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ARTICLE

A Fitting Program for Structural Determination of Molecular Clusters from Rotational Spectroscopy[†]

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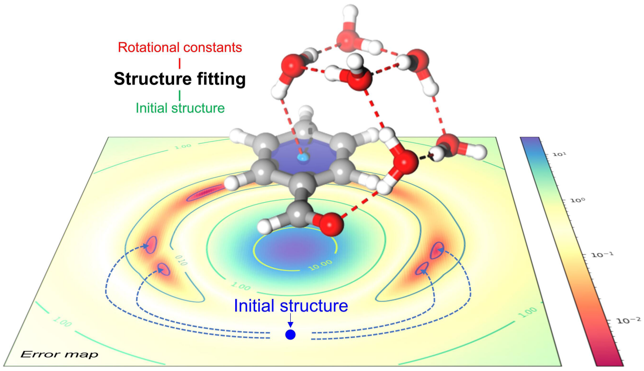

The characterization of the structures of molecular clusters, which serve as building blocks for bulk substances, provides crucial insight into the interactions between constituent units. Chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy, combined with state-of-the-art quantum chemical calculations, is a powerful tool for characterizing the structures of molecular clusters, as the rotational spectra are directly related to the mass distribution of a molecule or cluster. However, determining the structures of large or complex clusters from experimental rotational spectra remains challenging due to their structural flexibility. *Ab initio* and density functional theory calculations for searching their stable structures could be significantly time-consuming and method-dependent. To address these challenges, we have developed an approach that relies on the experimental rotational constants to search for potential molecular structures without quantum chemical optimization. Our approach involves creating an initial set of conformers through either a semi-empirical sampling program or the quasi-Monte Carlo method. Afterward, the trust region reflective algorithm is utilized for structure fitting. This procedure enables us to quickly generate potential conformers and gain access to precise structural information. We apply our fitting program to water hexamer and benzaldehyde-water clusters, and the resulting topological structures align extremely well with the experimental results.

Key words: Molecular cluster, Microwave spectroscopy, Chirped pulse, Structure fitting, Fitting program

I. INTRODUCTION

Molecular clusters are groups of molecules held together by non-covalent interactions (NCIs) such as hydrogen bonding, van der Waals forces, and dipole-dipole interactions. These clusters as the building blocks for bulk substances provide crucial insight into the interactions between constituent units, which help us understand the behavior and properties of materials at the molecular level [1]. The characterization of cluster structures has been a long-standing research focus [2−5]. Many efforts have been dedicated to unveil the structures of bare gas-phase clusters, which is free from solvent and matrix effects [6−8].

The combination of Fourier transform microwave (FTMW) spectroscopy with supersonic-jet expansion techniques has enabled the investigations of weakly

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bound molecular complexes [9−13]. The primary spectroscopic parameters, *i.e.*, rotational constants, obtained from microwave spectra, are directly related to the mass distribution of the measured molecule. Thus, information of the molecular bond lengths and angles can be obtained from the rotational spectra. This technique combined with electrical discharge [14−17], laser ablation [18−20], or laser photolysis [21−24] has been applied to study the transient molecular species such as radicals, and ions. Many molecules of astrochemical, atmospheric and biological interest have been precisely described by microwave spectroscopy [25−28].

The developing chirped-pulse Fourier transform microwave (CP-FTMW) technique has significantly increased the acquisition rate of broadband spectra, by raising the single-shot bandwidth of microwave spectroscopy from approximately 0.5 MHz to more than 10 GHz [29]. The frequency resolution of better than 10 kHz enables each spectral signal acquisition with up to 10^6 resolution elements [10]. This allows for accurate and definite identification of chemical species, even within complex mixtures. Its high spectral resolution enables the discrimination of closely spaced rotational spectra of isotopologues. The primary advantage of rotational spectroscopy for determining molecular structure lies in its ability to use isotopic substitution to derive the coordinates of each atom in the principal axis system, without relying on any assumptions about initial structures [30]. Based on the Born-Oppenheimer approximation, the approach assumes that the positions of atoms within a molecule are not affected by isotopic substitution. Substituting each atom with a different isotope modifies the mass distribution, resulting in changes to the rotational constants. These alterations to the moments-of-inertia can then be translated into the coordinates of the atoms in the principal axis system (r_s). An alternative method to obtain the structural information is by adjusting certain structural parameters in an initial structure, which is generally obtained from high-level quantum chemical calculations, to alter the moments-of-inertia. The experimental moments-of-inertia are then duplicated in a least-squares fitting procedure, resulting in a fitted structure that represents the effective ground state structure (r_0).

