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Infrared Signatures of Isomer Selectivity and Symmetry Breaking in the $\text{Cs}^+(\text{H}_2\text{O})_3$ Complex Using Many-Body Potential Energy Functions

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A quantitative description of the interactions between ions and water is key to characterizing the role played by ions in mediating fundamental processes that take place in aqueous environments. At the molecular level, vibrational spectroscopy provides a unique means to probe the multidimensional potential energy surface of small ion–water clusters. In this study, we combine the MB-nrg potential energy functions recently developed for ion–water interactions with perturbative corrections to vibrational self-consistent field theory and the local-monomer approximation to disentangle many-body effects on the stability and vibrational structure of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster. Since several low-energy, thermodynamically accessible isomers exist for $\text{Cs}^+(\text{H}_2\text{O})_3$, even small changes in the description of the underlying potential energy surface can result in large differences in the relative stability of the various isomers. Our analysis demonstrates that a quantitative account for three-body energies and explicit treatment of cross-monomer vibrational couplings are required to reproduce the experimental spectrum.

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I. INTRODUCTION

Hydrated ions are ubiquitous in nature and industrial processes.^{1–10} Despite their central role in mediating several physicochemical transformations in aqueous environments, the driving forces and mechanisms that determine the hydration structure of different ions remain the subject of ongoing debate.^{11–25} At the molecular level, a fundamental understanding of ion hydration is tightly connected to the ability to accurately characterize the structure and dynamics of the surrounding water hydrogen-bond (HB) network. Due to their relatively small size, small ion–water clusters represent prototypical systems for detailed studies of the rearrangements of the water HB network since they can be investigated both experimentally, using high-resolution vibrational spectroscopy,^{26–49} and theoretically, using high-level molecular modeling.^{50–72} In the case of monoatomic ions, the charge of the ion dictates the bonding motifs of the surrounding water molecules, with the halide ions typically serving as HB-acceptors within the water HB network and the alkali-metal ions forming noncovalent, ion–dipole complexes.^{69–77}

Cesium occupies a special place in the periodic table since it is the most electropositive element and the most polarizable alkali metal.⁷⁸ When hydrated, cesium ions (Cs^+) form clusters that are predominantly bound by electrostatic interactions, which results in low-energy isomers that can interconvert, even at relatively low temperatures.^{26,52,69,74,79–81} Both experimental measurements^{36,37} and theoretical calculations^{59,69} have demonstrated that the most stable structures of small $\text{Cs}^+(\text{H}_2\text{O})_n$ clusters correspond to isomers in which the ion prefers to interact with a network of HB water molecules. A recent analysis of the hydration structure of Cs^+ in bulk water has shown that an accurate representation of individual low-order many-body interactions is necessary to quantitatively reproduce the experimental extended X-ray absorption fine structure (EXAFS) spectra.²⁵

Among small $\text{Cs}^+(\text{H}_2\text{O})_n$ clusters, $\text{Cs}^+(\text{H}_2\text{O})_3$ represents a particularly interesting case of isomer selectivity, displaying several low-energy isomers whose structures result from a subtle competition between water–water and ion–dipole interactions. This competition leads to a unique temperature dependence of the measured infrared spectrum of $\text{Cs}^+(\text{H}_2\text{O})_3$ as multiple isomers are populated, even at cryogenic temperatures.⁶⁹ Although often observed via tagging experiments, recent advances in cryogenic infrared spectroscopy have enabled the trapping of individual isomers of ion–water clusters and measurements of the associated infrared spectra.^{26,27,32,34–38,40,43,82–90} However, unambiguously dissecting and assigning isomer-specific spectroscopic signatures to de-

fined vibrational modes remains challenging for both experiment and theory. In this context, the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster serves as an excellent system for testing the accuracy of both many-body potential energy functions (PEFs) used to represent multidimensional potential energy surfaces (PESs) and anharmonic and/or reduced-dimensional vibrational models used to calculate vibrational spectra. Given the nature of the underlying interactions and the presence of several nearly isoenergetic isomers, $\text{Cs}^+(\text{H}_2\text{O})_3$ clearly places stringent demands on the quality of the PES required to correctly determine isomer populations and accurately predict the vibrational coupling across all isomers, which are the foci of the present study. The article is organized as follows: Section II describes the MB-nrg model used to describe Cs^+ –water interactions as well as the theoretical and computational methods used to characterize the isomeric equilibria and calculate the vibrational spectra. Section III presents the analysis of the relative stability of the low-energy $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers in the context of many-body energies as well as systematic comparisons of the vibrational spectra calculated using different levels of approximations. The results are discussed in Section III C in the context of existing challenges for accurate theoretical modeling of anharmonic vibrational spectra of molecular systems with several coupled degrees of freedom. Finally, Section IV summarizes the main points of our study and provides an outlook on future directions.

II. METHODS

A. Molecular Models

All calculations of the energetics, relative stability, and vibrational spectra of the $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers were performed with the many-body Cs^+ –water MB-nrg potential energy function (PEF)^{25,67} using in-house software that is available upon request. As discussed in detail in the original reference,⁶⁷ the MB-nrg Cs^+ –water PEF is based on the many-body expansion (MBE) of the interaction energy,⁹¹

$$E_N = \sum_{i=1}^N V^{1\text{B}}(i) + \sum_{i<j}^N V^{2\text{B}}(i,j) + \sum_{i<j<k}^N V^{3\text{B}}(i,j,k) + \cdots + V^{\text{NB}}(1,\dots,N) \quad (1)$$

Here, V^{1B} represents the distortion energy of an individual water molecule, and V^{nB} is the n -body (nB) Cs^+ –water energy defined recursively as

$$\begin{aligned}
 V^{nB}(1, \dots, n) = & E_n(1, \dots, n) - \sum_i V^{1B}(i) - \sum_{i < j} V^{2B}(i, j) - \dots \\
 & - \sum_{i < j < \dots < n-1} V^{(n-1)B}(i, j, \dots, (n-1))
 \end{aligned}
 \tag{2}$$

Since Eq. 1 converges quickly for molecular systems with electron densities localized on individual monomers, such as ion–water clusters, it provides an efficient theoretical/computational framework for the development of analytic PEFs for computer simulations. In particular, it has been shown that the low-order terms of Eq. 1 can be accurately determined using correlated electronic structure methods (e.g., coupled cluster with single, double, and perturbative triple excitations, i.e., CCSD(T), the current “gold standard” for chemical accuracy). Within the MB-nrg framework,^{66,67} 2B and 3B CCSD(T) reference energies are accurately fitted to physically motivated expressions representing permanent electrostatics, induction, and dispersion, which are supplemented by short-range permutationally invariant polynomials (PIPs)⁹² representing quantum-mechanical effects (e.g., Pauli repulsion, charge transfer, and penetration) in regions where the electron densities of individual monomers appreciably overlap. In the MB-nrg PEFs, all larger-than-3B terms of Eq. 1 are represented through classical many-body induction.

