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Quantum dynamical effects in liquid water: A semiclassical study on the diffusion and the infrared absorption spectrum

Jian Liu,¹ William H. Miller,^{1,a)} Francesco Paesani,^{2,b)} Wei Zhang,³ and David A. Case³ ¹Department of Chemistry and K. S. Pitzer Center for Theoretical Chemistry, University of California, Berkeley, California 94720-1460, USA and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460, USA ²Department of Chemistry and Center of Biophysical Modeling and Simulation, University of Utah,

315 South 1400 East Room 2020, Salt Lake City, Utah 84112, USA ³Department of Chemistry and Chemical Biology and BioMaPS Institute, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854-8087, USA

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The important role of liquid water in many areas of science from chemistry, physics, biology, geology to climate research, etc., has motivated numerous theoretical studies of its structure and dynamics. The significance of quantum effects on the properties of water, however, has not yet been fully resolved. In this paper we focus on quantum dynamical effects in liquid water based on the linearized semiclassical initial value representation (LSC-IVR) with a quantum version of the simple point charge/flexible (q-SPC/fw) model [Paesani et al., J. Chem. Phys. 125, 184507 (2006)] for the potential energy function. The infrared (IR) absorption spectrum and the translational diffusion constants have been obtained from the corresponding thermal correlation functions, and the effects of intermolecular and intramolecular correlations have been studied. The LSC-IVR simulation results are compared with those predicted by the centroid molecular dynamics (CMD) approach. Although the LSC-IVR and CMD results agree well for the broadband for hindered motions in liquid water, the intramolecular bending and O-H stretching peaks predicted by the LSC-IVR are blueshifted from those given by CMD; reasons for this are discussed. We also suggest that the broadband in the IR spectrum corresponding to restricted translation and libration gives more information than the diffusion constant on the nature of quantum effects on translational and rotational motions and should thus receive more attention in this regard. © 2009 American Institute of Physics. [doi:10.1063/1.3254372]

I. INTRODUCTION

Theoretical simulations of the dynamics of large molecular systems is at present an extremely active area of research, and as in most areas of theory, the accuracy of the treatment is inversely related to the ease of its application. It is thus useful to have a full "menu" of theoretical approaches from the very accurate, which may be difficult to apply to very large systems to much simpler and more approximate methods that are more readily applicable to complex molecular systems.

Perhaps the simplest theoretical approach to chemical dynamics is classical mechanics, i.e., classical molecular dynamics (MD) simulations (which are extremely wide spread nowadays), while the most accurate treatment is of course a complete solution of the time-dependent Schrödinger equation. Semiclassical (SC) theory^{1,2} stands between these two limits: it utilizes classical trajectories as "input," and thus contains classical dynamics, and incorporates quantum mechanics approximately, i.e., within the SC approximation. The SC approximation actually contains all quantum effects

at least qualitatively, and in molecular systems the description is usually quite quantitative. This was first demonstrated by work in the 1970s on small molecular systems (primarily scattering problems), $^{1-6}$ and more recently in applications to systems with many degrees of freedom by using various initial value representations (IVRs) of SC theory (primarily to calculate time correlation functions).^{7–57}

The SC-IVR approach is also intermediate between classical MD and a full quantum treatment with regard to ease of application, i.e., it is more difficult to apply than standard classical mechanics, but much easier (for large molecular systems) than a full quantum calculation. Within the SC-IVR framework, too, there is a "submenu" of approaches from the full SC-IVR treatment, which entails no additional approximations to other versions that introduce approximations beyond the SC approximation itself to make it easier to apply to complex systems.

The simplest (and most approximate) version of SC-IVR is its "linearized" approximation the (LSC-IVR),^{30,31,35,47,58–61} which leads to the classical Wigner model^{62–64} for time correlation functions; see Sec. III A for a summary of the LSC-IVR (where we also point out that there are other approaches, which lead to the classical Wigner model). The LSC-IVR/classical Wigner model cannot describe true quantum coherence effects in time correlation

^{a)}Author to whom correspondence should be addressed. Electronic mail: millerwh@berkeley.edu.

^{b)}Present address: Department of Chemistry and Biochemistry, University of California-San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA.

functions—more accurate SC-IVR approaches, such as the Fourier transform forward-backward IVR (FB-IVR) approach^{22,65} [or the still more accurate *generalized* FB-IVR (Ref. 24) and *exact* FB-IVR (Ref. 29)] of Miller *et al.*, are needed for this—but it does describe a number of aspects of the dynamics very well.^{30–35,47–51,60,66} e.g., the LSC-IVR has been shown to describe reactive flux correlation functions (which determine chemical reaction rates) quite well, including strong tunneling regimes,^{35,59,66} and correlation functions with linear operators^{30,32,34} and also nonlinear operators^{33,67} in systems with enough degrees of freedom for quantum rephasing to be unimportant.

For thermal time correlation functions for large systems, other trajectory-based approximated quantum methods that are comparable to the LSC-IVR include the "forward-backward semiclassical dynamics" (FBSD) approximation of Makri *et al.*,^{30,39–43,68–78} the centroid MD (CMD) of Voth *et al.*,^{79–94} and the ring polymer MD (RPMD) of Manolopoulos *et al.*,^{95–103} Similar to the LSC-IVR, all these trajectory-based approaches fail to capture true quantum interferences but do describe quantum decoherence and tunneling effects fairly well, and are relatively straightforward to apply to complex polyatomic molecular systems for the entire range of temperature for systems of chemical interests. See Refs. 33–35 and 104 for more discussions and comparisons.

The purpose of the paper is to study quantum dynamical effects in liquid water via LSC-IVR simulations of the infrared (IR) absorption spectrum and the translational diffusion constant, and compare the theoretical results predicted by the LSC-IVR with those given by the CMD obtained by several of us earlier.⁸⁸ To avoid the double-counting of quantum effects^{88,105} in previous simulations^{98,106–113} which were based on empirical models designed for classical simulations, we use the quantum version of the simple point charge/ flexible (q-SPC/fw) model developed by Paesani et al.⁸⁸ Section II first summarizes the relation between thermal correlation functions of the system and experimental observables for dynamical properties (i.e., IR absorption spectrum and diffusion constant). Then Sec. III briefly reviews the LSC-IVR methodology and the local Gaussian approximation (LGA) which is used to generate the local momentum distribution in the LSC-IVR, and further gives explicit LSC-IVR (LGA) formulations for the correlation functions investigated in the present study. Section IV presents the LSC-IVR simulation results with detailed analysis on how correlations between different molecules and atoms play roles in the dynamical properties, and compares the theoretical results for the IR spectrum and the diffusion constant simulated by the LSC-IVR to those given by the CMD and also to the experimental data followed by further discussions. Concluding remarks are given in Sec. V.

II. EXPERIMENTAL OBSERVABLES AND THERMAL CORRELATION FUNCTIONS

Most quantities of interest in the dynamics of complex systems can be expressed in terms of thermal time autocorrelation functions,¹¹⁴ which are of the form

$$C_{AB}(t) = \frac{1}{Z} \operatorname{Tr}(\hat{A}^{\beta} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}), \qquad (2.1)$$

where $\hat{A}^{\beta}_{\text{std}} = e^{-\beta \hat{H}} \hat{A}$ for the standard version of the correlation function, or $\hat{A}^{\beta}_{\text{sym}} = e^{-\beta \hat{H}/2} \hat{A} e^{-\beta \hat{H}/2}$ for the symmetrized version,¹¹⁵ or $\hat{A}^{\beta}_{\text{Kubo}} = \frac{1}{6} \int_{0}^{\beta} d\lambda e^{-(\beta-\lambda)\hat{H}} \hat{A} e^{-\lambda \hat{H}}$ for the Kubotransformed version.¹¹⁶ These three versions are related to one another by the following identities between their Fourier transforms,

$$\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} I_{AB}^{\text{Kubo}}(\omega) = I_{AB}^{\text{std}}(\omega) = e^{\beta\hbar\omega/2} I_{AB}^{\text{sym}}(\omega), \qquad (2.2)$$

where $I_{AB}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} C_{AB}(t)$, etc. Here $Z = \text{Tr}[e^{-\beta \hat{H}}](\beta = 1/k_B T)$ is the partition function and \hat{H} the (time-independent) Hamiltonian of the system, and \hat{A} and \hat{B} are operators relevant to the specific property of interest.

