Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary material for

Theoretical vibrational spectra of $OH^{-}(H_2O)_2$: Effect of quantum distribution and vibrational coupling

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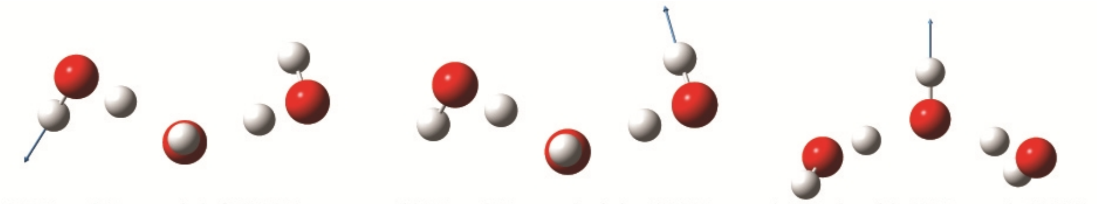
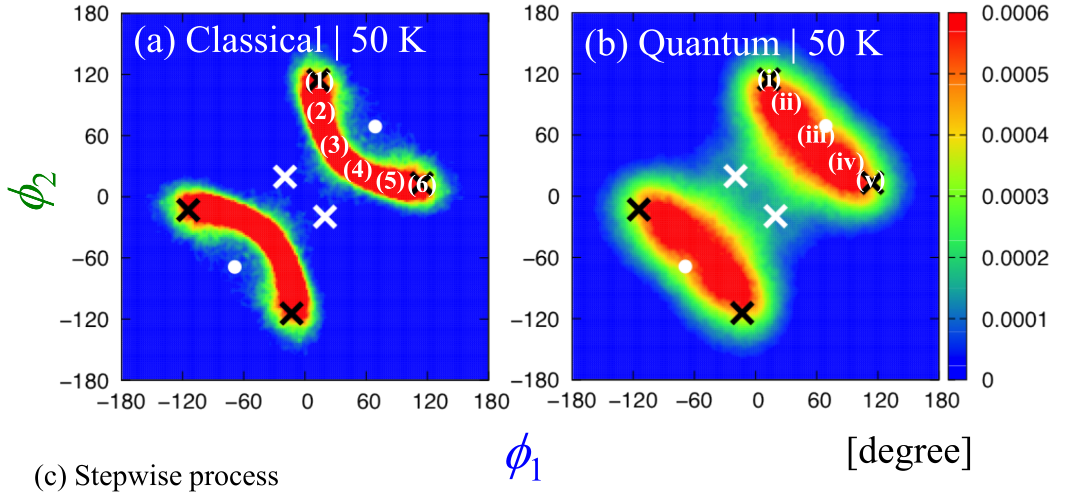
Summary on the schematic diagram of the vibrational modes considered for the free OH and hydroxide stretching, schematic images of the processes of conformation change between Conformer I; the detailed analysis on the definition of the angles for each conformer; the 2D, 4D, and 6D vibrational spectra for conformers II and C_2; the temperature dependence of the vibrational spectra and the spectra calculated using the vibrational perturbation theory are all available in the electronic supplementary material.

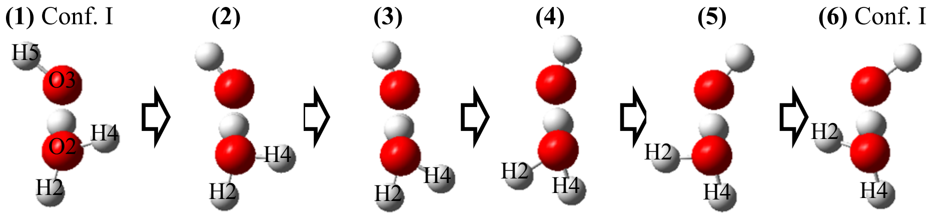


(a) Free OH stretch left (3937) (b) Free OH stretch right (3932) (c) Hydroxide OH stretch (3903)

Figure S1: Schematic diagram of the free OH and hydroxide stretching vibration that are considered in the present study. The harmonic frequencies, in cm^{-1}, are given in parenthesis.



