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Femtosecond electronic relaxation and real-time vibrational dynamics in 2’-hydroxychalcone†

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Abstract: Femtosecond ultrafast electronic relaxation and vibrational dynamics in 2’-hydroxychalcone after deep ultraviolet (DUV) excitation were observed by two types of pump-probe spectroscopy experiments, i.e., DUV-pump pulse and visible-broadband-probe pulse (DUV/Vis) experiments and DUV-pump and DUV-probe (DUV/DUV) pulses experiments. Time-dependent density functional theory (TDDFT) calculations were performed to elucidate relaxation dynamics from the third singlet electronic excited state S₃. The DUV/Vis experiments and TDDFT calculations have disclosed the ultrafast dynamics of internal conversion from the initial S₃ state (τ₁ ≈ 35 fs) towards the S₁ state via a rapid process through the S₃/S₂ conical intersection and proton transfer [OH: τ₂(H) ≈ 93 and OD: τ₂(D) ≈ 164 fs] before deactivation through the S₁/S₀ conical intersection (τ₃ ≈ 690 fs). Thanks to the ultrashort pump and probe pulses, real-time observation of vibrational modes coupled to the electronic excitation was realized providing both amplitudes and phases. Spectrogram analyses were performed based on the real-time spectra obtained by the DUV/Vis experiments, in which instantaneous vibrational frequencies reflecting molecular structural change after the impulsive excitation were visualized. The vibrational frequency of central C=C bond stretch decreases from ~1600 cm⁻¹ to ~1560 cm⁻¹ in about 200–500 fs and recovers by ~550 fs. Normal mode analyses along the decay path support the observed variation of the C=C stretching frequency. The temporal weakening of the central C=C bond is connected with the angle of the two aromatic rings which flip back to the initial conformation.

⁎ Electronic supplementary information (ESI) available: Calculated geometries, energies and normal modes at crucial points, recorded Raman spectra of 2’HC and formalisms for obtaining two-photon absorption cross-sections and molar absorption coefficients of transient species are supplied. See DOI: xxx.
Keyword:
2'-hydroxychalcone, femtosecond time-resolved pump-probe spectroscopy, TDDFT, conical intersection
1. Introduction

Ultrafast time-resolved (TR) spectroscopy is a powerful tool to investigate photochemical/physical dynamics of molecular systems. This paper reports on ultrafast dynamics of deep-ultraviolet (DUV) excited 2'-hydroxychalcone (2'HC), which undergoes internal conversion involving proton transfer in the excited states. Photo-induced spectral changes are monitored based on the pump-probe scheme at different probe wavelengths. The real-time vibrational dynamics is studied by the femtosecond time-resolved spectroscopy (TRS).

Chalcone compounds, most notably hydroxychalcone derivatives, are abundant in nature and reported to show rich pharmacological activity such as antibacterial and antioxidant activities. In particular, 2'HC undergoes cis-trans photoisomerization and subsequent dehydration reaction to give flavanone, as shown in Fig. 1(a), where the OH group plays an important role. The photochemistry of 2'HC analogues has been studied extensively in the last three decades. Favanone is an oxidized form of flavan, which is the basic skeleton of the vast family of flavonoid. The flavonoid family includes many kinds of metabolites of plants, such as flavanone, flavone, catechin, and anthocyanidin. Glycosides of anthocyanin, anthocyanin, are origins of various colours of flowers and fruits under specific pH conditions. Therefore, a TR study on chalcone compounds would provide a basic demonstration on the photodynamics in natural organic chemistry.

The photodynamics of the 2'HC compounds has been studied previously by several research groups using time-dependent or transient absorption experiments. Matsushima et al. have systematically studied the photocyclization processes of substituted 2'HC in various solvents using excitation by a high-pressure Hg lamp, and determined the quantum yields of photoproducts. Chou et al. have also studied transient species using UV-laser excitation, and Norikane et al. have reported nanosecond flash photolysis experiments in various solvents together with semi-empirical calculations. These studies have clarified that the photochemical reactions in Fig. 1(a) are initiated by the excited-state intramolecular-proton transfer (ESIPT) followed by the S\textsubscript{1}-T\textsubscript{1} intersystem crossing. However, the TR absorption spectra recorded in these experimental studies are limited in the delay time range longer than ~60 ns. Any ultrafast dynamics of 2'HC has not been elucidated in picosecond or femtosecond time regimes. The available semi-empirical calculations are only for the S\textsubscript{1} and T\textsubscript{1} states, and ab initio quantum chemical calculations are desired at sophisticated levels.

