMM proton-bound dimers containing either HCN or CH_3CN, there is no better agreement. Our calculations do, however, agree with the trend determined by Larson and McMahon[6] (blue dashed−dotted line in Figure 7) for normal proton bound dimers with no HDMM. On the basis of this discussion and the calculations presented here, it is concluded that it would be at best difficult to distinguish between proton-bound dimers with no or one HDMM using thermochemical measurements.

3.3. Infrared Spectra. Infrared spectroscopy is a technique which is very sensitive to the structure of a molecular species. Recently infrared spectra of gaseous ions have been made possible and are becoming more common with the advent of low-cost tunable infrared lasers. The infrared spectroscopy of proton-bound dimers has been the common interest of a number of groups very recently due to the very interesting anharmonic oscillation of the shared proton which, due mostly to its charge, is a very intense absorption. A relationship between the position of the O−H⁺−O asymmetric stretching absorption and the difference in proton affinity for heterogeneous proton-bound dimers was first established by Fridgen et al.,[20] although with the limited data ($\Delta PA < 30$ kJ mol⁻¹) the relationship could only be concluded to be linear. Recently, Roscioli et al.[21] extended the data set significantly out to a ΔPA of close to 500 kJ mol⁻¹, and a trend was observed in which the position of the O−H⁺−O asymmetric stretching absorption increases with increasing ΔPA to a maximum value which corresponds to a normal or slightly perturbed O−H stretch.

In Figure 8 the B3LYP/CBSB7 calculated wavenumber positions for the O−H⁺−O asymmetric stretching absorption is plotted against the proton affinity differences for all the
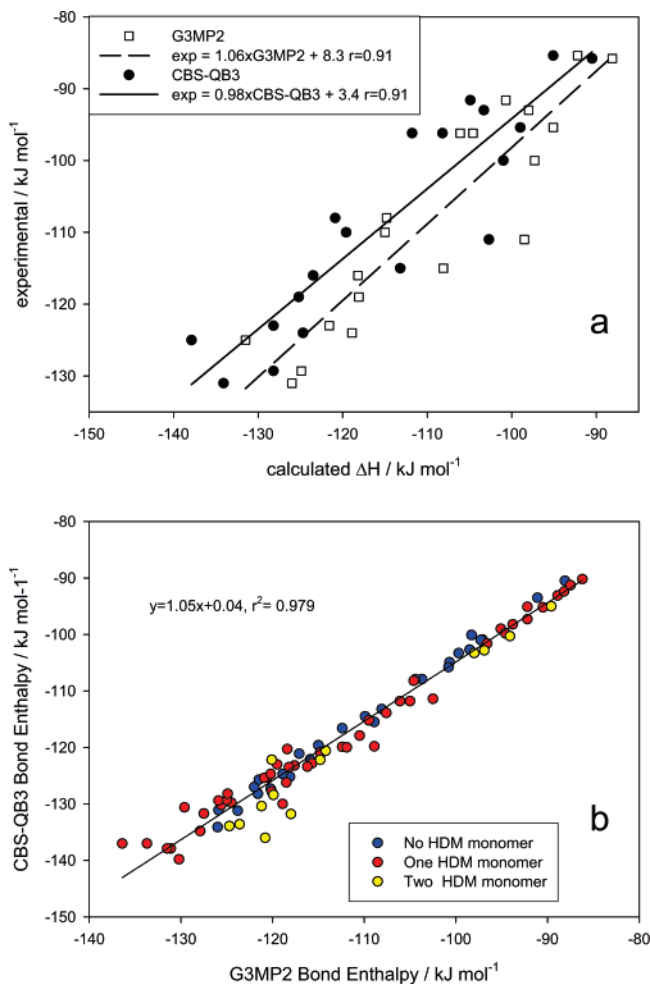
Figure 6. (a) G3MP2 and CBS-QB3 calculated bond enthalpies compared to experimental values and (b) correlation of the CBS-QB3 and G3MP2 bond enthalpies.
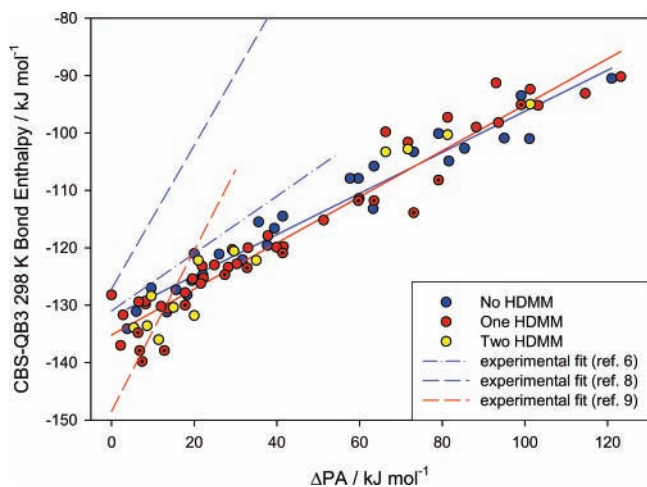

