Reduced Density Matrix Theory for Vibrational Absorption Line Shape in Energy Transfer Systems: Non-Condon Effects in Water

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Using the projection operator technique, a reduced density matrix theory for linear absorption spectrum of energy transfer systems is developed for the theoretical absorption line shape of the systems with non-Condon transitions. As an application, we considered a model system of OH vibrations of water. In the present model calculation, the OH vibration modes are coupled to each other *via* intra-molecular coupling mechanism while their intermolecular couplings are turned off. The time-correlation functions appearing in the formulation are calculated from a mixed quantum/classical mechanics method. The present theory is successful in reproducing the exact absorption line shape. Also the present theory was improved from an existing approximate theory, time-averaged approximation approach.

Key Words: Line shape, Vibration, Water, Energy transfer

Introduction

Spectroscopic studies have provided us with rich information about dynamics and structure in condensed phase. Such experimental data are interpreted by combining them with a theoretical modeling.[1-5] To achieve this goal, a formulation of response function which relates the dynamics of a system with experimental signals should precede. The most fundamental spectroscopy is absorption spectrum. Absorption spectrum can be theoretically calculated by considering the linear response function. Among the various approaches to calculate the response function, we recently developed a reduced density matrix approach[6] and it has been applied to understand the vibronic pattern of the absorption spectrum of energy transfer systems.[7] In that approach we derived a reduced density matrix using the projection operator technique initially developed by Mori[8] and Zwanzig.[9] As usual, the initial density matrix of bath was assumed to be in equilibrium. Also in order to calculate various time-correlation functions appearing in the formulation, we had to be based on the cumulant expansion technique for the fluctuation of bath which is valid for Gaussian processes.

For many interesting systems, the two assumptions invoked in the previous work, the initial equilibrium distribution of bath and Gaussian baths, are reasonably valid. However, it was recently shown that the vibrational transition of OH bonds in water is highly dependent on the configuration of bath; strongly hydrogen-bonded OH bonds have strong transition intensity while weakly or non-hydrogen-bonded OH bonds have weak transition intensity.[10] Therefore the initial state prepared by absorption of light should be in non-equilibrium configuration of bath. Also the assumption of Gaussian bath breaks down in the fluctuation dynamics of the OH transition frequency in water.[11] Therefore the previous approach may not be applied for the calculation of vibrational absorption spectrum of OH modes in water and it is desired to develop a new form of the reduced density matrix which is applicable to such a system. In this paper we will improve the previous approach by modi-

fying the projection operator to be suitable for the systems with non-Condon effects. Also, the various time-correlation functions appearing in the reduced density matrix approach will be calculated from the mixed quantum/classical mechanics (QM/CM) method going beyond the cumulant expansion technique.

Theory

Model Hamiltonian. We consider N chromophores with two vibrational states which are coupled to each other. The molecular Hamiltonian of such a system within one-exciton manifold reads

$$H = H^0 + H' \tag{1}$$

$$H^0 = |0\rangle h_0(q)\langle 0| + \sum_{n=1}^{N} |n\rangle h_n(q)\langle n| \tag{2}$$

$$H' = \sum_{n=1}^{N}\sum_{m=1}^{N}\left(|n\rangle h'_{nm}(q)\langle m| + c.c.\right) \tag{3}$$

Here q is the collective coordinate of bath. $h_n(q)$ is the Hamiltonian of the nth one-exciton state and $h'_{nm}(q)$ is the coupling Hamiltonian between the one-exciton states $|n\rangle$ and $|m\rangle$ which fluctuates due to the coupling to the bath degrees of freedom.