In principle, the structure of any given molecule can be determined from their rotational spectroscopy by the methods described above. However, the structural determination of a molecular cluster, especially for a large size cluster, is highly challenging. First, the determinations of the experimental structures need the spectroscopic parameters of corresponding isotopologues. But the fact that efficient production of high-density gas phase molecular clusters in a controllable manner is hardly achieved with current technology, makes the measurement of their isotopomers very difficult. Second, the energetically favored structures of large clusters are challenging to predict because they are influenced by various types of non-covalent interactions which are subtle. As the degrees of freedom and sizes of the clusters increase, their potential energy surfaces are often characterized by numerous quasi-degenerate and shallow local minima that are difficult to calculate. Therefore, the optimization of such complex systems becomes time-consuming and less accurate, even with the use of state-of-the-art DFT methods.

In this study, we develop a program to search for the possible r_0 structures of molecular clusters based on experimental rotational constants. The procedure for conformer searching involves generating a set of initial conformers followed by structural fitting using the experimental rotational constants. After structural optimization, the resulting structures are filtered to remove unreasonable conformations, and the remaining structures are ranked according to their relative energies. This method avoids *ab initio* energy calculations, and the optimization process are solely based on mathematical principles, making its computational cost negligible in comparison with *ab initio* or DFT calculations. Besides the rapid selection of the candidate structures from plenty of structures, the other advantage of this program is the accurate determination of the structural parameters.

We have tested our program on the clusters of benzaldehyde-water [31] and water hexamer [7]. The test results show that our method can efficiently produce the cluster structures without manual intervention or tuning, using only the experimental parameters as the optimization target. These advantages indicate that our program can serve as an efficient tool for fitting the structures of molecular clusters from microwave spectroscopy.

II. EXPERIMENTS

A. Experimental method

We have set up a CP-FTMW spectrometer at Fudan University recently, with a single-shot signal acquisition

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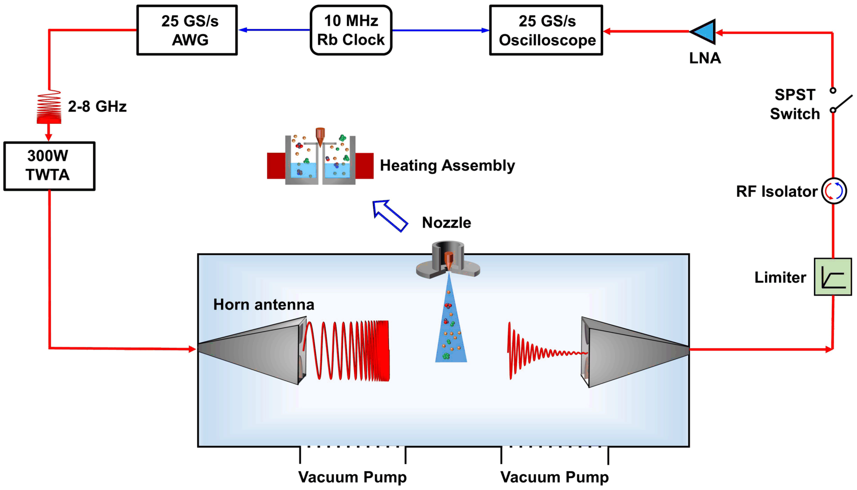

FIG. 1 Diagram of CP-FTMW spectrometer at Fudan University.

covering 2−8 GHz frequency range. Its schematic diagram is depicted in FIG. 1. In brief, a pulsed supersonic jet was produced by expanding the gas mixture into a vacuum chamber, and chirped pulses covering the frequency range of 2−8 GHz were emitted into the chamber to interact with the molecular beam. The resulting response of the chirped pulse in the limit of a strong driving field was referred to as rapid adiabatic passage (RAP) [32]. Once the excitation pulse dissipated, the particle population underwent redistribution and emitted coherent light, ultimately producing the free induction decay (FID) signal. This signal was then gathered and examined for analysis.

