Fundamental absorption frequencies and mean structures at vibrational ground state from quasi-classical direct ab initio MD: Triatomic molecule

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Abstract

The fundamental frequencies and the mean values of the internal coordinates are extracted from the trajectories of classical dynamics based on the relation between the classical and the quantum mechanical frequencies using quasi-classical direct ab initio molecular dynamics, where the oscillator amplitude is specified by setting the total energy equal to the harmonic vibrational energy. This method is applied to a triatomic molecule H_2O. The harmonic frequencies, the fundamental absorption frequencies, and the mean structures are obtained in good agreement with experimentally observed values with the theoretical level of MP2 using the aug-cc-pVTZ basis set.

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1. Introduction

There are various methods to analyze vibrations of molecules based on ab initio molecular orbital theory. One of them is a normal vibrational analysis, which approximates a molecule as a combination of harmonic oscillators. It conveniently gives harmonic frequencies with low cost. Recent progresses in the implementations of ab initio MO theory and in computer power also enabled various vibrational analyses considering anharmonicity [1-4].

It is well appreciated that molecular dynamics (MD) is a useful and powerful technique [5] to evaluate changes in molecular structures or properties along time evolution. Using classical MD, vibrational analyses of molecules are also done widely. Although this method may take account of anharmonicity, the following two points should be taken into consideration.

First, the correspondence between classical and quantum mechanical frequencies should be considered [6]. Although microscopic phenomena such as absorption of electromagnetic ray are ruled by quantum mechanics, MD treats molecules based on classical mechanics. Secondly, the potential energy surface (PES) on which dynamics run should be accurate. In general, the accuracy of the PES depends on the model functions which should have been constructed in advance and are used to perform molecular dynamics simulation. It is difficult, however, to construct an appropriate potential energy function enough to calculate dynamics properly from which vibrational properties involving anharmonicity can be extracted.

To consider these two points, we use quasi-classical direct ab initio MD. Aida et al. showed that the fundamental frequency of D_2 can be obtained fairly accurately using quasi-classical direct ab initio MD with full-SDCI/aug-cc-pVTZ level of theory [7]. In this letter, we present that the method can be also applied to triatomic molecules including couplings between vibrational modes. This is the basis for future studies of more extension of this analysis to larger molecules or clusters.

In addition to the fundamental frequencies, we show that the ‘mean molecular structures’ can be derived from quasi-classical direct ab initio MD. There are various kinds of 'mean molecular structures according to the definitions [8,9]. It is well-known that there are intrinsic and sizable differences between the equilibrium structure and the experimentally derived structures [10]. We obtain the mean values of the internal coordinates at the vibrational ground state from quasi-classical direct ab initio MD according to the definitions. These theoretical mean structures are found to be in good agreement with those respective experimental structures.

2. Fundamental frequencies

2-1. *Frequency of classical oscillator*

When an oscillator's vibrational amplitude is small, each vibrational mode of the classical oscillator is approximately independent. In such a case, the classical mechanical frequency of mode *i* ($\nu_i^{\text{classical}}$) is represented as follows [11]:

$$\nu_i^{\text{classical}} = \frac{\partial E}{\partial J_i} \tag{1}$$

Here, E is the total energy of the system, and J_i is the action variable of mode *i* defined by

$$J_i = \oint p_i dq_i \tag{2}$$

2-2. *Frequency of quantum oscillator*

For a quantum oscillator, the vibrational frequency is expressed as the separation of the relevant energy levels. Here, we describe two vibrational energy levels as two vectors,

$$\mathbf{n}' = (n'_1, n'_2, ..., n'_i, ...n'_{\mathrm{N}}) \tag{3}$$

and

$$\mathbf{n}'' = (n''_1, n''_2, ..., n''_i, ...n''_{\mathrm{N}}), \tag{4}$$

where n'_j and n''_j (j=1,2,…,N) are vibrational quantum numbers and N is the degree of the freedom. The frequency of a quantum oscillator with the transition from $\mathbf{n}'$ to $\mathbf{n}''$ is expressed as follows:

$$\nu_{\mathbf{n}'\to\mathbf{n}''}^{\text{quantum}} = \frac{1}{h}(E_{\mathbf{n}''}^{\text{quantum}} - E_{\mathbf{n}'}^{\text{quantum}}) \tag{5}$$

According to the quantum mechanics, the action variable of a quantum oscillator is represented by

$$J_i = h(n_i + \frac{1}{2}) \tag{6}$$

2-3. *Relationship between frequencies of classical and quantum oscillator* [12]

