

Anharmonicity and the Eigen-Zundel Dilemma in the IR Spectrum of the Protonated 21 Water Cluster

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Abstract: The infrared anharmonic spectra for the $\text{H}^+(\text{H}_2\text{O})_3$, $\text{H}^+(\text{H}_2\text{O})_4$, and $\text{H}^+(\text{H}_2\text{O})_{21}$ water clusters have been reported using vibrational second-order perturbation theory at the B3LYP level with 6-31+G(d) and 6-311++G(3df,3pd) basis sets. The anharmonicity results crucial for the evaluation of the protonated water clusters and the anharmonic corrections can be larger than 500 cm^{-1} , resulting in a shift of the H_3O^+ asymmetric stretchings near the region of 2000 cm^{-1} .

1. Introduction

Understanding the hydrated proton is of paramount importance for the knowledge of fundamental processes in chemistry and biology, and the investigation of protonated water clusters has been proven to be essential for understanding the nature of protons in solution.¹ From a conceptual point of view, the proton in the water clusters can be mainly located in two places. In the Eigen form (H_3O^+),² the proton is strongly linked by a single bond to the oxygen atom of a water molecule, while in the Zundel form,³ it lies midway between the oxygen atoms of two water molecules ($\text{H}_2\text{O}-\text{H}^+-\text{H}_2\text{O}$). The Grotthuss mechanism⁴ has been used to explain the proton transfer mechanism.

The structure and vibrational spectra of the protonated water clusters, $\text{H}^+(\text{H}_2\text{O})_n$, have been a challenge for chemists in the recent decades. In the small size regime ($n \leq 11$), experimental and theoretical works have allowed characterization of the Eigen and Zundel motifs.^{5–9} The structural identification of protonated water clusters with medium and large sizes has been more complicated. In 2004, as shown in the seminal works by Miyazaki et al.⁶ and Shin et al.,⁷ the authors were capable of isolating the protonated water clusters $\text{H}^+(\text{H}_2\text{O})_n$ with $n = 6–27$ in gas phase and of measuring their infrared (IR) spectra from 2000 to 4000 cm^{-1} . Both works confirm that protonated water clusters are chains, two-dimensional nets, and three-dimensional cage structures at small, intermediate, and large sizes, respectively.

Moreover, special attention has been paid to the vibrational spectrum of the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster.

Mass spectroscopy studies by Lin¹⁰ and Searcy and Fenn¹¹ found that $\text{H}^+(\text{H}_2\text{O})_{21}$ shows a large mass peak intensity with respect to its neighboring clusters. This fact was ascribed to an exceptional stability of this cluster, and from that moment, $\text{H}^+(\text{H}_2\text{O})_{21}$ was known as having the “magic number” of protonated water clusters. It was proposed that its stability is caused by its structure, and a distorted pentagonal dodecahedron cage, with a neutral water molecule encaged in the cavity, and a proton over the surface was suggested as an Eigen form. This hypothesis has been confirmed by theoretical calculations,^{12,13} predicting that dodecahedral with an Eigen motif located at the cluster surface is the most stable conformer. Nevertheless, as far as we know, experimental confirmation of this hypothesis has not been reported yet.

In the infrared predissociation spectra (IRPD) series of $\text{H}^+(\text{H}_2\text{O})_n$, with $n = 6–27$, obtained by Miyazaki et al.⁶ and Shin et al.,⁷ it was found that the O–H stretching band of two-coordinated single-acceptor–single-donor (AD) water molecules disappears at the magic number cluster. This fact is significant, because it supports the idea of a highly symmetric structure for $\text{H}^+(\text{H}_2\text{O})_{21}$, i.e., a pentagonal dodecahedron cage with an internal water. However, these experimental results do not answer the question of whether the correct model for $\text{H}^+(\text{H}_2\text{O})_{21}$ is an Eigen or a Zundel motif. The characteristic intense O–H stretching vibration band, predicted near 2500 cm^{-1} , for the Eigen structure does not appear in the experimental IR spectrum measured in the $2000–4000\text{ cm}^{-1}$ range.^{6,7} This result supports the possibil-

