

# Quantum fluctuation and vibrational dynamics of aqueous $\text{Cu}^+$ and $\text{Ag}^+$ clusters



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## ARTICLE INFO

### Article history:

Available online 24 March 2013

### Keywords:

Ring polymer molecular dynamics  
Aqueous  $\text{Cu}^+$  and  $\text{Ag}^+$  clusters  
Path integral simulation  
Anharmonicity

## ABSTRACT

The structures and infrared spectra of  $\text{Ag}^+(\text{H}_2\text{O})_n$  ( $n = 1-4$ ) and  $\text{Cu}^+(\text{H}_2\text{O})$  are studied by “on-the-fly” *ab initio* MD, *ab initio* PIMD, and *ab initio* RPMD simulations. It is found that the anharmonicity due to nuclear quantum and thermal effects acts differently depending on the system as well as the type of vibrational mode. In the low-frequency region, the spectra become a broad band as the cluster size increases due to the complex mode couplings, which is qualitatively different from the harmonic spectra. In contrast, the HOH bending modes are systematically red-shifted by a small amount due to the anharmonicity. The OH stretching modes are found to be also red-shifted, but the amount of shift is more dependent on the system. Consequently, these effects cannot be described by unique scaling of harmonic frequencies.

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## 1. Introduction

Ion–water complexes, or in general, ion solvation in aqueous environment, share the flexible nature due to highly anharmonic vibrations between the ion and water as well as structural rearrangements of the hydration shell. While thermal excitation would be the main origin for such large-amplitude motions for heavy atoms, nuclear quantum effect, e.g. zero-point vibration and tunneling, is considered to have an important contribution for light atoms such as hydrogen. For instance, the quantum mechanical nature of the structural fluctuation in ion–water complexes has been frequently pointed out from path integral simulations [1–15].

Among the ion–water complexes,  $\text{Ag}^+(\text{H}_2\text{O})_n$  and  $\text{Cu}^+(\text{H}_2\text{O})_n$  are two species that have been produced size-selectively [16–22]. Recently from the infrared (IR) photo-dissociation spectra, it has been suggested that  $\text{Cu}^+$  and  $\text{Ag}^+$  can be coordinated by 2 and 3 water molecules, respectively, in the first hydration shell by lino et al. [23–25]. This conclusion is consistent with the results of the corresponding static *ab initio* calculations. It has been reported that the 2 + 0 and 2 + 1 structures are the most stable ones for  $\text{Cu}^+(\text{H}_2\text{O})_2$  and  $\text{Cu}^+(\text{H}_2\text{O})_3$ , respectively [26–28], while the 3 + 0 and 3 + 1 structures are the most stable ones for  $\text{Ag}^+(\text{H}_2\text{O})_3$  and  $\text{Ag}^+(\text{H}_2\text{O})_4$ , respectively [26,29]. However, it is known well that the simple computed IR spectra in the standard harmonic analysis results in disagreement with the corresponding experiments. Thus, a traditional correction is often used to multiply the frequencies by a cer-

tain scaling factor, but this is no more than an empirical treatment. Basically, in order to improve the quality of the computation of vibrational spectra, it is necessary to explicitly include the effects of anharmonicities and mode couplings as well as quantum effects of vibration into the theoretical model.

One such approach is ring polymer molecular dynamics (RPMD) developed by Craig and Manolopoulos [30–32], which is an extension of the classical molecular dynamics to include nuclear quantum effects. The RPMD method has access to quantum correlation functions within a quasi-classical approximation based on the path integral formalism [33–36]. The infrared spectrum is available via the Fourier transform of approximate Kubo-transformed dipole autocorrelation function evaluated from the RPMD trajectories. The RPMD method can be combined with *ab initio* electronic structure calculations in order to obtain quasi-classical vibrational spectra from first principles [37,38]. Although it has been argued recently that RPMD is theoretically problematic in causing artificial resonances in vibrational spectra [39,40], it is one of the feasible ways that has direct access to approximate quantum dynamics of complex many-body systems. The RPMD method has been already used to compute infrared spectra of liquid water [39], hydrazine [42] and aromatic molecules [43,44].

In this paper,  $\text{Ag}^+(\text{H}_2\text{O})_n$  and  $\text{Cu}^+(\text{H}_2\text{O})$  are studied by *ab initio* MD and *ab initio* PIMD methods, which are able to simulate structural fluctuations in thermodynamic equilibria based on classical and quantum statistics, respectively. Then, by running a swarm of trajectories starting from these equilibrium configurations, the vibrational spectra are computed using *ab initio* MD and *ab initio* RPMD methods. We compare these results with the conventional static *ab initio* calculations and harmonic normal mode analysis

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to elucidate the influence of structural fluctuations, anharmonicity, and nuclear quantum effects on the vibrational infrared spectra of  $\text{Ag}^+(\text{H}_2\text{O})_n$  and  $\text{Cu}^+(\text{H}_2\text{O})$ .

## 2. Method

We have followed the standard procedure [40] to carry out “on-the-fly” Born–Oppenheimer *ab initio* MD, *ab initio* PIMD [45–49], and *ab initio* RPMD simulations [37,42] as well as the static *ab initio* calculations followed by harmonic analysis. All these *ab initio* simulations are performed by using the MP2 method with 6–31 + G\* basis set for O and H atoms, and def2-SVP basis set for Cu and Ag atoms using Gaussian03 [50] linked to our code [51]. The dipole trajectories of *ab initio* MD/RPMD simulations have been computed with the same MP2 level of *ab initio* electron structure method.

