

# Infrared Spectroscopy of Neutral Distrontium Hydroxides Unravels Configuration Transformation in Growing Water Clusters

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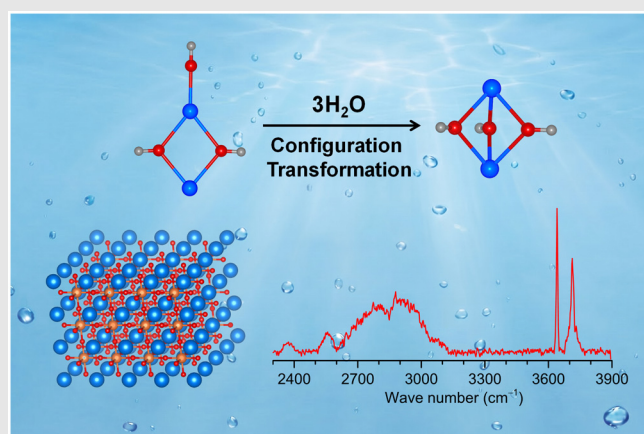
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Elucidating the hydration dynamics of polynuclear metals is vital for understanding the fundamental physicochemical properties of various interfacial processes. Nevertheless, the structural characterization of these neutral complexes is hindered by the inherent difficulties associated with experimental size selection. Here, the microhydration pathways and structural transformations of neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) clusters were unveiled through size-selected infrared-vacuum ultraviolet spectroscopy, coupled with quantum chemical calculations as well as ab initio molecular dynamics simulations. The results reveal that three water molecules are sufficient to trigger the configuration transformation from  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  to  $\text{Sr}_2(\mu_2\text{-OH})_3$ . This intriguing transition is found to be driven by hydration-induced structural deformation, achieving thermodynamic stability through the rearrangement of the hydrogen-bonding network. The current system affords a model for clarifying the metal-oxygen skeleton and hydration dynamics in the microenvironment of

perovskite catalysts and opens new avenues for systematic understanding of hydration-driven lattice rearrangements, active site modulation, and catalyst activation.



**Keywords:** hydration, cluster, hydrogen-bonding network, configuration transformation, infrared-vacuum ultraviolet spectroscopy

## Introduction

Exploring configuration transformation and reaction kinetics in hydration environments is of fundamental significance for unraveling physicochemical processes such as catalytic conversion, metal corrosion, aerosol nucleation, and functional materials.<sup>1–4</sup> During stepwise hydration, the water hydrogen-bonding network can induce adjustments to the core skeleton and coordination microenvironment, with the specific conformational transition of the system being subsequently driven on the potential energy surface. As a representative example, in heterogeneous catalysis and water splitting, hydration-induced effects have been demonstrated to effectively drive the structural rearrangement and topological dimensional transition of polynuclear metal active sites (e.g.,  $\text{Mn}_4\text{O}_4^+$ ) from a two-dimensional cyclic configuration to a three-dimensional cuboidal configuration.<sup>5</sup> This is considered a crucial kinetic prerequisite for lowering the O–H bond activation barrier of water molecules and unlocking highly efficient catalytic channels. Together with advanced quantum chemical calculations, the studies of hydration-driven configurational evolution at the molecular level have provided important insights into the microscopic mechanisms underlying complex processes.

Over the past decades, owing to advances in technology, the hydration processes of alkaline earth metal cations have been extensively investigated both experimentally and theoretically.<sup>6–16</sup> For instance, photodissociation spectroscopic studies of  $\text{Sr}^+(\text{H}_2\text{O})_n$  have shown that for  $n \leq 4$ , the clusters retain the  $\text{Sr}^+(\text{H}_2\text{O})_n$  solvation structure; starting at  $n \geq 5$ , the system undergoes a dehydrogenation reaction, dominantly generating the hydroxide products characterized by the compositions of  $\text{Sr}^+(\text{H}_2\text{O})_{n-1}$ .<sup>6</sup> Analogously, the  $\text{Sr}^{2+}(\text{H}_2\text{O})_n$  solvation structures have also been detected by using gas-phase ion equilibria techniques coupled with photodissociation dynamics.<sup>7,8</sup> Recently, a spectroscopic study of neutral  $\text{BaOH}(\text{H}_2\text{O})_n$  clusters revealed that at a critical hydration number of  $n = 3$ , the hydrogen-bonding network can spontaneously drive the structural conversion of a contact ion pair (CIP) into a solvent-shared ion pair (SIP).<sup>16</sup> Yet, experimental identification of configuration transformation in neutral polynuclear metal hydrates has not been achieved, because the size selection of these neutral complexes is hampered by the absence of charge.

In this work, a size-specific infrared-vacuum ultraviolet (IR-VUV) spectroscopic investigation on the stepwise hydration of a representative neutral binuclear metal hydroxide system ( $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$ ) is reported. Distinct OH stretching vibrational spectra recorded in the 2400–3700  $\text{cm}^{-1}$  region provide the first experimental evidence for a configuration transformation in neutral distrontium hydrates, indicating that three water molecules are able to drive the structural core transition from

$\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  to  $\text{Sr}_2(\mu_2\text{-OH})_3$ . The mechanism and implications of such a configuration transformation are discussed.