The rotational spectra of benzaldehyde-water clusters in the 2−8 GHz range were recorded by our CP-FTMW spectrometer. And the experiment was carried out as the following: a custom-made reservoir was employed, which is designed as part of a pulsed valve (general valve series 9) and positioned proximal to the valve orifice. This reservoir was maintained at ambient temperature and used to hold benzaldehyde. Distilled water was held in a second reservoir, which was located upstream of the gas pipeline, outside of the vacuum chamber. Samples of varying $H_2{}^{16}O/H_2{}^{18}O$ ratios were utilized for isotopologues. The experimental setup employed neon gas as the carrier gas with a backing pressure of 3 bars. The gas mixture was expanded through the nozzle with a diameter of 0.8 mm, generating a pulsed supersonic jet in a vacuum chamber. The frequency of the jet was set to 9 Hz. After a delay of around 900 μs, a horn antenna broadcast eight chirped pulses with a 4 μs duration spanning the 2−8 GHz into the vacuum chamber. These chirped pulses were generated by an arbitrary waveform generator operating at a sampling rate of 25 GS/s and amplified by a traveling wave tube amplifier with a minimum gain of 55 dB (300 W). The macroscopic dipole moment of the ensemble of molecules was probed by collecting eight FID signals, 40 μs for each, using another horn antenna, which were then recorded in the time domain with a digital oscilloscope with sample rate of 25 GS/s. The signals were subsequently transformed into the frequency domain using Fourier transformation with a Kaiser-Bessel window function. In order to decrease sample consumption and measurement time, a fast-frame data acquisition method was implemented that allowed for eight or more excitation and emission cycles during each supersonic expansion. The accuracy of the frequency measurement of the spectra was better than 15 kHz, and the resolution was better than 25 kHz.

B. Computational methods

The fitting program for the structures of molecular clusters was implemented using Python 3. The script is briefly divided into three components: preprocessing the coordinates data, fitting the rotational constants of the initial coordinates to the experimental ones by adjusting the initial coordinates, regenerating the coordinates. Initially, the input coordinates of the molecular cluster in the *xyz* format are split according to constituted monomers. Each monomer, except for the first one, is represented by a transform array of length six. The first three elements of this array represent the

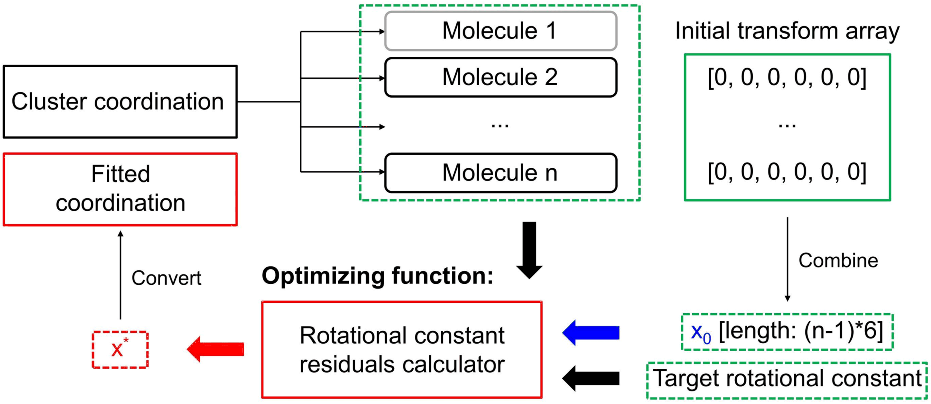

FIG. 2 Structure fitting workflow. Where x_0 is the variable to optimize and x^* is the result. The function accepts x_0, target rotational constant and molecule list as variables, and calculate difference between target value and one at x_0. Optimizing algorithm is able to find x^* that minimizes residual of the function.