Absorption Line Shape. The time-domain expression of the absorption line shape is given by[12]

$$I(\omega) = 2\operatorname{Re}\int_0^\infty dt\, e^{i\omega t}\phi(t). \tag{4}$$

Here $\phi(t) \equiv Tr\{\mu\rho(t)\}$ is the linear response function where μ is the molecular dipole operator along the direction of electric field and Tr denotes the trace over the quantum states of the

system and baths. $\rho(t) \equiv e^{-\frac{i}{\hbar}Ht} \mu \rho^{eq} e^{\frac{i}{\hbar}Ht}$ can be regarded as an effective density matrix at time t having evolved from $\mu \rho^{eq}$ at time zero where ρ^{eq} is the equilibrium density matrix. Assuming that only the ground state of the system is populated in equilibrium and ignoring the contribution of the permanent dipole moments (which are irrelevant to the absorption spectrum), the initial effective density matrix can be written as

$$\mu \rho_{eq} = \sum_{n=1}^{N} |n\rangle \rho_{n0} \langle 0| \qquad (5)$$

with $\rho_{n0} \equiv \mu_n \rho_0^{eq}$, the transition-dipole-weighted equilibrium bath density matrix subject to the ground state of system. $\mu_n(q) \equiv \langle n|\mu(q)|0\rangle$ is the transition dipole moment between the ground and nth one-exciton state which is dependent on the bath coordinate (non-Condon case). The initial effective density matrix consists of the coherences between the one-exciton states and ground state of a statistical ensemble weighted by their transition dipole moments. The spontaneous evolution of the coherences determines of the absorption spectrum and we need to develop a methodology for the description of the time evolution of density matrix.

Inserting the density matrix into the response function, we have

$$\phi(t) = Tr\left\{ \mu e^{-\frac{i}{\hbar}Ht} \sum_{n=1}^{N} |n\rangle \rho_{n0} \langle 0| e^{\frac{i}{\hbar}Ht} \right\} \qquad (6)$$

The response function describes the energy transfer process from a donor state $|n\rangle$ to an acceptor state.

Projection Operator. The inhomogeneous term in the kinetic equations derived by using projection operator technique can be removed by defining a projection operator to project density matrix onto its initial density matrix. In usual cases, initial density matrix of bath is well approximated as equilibrium one. However, if Condon approximation for transition dipole breaks down as shown in the vibration transition of water,[10] the initial density matrix of bath relevant to the absorption spectrum should substantially deviates from that of equilibrium state because of preferential excitation of chromophores depending on bath configuration. Therefore in order to take into account such a non-Condon effect, we need to introduce a projection operator associated with non-equilibrium density matrix of bath.

For that, noting the form of the initial condition Eq. (5), we introduce a projection operator P defined by

$$P \times f = \sum_{n=1}^{N} |n\rangle \rho_{n0} \langle 0| \langle f \rangle_{n0} \qquad (7)$$

where

$$\langle f \rangle_{n0} \equiv \frac{Tr_q(\mu_n \langle n|f|0\rangle)}{Tr_q(\mu_n \rho_{n0})} \qquad (8)$$

and its complementary one $Q = 1 - P$ where Tr_q denotes the quantum/classical traces over the bath variables. The operator P projects a matrix in the Hilbert space of the baths onto the initial effective density matrix ρ_{n0} which is dependent on the state of system (non-Condon effect). We can see that the projection operators have the following properties: $P\mu\rho^{eq} = \mu\rho_{eq}$ and $Q\mu\rho^{eq} = 0$.

Quantum Kinetic Equation. Time-evolution of the effective density matrix, $\rho(t) = e^{-\frac{i}{\hbar}Ht} |n\rangle \mu_n \rho_0^{eq} \langle 0| e^{\frac{i}{\hbar}Ht}$, is described by the Liouville equation

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}(L^0 + L')\rho(t) \qquad (9)$$

with $L^0\rho = [H^0, \rho]$ and $L'\rho = [H', \rho]$. In the interaction picture, Eq. (9) becomes

$$\frac{d}{dt}\rho^I(t) = -\frac{i}{\hbar}L'(t)\rho^I(t) \qquad (10)$$

where $L'(t) \equiv e^{\frac{i}{\hbar}L^0 t} L' e^{-\frac{i}{\hbar}L^0 t}$ and $\rho^I(t) \equiv e^{\frac{i}{\hbar}L^0 t}\rho(t)$.