For the Cs^+ –water MB-nrg PEF, the 2B energies were calculated⁶⁷ in the complete basis set (CBS) limit via a two-point extrapolation^{93,94} between the values obtained with the correlation-consistent polarized valence triple zeta (aug-cc-pVTZ for H₂O, and cc-pwCVTZ for the metal ions) and quadruple zeta (aug-cc-pVQZ for H₂O, and cc-pwCVQZ for the metal ions) basis sets.^{95–98} The 3B $\text{Cs}^+(\text{H}_2\text{O})_2$ energies were obtained²⁵ at the CCSD(T) level of theory using the cc-pwCVTZ basis set for Cs^+ and the aug-cc-pVTZ basis set for the O and H atoms, and corrected for basis set superposition error using the counterpoise method.⁹⁹

As in all other MB-nrg PEFs,^{66,67,100} the water–water interactions in the Cs^+ –water MB-nrg PEF are described by the MB-pol PEF,^{101–103} which has been shown to accurately reproduce water properties across all phases,^{104,105} including the isomeric equilibria and tunneling splittings in small water clusters,^{106–108} the structural, thermodynamic, and dynamical properties as well as vibrational spectra of liquid water,^{103,109–112} the sum-frequency generation spectra of the air/water interface,^{113,114} and the energetics and vibrational spectra of various ice phases.^{115–117}

B. Molecular Dynamics Simulations

Following Ref. 69, the structures of the $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers and associated relative stability as a function of temperature were obtained from replica exchange path-integral molecular dynamics (REPIMD) simulations. The REPIMD simulations were carried out in the temperature range from 10 K to 200 K (with the temperatures distributed linearly in a logarithmic scale) using the (2B+NB)-MB-nrg and (2B+3B+NB)-MB-nrg PEFs introduced in Refs. 67 and 25, which include explicit 2B, and both 2B and 3B interaction terms (Eq. 1), respectively. Following Refs. 118 and 119, each atom was described by a Feynman's ring polymer with $P = 64$ beads¹²⁰ using the normal-mode representation of the ring polymers, which guarantees efficient sampling of the quantum partition function in PIMD simulations.¹²¹ The fast Fourier transform algorithm was used to convert between Cartesian and normal-mode coordinates. The temperature was controlled with Nosé-Hoover chains of four thermostats coupled to each degree of freedom.¹²² It should be noted that, although the exact quantum properties can only be recovered in the limit of an infinite number of beads, Refs. 118 and 119 show that the free-energy differences in isomeric equilibria of water clusters converge more quickly and REPIMD simulations with 64 beads are sufficient to determine the relative stability of the different isomers as a function of temperature.

After an equilibration time of 1 ns, the populations of the different isomers were obtained from 3 ns of REPIMD simulations carried out with a timestep of 0.2 fs. Instantaneous $\text{Cs}^+(\text{H}_2\text{O})_3$ configurations were extracted every 2 ps from each replica along the REPIMD trajectories and quenched to the nearest (local) minimum-energy configurations using linear search combined with conjugate gradient optimizations (with a threshold of 10^{-8} kcal mol⁻¹ Å⁻¹ for the gradients).¹²³ Each quenched structure was then assigned to a specific isomer using structural criteria based on root-mean-square deviations from the optimized isomer configurations. It should be noted that isomeric equilibria for $\text{Cs}^+(\text{H}_2\text{O})_3$ were already reported in Ref. 69 at both classical (REMD) and quantum (REPIMD) levels using the (2B+NB)-MB-nrg PEF.

C. Vibrational Models

The infrared spectrum was calculated for each of the six $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers shown in Fig.1. Each lineshape was then weighted by the populations that were extracted from the REPIMD trajectories at a temperature of 30 K and summed. All vibrational calculations were performed numer-

ically by expanding the eigenstates in a basis of harmonic oscillator functions. Gauss-Hermite quadrature was used for evaluation of the potential energy and dipole matrix elements.^{124–126} The theoretical methods used in these calculations included harmonic normal-mode analysis; local-mode vibrational self-consistent field theory (VSCF);^{127,128} second-order, local-mode vibrational degenerate perturbation theory (VDPT2)¹²⁹ on VSCF states; the local-monomer approximation (LMon);^{130–137} and a perturbatively corrected local-monomer model (cLMon) that included two-mode, cross-monomer couplings.¹³⁸ Across all models, the small system sizes allowed ten quanta of excitation to be included along each mode. All potential energy and dipole moment calculations were conducted with the (2B+3B+NB) MB-nrg potential energy and dipole functions. A full description of the cLMon model, including intensity corrections, is provided in the Supplementary Material.

Following the procedure outlined in Ref. 137, the local-mode approach with frequency windowing effectively localizes a water cluster’s corresponding high-frequency bending and stretching modes independently, and exactly, onto independent monomers. This local transformation was shown to reduce the amount of intra-molecular mode coupling in the vibrational n -mode expansion, often converging after only two-mode couplings. For this work, the VSCF calculations were performed using this local-mode representation with a many-body expansion of the PES, including up to two-mode couplings (2-MR). The VDPT2 calculations were conducted on the corresponding local-mode VSCF states.¹²⁹ For a direct comparison between the LMon, cLMon, VSCF, and VDPT2 results, only the localized water bending and stretching modes of each isomer were included in all the calculations.

D. Tagged Isomers and Comparison with Experiments

In Section III, the experimental spectra reported in Ref. 84 are used in the comparisons with the theoretical spectra calculated using the methods discussed above. The experiments were conducted with both argon- and deuterium-tagged clusters at trap temperatures of 7 K and 12 K respectively. For the argon-tagged isomers, preliminary calculations with MP2/def2-TZVPP (see Supplementary Material) suggest that, in the minimum-energy configurations, the argon atom binds to Cs^+ in each of the four isomers identified from the REPIMD simulations (see Results).^{139–143} Since both structural and computed harmonic force constants were found to be insensitive to the placement of these single argon tags, we directly compare our calculated untagged spectra with the argon-tagged

results.