A. Infrared spectrum

The experimental IR spectrum is given in terms of two frequency-dependent properties—the Beer–Lambert absorption constant $\alpha(\omega)$ and the refractive index $n(\omega)$. According to the Fermi Golden Rule of time-dependent perturbation theory in quantum mechanics, these quantities are related to the dipole absorption line shape $I_{\mu\mu}^{\text{std}}(\omega)$ by

$$n(\omega)\alpha(\omega) = \frac{\pi\omega}{3\hbar c V \varepsilon_0} (1 - e^{-\beta\hbar\omega}) I_{\mu\mu}^{\rm std}(\omega), \qquad (2.3)$$

where $I_{\mu\mu}^{\text{std}}(\omega)$ is the Fourier transform of the (standard) collective dipole autocorrelation function, i.e.,

$$I_{\mu\mu}^{\text{std}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle_{\text{std}}$$
$$\equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} C_{\mu\mu}^{\text{std}}(t).$$
(2.4)

Here μ is the total dipole moment of the system.

Integrating the right-hand side (RHS) of Eq. (2.4) twice by parts, one obtains the relation

$$\omega^{2} I_{\mu\mu}^{\text{std}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle_{\text{std}} \equiv I_{\dot{\boldsymbol{\mu}}\dot{\boldsymbol{\mu}}}^{\text{std}}(\omega),$$
(2.5)

where $\hat{\mu}$ is the dipole-derivative operator (the change of the total dipole moment over time). By virtue of Eqs. (2.2) and (2.5), Eq. (2.3) can also be expressed as

$$n(\omega)\alpha(\omega) = \frac{\pi}{3\hbar c V \varepsilon_0} I^{\text{Kubo}}_{\mu\mu}(\omega), \qquad (2.6)$$

which shows that the most direct correlation function for the experimental observable $n(\omega)\alpha(\omega)$ is actually $C_{\dot{\mu}\dot{\mu}}^{\text{Kubo}}(t)$.

For a simple point charge model for water, the total dipole moment operator $\hat{\mu}$ is given by

$$\hat{\boldsymbol{\mu}} = \sum_{i=1}^{N_m} \left(q_{\rm H} \hat{\mathbf{r}}_{{\rm H},1}^i + q_{\rm H} \hat{\mathbf{r}}_{{\rm H},2}^i - q_{\rm O} \hat{\mathbf{r}}_{\rm O}^i \right) = \sum_{i=1}^{N_m} \sum_{j=1}^2 q_{\rm H} (\hat{\mathbf{r}}_{{\rm H},j}^i - \hat{\mathbf{r}}_{\rm O}^i),$$
(2.7)

where N_m is the number of molecules in the system, $\hat{\mathbf{r}}_{H,j}^i$ is the position of the *j*th hydrogen atom of the *i*th water molecule, $\hat{\mathbf{r}}_O^i$ is that of the oxygen atom of the *i*th water molecule, and the charge of the oxygen atom q_O is twice of that of hydrogen atom q_H . The dipole-derivative operator $\hat{\boldsymbol{\mu}}$ is then given by

$$\hat{\boldsymbol{\mu}} = q_{\rm H} \sum_{i=1}^{N_m} \sum_{j=1}^{2} \left(\hat{\mathbf{p}}_{{\rm H},j}^i / m_{\rm H} - \hat{\mathbf{p}}_{\rm O}^i / m_{\rm O} \right),$$
(2.8)

where $\hat{\mathbf{p}}_{\mathrm{H},j}^{i}$ and $\hat{\mathbf{p}}_{\mathrm{O}}^{i}$ are the corresponding momenta, and m_{H} and m_{O} the atom masses.

Obviously the sum of all relative velocities of the hydrogen atom to the oxygen atom in each water molecule is involved in Eq. (2.8), i.e., the collective dipole-derivative autocorrelation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ in Eq. (2.6) is given by

$$\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle = q_{\rm H}^2 \left\langle \left(\sum_{i=1}^{N_m} \sum_{j=1}^2 (\hat{\mathbf{p}}_{{\rm H},j}^i(0)/m_{\rm H} - \hat{\mathbf{p}}_{\rm O}^i(0)/m_{\rm O}) \right) \\ \cdot \left(\sum_{i'=1}^{N_m} \sum_{j'=1}^2 (\hat{\mathbf{p}}_{{\rm H},j'}^{i'}(t)/m_{\rm H} - \hat{\mathbf{p}}_{\rm O}^{i'}(t)/m_{\rm O}) \right) \right\rangle.$$
(2.9)

If one ignores the cross-terms between different molecules in the correlation function, then

$$\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle \approx \sum_{i=1}^{N_m} \langle \hat{\boldsymbol{\mu}}_{water,i}(0) \cdot \hat{\boldsymbol{\mu}}_{water,i}(t) \rangle$$
$$= q_{\rm H}^2 \sum_{i=1}^{N_m} \left\langle \left(\sum_{j=1}^2 \left(\hat{\mathbf{p}}_{{\rm H},j'}^i(0) / m_{\rm H} - \hat{\mathbf{p}}_{\rm O}^i(0) / m_{\rm O} \right) \right) \right.$$
$$\cdot \left(\sum_{j'=1}^2 \left(\hat{\mathbf{p}}_{{\rm H},j'}^i(t) / m_{\rm H} - \hat{\mathbf{p}}_{\rm O}^i(t) / m_{\rm O} \right) \right) \right\rangle.$$
(2.10)

Further neglecting the cross-terms between relative velocities for different H-atoms to O-atom in the same water molecule, one has

$$\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle \approx \sum_{i=1}^{N_m} \sum_{j=1}^{2} \langle \hat{\boldsymbol{\mu}}_{\text{HO},i,j}(0) \cdot \hat{\boldsymbol{\mu}}_{\text{HO},i,j}(t) \rangle$$

$$= q_{\text{H}}^2 \sum_{i=1}^{N_m} \sum_{j=1}^{2} \langle (\hat{\mathbf{p}}_{\text{H},j}^i(0)/m_{\text{H}} - \hat{\mathbf{p}}_{\text{O}}^i(0)/m_{\text{O}})$$

$$\cdot (\hat{\mathbf{p}}_{\text{H},j}^i(t)/m_{\text{H}} - \hat{\mathbf{p}}_{\text{O}}^i(t)/m_{\text{O}}) \rangle.$$
(2.11)

Finally, since the mass of the oxygen atom is ~16 times of that of the hydrogen atom, it is also reasonable to neglect the velocity of the oxygen atom and further approximate the correlation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ in terms of the velocity

(momentum) autocorrelation function of a single hydrogen atom

$$\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle \approx (q_{\mathrm{H}}/m_{\mathrm{H}})^{2} \sum_{i=1}^{N_{m}} \sum_{j=1}^{2} \langle \hat{\mathbf{p}}_{\mathrm{H},j}^{i}(0) \cdot \hat{\mathbf{p}}_{\mathrm{H},j}^{i}(t) \rangle$$
$$\equiv 2N_{m} (q_{\mathrm{H}}/m_{\mathrm{H}})^{2} C_{\mathbf{p}_{\mathrm{H}}\mathbf{p}_{\mathrm{H}}}(t), \qquad (2.12)$$

which was used by Lobaugh and Voth¹⁰⁸ and Poulsen *et al.*^{109,113} to simulate quantum dynamic effects of the IR spectrum.