## Experimental and Computational Methods

### Experimental method

The present experiment was conducted utilizing an IR-VUV apparatus (detailed experimental procedures are described in the [Supporting Information](#)).<sup>17–19</sup> Neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  species were produced by subjecting a high-purity (99.9%) strontium target to laser ablation within a supersonically expanded helium and water vapor mixture. The 193 nm laser, generated by an ArF excimer laser, was introduced at a time delay of 130 ns following the excitation of the  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  clusters by a tunable IR laser, which was produced via an optical parametric oscillator/optical parametric amplifier system pumped by the 1064 nm laser. To confirm a linear correlation between the predissociation yield and the applied photon fluence, the depletion signal was systematically characterized with respect to variations in the IR laser power.

### Computational method

To determine the most stable isomers of the neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1\text{--}5$ ) species, extensive structural searches were executed by utilizing the Molclus program<sup>20</sup> within the framework of density functional theory (comprehensive computational details are provided in the [Supporting Information](#)). Structural optimizations and harmonic vibrational frequency analyses for the identified isomers were executed by utilizing the Gaussian 16 package<sup>21</sup> at the B3LYP-D3(BJ)/def2-TZVP theoretical level. Both the relative energies of the isomers at 0 K and the energy barriers associated with the reaction pathways were evaluated, with zero-point vibrational energy (ZPVE) corrections applied. Calculated harmonic frequencies were uniformly scaled by 0.961 to correct for the inherent limitations attributed to the theoretical methods.<sup>22</sup> Spectral broadening of the theoretical harmonic frequencies was accomplished by applying a Gaussian line-shape function with a 10  $\text{cm}^{-1}$  full width at half maximum. The interaction energies during the stepwise hydration process were decomposed and analyzed by using the sobEDA method<sup>23</sup> at the B3LYP-D3(BJ)/def2-TZVP theoretical level.

The ab initio molecular dynamics (AIMD) simulations were executed by utilizing the CP2K software package.<sup>24</sup> During the simulations, an initial 5 ps dynamics equilibration was executed; upon completion, the system was switched to a microcanonical ensemble (NVE) for data collection. For different simulation temperatures (50, 100,

and 150 K), the total trajectory length was set to 150 ps. Subsequently, each trajectory was segmented into multiple 10-ps sub-trajectories. A Fourier transform was applied to each sub-trajectory independently, and the transformed results were accumulated to yield the final dipole time-correlation function spectra at the corresponding temperatures. This scheme naturally incorporated dynamical and anharmonic effects, although low-temperature quantum effects were excluded from the current simulations. The IR spectra obtained from the AIMD simulations were not scaled. Note that because ZPVE corrections and nuclear quantum effects were not explicitly accounted for in the AIMD simulations, the simulation temperatures did not strictly correspond to the actual experimental temperatures.

## Results and Discussion

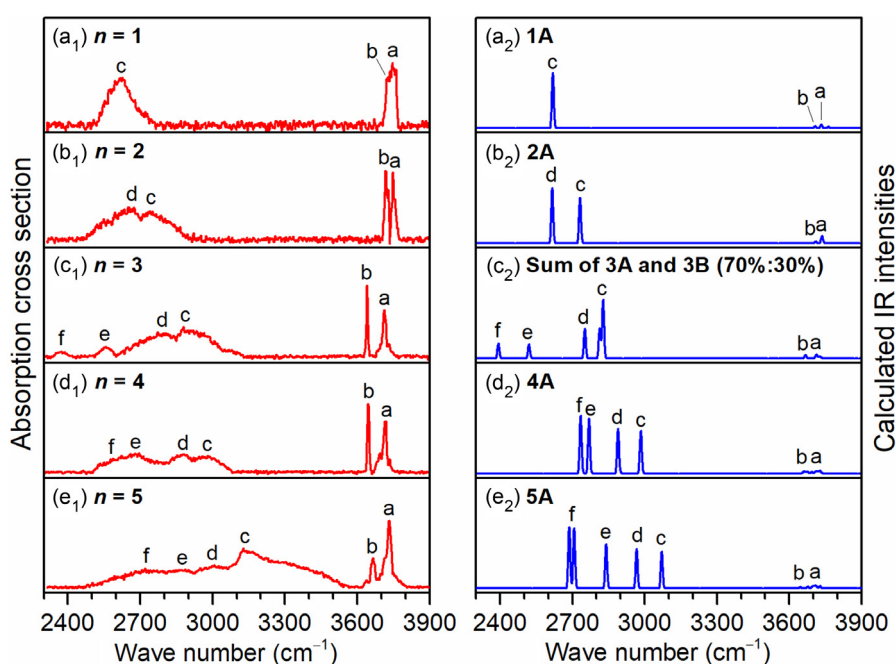
### IR spectral assignment and structural identification

