Hydrated Proton

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Strong Isotope Effects in the Infrared Spectrum of the Zundel Cation**

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Protonated water clusters $H(H_2O)_n^+$ of various sizes and geometries have captured the attention of many researchers in recent years owing to their importance in many areas of chemistry and biology. Advancement in understanding the dynamics and spectroscopy of these clusters has been possible as improvements were made in the measurement of infrared (IR) action spectra in the gas phase.[1–6] To assign the recorded spectra and extract information pertaining to the structure and dynamics of the clusters, computational simulations are required. Such simulations are difficult because of the coupled anharmonic interatomic-potentials that govern the motion of these systems and are characterized by several accessible minima connected through shallow barriers.

The protonated water dimer $H(H_2O)_2^+$, also known as the Zundel cation, has recently been the subject of intense research efforts both from experimental[2–6] and theoretical[5–14] perspectives. Multiphoton free electron laser (FEL) spectroscopy,[2,3] and predissociation studies using argon[4–6] and neon[5,6] as the tagging agents have been used to assign the vibrational modes of the water clusters. The spectrum obtained with neon tagging is very close to the linear absorption spectrum of the bare Zundel cation. The spectral assignment and the complete understanding of the system was accomplished following a full-dimensional quantum-dynamic simulation.[12,13] IR spectra of various isotopically substituted forms of the Zundel cation have been recently measured using the messenger predissociation technique with argon tagging in the range of 600–4000 cm^{-1}.[6] The large variation observed in the spectral features of the different isotopomers clearly indicates the complex nature of cluster dynamics that is dominated by anharmonicities and Fermi resonances.

Herein we report the computation and the assignment of the IR spectra of isotopically substituted forms of the Zundel cations $D(D_2O)_2^+$, $H(D_2O)_2^+$, and $D(H_2O)_2^+$. Furthermore, the spectra are compared to that of the non-deuterated $H(H_2O)_2^+$ cation.[12,13] The effect of a full or partial deuteration of the cation not only leads to line shifts, but significantly changes their intensities and modifies the assignment of the infrared signatures of the isotopologues. The changes in the IR spectra are the consequences of alterations of the coupling patterns among the vibrational modes as a result of deuteration. Computations of the IR spectra are performed by integrating the vibrational time-dependent Schrödinger equation in full dimension (15 D). The calculations are carried out by the multiconfiguration time-dependent Hartree (MCTDH) method, a general wavepacket–propagation algorithm.[15] The simulated spectra are then calculated by Fourier transform of an autocorrelation function using the initial state as the dipole-operated ground state,[13] the spectral resolution being limited by the length of the time-propagation. The autocorrelation function has a length of 2000 fs and the obtained spectral peaks have full widths at half maximum of 18 cm^{-1}.

Figure 1a shows the computed MCTDH spectrum for $H(H_2O)_2^+$ and is compared with the spectra from the Reference [6], which were measured using neon and argon as tagging agents. The agreement of the computed IR linear absorption spectrum with the neon-tagging spectrum is excellent. The argon-tagging spectrum shows splitting and broadening of spectral features due to the stronger interaction of argon with the cation. For the deuterated species, only the argon-tagged spectra have been measured to date,[6] and Figure 1b shows a comparison of the computed $D(D_2O)_2^+$ spectrum with that of the experimental data. Although the spectrum using argon tagging has relatively broad features, the positions of the main absorption bands are in good agreement in with the theory.

The interpretation of the IR spectra requires not only definite assignments of the spectral lines to their respective vibrational modes, but an understanding of the origin of such modes as well. Zeroth-order states are used as a tool to perform such assignments. These states correspond to the well-defined local excitations of the system, such as the bending modes of the water molecules, or the one-quantum excitation of the proton-transfer mode. These zeroth-order states are constructed as products of eigenfunctions of low dimensional Hamiltonians. A detailed definition and the procedures for obtaining those states in the context of MCTDH was presented elsewhere.[13] Herein $|\Phi_l\rangle$ refers to the vibrational wavefunction of a zeroth-order state, whereas $|\Psi_m\rangle$ corresponds to a vibrational eigenstate. The quantities used for assignment of the IR absorptions are the $|\langle\Phi_l|\Psi_m\rangle|^2$ products, which indicate the extent to which a particular