translation position, while the last three correspond to the orientation expressed in Euler angle. These transform arrays are concatenated to form the input variable for the following optimization. The core process of fitting program is based on trust region reflective (TRR) algorithm. TRR algorithm is a nonlinear optimization algorithm used to find global or local minimum of an unconstrained optimization problem. The basic idea of the TRR algorithm is to compute the gradient and Hessian matrix of the objective function at each iteration, and then construct a quadratic model. The algorithm then seeks a minimum of the quadratic model within a trust region, which limits the search to a certain region around the current point. In our case, TRR algorithm is implemented by least-square fit function using scipy package. This function would optimize the input to minimize the cost, which is expressed as the sum of related error of rotational constants in our program. The cost function accepts the overall transformation array, and transforms it to the structure of an optimized cluster. Then the rotational constants of the cluster with the new structure is calculated, giving the deviation related to the target rotational constants, which is the objective of the optimizing function. The function minimizes these deviations by adjusting transformation array. During this process, the structures of individual molecules remain constant. A new transformation array is given when optimizing process is finished, and the final cluster structure is converted to text as output. The whole process is summarized in FIG. 2.

A sampling program, such as CREST [33] and ABCluster [34], is required in our workflow, which performs structure sampling and provides proper initial structures. In our case, CREST is chosen for initial conformer generation. Random sampling is an alternative method to obtain initial structures. By using a quasi-Monte Carlo (QMC) [35] engine to generate random sets of initial transform arrays, more comprehensive starting points can be obtained. However, the results from the QMC method require filtering the energetically favored structures further, and this process is considerably time-consuming due to the mostly unreasonable starting structures.

III. RESULTS AND DISCUSSION

In a previous report, water hexamer has been examined in a pulsed supersonic expansion using CP-FTMW, three isomers were unambiguously identified as cage, prism, and book conformers, respectively [7]. The oxygen coordination was deduced using isotopic rotational constants through the Kraitchman equation, resulting in the r_s structure. The oxygen framework of three water hexamers was determined using 18 single ^{18}O-substituted isotopologues. Their r_0 structures were fitted using calculated r_e structure and experimentally rotational constants of isotopic species, as shown in Ref.[7] and FIG. 3.

In this work, we utilized our structural fitting program to optimize the structures of water hexamer which have been further compared with the experimental ones. Total 91 conformers of water hexamer are initially produced by CREST. These structures have been selected as the initial structures for the structural optimization with our fitting program. Totally, four prism structures, four cage structures, and seven book structures were

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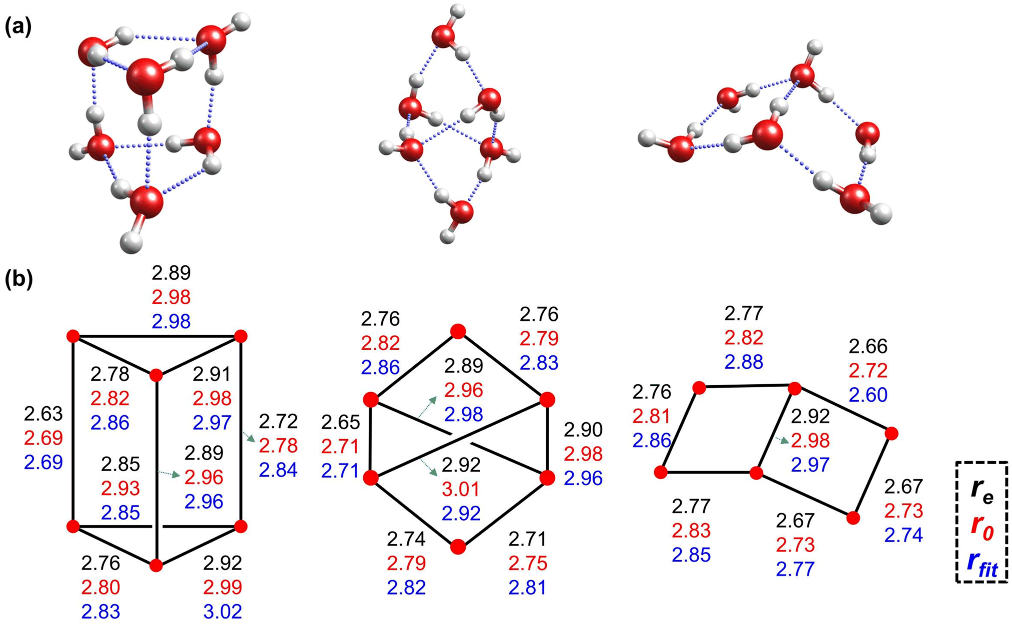