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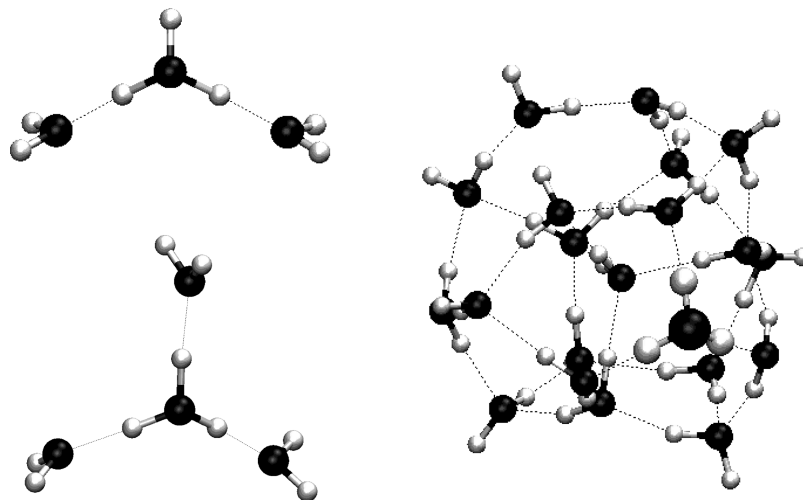


Figure 1. Optimized geometries for the protonated water clusters studied in this work. The atoms of the H_3O^+ cation in $\text{H}^+(\text{H}_2\text{O})_{21}$ are enlarged.

ity of a Zundel structure. Nevertheless, the peculiar proton oscillation of the Zundel motif appears around 1100 cm^{-1} , which is below the experimental measured IR spectrum (in the $2000\text{--}4000\text{ cm}^{-1}$ range), and therefore, the Zundel motif cannot be confirmed.

The discrepancy between *ab initio* results and the experimental spectrum was addressed by the fact that the theoretical calculations do not include thermodynamic factors, like the effect of temperature^{6,7} and the possible contributions from more than one structural isomer of a given cluster.^{7,14} After these works, several authors¹⁵ evaluated these thermodynamic factors for $\text{H}^+(\text{H}_2\text{O})_{21}$, and it has been concluded that they have an important role in the vibrational spectrum. For instance, the nonappearance of the OH stretching vibrations for the hydronium in the experimental IRDP spectrum ranging from 2000 to 4000 cm^{-1} has been attributed to a reduction of their vibrational intensities due to thermodynamic effects.

In 2009, Duncan and co-workers¹⁶ reported the IRPD spectra of $\text{D}^+(\text{D}_2\text{O})_n$ ($n = 18\text{--}24$), including $\text{H}^+(\text{H}_2\text{O})_{21}$, using a pulsed ring discharge source instead of the pulsed spark source previously employed.⁷ The IRPD spectrum of $\text{H}^+(\text{H}_2\text{O})_{21}$ is expanded to 1000 cm^{-1} , and in accordance with the previous results, the expected band around 2500 cm^{-1} of the O–H stretching vibrations of H_3O^+ was not detected. No other bands were found in the expanded lower frequency range of the spectrum. The pulsed ring discharge source makes larger ion signals, although the ions are not quite as cold as those produced with the laser spark. Then, in these new experiments, the role of the temperature becomes even more important. In addition, Douberly et al.¹⁶ pointed out that dissociation energies or the dynamical rate of dissociation at lower energies might be the problem due to the lack of a signal of the IRPD spectrum below 3100 cm^{-1} , so that further IR spectroscopy of clusters at a well-defined cold temperature would be extremely valuable.

In this work, we present a different and complementary point of view of this problem. We calculate the IR anharmonic spectra for the most stable conformers of the $\text{H}^+(\text{H}_2\text{O})_3$, $\text{H}^+(\text{H}_2\text{O})_4$, and $\text{H}^+(\text{H}_2\text{O})_{21}$ water clusters, all of

them having an Eigen structure. In the incoming paragraphs, we will show that the O–H stretching vibrations of H_3O^+ have red-shifts larger than 500 cm^{-1} , and therefore anharmonicity can also play a crucial role in the characterization of the IR spectra of the $\text{H}^+(\text{H}_2\text{O})_{21}$ water cluster.