III. RESULTS

A. Structural Analysis

Within the range of temperatures at which the REPIMD simulations were performed, five and six different $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers were found with the (2B+NB)-MB-nrg and (2B+3B+NB)-MB-nrg PEFs, respectively. Fig. 1 shows the isomer structures and relative energies with respect to the minimum-energy structure calculated with both (2B+NB)- and (2B+3B+NB)-MB-nrg PEFs, along with their relative harmonic zero-point corrected energies in parentheses. Although the isomer energies obtained with (2B+NB)-MB-nrg PEF do not differ by more than 0.2 kcal/mol from the corresponding energies calculated with the (2B+3B+NB)-MB-nrg PEF (with the exception of isomer **C3**), the relative populations of the different isomers change substantially as a function of the temperature. This temperature sensitivity is, of course, one of the central motivations for cryogenic, mass spectrometry-based spectroscopy techniques. It also, however, places considerable demands on PEFs that far exceed the inherent errors of many modern quantum chemical techniques, such as density functional theory.

While both PEFs predict isomer **C2** to be the ground-state structure of $\text{Cs}^+(\text{H}_2\text{O})_3$ after accounting for harmonic zero-point energy corrections, they predict the opposite order for isomers **C1** and **C5**, which has large effects on the temperature-dependence of the corresponding isomeric equilibria. In particular, isomer **C1**, which corresponds to the second-lowest energy isomer for the (2B+NB)-MB-nrg PEF and the minimum-energy isomer for (2B+3B+NB)-MB-nrg PEF, is found ~ 0.7 kcal/mol above isomer **C1** when harmonic zero-point energy corrections are included. On the other hand, isomer **C5**, which is predicted to lie ~ 3 kcal/mol above isomer **C1** by both PEFs, becomes thermodynamically competitive with isomer **C1** upon inclusion of harmonic zero-point energy corrections. This effect is explained by considering that the three water molecules in isomer **C5** effectively behave as Cs^+ -pinned free rotors, which leads to relatively higher entropy and, consequently, lower free energy, even at low temperatures. As a result of the subtle balance between enthalpic and entropic contributions, isomer **C5** only acquires substantial population in the REPIMD simulations carried out with the (2B+3B+NB)-MB-nrg PEF. While isomer **C6** is completely absent from the REPIMD simulations carried out with the (2B+NB)-MB-nrg PEF, it

FIG. 1. (a) Molecular structures of the six lowest-energy isomers of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster along with their relative energies and harmonic zero-point corrected energies calculated with both the (2B+NB)-MB-nrg and (2B+3B+NB)-MB-nrg PEFs. (b) Thermodynamic populations of the six lowest-energy isomers of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster calculated using REPIMD simulations with (2B+NB)-MB-nrg (left) and (2B+3B+NB)-MB-nrg (right) between 0 K and 200 K. Color scheme: isomer C1 = green, isomer C2 = blue, isomer C3 = violet, isomer C4 = magenta, isomer C5 = red, isomer C6 = black.

appears at high temperature in the REPIMD simulations performed with the (2B+3B+NB)-MB-nrg PEF. Moreover, while both MB-nrg PEFs predict isomer C1 and isomer C2 to be separated by less than 0.05 kcal/mol in their respective minimum-energy configurations, isomer C1 is only stable between ~ 20 K and ~ 120 K in the REPIMD simulations with the (2B+3B+NB)-MB-nrg PEF and essentially absent from isomeric equilibria predicted by the REPIMD simulations with the (2B+NB)-MB-nrg PEF. The differences in the relative stability of the $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers predicted by the two MB-nrg PEFs in the temperature range from 0 K to 200 K highlight the high

sensitivity of the corresponding isomeric equilibria to the details of the underlying PES. To further emphasize this point, the results of REPIMD simulations carried out with a previous version of the (2B+3B+NB)-MB-nrg PEF, which displays slightly higher errors relative to the reference CCSD(T) 3B energies, are reported in the Supplementary Material.

B. Spectroscopic Analysis

Given the differences between the (2B+NB)-MB-nrg and (2B+3B+NB)-MB-nrg PEFs discussed in Section III.A, the analysis of the infrared spectra of the $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers was only carried out using the (2B+3B+NB)-MB-nrg PEF. The infrared spectrum calculated with all methods described above is shown in Fig. 2, whereas the complete list of monomer bending and stretching fundamental frequencies is provided in Table I. At 30 K, the ensemble reflects substantive contributions from isomers **C1**, **C2**, and **C5**, with the largest contribution stemming from isomer **C2**. The spectra of each isomer, in isolation, are shown in Fig. 3. The following analysis will include both a discussion of the accuracy of the methodology and an assessment of the isomer populations, in the context of existing experimental spectra.

1. Hydrogen-Bonded OH-stretch Region

Because isomer **C2** exhibits C_{2v} symmetry, cross-monomer coupling occurs between the hydrogen-bond-donating water molecules’ fundamental stretching frequencies, with intensities that are modulated by the charge fluctuation on the proton acceptor. Peaks **(A8)** and **(A10)** track the fundamental O-H stretching transitions of the hydrogen-bonded (HB) water molecules across all vibrational methods for **C2**. Experimentally, this doublet peak spacing, which is related to the strength of this cross-monomer coupling, was measured as $\Delta_{HB}^{Exp} = 14 \text{ cm}^{-1}$ ($3538/3552 \text{ cm}^{-1}$).

