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Supplementary Information for:

Fundamental frequency from classical molecular dynamics

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I. Classical normal form theory[37]

[37] T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.*, 2002, **123**, 79–152.

Here we describe the essence of the review[37] by Komatsuzaki and Berry about the classical NFT that is necessary for the explanation of the analysis and calculations of our present paper. The theory described here is also called as Lie canonical perturbation theory (LCPT). LCPT is a convenient method to perform canonical transformation by perturbative calculation and obtain the Hamiltonian in normal form and the corresponding dynamical variables. Here we give a brief description of LCPT.

By means of LCPT, one can transform the original Hamiltonian, H, and dynamical variables, $\mathbf{J}$, $\mathbf{\Theta}$, $\mathbf{p}$, and $\mathbf{q}$, into new ones, $\overline{H}$, $\overline{\mathbf{J}}$, $\overline{\mathbf{\Theta}}$, $\overline{\mathbf{p}}$, and $\overline{\mathbf{q}}$, respectively. Moreover, if the generating function W used for LCPT is properly chosen, we can obtain the new Hamiltonian in normal form, namely;

$$H(\mathbf{J},\mathbf{\Theta}) \overset{W}{\rightarrow} \overline{H}(\overline{\mathbf{J}}) = \sum_{i=0}^{\infty} \varepsilon^i \overline{H}_i(\overline{\mathbf{J}}) \ . \qquad \text{(B1)}$$

Here, the Hamiltonian in normal form means that it is represented only by $\overline{\mathbf{J}}$.

I-1. Definitions and assumptions

For a parameter ε, Lie transformation, $\hat{T}$, is defined as follows:

$$\hat{T}\mathbf{z} \equiv \exp\left[-\varepsilon \hat{L}_W\right]\mathbf{z} \ , \qquad \text{(B2)}$$

where **z** represents a vector whose components are the dynamical variables **p** and **q** and $\hat{L}_W$ is defined as

$$\hat{L}_W \mathbf{z} \equiv \{W, \mathbf{z}\}, \tag{B3}$$

where W is a polynomial of **p** and **q** and { } is the Poisson bracket defined by

$$\{W, \mathbf{z}\} \equiv \sum_{i=1}^{N} \left(\frac{\partial W}{\partial q_i}\frac{\partial \mathbf{z}}{\partial p_i} - \frac{\partial \mathbf{z}}{\partial q_i}\frac{\partial W}{\partial p_i}\right) . \tag{B4}$$

The inverse transformation is defined as follows.

$$\hat{T}^{-1}\mathbf{z} \equiv \exp\left[\varepsilon \hat{L}_W\right]\mathbf{z} \tag{B5}$$

It is proven that the Lie transformation and the inverse transformation, Eqs. (B2) and (B5), are canonical transformation if **p** and **q** are canonical. If the right hand sides of Eqs. (B2) and (B5) are expressed as the Taylor expansions with respect to ε, $\hat{T}$ and $\hat{T}^{-1}$ are represented by

$$\hat{T} = \sum_{i=0}^{\infty} \frac{(-\hat{L}_W)^i}{i!}\varepsilon^i \quad , \tag{B6}$$

and

$$\hat{T}^{-1} = \sum_{i=0}^{\infty} \frac{(\hat{L}_W)^i}{i!}\varepsilon^i \quad . \tag{B7}$$

On the basis of Eq. (B6), Eq. (B8) can be proven. See ref 37.

$$\hat{T} f(\mathbf{z}) = f(\bar{\mathbf{z}}) \quad , \tag{B8}$$

where

$$\bar{\mathbf{z}} \equiv \hat{T}\mathbf{z} \ . \qquad \text{(B9)}$$

If we define a function $\bar{f}$ as

$$\bar{f}(\mathbf{z}) \equiv \hat{T}f(\mathbf{z}) \ , \qquad \text{(B10)}$$

operating $\hat{T}^{-1}$ on both sides of Eq. (B10) leads to

$$f(\mathbf{z}) = \hat{T}^{-1}\bar{f}(\mathbf{z}) \ . \qquad \text{(B11)}$$

On the basis of Eq. (B7), Eq. (B12) is also proven.[37]

$$\hat{T}^{-1}\bar{f}(\mathbf{z}) = \bar{f}(\bar{\mathbf{z}}) \ . \qquad \text{(B12)}$$

From the combinations of Eqs. (B8) and (B10), and Eqs. (B11) and (B12), we can obtain Eqs. (B13a) and (B13b), respectively.

$$\bar{f}(\mathbf{z}) = f(\bar{\mathbf{z}}) \ . \qquad \text{(B13a)}$$

$$f(\mathbf{z}) = \bar{f}(\bar{\mathbf{z}}) \ . \qquad \text{(B13b)}$$

Note that Eqs. (B13a) and (B13b) mean that although the functional forms of f and $\bar{f}$ are different, the functional value f at the point $\bar{\mathbf{z}}$ ($\mathbf{z}$) is equal to the functional value $\bar{f}$ at $\mathbf{z}$ ($\bar{\mathbf{z}}$). Furthermore, operation of $\hat{T}^{-1}$ on Eq. (B8) leads to

$$f(\mathbf{z}) = \hat{T}^{-1}f(\bar{\mathbf{z}}) \ . \qquad \text{(B14)}$$

As a result of Eqs. (B13b) and (B14), we can obtain Eq. (B15).

$$\bar{f}(\bar{\mathbf{z}}) = T^{-1}f(\bar{\mathbf{z}}) \qquad \text{(B15)}$$

Here we give the premises of LCPT: the generating function W, original hamiltonian H, and New Hamiltonian $\overline{H}$ are expandable as the power series in ε as follows.

$$W = \sum_{i=0}^{\infty} \varepsilon^i W_{i+1} \tag{B16}$$

$$H = \sum_{i=0}^{\infty} \varepsilon^i H_i \tag{B17}$$

$$\overline{H} = \sum_{i=0}^{\infty} \varepsilon^i \overline{H}_i \tag{B18}$$

On the basis of the definition of Eq. (B3) and the assumption of Eq. (B16), we can also express $\hat{L}_W$ as the expansion as follows.

$$\hat{L}_W = \sum_{i=0}^{\infty} \varepsilon^i \hat{L}_{i+1} \ , \tag{B19}$$

where

$$\hat{L}_i \equiv \{W_i, \quad\} \ . \tag{B20}$$

Using Eq. (B19), we can express Eqs. (B6) and (B7) as the expansions as follows.

$$\hat{T} = \sum_{i=0}^{\infty} \frac{\varepsilon^i}{i!} \left(\sum_{j=0}^{\infty} \varepsilon^j (-\hat{L}_{j+1}) \right)^i \tag{B21a}$$

$$\hat{T}^{-1} = \sum_{i=0}^{\infty} \frac{\varepsilon^i}{i!} \left(\sum_{j=0}^{\infty} \varepsilon^j \hat{L}_{j+1} \right)^i \tag{B21b}$$

Eqs. (B10) and (B21a) or Eqs. (B15) and (B21b) indicate the advantage of LCPT that after W is once established through each order, we obtain the new transformed physical quantity $\bar{f}$ as a function of $\mathbf{z}$ ($\overline{\mathbf{z}}$) from f as a function of $\mathbf{z}$ ($\overline{\mathbf{z}}$). Therefore, we can express the

new Hamiltonian $\overline{H}$, action variable $\overline{J}_k$, angle variable $\overline{\Theta}_k$, and frequency $\overline{\omega}_k$ of mode k straightforwardly as functions of $\mathbf{z}$ ($\overline{\mathbf{z}}$) by means of the transformations $\hat{T}$ ($\hat{T}^{-1}$) as shown in I-2, I-3, and I-4.