2. Computational Methods

The B3LYP¹⁷ exchange-correlation functional with 6-31+G(d) and 6-311++G(3df,3pd) basis sets¹⁸ has been used to optimize the geometries of $\text{H}^+(\text{H}_2\text{O})_3$, $\text{H}^+(\text{H}_2\text{O})_4$, and $\text{H}^+(\text{H}_2\text{O})_{21}$ (Figure 1), with the H_3O^+ sitting on the surface of the water cage, and to calculate their frequencies. All of the protonated water clusters of this work show an Eigen motif. The most stable conformer of $\text{H}^+(\text{H}_2\text{O})_{21}$ with the hydronium ion sitting on the surface, obtained by Hodges and Wales,¹² has been used as the initial geometry of the optimization process.

In recent years, many different methodologies have been implemented to evaluate vibrational wave functions including anharmonicity. In the VSCF¹⁹ procedure, each mode vibrates at the average potential generated by all other modes. The correlation between modes can be introduced through post-VSCF procedures such as perturbation theory (VMP2),²⁰ configuration interaction (VCI),²¹ and coupled-cluster techniques (VCC).²² The present work is focused on the vibrational second-order perturbation theory (VPT2)²³ treatment implemented by Barone.²⁴ The second-order perturbation theory correction is applied to a potential energy surface (PES) approximated by a Taylor series with normal coordinates, q_i , that includes the quadratic, all cubic, and semidiagonal quartic force constants.

$$V(q_1, q_2, \dots, q_N) \cong \frac{1}{2} \sum_i w_i q_i^2 + \frac{1}{6} \sum_{ijk} f_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} q_i q_j q_k q_l \quad (1)$$

The cubic and semidiagonal quartic force constants are computed using a finite difference approach, which linearly scales with the number of normal modes. For instance, in

Table 1. Calculated Harmonic and Anharmonic Vibrational Frequencies (in cm^{-1}) and Harmonic Intensities (in $\text{km}\cdot\text{mol}^{-1}$) at the B3LYP Level Using 6-311++G(3df,3pd) and 6-31+G(d) (in parentheses) Basis Sets for $\text{H}^+(\text{H}_2\text{O})_3$

| mode | <i>I</i> (har) | ν (har) | ν (anhar) | ν (exp) ^a |
|--|-----------------|-----------------|-----------------|--------------------------|
| H ₂ O asym. stretching | 374.7 (402.0) | 3876.1 (3831.3) | 3699.1 (3650.4) | 3724 |
| H ₂ O asym. stretching | 2.2 (2.6) | 3875.6 (3830.8) | 3697.9 (3649.7) | 3724 |
| H ₃ O ⁺ free OH stretching | 164.4 (145.7) | 3801.4 (3737.4) | 3616.3 (3546.8) | 3580 |
| H ₂ O sym. stretching | 43.4 (74.3) | 3787.6 (3728.8) | 3620.5 (3559.4) | 3639 |
| H ₂ O sym. stretching | 123.1 (121.8) | 3787.1 (3729.0) | 3621.4 (3564.1) | 3639 |
| H ₃ O ⁺ sym. stretching | 1116.5 (1175.2) | 2566.7 (2611.9) | 2564.1 (2542.2) | 2420 |
| H ₃ O ⁺ asym. stretching | 4137.9 (3990.3) | 2382.0 (2440.8) | 1802.1 (1848.6) | 1880 |

^a The experimental vibrational frequencies are obtained from ref 8, where $\text{H}^+(\text{H}_2\text{O})_3$ has been tagged with Ar.