B. Diffusion constant

The self-diffusion constant of a single water molecule can be obtained from the center-of-mass momentum autocorrelation function

$$D = \frac{1}{3} \int_0^\infty dt C_{\mathbf{p}_{H_2O} \mathbf{p}_{H_2O}}^{\text{Kubo}}(t) / m_{\text{H}_2O}^2, \qquad (2.13)$$

where the center-of-mass momentum of single water molecule $\hat{\mathbf{p}}_{\mathrm{H}_{2}\mathrm{O}}$ is the sum of the momenta of the two hydrogen atoms and that of the oxygen atom of the water molecule

$$\hat{\mathbf{p}}_{H_2O} = \sum_{j=1}^{2} \hat{\mathbf{p}}_{H,j} + \hat{\mathbf{p}}_O.$$
 (2.14)

Again, since the oxygen atom is much heavier than the hydrogen atom, a reasonable way is to use the oxygen momentum autocorrelation to calculate the diffusion constant, i.e.,

$$D = \frac{1}{3} \int_0^\infty dt C_{\mathbf{p}_0 \mathbf{p}_0}^{\text{Kubo}}(t) / m_0^2, \qquad (2.15)$$

which was used by Poulsen et al. 109,113

III. SIMULATION METHODOLOGY

A. Linearized semiclassical initial value representation

The SC-IVR approximates the forward (backward) time evolution operator $e^{-i\hat{H}t/\hbar}$ ($e^{i\hat{H}t/\hbar}$) by a phase space average over the initial conditions of forward (backward) classical trajectories.^{1,25,28,29} By making the approximation that the dominant contribution to the phase space averages comes from forward and backward trajectories that are infinitesimally close to one another, and then linearizing the difference between the forward and backward actions (and other quantities in the integrand), Wang *et al.*^{59,60} (see also Ref. 14) obtained the LSC-IVR, or classical Wigner model for the correlation function in Eq. (2.1),

$$C_{AB}^{\text{LSC-IVR}}(t) = Z^{-1} (2\pi\hbar)^{-N} \int d\mathbf{x}_0 \int d\mathbf{p}_0 A_w^\beta(\mathbf{x}_0, \mathbf{p}_0) B_w(\mathbf{x}_t, \mathbf{p}_t), \quad (3.1)$$

where A_w^{β} and B_w are the Wigner functions⁶² corresponding to these operators,

$$O_{w}(\mathbf{x},\mathbf{p}) = \int d\mathbf{\Delta}\mathbf{x} \langle \mathbf{x} - \mathbf{\Delta}\mathbf{x}/2 | \hat{O} | \mathbf{x} + \mathbf{\Delta}\mathbf{x}/2 \rangle e^{i\mathbf{p}^{T}\mathbf{\Delta}\mathbf{x}/\hbar}, \quad (3.2)$$

for any operator \hat{O} . Here *N* is the number of degrees of freedom in the system, and $(\mathbf{x}_0, \mathbf{p}_0)$ is the set of initial conditions (i.e., coordinates and momenta) for a classical trajectory, $(\mathbf{x}_t(\mathbf{x}_0, \mathbf{p}_0), \mathbf{p}_t(\mathbf{x}_0, \mathbf{p}_0))$ being the phase point at time *t* along this trajectory.

The classical Wigner model is an old idea,^{62–64,117} but it is informative to realize that it is contained within the general SC-IVR formulation, namely, as a specific approximation to it;^{59,60} more accurate implementations of the SC-IVR approach would be expected to lead to a more accurate description. It should also be noted that there are other approximate routes which lead to the classical Wigner model for correlation functions (other than simply postulating it); e.g., Pollak and Liao constructed a quantum transition state theory using the parabolic approximation for the dynamics in Eq. (3.1) for the flux-side correlation function,¹¹⁸ and Shi and Geva¹¹⁹ derived Eq. (3.1) by linearizing forward and backward paths in a Feynman path integral representation of the forward and backward propagators, as did Poulsen et al.¹²⁰ independently somewhat later [using the Feynman-Kleinert (FK) approximation for the LSC-IVR/Classical Wigner method, they called it the FK linear path integral^{109,113,120,121}]. Moreover, Liu and Miller³¹ have recently shown that the exact quantum time correlation function can be expressed in the same form as Eq. (3.1), with an associated dynamics in the single phase space, and it was furthermore demonstrated that the LSC-IVR is its classical limit $(\hbar \rightarrow 0)$, high temperature limit $(\beta \rightarrow 0)$, and harmonic limit.

The LSC-IVR can treat both linear and nonlinear operators in a consistent way,³³ can be applied to nonequilibrium, as well as the above equilibrium correlation functions, and can also be used to describe electronically nonadiabatic dynamics, i.e., processes involving transitions between several potential energy surfaces. These merits of the LSC-IVR make it a versatile tool to study a variety of quantum mechanical effects in chemical dynamics of large molecular systems.

B. Local Gaussian approximation

Calculation of the Wigner function for operator \hat{B} in Eq. (3.1) is usually straightforward; in fact, \hat{B} is often a function only of coordinates or only of momenta, in which case its Wigner functions is simply the classical function itself. Calculating the Wigner function for operator \hat{A}^{β} , however, involves the Boltzmann operator with the total Hamiltonian of the complete system, so that carrying out the multidimensional Fourier transform to obtain it is far from trivial. Furthermore, it is necessary to do this in order to obtain the distribution of initial conditions of momenta \mathbf{p}_0 for the real time trajectories. To accomplish this task, several approximations have been introduced for the LSC-IVR, which include the harmonic approximation by Wang *et al.*,⁵⁹ the more general *local* harmonic approximation by Shi and Geva,⁴⁷ the FK approximation by Poulsen *et al.*,¹²⁰

Gaussian approximation by Liu and Miller.^{30–34} More recently, Liu and Miller have proposed an LGA that improves on all these approximations for treating imaginary frequencies,³⁵ and this is what we have used for the study of liquid water in this paper. Below we briefly summarize the LGA.

As in the standard normal-mode analysis, mass-weighted Hessian matrix elements are given by

$$\mathbf{H}_{kl} = \frac{1}{\sqrt{m_k m_l}} \frac{\partial^2 V}{\partial x_k \, \partial \, x_l},\tag{3.3}$$

where m_k represent the mass of the *k*th degree of freedom. The eigenvalues of the mass-weighted Hessian matrix produce normal-mode frequencies $\{\omega_k\}$, i.e.,

$$\Gamma^T \mathbf{H} \mathbf{T} = \mathbf{\lambda},\tag{3.4}$$

with λ a diagonal matrix with the elements $\{(\omega_k)^2\}$ and **T** an orthogonal matrix. If **M** is the diagonal "mass matrix" with elements $\{m_k\}$, then the mass-weighted normal mode coordinates and momenta $(\mathbf{X}_0, \mathbf{P}_0)$ are given in terms of the Cartesian variables $(\mathbf{x}_0, \mathbf{p}_0)$ by

$$\mathbf{X}_0 = \mathbf{T}^T \mathbf{M}^{1/2} \mathbf{x}_0, \tag{3.5}$$

and

$$\mathbf{P}_0 = \mathbf{T}^T \mathbf{M}^{-1/2} \mathbf{p}_0. \tag{3.6}$$

The Fourier transform of Eq. (3.2) then gives the Wigner function of \hat{A}^{β} as

$$A_{w}^{\beta}(\mathbf{x}_{0},\mathbf{p}_{0}) = (2\pi\hbar)^{N} \langle \mathbf{x}_{0} | e^{-\beta H} | \mathbf{x}_{0} \rangle$$
$$\times \prod_{k=1}^{N} \left[\left(\frac{\beta}{2\pi Q(u_{k})} \right)^{1/2} \exp \left[-\beta \frac{(P_{0,k})^{2}}{2Q(u_{k})} \right] \right],$$
$$\times f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}), \qquad (3.7)$$

where $u_k = \beta \hbar \omega_k$, $P_{0,k}$ is the *k*th component of the massweighted normal-mode momentum \mathbf{P}_0 [in Eq. (3.6)] and the quantum correction factor is given by

$$Q(u) = \begin{cases} \frac{u/2}{\tanh(u/2)} & \text{for real } u\\ = \frac{1}{Q(u_i)} = \frac{\tanh(u_i/2)}{u_i/2} & \text{for imaginary } u(u = iu_i). \end{cases}$$
(3.8)

