Intramolecular proton transfer from one ether oxygen to another

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ABSTRACT

Proton transfer in the conjugate acid cation of a symmetric diether, 1,5-dimethoxy-3,3-dimethylpentane (**1**), is explored both theoretically and experimentally via IRMPD spectroscopy. The optimized geometry of the cation has one oxygen pyramidalized (sum of the three angles $\Sigma = 345^\circ$), while the other oxygen has a virtually planar geometry (if one includes the strongly hydrogen bonded $\text{O} \cdots \text{H}$, the three bond angles sum to $\Sigma' = 357^\circ$). Assuming that this geometry is not preserved upon intramolecular proton transfer from one oxygen to the other, two alternatives remain: either the two oxygens trade geometries (Σ and Σ' change places via a transition state that has a mirror plane of symmetry) or else both oxygens become pyramidalized. Because the asymmetric stretch couples with other vibrational modes of the cation, special attention is paid to the classical turning points at the zero point level corresponding to the lowest frequency vibration that shows a deuterium isotope effect, which occurs experimentally around 895 cm^{-1} . This stretching vibration has a lower frequency than the bands assigned to $\text{O} \cdots \text{H}-\text{O}$ bends, and it shifts to still lower frequency in the deuterated ion. Because a normal modes calculation matches this vibration, we conclude that the potential energy surface matches a single-well and does not correspond to a double-well minimum.

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1. Introduction

Intramolecular proton transfer may appear simple, but it can display complexities upon closer scrutiny. For example, proton transit between two amine groups would seem to behave in a relatively straightforward fashion: trivalent nitrogen has only one lone pair, so the H^+ in a monoprotonated diamine moves from one lone pair to the other. Complications arise even in a symmetric case, however, because situating the proton midway between the two basic atoms often corresponds to a local maximum. As a consequence, the potential energy surface for the $\text{N}-\text{H} \cdots \text{N}$ asymmetric stretch constitutes a double-well minimum, for which the harmonic (normal modes) approximation predicts an asymmetric stretching frequency much higher than experiment reveals [1]. Moreover, the asymmetric $\text{N}-\text{H} \cdots \text{N}$ stretch has a frequency lower than the two $\text{N}-\text{H} \cdots \text{N}$ bending vibrations, which also represents unusual behavior.

Intramolecular proton transfer between two ether groups looks even more complex than intramolecular transfer between amines, because each oxygen has two lone pairs. Intermolecular H^+ trans-

fer between two separate ethers has been studied extensively by experiment and theory [2–4], and the predicted IR spectra match the experimentally observed IRMPD spectra in the gas phase quite well. $\text{O} \cdots \text{H}-\text{O}$ bends appear at higher frequencies than do $\text{O} \cdots \text{H}-\text{O}$ asymmetric stretches, which seems to be characteristic of many proton-bound dimers. DFT calculations on the proton-bound dimer of dimethyl ether using the 6–31G* basis set [2] (or MP2 calculations using a larger basis set [4]) predict that both oxygens are pyramidalized. In the proton-bound dimer of dimethyl ether at these computational levels the bridging proton turns out to be virtually equidistant from both oxygens, which calculations at higher levels confirm. Among the protonated species previously examined is the conjugate acid of diglyme, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, [3] which has an intramolecular ionic hydrogen bond, but it remains unclear (as of this writing) which oxygen bears the proton and which is the bonding partner.

1,5-Dimethoxy-3,3-dimethylpentane, **1**, having two oxygens equivalent by symmetry, removes this ambiguity. The bridging proton in the conjugate acid of **1**, however, does not lie equidistant between the two oxygens. This paper addresses the question as to what the asymmetric stretch potential looks like when symmetry is broken in this manner. It makes use of IR Multiple Photon Dissociation (IRMPD) spectroscopy of gaseous positive ions to assess whether the potential surface for the fundamental $\text{O} \cdots \text{H}-\text{O}$ stretch

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is symmetrical or unsymmetrical. As in the case of intermolecular proton-bound dimers [2–4], a match between experiment and theory demonstrates a single-well potential minimum, whereas a severe mismatch suggests a double-well minimum.