The VUV-ionized mass spectra for the IR spectral measurement of each individual cluster  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) are displayed in Supporting Information Figure S1a-e, respectively. There is no negative signal of depletion efficiency of the VUV-ionized mass signal intensity of  $[\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n]^+$  with and without IR excitation, indicating that no spectral contribution comes from larger clusters (Supporting Information Table S1). Distinct vibrational features, which serve as structural fingerprints,

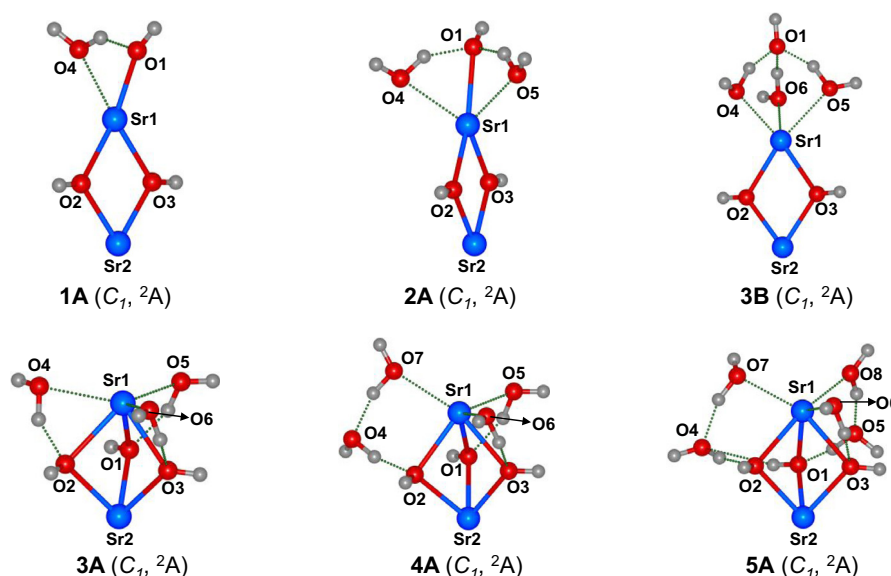
are identified from the experimentally measured IR spectra of the individual  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) complexes, as depicted in Figure 1a1-e1. Consequently, the absence of spectral contamination within the IR-VUV measurement scheme is verified, which aligns with previous validations in neutral water and hydrated cluster investigations.<sup>16,25,26</sup>

As shown in Figure 1a1-e1, three (a-c), four (a-d), six (a-f), six (a-f), and six (a-f) characteristic bands were resolved within the experimentally measured spectra of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ), respectively. Notably, band b appears as a small shoulder for the  $n = 1$  cluster, slightly red-shifts to  $3720\text{ cm}^{-1}$  for  $n = 2$ , remarkably red-shifts to  $3641\text{ cm}^{-1}$  for  $n = 3$ , and exhibits virtually unchanged frequency when as many as five water units are incorporated into the cluster, indicative of a configuration transformation at  $n = 3$ .

To elucidate the experimentally measured IR spectra and determine the structural configurations of the  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) species, quantum chemical computations were executed at the B3LYP-D3(BJ)/def2-TZVP theoretical level. The geometric structures and electronic states of identified isomers are presented in Figure 2, with their respective theoretical IR spectra provided in Figure 1a2-e2. The experimentally obtained IR spectra are contrasted with the calculated harmonic vibrational spectra for the remaining isomers in Supporting Information Figures S2-S6, respectively. Detailed assignments of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) are provided within Table 1, Supporting Information Tables S2 and S3,



**Figure 1** | Experimentally measured versus simulated IR spectra for the neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ). Calculations were carried out at the B3LYP-D3(BJ)/def2-TZVP theoretical level, with a uniform scaling factor of 0.961 applied to the harmonic vibrational frequencies.



**Figure 2** | Identified structures of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) computed at the B3LYP-D3(BJ)/def2-TZVP theoretical level (Sr, Blue; O, red; and H, gray). The Sr and O atoms are labeled for discussion.

respectively. All stepwise water addition reactions for the formation of isomers  $n\text{A}$  and  $n\text{B}$  are calculated to be exothermic by about 12–21 kcal/mol at the B3LYP-D3(BJ)/def2-TZVP theoretical level, indicating these hydration processes are both thermodynamically favorable and kinetically feasible.