For the LMon approximation, which lacks explicit cross-monomer coupling, and the local-mode VSCF approximation, which averages over all cross-monomer couplings, the two resulting fundamental transitions were computed to be degenerate. Therefore, the symmetry of this cluster makes it a fruitful testing ground for the handling of mode-coupling effects. The normal-mode harmonic approximation, for example, did not predict the proper peak placement but *did* break the degeneracy and reproduced the doublet structure, albeit with a slight overestimation of the doublet splitting ($\Delta_{HB}^{Harm} = 27 \text{ cm}^{-1}$). This effect suggests that a substantive contribution to this splitting

must stem from bilinear, cross-monomer coupling terms. The cLMon method, which includes these—and higher-order—couplings, yielded more accurate peak placements, but the doublet split-

FIG. 2. Comparison between thermally weighted infrared spectra calculated in the bending (HOH bend), hydrogen-bonded (HB OH) and free (free OH) OH stretching regions using: (A) harmonic approximation, (B) local-monomer approximation (LMon), (C) corrected local-monomer approximation (cLMon), (D) two-mode vibrational self-consistent field theory (VSCF), (E) two-mode corrected second-order vibrational degenerate perturbation theory (VDPT2). (F) Experimental argon-tagged spectrum measured at a trap temperature of 7 K. The spectra were calculated using the REPIMD isomer populations at 30 K, and the linewidths were broadened by a Lorentzian function with a width of 5 cm⁻¹. The intensities of the calculated spectra have been magnified by 2.5x in the HOH bend region. The color scheme is the same employed in Fig. 1 to identify the isomers: green = isomer C1, blue = isomer C2, red = isomer C5.

ting ($\Delta_{HB}^{cLMon} = 46 \text{ cm}^{-1}$) was overestimated. This latter result indicates that subtle competition is present among the aforementioned bilinear couplings, higher-order cross-monomer couplings, and additional anharmonic couplings involving other modes. The presence of splitting engendered by inclusion of the cross-monomer couplings is encouraging, although the overestimation

FIG. 3. Computed, un-weighted VDPT2 spectra of all six $\text{Cs}^+(\text{H}_2\text{O})_3$ isomers in the HOH bend and OH stretch regions. (A) **C1** (green), (B) **C2** (blue), (C) **C3** (violet), (D) **C4** (magenta), (E) **C5** (red), (F) **C6** (black), (G) Experimental argon-tagged spectrum measured at a trap temperature of 7 K, (H) Experimental D_2 -tagged spectrum measured at a trap temperature of 12 K. The computed spectra in the HOH bending region between 1500 and 1700 cm^{-1} have been magnified by 2.5x to highlight the underlying lineshape. The calculated linewidths were broadened by a 5- cm^{-1} Lorentzian function.

TABLE I. Calculated harmonic, local-monomer (LMon), corrected local-monomer (cLMon), two-mode vibrational self-consistent field theory (VSCF), two-mode corrected second-order vibrational degenerate perturbation theory (VDPT2), and experimental infrared transition frequencies (cm^{-1}) for the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster at 30 K. The peaks **A6**, **A14**, and **A21** originating from isomer **C5** have a ~ 3 -fold degeneracy. The experimental values were taken from Ref. 84. The * indicates two possible assignments for the peak at 3712 cm^{-1} (see main text for details).

Peak	Harm	LMon	cLMon	VSCF	VDPT2	Experiment	Isomer
Water bending fundamentals (HOH bend)							
A1	1626	1566	1555	1568	1553	1604	C1
A2	1645	1566	1563	1568	1571	1604	C1
A3	1645	1566	1574	1568	1571	1604	C1
A4	1657	1594	1584	1598	1589	1617	C2
A5	1667	1612	1601	1615	1601	1617	C2
A6	1677	1612	1612	1616	1613	1648	C5
A7	1694	1612	1632	1615	1629	1630	C2
Hydrogen-bonded stretch fundamentals (HB OH)							
A8	3696	3506	3484	3503	3488	3538	C2
A9	3724	3553	3536	3565	3529	3576	C1
A10	3723	3506	3530	3503	3518	3552	C2
A11	3748	3553	3555	3565	3555	3598	C1
A12	3748	3553	3561	3565	3555	3598	C1
Free hydrogen stretch fundamentals (Free-OH)							
A13	3809	3634	3631	3655	3626	3630	C2
A14	3817	3642	3642	3669	3634	3641	C5
A15	3878	3682	3678	3661	3684	3712*	C1
A16	3878	3682	3682	3661	3684	3712*	C1
A17	3855	3682	3689	3661	3691	3712*	C1
A18	3886	3688	3687	3655	3694	3692	C2
A19	3889	3697	3697	3688	3698	3703	C2
A20	3891	3697	3698	3688	3699	3703	C2
A21	3908	3706	3706	3671	3714	3712*	C5

of this splitting suggests that such reduced-dimensional constructions should be used with some

caution. Overall, the VDPT2 method provided the closest agreement with experiment in this region, in terms of both peak positions (red-shifted by 35-50 cm^{-1}) and doublet splitting ($\Delta_{HB}^{VDPT2} = 30 \text{ cm}^{-1}$). The presence of these remnant errors is suspected to stem from the restriction of the anharmonic calculations to the bend and stretch motions; low-frequency modes likely modulate the anharmonic couplings, as well, and will be discussed in a subsequent section.

Of course, any analysis of these spectral signatures must admit the possibility that other isomers are present. In this HB region, isomer **C1** (Fig. 3) actually exhibits better computed (VDPT2) alignment with the Ar-tagged experimental spectrum. The *relative C2/C1* spectra, however, when combined with the absence of computed transitions in this region from any other isomers, are consistent with the Ar- and D₂-tagged experimental spectra. Specifically, isomer **C2** is assigned a dominant role in the Ar-tagged spectrum, whereas isomer **C1** dominates the HB region when D₂-tagged. Previous analyses⁸⁴ have suggested the presence of multiple isomers in this region due to the tag, and indeed, the tag imparts non-negligible shifts to the experimentally observed spectra. The present analysis changes the assignment of one of these isomers, although it cannot assess whether this effect is a shift in the thermodynamics due to the tag or a kinetic-trapping effect.

2. *Free-OH Region*

All five vibrational models predict a bright doublet feature specific to the free-OH fundamental transitions of isomer **C2**. The feature with the largest oscillator strength (**A19,A20**), is assigned to the fundamental free-OH stretching modes on both of the water molecules mirrored across the C₂ axis. The fundamental transition frequencies of these modes remain nearly degenerate, even with the inclusion of cross-monomer coupling. The deviation from experiment comes from peak (**A18**), which is assigned to the high-frequency free-OH transition of the HB acceptor. Across all five computational models, the computed frequency of this transition is red-shifted, relative to the free-OH fundamental transition frequencies of the flanking (symmetry-mirrored) water molecules. The method that predicts the least splitting between (**A18**) and (**A19,20**) is VDPT2, which exhibits a splitting of $\Delta_{Free-OH}^{VDPT2} = \sim 5 \text{ cm}^{-1}$. As a result, (**A18**) would require the least shifting to align with the 3703 cm^{-1} peak from the experimental trace. Alternatively, a resonant vibrational interaction could acquire intensity to the blue of (**A19**)/(**A20**), or another isomer could contribute to this lineshape. Consistent with the latter possibility, isomer **C4** nicely matches both the position and lineshape in this region of the spectrum (see Fig. 3), but it nonetheless must exist as a relatively

minor isomer, however, because of its lack of transitions in the HB region.