I-2. New Hamiltonian

If we replace in Eq. (B15) f and $\bar{f}$ by H and $\overline{H}$, respectively, and express $\hat{T}^{-1}$, H, and $\overline{H}$ by their expansions, i.e. Eqs. (B21b), (B17), and (B18), we can obtain the representation of $\overline{H}$ with respect to $\hat{L}_m H_n$ in the following way.

$$\sum_{n'=0}^{\infty} \varepsilon^{n'} \overline{H}_{n'} = \sum_{l=0}^{\infty} \frac{\varepsilon^l}{l!} \left(\sum_{m=0}^{\infty} \varepsilon^m \hat{L}_{m+1} \right)^l \sum_{n=0}^{\infty} \varepsilon^n H_n \qquad \text{(B22)}$$

The parameter ε which is introduced as a parameter for Lie transformation, Eq. (B2), is the perturbation parameter. We obtain Eqs. (B23a)–(B23e) at each order of ε from Eq. (B22).

$$\varepsilon^0 : \overline{H}_0 = H_0 \qquad \text{(B23a)}$$

$$\varepsilon^1 : \overline{H}_1 = H_1 + \hat{L}_1 H_0 = H_1 + \{W_1, H_0\} \qquad \text{(B23b)}$$

$$\begin{aligned} \varepsilon^2 : \overline{H}_2 &= \frac{1}{2} \hat{L}_1^{\,2} H_0 + \hat{L}_2 H_0 + \hat{L}_1 H_1 + H_2 \\ &= \frac{1}{2} \{W_1, \{W_1, H_0\}\} + \{W_2, H_0\} + \{W_1, H_1\} + H_2 \end{aligned} \qquad \text{(B23c)}$$

$$\varepsilon^3 : \overline{H}_3 = \frac{1}{6}\hat{L}_1{}^3 H_0 + \frac{1}{2}\hat{L}_1\hat{L}_2 H_0 + \frac{1}{2}\hat{L}_2\hat{L}_1 H_0 + \frac{1}{2}\hat{L}_1{}^2 H_1 + \hat{L}_3 H_0 + \hat{L}_2 H_1 + \hat{L}_1 H_2 + H_3$$
$$= \frac{1}{6}\{W_1,\{W_1,\{W_1,H_0\}\}\} + \frac{1}{2}\{W_1,\{W_2,H_0\}\} + \frac{1}{2}\{W_2,\{W_1,H_0\}\}$$
$$+ \frac{1}{2}\{W_1,\{W_1,H_1\}\} + \{W_3,H_0\} + \{W_2,H_1\} + \{W_1,H_2\} + H_3$$

(B23d)

$$\varepsilon^4 : \overline{H}_4 = \frac{1}{24}\hat{L}_1{}^4 H_0 + \frac{1}{6}\hat{L}_1\hat{L}_2\hat{L}_1 H_0 + \frac{1}{6}\hat{L}_2\hat{L}_1{}^2 H_0 + \frac{1}{6}\hat{L}_1{}^2\hat{L}_2 H_0 + \frac{1}{6}\hat{L}_1{}^3 H_1$$
$$+ \frac{1}{2}\hat{L}_1{}^2 H_2 + \frac{1}{2}\hat{L}_2{}^2 H_0 + \frac{1}{2}(\hat{L}_1\hat{L}_2 + \hat{L}_2\hat{L}_1)H_1 + \frac{1}{2}(\hat{L}_1\hat{L}_3 + \hat{L}_3\hat{L}_1)H_0$$
$$+ \hat{L}_1 H_3 + \hat{L}_2 H_2 + \hat{L}_3 H_1 + \hat{L}_4 H_0$$
$$+ H_4$$
$$= \frac{1}{24}\{W_1,\{W_1,\{W_1,\{W_1,H_0\}\}\}\} + \frac{1}{6}\{W_1,\{W_2,\{W_1,H_0\}\}\} + \frac{1}{6}\{W_2,\{W_1,\{W_1,H_0\}\}\}$$
$$+ \frac{1}{6}\{W_1,\{W_1,\{W_2,H_0\}\}\} + \frac{1}{6}\{W_1,\{W_1,\{W_1,H_1\}\}\} +$$
$$+ \frac{1}{2}\{W_1,\{W_1,H_2\}\} + \frac{1}{2}\{W_2,\{W_2,H_0\}\} + \frac{1}{2}\{W_1,\{W_2,H_1\}\}$$
$$+ \frac{1}{2}\{W_2,\{W_1,H_1\}\} + \frac{1}{2}\{W_1,\{W_3,H_0\}\} + \frac{1}{2}\{W_3,\{W_1,H_0\}\}$$
$$+ \{W_1,H_3\} + \{W_2,H_2\} + \{W_3,H_1\} + \{W_4,H_0\} + H_4$$

(B23e)

I-3. New momenta and coordinates

The new momenta $\overline{\mathbf{p}}$ and coordinates $\overline{\mathbf{q}}$ are also obtained in as follows.

$$\overline{p}_k = \hat{T}p$$
$$= p_k + \varepsilon(-\hat{L}_1)p_k + \varepsilon^2(-\hat{L}_2 + \frac{1}{2}\hat{L}_1{}^2)p_k + \ldots \quad \text{(B24a)}$$
$$= p_k - \varepsilon\{W_1,p_k\} - \varepsilon^2(\{W_2,p_k\} - \frac{1}{2}\{W_1,\{W_1,p_k\}\}) + \ldots$$

$$\overline{q}_k = q_k - \varepsilon\{W_1, q_k\} - \varepsilon^2(\{W_2, q_k\} - \frac{1}{2}\{W_1, \{W_1, q_k\}\}) + \ldots \quad \text{(B24b)}$$

In our MD calculations, we set up the initial conditions for the trajectory calculations with respect to the new variables in *Step 3* and then express them by the original variables by means of inverse transformation in *Step 4*. For this reason, here we show that the original variables can be also represented with respect to the new variables as follows.

$$\begin{aligned} p_k &= \hat{T}^{-1}\overline{p}_k \\ &= \overline{p}_k + \varepsilon(\hat{L}_1)\overline{p}_k + \varepsilon^2(\hat{L}_2 + \frac{1}{2}\hat{L}_1^{\,2})\overline{p}_k + \ldots \quad \text{(B25a)} \\ &= \overline{p}_k + \varepsilon\{W_1, \overline{p}_k\} + \varepsilon^2(\{W_2, \overline{p}_k\} + \frac{1}{2}\{W_1, \{W_1, \overline{p}_k\}\}) + \ldots \end{aligned}$$

$$q_k = \overline{q}_k + \varepsilon\{W_1, \overline{q}_k\} + \varepsilon^2(\frac{1}{2}(\{W_2, \overline{q}_k\} + \{W_1, \{W_1, \overline{q}_k\}\}) + \ldots \quad \text{(B25b)}$$