Then we can write the effective density matrix $\rho(t)$ as a sum of two terms:

$$\rho(t) = e^{-\frac{i}{\hbar}L^0 t}(P + Q)\rho^I(t). \qquad (11)$$

The P- and Q-projected parts in Eq. (11) are solved by the standard method. Operating the projection operators on the kinetic equation, Eq.(10), we obtain the two coupled kinetic equations for the two parts of the density matrix:

$$\frac{d}{dt}P\rho^I(t) = -\frac{i}{\hbar}PL'(t)(P + Q)\rho^I(t) \qquad (12)$$

$$\frac{d}{dt}Q\rho^I(t) = -\frac{i}{\hbar}QL'(t)(P + Q)\rho^I(t) \qquad (13)$$

Noting the initial condition for the Q-projected part, $Q\rho^I(0) = Q\mu\rho^{eq} = 0$, we can easily solve Eq. (13) to obtain

$$Q\rho^I(t) = -\frac{i}{\hbar}\int_0^t G_+^Q(t,s)QL'(s)P\rho^I(s)ds \qquad (14)$$

where $G_+^Q(t,s) = \exp_+\left[-\frac{i}{\hbar}Q\int_s^t duL'(u)\right]$ is the forward propagator of the Q-projected part. $\exp_+[\cdot\cdot]$ is the time-ordered exponential operator. Noting that $\rho^I(s)$ in the right hand side (RHS) of Eq. (14) can be written as a product of the propagator, $G_+(s,t) \equiv \exp_+\left\{-\frac{i}{\hbar}\int_t^s duL'(u)\right\}$, and the density

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matrix at a local time t, $\rho^I(t)$, we can rewrite Eq. (14), a time-nonlocal equation, as a time-local equation,[13]

$$Q\rho^I(t) = -\Sigma(t)\rho^I(t) \tag{15}$$

where

$$\Sigma(t) \equiv \frac{i}{\hbar}\int_0^t G_+^Q(t,s)QL'(s)PG_+(s,t)ds . \tag{16}$$

Inserting $P+Q=1$ into the RHS of Eq. (15), we obtain the formal solution for $Q\rho^I(t)$,

$$Q\rho^I(t) = -\left(1+\Sigma(t)\right)^{-1}\Sigma(t)P\rho^I(t) \tag{17}$$

which is written in terms of the P-projected part. Adding the P- and Q-projected parts and using the operator identity, $\left(A+B\right)^{-1} = A^{-1} - \left(A+B\right)^{-1}BA^{-1}$, we can express the density matrix $\rho^I(t)$ in terms of the P-projected density matrix and the matrix $\Sigma(t)$:

$$\rho^I(t) = \left(1+\Sigma(t)\right)^{-1}P\rho^I(t) \tag{18}$$

and the original density matrix is given by

$$\rho(t) = e^{-\frac{i}{\hbar}L^0 t}\left(1+\Sigma(t)\right)^{-1}\sum_{n=1}^N |n\rangle\rho_{n0}\langle 0|\langle \rho^I(t)\rangle_{n0} . \tag{19}$$

Inserting Eq. (19) into Eq. (6), we obtain the linear response function

$$\phi(t) = \sum_{n=1}^N T_{n0}(t)\langle\rho^I(t)\rangle_{n0} \tag{20}$$

where

$$T_{n0}(t) = Tr\left(\mu e^{-\frac{i}{\hbar}L^0 t}\left(1+\Sigma(t)\right)^{-1}|n\rangle\rho_{n0}\langle 0|\right). \tag{21}$$

Expanding $T_{n0}(t)$ with respect to $\Sigma(t)$, we have

$$T_{n0}(t) = \sum_{i=0}^\infty T_{n0}^{(i)}(t) \tag{22}$$

where

$$T_{n0}^{(i)}(t) = Tr\left(\mu e^{-\frac{i}{\hbar}L^0 t}\left(-\Sigma(t)\right)^i|n\rangle\rho_{n0}\langle 0|\right). \tag{23}$$

Up to this point the formulation has been derived exactly.