With femtosecond time resolution, the ultrafast electronic relaxation processes and vibrational wavepacket dynamics can be observed simultaneously. Especially, the latter allows direct observation of the amplitudes of vibrational modes which are coupled to the impulsively-triggered electronic transition by a femtosecond pulse. This methodology is the real-time vibrational spectroscopy (RTVS) and advantageous over conventional TR vibrational spectroscopies including TR infrared (IR)-absorption and TR Raman spectroscopies. These cannot provide vibrational phase information. Furthermore, RTVS can provide the information of ‘instantaneous’ vibrational frequencies via
spectrogram analysis (SA) using gated Fourier transform (FT) of the real-time traces. These methods, RTVS and SA, clarify various ultrafast phenomena in photochemical processes including *cis-trans* isomerization, \(^9\) Claisen rearrangement, \(^10\) Varieties of photophysical processes have also been observed such as dynamic vibrational mode coupling, \(^11\) chirping of molecular vibrational frequency, \(^12\) dynamic Duschinsky rotation \(^13\) and time-dependent Herzberg-Teller coupling. \(^14,15\)

In contrast to 2′HC, 2-hydroxychalcone (2HC) analogues which possess the OH group at the other ring [see Fig. 1(a) for atom numbering] undergo cyclization to give strongly-coloured flavylvium (anthocyanidin) compounds. \(^16,17\) In general, the chalcone analogues exhibit UV absorption at about 390 nm whereas the flavylvium analogues show absorption in a visible (Vis) region around 540 nm. Related to the cyclization reaction which gives the basic unit of anthocyanidin, Pina and co-workers have studied the photodynamics of a 2HC analogue, 4-(dimethylamino)chalcone, using picosecond TR absorption spectroscopy, \(^17\) and proposed a solvent-dependent photoisomerization process involving proton-transferred intermediate species that are produced after *trans-cis* isomerization. The proton transfer is mediated by solvent water.

The distinct absorption change upon cyclization from chalcone to flavylvium analogues can be used as a molecular switching system. \(^18\) Namely, *trans*-2-hydroxy-4′-methoxy-chalcone photoisomerizes to the *cis* form (‘write’ by photons), and preferentially interconvert towards 4′-methoxy-flavylvium cation at low pH < 1 (‘lock’). The different UV (~390 nm) and Vis (~540 nm) absorption bands of the chalcone and flavylvium compounds prevent a reverse photoreaction. The written state is stable unless pH is increased. The hydration reaction by increasing pH > 1 will ‘unlock’ the cationic state, and the *cis-trans* backward reaction will ‘erase’ the switched state.

The radiative and non-radiative decay mechanisms of other chalcone derivatives have also been studied extensively, \(^19-21\) in which locally excited (LE) and twisted intramolecular charge-transfer (TICT) states are involved. The fluorescence quantum yields and energy levels of all-planar emissive LE state (E*), C-C bond-twisted more-emissive TICT polar state (A*) and C≡C bond-twisted less-emissive biradical state (P*) have been discussed in relation with conical intersections between them. \(^20\) Mechanistic and solvatokinetic effects which stem from the C≡C bond twist have also been discussed. \(^19,20\) The internal rotation in the ground and excited states of substituted stilbene \(^22\) and ketone \(^23\) as well as chalcone and C=C/C-bridged analogues \(^24,25\) have been basic model systems in the photochemistry of \(\pi\)-conjugated systems.