Instead, other isomers are considered as possibilities for the contribution to the free-OH line-shape. One possible assignment is the transition (**A21**), which is assigned to isomer **C5** and is thermodynamically populated even at ~ 30 K. The intensity of this transition arises from the three-fold degeneracy of the antisymmetric stretch modes of each of the water molecules. Across all models, (**A21**) is positioned to the blue of (**A19**, **A20**), which is consistent with the peak position in the experimental spectrum; however, either the isomer populations would need to adjust or the dipole response would need to increase in order to better align with the measured intensity. A more likely assignment involves isomer **C1**. Although its computed free-OH stretch sits to the red of the free-OH doublet in **C2**, a relatively minor blue-shift (due to inaccuracies in the PEF and/or the anharmonic simulations) would bring it into congruence with the “missing” shoulder in the spectrum. This assignment is consistent with the tagging dependence of the spectra, where the blue-shifted bands in the HB region (and red-shifted bands in the HOH bend, discussed below) account for the Ar and D₂ cases, as well. These assignments, when combined with the known tagging effects, suggest that isomer-selective, double-resonance experiments could add considerable clarity to the observed spectra.

3. *HOH Bending Region*

The HOH bending transitions [(**A4**) and (**A5**)] in isomer **C2** were computed via VDPT2 to be red-shifted, relative to the Ar-tagged experimental values, by 28 and 16 cm⁻¹, respectively. This behavior is likely the result of neglecting coupling to low-frequency modes. The strongest evidence for this explanation is that the feature is non-trivially modulated by including partial low-frequency mode coupling in the local-mode VSCF and VDPT2 models (Supporting Information). On the other hand, the relative shift between the Ar- and D₂-tagged spectra reflects shifting relative population of isomers **C2** and **C1** in this bending region, which is consistent with the behavior observed in the HB region. The population of isomer **C1** is exquisitely sensitive to both its relative energy and the temperature, and different tagging configurations could certainly alter either component. The bending transition in isomer **C5** actually matches the experimentally observed transition the best (in the Ar-tagged case). Although its presence cannot be ruled out—and, indeed, is predicted by the REPIMD populations—the spectra alone are insufficient to disentangle whether it makes a substantial contribution. Instead, isomers **C1** and **C2**, with their already-established caveats in-

volving the influence of low-frequency modes, appear to comprise the main contributions to the experimental spectra.

C. Discussion

Guided by the combination of the computed VDPT2 spectra and the Ar- and D₂-tagged experimental spectra, the present analysis suggests that the infrared spectrum primarily arises from isomers **C2** and **C1**, with possible additional contributions from isomer **C5**. Although the relative fractions may differ, this qualitative result is consistent with the isomer populations computed via REPIMD.

Both the spectra and the populations are sensitive to the details of the underlying PES (which also does not yet include the tag atom/molecule). To emphasize this sensitivity, infrared spectra calculated with the same five theoretical models used in Figs. 2 and 3 but an earlier version of the (2B+3B+NB)-MB-nrg PEF, associated with slightly larger errors relative to the reference CCSD(T) 3B energies, are reported in the Supplementary Material. Interestingly, both cLMon and VDPT2 infrared spectra calculated with less accurate (2B+3B+NB)-MB-nrg PEF appear to be in better agreement with the experimental spectrum, which suggests that error compensation between inaccuracies in the PES and approximations in the vibrational models may occur, or that the “true” PES is within the intrinsic error associated with CCSD(T) calculations. Future analyses of Cs⁺(H₂O)₃ vibrational spectra will focus on three-mode couplings in the VSCF and VDPT2 frameworks, as well as the role of low-frequency modes.

An interesting result of the present analysis is the breakdown of the local-monomer approximation when treating the symmetric isomer **C2**. Unexpectedly, the inclusion of two-mode, cross-monomer couplings overestimates the doublet splitting in the HB OH region. This result likely suggests that higher-order couplings (e.g., three-mode couplings) are required to properly account for the symmetry breaking. However, the tensor integrals that would be required to account for three-mode couplings in the cLMon model would notably increase the computational expense and complexity. The allure of the local-monomer approximation is simplicity, and these higher order corrections would likely push the model beyond the limits of practical computation for general anharmonic systems. Alternatively, if low-frequency modes are the source of remnant discrepancies, local-monomer extensions involving translations and rotations of the monomers could perhaps account for these contributions. These remaining questions about the accuracy of the theoretical methods used to calculate vibrational spectra of the Cs⁺(H₂O)₃ cluster make a direct assess-

ment of the accuracy of the corresponding MB-nrg PEF difficult. The calculations have, however, qualitatively determined the dominant contributors to the overall spectrum, which suggests that the (2B+3B+NB)-MB-nrg PEF should, at least, provide a semi-quantitative representation of Cs^+ –water interactions, in agreement with the analysis of Ref. 25.

IV. CONCLUSIONS

The tendency of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster to form several thermodynamically competitive isomers makes this system an interesting case for testing the accuracy of many-body PEFs and reduced-dimensionality vibrational models. Although an explicit representation of 3B energies appears to have minimal effects on the energy differences among the various isomers, these minimal differences still have notable repercussions on the relative stability of the isomers in the 0 K-200 K temperature range. Importantly, our analysis shows that, after including zero-point energy, the lowest-energy isomer of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster belongs to the C_{2v} symmetry point group for which standard theoretical models (such as LMon and local-mode VSCF models) fail to correctly predict the OH-stretch vibrational transitions in the hydrogen-bonded region of the spectrum. This effect is due to the inability of these models to reproduce the symmetry-breaking, which results from the C_{2v} symmetry. Symmetry breaking is reproduced, although overestimated, by perturbative models, such as cLMon and VDPT2. Since the local-monomer approximation is, however, a nice interpretive model of vibrational spectra of small aqueous clusters, an extension of this model (cLMon), which includes the effects of cross-monomer coupling, was presented. The cLMon method represents a clear improvement upon LMon. Interestingly, couplings beyond bilinear terms were found to be necessary for accurately capturing the symmetry breaking. The most important lesson gleaned from this analysis is that a quantitative match of theoretical and experimental spectra requires both a highly accurate representations of the underlying PES and a nearly exact theoretical treatment of the vibrational structure, which calls into question theoretical approaches based on classical molecular dynamics and density functional theory.^{82,84} Reduced-dimensional approximations also appear to leave many unanswered questions, and this assessment is particularly true when trying to predict sensitive doublet splittings.