In general, protonation of an ether results in a pyramidalized oxygen. For example, the three bond angles around Me_2OH^+ sum to $\Sigma = 339^\circ$ [5]. In other words, the lone pair coplanar with the two C–O bonds has lower basicity than one out of the plane. For α,ω -dimethoxyalkanes, an unsymmetrical, strong hydrogen bond prevails in the conjugate acid ions. The protonated α,ω -dimethoxyalkane oxygen having the shorter O–H distance again has a pyramidal geometry, while (in the optimized structure) the longer O...H distance (corresponding to the strong hydrogen bond) has a very nearly planar orientation of the O...H relative to the two C–O bonds. This structural feature suggests that the potential surface for proton motion might correspond to transit from the more basic lone pair of one oxygen to the less basic lone pair of the other. Eq (1) depicts a typical case for a protonated, symmetrical diether, the conjugate acid of **1**. DFT predicts for the optimized geometry that the three angles around the protonated oxygen sum to roughly $\Sigma = 345^\circ$, while the three angles around the other oxygen (including the O...H) sum to nearly $\Sigma' = 357^\circ$.

This report focuses on 1,5-dimethoxy-3,3-dimethylpentane, **1**, an aliphatic diether whose conjugate acid gives one of the closest approaches between the two oxygen atoms. The first objective has been computationally to seek out the most basic α,ω -dimethoxyalkane having chemically equivalent oxygens, so that its conjugate acid ion can form in sufficient abundance via electrospray mass spectrometry (ESI). The second objective compares computation with experiment to explore the vibrational spectrum of the conjugate acid (as well as its deuterated analogue) in the gas phase by means of IRMPD spectroscopy (which leads to methanol expulsion) to decide between alternative potential surfaces.

The geometries at the classical turning points of the zero point level of the asymmetric stretch vibration have much more chemical relevance than the computationally optimized geometry. Three limiting cases for proton transfer can be imagined:

1. The geometry at the zero point level might transform such that the oxygens are pyramidalized at one (or both) of the classical turning points.

Fig. 1. 3-Dimensional representation of the DFT equilibrium geometry of the conjugate acid of **1** (B3LYP/AUG-cc-pVTZ). The predicted dihedral angle between the methoxy groups is 102° .

2. Alternatively, the oxygens might exchange geometries; i.e. the planar oxygen at one classical turning point becomes pyramidalized at the other classical turning point, while the pyramidal oxygen becomes planar in turn.
3. The optimized geometry described above at the bottom of the potential well (one oxygen virtually planar while the other oxygen is pyramidalized) might describe the geometry at both classical turning points of the zero point level.

The last choice appears chemically unreasonable, for it predicts that intramolecular H^+ -transfer yields a protonated oxygen that remains planar. We discard this last option without further discussion, since calculations do not justify it. This paper will treat only the first two cases.

2. Experimental

Ions were generated in an electrospray ionization (ESI) source. For the FTICR experiments, [6] solutions containing mM concentrations of **1** were introduced at 10–50 $\mu\text{L}/\text{min}$ flow rates, while for the quadrupole ion trap experiments [7] (owing to increased sensitivity), 1 μM solutions of **1** were introduced at a flow rate of 120 $\mu\text{L}/\text{h}$. In both cases, the ions were guided to an ion trap (ICR cell or quadrupole ion trap) where protonated **1** ($m/z = 161$ or 162 for the deuterated species) was mass isolated and irradiated by the tunable infrared beam from the FELIX free electron laser. In the experiments reported here, FELIX was set to produce 6 μs long pulses in the 300–1800 cm^{-1} frequency range with an energy up to 40 mJ/pulse at a repetition rate of 5 Hz and a bandwidth of 0.4% of the center frequency. The wavelength is calibrated using a grating spectrometer. Resonant absorption of the infrared radiation leads to an increase of the internal energy of the ion which results in dissociation. An infrared spectrum is obtained by monitoring the dissociation yield as function of the laser frequency. The yield at each infrared point is obtained from averaged mass spectra and is linearly corrected for the frequency dependent laser power.