For quasi-classical treatment [7] of molecules, in which they are treated classically but with consideration of quantum mechanical elements, the relationship between the frequencies of a classical and a quantum oscillators should be elucidated. For this purpose, Eq. (5) is transformed using Eqs. (1) and (6) as follows.

$$\begin{aligned}\nu_{\mathbf{n}'\to\mathbf{n}''}^{\text{quantum}} &= \frac{1}{h}(E_{\mathbf{n}''}^{\text{quantum}} - E_{\mathbf{n}'}^{\text{quantum}}) \cong \frac{1}{h}\sum_{j=1}^{N}\left(\frac{\partial E^{\text{quantum}}}{\partial n_j}\right)_{(\mathbf{n}'+\mathbf{n}'')/2}(n_j'' - n_j') \\ &= \frac{1}{h}\times h\sum_{j=1}^{N}\left(\frac{\partial E^{\text{quantum}}}{\partial J_j}\right)_{(\mathbf{n}'+\mathbf{n}'')/2}(n_j'' - n_j') \\ &= \sum_{j=1}^{N}\nu_j^{\text{classical}}(n_j'' - n_j')\end{aligned} \tag{7}$$

Note that the partial derivative is performed at the mean state,

$$\frac{\mathbf{n}' + \mathbf{n}''}{2} = (\frac{n_1' + n_1''}{2}, \frac{n_2' + n_2''}{2}, \ldots, \frac{n_i' + n_i''}{2}, \ldots, \frac{n_{\mathrm{N}}' + n_{\mathrm{N}}''}{2}) \quad , \tag{8}$$

which corresponds to the 'energy level' of the classical oscillator, of which the vibrational frequency is $\nu_j^{\text{classical}}$ (j=1,…,N). $E_{\mathbf{m}}^{\text{quantum}}$ corresponds to the energy of one vibrational state **m** which consists of a combination of quantum oscillators including coupling between the oscillators. Thus, the expression of a quantum mechanical frequency is obtained in terms of the motions of the classical oscillators.

2-4. *Quasi-classical treatment of triatomic molecules*

Based on the general relationship between classical and quantum mechanical frequencies derived above, here we show the procedure how to get the fundamental frequencies of a non-linear triatomic molecule H_2O.

The lower vibrational energy levels of a triatomic molecule are expressed by

$$\mathbf{0} = (0,0,0)\,, \tag{9-a}$$

$$\mathbf{1}_1 = (1,0,0)\,, \tag{9-b}$$

$$\mathbf{1}_2 = (0,1,0)\,, \tag{9-c}$$

and

$$\mathbf{1}_3 = (0,0,1)\,, \tag{9-d}$$

where the elements of vectors are vibrational quantum numbers of vibrational modes 1, 2, and 3, which correspond to symmetric stretching, bending, and antisymmetric stretching, respectively. For example, if they are represented in terms of the harmonic frequency ω_i within the framework of harmonic approximation, the element 0, means the zero point harmonic vibrational energy $\omega_i/2$, and 1 means the first excited energy $3\omega_i/2$, since the harmonic energy is represented by $E_{harm} = \sum_i \omega_i(n_i + 1/2)$. According to Eq. (7), fundamental frequencies of the modes 1, 2 and 3 are expressed in terms of the frequencies of the classical oscillators in the following way:

$$\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_1} \cong \nu^{\text{classical}}_1 \quad , \tag{10-a}$$

$$\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_2} \cong \nu^{\text{classical}}_2 \quad , \tag{10-b}$$

and

$$\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_3} \cong \nu^{\text{classical}}_3 \quad , \tag{10-c}$$

when the energy levels of the classical oscillators are,

$$\frac{\mathbf{0}+\mathbf{1}_1}{2}=(\frac{1}{2},0,0)\,, \tag{11-a}$$

$$\frac{\mathbf{0}+\mathbf{1}_2}{2}=(0,\frac{1}{2},0)\,, \tag{11-b}$$

and

$$\frac{\mathbf{0}+\mathbf{1}_3}{2}=(0,0,\frac{1}{2})\,, \tag{11-c}$$

respectively, according to Eq. (8). Thus, the fundamental frequencies of the mode 1 ($\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_1}$), the mode 2 ($\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_2}$), and the mode 3 ($\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_3}$) are obtained from the motions of classical oscillators, in which the energy levels are set to those in Eqs (11-a), (11-b), and (11-c), respectively.