Table 2. Calculated Harmonic and Anharmonic Vibrational Frequencies (in cm^{-1}) and Harmonic Intensities (in $\text{km}\cdot\text{mol}^{-1}$) at the B3LYP Level Using 6-311++G(3df,3pd) and 6-31+G(d) (in parentheses) Basis Sets for $\text{H}^+(\text{H}_2\text{O})_4$

| Mode | <i>I</i> (har) | ν (har) | ν (anhar) | ν (exp) ^a |
|--|-----------------|-----------------|-----------------|--------------------------|
| H ₂ O asym. stretching | 402.9 (359.4) | 3884.1 (3834.7) | 3699.0 (3645.6) | 3730 |
| H ₂ O asym. stretching | 37.1 (49.6) | 3883.6 (3834.3) | 3697.7 (3643.4) | 3730 |
| H ₂ O asym. stretching | 32.3 (88.5) | 3883.4 (3833.9) | 3711.0 (3668.8) | 3730 |
| H ₂ O sym. stretching | 1.4 (3.9) | 3796.3 (3732.6) | 3622.0 (3562.5) | 3644 |
| H ₂ O sym. stretching | 74.1 (72.8) | 3795.2 (3731.7) | 3616.2 (3556.9) | 3644 |
| H ₂ O sym. stretching | 73.6 (69.3) | 3795.0 (3731.3) | 3632.3 (3581.9) | 3644 |
| H ₃ O ⁺ asym. stretching | 2994.0 (2853.3) | 2856.7 (2869.0) | 2622.5 (2609.1) | 2665 |
| H ₃ O ⁺ asym. stretching | 2990.3 (2856.7) | 2856.3 (2868.6) | 2621.8 (2617.6) | 2665 |

^a The experimental vibrational frequencies are obtained from ref 8, where $\text{H}^+(\text{H}_2\text{O})_4$ has been tagged with Ar.

the case of $\text{H}^+(\text{H}_2\text{O})_{21}$, it implies 373 frequency calculations. The VPT2 method has been successfully applied to reproduce the vibrational properties for a large variety of systems.²⁵ All calculations have been carried out using Gaussian 03.²⁶

3. Results and Discussion

The first step of the present work has been devoted to validating the VPT2 methodology used to evaluate the IR spectrum of $\text{H}^+(\text{H}_2\text{O})_{21}$ with a potential energy surface (PES) obtained at the B3LYP/6-31+G(d) level.²⁷ To this end, we have computed the IR spectra of $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$, for which accurate experimental IR spectra have been recently reported.^{7,9} Tables 1 and 2 contain the experimental and calculated harmonic and anharmonic vibrational frequencies and harmonic intensities of selected vibrational frequencies for $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$ systems, respectively, obtained at B3LYP level of theory using 6-31+G(d) and 6-311++G(3df,3pd) basis sets. The Supporting Information contains all of the harmonic and anharmonic vibrational modes for the protonated water clusters studied in this work.

The first important conclusion is that the augmentation of the basis set from 6-31+G(d) to 6-311++G(3df,3pd) is not crucial for the evaluation of the IR anharmonic spectra of $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$ (for more details, see the Supporting Information). The second important conclusion is that the H_3O^+ stretchings present important anharmonic red-shifts, e.g., around 300 cm^{-1} for the $\text{H}^+(\text{H}_2\text{O})_4$ system and up to 592.1 cm^{-1} for the asymmetric stretching of H_3O^+ for $\text{H}^+(\text{H}_2\text{O})_3$.²⁸ Moreover, the introduction of anharmonicity through the VPT2 methodology produces a considerable improvement of the harmonic vibrational frequencies. The differences of the harmonic vibrational frequencies with respect to the experimental values range between 98.4 and 560.8 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_3$ and between 88.6 and 204 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_4$, while the differences between anharmonic and experimental vibrational frequencies range between 20.6 and

144.1 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_3$ and between 22.0 and 84.4 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_4$. These results illustrate the relevance of the anharmonicity in the evaluation of the vibrational spectra for protonated water clusters. In addition, we can conclude that the VPT2 methodology with the PES obtained at the B3LYP/6-31+G(d) level represents an effective and reliable choice for obtaining a semiquantitative reproduction of the experimental spectra of $\text{H}^+(\text{H}_2\text{O})_{21}$.