The diol corresponding to compound **1** was prepared by reduction of 3,3-dimethylglutaric anhydride (Aldrich) with an excess of lithium aluminum hydride. This diol was dissolved in dry THF, doubly deprotonated with an excess of pentane-washed sodium hydride, then treated with an excess of iodomethane, refluxed, followed by aqueous workup, removal of solvent, and two successive distillations. Unless otherwise stated, DFT calculations were optimized using the B3LYP/AUG-cc-pVTZ basis set. Normal mode calculations on optimized geometries were performed at that level and vibrational frequencies above 800 cm^{-1} are scaled by 0.97 [8]. Comparison with MP2/6-311++G** optimizations shows that the difference between the minimum and the C_s geometry is 7.5 kJ/mol, versus 2.2 kJ/mol at the DFT level.

3. Results

Previous investigations have portrayed proton-bound homodimers of ethers as having two nearly equivalent O–H bond distances [2–4], which our B3LYP/AUG-cc-pVTZ calculations corroborate. For the intramolecular hydrogen bond in protonated **1**, however, the O–H and H...O bond lengths differ by about 0.177 Å. We ascribe this variation to constraints upon the rotations of the methoxy groups.

DFT modelling indicates that 1,5-dimethoxypentane is the most basic of the α,ω -dimethoxy-*n*-alkanes, consistent with previously published experimental data [9]. Based on the Thorpe-Ingold effect [10], one would expect dimethyl substitution of one of the carbons in the methylene chain to favor further cyclization of the conjugate acid. Whereas the fully extended conformation is calculated to have the lowest energy for neutral **1**, protonation on

Fig. 2. **A.** Asymmetric O...H–O stretch potential for protonated **1** calculated by DFT as a series of 18 points by optimizing geometries with **r** held at a variety of fixed distances without constraining any other degrees of freedom. The heavy line at the top of the curve stands for the zero-point level of the lowest frequency harmonic vibration having substantial asymmetric stretch character; **B.** DFT-calculated asymmetric O...H–O stretch coordinate for protonated **1**, assuming a C_s transition state ($\mathbf{r}=\mathbf{R}$), which passes the bridging proton from the more basic lone pair on one oxygen directly to the more basic lone pair on the other oxygen. The C_s geometry in **B** corresponds to the minimum having a mirror plane of symmetry. By virtue of the symmetry constraint, this geometry has a higher electronic energy than the $\mathbf{r}=\mathbf{R}$ point in **A**. As in **A**, the heavy line at the top of the curve stands for the zero-point level of the lowest frequency harmonic vibration with substantial asymmetric stretch character, and the curve represents the best quartic fit to the points below that zero point level.

oxygen leads to a cyclic conformation, as depicted in Eq. (1), where the proton forms a covalent bond to one oxygen and an ionic hydrogen bond to the other. When compared to the fully extended conformations of the neutral α,ω -diethers (i.e. the most stable geometries), 1,5-dimethoxy-3,3-dimethylpentane, **1**, is calculated to be 13 kJ/mol more basic than 1,5-dimethoxypentane. Therefore we chose dimethyl compound **1** as a neutral diether (in which the two oxygens are chemically equivalent), whose conjugate acid can most easily be formed by ESI mass spectrometry.

According to DFT calculations, the two oxygens of protonated 1,5-dimethoxypentane lie slightly more than 2.40 Å apart, while the two oxygens of protonated 1,5-dimethoxy-3,3-dimethylpentane lie slightly less than 2.40 Å apart. Both have a nearly linear OHO angle (calculated to be between 178° and 179°). Both conjugate acid ions have a conformation very similar to a cycloheptane chair, but with a long bond corresponding to the near-linear OHO linkage. DFT modelling predicts both ions to be unsymmetrically bridged in their optimized geometries, with the shorter OH distance being 1.11 Å. The longer OH distance is slightly greater than 1.30 Å for protonated 1,5-dimethoxypentane and slightly less than 1.29 Å for protonated 1,5-dimethoxy-3,3-dimethylpentane.