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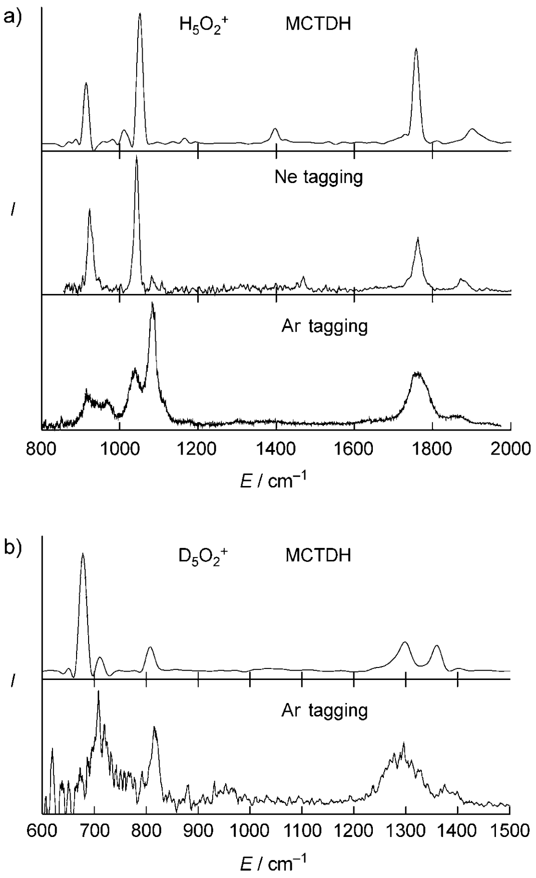

Figure 1. Comparison of MCTDH spectra with available experimental data from the literature [6] for a) $H(H_2O)_2^+$ and b) $D(D_2O)_2^+$.

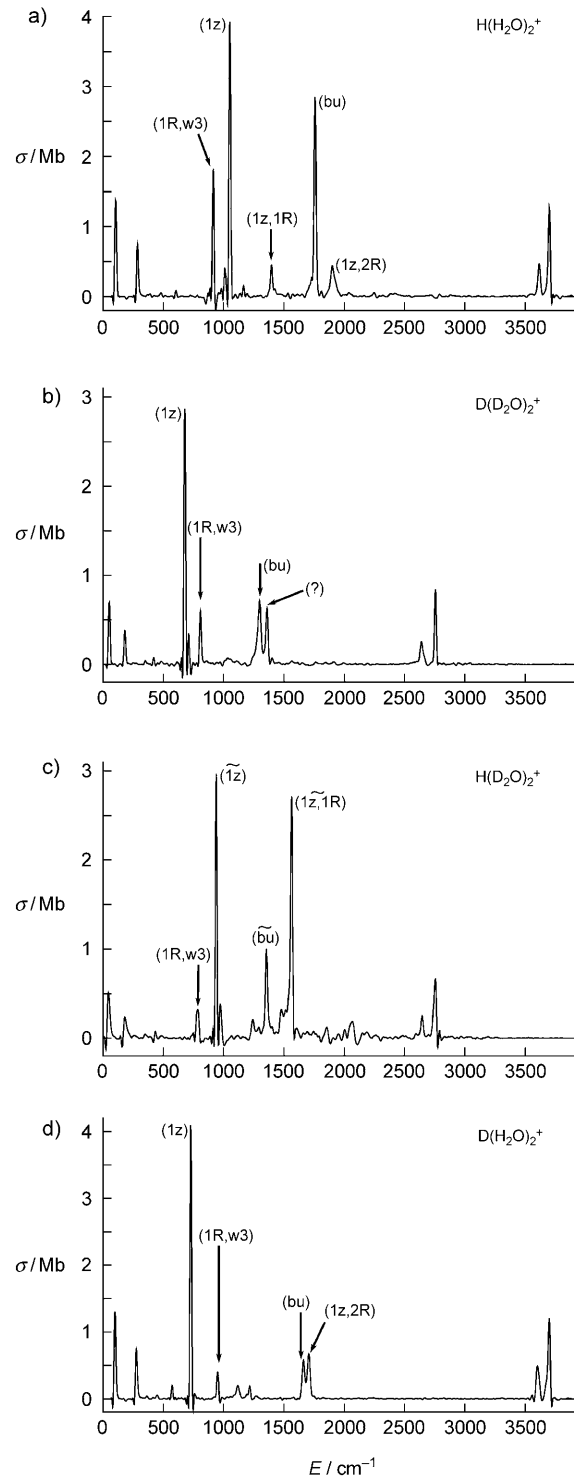

Figure 2. Computed IR spectra of the a) $H(H_2O)_2^+$, b) $D(D_2O)_2^+$, c) H-$(D_2O)_2^+$, and d) $D(H_2O)_2^+$ isotopologues of the Zundel cation, with the corresponding assignments for the most intense absorptions. σ = cross section.