Finally, it is interesting here to compare the IR spectra of both clusters, according to the results reported by Headrick et al.⁸ In the case of the $\text{H}^+(\text{H}_2\text{O})_3$ cluster, the Eigen signature appears at 1880 cm^{-1} . On the contrary, in the case of the $\text{H}^+(\text{H}_2\text{O})_4$ cluster, the Eigen core is fully hydrated, and the corresponding band appears at 2665 cm^{-1} . In both cases, our anharmonic calculations predict quite well the experimental bands, and they are also in good agreement with the theoretical values reported in the same work. These results are very interesting because they clearly show that the Eigen signature can cover a wide range of frequencies. For instance, the OH stretch of the isolated H_3O^+ appears near 3500 cm^{-1} ,²⁹ and it is red-shifted up to 2665 cm^{-1} for the $\text{H}^+(\text{H}_2\text{O})_4$ cluster and up to 1880 cm^{-1} for the $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_5$ clusters.⁸

Regarding the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster, Figure 2 shows the harmonic and anharmonic computed IR spectra, whereas the calculated values and relative intensities of the H_3O^+ stretchings are reported in Table 3.

At the first sight of Figure 2, one can see important dissimilarities between harmonic and anharmonic IR spectra. From 3000 to 4000 cm^{-1} , the symmetric and asymmetric stretchings of water molecules and the OH stretching bands of three-coordinated double-acceptor–single-donor (AAD) water molecules appear. These vibrational modes show different red-shift anharmonic corrections, ranging from 170 to 310 cm^{-1} .²⁸ These red-shift anharmonic corrections lead to a reorganization of the vibrational modes and an important