In this paper, we present multichannel TR absorption spectroscopy experiments in the femtosecond time regime for *trans*-2′HC. After 2′HC absorbs a 9-fs DUV pump pulse, it undergoes photochemical/photophysical processes until it returns to the electronic ground state or reaches flavanone through the multiple processes. \(^4\) The DUV pulse duration of 9 fs is the world shortest ever used for TR spectroscopy except in our previous two papers. \(^26,27\) Based on experimental and theoretical results, we discuss the ultrafast relaxation and vibronic processes on the electronic excited state surfaces. We demonstrate experimental determination of wavelength-dependent lifetimes and absolute molar
absorption coefficients of transient species. The two types of experiment are performed; the DUV pump/Vis probe (实验 A) and DUV pump/UV probe experiments (实验 B).

2. Experimental

Our experimental setup has been reported previously.\textsuperscript{26,28,29} Briefly, the ultrafast TR difference absorption/emission spectra [$\Delta A(\lambda, t_d)$] are recorded using a polychromator coupled to a 128-channel lock-in amplifier (MCLIA) and a piezo-controlled optical delay stage. The multi-channel detection at 128 different probe wavelengths $\lambda$ at delay time $t_d$ accumulates the difference absorbance signal as $\Delta A$ with pump on and off. Thus, two-dimensional (2D) spectra $\Delta A(\lambda, t_d)$ of RTVS are obtained as contours on the 2D map. The $\Delta A$ spectra in the Vis or DUV regions monitor ultrafast electronic relaxations and real-time amplitudes of vibrations coupled to the corresponding electronic states at relevant $t_d$.

The multiplex capability for different wavelength has experimental advantages over single-wavelength detection by several factors, since it can trace electronic and vibrational dynamics at the same time. The advantages are listed in detail as follows.

1. Experimental errors due to inevitable laser intensity fluctuations and spectral change due to various non-linear optical processes in the DUV pulse generation stage can be significantly reduced.
2. Data taking time for the multichannel experiments is reduced by more than 100 times from single channel experiments.
3. Mechanical and temperature instability that a large number of optical components in the system could suffer from can be minimized.

The intensity fluctuation and spectral change of the ultrashort DUV pulse system in (1) arises from the multiple nonlinear optical (NLO) pulse generation mechanisms including the self-phase modulation, self-focusing, stimulated Raman gain and loss, the parametric four-wave mixing and supercontinuum generation.\textsuperscript{30}

Further advantage is that the 2D map of $\Delta A(\lambda, t_d)$ can elucidate both behaviors of intensity dynamics and spectral change. That is, quantitative analyses of the $\Delta A$ contour map allow reliable determinations of the ultrafast dynamics in case of ‘cross-talk’ between the intensity change at some specific spectral components (we call this vertical change) and spectral shift (horizontal change). Single-channel analyses cannot discriminate such a spectral change from a temporal change.

A 798 nm fundamental-frequency output from a Ti: sapphire regenerative amplifier (35 fs, 798 nm, 3 mJ, 1 kHz) is separated into two beams for the purpose of generating the DUV pump pulse (260–280 nm) and the Vis broadband probe pulse (500–650 nm) in experiment A. The DUV pulse is used also as the probe pulse in experiment B as mentioned above.

One of the two split fundamental-frequency pulses is used to generate the DUV pump pulse as follows. It is separated into two beams again. One beam is frequency doubled in a BBO (beta barium borate, $\beta$-BaB$_2$O$_3$) crystal to produce 399 nm pulse and then negatively chirped by diffraction with a
grating pair two times. The other beam is focused into a Kr-filled hollow-core fiber and converted to positively-chirped near-infrared (NIR) supercontinuum by the self-phase modulation. The amount of positive chirp is adjusted with chirped mirrors. Both of the beams are finally overlapped spatially and temporally in an Ar-filled hollow core fiber, and converted to a chirped DUV pump pulse based on the parametric four-wave mixing scheme. The maximal spatial overlap of the beams in the Ar-filled hollow core fibers is attained with piezo-controlled feedback mirrors by utilizing the intensity of reduced DUV pulse as an error signal. The negative group-velocity dispersion of the DUV pump pulse is compensated by travelling through air, resulting in nearly FT-limited FWHM (full width at half maximum) duration of 9 fs. The time resolution of the TR measurements is estimated to be ~12 fs from time convolution of the pump and probe pulses.

