Supporting Information of

Quantum Vibration Perturbation Approach with Polyatomic Probe in Simulating Infrared Spectra

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1 The details of replace the molecule in clusters

To use the QVP method, the essential step is to replace the molecule you study in the trajectory with the isolated one, or say, to replace it with the un-perturbed one. Considering the fact that motions you do not directly study, even when the motion is an intramolecular one, should be considered as the ‘environment’, this kind of replacement is not that straight forward.

To replace the in-cluster molecule with the isolated one, we need the following steps.

1. Translate and rotation;
2. Project the IR-active vibration out;
3. Add the vibrating coordinates in;
4. Rotate and translate back.

Let us define the symbols first. Cartesian coordinates of the atoms in N-atom the chromophore are denoted by $\mathbf{R}$ and the equilibrium geometry $\mathbf{R}_\mathrm{e}$. The ith normal mode coordinate is written as Q_i and we have

$$\mathbf{R} = \mathbf{R}_\mathrm{e} + \sum_{i=1}^{3N} Q_i \cdot \boldsymbol{\xi}_i, \tag{1}$$

where $\boldsymbol{\xi}_i$ stands for the ith normal mode's vector. For in-trajectory molecule, $\mathbf{R}'$ is used to denote Cartesian coordinates. x_i, y_i, z_i and x'_i, y'_i, z'_i are used to describe the Cartesian coordinate in three orthogonal orientations of the ith atom. Note that the $\mathbf{R}$ and its ‘friends’ are all column vectors.

First, we define the translation vector. Calculate centre of mass for the in-cluster molecule

$$\alpha'_\mathrm{COM} = \frac{\sum_i m_i \alpha'_i}{\sum_i m_i} \quad (\alpha = x, y, z). \tag{2}$$

and the translation **t** can be easily defined as

$$\mathbf{t} = (\underbrace{x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, \ldots, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, \ldots, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}}_{3N})^{\mathsf{T}}. \tag{3}$$

Then, rotation. Here, we follow the Kabsch algorithm. The main idea is introduced as follow.

Consider we have two molecular structures with a little bit deformation, say **X** and **Y**, in Cartesian coordinates, with their centres of mass as the origins. For convenience, **X** and **Y** are $N \times 3$ matrices, corresponding to equilibrium structure and the one in MD trajectory respectively. Note that in this document, $N \times M$ means that the matrix has N rows and M columns. In FORTRAN, we write such matrix as

```
REAL*8::X(N,M)
```

for example, whose multiplication can be treated using `MATMUL()` function in FORTRAN. Therefore, the covariance matrix **C** is written

$$\mathbf{C} = \mathbf{Y}^{\mathsf{T}} \mathrm{diag}(\mathbf{m}) \mathbf{X} \tag{4}$$

and it is a 3×3 matrix, where **m** is vector formed by atomic masses. Further, you get the square of **C**, $\mathbf{C}^2$

$$\mathbf{C}^2 = \mathbf{C}^{\mathsf{T}} \mathbf{C}. \tag{5}$$

$\mathbf{C}^2$ is then a real symmetry matrix. Diagonalize it, you get the eigenvectors, which form a 3×3 matrix $\mathbf{A}'$, and eigenvalue $\lambda_i (i = 1, 2, 3)$. Sort the eigenvectors with their corresponding eigenvalues decreasing. Let us call the matrix formed by the sorted eigenvectors **A**. To deal with plane molecules, we let column vectors in **A** obey $\mathbf{A}_3 = \mathbf{A}_1 \times \mathbf{A}_2$ to deal with plane molecules. Then we calculate

$$\mathbf{B}' = \mathbf{C}\mathbf{A}. \tag{6}$$

Normalize $\mathbf{B}'$ to get **B**. Generally, column vectors in **B** should obey $\mathbf{B}_3 = \mathbf{B}_1 \times \mathbf{B}_2$. The rotation matrix is then

$$\hat{U} = \mathbf{B}\mathbf{A}^{\mathsf{T}}, \tag{7}$$

which can operate on X^{T}

$$\mathbf{X}'^{\mathsf{T}} = \hat{U} \mathbf{X}^{\mathsf{T}} \tag{8}$$

to minimize sRMSD of the two structures, which reads

$$\mathrm{sRMSD} = \left(\frac{1}{N} \sum_{i=1}^{N} d_i^2 \right)^{1/2}, \tag{9}$$

where

$$d_i = [(\mathbf{Y}_{ix} - \mathbf{X}'_{ix})^2 + (\mathbf{Y}_{iy} - \mathbf{X}'_{iy})^2 + (\mathbf{Y}_{iz} - \mathbf{X}'_{iz})^2]^{1/2}. \tag{10}$$