3. Mean structures

Various 'mean structures' have been proposed [8,9]. In this letter we show structural parameters of three types of structures R_0, R_z, and R_g from quasi-classical direct ab initio MD by setting the vibrational ground state. We present in this section the formalization of the parameters for the O-H distance and the H-O-H angle corresponding to these structures R_0, R_z, R_g in terms of the Cartesian coordinates.

We use the bracket $\langle\ \rangle$ to indicate the expectation or mean value over the ground vibrational eigenstate. In the framework of MD, $\langle\ \rangle$ means the average over the trajectory which mimics the vibrational ground state. We refer to this trajectory as 'ground state trajectory' described in subsection 4-2.

3-1. *Effective structure R_0*

An effective structure R_0 corresponds to the one which is obtained from the rotational constants in the vibrational ground state from measurements of microwave or IR spectroscopy.

Theoretically, the effective structure is defined as follows. The structure of a water molecule is set on the *x*-*z* plane in the Cartesian coordinate system, the origin of which is the center of the mass and the principal axis is z-axis. When the structure of a water molecule is R_0 with the C_{2V} symmetry, the tensor of inertia is automatically diagonalized; thus,

$$I_0 = \begin{pmatrix} \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha({y_{0\alpha}}^2 + {z_{0\alpha}}^2) & -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha x_{0\alpha} y_{0\alpha} & -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha x_{0\alpha} z_{0\alpha} \\ -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha y_{0\alpha} x_{0\alpha} & \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha({z_{0\alpha}}^2 + {x_{0\alpha}}^2) & -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha y_{0\alpha} z_{0\alpha} \\ -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha z_{0\alpha} x_{0\alpha} & -\sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha z_{0\alpha} y_{0\alpha} & \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha({x_{0\alpha}}^2 + {y_{0\alpha}}^2) \end{pmatrix}$$
$$= \begin{pmatrix} \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha {z_{0\alpha}}^2 & 0 & 0 \\ 0 & \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha({z_{0\alpha}}^2 + {x_{0\alpha}}^2) & 0 \\ 0 & 0 & \sum\limits_{\alpha=\mathrm{H,H',O}} m_\alpha {x_{0\alpha}}^2 \end{pmatrix} \quad (12)$$

The diagonal terms,

$$I_0^a = \sum_\alpha m_\alpha {z_{0\alpha}}^2 , \quad (13\text{-a})$$

$$I_0^b = \sum_\alpha m_\alpha {x_{0\alpha}}^2 , \quad (13\text{-b})$$

and $$I_0^c = \sum_\alpha m_\alpha ({x_{0\alpha}}^2 + {z_{0\alpha}}^2) , \quad (13\text{-c})$$

are related to the rotational constants of the vibrational ground state in the following way.

$$A_0 = (h/8\pi^2)(1/I_0^a) , \quad (14\text{-a})$$

$$B_0 = (h/8\pi^2)(1/I_0^b) , \quad (14\text{-b})$$

$$C_0 = (h/8\pi^2)(1/I_0^c) \quad . \quad (14\text{-c})$$

Based on the structural parameters for each time step of quasi-classical direct ab initio MD at the vibrational ground state, we can obtain the inertia moments for each time step. The rotational constants are equal to the corresponding mean values over the trajectory; namely,

$$A_0 = \langle A \rangle = (h/8\pi^2)\langle 1/I^a \rangle , \tag{15-a}$$

$$B_0 = \langle B \rangle = (h/8\pi^2)\langle 1/I^b \rangle , \tag{15-b}$$

$$C_0 = \langle C \rangle = (h/8\pi^2)\langle 1/I^c \rangle \quad . \tag{15-c}$$

As shown in Eq. (13), to obtain the elements of the R_0 structure, $x_{0\alpha}$, $y_{0\alpha}$, and $z_{0\alpha}$ (α = H, H', O), the inertia moments of vibrational ground state, I_0^a, I_0^b and I_0^c are required. Thus, from Eqs. (14) and (15) one way to obtain R_0 from MD is reduced to calculating the average of reciprocals of inertia moments over the 'ground state trajectory', namely, $\langle 1/I^a \rangle$, $\langle 1/I^b \rangle$, and $\langle 1/I^c \rangle$. If $x_{0\alpha}$, $y_{0\alpha}$, and $z_{0\alpha}$ are obtained, the structural parameters of r_0 and θ_0, the distance of O-H bond and the angle of H-O-H, can be obtained as follows:

$$r_0 = |\mathbf{OH}_0| = \sqrt{(x_{0\mathrm{O}} - x_{0\mathrm{H}})^2 + (y_{0\mathrm{O}} - y_{0\mathrm{H}})^2 + (z_{0\mathrm{O}} - z_{0\mathrm{H}})^2} \tag{16}$$

$$\begin{aligned}\theta_0 &= \arccos \frac{\mathbf{OH}_0 \cdot \mathbf{OH}'_0}{|\mathbf{OH}_0||\mathbf{OH}'_0|} \\ &= \arccos \frac{((x_{0\mathrm{O}} - x_{0\mathrm{H}}) \cdot (x_{0\mathrm{O}} - x_{0\mathrm{H}'}) + (y_{0\mathrm{O}} - y_{0\mathrm{H}}) \cdot (y_{0\mathrm{O}} - y_{0\mathrm{H}'}) + (z_{0\mathrm{O}} - z_{0\mathrm{H}}) \cdot (z_{0\mathrm{O}} - z_{0\mathrm{H}'}))}{\sqrt{(x_{0\mathrm{O}} - x_{0\mathrm{H}}) + (y_{0\mathrm{O}} - y_{0\mathrm{H}}) + (z_{0\mathrm{O}} - z_{0\mathrm{H}})}\sqrt{(x_{0\mathrm{O}} - x_{0\mathrm{H'}}) + (y_{0\mathrm{O}} - y_{0\mathrm{H'}}) + (z_{0\mathrm{O}} - z_{0\mathrm{H'}})}}\end{aligned} \tag{17}$$

Here, one of the two hydrogen atoms is denoted as H and the other as H'.

3-2. *Zero point mean structure R_z*

R_z is the zero point mean structure. Thus, this value is more physically clear than R_0. The parameter r_z is obtained as the magnitude of the mean value of the vector **OH**; namely,

$$r_z = |\langle \mathbf{OH} \rangle| \quad . \tag{18}$$

Here, the vector **OH** is defined as

$$\mathbf{OH} = \begin{pmatrix} x_{\mathrm{H}} - x_{\mathrm{O}} \\ y_{\mathrm{H}} - y_{\mathrm{O}} \\ z_{\mathrm{H}} - z_{\mathrm{O}} \end{pmatrix} \tag{19}$$

Thus,

$$\langle \mathbf{OH} \rangle = \begin{pmatrix} \langle x_{\mathrm{H}} - x_{\mathrm{O}} \rangle \\ \langle y_{\mathrm{H}} - y_{\mathrm{O}} \rangle \\ \langle z_{\mathrm{H}} - z_{\mathrm{O}} \rangle \end{pmatrix} = \begin{pmatrix} \langle x_{\mathrm{H}} \rangle - \langle x_{\mathrm{O}} \rangle \\ \langle y_{\mathrm{H}} \rangle - \langle y_{\mathrm{O}} \rangle \\ \langle z_{\mathrm{H}} \rangle - \langle z_{\mathrm{O}} \rangle \end{pmatrix} \quad . \tag{20}$$

The parameter θ_z is obtained as the angle between two OH bonds; namely,

$$\theta_z = \arccos \frac{\langle \mathbf{OH} \rangle \cdot \langle \mathbf{OH'} \rangle}{\left| \langle \mathbf{OH} \rangle \right| \left| \langle \mathbf{OH'} \rangle \right|} \tag{21}$$

Therefore, using the mean values of atomic coordinates, $\langle x_\alpha \rangle$, $\langle y_\alpha \rangle$, $\langle z_\alpha \rangle$, over the ‘ground state trajectory’, r_z and θ_z can be obtained.

3-3. *R_g Structure*

The R_g structure is the center of gravity of the probability distribution function, and is derived by electron diffraction experiments. Theoretically, the mean value of OH distance, r_g, corresponds to the R_g structure [13]; namely,

$$r_g = \left\langle \sqrt{(x_{\mathrm{H}} - x_{\mathrm{O}})^2 + (y_{\mathrm{H}} - y_{\mathrm{O}})^2 + (z_{\mathrm{H}} - z_{\mathrm{O}})^2} \right\rangle \tag{22}$$

Therefore, to calculate r_g from MD, we need to calculate the distances at each step of the ‘ground state trajectory’ and average it over the trajectory.

4. Computational details

4-1. *Fundamental frequencies*

The theory described in Section 2 is applied to H_2O, a non-linear triatomic molecule. The procedure is as follows.