I-4. New action variable

If in Eq. (B13a) f is replaced with the action variable J_k of mode *k*, the new action variable $\overline{J}_k$ can be obtained as follows.

$$\begin{aligned} \overline{J}_k(\mathbf{p}, \mathbf{q}) &= \hat{T}J_k(\mathbf{p}, \mathbf{q}) \\ &= J_k(\overline{\mathbf{p}}, \overline{\mathbf{q}}) \\ &= \frac{1}{2\omega_k}(\overline{p}_k^{\,2} + \omega_k^{\,2}\overline{q}_k^{\,2}) \end{aligned} \quad \text{(B26)}$$

I-5. Determination of *W*

When $\overline{H}$ is in normal form, it depends on $\overline{\mathbf{J}}$ but does not depend on $\overline{\mathbf{\Theta}}$. Therefore, canonical transformation at a certain perturbation order *i* should be done to make $\overline{H}_i$

independent of $\overline{\boldsymbol{\Theta}}$. We show here how to determine W_1 to obtain the new Hamiltonian $\overline{H}_1$. The procedures to determine the higher order generating functions are likewise.

According to the procedure of perturbation theory, solutions of a certain perturbation order *i* are determined using the variables obtained at the perturbation order $i-1$. Therefore, W_1 is determined so that $\overline{H}_1$ depends only on the zeroth order action variables **J**, and is independent of the zeroth order angle variables, $\boldsymbol{\Theta}$. The equations of motion for zerothe order are given by

$$\frac{\partial H_0}{\partial p_i} = \frac{dq_i}{d\tau} \ , \tag{B27a}$$

and

$$\frac{\partial H_0}{\partial q_i} = -\frac{dp_i}{d\tau} \ , \tag{B27b}$$

Where H_0 is given by Eq. (2). The solutions of Eqs. (B27a,b) are given by

$$q_k = \sqrt{\frac{2J_k}{\omega_k}} \cos\Theta_k \tag{B28a}$$

and

$$p_k = -\sqrt{2J_k\omega_k} \sin\Theta_k \ , \tag{B28b}$$

where

$$\Theta_k = \omega_k\tau + \beta_k \ . \tag{B29}$$

For the canonical transformation at first order perturbation, here we follow Eq. (B23b). Functional form of H_1 is given by Eq. (3) and it is expressed by using Eq. (B28a) as follows.

$$\begin{aligned} H_1 &= \frac{1}{6}\sum_{i,j,k}^{N} c_{ijk}\sqrt{\frac{2J_i}{\omega_i}\frac{2J_j}{\omega_j}\frac{2J_k}{\omega_k}}\cos\Theta_i\cos\Theta_j\cos\Theta_k \\ &= \frac{1}{24}\sum_{i,j,k}^{N} c_{ijk}\sqrt{\frac{2J_i}{\omega_i}\frac{2J_j}{\omega_j}\frac{2J_k}{\omega_k}}\{\cos(\Theta_i-\Theta_j-\Theta_k)+\cos(\Theta_i+\Theta_j-\Theta_k) \\ &\quad +\cos(\Theta_i-\Theta_j+\Theta_k)+\cos(\Theta_i+\Theta_j+\Theta_k)\} \end{aligned} \tag{B30}$$

Because all terms in H_1 depend on $\boldsymbol{\Theta}$, W_1 must be determined so that all terms of H_1 is canceled. Therefore, from Eq. (B23b), we can determine W_1 by requiring Eqs. (B31) and (B32) to be satisfied.

$$\{W_1, H_0\} = -H_1 \tag{B31}$$

$$\overline{H}_1 = 0 \tag{B32}$$

The left hand side of Eq. (B31) is transformed as follows.

$$\begin{aligned} \{W_1, H_0\} &= \sum_{j=1}^{N}\left(\frac{\partial W_1}{\partial q_j}\frac{\partial H_0}{\partial p_j}-\frac{\partial H_0}{\partial q_j}\frac{\partial W_1}{\partial p_j}\right) \\ &= \sum_{j=1}^{N}\left(\frac{\partial W_1}{\partial q_j}\frac{dq_j}{d\tau}+\frac{dp_j}{d\tau}\frac{\partial W_1}{\partial p_j}\right)=\frac{dW_1}{d\tau} \end{aligned} . \tag{B33}$$

By integrating Eq. (B33) and using Eqs. (B28a), (B29) , (B30) and (B31), W_1 is determined as follows:

$$
\begin{aligned}
W_1 &= -\int_0^{\tau} d\tau H_1 \\
&= -\frac{1}{6}\sum_{i=1}^{N} c_{ijk}\{\frac{1}{\omega_i+\omega_j-\omega_k}(-\frac{p_i q_j q_k}{\omega_i}-\frac{p_i p_j p_k}{\omega_i\omega_j\omega_k}-\frac{q_i p_j q_k}{\omega_j}+\frac{q_i q_j p_k}{\omega_k}) \\
&+\frac{1}{\omega_i+\omega_j+\omega_k}(-\frac{p_i q_j q_k}{\omega_i}+\frac{p_i p_j p_k}{\omega_i\omega_j\omega_k}-\frac{q_i p_j q_k}{\omega_j}-\frac{q_i q_j p_k}{\omega_k}) \\
&+\frac{1}{\omega_i-\omega_j+\omega_k}(-\frac{p_i q_j q_k}{\omega_i}-\frac{p_i p_j p_k}{\omega_i\omega_j\omega_k}+\frac{q_i p_j q_k}{\omega_j}-\frac{q_i q_j p_k}{\omega_k}) \\
&+\frac{1}{\omega_i-\omega_j-\omega_k}(-\frac{p_i q_j q_k}{\omega_i}+\frac{p_i p_j p_k}{\omega_i\omega_j\omega_k}+\frac{q_i p_j q_k}{\omega_j}+\frac{q_i q_j p_k}{\omega_k})\}
\end{aligned}
\quad . \quad \text{(B34)}
$$

We can also determine W_i with $i > 1$ in the same way. Note that the order of W_i with respect to **p** and **q** is i+2.

II. Quantum normal form theory[36]

[36] H. Waalkens, R. Schubert and S. Wiggins, *Nonlinearity*, 2008, **21**, R1-R118.

Here we describe the essential materials for our calculation as to quantum NFT that is written in the review by Waalkens and co-workers,[36] modifying in the way applicable to our analysis.

In the NFT for quantum mechanics, the canonical transformation for classical mechanics is replaced by the unitary transformation, and the dynamical variables of classical mechanics are treated with the corresponding operators in quantum mechanics.

To calculate the quantum frequency ω_m^{qu}, the energy eigenvalue must be derived. If we

represent $\hat{J}_k$ as

$$\hat{J}_k = \frac{1}{2\omega_k}(\hat{p}_k{}^2 + \omega_k{}^2\hat{q}_k{}^2) \ , \qquad \text{(S1)}$$

where $\hat{p}_k$ and $\hat{q}_k$ are operators of p_k and q_k, respectively, the eigenfunctions of $\hat{J}_k$ (k = 1–N) are equivalent to those of the harmonic oscillators, and the eigenvalues are equivalent to those of the harmonic oscillators multiplied by $1/\omega_k$. Therefore, the vibrational energy eigenvalue is easily obtained if the Hamiltonian is expressed only by $\hat{J}_k$. For this reason, the energy eigenvalue is obtained by a unitary transformation so that the new Hamiltonian $\hat{H}'$ is written only in terms of $\hat{J}_k$. In this respect, the direction of the transformation is the same as in classical mechanics, in which $\overline{H}$ depends only on $\overline{J}_k$, despite the differences stated above.

