## Supporting Information for

## Non-Born-Oppenheimer Molecular Dynamics Observed by Coherent Nuclear Wave Packets

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# **1.** NUV pump-visible probe transient absorption (TA) experiment setup with a temporal resolution of 11 fs.

The optical layout of this experiment is represented in Figure S1. The output of a Ti:sapphire amplifier (1 kHz, 0.6 mJ per pulse) is focused into a 1 m-long hollow-core fiber with a diameter of 200 µm placed in a Ne gas-filled chamber. The Ne gas was flowed from the beam input side to the output side by a mass-flow controller with a flow rate of 50 cc/min. The gas flow generates a pressure distribution in the hollow-core so that the pressure gradually increases from the input side to the output side, and the pressure at the output side of the chamber was 2.1 bar. The gas flow eliminates unexpected impurities in the chamber, and the pressure distribution enhances the selfphase modulation efficiency by reducing unnecessary natural broadening by Ne gas. The details about the supercontinuum generation with a noble gas are described elsewhere.<sup>1-2</sup> The supercontinuum output was compressed by a set of double-angle multilayer mirrors,<sup>3</sup> and a wedge prism pair. A small portion of the supercontinuum, which was reflected from a wedge prism, was used as probe beam, and the other portion was used to generate the second harmonic pump beam using a 20 µm-thick BBO crystal. A UV chirped mirror pair not only separates the pump beam from the fundamental beam but also compresses it. The spectral width and tuning range of the pump was decided by the spectral bandwidth of the UV chirped mirrors in Figure S1. The pulse energy of the pump beam was reduced from 300 nJ to 10 nJ by rotating the optic axis of the BBO crystal to avoid high-order processes at the sample. The pulse energy of the probe was < 200 pJ at the sample position. The pump and probe spectra at the sample position are presented in Figure 1b. The detection wavelength was chosen to be the saddle point of the red or blue side of the stimulated emission, at which the vibrational oscillations are intense.<sup>4</sup> We chose the red side of the emission spectra of 10-hydroxybenzo[h]quinoline (HBQ) and 2-(2'-hydroxyphenyl)benzothiazole (HBT) to measure wave packet oscillations to avoid the contributions of excited-state absorption at the blue sides of the emission spectra. The time resolution of the experiment was about 11 fs, which is shown and explained in Figure 1e, based on the impulsive Raman spectrum of ethanol (Figure S2).

HBQ and HBT were purchased from TCI (Tokyo Chemical Industry, Co.) and used without further purification. The absorbance of the samples was 0.4 in ethanol for the thickness of 100  $\mu$ m. The samples were flowed continuously with a wire-guided flow cell<sup>5</sup> to minimize photo-

degradation. In this TA setup, the Rayleigh length at the sample is longer than the thickness of the sample (100  $\mu$ m) due to the long focal length (30 cm) of the focusing optics. Thus, the probe spectrum should show not only the resonant response of the sample but also the non-resonant response of the cell-wall, in case we used a typical flow cell. The use of the wire-guided cell enabled us to eliminate the non-resonant response of the cell wall.



**Figure S1**. BB: broadband, CM: chirped mirror, HS: Harmonic separator, FS: fused silica window. The blue line indicates the optical path of the pump beam. The pump is generated at the BBO crystal via second harmonic generation of the supercontinuum light, and compressed by a UV CM pair and a FS window. A small portion of the supercontinuum was chosen for the probe beam.



**Figure S2**. The Raman spectra of ethanol measured with the TA setup described in Figure S1 (red) and spontaneous Raman spectrum of ethanol (black). The spontaneous Raman spectrum is calibrated by the time resolution of TA with the calibration factor of  $\exp[-(\pi\Delta t v)^2/4\ln 2]$ , where v and  $\Delta t$  are the frequency and pulse width in full-width at half-maximum, respectively.

Nonpolar aprotic solvents are typically used for ESIPT study because of the possibility of intermolecular hydrogen bonding with solvent, which may disrupt ESIPT.<sup>6</sup> In this study, we used a wire-guide sampling system to achieve the highest time-resolution and high signal to noise ratio by eliminating scattering and the non-resonant response from the cell windows. Cyclohexane that we normally have used were not compatible with the wire-guide sampling apparatus. However, we believe that the intermolecular hydrogen bonding is nearly absent for HBQ and HBT in ethanol. It was reported that the ESIPT rates and coherent vibrational spectra (CVS) of HBQ and HBT are the same in both cyclohexane and methanol.<sup>7</sup> This indicates that the intermolecular hydrogen bonding solvent methanol. Because ethanol is less polar and shows weaker hydrogen-bonding ability than methanol, the possibility of intermolecular hydrogen bonding between HBQ (and HBT) and ethanol can be neglected.