That is all for rotation. Note that $\hat{U}$ is an orthogonal matrix, which obeys

$$\hat{U}\hat{U}^{\mathsf{T}} = \hat{U}^{\mathsf{T}}\hat{U} = \mathbf{I}. \tag{11}$$

Notice again that the rotation operator is a 3×3 matrix. It is easy to write it as a $3N \times 3N$ matrix. However, in order to consist with the literature and for the elegance of mathematics, we perform all the rotation in **X** and **Y** and the vibration in **R** and its 'prime versions'. In this document, for elegance, I will omit all the $X \leftrightarrow \mathbf{R}$ conversion. In FORTRAN, use the following codes to complete this

```
X=TRANSPOSE(RESHAPE(R,(/3,N/)))
```

and

```
R=RESHAPE(TRANSPOSE(X),(/3*N/))
```

To project the studying motion $\boldsymbol{\xi}_\mathrm{s}$ out, the in-cluster molecule is first moved to the isolated molecule's place and then perform the projection. We have

$$\mathbf{R}'' = \hat{U}^\mathsf{T}(\mathbf{R}' - \mathbf{t}). \tag{12}$$

Also, we have the displacement coordinate

$$\Delta\mathbf{R}'' = \mathbf{R}'' - \mathbf{R}_\mathrm{e}, \tag{13}$$

and the so-called mass-weighted version of displacement coordinate $\Delta\tilde{\mathbf{R}}''$ got from multiply $\sqrt{m_i}$ to the ith atom's displacement. Then project the motion studied $\boldsymbol{\xi}_\mathrm{s}$ out,

$$\Delta'\tilde{\mathbf{R}}'' = \Delta\tilde{\mathbf{R}}'' - [\tilde{\boldsymbol{\xi}}_\mathrm{s}^\mathsf{T}\Delta\tilde{\mathbf{R}}''] \cdot \tilde{\boldsymbol{\xi}}_\mathrm{s} \tag{14}$$

to make sure the 'environment' motions remains untouched and the motion we want to use QVP to deal with fix to Q_s^e. Note that all symbols with a tilde mean the mass-weighted ones. After that we have to add the motion back (in quantum mechanics picture, or in this case, PODVR grids). We have the jth PODVR grid

$$\mathbf{R}_j''' = \mathbf{R}_\mathrm{e} + \Delta'\mathbf{R}'' + r_j \cdot \boldsymbol{\xi}_\mathrm{s}. \tag{15}$$

The final in-cluster coordinate then be

$$\mathbf{R}_j'''' = \hat{U}\mathbf{R}_j''' + \mathbf{t}, \tag{16}$$

and is used to replace the one in trajectory.

Some comments should be made to the method presented here. Readers may have noticed that all steps described here are reversible. Therefore, this method honestly represents the molecule's shape and position in clusters. The reason why we do not use vibration modes directly is that the linear normal mode is not a good way to represent the rotation, which may lead to mistakes.

2 Optimized geometry and normal modes

We optimized the formic acid monomer at the CCSD(T)-F12b/cc-pVTZ-F12 level, and obtained the equilibrium structure $\mathbf{R}_\mathrm{e}^\mathrm{ch}$ of formic acid (in Table S1) and the corresponding C=O stretching vibration mode (in Table S3). The atomic numbers in all Tables corresponds to those appearing in Figure S1. (The digits of the coordinates and wave function in the tables are derived from the direct output of the software package, and do not represent significant digits)

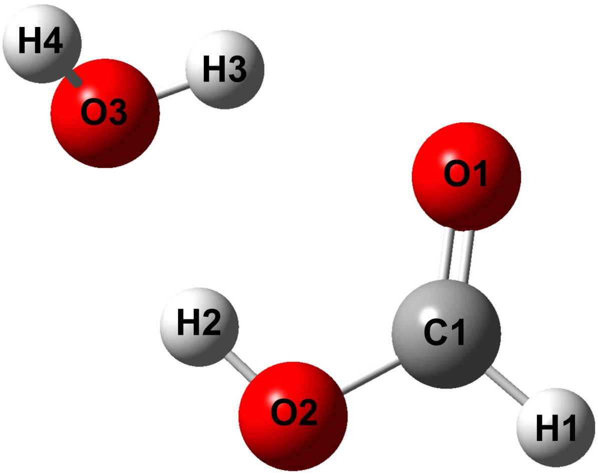

Figure S1: Optimized $HCOOH \cdot H_2O$ cluster structure. In this cluster, the configuration of the formic acid molecule is similar to the optimized formic acid monomer, both are a *trans* structures.

Table S1: Optimized geometry of formic acid (HCOOH) at CCSD(T)-F12b/cc-pVTZ-F12 level. All coordinates are in Ångström (Å).