The other separated fundamental-frequency pulse is spectrally broadened by focusing into a 2-mm thick sapphire plate and converted to a Vis-to-NIR broad-band probe pulse by supercontinuum generation including self-phase modulation and other NLO processes. The intensity and spectrum are optimized to obtain a stable clean ultrashort pulse by adjusting a variable neutral density filter placed in front of the sapphire plate.

The multichannel detected probe signal is recorded at each delay time $t_d$. The optical delay is controlled stepwise by a translation stage that holds a pair of mirrors perpendicularly. The probe pulse after a sample cell is guided through a bundle fiber towards a polychromator, in which the probe pulse is dispersed by a grating [Vis: 300 grooves/mm and 500-nm bandwidth (BW); DUV: 1800 grooves/mm and 300-nm BW]. The multi-colour signals are detected by 128 avalanche photodiodes that are aligned parallel to the spectral dispersion. The output signal is coupled to the 128-channel multi-channel lock-in-amplifier (MCLIA) through a multi-mode fiber bundle. The MCLIA is operated with the time constant of 3 s. The signals are accumulated as a 2D map of difference absorbance $\Delta A(\lambda, t_d)$ using a mechanical chopper operated at 1 kHz. The lock-in detection is performed in synchronous with the chopper through a low-pass filter.

A methanol solution sample of trans-2’HC is spewed into a 0.5-mm thick cell which is connected to a circulating pump through a tube. This setup makes it possible to avoid optical or thermal damages. The circulation speed is adjusted for a sample solution in a focused volume not to experience double excitations. The concentration of the sample is 0.1 and 0.01 mol/L for the Vis and DUV probes, respectively. The latter concentration is optimized for the transmitted probe DUV light to be intense enough for detection with a high signal to noise ratio. Typical pulse energies of the pump and probe are 90 and 10 nJ, respectively. The static electronic absorption spectra of 2’HC are recorded using a UV/Vis spectrometer (Shimadzu UV-3101). The H/D substitution of deuterated 2’HC is confirmed by NMR experiments in CCl$_4$ solutions.

The group velocity dispersion (GVD) in any media broadens the pulse duration. However, as long as the penetration depth of the pump pulse into the media (solution in this case) is sufficiently small, the time resolution of $\Delta A$ is effectively unchanged since the induced ultrafast phenomena that contribute
to ΔA take place within the depth. The thickness of the cell can thus be arbitrarily selected if the probe pulse is intense enough to be detected after passing through the cell. In the present experiments the DUV pump or DUV probe pulse is strongly absorbed by 2′HC, whereas the Vis probe pulse is transparent to the solvent and 2′HC and can be absorbed only by transient species.

The intensity $I$ of light in the linear absorption regime is attenuated exponentially as a function of the path length $l$, and the penetration depth $\delta_p$ is defined to be the inverse of the absorption coefficient $\alpha$:

$$I(l) = I_0 e^{-\alpha l},$$  \hfill (1)

$$\delta_p = \frac{1}{\alpha}. \hfill (2)$$

Comparison with the Lambert-Beer law gives a relation of $\delta_p$ with the molar absorption coefficient $\varepsilon$ and concentration $c$:

$$A = -\log_{10} \left( \frac{I}{I_0} \right) = \varepsilon cl,$$  \hfill (3)

$$\delta_p = \frac{1}{\varepsilon c \ln 10}. \hfill (4)$$

Using the expression of $\delta_p$ in Eq. (4), the GVD broadening of the DUV pump pulse can be estimated. The GVD of methanol is 229.76 fs²/mm and $\varepsilon$ of 2′HC is 0.50×10⁴ mol⁻¹ L cm⁻¹ at 270 nm.⁶ The shorter- and longer-wavelength edges of the pump pulse are located around 260 and 280 nm, respectively, as in Fig. 1(b). Using the concentration 0.1 mol/L of 2′HC for the Vis probe experiments, the penetration depth of the DUV pump pulse is estimated to be $\delta_p = 8.7$ and 5.8 μm at 260 and 280 nm, respectively. Corresponding GVD broadening is only 0.20 and 0.13 fs, being almost negligible. In the case of the DUV probe experiments, these values are one order magnitude larger due to the low concentration of 0.01 mol/L. Nonetheless, the broadening of the 260 and 280 nm components of the pump pulse is only 2.0 and 1.3 fs, respectively.