#### 2. Coherent vibrational spectrum (CVS) simulation in non-BO regime.

When a molecule is resonantly excited by an ultrashort optical pulse, a coherent wave packet is generated on the excited state of the molecule because of the different gradients of the groundand excited-potential energy surfaces (PESs). The oscillation amplitude of each vibrational mode in the coherent nuclear wave packet is determined by the Huang-Rhys factor. Conventionally, the Huang-Rhys factor can be calculated semi-classically by comparing the equilibrium configurations of the ground and excited states, as described in scheme **1**. In scheme **2**, we numerically calculated the gradient of the excited-PES for the molecular configuration optimized at the ground state to describe the propagation of nuclear wave packet trapped in the E<sup>\*</sup> surface. The energy minimum geometry of E<sup>\*</sup> ( $q_{E^*,0}$ ) is calculated numerically by propagating all the vibrational modes of E at  $q_{E,0}$  with an approximation that the normal modes of E and E<sup>\*</sup> are the same. Then the position ( $q_{E^*}(t)$ ) and the momentum ( $p_{E^*}(t)$ ) of an initial nuclear wave packet on the E<sup>\*</sup> surface can be expressed as

$$\boldsymbol{q}_{E^{*}}(t) = \boldsymbol{q}_{E,0} + \sum_{i=1}^{N_{v}} \delta_{E,i} \cdot e^{-\left(\omega_{E^{*},i} \Delta t_{p}/2\pi\right)^{2}} \left(1 - \cos\left[\omega_{E^{*},i}t\right]\right) \hat{v}_{E^{*},i}, \qquad (S1)$$

and 
$$\boldsymbol{p}_{E^*}(t) = \sum_{i=1}^{N_v} \omega_{E^*,i} \delta_{E,i} e^{-(\omega_{E^*,i} \Delta t_p/2\pi)^2} \sin \left[ \omega_{E^*,i} t \right] \hat{v}_{E^*,i},$$
 (S2)

where  $\hat{v}_{E^*,i}$  is the unit vector of the *i*-th vibrational coordinate.  $\delta_{E,i}$  is the geometrical displacement between  $\boldsymbol{q}_{E^*,0}$  and  $\boldsymbol{q}_{E,0}$  projected on the *i*-th vibrational mode (black lines in Figure S3). The Gaussian functions in Eqs. (S1) and (S2) consider the pulse duration of the pump pulse, where  $\Delta t_p$  were 11 fs in full-width at half-maximum. The pump pulse cannot generate coherences at the vibrational modes with the period shorter than  $\Delta t_p$ . Thus, the amplitude of the wave packet is attenuated by the Gaussian functions in Eqs. (S1) and (S2). Subsequently, the propagating wave packet suffers from excited-state intramolecular proton transfer (ESIPT) with a specific probability, which corresponds to the time-dependent coupling strength. The configuration of the proton transferred  $E^*(\boldsymbol{q}_{E^*,PT}(t))$  is given as

$$q_{E^*,PT}(t) = q_{E^*}(t) + q_{PT}(t)$$
. (S3)

 $q_{PT}(t)$  describes the proton motion during ESIPT. The electronic structure changes as soon as ESIPT completes, which implies an abrupt change in the gradient of PES. Then, the vibrational modes of E<sup>\*</sup> constructing the nuclear wave packet should be expanded into the vibrational modes of K<sup>\*</sup>. A mode-mixing matrix  $\hat{M}$ , <sup>8</sup> which represents the transformation matrix between the vibrational coordinates of E<sup>\*</sup> ( $\hat{v}_{E^*,i}$ ) and K<sup>\*</sup> ( $\hat{v}_{K^*,j}$ ), is used to transform from  $q_{E^*,PT}(t)$  to  $q_{K^*}(t)$ and  $p_{E^*}(t)$  to  $p_{K^*}(t)$ , which are the functions of  $\hat{v}_{K^*,j}$ .