As noted at the end of the Introduction, we reject the last option for proton transfer (where both classical turning points at the zero point level preserve the bond angles of the optimized geometry) as chemically unreasonable. Fig. 2 depicts the other two options, two alternative potential surfaces for intramolecular transfer of a proton from one oxygen to the other. The heavy line at the top of both curves represents the zero point energy for the lowest frequency vibration with asymmetric stretch character estimated from the experimental data.

The solid curve in Alternative **A** represents the best quartic fit to a series of points optimized with one O–H distance (**r**) held fixed at various values from 1.00 Å (at the far right) to 1.44 Å (to the far left) in 0.02–0.03 Å steps. The x-axis, though, has converted the values of **r** and **R** to the normal coordinate $(\mathbf{R}-\mathbf{r})/\sqrt{2}$. We have applied no other constraint besides fixing the value of **r**.

Alternative **B** shows a potential curve that more closely resembles the structure of proton-bound ether homodimers (which approach a C_s geometry with the proton equidistant between the two oxygens) and also the intramolecular transfer between two chemically equivalent amines: the midpoint of that curve is a potential energy maximum, for it imposes C_s symmetry where $\mathbf{r}=\mathbf{R}$. Because of this symmetry constraint, this geometry has an elec-

tronic energy higher than the point where $\mathbf{r}=\mathbf{R}$ in Alternative **A**. The C_s geometry constitutes the global minimum for a species having a mirror plane of symmetry and corresponds to the second option listed at the end of the Introduction: the planar and the pyramidalized oxygens trade geometries (i.e. Σ and Σ' exchange atoms). This paper has the purpose the differentiating the two alternatives, **A** and **B**, by means of the IRMPD spectra.

According to the DFT calculations, the asymmetric O...H–O stretch mixes with skeletal modes to a greater extent than does the corresponding N...H–N stretch of protonated diamines [1]. This renders it difficult to differentiate the curves in Fig. 2 on the basis of a reduced dimensional treatment. As noted above, the heavy solid line at the top of both curves represents the scaled harmonic zero point level for the lowest frequency O...H–O stretch that exhibits substantial dependence upon substitution of deuterium for the bridging hydrogen.

A quartic polynomial, as shown in Alternative **A**, gives an extremely good fit to the points in the domain of interest. The dashed curve in Alternative **A** shows the best parabolic fit to these same points. While this harmonic approximation does not match the points particularly well, the Hooke's Law spring constant of that quadratic fit comes close to the restoring force at the bottom of the solid curve. To the left of the y-axis, close to $\mathbf{r}=1.300$ and $\mathbf{R}=1.114$, the bondlengths are very nearly the reverse of the distances in the optimized geometry ($\mathbf{r}=1.111$ and $\mathbf{R}=1.288$), but here both oxygens are pyramidalized (the sums of the three angles are $\Sigma=348^\circ$ and $\Sigma'=345^\circ$, respectively), rather than just one of them. Alternative **A** thus corresponds to the first option listed at the end of the Introduction.

At the right hand classical turning point of the zero point level for both alternatives, one oxygen is pyramidalized, while the other oxygen is planar with respect to the hydrogen-bonded proton and the two carbons. Both oxygens are pyramidalized at the left hand classical turning point of Alternative **A** ($\Sigma=342^\circ$ and $\Sigma'=348^\circ$), while (because the calculated points to the left of the y-axis in Alternative **B** simply reflect the half-dozen points to the right of the potential energy minimum) the other oxygen is pyramidalized ($\Sigma=343^\circ$) and the one is planar ($\Sigma'=360^\circ$).

The curve in Alternative **B** represents the best quartic fit to the minimized energies of the four points to its right of the optimized structure (as in Alternative **A**) and the point corresponding to the optimized C_s geometry in the middle. This constitutes a double-well potential having its transition state about 2.1 kJ/mol above the

Fig. 3. A. Experimental IRMPD spectra of protonated (black curve) and deuterated (red curve) **1**, as detected by expulsion of methanol or methanol-*d*. The red stick spectra indicate the positions of the four most intense bands having O...H–O bending character (dashed lines) and the two most intense bands having O...H–O stretching character (solid lines) calculated at B3LYP/aug-cc-pVTZ (harmonic frequencies scaled by 0.97). These normal modes mix with other vibrations of the cation. B. Calculated B3LYP/aug-cc-pVTZ infrared spectrum of protonated (red curve) and deuterated (black curve) **1** both scaled by 0.97. The calculated harmonic intensity of the 1614 cm^{-1} absorption is offscale but can be gauged relative to the calculated 1546 cm^{-1} absorption based on the heights of the dashed lines in A.

global minimum. As shown, the quartic fit to the data below the zero point level does not match the calculated points particularly well, especially with regard to the C_s transition state (where $\mathbf{R} = \mathbf{r}$).