Figure 7. Plot of the CBS-QB3 bond enthalpies for heterogeneous proton-bound dimers vs the difference in proton affinities of the neutral monomers. See text for details.

proton-bound dimers considered in this study (see Tables S7–S9 in the Supporting Information for the actual values). The calculations predict a trend similar to that of the experimental data.[20–23] If a scaling factor of 0.84 is used, the experimental and predicted trend line would be virtually indistinguishable. What is significant is that while the proton-bound dimers which contain no HDMM generally follow this trend, the other sets
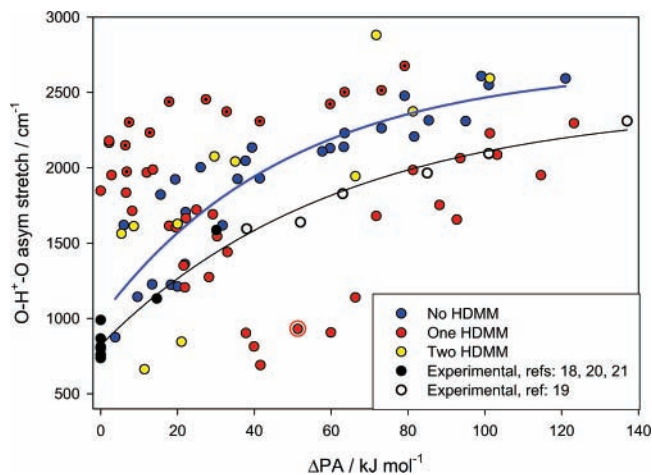

Figure 8. Plot of the $O-H^+-O$ asymmetric stretching vibration for heterogeneous proton-bound dimers vs the difference in proton affinities of the neutral monomers.

of proton-bound dimers do not follow this trend. For example, the NH_2CN/CH_3OH proton-bound dimer (indicated in red outline in Figure 8) has a proton affinity difference of 51.3 kJ mol^{-1} in favor of cyanamide. On the basis of this proton-affinity difference, one might expect that the structure of the proton-bound dimer would have the proton covalently bound to the cyanamide molecule and the asymmetric stretching vibration would occur at above 1500 cm^{-1} if the experimental curve is used as a guide. However, using a scaling factor of 0.84, the band is predicted by the B3LYP/CBSB7 calculations to occur at about 780 cm^{-1}. The reason for such a large predicted shift from the experimentally determined trend is the structural anomaly which is the topic of this paper: The proton in the NH_2CN/CH_3OH proton-bound dimer is slightly closer to methanol than cyanamide by 0.154 Å.

While an observation of an asymmetric stretch which does not conform to this trend might be an indication of the structure, or the anomalous structure, of the heterogeneous proton-bound dimer, the region of the infrared spectra from 800 to 2000 cm^{-1} is fairly congested and it may be difficult to confirm the assignment of bands in this region to the asymmetric stretching oscillation. To be a sensitive indicator of the structure of the proton-bound dimer, the band must be sensitive to the position of the binding proton, which would tend to rule out $C-H$ stretches. The $C-O$, $C=O$, or $C=N$ stretches would probably be sensitive to the position of the proton but suffer also from the fact that they occur in a region of the spectrum which is congested. However, the $O-H$ stretch of proton-bound dimers containing alcohols occurs in an uncongested region of the spectrum and should also be sensitive to the position of the proton. For example in a methanol proton-bound dimer, as the binding proton gets closer to the methanol oxygen, it would be expected that the free $O-H$ bond would weaken and the $O-H$ stretch would shift to a lower wavenumber position in the infrared spectrum. At the two extremes the $O-H$ stretch for proton-bound dimers should fall between the $O-H$ stretch of neutral methanol and that of protonated methanol. In Figure 9, a plot of the predicted position of the $O-H$ stretch is plotted against the proton–oxygen bond length in methanol-containing proton-bound dimers. The predicted $O-H$ stretches have been scaled by 0.96, a common scaling factor for density functional calculations, and brings the calculated value for neutral methanol (3839 cm^{-1}) into line with the experimental value (3681 cm^{-1}).[24] The two extremes mentioned above are shown by the solid horizontal lines in Figure 9. Also shown are the homogeneous
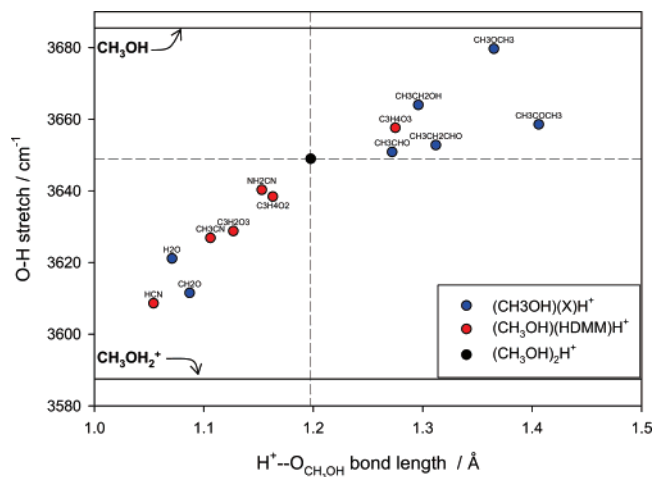
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Figure 9. Position of the methanol-free OH stretching vibration in methanol-containing proton-bound dimers vs the H^+-OH bond length. Wavenumber positions have been scaled by 0.96.