The total attenuation factors of the DUV probe pulse after transmitted through the 0.5 mm thickness are calculated to be 3.2×10⁻³, 1.8×10⁻³ and 0.2×10⁻³ at the wavelengths 260 nm, 270 nm and 280 nm, respectively, from the molar absorption coefficients 0.50×10⁴, 0.55×10⁴ and 0.75×10⁴ mol⁻¹ L cm⁻¹.⁶ These values correspond to the absorbance of ~3, and the attenuated probe pulse can still provide a sufficient intensity to be detected. The attenuation of the Vis probe pulse is almost negligible as noted above.

3. Computational details

Calculations of the usual linear-response time-dependent density functional theory (TDDFT)³²,³³ are performed to elucidate the molecular deformations and decay dynamics of 2′HC in the electronic
excited states after photoexcitation to the \( S_3 \) state. Critical points are optimized along the decay path departing from the initial structure (denoted by \( S_{3FC} \)) under the Franck-Condon approximation towards the conical intersection between the first excited and the ground electronic states (denoted by \( S_1/S_0 \)). The connectivity of the critical points is confirmed by following intrinsic reaction coordinates (IRC) and meta-IRCs (the steepest descent path in the mass-weighted coordinate). In the TDDFT calculations, the \( \omega B97XD \) functional\(^{35} \) is employed along with the 6-31G(d) basis set, because the \( \omega B97XD \) functional is known to be one of the best choices to describe excited states by the TDDFT calculations.\(^{36} \) As a result, the present calculations are in good agreement with the experimental observation. It is recalled that the TDDFT calculation in general provides only a qualitative description of the excited states.

Normal mode analyses are applied to several potential minima in methanol and utilized to investigate the decay dynamics and deformation components along the decay path. The \( S_0/S_1 \) geometry is optimized by using spin-flip TDDFT (SF-TDDFT) calculations.\(^{37,39} \) Also, the most energetically preferred decay channels are systematically searched by using the seam model function (SMF) / single component artificial force induced reaction (SC-AFIR) method\(^{40,41} \) with the SF-TDDFT method in the vacuum. In the SMF/SC-AFIR search, eleven atoms around C1', i.e. C1', C2', C3', C6', O11, H14, O10, C9, H13, C8 and C7 are accounted as the target atoms for the SC-AFIR scheme.\(^{42} \) In the SF-TDDFT calculations, the BHHLYP functional\(^{43,44} \) with the 6-31G(d) basis set is used.

The solvent effect on the decay path is examined for 2'HCl in methanol compared to that in the vacuum. All of the optimized structures in methanol and in the vacuum are shown in Table S1 and S2. The solvent effect is taken into account using the CPCM (conductor-like polarizable continuum model)\(^{45-48} \) TDDFT energies and gradients are computed using the Gaussian 09 program package,\(^{49} \) and SF-TDDFT energies and gradients are obtained using the GAMESS program package.\(^{50,51} \) All of geometry optimizations, meta-IRC calculations and the SMF/SC-AFIR search are performed by using a developmental version of the GRRM (Global Reaction Route Mapping) program.\(^{52} \)