FIG. 3 Structures and structural parameters of water hexamer. (a) From left to right: r_0 structures of prism, cage, and book conformers; (b) skeletons of corresponding three conformers, red circles stand for oxygen. r_e, r_0, and fitted structure (r_fit) have bond length in Å colored as black, red, and blue.

produced by the fitting program with a semi-empirical GFN2-xtb [36] energy threshold of 10 kJ/mol. The structural parameters of the fitted structures of water hexamer are shown in FIG. 3. The sketches of oxygen frameworks are shown in FIG. 3(b), and the distances between oxygen atoms are listed for comparison with the experimental (r_0) and calculated (r_e) values. It can be observed that the structural parameters (r_fit) of energy-favored structures fitted by our program are in good agreement with the experimental parameters of Ref.[7] and the r_e parameters calculated at the B3LYP-D4/def2-TZVP level of theory. The maximum deviations between the bond lengths of program fitted structures and r_0 structures are 0.08 Å, 0.09 Å, and 0.12 Å in prism, cage, and book conformers, respectively. In addition to the experimentally observed book conformers, our program predicts another book conformer (see FIG. S3 in Supplementary materials, SM) that is consistent with the experimental isotopic coordinates, wherein the direction of the right-side water tetramer is counterclockwise instead of clockwise as in the observed conformer. Moreover, all the fitted conformers have been further validated by the experimental parameters of the isotopic species.

We have investigated the structures of the clusters of PhCHO-$(H_2O)_{1-6}$ using CP-FTMW spectrometer (see FIG. 4 or Ref.[31]). There are two energetically similar isomers associated with the PhCHO-H_2O complex, with each isomer corresponding to a water molecule that is situated on one side or the other of the carbonyl group through an OH$\cdots$O hydrogen bond (HB) within the PhCHO molecule plane. One isomer features a secondary, weak CH$\cdots$O HB between the oxygen atom of water and the hydrogen atom of the aldehyde group. The second isomer features a secondary, weak CH$\cdots$O HB between the oxygen atom of water and the hydrogen atom of the phenyl ring. Similarly, PhCHO-$(H_2O)_2$ complex has two conformers, in which the water dimer is stabilized by a HB with one end anchored at the aldehyde oxygen through HB and the other end interacting with either the aldehyde hydrogen or the C$-$H bond of phenyl ring. In the PhCHO-$(H_2O)_3$ cluster, chain-like water trimer coupling with the aldehyde group forms a cycle. The PhCHO-$(H_2O)_{1-3}$ clusters have near planar structures, while in the PhCHO-$(H_2O)_{4-6}$ clusters, the water molecules form four-member ring, five-member ring, and book-shape structures above the phenyl ring. In these clusters, OH$\cdots$O and OH$\cdots\pi$ non-covalent bonds dominate the interactions between water oligomers and benzaldehyde. As the size of the cluster increases, the measurement of isotopologues and the structure determination become more difficult. As a result, we have not experimentally determined the structural details of PhCHO-$(H_2O)_{4-6}$ clusters.

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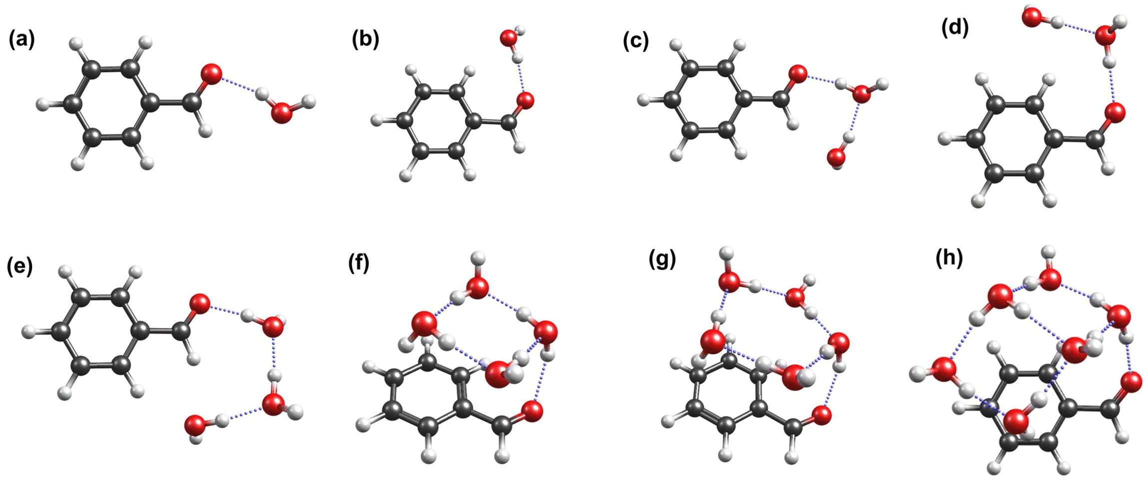