1. The molecular structure is optimized by means of ab initio MO.
2. The normal vibrational analysis is done at the optimized structure, and the harmonic frequencies ω_1, ω_2, and ω_3 are obtained.
3. Three trajectories (Case-1, Case-2 and Case-3) of direct ab initio MD are run. The initial geometry for each of the trajectories is the optimized geometry and the initial velocity is as follows: the direction is along the normal mode, and the magnitude is as much as the molecule can oscillate with the energy levels of Eq. (11). Using harmonic frequencies which are obtained in Step 2, the energy levels of Case-1, Case-2 and Case- 3 are $[3\omega_1/2, \omega_2/2, \omega_3/2]$, $[\omega_1/2, 3\omega_2/2, \omega_3/2]$, and $[\omega_1/2, \omega_2/2, 3\omega_3/2]$, respectively. Here, the square brackets specify that the levels are expressed not in terms of quantum numbers as in Eq. (3) or Eq. (4) but the harmonic frequencies.
4. Fourier transformation of the velocity auto-correlation function of Case-1 gives the fundamental frequency $\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_1}$; that of Case-2 gives $\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_2}$ and that of Case-3 gives $\nu^{\text{quantum}}_{\mathbf{0}\to\mathbf{1}_3}$.

Concerning the quasi-classical MD, we use the method of direct ab initio MD, in which the trajectories are calculated by integrating Newton's equations of motion with the energies and forces obtained directly from ab initio MO calculations at each time step. The classical nuclear trajectories are integrated with constant total energy using a fourth-order Gear predictor-corrector algorithm [14], and the time step of 0.1 fs is used to ensure the numerical accuracy. The total number of the steps is 8000 for each simulation. The level of the theory used is MP2/aug-cc-pVTZ and the program used is HONDO2004 [15].

The Fourier transformation method we use is the Fast Fourier Transformation (FFT) [16]. The spectral resolution is estimated to be 1.27 cm^{-1}.

4-2. *Mean structures*

In section 3 we referred to the trajectory which mimics the vibrational ground state as 'ground state trajectory.' In order to simulate the vibrational ground state, we run the Case-4 trajectory of quasi-classical direct ab initio MD for 'ground state trajectory' in the following way. The initial geometry is the optimized geometry same as the above cases but the initial velocities of each vibrational mode are as much magnitudes as the zero point vibrational energies [$\omega_1/2$, $\omega_2/2$, $\omega_3/2$] for respective modes, so that this trajectory mimics the quantum mechanical zero point vibrational eigenstate. The time step is 0.1 fs and the total number of steps is 30000. The R_0 structure is obtained by calculating $1/I^a$, $1/I^b$, and $1/I^c$ at each time step and averaging them, the R_z structure by averaging atomic coordinates, and the R_g structure by averaging distance $|\mathbf{OH}|$ over the total MD steps (that is 3 ps) of Case-4.

5. Results and discussion

5-1. *Fundamental frequencies*

Calculated fundamental frequencies from quasi-classical direct ab initio MD are summarized in Table 1 together with experimentally obtained fundamental frequencies. The calculated harmonic frequencies based on the normal mode analysis at the optimized geometry with the same level of theory are shown in Table 2. On calculating the fundamental frequency of vibrational mode *i* from quasi-classical direct ab initio MD, the state of the oscillator of the mode *i* is equal to n_i=1/2, and those of the other modes j ($\neq i$) are equal to n_j=0.

For comparison, the results of the other methods to calculate fundamental frequencies are shown in table 1. One is the second order perturbation theory implemented in the program package Gaussian 03 [21], which calculates anharmonic constants and fundamental frequencies from second, third, and quartic potential derivatives with respect to normal coordinates [1]. The other is direct VCI (Virtual Configuration Interaction). The results were taken from Ref. [4], in which the eigenvalues of anharmonic vibrational eigenstates were calculated self-consistently based on variational principle including the couplings of vibrational modes using global PES with MP2/aug-cc-pVTZ.

As shown in Tables 1 and 2, both of the fundamental and the harmonic frequencies at the level of MP2/aug-cc-pVTZ are satisfactory and consistently agree well with the experimental values, for all of these three methods, i.e., our method, the second order perturbation theory and direct VCI. It is expected that when the level of theory is higher, the degree of the agreement would become better, taking account of the fact that the harmonic frequencies at the level of CCSD(T)/aug-cc-pVQZ agree quite well with the estimated values based on the CVRQD PESs [19] and also with the experimental values (see Table 2). Since all of the three methods provide almost the same values, we can regard all of those methods are in similar quality in the case of H_2O. Our method does not require the PES of the system in advance, nor higher order derivatives. Therefore, it is possible to apply our method to any system, especially to a larger molecular system. Furthermore, our method can apply to get any frequencies other than fundamental frequencies.