$$\boldsymbol{q}_{K^*}(t) = \sum_{j=1}^{N_v} \sum_{i=1}^{N_v} \left[ \left\{ M_{ji} \left( \left( \boldsymbol{q}_{E^*}(t) - \boldsymbol{q}_{E,0} \right) \cdot \hat{\boldsymbol{v}}_{E^*,i} \right) \right\} + \delta_{K,j} \right] \hat{\boldsymbol{v}}_{K^*,j} , \qquad (S4)$$

and 
$$\boldsymbol{p}_{K^*}(t) = \sum_{j=1}^{N_v} \sum_{i=1}^{N_v} M_{ji} \left( \boldsymbol{p}_{E^*}(t) \cdot \hat{\boldsymbol{v}}_{E^*,i} \right) \hat{\boldsymbol{v}}_{K^*,j}.$$
 (S5)

Note that the total energy is not conserved in the vibrational coordinate transformation (Eqs. (S4) and (S5)) because of the electronic-to-vibrational energy conversion.  $\delta_{K,j}$  is the displacement between  $q_{E^*,PT}(t)$  and  $q_{K^*}(t)$  projected on the *j*-th vibrational coordinate of K<sup>\*</sup> (red lines in Figure S3). Because TA visualizes molecular dynamics through the transition energy of a molecular ensemble, the amplitude of the wave packet measured in TA should be proportional to the total energy of the oscillating vibrational modes. Then the amplitude,  $A_{K^*,j}(t)$ , and phase,  $\theta_{K^*,j}(t)$ , of the wave packet can be calculated from the Eqs. (S4) and (S5) as

$$A_{K^{*},j}(t) = \frac{1}{2} \left( \mu_{K^{*},j} \omega_{K^{*},j}^{2} \left( \left( \boldsymbol{q}_{K^{*},j}(t) - \boldsymbol{q}_{K^{*},0} \right) \cdot \hat{v}_{K^{*},j} \right)^{2} + \frac{\left( \boldsymbol{p}_{K^{*}}(t) \cdot \hat{v}_{K^{*},j} \right)^{2}}{\mu_{K^{*},j}} \right) e^{-\left( \omega_{K^{*},j} \Delta t_{pr}/2\pi \right)^{2}}, \quad (S6)$$

and 
$$\theta_{K,j}(t) = \tan^{-1} \left( \frac{\boldsymbol{p}_{K^*}(t) \cdot \hat{v}_{K^*,j}}{\mu_{K^*,j} \omega_{K^*,j} \left( \boldsymbol{q}_{K^*}(t) - \boldsymbol{q}_{K^*,0} \right) \cdot \hat{v}_{K^*,j}} \right) + \pi H \left[ \left( \boldsymbol{q}_{K^*}(t) - \boldsymbol{q}_{K^*,0} \right) \cdot \hat{v}_{K^*,j} \right], \quad (S7)$$

where H is the Heaviside step function. A Gaussian function in Eq. (S6) considers the low-pass filtering effect due to the pulse duration of the probe pulse as similar as the low-pass filtering effect

of pump pulse in Eqs. (S1) and (S2). Note that Eqs. (S6) and (S7) describe a single molecular vibration. The measured wave packet oscillation must be represented as a function of pump-probe time-delay (t' in Eq. (2)), because TA data show the ensemble-averaged wave packet. In Eq. (2), we used the experimentally measured enol depopulation function as the proton transfer probability density to obtain the ensemble-averaged wave packet.



**Figure S3**. The vibrational displacement between E and E<sup>\*</sup> ( $\delta_E$ , black), and between E<sup>\*</sup> and K<sup>\*</sup> ( $\delta_K$ , red) for HBQ (top) and HBT (bottom), respectively. The displacement of each mode is converted to the vibrational reorganization energy for convenience.

**3.** Effect of proton motion during ESIPT on the coherent vibrational spectrum (CVS) simulation.



**Figure S4.** (a) The theoretical (black) and experimental (red) coherent vibrational spectra (CVS) of HBQ. The theoretical spectra are calculated by scheme **2** described in the main text. The contribution of OH stretching mode is removed for the dashed line. The experimental data were analyzed by the linear prediction and singular value decomposition to eliminate the contribution of out-of-plane modes and the solvent Raman peaks. (b) The Dushinsky (mode mixing) matrix of HBQ. The dashed lines indicate two vibrational modes of K\* representing the non-BO character of the ESIPT in HBQ.