V. SUPPLEMENTARY MATERIAL

Sensitivity analysis of the energetics, structures, and vibrational spectra calculated for the $\text{Cs}^+(\text{H}_2\text{O}_3)$ isomers using two MB-nrg PEFs that adopt slightly different representations of three-body energies. Theoretical and computational details of the corrected local monomer (cLMon) method, comparisons of MP2 Ar tagged and untagged vibrational frequencies, and comparisons of the vibrational spectra calculated with VDPT2 in the low-frequency region.

VI. DATA AVAILABILITY

Any data generated and analyzed for this study that are not included in this Article and its Supplementary Material are available from the authors upon request.

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Supplementary Material

Infrared Signatures of Isomer Selectivity and Symmetry Breaking in the $\text{Cs}^+(\text{H}_2\text{O})_3$ Complex Using Many-Body Potential Energy Functions

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I. ACCURACY OF THE MB-nrg PEFs

A. 3B energies

To investigate how the details of the MB-nrg PEFs affect the calculations of the infrared spectrum, a second (2B+3B+NB)-MB-nrg PEF, hereafter referred to as MB-nrg PEF2, was developed using the same 2B and 3B CCSD(T) training sets used in Refs. 1 and 2 to develop the (2B+3B+NB)-MB-nrg PEF, hereafter referred to as MB-nrg PEF1, described in the main text. The MB-nrg PEF2 differs from MB-nrg PEF1 only in the 3B PIP, i.e., MB-nrg PEF1 and PEF2 share the same representations of permanent permanent electrostatics, induction, dispersion, and 2B PIP. Fig. 1 shows correlation plots between the 3B CCSD(T) reference energies, calculated with aug-cc-pVTZ (AVTZ) basis set³ and corrected for the basis set superposition error using the counterpoise method (CP),⁴ and the corresponding values obtained with MB-nrg PEF1 (left panel) and MB-nrg PEF2 (right panel). The root-mean squared deviations (RMSDs) associated with the two PEFs are 0.06 kcal/mol and 0.15 kcal/mol, respectively, indicating that MB-nrg PEF2 is less accurate than MB-nrg PEF1 relative to the CCSD(T) reference.

FIG. 1. Correlation plots between the 3B CCSD(T) reference energies and the corresponding values calculated with the MB-nrg PEF1 (left panel) and MB-nrg PEF2 (right panel).

B. Structural Analysis

Following the same approach described in the main text, REPIMD simulations were carried out with the MB-nrg PEF2 between 10 K and 200 K. As shown in Fig. 2, only 5 of the 6 isomers of the $\text{Cs}^+(\text{H}_2\text{O})_3$ clusters predicted by the MB-nrg PEF1 are found with the MB-nrg PEF2, with isomers **C2** and **C3** becoming the lowest-energy and fifth lowest-energy isomers before including the corresponding zero-point energies, respectively. Considering that isomer **C6** is predicted not to be stable by the MB-nrg PEF2, the REPIMD populations of the remaining isomers are qualitatively similar to those found with the MB-nrg PEF1.

II. SPECTROSCOPIC ANALYSIS

A. Corrected Local-Monomer Model (cLMon)

When the local-monomer approach is applied to the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster, the following nine-dimensional Hamiltonian is obtained:

$$\hat{H}_{9d} = \sum_M^3 \frac{\hat{P}_{M,HOH}^2}{2m_{M,HOH}} + \frac{\hat{P}_{M,S1}^2}{2m_{M,S1}} + \frac{\hat{P}_{M,S2}^2}{2m_{M,S2}} + V(\vec{q}_{M,HOH}, \vec{q}_{M,S1}, \vec{q}_{M,S2}) \quad (1)$$

Here, M is a summation over monomers and $\vec{q}_{M,HOH}$, $\vec{q}_{M,S1}$, and $\vec{q}_{M,S2}$ are the set of HOH bending, and S1 and S2 OH-stretching modes localized on monomer M . The monomer-specific, three-dimensional PESs, $V(\vec{q}_{M,HOH}, \vec{q}_{M,S1}, \vec{q}_{M,S2})$, include all intra-mode vibrational coupling. Solutions to the vibrational Schrödinger equation for the Hamiltonian (Eq. 1) were obtained by expanding the eigenstates numerically in a basis of three-dimensional, direct-product harmonic oscillator basis states using Gaussian quadrature for the integration of the PES. The relatively small system size allowed for ten quanta of excitation in each of the HOH, S1, and S2 oscillators respectively. The resulting nine-dimensional eigenstates of this separable Hamiltonian were written as a tensor-product of the three-dimensional eigenfunctions. Expressed in terms of the harmonic oscillator basis functions, the tensor-product states take the form of Eq. 2.

$$|\Psi_{\alpha,\beta,\gamma}\rangle = \sum_{ijk} \sum_{lmn} \sum_{opq} C_{ijk} C_{lmn} C_{opq} |i, j, k, l, m, n, o, p, q\rangle \quad (2)$$

FIG. 2. (a) Molecular structures of the six lowest-energy isomers of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster along with their relative energies and harmonic zero-point corrected energies calculated with both MB-nrg PEF1 and MB-nrg PEF2. (b) Thermodynamic populations of the six lowest-energy isomers of the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster calculated using REPIMD simulations with MB-nrg PEF1 (left) and MB-nrg PEF2 (right) between 0 K and 200 K. Color scheme: isomer C1 = green, isomer C2 = blue, isomer C3 = violet, isomer C4 = magenta, isomer C5 = red, isomer C6 = black

The quantum numbers α, β, γ refer to monomers 1, 2, and 3 respectively. Likewise, the quantum numbers of the three-dimensional basis functions are i, j, k for monomer 1, l, m, n for monomer 2, and o, p, q for monomer 3.