Now we take the lowest order approximation with respect to L' in the matrix $\Sigma(t)$ and then the two propagators in the integrand of Eq. (16) become the identity matrix and $\Sigma(t)$ is approximated as

$$\Sigma(t) \approx \frac{i}{\hbar}\int_0^t ds QL'(s)P \tag{24}$$

That is the only approximation in the present formulation. The lowest order approximation should be valid only when the perturbation Hamiltonian (inter-chromophore couplings), Eq. (3), is small. Therefore the present theory may not be applicable for large coupling cases in which energy transfer occurs more rapidly than any other time scales of the system. Then all $T_{n0}^{(i)}(t)$ for $i \geq 2$ vanish due to the multiplication of the projection operators P and Q. In this case, the matrix $T_{n0}(t)$ in Eq. (20) is given simply by a sum of two terms:

$$T_{n0}(t) \approx T_{n0}^{(0)}(t) + T_{n0}^{(1)}(t) \tag{25}$$

where

$$T_{n0}^{(0)}(t) = \left\langle\mu_n(t)\Lambda_n^-(t)\mu_n\right\rangle_0 \equiv \Gamma_n^{(0)}(t) \tag{26}$$

$$T_{n0}^{(1)}(t) = -\sum_{m=1}^N\frac{i}{\hbar}\int_0^t ds\left\{\Gamma_{mn}^{(1)}(t,s) - \Gamma_m^{(0)}(t)\Theta_{mn}^{(1)}(s)\right\} \tag{27}$$

with $\Lambda_m^-(t) \equiv e^{\frac{i}{\hbar}h_0 t}e^{-\frac{i}{\hbar}h_m t} = e_+^{-i\int_0^t d\tau\omega_m(\tau)}$ and $\omega_m(t) \equiv e^{\frac{i}{\hbar}h_0 t}(h_m - h_0)e^{-\frac{i}{\hbar}h_0 t}$. The auxiliary functions in Eq. (27) are defined as

$$\Theta_{mn}^{(1)}(t) \equiv \left\langle\mu_m\tilde{h}_{mn}'(t)\mu_n\right\rangle_0/\left\langle\mu_m^2\right\rangle_0 \tag{28}$$

$$\Gamma_{mn}^{(1)}(t,s) \equiv \left\langle\mu_m(t)\Lambda_m^-(t)\tilde{h}_{mn}'(s)\mu_n\right\rangle_0 \tag{29}$$

where $\tilde{h}_{mn}'(t) \equiv \Lambda_m^+(t)h_{mn}'(t)\Lambda_n^-(t)$ with $\Lambda_m^+(t) \equiv e^{\frac{i}{\hbar}h_m t}e^{-\frac{i}{\hbar}h_0 t} = e_-^{i\int_0^t d\tau\omega_m(\tau)}$.

Another quantity in Eq. (20), the reduced density matrix $\langle\rho^I(t)\rangle_{n0}$, is obtained by numerically solving the following kinetic equation which is derived by inserting Eq. (18) into Eq. (12):

$$\frac{d}{dt}\langle\rho^I(t)\rangle_{n0} = -\sum_{m=1}^N\left[k_{nm}^S(t) + k_{nm}^D(t)\right]\langle\rho^I(t)\rangle_{m0} \tag{30}$$

where the elements of the rate matrices are, to the second order with respect to L', given as

$$k_{nm}^{S}(t) = \frac{i}{\hbar}\Theta_{nm}^{(1)}(t)$$

$$k_{nm}^{D}(t) = \frac{1}{\hbar^2}\sum_{k=1}^{N}\int_0^t ds\left\{\Theta_{nkm}^{(2)}(t,s) - \Theta_{nk}^{(1)}(t)\Theta_{km}^{(1)}(s)\right\} \tag{31}$$

where

$$\Theta_{ij}^{(1)}(t) \equiv \left\langle \mu_i \Lambda_i^+(t) h_{ij}'(t) \Lambda_j^-(t) \mu_j \right\rangle_0 \Big/ \left\langle \mu_i^2 \right\rangle_0 \tag{32}$$

$$\Theta_{ikj}^{(2)}(t,s) \equiv \left\langle \mu_i \tilde{h}_{ik}'(t) \tilde{h}_{kj}'(s) \mu_j \right\rangle_0 \Big/ \left\langle \mu_i^2 \right\rangle_0. \tag{33}$$

The initial condition for the reduced density matrix is given by

$$\left\langle \rho^I(0) \right\rangle_{m0} = \frac{Tr_q\left(\mu_m \rho_{m0}\right)}{Tr_q\left(\mu_m \rho_{m0}\right)} = 1 \tag{34}$$