zeroth-order vibration participates in a given spectral line. Although each spectral line contains contributions from all or some of the considered zeroth-order states (non-vanishing $|\langle \Phi_l | \Psi_m \rangle|^2$), there is usually a zeroth-order state that contributes to a specific transition appreciably more than the others. Thus, a given spectral line is referred to as the observed transition and the corresponding eigenstate as $|\Psi_{obs}\rangle$, as it is possible to identify a zeroth-order state $|\Phi_{obs}\rangle$, which contributes largely to $|\Psi_{obs}\rangle$. In the case of very large couplings of the vibrational modes, it may not be possible to clearly deconvolute the spectrum such that one-to-one assignments of spectral peaks to zeroth-order states can be achieved, because some transitions have similar contributions from two or more zeroth-order states. A table containing the most important $|\langle \Phi_l | \Psi_i \rangle|^2$ elements for the four considered isotopologues is provided in the Supporting Information.

Figure 2 presents the computed IR spectra of $H(H_2O)_2^+$, $D(D_2O)_2^+$, $H(D_2O)_2^+$, and $D(H_2O)_2^+$. The IR spectrum of $H(H_2O)_2^+$ was discussed in References [12] and [13] and has been reintroduced herein as a reference spectrum to compare the spectra of the various isotopologues. The lowest frequency region of the four spectra is composed of two lines related to combinations of the one-quantum wagging motion and the internal rotation of one monomer with respect to the other. The highest frequency regime on the other hand, is composed of two lines related to the terminal O–H (O–D) vibrations of the water molecules. Neither the assignment of the peaks just discussed in the lowest and highest energy domain, nor their relative positions, change after deuteration. Only the expected red shifts take place for $D(D_2O)_2^+$ and $H(D_2O)_2^+$, that is, upon substitution of the terminal hydrogen atoms by deuterium.

The situation, however, is much more complex in the spectral region between 600 and 2000 cm^{-1}. The middle range of the $H(H_2O)_2^+$ spectrum in Figure 2a features five distinct absorptions between 900 and 1900 cm^{-1} that originate from a set of five coupled zeroth-order states[12,13]: 1) $|\Phi_{1R,w_3}\rangle$, a combination of a two-quanta asymmetric wagging (w_3) mode and the one-quantum ($1R$) mode (where R is the O–O stretching coordinate), 2) $|\Phi_{1z}\rangle$, the one-quantum asymmetric proton stretch along the central O–O axis (z refers to the proton position along the O–O axis), 3) $|\Phi_{1z,1R}\rangle$, a combination of the $1z$ and $1R$ excitations, 4) $|\Phi_{1z,2R}\rangle$, a combination of the $1z$ and two-quanta O–O excitations, and 5) $|\Phi_{bu}\rangle$, the ungerade bending mode of water.

The most intense line of the $H(H_2O)_2^+$ spectrum centered at 1040 cm^{-1} is related to the $1z$ transition, as the displacement of the central proton along the O–O axis causes the largest variation of the dipole moment. Although the $|\Phi_{1z}\rangle$ state has a large contribution to this eigenstate, the second most important contribution to this line arises from the $|\Phi_{1R,w_3}\rangle$ state. The situation is however reversed for the transition centered at 915 cm^{-1}, in which the leading contribution is the $|\Phi_{1R,w_3}\rangle$ state, and the second most important contribution is $|\Phi_{1z}\rangle$. Therefore, the doublet of peaks centered at about 1000 cm^{-1} in $H(H_2O)_2^+$ arises from a Fermi resonance between the strongly coupled zeroth-order states $|\Phi_{1z}\rangle$ and $|\Phi_{1R,w_3}\rangle$.[12–14] The next three lines of the spectrum correspond to the 1415 cm^{-1} ($1z$,$1R$), 1750 cm^{-1} (bu) and 1905 cm^{-1} ($1z$,$2R$) transitions. All three transitions, and bu in particular, have a significant contribution from the $|\Phi_{1z}\rangle$ zeroth-order state, from which they obtain a large part of their spectral intensity.[13] Moreover, the strong coupling between the $|\Phi_{1z}\rangle$ and $|\Phi_{bu}\rangle$ modes is responsible for shifting the bu and $1z$ modes, respectively, by about 150 cm^{-1} higher and lower with respect to their estimated uncoupled positions.[13,14]