DFT calculations (even ones that take anharmonicity into account) do a poor job for double-well potentials [1]. The qualitative feature of such potentials is that the hump in the middle raises the zero point level ($v=0$) more than the $v=1$ level, such that DFT predictions of vibrational frequencies are much too high. Hence, if DFT modelling does a moderately good job of predicting the O...H–O asymmetric stretch, that argues for Alternative **A** as opposed to Alternative **B**.

The abundance of the m/z 161 conjugate acid ion from protonated **1** proved sufficient to record an IRMPD spectrum using FELIX, which Fig. 3A displays in black. Superimposed on that experimental spectrum is the noisier IRMPD spectrum of m/z 162 from ESI of the same compound in D_2O /methanol- d_4 . Under similar experimental conditions, multiple photon dissociation of the d_1 ion gives a lower dissociation yield than for the entirely protonated cation, leading to lower intensities in the IRMPD spectrum. This difference in intensities agrees with the theoretical prediction in Fig. 3B (roughly a factor of 2).

The spectrum bears a resemblance to the IRMPD spectra of the proton-bound dimer of dimethyl ether with at least one differ-

ence: the strong band observed in Fig. 3 near 895 cm^{-1} is not to be found in either of the published spectra of proton-bound dimer of dimethyl ether. [2,3] Because this 895 cm^{-1} band vanishes with deuteration (and because it coincides with a DFT-predicted band corresponding to an OH...O stretch), we assign that band to an asymmetric stretching vibration of the bridging proton between two oxygens.

Fig. 4 reproduces the low frequency vibrational spectrum of protonated **1** recorded using a quadrupole trap, with excitation provided also by FELIX. The curve shown as a solid black line is the infrared spectrum obtained under normal operation conditions of the quadrupole ion trap, where helium is used to cool the ions to enhance their trapping efficiency. Diminishing the helium pressure lowers the cooling rate of the ions, which allows weak infrared bands to reach the dissociation threshold as well (at the cost of the total amount of stored ions), as can be seen in Fig. 4 (dashed curve). The intense band around 750 cm^{-1} in that spectrum is the same as the lowest band of the red trace in Fig. 3A, but broader. In general, harmonic DFT predictions in the domain of Fig. 4 do not require scaling to match experimental frequencies; hence, the calculated theoretical curve (silhouette) shown in Fig. 4 is not scaled. Of particular interest is the discrepancy between the theoretical predictions for the most intense IR absorptions below 750 cm^{-1} (406 and 451 cm^{-1}) and the experimentally observed bands around 450 and 515 cm^{-1} . It might be that one band agrees with an experimental frequency exactly as predicted and the other is shifted by 110 cm^{-1} from the calculated normal mode. Or both bands could shift to the blue by approximately $60 \pm 5 \text{ cm}^{-1}$ relative to the DFT calculation. Finally (which seems least likely), one band could shift to the blue and the other to the red. In any event, the lower frequency experimental band (which appears only when helium is not introduced into the ion trap) could match either the higher frequency calculated position or the lower frequency calculated position (which corresponds to the scissors motion of the *gem*-dimethyl group). It is not possible to distinguish these choices at this time.