As illustrated in Supporting Information Figure S2, with regard to the  $n = 1$  cluster, the global minimum structure is identified as the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})(\text{H}_2\text{O})$  configuration (labeled 1A) with the  $^2\text{A}$  electronic state, in which the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  core has two bridging OH groups and one terminal OH group. In this configuration, a hydrogen bond is formed between the terminal OH group and the solvating water ligand coordinated to the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  core. Meanwhile, a distinct  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})$  structure with three bridging OH units is exhibited by isomer 1B, which is located 1.93 kcal/mol above isomer 1A on the potential energy surface at the B3LYP-D3(BJ)/def2-TZVP theoretical level (Supporting Information Figure S2c). The calculated harmonic vibrational spectrum of isomer 1A exhibits the best agreement with the experimentally acquired spectrum. In contrast, the predicted absorption peak at  $2797\text{ cm}^{-1}$  in isomer 1B is not experimentally observed. Thus, the existence of isomer 1B could be excluded. As shown in Supporting Information Figure S2d, the simulated IR spectrum of  $\text{Sr}_2(\text{OH})_2(\text{H}_2\text{O})_2$  is remarkably discrepant from the experimental IR spectrum of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})$ , thus excluding spectral contamination. Similarly, the preference of the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  configuration is also found for  $n = 2$  (Supporting Information Figure S3).

An inversion in the relative energies of the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  and  $\text{Sr}_2(\mu_2\text{-OH})_3$  configurations is observed

at  $n = 3$ . The most stable isomer (3A) is found to have the  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_3$  structure (Supporting Information Figure S4). Isomer 3B has the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})(\text{H}_2\text{O})_3$  structure with two bridging and one separated OH groups, which is determined to be destabilized by 1.78 kcal/mol when compared with isomer 3A at the B3LYP-D3(BJ)/def2-TZVP theoretical level. Furthermore, the single-point energy evaluations conducted on isomers 3A and 3B at the B2PLYPD3/def2-TZVPP and CCSD(T)/def2-TZVPP theoretical levels indicate that isomer 3B is 2.82 and 3.54 kcal/mol higher in energy than isomer 3A, respectively, confirming the B3LYP-D3(BJ)/def2-TZVP calculated results. In the calculated spectrum of isomer 3A, the calculated stretching modes associated with the bridging O(1)H, O(2)H, and O(3)H units ( $\sim 3666\text{ cm}^{-1}$ ) are correlated with the experimentally observed spectral feature b ( $3641\text{ cm}^{-1}$ ) (Table 1). An acceptable alignment with the experimental bands d ( $2799\text{ cm}^{-1}$ ), e ( $2557\text{ cm}^{-1}$ ), and f ( $2364\text{ cm}^{-1}$ ) is demonstrated by the corresponding theoretical hydrogen-bonded stretching frequencies ( $2752$ ,  $2520$ , and  $2394\text{ cm}^{-1}$ ) derived from the calculated harmonic spectrum of isomer 3B. As presented in Figure 1c2 and Supporting Information Figure S4, the experimental spectrum is best reproduced by the sum IR spectrum of a 70% (3A): 30% (3B) mixture, which is well supported by the calculated relative energies. The experimental spectrum is assigned to isomers 3A and 3B, which is supported by the consistency between the calculated and experimental spectra. As shown in Figure 3, the largest barrier of elementary processes for the  $3\text{B} \rightarrow 3\text{A}$  isomerization is calculated to be 5.82 kcal/mol at the B3LYP-D3(BJ)/def2-TZVP level of theory. Prior to the structural

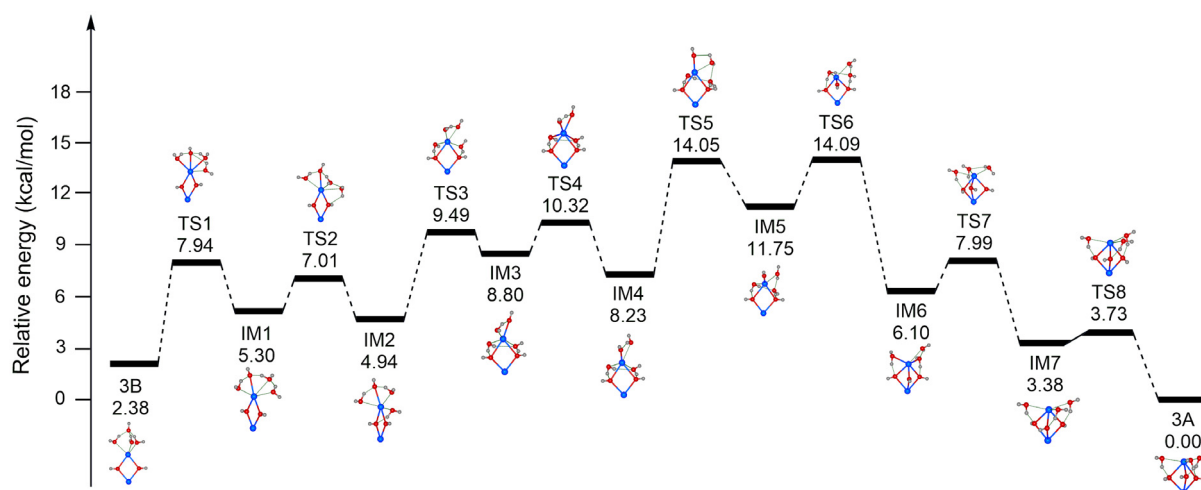
**Table 1** | Comparative Analysis of the Experimental Band Positions ( $\text{cm}^{-1}$ ) of Neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_3$  Cluster to the Calculated Values of the Most Stable Structures Determined at the B3LYP-D3(BJ)/def2-TZVP Theoretical Level (IR Intensities are Denoted Within Parentheses in Units of  $\text{km/mol}$ , and the Calculated Harmonic Vibrational Frequencies are Corrected by a Scaling Factor of 0.961)