The IR spectrum of $D(D_2O)_2^+$ is shown in Figure 2b. The $1z$ peak is found at 678 cm^{-1} and is, as in $H(H_2O)_2^+$, the most intense IR absorption. The ($1R$,w_3) peak is found at 807 cm^{-1}. The characteristic doublet observed at about 1000 cm^{-1} in $H(H_2O)_2^+$ is also found in $D(D_2O)_2^+$, but with its constituent peaks in reverse order. The bu peak is found at 1298 cm^{-1}, about 450 cm^{-1} lower in wavenumber compared to its position in $H(H_2O)_2^+$. Neither the ($1z$,$1R$) nor ($1z$,$2R$) peak appear in the spectrum of $D(D_2O)_2^+$. After deuteration, the coupling between the z (proton position) and R (O–O distance) modes is reduced because the system remains in deeper, less anharmonic regions of the potential, thus reducing the possibility for direct absorption of the ($1z$,$1R$) and ($1z$,$2R$) combinations. Close to the bu peak, a line is found that is unassigned. This unknown state borrows part of the intensity from bu to become more intense in the spectrum of $D(D_2O)_2^+$. This absorption is also seen as a shoulder in the bu peak obtained from the experiments.[6] The exact nature of this absorption will be addressed later.

The most complex of all considered spectra is $H(D_2O)_2^+$ (Figure 2c). The deuteration of the external positions brings the position of the zeroth-order state $|\Phi_{bu}\rangle$ to a lower frequency by about 300 cm^{-1}, whereas the zeroth-order states $|\Phi_{1z}\rangle$ and $|\Phi_{1z,1R}\rangle$ remain mostly unaffected. This results in a situation in which $|\Phi_{bu}\rangle$ is found between $|\Phi_{1z}\rangle$ and $|\Phi_{1z,1R}\rangle$. These three zeroth-order states strongly couple to each other and are responsible for the triplet absorption with peaks at 938, 1355, and 1564 cm^{-1}, for which the peak at 938 cm^{-1} has almost equal contribution from $|\Phi_{1z}\rangle$ and $|\Phi_{bu}\rangle$. The central peak at 1355 cm^{-1} has almost equal participation from $|\Phi_{1z}\rangle$, $|\Phi_{bu}\rangle$, and $|\Phi_{1z,1R}\rangle$. On the other hand, the peak at 1564 cm^{-1} is a mixture of $|\Phi_{bu}\rangle$ and $|\Phi_{1z,1R}\rangle$ with a slightly larger contribution of the latter. The strong couplings shape the middle region of the spectrum and are reflected in the loss of diagonal dominance of the matrix composed of the $|\langle\Phi_l|\Psi_m\rangle|^2$ elements for $H(D_2O)_2^+$ (see the Supporting Information). The use of a tilde in these three assignments in Figure 2c indicates that the tag assignments are somewhat arbitrary because of the strong mixings of the underlying zeroth-order states. The ($1R$,w_3) peak is of reduced intensity owing to its red shift and is consequently decoupled from the zeroth-order $1z$ state. The ($1z$,$2R$) state is located far from peaks from which it can borrow intensity and shows no IR absorption.

In contrast to $H(D_2O)_2^+$, deuteration of the central position alone in $D(H_2O)_2^+$ leads to the simplest and most diagonally dominant IR spectrum of this series. In this case the zeroth-order $1z$ peak shifts to lower frequencies and decouples itself from the ($1R$,w_3) peak. The peak at 785 cm^{-1} is clearly assigned to $1z$ and is decoupled from bu. This decoupling brings the position of the bu peak down to 1662 cm^{-1}, which is closer to the bending frequency of an isolated water molecule, and explains the reduced intensity. Note that the position of bu at 1758 cm^{-1} in $H(H_2O)_2^+$ was due to the strong coupling with the central proton $1z$ mode. Owing to the isotopic substitution, the ($1z$,$2R$) peak is shifted down in wavenumber to a position that is relatively close to the bu.

In conclusion, quantum-dynamic simulations and assignments are presented for the most important peaks for the IR spectra of the $D(D_2O)_2^+$, $H(D_2O)_2^+$ and $D(H_2O)_2^+$ isotopologues of the Zundel cation in the spectral range 0–4000 cm^{-1}. Dramatic differences are found between the spectra of the various isotopologues. These differences are present because of the soft, anharmonic, and coupled potential of the Zundel cation, for which the dynamics and spectroscopy are strongly dominated by Fermi resonances between various zeroth-order vibrations. The most complex spectrum is $H(D_2O)_2^+$, in which the deuteration of the external positions results in confinement of the IR-active modes to a narrow spectral range and leads to large mixings between the zeroth-order $1z$, bu, and ($1z$,$1R$) vibrations. Conversely, deuteration of the internal position in $D(H_2O)_2^+$ induces a decoupling of the motion of the central proton with respect to the motions of the water moieties. Precise assignments of all peaks were achieved for these clusters. The calculations present important fundamental information on the dynamics and spectroscopy of protonated water clusters, in particular on their dramatic isotope effects, and represent a step forward in our understanding of these complex systems.

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