The unitary transformation is performed through the Hamiltonian in symbolic representation rather than directly. This is because the symbols are much easier to treat than the operators. Weyl quantization is used here to associate operators in a Hilbert space with functions in a phase space. In the context of Weyl quantization, a variable $A(\mathbf{p},\mathbf{q})$, which is a function of **p** and **q**, is called a (Weyl) symbol of the corresponding operator $\hat{A}$. Thus, the transformation is performed in three steps rather than directly. In *Step 1*, operators $\hat{p}_k$, $\hat{q}_k$, $\hat{J}_k$, and $\hat{H}$ are replaced by the corresponding symbols. In *Step 2*, unitary transformation is

performed for the symbols. In *Step 3*, the symbols are quantized by Weyl quantization. Bellow, H' is the symbol of the Hamiltonian in the quantum normal form, and $\hat{H}'$ is the operator in the quantum normal form.

The procedures are described below.

Step 1:

By means of Weyl quantization, the operators of coordinate $\hat{q}_k$ and momentum $\hat{p}_k$ of mode *k* act on a wave function according to

$$\hat{q}_k \psi(q) = q_k \psi(q), \tag{S2}$$

$$\hat{p}_k \psi(q) = \frac{\mathrm{h}}{\mathrm{i}} \frac{\partial \psi(q)}{\partial q_k}. \tag{S3}$$

Weyl quantization extends these prescriptions to general functions of **q** and **p** by requiring that the quantization of the exponential function

$$e^{\frac{\mathrm{i}}{\mathrm{h}}(\langle \xi_{\mathbf{p}}, \mathbf{q} \rangle + \langle \xi_{\mathbf{q}}, \mathbf{p} \rangle)} \tag{S4}$$

is the phase space translation operator

$$\hat{T}(\xi_{\mathbf{q}}, \xi_{\mathbf{p}}) = e^{\frac{\mathrm{i}}{\mathrm{h}}(\langle \xi_{\mathbf{p}}, \hat{\mathbf{q}} \rangle + \langle \xi_{\mathbf{q}}, \hat{\mathbf{p}} \rangle)}, \tag{S5}$$

where $\xi_{\mathbf{q}}$ and $\xi_{\mathbf{p}}$ are real numbers, and the bracket $\langle , \rangle$ is the scalar product. Using Fourier inversion, we can represent a function in phase space as

$$A(\mathbf{q},\mathbf{p}) = \frac{1}{(2\pi\hbar)^{2N}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\xi_{\mathbf{q}} d\xi_{\mathbf{p}} \overline{A}(\xi_{\mathbf{q}},\xi_{\mathbf{p}}) e^{\frac{\mathrm{i}}{\hbar}(\langle \xi_{\mathbf{p}},\mathbf{q}\rangle + \langle \xi_{\mathbf{q}},\mathbf{p}\rangle)}, \tag{S6}$$

where

$$\overline{A}(\xi_{\mathbf{q}},\xi_{\mathbf{p}}) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\mathbf{q} d\mathbf{p} A(\mathbf{q},\mathbf{p}) e^{-\frac{\mathrm{i}}{\hbar}(\langle \xi_{\mathbf{p}},\mathbf{q}\rangle + \langle \xi_{\mathbf{q}},\mathbf{p}\rangle)} \tag{S7}$$

is the Fourier transform of $A(\mathbf{q},\mathbf{p})$. The Weyl quantization Op[A] of A is then defined by replacing the factor $e^{\frac{\mathrm{i}}{\hbar}(\langle \xi_{\mathbf{p}},\mathbf{q}\rangle + \langle \xi_{\mathbf{q}},\mathbf{p}\rangle)}$ in Eq. (S6) by the operator $\hat{T}(\xi_{\mathbf{q}},\xi_{\mathbf{p}})$, i.e.,

$$\hat{A} \equiv \mathrm{Op}[A] \equiv \frac{1}{(2\pi\hbar)^{2N}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\xi_{\mathbf{q}} d\xi_{\mathbf{p}} \overline{A}(\xi_{\mathbf{q}},\xi_{\mathbf{p}}) \hat{T}(\xi_{\mathbf{q}},\xi_{\mathbf{p}}) , \tag{S8}$$

where Op[ ] is defined as replacing the symbol inside the bracket with the corresponding operator by the Weyl quantization. The quantization can also be inverted, as follows:

$$A(\mathbf{q},\mathbf{p}) = \mathrm{Tr}[\hat{T}(\mathbf{q},\mathbf{p})^{*} \mathrm{Op}[A]] . \tag{S9}$$

As noted above, the function A is called a (Weyl) symbol of the operator $\hat{A}$. The symbols of the Hamiltonian and action variables are obtained from Eq. (S9).

Step 2:

The unitary transformation of an operator $\hat{f}$ is given by

$$\hat{f}' = e^{-\frac{\mathrm{i}}{\hbar}\varepsilon\hat{W}} \hat{f} e^{\frac{\mathrm{i}}{\hbar}\varepsilon\hat{W}} , \tag{S10}$$

where ε is a perturbation parameter for performing the unitary transformation using perturbation theory, $\hat{W}$ =Op[W], and W is a polynomial of **p** and **q**. As in the symbolic representations of operators, the unitary transformation is also represented by symbols. It is

easily derived that Eq. (S10) is represented by the corresponding symbols as

$$f' = \sum_{l=0}^{\infty} \frac{\varepsilon^l}{l!} \hat{M}_W{}^l f \,, \tag{S11}$$

where $\hat{M}_W$ is defined as

$$\hat{M}_W \equiv \sum_{k=0}^{\infty} C_k W[\langle \overrightarrow{\partial}_{\mathbf{q}}, \overrightarrow{\partial}_{\mathbf{p}} \rangle - \langle \overleftarrow{\partial}_{\mathbf{q}}, \overrightarrow{\partial}_{\mathbf{p}} \rangle]^{2k+1} \,, \tag{S12}$$

where

$$C_k = (\frac{\mathrm{h}}{2})^{2k} \frac{(-1)^k}{(2k+1)!} \,. \tag{S13}$$

The operators $\overrightarrow{\partial}_{\mathbf{q}}$, $\overleftarrow{\partial}_{\mathbf{p}}$, $\overleftarrow{\partial}_{\mathbf{q}}$, and $\overrightarrow{\partial}_{\mathbf{p}}$ on the right-hand side of Eq. (S12) are partial derivatives with respect to **p** or **q** as indicated by the subscripts, and the arrows specify whether they act on the left or the right. For example, operation of the term in Eq. (S12) with *k* equal to zero on *H* is expressed as

$$C_0 W[\langle \overrightarrow{\partial}_{\mathbf{q}}, \overleftarrow{\partial}_{\mathbf{p}} \rangle - \langle \overleftarrow{\partial}_{\mathbf{q}}, \overrightarrow{\partial}_{\mathbf{p}} \rangle] H = \sum_{j=1}^{N} (\frac{\partial W}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial H}{\partial q_j} \frac{\partial W}{\partial p_j}) \,. \tag{S14}$$