| Species                                          | Isomers | Label | Exptl | Calcd       | Mode                                                                            |
|--------------------------------------------------|---------|-------|-------|-------------|---------------------------------------------------------------------------------|
| $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_3$ | 3A      | a     | 3712  | 3713 (6)    | Symmetric H-donor-free OH stretching mode of O(4)H, O(5)H, and O(6)H groups     |
|                                                  |         |       |       | 3712 (49)   | Antisymmetric H-donor-free OH stretching mode of O(4)H, O(5)H, and O(6)H groups |
|                                                  |         |       |       | 3712 (48)   | Antisymmetric H-donor-free OH stretching mode of O(4)H, O(5)H, and O(6)H groups |
|                                                  |         | b     | 3641  | 3667 (7)    | Antisymmetric bridging OH stretching mode of O(1)H, O(2)H, and O(3)H groups     |
|                                                  |         |       |       | 3667 (1)    | Antisymmetric bridging OH stretching mode of O(1)H, O(2)H, and O(3)H groups     |
|                                                  |         |       |       | 3666 (95)   | Symmetric bridging OH stretching mode of O(1)H, O(2)H, and O(3)H groups         |
|                                                  |         | c     | 2878  | 2828 (1812) | Symmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups         |
|                                                  |         |       |       | 2814 (466)  | Antisymmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups     |
|                                                  |         |       |       | 2813 (466)  | Antisymmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups     |
|                                                  | 3B      | a     | 3712  | 3730 (49)   | H-donor-free OH stretching mode of O(6)H group                                  |
|                                                  |         |       |       | 3726 (50)   | H-donor-free OH stretching mode of O(5)H group                                  |
|                                                  |         |       |       | 3723 (17)   | H-bonded OH stretching mode of separated O(1)H group                            |
|                                                  |         |       |       | 3722 (48)   | H-donor-free OH stretching mode of O(1)H group                                  |
|                                                  |         |       |       | 3710 (28)   | Antisymmetric stretching mode of bridging O(2)H and O(3)H groups                |
|                                                  |         |       |       | 3708 (3)    | Symmetric stretching mode of bridging O(2)H and O(3)H groups                    |
|                                                  |         | d     | 2799  | 2752 (2144) | Symmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups         |
|                                                  |         | e     | 2557  | 2520 (1006) | Antisymmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups     |
|                                                  |         | f     | 2364  | 2394 (1076) | Antisymmetric H-bonded OH stretching mode of O(4)H, O(5)H, and O(6)H groups     |

rearrangement to the global minimum, both isomers 3A and 3B are kinetically trapped owing to the helium expansion associated with the cold molecular beam, which is attributed to the magnitude of this barrier,<sup>27</sup> indicative of possible coexistence of isomers 3A and 3B. This phenomenon is paralleled by the experimental detection of low-lying isomers in other neutral cluster systems.<sup>28–32</sup>

For  $n \geq 4$ , the most stable isomers are identified as the  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_n$  configurations with the  $^2\text{A}$  electronic state (Supporting Information Figures S5 and S6), in which water molecules are sequentially inserted into the

$\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_3$  cluster, thereby forming the hydrogen-bonding networks. At the B3LYP-D3(BJ)/def2-TZVP theoretical level, relative energy elevations of 4.59 and 1.39 kcal/mol are calculated for isomers 4B (Supporting Information Figure S5c) and 5B (Supporting Information Figure S6c) with respect to isomers 4A and 5A, respectively. Similarly, the computed harmonic vibrational spectra of isomers 4A and 5A agree best with the experimental spectra. By comparison, the predicted vibrational features at  $3302\text{ cm}^{-1}$  for isomer 4B and the band at  $3156\text{ cm}^{-1}$  for isomer 5B are not experimentally



**Figure 3** | Potential energy profiles associated with the 3B to 3A isomerization. Relative energies calculated at the B3LYP-D3(BJ)/def2-TZVP theoretical level are listed in kcal/mol. The abbreviation “IM” is abbreviated as intermediate, and the transition state is denoted as “TS.” The corresponding optimized geometries are depicted in the inset (Sr, Blue; O, red; and H, gray).