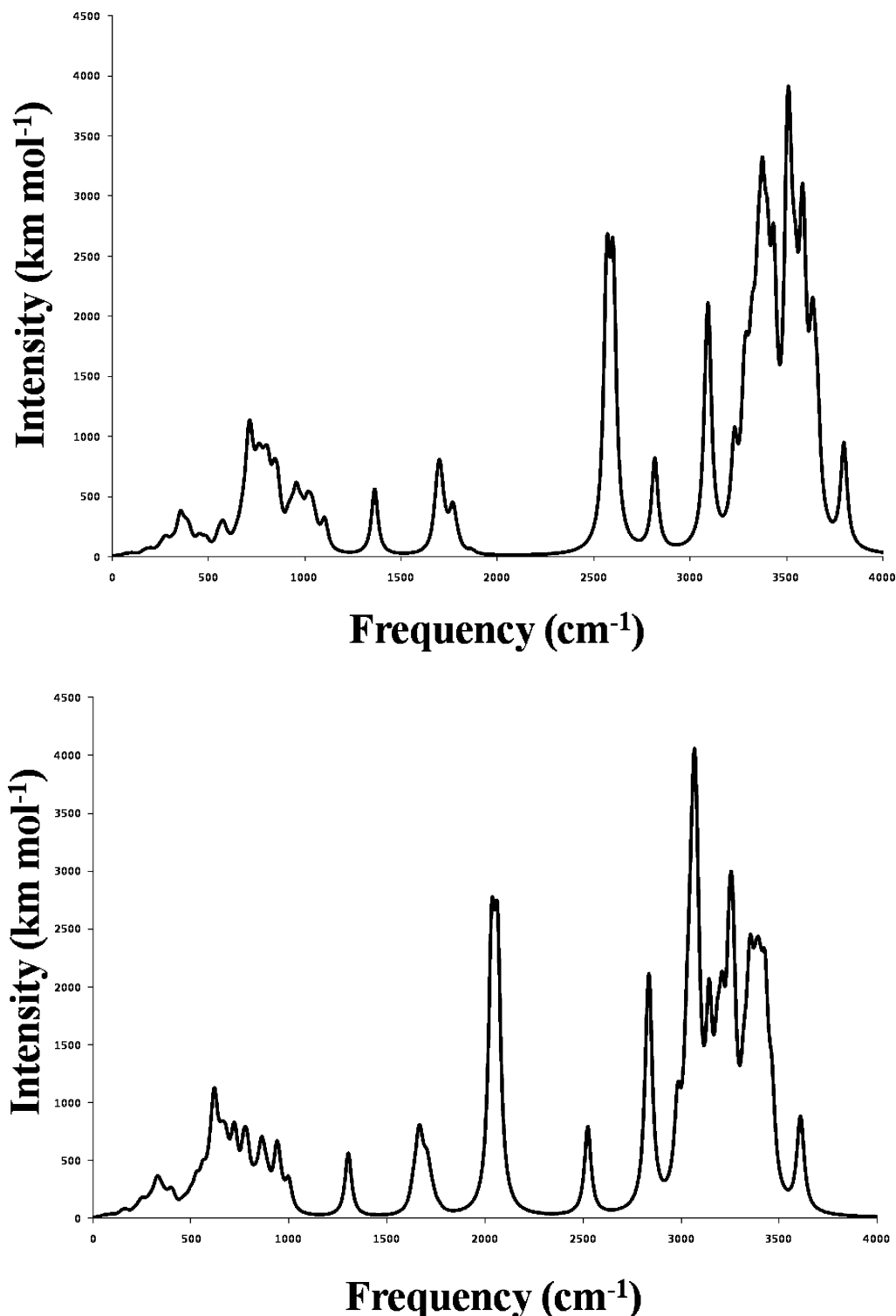


Figure 2. Computed harmonic (top) and anharmonic (bottom) spectra for the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster with H_3O^+ located on the surface of the cage, obtained at the B3LYP/6-31+G(d) level of theory.

change of the IR spectrum shape, so that the shape of the anharmonic computed IR spectrum of the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster is more similar to the experimental IRPD spectrum reported by Shin et al.⁷ and Douberly et al.¹⁶ than that predicted by the harmonic approach.

Below 3000 cm^{-1} , the “problematic” stretching bands of H_3O^+ are found. First, our calculations predict a less intense band ($761\text{ km}\cdot\text{mol}^{-1}$), which is located at 2523.3 cm^{-1} , that corresponds to the H_3O^+ symmetric stretching. This band has

an important anharmonic correction of 292.5 cm^{-1} . Second, our calculations predict at 2062.9 and 2033.2 cm^{-1} two intense bands (2030 and $2080\text{ km}\cdot\text{mol}^{-1}$), corresponding to the fingerprint vibrational frequencies of the H_3O^+ asymmetric stretchings. It is important to remark here that, for these two bands, the anharmonic corrections are larger than 500 cm^{-1} in a similar way to that previously discussed for the $\text{H}^+(\text{H}_2\text{O})_3$ cluster. Finally, below 1800 cm^{-1} , the harmonic and anharmonic vibrational IR spectra are quite

Table 3. Calculated Harmonic and Anharmonic Vibrational Frequencies (in cm^{-1}) and Harmonic Intensities (in $\text{km}\cdot\text{mol}^{-1}$) at the B3LYP/6-31+G(d) Level of H_3O^+ Stretching for the $\text{H}^+(\text{H}_2\text{O})_{21}$ Cluster with H_3O^+ Located on the Surface of the Cage

| mode | I (har) | ν (har) | ν (anhar) |
|---|-----------|-------------|---------------|
| H_3O^+ sym. stretching | 761.4 | 2815.8 | 2523.3 |
| H_3O^+ asym. stretching | 2030.4 | 2599.8 | 2062.9 |
| H_3O^+ asym. stretching | 2079.9 | 2567.2 | 2033.2 |

analogous, and they contain vibrational bending frequencies of water molecules with anharmonic corrections smaller than 100 cm^{-1} .