For the derivation of Eq. (S11), see the reference.[36] The equation for the new Hamiltonian represented by H' is obtained if f and f' are replaced by H and H', respectively, in Eq. (S11). W, H, and H' are assumed to be represented by their series expansions in the following way.

$$W = \sum_{i=0}^{\infty} \varepsilon^i W_{i+1} \tag{S15}$$

$$H = \sum_{i=0}^{\infty} \varepsilon^i H_i \tag{S16}$$

$$H' = \sum_{i=0}^{\infty} \varepsilon^i \overline{H}_i \tag{S17}$$

Using (S15), $\hat{M}_W$ can be expressed as

$$\begin{aligned} \hat{M}_W &= \sum_{m=0}^{\infty} \varepsilon^m W_{m+1} \sum_{k=0}^{\infty} C_k [\langle \hat{\partial}_{\mathbf{q}}^{\mathbf{W}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{V}} \rangle - \langle \hat{\partial}_{\mathbf{q}}^{\mathbf{V}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{W}} \rangle]^{2k+1} \\ &= \sum_{m=0}^{\infty} \varepsilon^m \hat{M}_{m+1} \end{aligned}, \tag{S18}$$

where

$$\hat{M}_m \equiv W_m \sum_{k=0}^{\infty} C_k [\langle \hat{\partial}_{\mathbf{q}}^{\mathbf{W}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{V}} \rangle - \langle \hat{\partial}_{\mathbf{q}}^{\mathbf{V}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{W}} \rangle]^{2k+1} \quad . \tag{S19}$$

To compare the terms at certain orders of ε, Eq. (S18) is inserted into Eq. (S11), and f' and f are replaced by the expansions of H' and H, respectively, as follows.

$$\begin{aligned} \sum_{n'=0}^{\infty} \varepsilon^{n'} H'_{n'} &= \sum_{l=0}^{\infty} \frac{\varepsilon^l}{l!} \hat{M}_W{}^l H \\ &= \sum_{l=0}^{\infty} \frac{\varepsilon^l}{l!} \left\{ \sum_{m=0}^{\infty} \varepsilon^m W_{m+1} \sum_{k=0}^{\infty} C_k [\langle \hat{\partial}_{\mathbf{q}}^{\mathbf{W}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{V}} \rangle - \langle \hat{\partial}_{\mathbf{q}}^{\mathbf{V}}, \hat{\partial}_{\mathbf{p}}^{\mathbf{W}} \rangle]^{2k+1} \right\}^l \sum_{n=0}^{\infty} \varepsilon^n H_n \\ &= \sum_{l=0}^{\infty} \frac{\varepsilon^l}{l!} \left\{ \sum_{m=0}^{\infty} \varepsilon^m \hat{M}_{m+1} \right\}^l \sum_{n=0}^{\infty} \varepsilon^n H_n \end{aligned} \tag{S20}$$

Consequently, the following recursive equations are obtained.

$$\varepsilon^0 : H'_0 = H_0 \tag{S21}$$

$$\varepsilon^1 : H'_1 = H_1 + \hat{M}_1 H_0 \tag{S22}$$

$$\varepsilon^2 : H'_2 = \frac{1}{2}\hat{M}_1{}^2 H_0 + \hat{M}_2 H_0 + \hat{M}_1 H_1 + H_2 \tag{S23}$$

$$\varepsilon^3 : H'_3 = \frac{1}{6}\hat{M}_1{}^3 H_0 + \frac{1}{2}\hat{M}_1\hat{M}_2 H_0 + \frac{1}{2}\hat{M}_2\hat{M}_1 H_0 + \frac{1}{2}\hat{M}_1{}^2 H_1 + \hat{M}_3 H_0 + \hat{M}_2 H_1 + \hat{M}_1 H_2 + H_3 \tag{S24}$$

$$\begin{aligned}\varepsilon^4 : H'_4 = {} & \frac{1}{24}\hat{M}_1{}^4 H_0 + \frac{1}{6}\hat{M}_1\hat{M}_2\hat{M}_1 H_0 + \frac{1}{6}\hat{M}_2\hat{M}_1{}^2 H_0 \\ & + \frac{1}{6}\hat{M}_1{}^2\hat{M}_2 H_0 + \frac{1}{6}\hat{M}_1{}^3 H_1 + \frac{1}{2}\hat{M}_1{}^2 H_2 + \frac{1}{2}\hat{M}_2{}^2 H_0 \\ & + \frac{1}{2}\hat{M}_1\hat{M}_2 H_1 + \frac{1}{2}\hat{M}_2\hat{M}_1 H_1 + \frac{1}{2}\hat{M}_1\hat{M}_3 H_0 + \frac{1}{2}\hat{M}_3\hat{M}_1 H_0 \\ & + \hat{M}_1 H_3 + \hat{M}_2 H_2 + \hat{M}_3 H_1 + \hat{M}_4 H_0 + H_4\end{aligned} \tag{S25}$$

As is written in the review,[36] the classical and quantum normal forms are very similar. In our description, one can see the perturbation equations Eqs. (S22)–(S25) are the same as the classical versions, Eqs. (B23a)–(B23e), if the operators $\hat{M}_m$ are replaced by the classical analogue L_m. In addition to the difference between $\hat{M}_m$ and L_m, other differences arise in the process of *Step 3*. The result is given in the main text.

III. Frequency of H_2O

The frequencies of H_2O are plotted in Fig. A. The symbols (open circle, filled triangle, open square) and the numbers in parenthesis have the same meaning as those in Fig. 1 and Table 1 in the text. Filled triangles indicate the classical mechanical frequencies obtained