Atom	x	y	z
C1	1.4826235247	−1.4520071867	−0.0446257725
H1	2.4244170923	−2.0075890921	−0.0121827777
O1	1.3879588299	−0.2599719683	−0.1374121039
O2	0.4449603033	−2.3006934343	0.0347312820
H2	−0.3580224001	−1.7622451186	0.0019663721

Table S2: Optimized geometry of formic acid (HCOOH) at M06-2X/cc-pVTZ level. All coordinates are in Ångström (Å).

Atom	x	y	z
C1	1.4835555453	−1.4473187601	−0.0436571479
H1	2.4222899324	−2.0102853903	−0.0138699138
O1	1.3908564621	−0.2624006979	−0.1370812894
O2	0.4491978524	−2.2929588309	0.0368125088
H2	−0.3639624422	−1.7695431208	0.0002728423

Table S3: C=O stretching mode of optimized formic acid (HCOOH) at CCSD(T)-F12b/cc-pVTZ-F12 level.

Atom	x	y	z
C1	−0.00556	0.22037	−0.01730
H1	−0.17962	−0.03326	0.00479
O1	0.01325	−0.14714	0.01144
O2	−0.00290	−0.02319	0.00186
H2	0.08166	0.11273	−0.00988

[a] Coordinate unit is Å.

3 PODVR grids number

In the QVP method, in order to describe the vibration potential energy curve of the reference state with fewer grid points, we use the PODVR method. Of course, the more DVR grids are used, the more accurate the description of the potential energy curve is. However, this will greatly increase the computational cost. Therefore, we need to test the optimal number of DVR points for different systems, minimize the number of DVR grids with little impact to the results.

We used different DVR grid numbers to describe the C=O stretching vibration potential energy curve of the formic acid molecule, and solved the one-dimensional Schrödinger equation to obtain the vibration frequencies under different numbers of grid points, the results are shown in Table S4 and Figure S2.

Table S4: When the QVP method takes the different number of DVR grids, the change of the instantaneous frequency of the reference structure is displayed by the red line in Figure S2.

DVR grid number	Energy
4	1799.12
5	1801.05
10	1801.24
20	1801.12
50	1801.12

[a] energy unit is cm^{-1}.

From the Figure S2 and Table S4 we can find that as the number of DVR grid points increasing, the vibration frequency results show a convergence trend, but Figure S2 also shows that when we take the DVR grid number = 4, compared to the DVR grid number = 5, The results have changed a lot, which shows that we can use 5 DVR grids to minimize the computational cost without large changes in results. The vibrational wave function represented by these five points is shown in Table S5.

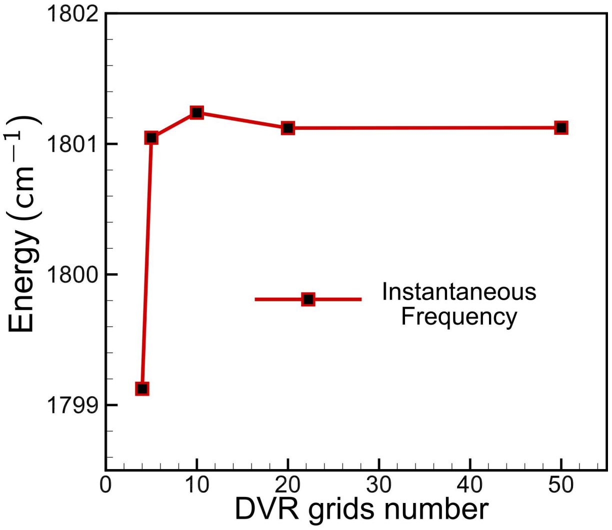

Figure S2: Convergence of energy level calculation. We took different DVR grid numbers on the instantaneous C=O stretching vibration frequency of formic acid molecule to solve Schrödinger equation. The black dots in the figure indicate the instantaneous vibration frequency of the reference state structure corresponding to the number of DVR grids, and the red line indicates the change tendency.

Table S5: The wave function of C=O stretching vibration mode at every PODVR grid.

Q_s	Excited State	Ground State
−0.1180160891	−0.2172508959	0.0583506568
−0.0636952246	−0.6413992163	0.3497844921
−0.0161991993	−0.2398865269	0.7055062850
0.0298278461	0.5741734451	0.5882891718
0.0791020874	0.3926683112	0.1744211629

^{a} Coordinate unit is Å.

4 Cluster structures

To test if the “low level" method to predict molecular structure without ruining the accuracy of geometry. Geometry of $HCOOH \cdot H_2O$ was optimized on both CCSD(T)-F12b/cc-pVTZ-F12 and M06-2X/cc-pVTZ levels. Using Kabcsh algorithm, and calculated the RMSD between two structure, the two origin optimized structures are showed in Table S6 and Table S7.