FIG. 4 Experimentally observed structures of the PhCHO-$(H_2O)_{1-6}$ clusters [31].

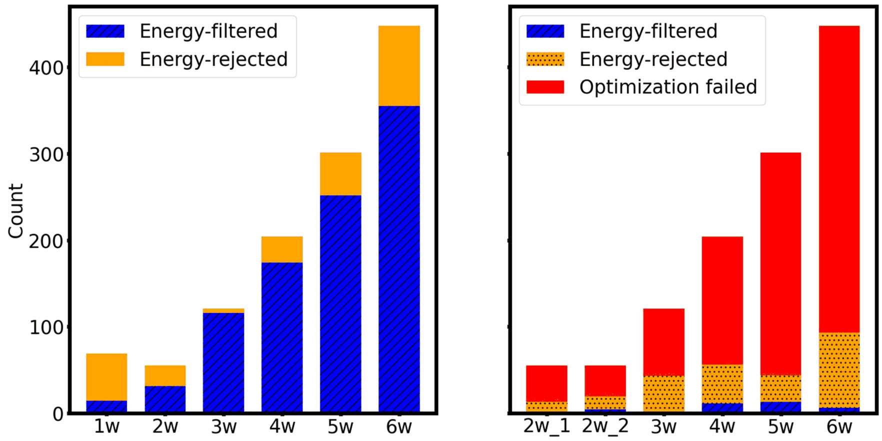

FIG. 5 CREST results (left panel) and program optimization results (right panel). "Energy-filtered": energetically favorable conformers filtered by a 20 kJ/mol threshold; "Energy-rejected": conformers that are excluded by the energy filter; "Optimization failed": optimization failed towards the target rotational constants. Energy-filtered number of PhCHO-$(H_2O)_2$_1 and PhCHO-$(H_2O)_3$ is 1. xw denotes PhCHO-$(H_2O)_x$, _1 and _2 denote conformer 1 and conformer 2.

Therefore, we applied the structural fitting program to reinvestigate this system. CREST was employed to generate candidate conformers for all the benzaldehyde-water clusters. Totally, 69, 55, 121, 204, 301, and 448 candidates are generated for the PhCHO-$(H_2O)_{1-6}$ species, respectively. Based on the fitting algorithm, we optimized all candidates to reproduce the experimental rotational constants. Any structure that cannot be successfully optimized, *i.e.*, cannot be optimized to the target value or optimized to incorrect structures, is excluded from the pool of candidate structures. This process shrinks the candidate number of PhCHO-$(H_2O)_{1-6}$ species to 69/44 (two conformers, same in PhCHO-$(H_2O)_2$), 13/19, 43, 56, 44, and 93, respectively. After the initial optimization, the structures undergo the energetical examination by the GFN2-xtb method with an energy threshold of 20 kJ/mol to eliminate the irrational structures generated by the fitting algorithm. After this procedure, we are able to further reduce the optimized candidate number to 35/10, 1/4, 1, 11, 13, and 6, for PhCHO-$(H_2O)_{1-6}$ species, respectively. Except for the mono-hydrate specie, the number of candidates is much smaller than that obtained from the direct energy screening by CREST method with the same energy threshold (14, 31, 116, 174, 252, and 355 for PhCHO-$(H_2O)_{1-6}$, respectively). The comparison is summarized in FIG. 5 and Table S6 in SM. After going through this process, the majority of the candidate number is reduced to less than 10% of the original CREST results. It is worth noting that, for PhCHO-H_2O species, most