(c) Stepwise process



(d) Concerted process

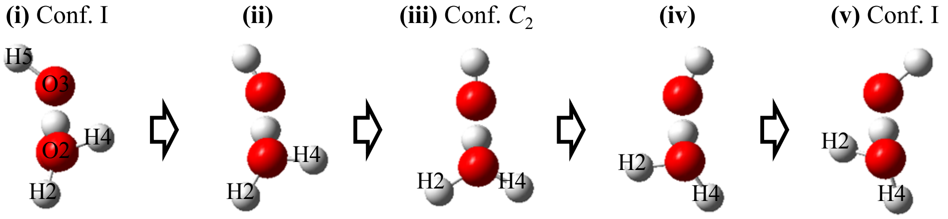


Figure S2: Two-dimensional distributions of ϕ_1 and ϕ_2 in (a) classical and (b) quantum simulations at 50 K similar to Figure 2 in the body text and schematic images of (c) the stepwise process of conformation changes from (1) to (6) seen along H5 atom rocking motion coordinate ϕ_4 seen in classical simulations and (d) the concerted process of the conformation changes seen in quantum simulations from lateral views.

Detailed discussion on definition of the conformations

To confirm if the definition of the conformers given in Figure S3, does not give artificial dependence on the population given in Table 3 of the main text, we have defined the conformers by using a different definition. We defined that the distribution region of Conformers I, II, and C_2 as $\phi_3: \pm 60 \sim \pm 180° \; and \; \phi_4: \pm 15 \sim \pm 30°$; $\phi_3: -60 \sim 60° \; and \; \phi_4: \pm 15 \sim 30°$; and $\phi_3: \pm 180 \sim \pm 60° \; and \; \phi_4: -15 \sim 15°$,respectively. Schematic image of these definitions is shown in electronic supplementary information Figure S4. As given in Table S1, the population obtained using this definition give similar trends as those given in Table 3 of the main text, where the dominant population at 50 K for the quantum and classical comes from conformer I and C_2. As the temperature increases, the population of conformer II increases to be about one quarter of the population at 150 K in the quantum simulation. Furthermore, the population of the C_2 conformer becomes nearly equal between the classical and quantum simulations at 150 K. Therefore, we believe that the general trends in population obtained in the present calculation will not vary greatly with the definition in the ϕ_3 and ϕ_4 angle spaces.

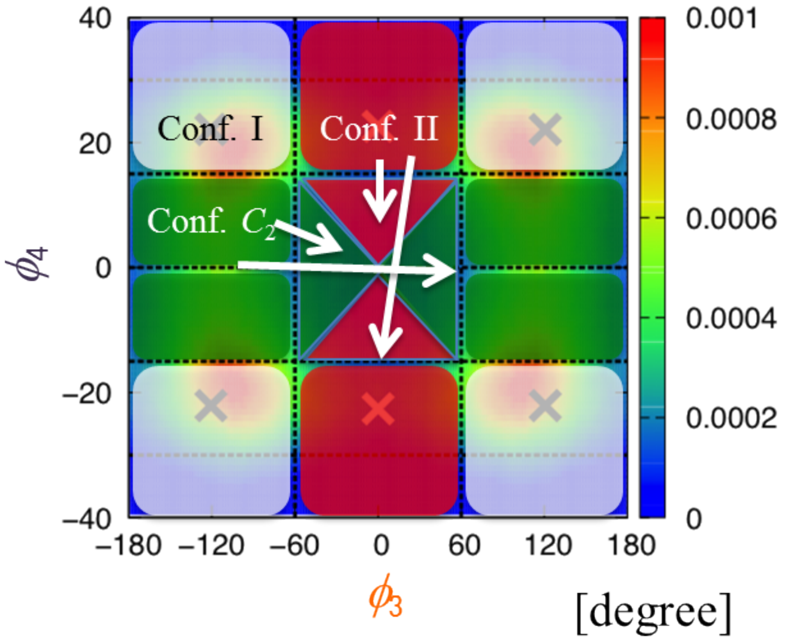


Figure S3: The definitions of the area for each conformer shown in Table 3. White, red, and green areas represent the defined areas of Conformers I, II, and C_2.