Table S8: Two different methods are used to optimize the $HCOOH \cdot H_2O$ cluster, the length of the formic acid C=O and the length of the hydrogen bond formed by the C=O bond with water. All coordinates are in Ångström (Å).

	CCSD(T)-F12	M06-2X
C=O length	1.21059	1.20554
Hydrogen Bond length	2.00636	1.99504

Table S6: Optimized geometry of $HCOOH \cdot H_2O$ at CCSD(T)-F12b/cc-pVTZ-F12 level.

Atom	x	y	z
C1	1.6197332722	−1.4959643224	−0.0206650281
H1	2.4568729330	−2.1963955523	0.0515307383
O1	1.7631206488	−0.2981000190	−0.1211101101
O2	0.4596824978	−2.1360723417	0.0178478629
H2	−0.2580401616	−1.4672154548	−0.0500799754
O3	−0.9814177867	0.1502011128	−0.2880238968
H3	−0.0769771926	0.4934408753	−0.2350044172
H4	−1.4983330778	0.6583531852	0.3392124344

^{a} Coordinate unit is Å.

Table S7: Optimized geometry of $HCOOH \cdot H_2O$ at M06-2X/cc-pVTZ level.

Atom	x	y	z
C1	1.6144990944	−1.4881421303	0.0048732240
H1	2.4353736910	−2.2007950786	0.1366264820
O1	1.7803073014	−0.3023234405	−0.1279903870
O2	0.4494996732	−2.1077109507	0.0087877793
H2	−0.2638862480	−1.4370942826	−0.1197338018
O3	−0.9785525055	0.1420284511	−0.3989909107
H3	−0.0809019340	0.5069553710	−0.3785222551
H4	−1.4716979394	0.5953295435	0.2880439014

^{a} Coordinate unit is Å.

5 The vibrational relaxation time

To estimate the relaxation time T_1, time-dependent perturbation theory (Fermi's Golden Rule) is utilized. The quantum mechanical vibrational population relaxation rate T_{ij}^{-1} from state j to state i is

$$T_{ij}^{-1} = \hbar^{-2} \int_{-\infty}^{\infty} \mathrm{d}t \, \exp\big(\mathrm{i}\omega_{ij} t\big) \langle V_{ij}(t) V_{ji}(0) \rangle. \tag{17}$$

Similarly to the line shape theory, in this work, its semi-classical approximation is used instead

$$T_{ij}^{-1} = A(\omega_{ij}) \hbar^{-2} \int_{-\infty}^{\infty} \mathrm{d}t \, \exp\big(\mathrm{i}\omega_{ij} t\big) \langle V_{ij}^{\mathrm{cl}}(t) V_{ji}^{\mathrm{cl}}(0) \rangle. \tag{18}$$

In formulae above, ω_{ij} is the radian frequency difference between the two states, and V_{ij} is the off-diagonal element of the full Hamiltonian, or simplified as

$$\begin{aligned} V_{ij}^{\mathrm{cl}} &= \langle \phi_i | \hat{V}' | \phi_j \rangle \\ &= \int \mathrm{d}Q_s \, \phi_i^*(Q_s) V'(Q_s; t) \phi_j(Q_s), \end{aligned} \tag{19}$$

and the $A(\omega_{ij})$ is the Quantum Correction Function (QCF). In this work, we take the approximation that relaxation from the first vibrational excited state to the ground state dominates ($T_1 \approx T_{01}$).

Practical problems during the computation, however, prevent us from getting a reliable T_1 numerically.Different schemes of QCF can be selected, while the result may differ by ~ 70 times(Table S7). Getting a "correct" QCF is as difficult as to perform a nuclear quantum dynamics simulation,which is practically unaffordable. The high-frequency noise from a numerical simulation is also one of the difficulties in this study. To get a meaningful result, the function $\log_{10} T_{01}^{\mathrm{cl}}(\omega_{01})$ is firstly smoothed and then the value at $\omega_{01} = 1767\,\mathrm{cm}^{-1}$ is taken from the full spectrum. In conclusion, T_1 of the value 7.76 ps is obtained with the Schofield QCF. Due to the factors discussed above, this value is only taken as an initial guess of T_1.

Table S9: Value of different Quantum Correction Function.

QCF Type	Value of QCF	Reference
None	1.00	-
Standard	2.00	Ref1–3
Harmonic/Schofield	24.22	Ref4–6
Harmonic	8.47	Ref2, 7–9
Schofield	69.21	Ref10
Bader	4.24	Ref7

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