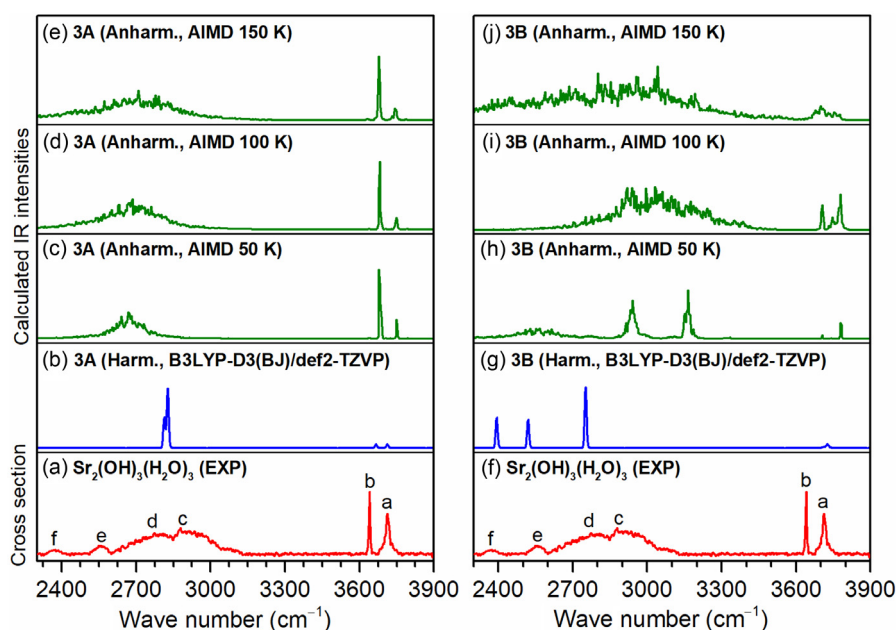
observed, indicating that isomers 4B and 5B negligibly contribute to the experimental spectra.

### AIMD simulation analysis

It can be seen from the above analyses that the experimental spectral features of flexible hydrogen-bonding networks of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  cannot be fully described by the static harmonic vibrational spectra. To capture the spectral broadening effects induced by hydrogen-bonding interactions, the determined  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  isomers were subjected to AIMD simulations across a range of temperatures. Considering that the configuration transformation of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  occurs at  $n = 3$ , the analysis of the AIMD results is concentrated on isomers 3A and 3B (Figure 4a–j), while the data for the remaining isomers are presented correspondingly (Supporting Information Figures S7–S10). The experimental spectrum is evaluated in conjunction with the AIMD spectra at 50, 100, and 150 K for isomers 3A and 3B, and is presented in Figure 4. As the simulation temperature is elevated, the spectral bands of isomers 3A and 3B within the 2300–3500  $\text{cm}^{-1}$  region are progressively broadened. The AIMD spectra at 150 K exhibit the most satisfactory concordance with the experimentally measured spectrum, which is comparable to the temperature of the cluster beam source in laser vaporization (100–150 K). Supporting Information Figures S11 and S12 show the plot of vibrational density of states derived from the AIMD simulations, which reflect the contributions of the O–H stretching vibrations from distinct OH groups to the spectral features in the 2300–3500  $\text{cm}^{-1}$  region. For isomers 1A, 2A, 4A, and 5A, the AIMD spectra at 100 K agree best with the experimental spectra (Supporting Information Figures S7–S10). The

optimum AIMD temperature of  $n = 3$  (150 K) is higher than that of other clusters (100 K), which is in accord with the large amplitude motions of hydrogen bonds caused by the configuration transformation (vide infra).

Statistical mechanical evidence for evaluating the dynamic stability of hydrogen-bonding networks is derived from the analysis of AIMD trajectories for isomers 3A and 3B at 150 K (Supporting Information Figures S13 and S14). During the AIMD simulation of isomer 3A, the distribution of the Sr(1)⋯Sr(2) distance (Supporting Information Figure S13a), the Sr(1)⋯O( $m$ ) distances (Supporting Information Figures S13b,c), and the O(4)H⋯O(2) hydrogen bond length (Supporting Information Figure S13d) all exhibit typical Gaussian characteristics, with their fluctuation amplitudes consistently confined within a narrow range of 0.4–0.8 Å. This confirms the excellent structural robustness of the  $\text{Sr}_2(\mu_2\text{-OH})_3$  core configuration of isomer 3A during the finite-temperature dynamics. In contrast, in the AIMD simulations of isomer 3B, drastic fluctuations are observed for the Sr(1)⋯O( $m$ ) distances (Supporting Information Figures S14b–e) and the O( $n$ ) H⋯O(1) hydrogen-bond lengths (Supporting Information Figures S14f–h). For instance, the distribution ranges of the Sr(1)⋯O(1) and Sr(1)⋯O(5) distances are significantly broadened to 3.5–5.4 and 2.1–4.8 Å, respectively. In particular, the distribution range of the O(4)H⋯O(1) hydrogen bond (2.3–4.3 Å) exhibits a substantial increase as compared to its static bond length (~1.54 Å), suggesting the near-complete cleavage of this hydrogen bond during the simulation. Simultaneously, the bond length distribution interval of O(5)H⋯O(1) narrows to 0.9–1.2 Å, revealing a large fluctuation of hydrogen from O(5) to O(1). These microscopic dynamical features indicate the poor



**Figure 4** | Comparison of experimental IR spectrum of neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_3$  cluster [(a) and (f)], B3LYP-D3(BJ)/def2-TZVP calculated harmonic IR spectra of isomers 3A (b) and 3B (g) and anharmonic IR spectra generated by AIMD simulations at 100, 150, and 200 K of isomers 3A (c–e) and 3B (h–j).

thermal stability of the 3B configuration, characterized by a flexible hydrogen-bonding network that is highly liable to rearrange at finite temperatures. Such structural fluxionality not only elucidates the discrepancies between the AIMD spectrum and the static harmonic vibrational spectrum of isomer 3B, but also corroborates the instability of the 3B structure.