In Eq. (3.7),

$$f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}) = \int \mathbf{d}\Delta \mathbf{x} \frac{\left\langle \mathbf{x}_{0} - \frac{\Delta \mathbf{x}}{2} \middle| \hat{A}^{\beta} \middle| \mathbf{x}_{0} + \frac{\Delta \mathbf{x}}{2} \right\rangle}{\langle \mathbf{x}_{0} \middle| e^{-\beta \hat{H}} \middle| \mathbf{x}_{0} \rangle} e^{i\Delta \mathbf{x}^{T} \cdot \mathbf{p}_{0}/\hbar}$$
$$\int \mathbf{d}\Delta \mathbf{x} \frac{\left\langle \mathbf{x}_{0} - \frac{\Delta \mathbf{x}}{2} \middle| e^{-\beta \hat{H}} \middle| \mathbf{x}_{0} + \frac{\Delta \mathbf{x}}{2} \right\rangle}{\langle \mathbf{x}_{0} \middle| e^{-\beta \hat{H}} \middle| \mathbf{x}_{0} \rangle} e^{i\Delta \mathbf{x}^{T} \cdot \mathbf{p}_{0}/\hbar},$$
(3.9)

is a function depending on the operator \hat{A}^{β} . For example, when $\hat{A}^{\beta} = e^{-\beta \hat{H}} \hat{\mathbf{x}}$, one has

$$f_A(\mathbf{x}_0, \mathbf{p}_0) = \mathbf{x}_0 + \frac{i\beta\hbar}{2} \mathbf{M}^{-1/2} \mathbf{T} \mathbf{Q}(\mathbf{u})^{-1} \mathbf{P}_0, \qquad (3.10)$$

where $\mathbf{Q}(\mathbf{u})$ is the diagonal quantum correction factor matrix with the elements $\{Q_k \equiv Q(u_k)\}$.

The explicit form of LSC-IVR correlation function [Eq. (3.1)] with the LGA is thus given by

$$C_{AB}^{\text{LSC-IVR}}(t) = \frac{1}{Z} \int \mathbf{d} \mathbf{x}_0 \langle \mathbf{x}_0 | e^{-\beta \hat{H}} | \mathbf{x}_0 \rangle \int \mathbf{d} \mathbf{P}_0 \prod_{k=1}^N \left[\left(\frac{\beta}{2 \pi Q(u_k)} \right)^{1/2} \\ \times \exp \left[-\beta \frac{(P_{0,k})^2}{2 Q(u_k)} \right] \right],$$
$$\times f_A(\mathbf{x}_0, \mathbf{p}_0) B(\mathbf{x}_t, \mathbf{p}_t). \tag{3.11}$$

Below we show the explicit LSC-IVR formulations of the correlation functions considered in Secs. II A and II B.

C. Explicit formulations

For convenience, for the system consisting of N_m water molecules with the total degrees of freedom $N=9N_m$, one labels the order of the dimensions as x, y, z for each atom and that of the atoms as H, H, and O for each molecular. For instance, 9(i-1)+3(j-1)+k represents the *k*th dimension of the *j*th atom in the *i*th molecule; k=1,2,3 stand for x,y,z, respectively; j=1,2,3 depicts the first H-atom, the second one, and the O-atom, respectively. For the operator $\hat{A}^{\beta} = \hat{\mu}^{\beta}_{Kubo}$, by virtue of the relation

$$\hat{\boldsymbol{\mu}}_{\text{Kubo}}^{\beta} = \frac{i}{\hbar\beta} [\hat{\boldsymbol{\mu}}, e^{-\beta\hat{H}}], \qquad (3.12)$$

or

$$\hat{\mathbf{p}}_{\text{Kubo}}^{\beta} = \frac{i}{\hbar\beta} \mathbf{M}[\hat{\mathbf{x}}, e^{-\beta\hat{H}}], \qquad (3.13)$$

and Eq. (3.10), it is straightforward to show

$$\hat{\mathbf{p}}_{\text{Kubo}}^{\beta} = \mathbf{M}^{1/2} \mathbf{T} \mathbf{Q}(\mathbf{u})^{-1} \mathbf{P}_0, \qquad (3.14)$$

with the relation between the momentum vector \mathbf{p}_0 and the mass-weighted normal-mode momentum vector \mathbf{P}_0 given in Eq. (3.6). So *k*th component of the Kubo-transformed operator $(\hat{\mathbf{p}}_{\text{H},j}^i)_{\text{Kubo}}^{\beta} = \frac{1}{\beta} \int_0^{\beta} d\lambda e^{-(\beta-\lambda)\hat{H}} \hat{\mathbf{p}}_{\text{H},j}^i e^{-\lambda\hat{H}}$ can be shown as

$$(\hat{p}_{\mathrm{H},j,k}^{i})_{\mathrm{Kubo}}^{\beta} = \sqrt{m_{\mathrm{H}}} \sum_{l=1}^{N} T_{9(i-1)+3(j-1)+k,l} Q(u_{l})^{-1} P_{0,l}, \quad (3.15)$$

with $P_{0,l}$ as the *l*th component of the vector \mathbf{P}_0 and T_{mn} the element of the matrix **T**. Similarly, for the operator $(\hat{\mathbf{p}}_O^i)_{\text{Kubo}}^{\beta}$, one has

$$(\hat{p}_{\mathrm{O},k}^{i})_{\mathrm{Kubo}}^{\beta} = \sqrt{m_{\mathrm{O}}} \sum_{l=1}^{N} T_{9(i-1)+6+k,l} Q(u_{l})^{-1} P_{0,l}.$$
 (3.16)

For the Kubo-transformed correlation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$, one has

$$f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}) \cdot B(\mathbf{x}_{t},\mathbf{p}_{t}) = q_{H}^{2} \sum_{k=1}^{3} \left\{ \left[\sum_{i=1}^{N_{m}} \sum_{j=1}^{2} \left((m_{H})^{-1/2} \sum_{l=1}^{N} T_{9(i-1)+3(j-1)+k,l} Q(u_{l})^{-1} P_{0,l} - (m_{O})^{-1/2} \sum_{l'=1}^{N} T_{9(i-1)+6+k,l'} Q(u_{l'})^{-1} P_{0,l'} \right) \right] \times \left(\sum_{i'=1}^{N_{m}} \sum_{j'=1}^{2} \left(\hat{p}_{9(i'-1)+3(j'-1)+k}(t)/m_{H} - \hat{p}_{9(i'-1)+6+k}(t)/m_{O} \right) \right) \right\}.$$
(3.17)