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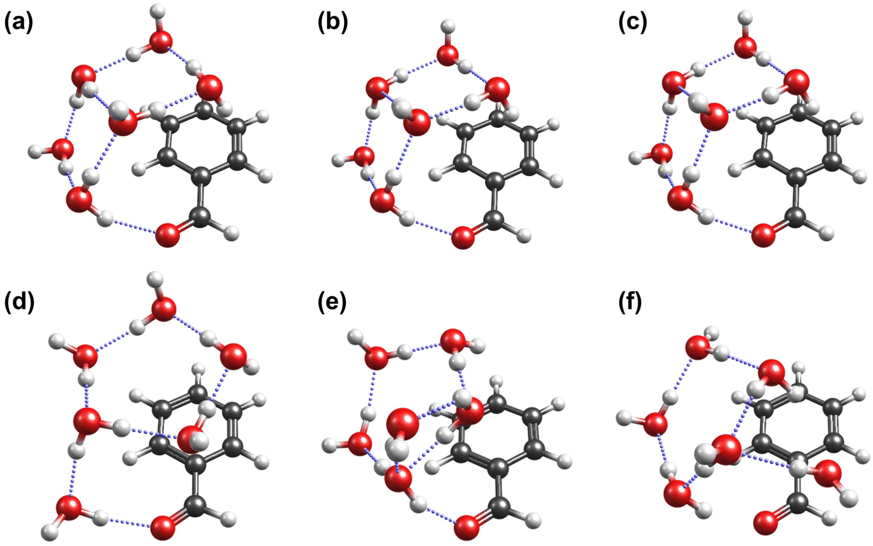

FIG. 6 Optimized conformers of PhCHO-$(H_2O)_6$ from the fitting program, energetically ranked by GFN2-xtb method from the lower to the higher one (a−f).

of the program fitted conformers differ only in the orientations of the OH bonds of water molecule, which are actually identical in the vibrationally averaged structures [31, 37]. In the original CREST output, there are many structures far from the experimental results, and the fitting process can optimize them to the experimentally observed configuration.

Taking PhCHO-$(H_2O)_6$ species as an example, among the top 52 predicted structures of the output of CREST, the cubic or quasi-cubic water hexamer is prominent. Notably, no experimentally observed book isomer is present in these structures. With the further DFT optimization at the B3LYP-D4/def2-TZVP level of theory (without ZPE and BSSE corrections), all the energetically favorable structures are arranged in a cubic or quasi-cubic manner, and the book-shaped water hexamer does not appear until the twentieth structure in the energetical rank. Impressively, our structural fitting program can optimize the CREST results into six conformers. Among these conformers, three low-energy ones include a book-shaped water hexamer, while the other three have water molecules forming a pentagonal ring, as depicted in FIG. 6. This result shows that the structural fitting program can rapidly identify the experimentally observed conformer of PhCHO-$(H_2O)_6$, with significantly higher efficiency compared with conventional way by DFT calculations.

It is worth noting that the length of the transformation array exceeds the number of available rotational constants. As a result, an overdetermined equation is being solved, which theoretically has an infinite number of solutions and can result in the countless local minima. This emphasizes the importance of choosing an appropriate initial structure for achieving the desired optimization results. Sampling tools like CREST are not always capable of providing the optimal starting structure. Escaping from local minima is a crucial research objective in global optimization, and the Monte Carlo method is a direct and straightforward approach that is widely used in molecular simulations [38, 39]. The Monte Carlo method identifies the minimum point through a large number of random samples, and in theory, the global minimum point can be found as the number of samples approaches infinity.