### Mechanism of configuration transformation

A principal finding of the current study is that the structural transition of the  $\text{Sr}_2(\text{OH})_3$  core is induced by the coordination of the third water molecule. To elucidate the mechanism of this configuration transformation, calculations at the B3LYP-D3(BJ)/def2-TZVP theoretical level were carried out to execute the energy decomposition analysis (EDA). The analysis results (Supporting Information Table S4) reveal that in the initial hydration stages ( $n = 1$ –3), for the growth pathway of the  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_n$  isomers ( $1\text{B} \rightarrow 2\text{B} \rightarrow 3\text{A}$ ), the components of the interaction energy ( $\Delta E_{\text{int}}$ ) exhibit stable and regular evolutionary characteristics. With the sequential addition of water molecules, a gradual increase is observed for the electrostatic interaction energy ( $\Delta E_{\text{els}}$ ) ( $-44.89 \text{ kcal/mol} \rightarrow -45.85 \text{ kcal/mol} \rightarrow -45.86 \text{ kcal/mol}$ ), while the orbital interaction energy ( $\Delta E_{\text{orb}}$ ) is gradually decreased ( $-23.03 \text{ kcal/mol} \rightarrow -22.88 \text{ kcal/mol} \rightarrow -21.94 \text{ kcal/mol}$ ). Importantly, a distinct decreasing trend is observed for the Pauli repulsion energy ( $\Delta E_{\text{rep}}$ ) ( $54.31 \text{ kcal/mol} \rightarrow 53.23 \text{ kcal/mol} \rightarrow 52.39 \text{ kcal/mol}$ ). This indicates that the  $\text{Sr}_2(\mu_2\text{-OH})_3$  core skeleton possesses robust structural

stability during the hydration process, and the system achieves stabilization primarily through the rearrangement of the hydrogen-bonding network. In contrast, for the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})(\text{H}_2\text{O})_n$  isomers ( $1\text{A} \rightarrow 2\text{A} \rightarrow 3\text{B}$ ), the  $\Delta E_{\text{int}}$  remains relatively stable for  $n = 1$ –2, but a pronounced jump is observed upon evolution to 3B ( $-27.39 \text{ kcal/mol} \rightarrow -27.36 \text{ kcal/mol} \rightarrow -30.12 \text{ kcal/mol}$ ). Simultaneously, the  $\Delta E_{\text{els}}$  also increases to  $-49.85 \text{ kcal/mol}$ .

It is noteworthy that the binding energy ( $\Delta E_{\text{bind}}$ ) is determined not only by the  $\Delta E_{\text{int}}$  but also by the deformation energy ( $\Delta E_{\text{def}}$ ), which is quantified as the energy required when the isolated fragments are deformed into the structural configurations exhibited within the complex.<sup>33</sup> The atomic distances of  $\text{Sr}(1)\cdots\text{O}(1)\text{H}$  and  $\text{Sr}(1)\cdots\text{Sr}(2)$  within isomers  $n\text{A}$  and  $n\text{B}$  and their basic structural units, along with the deformation energies induced by the binding of an individual water molecule, are detailed in Supporting Information Table S5. As revealed by recent investigations focused on the microhydration mechanisms of alkaline earth metal hydroxides, the microhydration environment can induce the dissociation of the  $\text{Ba-OH}$  bond, promoting the structural evolution of the system toward a SIP configuration, starting with a CIP.<sup>16</sup> The significant variations in the EDA data for the 3B configuration reflect that a pronounced elongation of the  $\text{Sr}(1)\cdots\text{O}(1)\text{H}$  distance is induced by the coordination of the third water molecule (from 2.52 to 3.33 Å, as detailed in Supporting Information Table S5). This elongation causes a substantial deformation of the

$\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  core skeleton, thereby reducing the thermodynamic stability of the system, which is also corroborated by the aforementioned AIMD analysis. Consequently, although isomer 3B exhibits a higher  $\Delta E_{\text{int}}$  than 3A, its fundamental  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  skeleton undergoes significant structural deformation. The substantial increase of  $\Delta E_{\text{def}}$  (12.44 kcal/mol) results in a higher thermodynamic stability for isomer 3A as compared to isomer 3B.