4. Discussion

Previous work [1] has shown that double-well potential surfaces for proton transfer tend to lead to unusually low asymmetric stretch frequencies for the proton in transit, far below 1000 cm^{-1} . The situation is rendered more complex here, though, because both the O...H–O asymmetric stretch and the O...H–O bending frequencies exhibit even greater mixing with skeletal modes. In the present case, harmonic DFT calculations still predict that the vibrations having O...H–O asymmetric stretch character have lower frequencies than vibrations having O...H–O bending character. On the one hand, such behavior is not typical of covalently bonded molecules. On the other hand, the predicted (scaled) harmonic normal mode frequencies (corresponding to Fig. 3B) align fairly well with the IRMPD spectra, as indicated by the solid (O...H–O asymmetric stretch) and dashed (O...H–O bends) lines superimposed upon the experimental spectra in Fig. 3A. These lines represent, respectively, the two most intense bands having asymmetric stretch character (solid lines) and the four most intense bands having O...H–O bending character (dashed lines).

Previous investigators have inferred that the proton-bound homodimer of dimethyl ether has two nearly equivalent O–H distances [2–4]. By contrast, the internal, ionic hydrogen bond of protonated **1** has distances relative to the bridging proton that differ by approximately 0.177 Å. With symmetry broken in this fashion, two alternatives present themselves, represented by Alternative **A** and Alternative **B** in Fig. 1. In **A**, the potential well possesses no symmetry but has a single minimum. In **B**, there is a local maxi-

Fig. 4. Experimental IRMPD spectrum of m/z 161 (protonated **1**) recorded in a quadrupole ion trap with helium buffer gas (solid black curve) and with diminished helium (dashed curve), compared to the unscaled DFT harmonic predicted IR spectrum (silhouette).

mum at the midpoint, and a double-well minimum results. In other words, preserving the C_s symmetry (which bimolecular, proton-bound ether homodimers exhibit) produces a small barrier in the intramolecular case. On the one hand, if the double-well minimum is a correct representation, then the calculated normal mode(s) for asymmetric stretching should be much lower than observed experimentally, as has been seen for protonated diamines [1]. This occurs because the hump in the middle pushes up the zero point level far more than it does the $v=1$ level. If, on the other hand, the positions of the calculated normal modes match experiment (as they do in the case of proton-bound ether homodimers [2–4]), then it seems more plausible to infer a single-well minimum.

The IRMPD spectrum of deuterated **1** (the black trace in Fig. 3A) shows that the second lowest energy band of the red trace in Fig. 3A (near 895 cm^{-1}) shifts to lower frequency. Because the asymmetric $\text{O}\cdots\text{D}-\text{O}$ stretch also couples with skeletal modes, one cannot state with certainty which of the corresponding red-shifted bands (at 800 and 845 cm^{-1} in the black trace, both of which have asymmetric stretch character according to computer animation) provides a better match. In any event, the 895 cm^{-1} band disappears upon replacement of the bridging H with bridging D.

The band positions in Fig. 3A correlate well with the scaled predictions, but many intensities do not. The most intense calculated band in the fingerprint region corresponds to one of the $\text{O}\cdots\text{H}-\text{O}$ bends (1585 cm^{-1} observed vs 1614 cm^{-1} predicted, which lies within the 35 cm^{-1} uncertainty due to anharmonicity [11]), but there is an equally intense experimental band around 1000 cm^{-1} , which is an order of magnitude stronger than predicted. In like fashion, the bands $\pm 300\text{ cm}^{-1}$ on either side of 1000 cm^{-1} also display intensities greater than predicted.

The two lowest bands in Fig. 4 also have some asymmetric stretch character, but, according to DFT calculations, do not shift more than 5 cm^{-1} upon deuteration (although this hypothesis has yet to be tested experimentally). Thus, we base most of our conclusions on the bands represented by the stick spectra in Fig. 3A. We assign the two highest frequency bands (represented by red dashed lines) to $\text{O}\cdots\text{H}-\text{O}$ bends, based on DFT calculations, and both shift to the red upon deuteration. The other two dashed lines and the higher frequency solid line lie in a congested region, making it difficult to assess whether they have shifted or not. The lower solid line shifts, and, based on its match with the calculated normal mode for an $\text{O}\cdots\text{H}-\text{O}$ asymmetric stretch, we infer that the harmonic approximation gives a good fit to the experimental data. Hence, we infer that Fig. 2A (a single-well potential) does correspond to an accurate representation of the potential energy surface for proton transit, rather than Fig. 2B.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ijms.2016.08.012>.

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