Similarly, one can show

$$f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}) \cdot B(\mathbf{x}_{t},\mathbf{p}_{t}) = q_{H}^{2} \sum_{k=1}^{3} \sum_{i=1}^{N_{m}} \left\{ \left[\sum_{j=1}^{2} \left((m_{H})^{-1/2} \sum_{l=1}^{N} T_{9(i-1)+3(j-1)+k,l} Q(u_{l})^{-1} P_{0,l} - (m_{O})^{-1/2} \sum_{l'=1}^{N} T_{9(i-1)+6+k,l'} Q(u_{l'})^{-1} P_{0,l'} \right) \right] \times \left(\sum_{j'=1}^{2} \left(\hat{p}_{9(i-1)+3(j'-1)+k}(t) / m_{H} - \hat{p}_{9(i-1)+6+k}(t) / m_{O} \right) \right) \right\}$$
(3.18)

for the Kubo version of the correlation function $\sum_{i=1}^{N_m} \langle \hat{\mu}_{water,i}(0) \cdot \hat{\mu}_{water,i}(t) \rangle_{Kubo}$ in the RHS of Eq. (2.10);

$$f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}) \cdot B(\mathbf{x}_{t},\mathbf{p}_{t}) = q_{H}^{2} \sum_{k=1}^{3} \sum_{i=1}^{N_{m}} \sum_{j=1}^{2} \left\{ \left((m_{H})^{-1/2} \sum_{l=1}^{N} T_{9(i-1)+3(j-1)+k,l} Q(u_{l})^{-1} P_{0,l} - (m_{O})^{-1/2} \sum_{l'=1}^{N} T_{9(i-1)+6+k,l'} Q(u_{l'})^{-1} P_{0,l'} \right) \times (\hat{p}_{9(i-1)+3(j-1)+k}(t)/m_{H} - \hat{p}_{9(i-1)+6+k}(t)/m_{O}) \right\}$$

$$(3.19)$$

for the Kubo version of the correlation function $\sum_{i=1}^{N_m} \sum_{j=1}^2 \langle \hat{\mu}_{HO,i,j}(0) \cdot \hat{\mu}_{HO,i,j}(t) \rangle_{Kubo}$ in the RHS of Eq. (2.11);

164509-6 Liu et al.

$$f_A(\mathbf{x}_0, \mathbf{p}_0) \cdot B(\mathbf{x}_t, \mathbf{p}_t) = (2N_m)^{-1} (m_{\rm H})^{-1/2} \sum_{k=1}^3 \sum_{i=1}^{N_m} \sum_{j=1}^2 \left\{ -\left(\sum_{l=1}^N T_{9(i-1)+3(j-1)+k,l} Q(u_l)^{-1} P_{0,l}\right) p_{9(i-1)+3(j-1)+k}(t) \right\}$$
(3.20)

for the Kubo-transformed correlation function $C_{\mathbf{p}_{H}\mathbf{p}_{H}}^{\text{Kubo}}(t)$ in Eq. (2.12);

$$f_{A}(\mathbf{x}_{0},\mathbf{p}_{0}) \cdot B(\mathbf{x}_{t},\mathbf{p}_{t}) = (N_{m})^{-1} \sum_{k=1}^{3} \sum_{i=1}^{N_{m}} \left\{ \left(\sqrt{m_{\rm H}} \sum_{j=1}^{2} \sum_{l=1}^{N} T_{9(i-1)+3(j-1)+k,l} Q(u_{l})^{-1} P_{0,l} + \sqrt{m_{\rm O}} \sum_{l'=1}^{N} T_{9(i-1)+6+k,l'} Q(u_{l'})^{-1} P_{0,l'} \right) \\ \times \left(\sum_{j=1}^{2} \hat{p}_{9(i-1)+3(j-1)+k}(t) + \hat{p}_{9(i-1)+6+k}(t) \right) \right\}$$
(3.21)

for the Kubo-transformed correlation function $C_{\mathbf{p}_{\mathrm{H},\mathrm{O}}\mathbf{p}_{\mathrm{H},\mathrm{O}}}^{\mathrm{Kubo}}(t)$; and

$$f_A(\mathbf{x}_0, \mathbf{p}_0) \cdot B(\mathbf{x}_t, \mathbf{p}_t) = (N_m)^{-1} (m_0)^{-1/2} \sum_{k=1}^3 \sum_{i=1}^{N_m} \left\{ \left(\sum_{l=1}^N T_{9(i-1)+6+k,l} Q(u_l)^{-1} P_{0,l} \right) p_{9(i-1)+6+k}(t) \right\} , \qquad (3.22)$$

for the Kubo-transformed correlation function $C_{\mathbf{p}_0\mathbf{p}_0}^{\text{Kubo}}(t)$.

Substituting the formula of $f_A(\mathbf{x}_0, \mathbf{p}_0) \cdot B(\mathbf{x}_t, \mathbf{p}_t)$ into Eq. (3.11), one gets the corresponding LSC-IVR approximation for the correlation function.¹²²

IV. RESULTS AND DISCUSSIONS

A. Simulation details

The q-SPC/fw model has been fully described in Ref. 88. It is a fully quantum model of liquid water at ambient conditions, which is exclusively based on the quantum results obtained from path integral MD (PIMD) and CMD simulations and enables these simulation results in an overall good agreement with the corresponding experimental values for a large set of equilibrium and dynamical properties. Here we use the LSC-IVR [i.e., Eq. (3.11)] to calculate the diffusion constant and the IR spectrum, with $\langle \mathbf{x}_0 | e^{-\beta \hat{H}} | \mathbf{x}_0 \rangle / Z$ in Eq. (3.11) evaluated by PIMD. One can refer to Sec. IIC of Ref. 35 for more details for the simulation procedure for the LSC-IVR.

The LSC-IVR (LGA) method has recently been implemented by us in the AMBER MD package,^{123,124} as has the PIMD method and the q-SPC/fw model several years earlier.⁸⁸ All LSC-IVR results in this paper have thus been obtained by employing the AMBER package. The simulations were carried out with a total of 216 water molecules in a cubic box with the periodic boundary condition. The shortrange interactions were truncated at 9.0 Å and the particle mesh Ewald method $^{125-127}$ was employed to calculate the long-range electrostatic interactions. As described in Ref. 88, a PIMD simulation was carried out in the NPT ensemble for 1 ns to obtain the density for liquid water at the ambient condition (T=298.15 K and P=1 atm), and then canonical equilibrium properties were obtained by PIMD for the NVT ensemble. In the PIMD simulation, 24 path integral beads were sufficient to give converged results,⁸⁸ and the temperature was controlled with the implementation of the Nosé-Hoover chains of four thermostats^{128,129} that were coupled to each path integral normal-mode.

For the LSC-IVR simulations, we first randomly select one of the path integral beads every 1 ps in the imaginary time propagation of the PIMD for the NVT ensemble, using

the configuration of the bead as the initial position \mathbf{x}_0 of the system, with its initial Cartesian momentum $\mathbf{p}_0 = \mathbf{M}^{1/2} \mathbf{T} \mathbf{P}_0$ sampled from the Gausssian distribution for the massweighted normal-mode momentum \mathbf{P}_0 in Eq. (3.11); a classical trajectory is then propagated from $(\mathbf{x}_0, \mathbf{p}_0)$ for 14 ps and the estimator $f_A(\mathbf{x}_0, \mathbf{p}_0) \cdot B(\mathbf{x}_t, \mathbf{p}_t)$ evaluated along the trajectory. Finally, this whole procedure is repeated to generate new trajectories, and one averages the property $f_A(\mathbf{x}_0, \mathbf{p}_0) \cdot B(\mathbf{x}_t, \mathbf{p}_t)$ for all real time trajectories until a converged result is obtained. About 300 such trajectories were enough to get good statistics for single atom or molecule self momentum correlation functions [i.e., $C_{\mathbf{p}_{H_2O}\mathbf{p}_{H_2O}}^{\text{Kubo}}(t)$, $C_{\mathbf{p}_H\mathbf{p}_H}^{\text{Kubo}}(t)$, and $C_{\mathbf{p}_O\mathbf{p}_O}^{\text{Kubo}}(t)$], while 40 000 trajectories were used to obtained converged results for correlation functions for the IR spectrum [i.e., $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$ and its approximations in Eqs. (2.10) and (2.11)]. For the real time dynamics in the LSC-IVR, the velocity-Verlet algorithm^{130,131} was employed with a time step $\Delta t = 0.5$ fs.