According to the aforementioned theory, the Monte Carlo method can be employed for initial conformations searching. By using semi-empirical energy calculations employed in GFN1-xtb [40], we can screen out the energetically unfavorable conformations, resulting in a series of possible conformers with rotational constants closely matching the experimental values. This approach is feasible for clusters with low optimization degrees of freedom, such as the PhCHO-$(H_2O)_3$ cluster with 18 variables. We conducted 10,000 random samplings of the cluster and obtained 1291 conformers. Among them, 29 conformers are within the energy threshold of 40 kJ/mol. Although the orientations of water molecules are not completely consistent with the correct configuration in most conformers, their positions are close to the experimentally observed con-

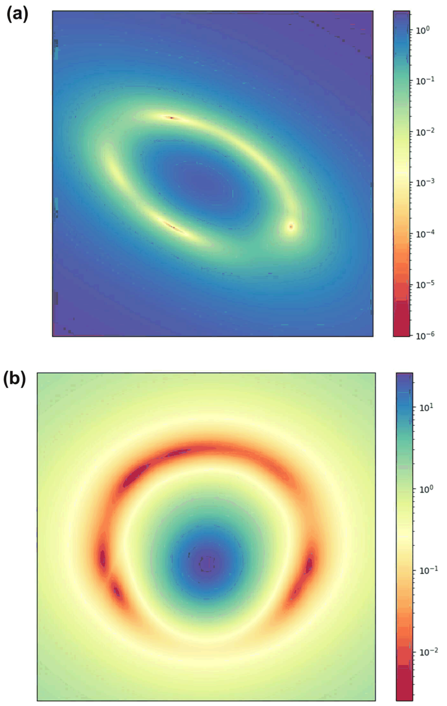

FIG. 7 Projections of transform array of PhCHO-$(H_2O)_6$. (a) Two-dimensional slice; and (b) principal component analysis projection. The color coding in the figure denotes the logarithmic relative error of the rotational constants between the sampling and the experiment, with red representing the lowest error and blue representing the largest error.

figuration. This method is more effective for smaller clusters, as exemplified by the 10 random samplings of PhCHO-$(H_2O)_1$, which finally results in six conformers. In these conformers, the position of the water molecules is consistent with the experimental observations. However, insufficient sampling may prevent obtaining the true structure if the degree of freedom of the system is considerably high. For instance, out of 7248 samples generated for the PhCHO-$(H_2O)_6$ cluster with 36 variables, none of the conformers were found to match the experimental result. These results indicate that randomized sampling methods are sufficiently efficient for small clusters, but are significantly time-consuming for larger clusters with more degrees of freedom, although they are theoretically feasible.

We examined the 36-dimensional sampling space of PhCHO-$(H_2O)_6$ and visualized it through slice and projection, which are depicted by the logarithmic relative error between the rotational constants of the sampling structures and the experimental ones, as shown in FIG. 7. The two-dimensional slice of this high-dimensional variable demonstrates that the local minima are not uniformly distributed throughout the entire space (FIG. 7(a)). This result suggests the existence of many regions in the sampling space where no conformer can meet the desired rotational constants. This can explain why conventional sampling programs, such as CREST used in this study, are struggled in searching the right structure. They can be caught in the "blue" whirlpool, and produce many structures deviating from the right ones. As we observed in the result of CREST, a lot of cubic structures are predicted. Furthermore, we used principal component analysis (PCA) to project the high-dimensional variable onto a two-dimensional plane (FIG. 7(b)). According to the findings, the local minima are distributed unevenly, with a dense belt-shaped region. This suggests that numeral local minima in close proximity area may exhibit comparable rotational constants. The inefficiency of Monte Carlo methods in exploring configurations for large cluster systems might be attributed to this factor.

IV. CONCLUSION

In summary, this study presents a structural fitting program that utilizes experimental rotational constants to search for r_0 structures of molecular clusters. This program involves creating an initial set of conformers through either a semi-empirical sampling program, such as CREST, or the quasi-Monte Carlo method. Afterward, the trust region reflective algorithm is utilized for structural fitting. The fitted results are further filtered by energy evaluation. This procedure enables us to quickly generate the potential conformers and gain access to precise structural information. Successful testing of the program on benzaldehyde-water clusters and water hexamers shows that it is a viable tool for identifying cluster structures without the need to perform *ab initio* calculations. This program facilitates the structural search and optimization for molecular clusters.

Supplementary material: Program source code, test platform, fitted structure and coordinates, and rotational constants of fitted benzaldehyde-water clusters are available.

V. ACKNOWLEDGMENTS

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