The two-mode, cross-monomer couplings were included using first-order degenerate pertur-

bation theory by expanding the corresponding cross-monomer coupled eigenstates in the basis of the nine-dimensional tensor-product local-monomer basis functions. This procedure required computing all two-mode cross-monomer potential energy surfaces. For two monomers M_A and M_B , the perturbation is then expressed as

$$\hat{V}'_{M_A, M_B} = \sum_I^3 \sum_J^3 V(\vec{q}_{M_A, I}, \vec{q}_{M_B, J}) - V(\vec{q}_{M_A, I}) - V(\vec{q}_{M_B, J}) \quad (3)$$

Integrating $\hat{V}'_{M_A, M_B}$ over the local-monomer basis functions gives the following Hamiltonian matrix elements:

$$\begin{aligned} \langle \alpha, \beta, \gamma \Psi | \hat{H}' | \Psi_{\alpha', \beta', \gamma'} \rangle &= \langle \alpha, \beta \Psi | \hat{V}'_{1,2} | \Psi_{\alpha', \beta'} \rangle \delta_{\gamma, \gamma'} \\ &+ \langle \alpha, \gamma \Psi | \hat{V}'_{1,3} | \Psi_{\alpha', \gamma'} \rangle \delta_{\beta, \beta'} \\ &+ \langle \beta, \gamma \Psi | \hat{V}'_{2,3} | \Psi_{\beta', \gamma'} \rangle \delta_{\alpha, \alpha'} \end{aligned} \quad (4)$$

As a result of the tensor-product integration, the nine-dimensional integrals in Eq. 4 simplify into the sum of nine two-dimensional integrals over cross-monomer pairs of modes. Although any number of local-monomer basis states could be used, we found that the twenty lowest-energy states were sufficient for the perturbative expansion. Since the coupled-monomer eigenstates are written in the local-monomer basis, the two-mode coupled dipole surfaces are expressed as

$$\hat{\vec{\mu}}_{M_A, M_B} = \sum_I^3 \sum_J^3 \vec{\mu}(\vec{q}_{M_A, I}, \vec{q}_{M_B, J}) - \vec{\mu}(\vec{q}_{M_A, I}) - \vec{\mu}(\vec{q}_{M_B, J}) - \vec{\mu}_0 \quad (5)$$

The main distinction from the functional form of the two-mode coupled PESs is that the cross-monomer dipole coupling requires the vector subtraction of the permanent dipole $\vec{\mu}_0$. The corresponding transition dipole correction, therefore, required integrating $\hat{\vec{\mu}}_{M_A, M_B}$ over the perturbatively corrected, cross-monomer eigenstates.

B. MP2 Argon-Tagged Results

The argon-tagged calculations were accomplished by first optimizing isomers **C1**, **C2**, **C5** without argon using MP2/def2-TZVPP. Using the resulting configurations, an argon atom was placed

in multiple configurations and further optimized to local minima. Harmonic frequencies were calculated for the corresponding isomers with the same level of theory and basis set. All calculations were performed with a development version of the Q-Chem 5.0 software⁵. The harmonic normal-mode frequencies are provided in Table I. A comparison between the argon-tagged and untagged structures are shown in Figures 3, 4, and 5.

FIG. 3. Comparison between the structures of the argon tagged (A) and untagged (B) isomer **C1**. Structural parameters were calculated using MP2/def2-TZVPP.

Clearly the argon, with this level of theory and basis set, exhibits a negligible effect on both the structures and harmonic frequencies. Likewise, the isomer ordering is consistent using MP2/def2-TZVPP and MB-nrg with the electronic energies **C1** at 0.00 kcal/mol, **C2** at 0.05 kcal/mol, and **C5** at 3.31 kcal/mol. While the argon tag could still impact free energies, the corresponding infrared spectrum, or even the kinetics of isomerization, these preliminary results suggest that the enthalpic effect is minimal.

C. VDPT2 Low-Frequency Comparison

The results of VDPT2 calculations using single-mode additions to the 9-dimensional results in the main text are shown in Fig. 6. Both the high- and low-frequency regions of the spectrum were impacted to some degree by this inclusion. In order to maintain a consistent comparison to

TABLE I. Calculated harmonic frequencies (cm^{-1}) for the argon-tagged and untagged $Cs^+(H_2O)_3$ isomers.

The frequencies were calculated using MP2/def2-TZVPP.

Mode	C1(Ar)	C1	C2(Ar)	C2	C5(Ar)	C5
1	0	—	7	—	7	—
2	0	—	26	—	12	—
3	41	—	39	—	13	—
4	94	94	44	40	16	10
5	94	94	63	64	21	13
6	110	111	132	131	36	13
7	182	181	161	161	42	45
8	182	181	176	176	51	45
9	210	210	209	210	94	88
10	323	323	219	223	139	139
11	323	323	238	243	140	141
12	383	384	248	253	142	141
13	416	417	257	264	279	282
14	416	417	362	363	284	291
15	492	491	471	472	287	291
16	549	548	482	485	320	326
17	549	548	610	613	325	326
18	769	768	670	674	328	328
19	1658	1657	1675	1675	1694	1695
20	1667	1667	1693	1693	1695	1695
21	1667	1667	1723	1724	1695	1695
22	3788	3790	3777	3776	3903	3904
23	3824	3825	3799	3798	3904	3904
24	3824	3825	3886	3888	3904	3904
25	3969	3969	3973	3972	3993	3993
26	3969	3969	3976	3975	3994	3994
27	3972	3972	3977	3977	3994	3994

the LMon and cLMon methods, only the results that include the bending and stretching regions are included in the main text. Based on this mode-coupling analysis, future investigation of the

FIG. 4. Comparison between the structures of the argon-tagged (A) and untagged (B) isomer **C2**. Structural parameters were calculated using MP2/def2-TZVPP.

FIG. 5. Comparison between the structures of the argon-tagged (A) and untagged (B) isomer **C5**. Structural parameters were calculated using MP2/def2-TZVPP.

low-frequency region is evidently warranted. Quadrature limitations prevented full-dimensional VDPT2 simulations in the present analysis, but these simulations will be pursued in future studies.