Mixed QM/CM Calculation. In order to calculate the various time correlation functions introduced in the previous sections, we utilize the mixed quantum/classical mechanics (QM/CM) method recently developed for water by Skinner group.[14-16] In the QM/CM method, the hindered-translational and librational degrees of freedom (called the bath) of the water molecules are approximately described by classical mechanics with a molecular dynamics simulation using SPC/E water model[17] at 300 K. The three vibrational modes of a water molecule in the liquid phase are represented by the basis of two local OH stretching modes and an HOH bending mode. Since the characteristic frequencies of those vibrational modes are much higher than thermal energy at room temperature, a quantum-mechanical description is required for them. The vibration energy, intra-molecular coupling and transition dipole of an OH bond calculated by quantum chemical method is mapped to the electric field exerted on the bond. Then by calculating the electric field in the classical molecular dynamics simulation, we can calculate the fluctuation dynamics needed in the above reduced density matrix approach. The approximations invoked in the approach and the details of the method can be referred to ref.[16]

Results and Discussion

In this paper we apply the formulation developed above to the absorption spectrum of the OH vibration in neat water. The OH vibration of a water molecule is coupled to other OH vibrations *via* intra- and/or inter-molecular couplings. The aim of the present section is not to calculate realistic absorption spectrum of water in quantitative way but to examine the validity of the present formulation by comparing the spectral prediction of the present theory with that of exact calculation and also with that of an existing approximate theory. Therefore, in order to reduce computation time, we turn the inter-molecular couplings off in our illustrative calculations.

First, we run NVE molecular dynamics simulation (MD) as described above with 128 SPC/E water molecules at the experimental density at 300 K. Periodic boundary conditions were
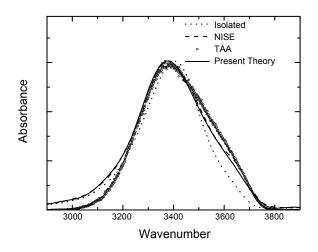

Figure 1. Comparison of theoretical absorption line shapes. For comparison we also put the theoretical line shape of uncoupled OH vibrations (denoted as "Isolated"). Each spectrum is normalized by its maximum value. The line shape predicted by TAA (solid circles) represents a distribution of time-averaged transition energies.

employed and the electrostatic forces were computed using an approximation to the Ewald sum. The time step for MD was 1 fs. After an equilibration period, we generate a trajectory of the molecular coordinates at every 10 fs for a time period of 200 ps which represents a series of bath conformations. One thousand starting points were selected at every 200 fs as different initial configurations of baths. For each selected configuration, we calculate the 1-ps trajectory of electric field exerted on every OH bond which is created by the presence of the partial charges of other water molecules. Then using the mapping relations developed by Skinner group,[14-16] the 1-ps trajectories of molecular properties required in various levels of theory are calculated.

The response function for the absorption spectrum can actually be calculated in a way numerically exact within the mixed QM/CM framework by numerical integration of time-dependent Schrödinger equation (NISE) for the density matrix, Eq. (9). The molecular Hamiltonian for the Schrödinger equation is time-dependent due to the coupling to fluctuating bath and is calculated using the mixed QM/CM method as described above. For the technical details of NISE, you can refer to ref.[16] Even though NISE approach is feasible for reasonably large systems, it is still desired to develop an approximate theory to calculate absorption spectrum in a large size of molecular assembly. The theoretical framework developed in the present paper is one candidate for them.

Another useful approximate theory is so called time-average approximation (TAA) recently developed by Auer and Skinner.[18] In that approach, fluctuating transition energies of chromophores are approximated as their average values taken over a short time period which was determined by analyzing Kubo model to be 76 fs for water. Then, the molecular Hamiltonian is assumed to be static as the time-averaged one and the static Hamiltonian is numerically diagonalized to give a distribution of eigen energies of the static molecular system. This approach was able to save computation time from the exact calculation.