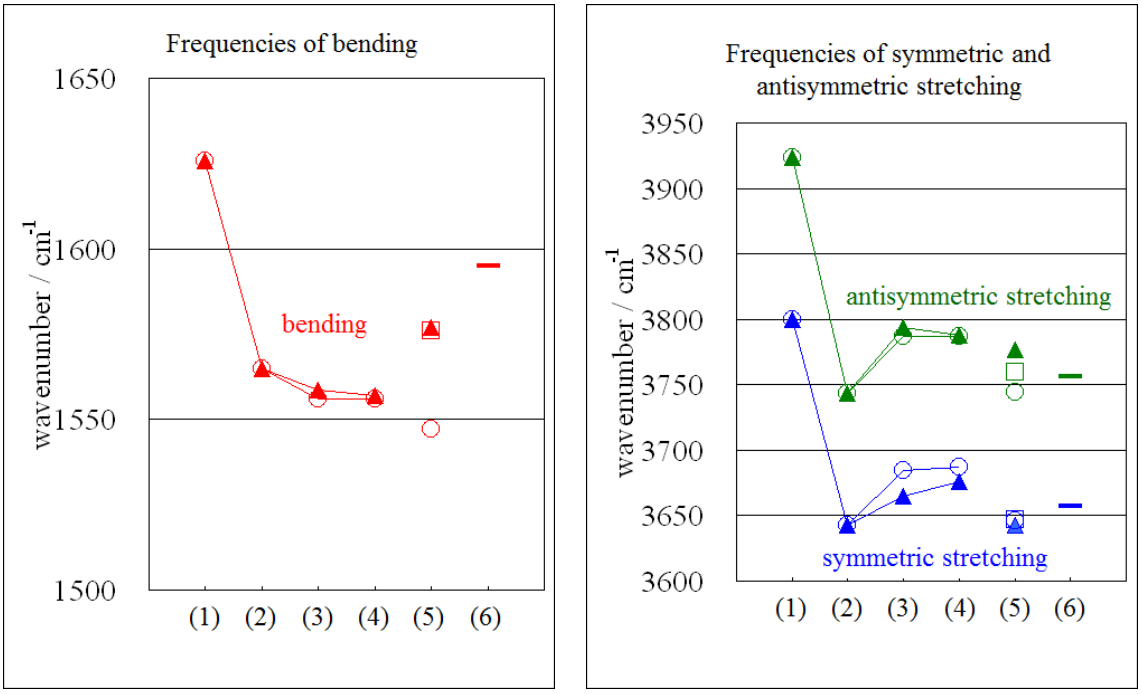


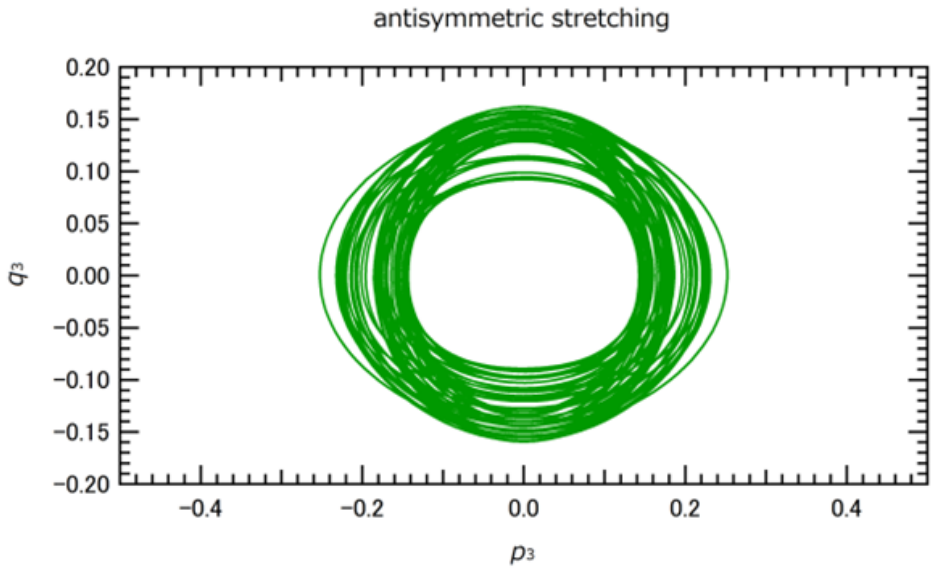
Fig. A

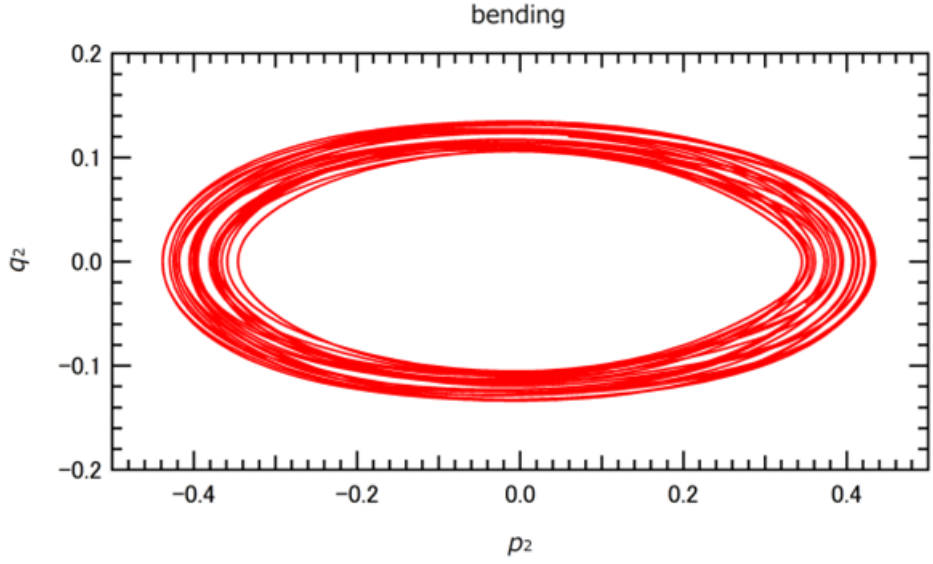
by (1) the zeroth-, (2) second-, and (3) fourth-order canonical perturbation, and by (4) FT of MD calculations on QFF PES. Filled triangles in the column of (5) indicate the classical mechanical frequencies from FT of direct ab initio MD calculation at the level of MP2/aug-cc-pVTZ. Circles indicate the quantum mechanical frequencies from (1) the zeroth-, (2) second-, and (3) fourth-order perturbation theory and from (4) cc-VSCF with QFF PES. Circles in the column (5) indicate the quantum mechanical frequencies from cc-VSCF with the direct PES at the MP2/aug-cc-pVTZ level of theory. Squares in the column (5) are the quantum mechanical frequencies from VCI with direct PES at the MP2/aug-cc-pVTZ level

of theory taken from the literature.[1]

IV. Trajectory

A trajectory in phase space generated with the initial condition of Eqs. (63)–(66) is shown in Fig B1. Blue, red, and green lines are the trajectories corresponding to symmetric stretching, bending, and antisymmetric stretching vibrational modes (normal modes), respectively. The trajectory is drawn in view of the original momenta (horizontal line) and coordinates (vertical line). Units for all momenta and coordinates are atomic units. The same trajectory but in view of the new momenta (horizontal line) and coordinates (vertical line)} in normal form is shown in Fig. B2. The color of lines and the units are same as Fig. B1.


antisymmetric stretching
0.20
0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
−0.20
q3
−0.4
−0.2
0.0
0.2
0.4
p3