5-2. *Mean structures*

Computational and experimental structural parameters are shown in Table 3. The equilibrium internal O-H distance r_e and H-O-H angle θ_e are obtained by means of the optimization procedure based on ab initio MO (MP2/aug-cc-pVTZ). The order of the size $r_e < r_g < r_z$ and the differences $r_g - r_e$ and $r_z - r_g$ are consistent with those obtained experimentally except for r_0. Although in general r_0 is considered to be greater than r_e, in the case of H_2O the experimentally obtained r_0 was reported to be smaller than r_e. Our method gives the value for r_0 greater than $\mathrm{r_e}$, which is consistent with most molecules. As shown in Table 3, the level of

CCSD(T)/aug-cc-pVQZ gives closer values of the equilibrium geometrical parameters to the best computational estimate in the literature based on the CVRQD PESs [19]. The equilibrium geometry as well as the mean geometries at the level of MP2/aug-cc-pVTZ are satisfactory and consistently agree well with the experimental geometries. To the best of our knowledge, this is the first *ab initio* evaluation of the mean structures, r_g, r_z and r_0, of H_2O without any force field parameters.

5. Conclusion

The fundamental frequencies of a non-linear triatomic molecule H_2O are obtained from quasi-classical direct ab initio MD by describing quantum mechanical eigenstates in terms of classical trajectories. In this way, quantum mechanical frequencies are obtained from classical trajectories with high numerical accuracy. It is important to control the energy levels of the classical oscillators, i.e., molecules with multiple vibrational degrees, to obtain the quantum mechanical frequencies from the trajectories. This study lays a foundation for the extension of vibrational analysis using quasi-classical direct ab initio MD to larger molecules or clusters.

By controlling the energy levels to be equal to the zero point vibrational state, the mean structures are obtained reasonably consistent with experimentally obtained values.

As a further application of the method described here, it is possible to obtain transition energy between any states and a mean structure of a specific excited state by controlling the energy levels properly.

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Table 1. Calculated and experimental fundamental frequencies (in cm^{-1}) of H_2O

	Q-C MD [a)]	Direct VCI [b)]	second-order [c)]	expt [d)]
ν_1	3640	3647	3646	3657.050
ν_2	1578	1576	1578	1594.74635
ν_3	3751	3760	3758	3755.929

a) Quasi-classical direct ab initio MD with MP2/aug-cc-pVTZ.

b) Direct Virtual Configuration Interaction with MP2/aug-cc-pVTZ taken from [4].

c) Second-order perturbation method with MP2/aug-cc-pVTZ.

d) Experimental values. ν_1 and ν_3 are taken from [17] and ν_2 from [18].

Table 2. Calculated and experimental harmonic frequencies (in cm^{-1}) of H_2O.

	MP2/ aug-cc-pVTZ [a]	CCSD(T)/ aug-cc-pVQZ [a]	CVRQD [b]	expt [c]
ω_1	3800	3834	3833.0	3832.17
ω_2	1626	1649	1648.8	1648.47
ω_3	3923	3944	3944.1	3942.53

a) Normal mode analysis by means of ab initio MO method.

b) Computational values taken from [19].

c) Experimental values taken from [20].

Table 3. Various mean structures [a)] of H_2O

	MP2/ aug-cc-pVTZ [b)]	CCSD(T)/ aug-cc-pVQZ [c)]	CVRQD [d)]	expt [e)]
r_e	0.9596	0.9588	0.95782	0.9572
θ_e	104.21	104.35	104.485	104.34
r_z	0.973			0.9714
θ_z	104.15			
r_g	0.976			0.974
r_0	0.962			0.956
θ_0	104.74			105.11

[a)] r_e and θ_e are the O-H length and H-O-H angle, respectively, at the equilibrium structure. r_z, r_g, r_0 and θ_z, θ_0 are the mean structures corresponding to the O-H length and H-O-H angle, respectively. See text for the definition. Lengths are in Ångstrom and angles are in degrees.

[b)] r_e and θ_e are the optimized geometrical parameters with MP2/aug-cc-pVTZ, and the other values are obtained from quasi-classical direct ab initio MD with MP2/aug-cc-pVTZ.

[c)] Optimized geometrical parameters with CCSD(T)/aug-cc-pVQZ.

[d)] Optimized geometrical parameters with CVRQD taken from [19].

[e)] Experimental values taken from [6, 20, 22].