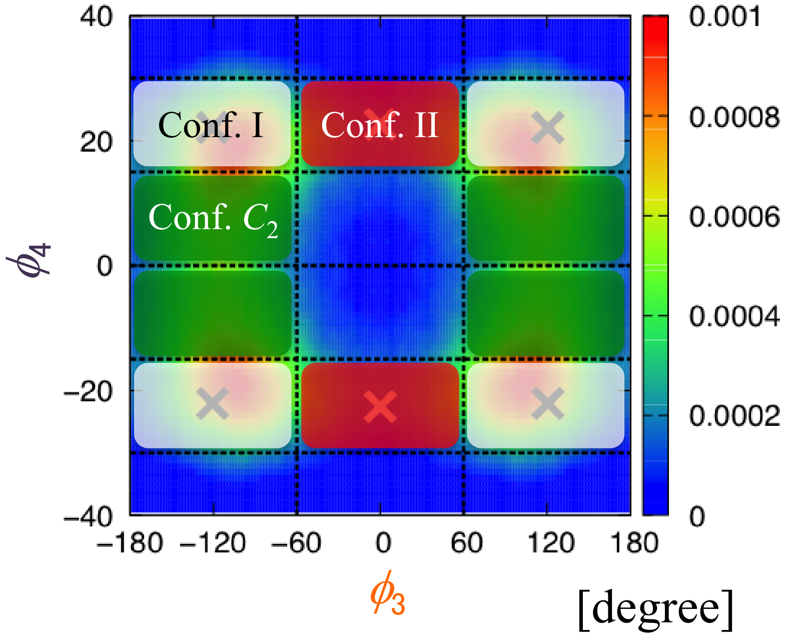


Figure S4: The definitions of the area for each conformer shown in Table S1. White, red, and green areas represent the defined areas of Conformers I, II, and C_2.

Table S1.: Populations of each conformer obtained from quantum and classical simulations at 50, 100, and 150 K. The results are just the same as Table 3 in the main text, but the probabilities are determined using the splitting given in Figure S4. Since this distribution does not use the full configuration space, they do not add up to 1. Thus the obtained population are rescaled so that they add up to “1.0”. Populations obtained from static electronic structure calculations are also shown.

%		50 K	100 K	150 K
Conformer I	Quantum	48.8	50.9	45.6
	Classical	92.1	64.6	59.2
	Static	70.0	57.8	51.9
Conformer II	Quantum	10.1	20.6	22.8
	Classical	3.0	11.1	15.3
	Static	30.0	42.2	48.1
Conformer C_2	Quantum	41.1	28.5	31.6
	Classical	4.9	24.3	25.5
	Static	-	-	-

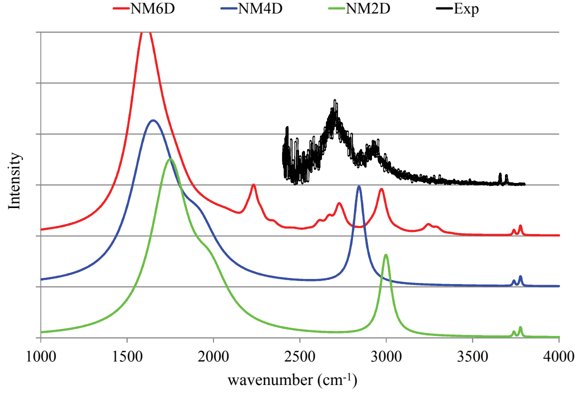
Details concerning the vibrational calculation

The vibrational problem was solved by diagonalizing the Hamiltonian matrix represented by the discrete variable representation (DVR) of the harmonic oscillator basis functions. We used the 6 normal modes (NM's) give in Fig 2 of the main text, and we calculated 7 grid points for each degree of freedom, except for the two van der Waals (VDW) stretching modes, in which we used 10. Therefore for the NM2D, NM4D, and NM6D calculation we performed single point calculation for the energy and dipole moment on 49, 2401, and 2.4×10^5 grid points. The large size Hamiltonian matrix was diagonalized using the iterative diagonalization procedures, Lanczos and Davidson methods. Using the obtained eigenvalues, eigenvectors and DMF, the integrated absorption intensities (km/mol) between the initial ground state, Ψ_0, and the vibrational excited states, Ψ_f, were calculated by,

$$A(\nu) \;=\; \frac{8N_A\pi^3}{300000\;hc}\,|<\Psi_0\,|\,\hat{\boldsymbol{\mu}}\,|\,\Psi_f>|^2\,\tilde{\nu}_{0f} \;=\; 2.506\,|\boldsymbol{\mu}_{0f}\,|^2\,\tilde{\nu}_{0f} \qquad (2),$$

where $\hat{\boldsymbol{\mu}}$ is the dipole moment function in Debye, $\tilde{\nu}_{0f}$ is the transition energy in cm^{-1} and $|\boldsymbol{\mu}_{0f}\,|$ is the absolute value of the transition moment vector.