B. Results and discussions

Figure 1 shows the normalized density distribution of local normal-mode frequencies of typical quantum configurations generated by the PIMD for the q-SPC/fw model for liquid water at the ambient condition (T=298.15 K and P=1 atm). One sees two peaks in the high real frequency regime (i.e., 16 < u < 19), related to the O–H (symmetric and antisymmetric) stretching modes, for which quantum effects are quite important. One also sees that even at room temperature, more than 17% of local frequencies are imaginary, with 7% in the "deep tunneling" imaginary frequency regime that have $u_i = \beta \hbar |\omega_i| \ge \pi$. The LGA is able to deal the entire imaginary frequency modes for $u_i \ge \pi$ in the LSC-IVR.

We first investigate the IR spectrum for the q-SPC/fw water model. Figure 2 shows the comparison of the correlation functions $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$ and



FIG. 1. Normalized density of local frequencies from the path integral calculations for the q-SPC/fw water model at T=298.15 K. Imaginary frequencies are plotted on the negative axis. Dotted line indicates the imaginary frequency for $\beta\hbar|\omega|=\pi$.

 $\sum_{i=1}^{N_m} \langle \hat{\boldsymbol{\mu}}_{water,i}(0) \cdot \hat{\boldsymbol{\mu}}_{water,i}(t) \rangle_{Kubo}$ and their corresponding IR spectra. The collective dipole-derivative autocorrelation function and the self dipole-derivative autocorrelation function are similar in the oscillation period but have subtle differences in the intensities. Figure 2(b) suggests that the collective behavior of all water molecules is significant for the intensity of the O–H stretching (high frequency) regime. The correlation among distinct water molecules decreases the peak for the asymmetric O–H stretch (~3675 cm⁻¹) and enhances that for the symmetric O–H stretch (~3590 cm⁻¹). It also causes a slight redshift (~15 cm⁻¹) of the peak for the H–O–H bending motion (~1468 cm⁻¹) but not the intensity. In addition, the correlation among distinct water molecules



FIG. 2. (a) Comparison of $\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle_{\text{Kubo}}$ (sum-water-Kubo) and $\sum_{i=1}^{N_m} \langle \hat{\boldsymbol{\mu}}_{\text{water},i}(0) \cdot \hat{\boldsymbol{\mu}}_{\text{water},i}(t) \rangle_{\text{Kubo}}$ (single-water-Kubo). The correlation functions are multiplied by $m_{\text{H}}/4k_B N_m q_{\text{H}}^2$ such that the unit is kelvin. (b) The corresponding IR spectra obtained from the correlation functions in panel (a).



FIG. 3. (a) Comparison of $\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle_{\text{Kubo}}$ (sum-water-Kubo) and $\sum_{i=1}^{N_m} \sum_{j=1}^2 \langle \hat{\boldsymbol{\mu}}_{\text{HO},i,j}(0) \cdot \hat{\boldsymbol{\mu}}_{\text{HO},i,j}(t) \rangle_{\text{Kubo}}$ (single-HO-Kubo). The correlation functions are multiplied by $m_{\text{H}}/4k_B N_m q_{\text{H}}^2$ such that the unit is kelvin. (b) The corresponding IR spectra obtained from the correlation functions in panel (a).

also induces a blueshift of the peak of the broadband for the hindered libration and restricted translation $(\sim 10-1100 \text{ cm}^{-1})$, and a slight change in intensity.

Figure 3 shows the correlation function $\Sigma_{i=1}^{N_m} \Sigma_{j=1}^2 \langle \hat{\mu}_{\text{HO},i,j}(0) \cdot \hat{\mu}_{\text{HO},i,j}(t) \rangle_{\text{Kubo}}$ and its corresponding IR spectrum, with $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$ and its IR spectrum also shown for comparison. Comparing with Fig. 2, one sees that the correlation between different components $\hat{\mu}_{\text{HO},i,j=1}$ and $\hat{\mu}_{\text{HO},i,j=2}$ in the same water molecule has significant influence on the H-O-H bending motion and the hindered motionsthe intensity of the bending peak is decreased, and the peak for the hindered motions is further redshifted and also changed in intensity. The intensity of the O-H stretching peaks is also affected by the intramolecular correlation.

For the further approximation to $\sum_{i=1}^{N_m} \sum_{j=1}^{2} \langle \hat{\mu}_{HO,i,j}(0) \rangle$ $\hat{\mu}_{\text{HO},i,i}(t)$ of ignoring the motion of the O-atom in the water molecule, the correlation function $2N_m(q_{\rm H}/m_{\rm H})^2 C_{\mathbf{p}_{\rm H}\mathbf{p}_{\rm H}}^{\rm Kubo}(t)$ and its corresponding IR spectrum are shown in Fig. 4, with $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{kubo}}$ and its IR spectrum as the usual reference. By comparison with Fig. 3, one sees that $2N_m(q_{\rm H}/m_{\rm H})^2 C_{\mathbf{p}_{\rm H}\mathbf{p}_{\rm H}}^{\rm Kubo}(t)$ does reproduce the O–H stretching regime and the bending regime of the IR spectrum given by $\sum_{i=1}^{N_m} \sum_{j=1}^2 \langle \hat{\mu}_{HO,i,j}(0) \cdot \hat{\mu}_{HO,i,j}(t) \rangle$ fairly well with only a slight decrease in the intensity. However, a large discrepancy occurs in the restricted translational motion ($\sim 10-400 \text{ cm}^{-1}$). This is not a surprise since the O-atom motion has the most important contribution to the restricted translation of the water molecule (also see below for discussion on diffusion con-



FIG. 4. (a) Comparison of $\langle \hat{\boldsymbol{\mu}}(0) \cdot \hat{\boldsymbol{\mu}}(t) \rangle_{\text{Kubo}}$ (sum-water-Kubo) and $2N_m(q_H/m_H)^2 C_{\text{P}_H\text{P}_H}^{\text{Kubo}}(t)$ (single-H-Kubo). The correlation functions are multiplied by $m_H/4k_BN_mq_H^2$ such that the unit is kelvin. (b) The corresponding IR spectra obtained from the correlation functions in panel (a).

stants); the IR spectrum given by the H-atom self momentum correlation function thus does not provide the correct physical picture.