Figure S4a shows two CVS simulation results calculated based on scheme 2 described in the main text. The dashed line represents the simulation result with setting  $q_{PT}(t)$  in Eq. (S3) as zero, whereas the black line assumes that the  $q_{PT}(t)$  is the same to the displacement of the OH stretching mode of E<sup>\*</sup> ([64] 3191 cm<sup>-1</sup>) with respect to the ESIPT, where the number in the rectangular bracket indicates the index of a vibrational mode. Note that the amplitude of [5] 251 cm<sup>-1</sup> mode of K<sup>\*</sup> is dramatically reduced by removing the contribution of proton motion. This indicates that the vibrational coherence of the [5] 251 cm<sup>-1</sup> mode is generated by the proton transfer process. The mode-mixing matrix (Figure S4b) shows strong coupling between the [64] 3191 cm<sup>-1</sup> mode

of  $E^*$  and [5] 251 cm<sup>-1</sup> mode of K<sup>\*</sup>. It can be concluded that the OH stretching motion is closely related to the proton transfer, because the contribution to the [64] 3191 cm<sup>-1</sup> mode is dominantly coming from the OH stretching motion.

Frequency	Mode	Frequency	scheme 1	scheme 2
exp. $(cm^{-1})$	index	calc. $(cm^{-1})$	$\lambda_i (\mathrm{cm}^{-1})$	$\lambda_i (\mathrm{cm}^{-1})$
237	5	251	3	170
396	9	402	116	114
543	13/16	527/565	35/92	26/82
688	19	683	19	109
794	25	808	0.5	8
842	27	853	55	26
990	32	993	64	32
1205	39	1185	31	23
1346	42/43	1305/1314	24/19	43

4. Description of the nuclear motions of the assigned vibrational peaks of HBQ.

**Table S1.** The vibrational reorganization energies ( $\lambda_i$ ) predicted by scheme 1 and 2 are also presented.  $\lambda_i$  predicted by scheme 2 is the peak value of the *i*-th mode in CVS<sub>2</sub>.

The 396 cm<sup>-1</sup> mode modulates mostly the distance between the pyridine and phenol groups, and the 688  $cm^{-1}$  mode is associated with the ring-breathing motion. Both the 396 and 688  $cm^{-1}$ modes vary the distance between the oxygen and nitrogen atoms significantly. The 543 cm<sup>-1</sup> mode is associated with an asymmetric ring-breathing motion, does not change the distances between the oxygen, nitrogen, and proton. High-frequency peaks at 842, 990, 1205, and 1346 cm<sup>-1</sup> and a broad feature around 1500 cm<sup>-1</sup> are observed owing to the high temporal resolution of the current experiment. The 842 and 990 cm<sup>-1</sup> modes involve asymmetric ring-breathing motions, the 1205 cm<sup>-1</sup> mode is a combination of rocking and scissoring of the hydrogens in the aromatic ring, and the 1346 cm<sup>-1</sup> mode involves in-plain proton bending together with C=O stretching. The broad peak around 1500 cm<sup>-1</sup> represents a superposition of the C-C stretching modes of the aromatic rings. The contribution of the N–H stretching is significant in the 842, 990, and 1346 cm<sup>-1</sup> modes, whereas it is negligible in the 1205 cm<sup>-1</sup> mode. Because the vibrational peaks appearing in CVS<sub>1</sub> reflect the geometrical difference between  $q_{E,0}$  and  $q_{K^*,0}$ , whereas CVS<sub>2</sub> reflects the geometrical differences between  $q_{E,0}$  and  $q_{E^{*},0}$  and between  $q_{E^{*},0}$  and  $q_{K^{*},0}$ , the vibrational modes predicted by both simulations with similar amplitudes should have small displacements between  $q_{E,0}$  and  $q_{E^*,0}$ along those modes.



**Figure S5.** Displacement vectors of the vibrational modes of (a, c) HBQ and (b, d) HBT, which are predicted to appear at the TA data by the scheme **2** only. The frequencies in the parentheses are the experimental values. The gray, white, red, blue and yellow colors indicate C, H, O, N and S atoms, respectively.

molecule		HBQ	HBT
Enol form	НОМО		
	LUMO		
Keto form	LUMO		

**Figure S6.** Molecular orbitals of HBQ and HBT. The molecular structure and molecular orbitals of HBQ (a - c) and HBT (d - f). The HOMOs (a, d) and LUMOs (b, e) of the enol-form HBQ and HBT. (c, f) The LUMOs of the keto-form HBQ and HBT.

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