### 4. Results and Discussion

#### 4.1 DUV pump – Vis-NIR probe experiments

Fig. 1(b) shows the electronic absorption spectrum of \textit{trans}-2’HC in methanol. The observed peak at \(~3.9\) eV and shoulder at \(~3.5\) eV are assigned, respectively, to the transitions from \( S_0 \) to \( S_0(\pi_2;\pi^*) \) and from \( S_0 \) to \( S_1(\pi_1;\pi^*) \) based on the calculated oscillator strengths, 0.99 for \( S_1(\pi_1;\pi^*) \), less than 0.001 for \( S_2(\pi_3;\pi^*) \) and 0.24 for \( S_3(\pi_2;\pi^*) \) in methanol. These transitions are approximately described as one-electron promotion among molecular orbitals \( \pi_1, \pi_2, \pi, \) and \( \pi^* \). The transition energies are calculated to be \(~3.81\) eV (\( S_1 \)), \(~3.96\) eV (\( S_2 \)) and \(~4.21\) eV (\( S_3 \)) in methanol. Thus, the present pump energy centered at \(~4.7\) eV (260–280 nm) is located in post resonant with the \( S_3\rightarrow S_0 \) absorption, as shown in Fig. 1(b). The present assignments are in line with the previous papers that have reported absorption and emission
spectra in various solvents for trans-2′HC, cis-2′HC and flavanone along with semi-quantitative calculations.\textsuperscript{4,6,53}

The Vis probe pulse in the energy range 1.9–2.6 eV (480–640 nm) is not resonant with the absorption from the ground state of trans-2′HC in Fig. 1(b). Therefore, negative $\Delta A$ due to bleaching of the $S_3^-\rightarrow S_0$ absorption will not appear in the Vis probe experiments. If trans-2′HC is converted to the triplet state, negative $\Delta A$ due to the Vis emission could in principle contribute in this visible range (Fig. 3 in Ref. 6). However, the time scale of the intersystem crossing is $\sim 1$ µs, which is far beyond the femtosecond time scale. Multiphoton ionization is unlikely under the present condition, since the ionization energy of aromatic molecules\textsuperscript{54} normally larger than 8 eV and the two-photon absorption crosssections of typical organic conjugated molecules are of the order of $\sigma_{\text{TPA}} = 6000 \text{ GM}$ (Göppert-Mayer unit, $10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$).

In the present study, the concentrations of the sample are $C_{\text{Vis}} = 6.02\times10^{19}$ molecule cm$^{-3}$ (0.1 mol/L) for the Vis probe experiments and $C_{\text{DUV}} = 6.02\times10^{18}$ molecule cm$^{-3}$ (0.01 mol/L) for the DUV probe experiments. Using $\sigma_{\text{TPA}}$ and $\delta_p$, the attenuation by two-photon absorbance $\Delta I_{\text{Vis}}$ of the pump pulse in the Vis probe experiments is estimated to be $\Delta I_{\text{Vis}} = 4.99\times10^{23}$ photon cm$^{-2}$ s$^{-1}$. This attenuated photon flux is negligible compared to the incident photon flux, $I_0 = 4.88\times10^{27}$ photon cm$^{-2}$ s$^{-1}$. Details are given in the Electronic Supplementary Information (ESI).

Fig. 2(a) presents a 2D difference absorption spectrum $\Delta A(\lambda, t_d)$ [or equivalent $\Delta A(\omega, t_d)$] between $S_3$-photoexcited and unexcited methanol solution of 2′HC in the delay time range from $-440$ fs to 1700 fs. The horizontal stripes on the central part of the contour map are not due to mechanical noise induced by the non-smooth stage motion which is carefully ruled out by blank-test experiment without a sample. It is attributed to temporal modulation of electronic spectra by coupled molecular vibrations that are induced impulsively by the pump pulse with duration shorter than the vibrational period. The temporal modulation of electronic transition probability between the ground and excited states is induced by the vibrational modes via vibronic coupling. From the FT of $\Delta A(\lambda, t_d)$ over a delay time range, we can obtain the vibrational frequencies of the coupled modes. The impulsively excited vibrational motion also induces the modulation of refractive index of transparent solvent by the non-resonant impulsive Raman effect. In fact, the FT of the time-dependent $\Delta A(\lambda, t_d)$ traces gives the vibrational frequencies of decaying 2′HC and the Raman-active vibration of methanol at 1035 cm$^{-1}$. Details are discussed in Section 4.8.