bending
0.2
0.1
0.0
−0.1
−0.2
q2
−0.4
−0.2
0.0
0.2
0.4
p2

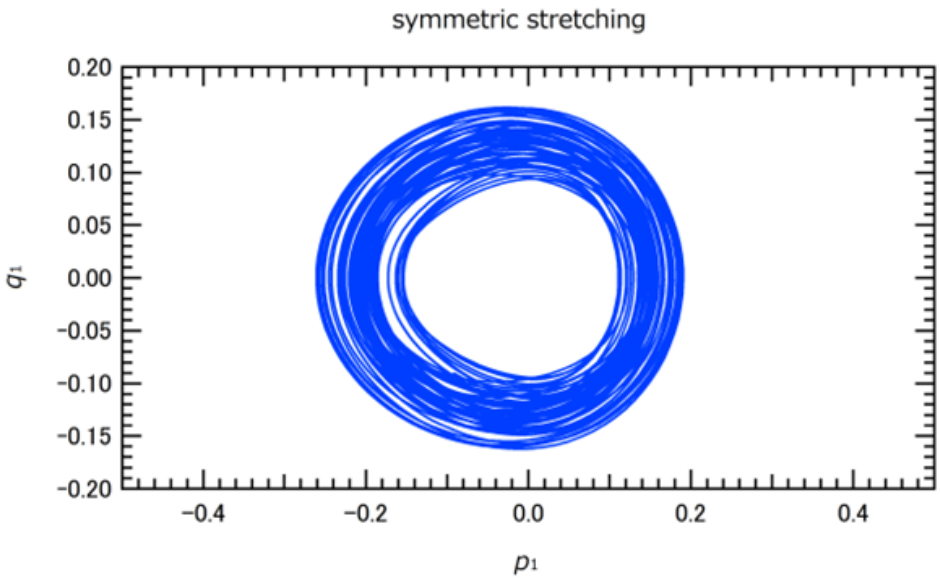
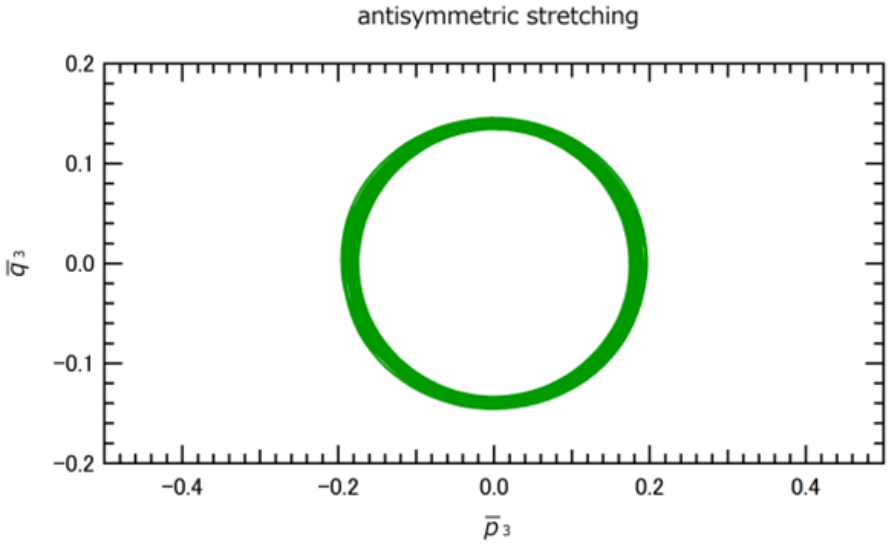

symmetric stretching
0.20
0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
−0.20
q_1
−0.4
−0.2
0.0
0.2
0.4
p_1

Fig. B1


antisymmetric stretching
0.2
0.1
0.0
−0.1
−0.2
$\overline{q}_3$
−0.4
−0.2
0.0
0.2
0.4
$\overline{p}_3$

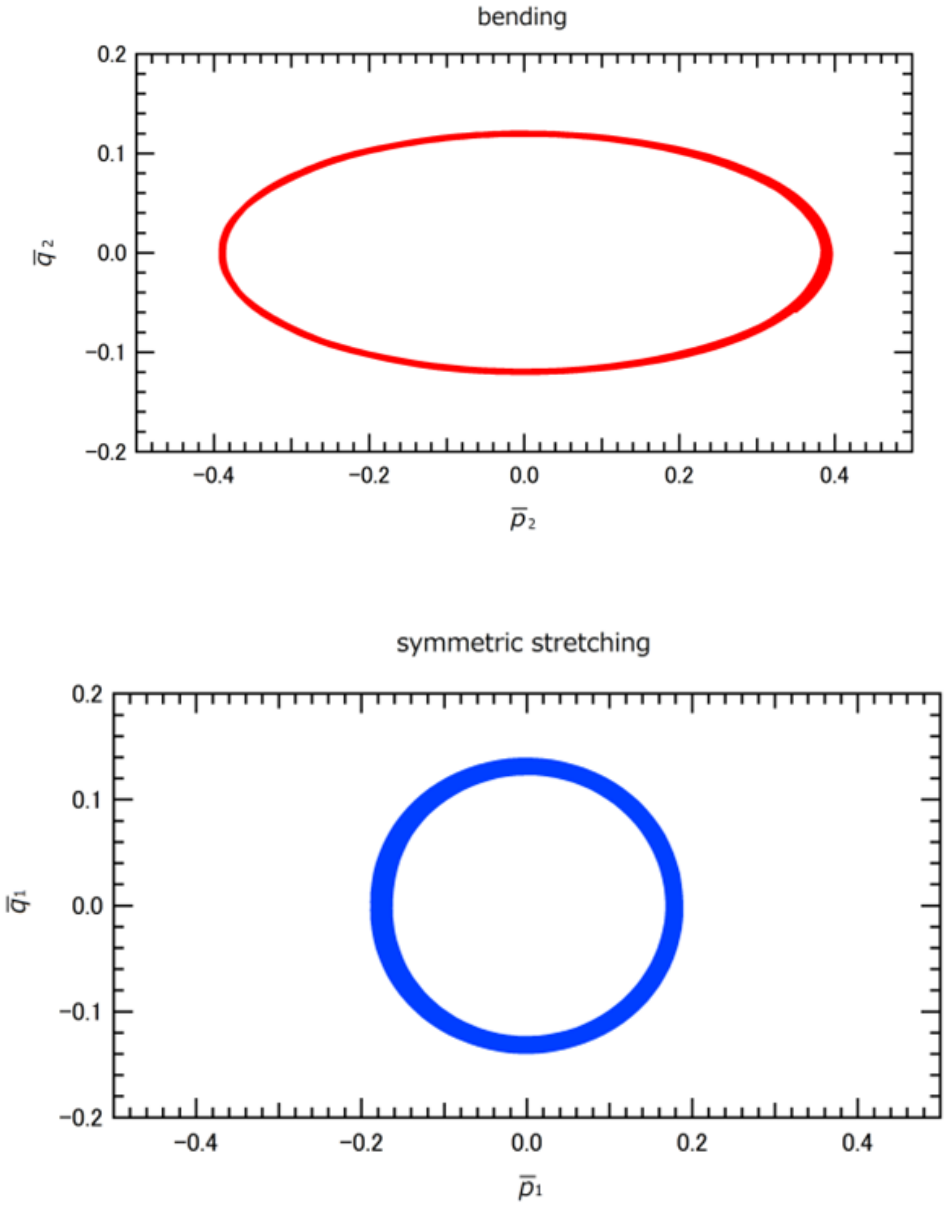
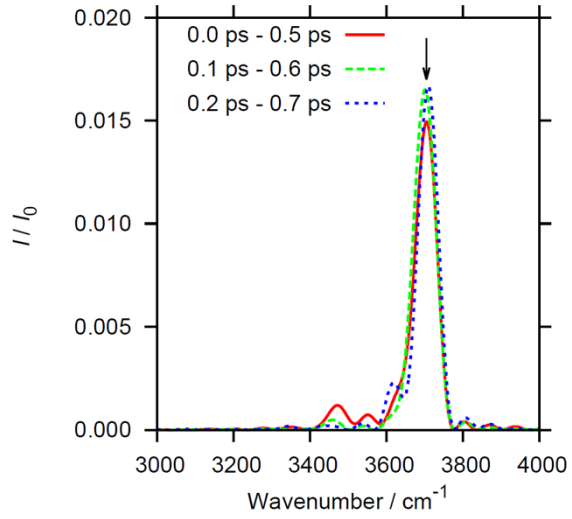

bending
0.2
0.1
0.0
−0.1
−0.2
$\overline{q}_2$
−0.4
−0.2
0.0
0.2
0.4
$\overline{p}_2$
symmetric stretching
0.2
0.1
0.0
−0.1
−0.2
$\overline{q}_1$
−0.4
−0.2
0.0
0.2
0.4
$\overline{p}_1$