FIG. 6. Role of low-frequency modes in anharmonic simulations. The spectra in the main text were computed by inclusion of only the water bending and O-H stretching vibrational modes (9-dimensional). As a preliminary assessment of the influence of low-frequency modes, VDTP2 spectra were computed by making single additions of modes from the remaining set of 15 modes. Traces are numbered as modes 0-14 to signify the identity of the additional mode.

D. Spectrum Comparison with PEF2

The infrared spectrum calculated with MB-nrg PEF2 is shown in Fig. 7, and a complete list of transition frequencies is provided in Table II. A direct comparison between the VDPT2 results for PEF1 and PEF2 is provided in Fig. 8.

FIG. 7. (a) Comparison between thermally weighted infrared spectra calculated in the bending (HOH bend), hydrogen-bonded (HB OH) and free (free OH) OH stretching regions for PEF2 using: (A) harmonic approximation, (B) local-monomer approximation (LMon), (C) corrected local-monomer approximation (cLMon), (D) two-mode vibrational self-consistent field theory (VSCF), (E) two-mode corrected second-order vibrational degenerate perturbation theory (VDPT2). (F) Experimental spectrum. All theoretical spectra were calculated using the isomer populations at 30 K (see Figure 2B) and the linewidths were homogeneously broadened by a Lorentzian lineshape with a width of 5 cm^{-1} . The calculated spectra are magnified by 2.5x in the HOH bend region. The color scheme is the same employed in the main text and Fig. 2 to identify the different isomers: green = isomer C1, blue = isomer C2, red = isomer C5.

1. Hydrogen-Bonded OH-stretch Region

As for MB-nrg PEF1, the infrared spectrum is dominated by isomer **C1**, with peaks (**A8**) and (**A10**) tracking the fundamental transitions across all vibrational methods. Experimentally, the spacing between the (**A8**) and (**A10**) peaks is 14 cm^{-1} . As discussed in the main text, the local-monomer approximation, which lacks explicit cross-monomer coupling, and the local-mode VSCF

FIG. 8. VDPT2 comparison between the spectrum calculated with PEF1 (top) and PEF2 (bottom). the linewidths were broadened by a Lorentzian line ship with a width of 5 cm^{-1} . both the intensities in the bend region for PEF1 and PEF2 have been magnified by 2.5x.

approximation, which averages over all cross-monomer couplings, predict the two fundamental transitions to be degenerate. The normal-mode harmonic approximation slightly overestimates the doublet splitting $\Delta_{HB}^{Harm} = 23 \text{ cm}^{-1}$. The VDPT2 method yields more accurate peak placements, but the doublet splitting ($\Delta_{HB}^{VDPT2} = 26 \text{ cm}^{-1}$) is still comparable to the harmonic approximation. For comparison, the the doublet splittings predicted by the corresponding calculations carried out with the MB-nrg PEF1 are: 27 cm^{-1} with the harmonic approximation, 46 cm^{-1} with cLMon, and 30 cm^{-1} with VDPT2.

2. Free-OH Region

As for MB-nrg PEF1, all five vibrational models also predict a bright doublet feature specific to the free-OH fundamental transitions of isomer **C2** with MB-nrg PEF2. The feature with the largest oscillator strength (**A19,A20**), is assigned to the fundamental free-OH stretching modes on each of the water molecules mirrored across the C_2 axis. The fundamental transition frequencies of these modes remain nearly degenerate, even with the inclusion of cross-monomer coupling. The deviation from experiment comes from peak (**A18**), which is assigned to the high-frequency free-OH transition of the HB acceptor. Across all five computational models, the computed frequency

of this transition is red-shifted relative to the free-OH fundamental transition frequencies of the flanking (symmetry-mirrored) water molecules. This result is surprising considering the near-degeneracy of the measured peaks. A distinct difference between PEF1 and PEF2 is the presence of peak **A21** since isomer **C5** has significantly higher thermal population with PEF2. While (**A21**) is degenerate with (**A19, A20**) in the LMon and cLMon models, the harmonic and VDPT2 models place the peak position of (**A21**) to the blue of (**A19, A20**), which is consistent with the peak position in the experimental spectrum.

3. *HOH Bending Region*

The differences between PEF1 and PEF2 are least noticable in the bending region. Other than a slight overall shift as shown in Figure 8, the only significant difference is the increased intensity of (**A6**) which arises from the increased thermal population of isomer **C5**.

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TABLE II. PEF2 Calculated harmonic, local-monomer (LMon), corrected local-monomer (cLMon), two-mode vibrational self-consistent field theory (VSCF), two-mode corrected second-order vibrational degenerate perturbation theory (VDPT2), and experimental infrared transition frequencies (cm^{-1}) for the $\text{Cs}^+(\text{H}_2\text{O})_3$ cluster at 30 K. The peaks **A6**, **A14**, and **A21** originating from isomer **C5** have a ~ 3 -fold degeneracy. The experimental values were taken from Ref. 6.

Peak	Harm	LMon	cLMon	VSCF	VDPT2	Experiment	Isomer
HOH bend							
A1	1631	1566	1552	1568	1560	1604	C1
A2	1640	1566	1564	1568	1568	1604	C1
A3	1640	1566	1577	1568	1568	1604	C1
A4	1654	1590	1589	1593	1587	1617	C2
A5	1669	1610	1600	1613	1603	1617	C2
A6	1678	1613	1613	1617	1614	1648	C5
A7	1688	1610	1620	1613	1623	1630	C2
Hydrogen-bonded OH stretch							
A8	3720	3535	3516	3532	3518	3538	C2
A9	3723	3548	3533	3554	3526	3576	C1
A10	3743	3535	3556	3532	3544	3552	C2
A11	3744	3548	3548	3554	3550	3598	C1
A12	3744	3548	3556	3554	3550	3598	C1
Free OH stretch							
A13	3801	3625	3623	3651	3618	3630	C2
A14	3819	3644	3643	3671	3637	3641	C5
A15	3877	3681	3678	3664	3684	3712*	C1
A16	3877	3681	3681	3664	3684	3712*	C1
A17	3877	3681	3682	3664	3684	3712*	C1
A18	3886	3687	3686	3651	3692	3692	C2
A19	3897	3707	3706	3670	3709	3703	C2
A20	3900	3707	3710	3670	3711	3703	C2
A21	3908	3707	3707	3670	3715	3712*	C5

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