Figure 5 shows the direct comparison of the IR spectrum based on the LSC-IVR approximation for $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{Kubo}$ for the q-SPC/fw water model to that obtained from the CMD method⁸⁸ for the same state point and for the same model, and also compared with experiment.¹³² This is more interesting since the IR spectrum, unlike the diffusion constant (see below), was not one of the dynamical properties that were used to adjust parameters of the q-SPC/fw based on the CMD in order to reproduce the experimental IR absorption spectrum. One sees very good agreement between the LSC-IVR and the CMD spectra and the experimental data for the shape and for the position of the peak



FIG. 5. Comparison of simulated IR absorption spectra based on the LSC-IVR (LGA) and the CMD methods using the q-SPC/fw model to the experimental results.

in the broadband arising from the hindered motions $(\sim 10-1100 \text{ cm}^{-1})$. The intensity of the broadband given by the LSC-IVR is slightly smaller than that given by the CMD and therefore closer to the experimental data. The small shoulder at $\sim 200 \text{ cm}^{-1}$, which arises from the contribution of dipole-induced dipole interactions, is absent from both the LSC-IVR and CMD simulations for the q-SPC/fw model. This is expected since any fixed point charge model is not able to describe electronic polarization. In the bending regime, the position of the peak given by the LSC-IVR is blueshifted from that given CMD (by around 18 cm⁻¹), and the experimental spectrum is further blueshifted $(\sim 1640 \text{ cm}^{-1})$; the intensity for the LSC-IVR result is smaller than that for the CMD result, but the experimental result is even smaller. Both LSC-IVR and CMD simulations for the q-SPC/fw model predict two separated peaks in contrast to the broad O-H stretching band observed in the experiment. This is largely because the simple uncoupled harmonic oscillators in the q-SPC/fw model fail to capture the significant anharmonicity of and do not account for the effect of hydrogen bonding on the intramolecular O-H vibrations, which is also evident from the redshifting of the O-H stretching band in the experimental spectrum.^{88,105} (Fig. 5 of Ref. 88 shows that the asymmetric O-H stretching band is stronger than the symmetric one in the CMD simulation for the q-SPC/fw model, while Fig. 5 of Ref. 105 shows the opposite. This is due to the fact that the CMD simulation in Fig. 7 of Ref. 88 employs a fully adiabatic CMD (A-CMD) (Ref. 81), while that in Ref. 105 uses only a partially adiabatic CMD (Ref. 87) (PA-CMD). Different levels approximation of the CMD model and the time steps involved in updating the CMD trajectory thus affect the high-frequency vibrational band).

We note that the O-H stretching peaks predicted by the LSC-IVR are blueshifted from those given by CMD, as is the bending band, as shown in Fig. 5 for the q-SPC/fw model. Without having exact quantum "benchmark" calculations it is of course not possible to say with certainty which result is more nearly correct. However we do note that Witt et al. have recently shown that the IR spectrum given by CMD is redshifted from the classical frequency when using a harmonic intramolecular potential for the diatomic molecular OH, the redshift being more pronounced the lower the temperature¹⁰⁴ (which Witt et al. claim to be due to the "curvature problem"); for a harmonic potential the classical and quantum frequencies are expected to be very similar, and the LSC-IVR is expected to be close to the exact result in this case since it is well-known to be exact for fully harmonic potentials.¹³³ Also, for a presumably more realistic *ab initio* based model-the TTM3-F, a flexible and polarizable model for water clusters and liquid water of Fanourgakis and Xantheas¹³⁴—it has been reported that both the O–H stretching band and the bending band given by CMD (or PA-CMD) calculations are redshifted from those in the experimental spectrum;^{91,135} here, however, one cannot be guaranteed that this discrepancy is not due to the potential. So even though one can make some plausible arguments that the blueshift of the LSC-IVR results from those given by CMD is in the correct direction, this is not definitive. Finally, we also point



FIG. 6. Comparison of two Kubo-transformed momentum autocorrelation functions. Solid line: $C_{\mathbf{P}_{Q}\mathbf{P}_{Q}}^{\mathrm{Kubo}}(t)/2m_{\mathrm{O}}k_{B}$ for single O-atom (single-O-Kubo). Dotted line: $C_{\mathbf{P}_{L_{Q}}\mathbf{O}\mathbf{P}_{L_{Q}}}^{\mathrm{Kubo}}(t)/(2m_{\mathrm{H_{2}O}}k_{B}$ for the center-of-mass of single water molecule (center-water-Kubo).

out that Paesani *et al.* have shown that the CMD spectral lines for HOD in D_2O (i.e., the O–H stretch) and for HOD in H_2O (i.e., the O–D stretch) agree well with the vibrational frequency distributions based on centroid configurations from A-CMD trajectories with the TTM3-F force field.⁹² Further comparisons with the vibrational frequency distributions based on configurations from individual path integral beads would be useful to help resolve the matter, as would LSC-IVR simulations for the TTM3-F model or more advanced ones.

Finally we consider the diffusion constant in the liquid water. Figure 6 shows the comparison between the correlation function $C_{\mathbf{p}_{H_2O}\mathbf{p}_{H_2O}}^{\text{Kubo}}(t)$, which relates to the diffusion of a single water molecule, and $C_{\mathbf{p}_0\mathbf{p}_0}^{\text{Kubo}}(t)$, which describes the diffusion of single O-atom. One sees that the overall long-time behavior of the two correlation functions is similar. This demonstrates that O-atom dynamics dominates the diffusion of single water molecule since the O-atom is much heavier than the H-atom. However, $C_{\mathbf{p}_0\mathbf{p}_0}^{\text{Kubo}}(t)$ shows oscillatory structure due to intramolecular interactions (i.e., the O-H stretching interactions and the bending motion), while the centerof-mass momentum correlation function $C_{\mathbf{p}_{H,0}\mathbf{p}_{H,0}}^{\text{Kubo}}(t)$ is much smoother. The LSC-IVR gives the diffusion constant for a single water molecule as $D_{\rm H_2O}^{\rm LSC-IVR} = 0.50 \pm 0.01$ Å²/ps, which is close to that for a single O-atom as $D_{O}^{\text{LSC-IVR}}$ = 0.56 ± 0.01 Å²/ps. Although the intramolecular motions should not affect the long time limit of the translational motion (i.e., the diffusion constant) of the water molecule, the center-of-mass momentum correlation function $C_{\mathbf{p}_{\mathrm{H}_{2}\mathrm{O}}\mathbf{p}_{\mathrm{H}_{2}\mathrm{O}}}^{\mathrm{Kubo}}(t)$ is more numerically favorable (to get better statistics).

Figure 7 further compares the LSC-IVR result for $C_{P_{H_2O}P_{H_2O}}^{Kubo}(t)$ to the CMD and classical results obtained by Paesani *et al.* in Ref. 88. One sees that they all share similar behavior. The CMD is closer to the LSC-IVR for short time but to the classical result for long time. As shown in Table I, the diffusion constant given by CMD is $D_{H_2O}^{CMD} = 0.25 \pm 0.01 \text{ Å}^2/\text{ps}$, which is only half of the LSC-IVR value and closer to the experimental result $D_{H_2O} = 0.23 \text{ Å}^2/\text{ps}$.¹³⁶ However, one should not read too much into the direct comparison with experiment since the diffusion constant is one of the dynamical properties that were



FIG. 7. Comparison of normalized Kubo-transformed center-of-mass momentum autocorrelation functions $C_{PH_2O}^{Kubo}(t)/C_{PH_2OPH_2O}^{Kubo}(0)$. Solid line: LSC-IVR (LGA). Dotted line: CMD. Dot-dashed line: classical result.