Fig. 2(b) shows TR difference transient absorption spectra $\Delta A(\lambda, t_d)$ at nine delay times in the probe range 1.95–2.60 eV (633–475 nm), whereas Fig. 2(c) are time dependences of difference absorbance at four wavelengths. The most prominent change in Fig. 2(b) is the abrupt decrease observed from 0 to 100 fs over almost entire frequency region. The following phenomena can be understood in terms of energy regions above and below $\sim 2.25$ eV. The intensity of the higher energy band above 2.25 eV
decreases gradually, whereas the lower energy band below 2.25 eV gains the intensity again from delay time \( t_d \approx 100 \) fs (red) and levels off towards \(-500 \) fs (green). It decreases again after \(-500 \) fs. These TRS suggest the existence of (a) a slow decreasing spectral component towards \(~1000 \) fs in the region above 2.25 V and (b) fast decreasing components in a short delay time up to \(-100 \) fs and following slower increasing components over 500–1000 fs below 2.25 eV.

To investigate the complicated behaviour more clearly, the time dependences of \( \Delta A \) are shown in Fig. 2(c) at probe photon energies 2.42 eV (512 nm), 2.33 eV (532 nm), 2.25 eV (551 nm) and 2.09 eV (594nm). The traces show remarkable differences among them. Namely, \( \Delta A \) at 2.42 eV seems to decrease with two decay constants before and after \(-200 \) fs. On the other hand, \( \Delta A \) at 2.25 and 2.09 eV display a sharp rise and fall around \( t_d = 0–100 \) fs, and a gradual increase towards \(-500 \) fs. These behaviours above and below 2.25 eV correspond to the slow process (a) and fast processes (b) mentioned above, respectively.

In principle, difference absorbance \( \Delta A \) can become positive or negative depending upon competitive contributions from absorption or stimulated emission. It can be reduced by population depletion of the initial state as well. Since \( \Delta A \) in the probe energy range of 1.95–2.60 eV does not overlap with the \( S_0 \) absorption shown in Fig. 1(b), the observed \( \Delta A \) is predominantly attributed to absorption or stimulated emission from transient excited states. The observed positive \( \Delta A \) indicates more intense absorption from the photoexcited singlet states than stimulated emission. The triplet states\(^5\) which are produced by spin flip are not involved in the present femtosecond experiments.

If multiple absorption/emission transitions spectrally overlap, it is not easy to determine whether \( \Delta A \) stems from spectral shift (horizontal change) or population change (vertical change). As a first approximation, the zeroth moment \( M_0(t) \) which defined as the frequency average by Eq. (5) is useful to evaluate the total change of \( \Delta A \),

\[
M_0'(t) = \frac{\int_{\omega_1}^{\omega_2} \Delta A(\omega, t) d\omega}{\omega_2 - \omega_1}.
\]  (5)

However, \( \Delta A \) includes optical frequency dependence of the transition probability, \( BI_\omega n_i \), where \( B \) is the Einstein B coefficient, \( I_\omega \) is specific intensity of radiation field and \( n_i \) is the number density of molecules in quantum level \( i \). Since \( I_\omega \) depends upon the energy, integrated photon distribution over space and time of the pulse, \( \Delta A \) reflects the different number of photons. It would be most fundamental to evaluate the contribution of the transition moment squared of each transition, which is proportional to \( B \).

Therefore, we calculate the zeroth-order moment \( M_0(t) \) of \( \Delta A \) that is divided by the transition energy as in Eq. (6). \( M_0(t) \) reflects the transition probability integrated over the photon energy range of the probe pulse. Since the spectral shape changes with time (horizontal change), it is of importance to calculate the zeroth moment to remove the ‘cross talk’ with intensity change (vertical change).
Calculated $M_0(t)$ in Fig. 2(d) displays the ultrafast decay of the total transition probability in the visible region. A sharp decrease appears in $t_1 < \sim 100$ fs and a slow increase and an even slower decrease follow in regions $t_2 = 100–400$ and $t_3 = 400–1600$ fs, respectively. There seems to be at least three decay processes. $M_0$ also displays vibronic fringes due to the coherent intramolecular vibrational relaxation more evidently.