Our predicted anharmonic spectrum shows large differences with respect to the experimental IRPD spectra reported in the literature^{6,7,16} in which neither the H_3O^+ stretching frequencies nor the vibrational bending frequencies below 1800 cm^{-1} are observed. According to previous works,^{7,14–16} these differences might be attributed to thermodynamic and dynamic effects, like the temperature and the contributions from more than one structural isomer of a given cluster. In addition, it is worth pointing out here that the calculations and experiments address different situations; namely, the calculations correspond to one-photon absorption spectra, and the experiment corresponds to multiphoton (predominantly two-photon) predissociation spectra. These factors can have an important role in the vibrational spectrum of $\text{H}^+(\text{H}_2\text{O})_{21}$, and consequently, they can lead to a reduction of the vibrational band intensities. For instance, they could explain the nonappearances of the symmetric H_3O^+ stretching vibration predicted around 2500 cm^{-1} and the asymmetric H_3O^+ stretching vibrations predicted around 2000 cm^{-1} in the experimental IR spectra. Our computed IR spectrum does not consider the effect of the temperature, and it corresponds to the most stable conformation of the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster. Thus, our results should mimic a spectrum measured at very low temperatures, where the thermodynamic and dynamic effects are reduced.

4. Conclusions

In the present work, we have studied the anharmonic effects of the $\text{H}^+(\text{H}_2\text{O})_3$, $\text{H}^+(\text{H}_2\text{O})_4$, and $\text{H}^+(\text{H}_2\text{O})_{21}$ water clusters, all of them having an Eigen structure, by using the VPT2 methodology with a PES obtained at the B3LYP level of theory using 6-31+G(d) and 6-311++G(3df,3pd) basis sets. Our results lead to the following conclusions:

For the $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$ clusters, experimental and other theoretical data are available, and they are in good agreement with the results obtained in this work. According to our calculations, the Eigen signature appears at 1802 cm^{-1} in the case of the $\text{H}^+(\text{H}_2\text{O})_3$ cluster and at 2622 cm^{-1} in the case of the $\text{H}^+(\text{H}_2\text{O})_4$ cluster (the experimental values are 1880 and 2665 cm^{-1} , respectively). In both cases, the anharmonic effects are shown to be very important, with red-shifts up to 580 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_3$ and up to 234 cm^{-1} for $\text{H}^+(\text{H}_2\text{O})_4$ with respect to the harmonic spectra.

Regarding to the $\text{H}^+(\text{H}_2\text{O})_{21}$ cluster, our calculations show that the anharmonic effects produce important red-shifts in

the computed bands. In the 3000 to 4000 cm^{-1} range, the computed anharmonic IR spectrum is more similar to the experimental spectrum than the harmonic one. Moreover, our calculations predict the symmetric and HO asymmetric stretchings of the Eigen signature to appear close to 2500 and 2000 cm^{-1} with red-shifts larger than 250 and 500 cm^{-1} , respectively, with respect to the computed harmonic value. The discrepancies between theoretical and experimental IR spectra have been attributed to thermodynamic and dynamic effects, and therefore, these results will be valid at very low temperatures. Regarding this point, and following a reviewer's comment, it is worth noting here that it will be very difficult to obtain a high enough concentration of ions to do a direct IR adsorption measurement, and at temperatures near 0 K , the IRPD technique would take more than two photons to observe dissociation on the time scale of the experiment.

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Supporting Information Available: All of the harmonic and anharmonic vibrational modes at the B3LYP level of theory using 6-31+G(d) and 6-311++G(3df,3pd) basis sets for the protonated water clusters studied in this work. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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- (27) It is important to remark that the harmonic and anharmonic vibrational spectra for the $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$ clusters were also evaluated at the MP2 level, and they compare quite well with the B3LYP and the experimental results.
- (28) It is important to remark that some of the largest anharmonic corrections to vibrational frequencies may suffer from some errors. They have been evaluated using a truncated PES and the perturbation theory. The coupling between anharmonic low and high frequency modes can generate very large cubic and quartic force constants, which could affect the convergence of the perturbation method. For instance, in the low frequency modes of $\text{H}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_4$, the VPT2 correction leads to negative vibrational frequencies. In order to fix these modes and to validate the VPT2 results for the highly anharmonic systems, it would be necessary to apply vibrational variational methods, i.e., vibrational configuration interaction (VCI) or vibrational coupled-cluster (VCC), and to use a full PES, although this point is outside the scope and possibilities of this work.
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