Figure 1 compares the predictions of the theories for the

OH vibrational transition in a model water system in which the inter-molecular couplings are turned off but the intra-molecular couplings remains on. The line shape predicted by the present theory is calculated by Eq. (4) along with Eqs. (20), (25), and (30). The complex kinetic equations for the present theory, Eq. (30), and the time-dependent Schrödinger equation for NISE are numerically solved by using the IMSL differential equation solver, IVMRK, which uses Runge-Kutta pairs of various orders. For TAA, the same set of initial bath configurations as employed in NISE and in the present theory was selected and for every initial configuration, the time-averages of transition energies were taken over the time period of 76 fs as dictated in ref.[18] from the trajectory starting from the initial configuration. More specifically, from a trajectory of molecular dynamics simulation, one prepares an ensemble of molecular configurations and constructs, for each element of the ensemble, its static molecular Hamiltonian by the time-average. Then one obtains an ensemble of eigen energies whose distribution corresponds to the line shape of TAA.

We first note that the exact line shape is broadened on both red and blue sides of spectrum as a result of intra-molecular couplings. Two approximate theories, TAA and the present theory, also predict broader spectra. All the three theories, NISE, TAA, and the present theory, succeed in predicting the red-shift (25 cm^{-1}) of spectrum caused by the intra-molecular couplings.

The present theory is almost completely in agreement with the exact calculation (NISE) except for the amplitude on the blue side shoulder around at 3650 cm^{-1}. Compared with NISE, the present theory predicts a little less amplitude on the blue side. Other than that, the present theory is excellent in reproducing the exact theoretical spectrum calculated by NISE. In particular, the complete agreement on the red side of spectrum between the present theory and NISE is very promising. In comparison, TAA fails in quantitative prediction of the red-side spectrum and also the spectral structure of TAA is not satisfactory on the blue side. In overall, the present theory works much better than the other approximate theory, TAA. This result illustrates the usefulness of the present theory in the theoretical calculation of absorption spectra for the systems with a large number of coupled chromophores which the exact calculation is not available for.

Summary

We developed a reduced density matrix theory for linear absorption spectrum using the projection operator technique. We suggest a new form of projection operator relevant to the systems with non-Condon effects in light-matter interaction. The time-correlation functions in the response function and in the kinetic parameters for the reduced density matrix were obtained to be well suitable for the systems with non-Condon effects. The present theory has been applied in the calculation of vibrational absorption spectrum of a model system of water molecules in which the OH bonds are coupled only *via* intra-molecular couplings. From the model calculations, we showed that the present theory works excellently in reproducing the exact absorption line shape. Also the present theory was compared with an existing approximate theory, TAA, and we found that the performance of theory is better in the present reduced density matrix approach. The present formulation can be easily extended to larger systems for which the exact calculation is not accessible.

References

1. Saven, J. G.; Skinner, J. L. *J. Chem. Phys.* **1993**, *99*, 4391.
2. Stephens, M. D.; Saven, J. G.; Skinner, J. L. *J. Chem. Phys.* **1997**, *106*, 2129.
3. Geva, E.; Skinner, J. L. *J. Phys. Chem. B* **1997**, *101*, 8920.
4. Burt, J. A.; Zhao, X.; McHale, J. L. *J. Chem. Phys.* **2004**, *120*, 4344.
5. Bhattacharyya, D.; Dutta, B. K.; Ray, B.; Ghosh, P. N. *Chem. Phys. Lett.* **2004**, *389*, 113.
6. Yang, M. *J. Chem. Phys.* **2005**, *123*, 124705.
7. Yang, M. *J. Mol. Spectrosc.* **2006**, *239*, 108.
8. Mori, H. *Prog. Theor. Phys.* **1965**, *33*, 423.
9. Zwanzig, R. *Phys. Rev.* **1961**, 124.
10. Schmidt, J. R.; Corcelli, S. A.; Skinner, J. L. *J. Chem. Phys.* **2005**, *123*, 044513.
11. Grigolini, P. *J. Mol. Struct.* **1991**, *250*, 119.
12. Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York.
13. Shibata, F.; Takahashi, Y.; Hashitsume, N. *J. Stat. Phys.* **1977**, *17*, 171.
14. Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2004**, *120*, 8107.
15. Auer, B.; Kumar, R.; Schmidt, J. R.; Skinner, J. L. *P. Natl. Acad. Sci. USA* **2007**, *104*, 14215.
16. Yang, M.; Skinner, J. L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 982.
17. Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.
18. Auer, B. M.; Skinner, J. L. *J. Chem. Phys.* **2007**, *127*, 104105.