Fig. B2

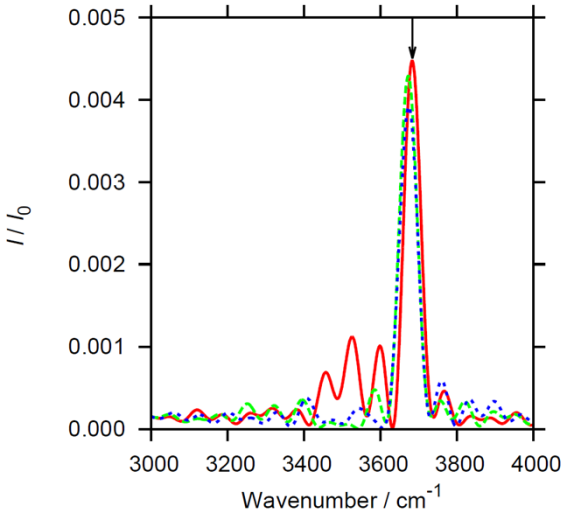
V. Power spectra of $C_{10}H_8$

Power spectra of $C_{10}H_8$ from the MD calculations for mode 1-8 frequencies are shown here. Intensity (I) is normalized by the total intensity (I_0). The black arrows indicate the peak positions of spectra in 0.0 ps -0.5 ps, from which we read $\omega^{cl(\infty)[0]}$.

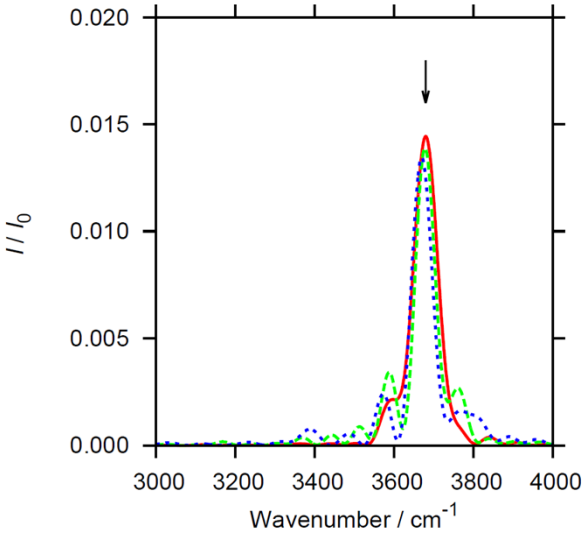
Mode 1



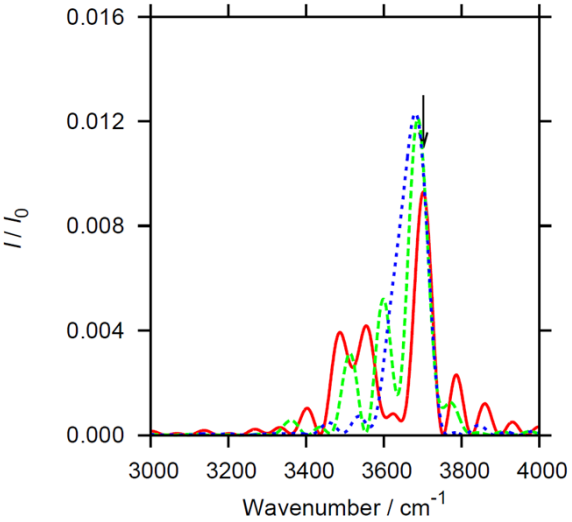
Mode 2



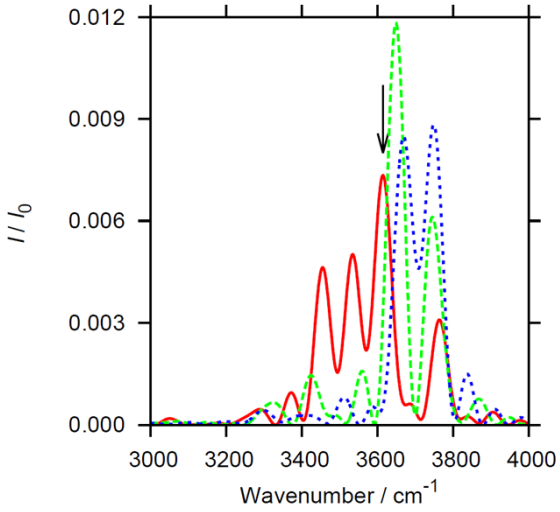
Mode 3



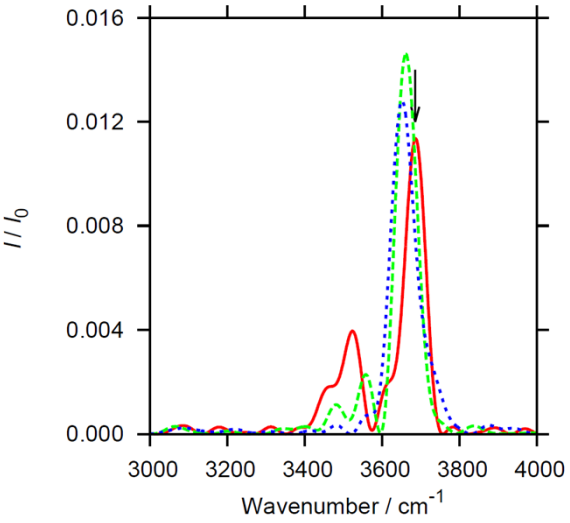
Mode 4



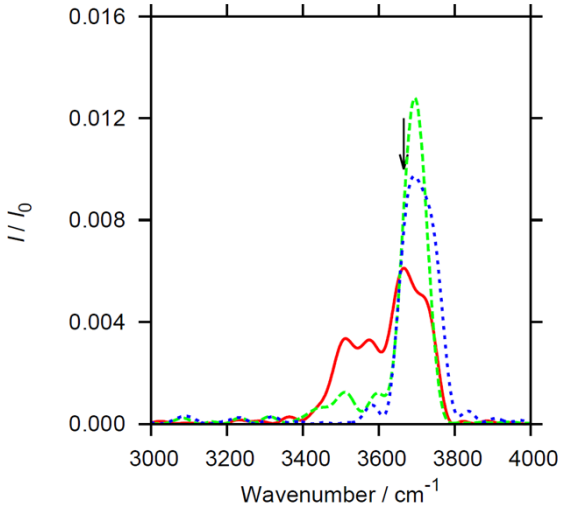
Mode 5



Mode 6



Mode 7



Mode 8