used to select the parameters of the q-SPC/fw model so that the CMD calculation reproduces the experimental value. More interesting are the relative values between different methods. The LSC-IVR suggests the ratio of diffusion constants $D_{\rm H_2O}^{\rm QM}/D_{\rm H_2O}^{\rm Classical}$ = 2.8, while the CMD gives 1.4. We note this is similar to the comparison of the diffusion con-stants of liquid parahydrogen.^{34,35} For example, as shown in Figs. 11 and 12 of Ref. 34 and Tables 1 and 3 of Ref. 35 for the state point T=14 K, the LSC-IVR (LGA) gives about 2.2 for the ratio $D_{\rm H_2}^{\rm QM}/D_{\rm H_2}^{\rm Classical}$ and the CMD suggests about 1.3, while the MEAC-corrected result (a more accurate value) lies at 1.5-1.8, which suggests that the LSC-IVR overestimates the diffusion constant while the CMD underestimates it. This is also the case for a higher temperature T=25 K. References 34 and 35 also show that the LSC-IVR approaches the MEAC-correction faster than the CMD as the temperature increases for the liquid hydrogen system. On the other hand, we (and also others¹³⁷) note that the CMD (or RPMD) has the merit to conserve the proposed phase distribution in its model and keep $\langle B(t) \rangle$ [i.e., set the operator A =1 for the correlation function $\langle A(0)B(t)\rangle$ invariant for either intermolecular or intramolecular modes, while the LSC-IVR does not have such a merit, although how this merit indeed reflects the accuracy of the true correlation function $\langle A(0)B(t)\rangle$ is very subtle (i.e., the quantum evolution of $e^{-i\hat{H}t/\hbar}\hat{A}^{\beta}e^{i\hat{H}t/\hbar}$ is *not* stationary for general operators $\hat{A} \neq 1$).^{32–35,43} It is not clear whether the exact result for the q-SPC/fw water model is between what LSC-IVR and CMD give. Since the temperature T=298.15 K for the liquid water system is relatively high (i.e., imaginary time $\hbar\beta$ ≈ 25.62 fs is short), the MEAC correction for the momentum correlation function is not so useful. It will be interesting

TABLE I. Diffusion constants for liquid water in the ambient condition (T=298.15 K). All simulations were performed with 216 water molecules in cubic box with periodic boundary conditions.

Models	Methods	$D_{\mathrm{H_2O}}(\mathrm{\AA^2/ps})$	$D_{\mathrm{H_2O}}^{\mathrm{QM}}/D_{\mathrm{H_2O}}^{\mathrm{Classical}}$
q-SPC/fw ^a	Classical	0.18 ± 0.01	
	LSC-IVR (LGA)	0.50 ± 0.01	2.8
	CMD	0.25 ± 0.01	1.4

^aReference 88.

to come up with other ways to analyze the accuracy of the correlation function itself in future.

While the present manuscript was in preparation, a paper by Habershon et al.¹⁰⁵ appeared that proposed another quantum version of a fixed charge flexible model-the q-TIP4P/F based on the TIP4P/2005 model of Abascal and Vega.¹³⁸ The O-H bonds are described by a quartic function which introduces anharmonicity and thus gives a broad O-H stretching band. By tuning the parameters, the q-TIP4P/F water model is also able to give very good agreement between a number of static properties and PIMD simulations and also between several dynamical properties (such as diffusion constants) and RPMD/PA-CMD simulations. For a few properties, the q-TIP4P/F seems to be more promising than the q-SPC/fw model. Habershon et al.¹⁰⁵ further argued that for water models that give a single broad O-H stretching band, the competition between the intramolecular and intermolecular guantum effects should give the ratio between the quantum and classical self-diffusion constants for the water molecule as $D_{\rm H_2O}^{\rm QM}/D_{\rm H_2O}^{\rm Classical} < 1.2$. Is this indeed the whole story?

Since it was found that intermolecular quantum effects tend to disrupt the hydrogen-bonding network, providing a less structured liquid for which both translational and rotational dynamics are more rapid,^{88,105} both the q-SPC/fw and q-TIP4P/F models adjusted the parameters for the intramolecular interactions so that the quantum single water dipole moment was large enough (which retarded the molecular motion) to compensate for the intermolecular quantum effects, so that diffusion constants predicted by the CMD or RPMD simulations agree with the experimental data. However, one should also keep in mind that the broadband corresponding to restricted translation and libration motions $(\sim 10-1100 \text{ cm}^{-1})$, rather than a single point (such as the diffusion constant) of the spectrum, tells a much more detailed story about the translational and rotational dynamics. Figure 5 of the present manuscript and Fig. 5 of Ref. 105 both suggest that the intensity of the broadband for hindered motions is actually larger than the experimental data (discard the discrepancy of the shoulder for the dipole-induced dipole interaction around 200 cm⁻¹) in either the q-SPC/fw or q-TIP4P/F model. Note that the intensity of the IR spectrum is proportional to the square of the dipole-derivate [cf. Eq. (2.6)], which means that quantum dynamical effects of the dipole-dipole interaction are actually overestimated in both the q-SPC/fw and q-TIP4P models. The statement that the competition between the intermolecular and intramolecular quantum effects gives $D_{\rm H_2O}^{\rm QM}/D_{\rm H_2O}^{\rm Classical} < 1.2$, mainly based on the RPMD simulation for the q-TIP4P/F model,¹⁰⁵ therefore needs further investigation. Whether or not electronic polarization is included in the models, not only diffusion constants but also the broad IR band for the restricted translation and libration should be considered in coming to a consistent conclusion about quantum effects on the translation and rotational motions in liquid water. For example, Fig. 5 shows that quantum dynamical effects of the dipole-dipole interaction estimated by the CMD (and very likely the RPMD) are larger than those estimated by the LSC-IVR, while the latter gives a broadband for hindered motions closer to the experimental data. This is one of the main reasons why the diffusion constant given by the LSC-IVR is larger than that by the CMD/RPMD.

V. CONCLUSIONS

In this paper we have applied the LSC-IVR (LGA) method for a quantum version of flexible water model (the q-SPC/fw model⁸⁸) to study quantum dynamical effects in liquid water at ambient conditions (T=298.15 K and P=1 atm). The translational diffusion constant and the IR absorption spectrum have been investigated.

In order to study the collective behaviors of molecules and of intramolecular atoms, comparisons are presented among the collective dipole-derivative correlation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$ and its several approximations [i.e., Eqs. (2.9)-(2.12)] and among the corresponding IR spectra. The detailed analysis suggests that the collective motion of all water molecules affects much the O-H stretching regime, causing a redshift in the bending regime and a blueshift in the libration regime. The intramolecular correlation has important contributions to the spectrum even in the regime for the hindered motions: directly using the H-atom self momentum correlation function 108,109,113 could not give a faithful description for the restricted translational regime (and also other regimes) of the IR spectrum (See Fig. 4); the collective dipole-derivative autocorrelation function $\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_{\text{Kubo}}$ is what one should rely on. A comparison of the self momentum correlation function of a single water molecule $C_{\mathbf{p}_{H_2O}\mathbf{p}_{H_2O}}^{\text{Kubo}}(t)$ and that of a single O-atom $C_{\mathbf{p}_0\mathbf{p}_0}^{\text{Kubo}}(t)$ is also presented, demonstrating that the intramolecular correlation between the O-atom and the H-atoms does affect the behavior of the correlation function [i.e., $C_{\mathbf{p}_{\mathrm{H},\mathrm{O}}\mathbf{p}_{\mathrm{H},\mathrm{O}}}^{\mathrm{Kubo}}(t)$ is much smoother].

Comparison of the IR spectra calculated by LSC-IVR and CMD for the q-SPC/fw water model shows that both the O-H stretching and bending bands given by LSC-IVR are blueshifted from those by CMD and that the intensities of the broadband for hindered motions and the bending band are lower than those given by CMD. It is also found that the translational diffusion constant calculated by LSC-IVR is nearly twice of that by CMD. We also point out that the broadband for the restricted translation and libration of the IR spectrum, which gives more detailed information than the diffusion constant, should be also taken into account when considering the role of quantum effects on the translation and rotational motions. Since the q-SPC/fw model is inadequate to describe dipole-induced dipole interactions that are important in liquid water, it will be very interesting to carry out LSC-IVR simulations based on a more physical model, e.g., an *ab initio* based, flexible and polarizable TTM3-F model¹³⁴ or even more advanced models for quantum dynamical effects for liquid water, and reconsider these issues.

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