During the subsequent hydration stages ( $n = 4-5$ ), the  $\text{Sr}_2(\mu_2\text{-OH})_3$  skeleton remains stable, and the additional water molecules are mainly involved in the construction of the peripheral hydrogen-bonding network. Based on the EDA results, a pronounced enhancement in  $\Delta E_{\text{orb}}$  is observed (4A,  $-28.37$  kcal/mol; 5A,  $-29.22$  kcal/mol), which compensates for the elevated  $\Delta E_{\text{xrep}}$  induced by increased steric hindrance. For the cluster growth from isomer 3B, as the primary electrostatic adsorption sites diminish, a systematic attenuation trend is observed for isomers 4B and 5B regarding their binding capacities for subsequent water molecules and the majority of the associated interaction energy components.

### Implications of configuration transformation

The experimental observation of the configuration transformation of neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  clusters during the hydration processes is particularly intriguing. Their basic Sr-O skeleton, characterized by bimetallic synergy, is highly correlated with the surface active sites of strontium-based complex perovskite materials (e.g.,  $\text{SrTiO}_3$  and  $\text{SrIrO}_3$ )<sup>34-40</sup> that are widely utilized in energy conversion applications. Furthermore, this microhydration process closely mimics the establishment of surface hydration microenvironment in authentic catalytic systems. For high-performance oxygen evolution reaction catalysts such as  $\text{SrIrO}_3$ , the adsorption energies of oxygenated intermediates on the bimetallic active centers are precisely optimized by such surface lattice rearrangements driven by the hydration microenvironment, thereby endowing the materials with superior catalytic activity.<sup>38,40</sup> Moreover, the deactivation of heterogeneous catalysts in aqueous solutions is predominantly attributed to active site poisoning or lattice deconstruction triggered by profound interfacial solvation.<sup>41-43</sup> The present insights suggest that the compact hydrogen-bonding network spontaneously formed around the polynuclear metal-oxygen skeleton likely manifests as a hydration layer occupying the catalytic active sites, or acts as a precursor that induces the irreversible leaching of active metals.

While the microhydration mechanisms of bimetallic species are revealed by the present study on gas-phase  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  clusters, the intrinsic differences between these isolated clusters and solid-state catalysts would be noted. In contrast to isolated gas-phase

clusters, the perovskite catalyst interface is strictly constrained by the bulk lattice, facilitating specific localized reconstructions. For instance, the complete depletion of Sr from approximately seven  $\text{SrIrO}_3$  monolayers has been experimentally observed, accompanied by a slight structural rearrangement that generates a highly active  $\text{IrO}_x$  surface layer.<sup>38</sup> Furthermore, while only a few discrete water molecules can be captured by gas-phase bimetallic clusters, continuous multilayer hydration structures stabilized by extended hydrogen-bonding networks are formed at authentic solid-liquid interfaces. Specifically, a complete layer of water molecules with a density of  $1.04 \times 10^{15} \text{ cm}^{-2}$  atop a surface hydroxylated layer was recently observed by in situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) studies on  $\text{SrTiO}_3$  surfaces.<sup>44</sup>

## Conclusion

The IR spectra of neutral  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  ( $n = 1-5$ ) clusters were measured by utilizing an IR-VUV spectroscopic technique. By combining these experimental results with quantum chemical calculations as well as AIMD simulations, the  $n \leq 2$  clusters were identified to adopt the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})(\text{H}_2\text{O})_n$  configuration and the  $n \geq 3$  clusters to have the  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_n$  configuration, revealing an intriguing configuration transformation at  $n = 3$ . Such a structural transition is found to be driven by a pronounced structural deformation of the  $\text{Sr}_2(\mu_2\text{-OH})_2(\eta^1\text{-OH})$  skeleton induced by the third water molecule, which subsequently generates a high deformation energy. Thereby, for the  $\text{Sr}_2(\mu_2\text{-OH})_3(\text{H}_2\text{O})_n$  configuration, the Pauli repulsion energy is effectively reduced and structural stability is maintained through the rearrangement of the hydrogen-bonding network, thus rendering it as the global minimum on the potential energy surfaces. The present system serves as a model for catalyst design strategies toward regulating active sites and prolonging catalyst lifetime through interfacial modification.

## Supporting Information

Supporting Information is available and includes detailed experimental and computational methods; mass spectra (Figure S1); Comparison of experimental IR spectra of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  and calculated IR spectra of isomers (Figures S2–S6); Comparison of experimental IR spectra of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  and AIMD simulated IR spectra (Figures S7–S10); Dipole time-correlation function spectra and density of state plots of isomers 3A and 3B (Figures S11 and S12); normal distribution of bond distances (Figures S13 and S14); calculated vertical ionization potentials (Table S1); comparison of the experimental band positions of  $\text{Sr}_2(\text{OH})_3(\text{H}_2\text{O})_n$  to the

calculated values of the most stable structures (Tables S2 and S3); sobEDA analysis results (Table S4); calculated bond distances and corresponding deformation energies (Table S5).

## Conflicts of Interest

There are no conflicts to declare.

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