(a) Conformer II



(b) C_2 isomer

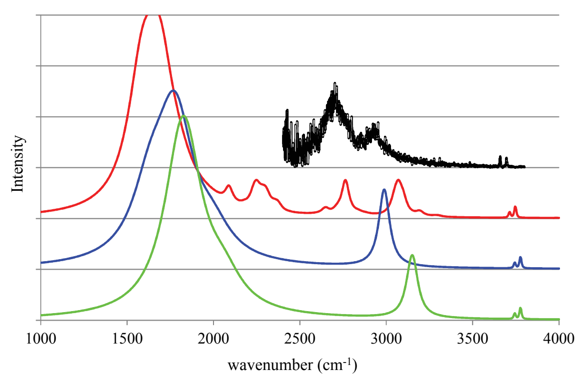


Figure S5: The theoretical vibrational spectra of (a) Conformer I and (b) C_2 isomer calculated by 2D, 4D, and 6D models are represented by green, blue and red lines, respectively. The experimental spectra of Johnson and coworkers, is also given in black lines.

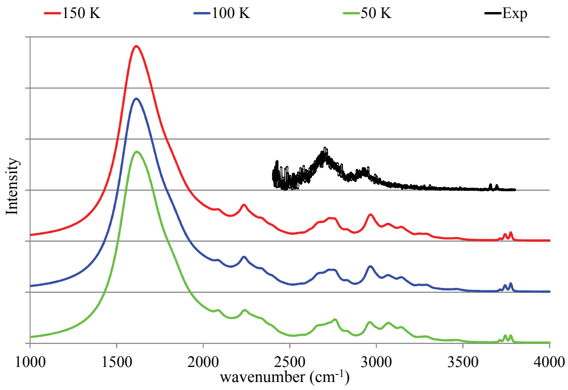


Figure S6: Vibrational spectra for OH-$(H_2O)_2$, calculated using the 6D model with the population calculated by PIMD methods. Results for 50, 100 and 150 K are given in green, blue and red lines. The experimental spectra of Johnson and coworkers, is also given in black lines.

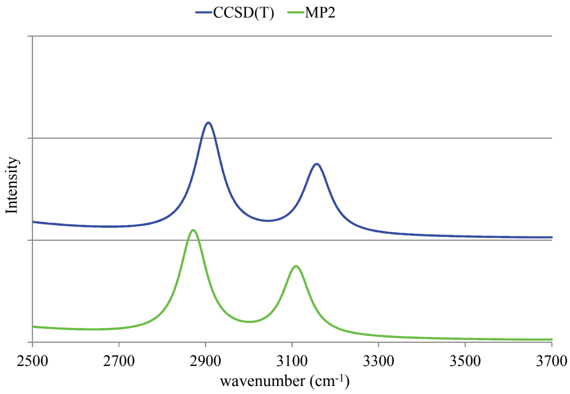


Figure S7: Vibrational spectra of conformer I calculate using the 4D model with the potential energy surface calculated by MP2 and CCSD(T) are given in green and blue lines for the region corresponding to the IHB OH stretching overtone.

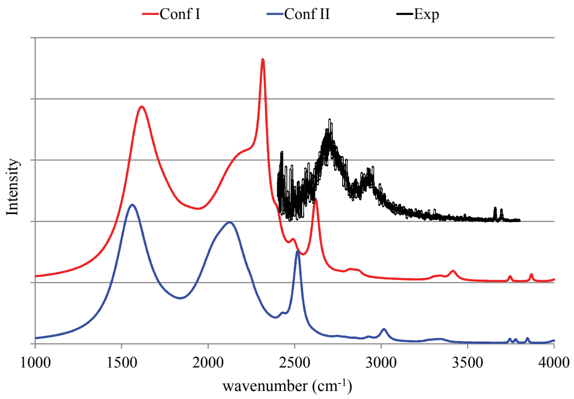


Figure S8: Vibrational spectra calculate using the vibrational perturbation theory for conformer I and II are given in red and blue lines, respectively. The experimental spectra of Johnson and coworkers, is also given in black lines.