methanol proton-bound dimer values (1.198 Å and 3649 cm^{-1} for an out of phase O−H stretch). Of importance is that the data fall into two quadrants on this plot. If the $H^+-O_{CH_3OH}$ bond is shorter than that in the homogeneous proton-bound dimer, then the O−H stretch approaches that of protonated methanol. Conversely if the $H^+-O_{CH_3OH}$ bond is longer than that in the homogeneous proton-bound dimmer, then the O−H stretch approaches the value for neutral methanol. Two specific examples which have been discussed previously are the proton-bound dimers containing methanol and either cyanamide or acetonitrile. Clearly, since it is predicted that the binding proton lies closer to methanol than the basic site of the other monomer, the free O−H stretch should be closer in magnitude to the out of phase OH stretch in protonated methanol.

What can be concluded from the plot of Figure 9 is that infrared spectra of these proton-bound dimers in the O−H stretching region should allow us to experimentally determine if this structural anomaly does in fact exist, and perhaps with experiments on a full complement of proton-bound dimers, it would be possible to at least qualitatively assess the degree of covalent bonding (i.e., similarity to $CH_3OH_2^+$) and the degree of electrostatic interaction (i.e., similarity to CH_3OH).

4. Conclusions

Through electronic structure calculations (CBS-QB3 and G3MP2) it has been shown that thermochemistry is probably not the best method in an attempt to distinguish the structure of heterogeneous proton-bound dimers with one highly polar monomer from proton-bound dimers containing low-polarity monomers. The enthalpy associated with forming the proton-bound dimer from its protonated and neutral monomers is shown to be linearly related to the difference in proton affinities as has been observed experimentally. However, unlike previous experimental studies, the linear correlation does not depend strongly on whether the basic sites are C=O, C=N, or O(H) n-donor bases. In fact, the calculations predict that it would be virtually impossible to tell the difference between proton-bound dimers containing the different types of monomers.

It has been shown that the best method to experimentally observe the "anomalous" structural differences between proton-bound dimers containing 0 and 1 high dipole moment monomer is spectroscopically. It was shown that the OHO asymmetric stretch is probably not the best infrared band to try to correlate

with structure. The best band to observe would be one which is in a region of the spectrum which is not masked by other absorptions and which is sensitive to the proximity of the binding proton. For example, it is shown that the methanol-free O−H stretch is very sensitive to the O−H$^+$ bond distance in methanol-containing heterogeneous proton-bound dimers. It is predicted that the free O−H stretch of the methanol/acetonitrile proton-bound dimer is more closely related to the O−H stretch in protonated methanol than the O−H stretch in neutral methanol. Observations of these bands should confirm that the proton is closer to methanol in the methanol/acetonitrile proton-bound dimer despite acetonitrile having a higher proton affinity. It is hoped that in the near future we will be in a position to measure these bands using matrix isolation spectroscopy and/or in the gas-phase by infrared multiple photon dissociation spectroscopy using a combination of a tunable OPO laser and FTICR spectrometer.

Supporting Information Available: Structural data, wavenumbers, binding energies, proton affinities, and plots of bond distance vs dipole moment and of bond enthalpies vs difference in proton affinities. This material is available free of charge via the Internet at http://pubs.acs.org.

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