To obtain the statistical averages and the density profiles, *ab initio* PIMD (*ab initio* MD) simulations were carried out for 40,000–74,000 steps (320,000 steps) with the Trotter number or the “number of beads” of  $P = 16$  ( $P = 1$ ). This was done for each system of  $\text{Ag}^+(\text{H}_2\text{O})_n/\text{Cu}^+(\text{H}_2\text{O})$  with the step size of  $dt = 0.1$  fs after the preliminary equilibration of 10,000 steps. The massive Nose–Hoover chain technique has been used to control the temperature at 300 K. In the *ab initio* RPMD and *ab initio* MD simulations, the initial positions and velocities have been taken from the above preliminary thermostated runs which generate classical and quantum canonical ensembles, respectively, at 300 K. Starting from 10

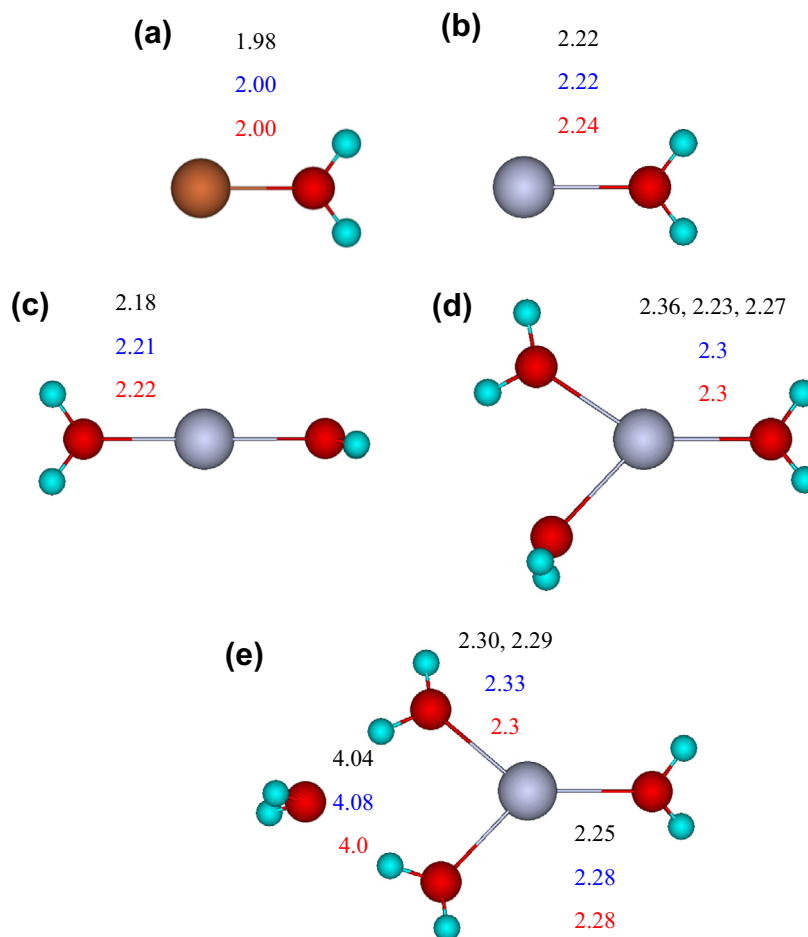
different (statistically independent) *ab initio* PIMD (*ab initio* MD) configurations thus obtained, *ab initio* RPMD (*ab initio* MD) simulations with  $P = 16$  ( $P = 1$ ) were carried out for 2 ps each (See Refs. [40,41] that discuss the restarting procedure for RPMD). This was done for each system of  $\text{Cu}^+(\text{H}_2\text{O})/\text{Ag}^+(\text{H}_2\text{O})_n$  with  $dt = 0.2$  fs. In order to properly compute the vibrational IR spectra in *ab initio* RPMD (*ab initio* MD) simulations, the thermostats were turned off and the rotational degrees of freedom were eliminated [40]. It has been checked that the total energy was conserved within the error of less than 0.001 hartree throughout the MD and RPMD trajectories. It took about 90 s per PIMD step (or RPMD step) for  $\text{Ag}^+(\text{H}_2\text{O})_4$  using the 3.0 GHz Xenon 16-core PC cluster. We note here that the resolution of the IR spectra obtained from Fourier transform of the trajectory of  $\tau = 2$  ps at temperature 300 K is

$$\lambda_{\text{ft}}^{-1} = \frac{1}{\tau c} = \frac{1}{2 \times 10^{-12}[\text{s}] \times 3.00 \times 10^{10}[\text{cm/s}]} \approx 16.7[\text{cm}^{-1}],$$

where  $c$  is the speed of light.

All the *ab initio* MD, PIMD and RPMD simulations were started from the global minimum configuration. It has been found that the conformational change did not occur in all these cases within the simulation time. Note that this situation is different from the experiments by lino et al. [24] done in the high energy regions, where multiple conformers may have been involved.

To our knowledge, it is difficult to assess the temperature of gaseous clusters generated in the jet spray, so there is no way to set exactly at the temperature corresponding to the experiment.



**Fig. 1.** The optimized geometries of (a)  $\text{Cu}^+(\text{H}_2\text{O})$ , (b)  $\text{Ag}^+(\text{H}_2\text{O})$ , (c)  $\text{Ag}^+(\text{H}_2\text{O})_2$ , (d)  $\text{Ag}^+(\text{H}_2\text{O})_3$ , and (e)  $\text{Ag}^+(\text{H}_2\text{O})_4$  obtained from static *ab initio* calculations. The numbers in black are the equilibrium Ag–O/Cu–O distances. The numbers in blue and red are the average Ag–O/Cu–O distances from *ab initio* MD and *ab initio* PIMD simulations, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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