Fig. 2(e) shows the FT of $\Delta A$ in the region of 0–2000 cm$^{-1}$. The trace at $\sim 1030$ cm$^{-1}$ in the power spectrum is assignable to the strongest Raman-active vibration of ground-state methanol at 1035 cm$^{-1}$ (presented in Fig. S1). However, the vibrational frequencies of 2′HC are not same as those at the ground state (Fig. S1),$^{55,56}$ since the photoexcited 2′HC molecule changes its vibrational frequencies on the way of decay processes. Detailed vibrational analyses on real-time frequency change on the excited states are discussed in Sec. 4.8.

### 4.2 Analyses on a sequential decay model

We can determine rate constants $k_1 - k_3$ for the three processes by fitting a decay curve at each wavelength on the 2D $\Delta A(\lambda, t_d)$ map. The decay processes are represented as $A (S_3) \rightarrow B \rightarrow C \rightarrow D (S_0^*)$, and corresponding rate equations are given by Eqs. (7)–(10). In the present experimental time scale, component D is long lived and $k_4$ can be approximately regarded to be zero.

\[
\frac{d[A]}{dt} = -k_1[A],
\]
\[
\frac{d[B]}{dt} = k_1[A] - k_2[B],
\]
\[
\frac{d[C]}{dt} = k_2[B] - k_3[C],
\]
\[
\frac{d[D]}{dt} = k_3[C] - k_4[D].
\]

Difference absorbance $\Delta A$ is obtained by subtracting the contribution of the ground state G from those of photoinduced species A–D as in Eq. (11),

\[
\Delta A = \varepsilon_A[A] + \varepsilon_B[B] + \varepsilon_C[C] + \varepsilon_D[D] - \varepsilon_G[G])l.
\]

where $\varepsilon_j$ ($j = A–D$ and G) and $l$ are molar absorption coefficients and the sample thickness, respectively.

The first process in the shortest delay time region is expected to be significantly fast. Thus, the apparatus function of a Gaussian function with FWHM 10 fs was convoluted with the exponential decay function. The resultant function represented with the complementary error function in Eq. (S16) was
applied for determination of $\tau_1$ after subtracting the longer decay components. Details are given in the ESI. Since the ratio of excited 2′HC to the ground state is estimated to be 0.83 % from the laser spectrum, laser power, focused spot size, the initial concentration $[A]_0$ is set to be $8.3 \times 10^{-4}$ molL$^{-1}$. The other initial concentrations are zero.

Fig. 3 presents determined relaxation lifetimes, rate constants, and molar absorption coefficients. The most remarkable result is the kinetic deuterium effect that appears clearly in $\tau_2$ in Fig. 3(b) and $k_2$ in Fig. 3(e). Thus, proton or hydrogen atom transfer is involved in the second process. In contrast, the first and third processes display small differences between the OH and OD analogues in $\tau_i$ [i = 1 and 3, Fig. 3(a) and (c)] and $k_i$ [Fig. 3(d) and (f)]. Since the first $k_1$ process is faster than the resolution of the probe pulse, a Gaussian apparatus function is convoluted with the exponential decay functions in the analyses. A special care was taken in fitting three $k_i$ values at each wavelength by performing several types of non-linear least-squares calculations, i.e., stepwise iterative or subtraction fitting and simultaneous global fitting. The former method is found to give $\tau_i$ and $k_i$ with smaller error. The obtained frequency-averaged lifetimes are $\tau_1 = 35 \pm 1$ fs, $\tau_2 = 93 \pm 1$ fs and $\tau_3 = 690 \pm 9$ fs for the OH analogues, and $\tau_1 = 38 \pm 1$ fs, $\tau_2 = 164 \pm 1$ fs and $\tau_3 = 759 \pm 13$ fs for the OD analogues. These ultrafast rate constants of 2’HC have been determined for the first time in this paper in a much shorter time regime than previous studies.$^4,6$

The second significant point is the wavelength dependences of $\tau_i$ and $k_i$, which have become obtainable in the present multichannel experiments. We call them $\tau_i$ and $k_i$ spectra, respectively. The rate constant $k_1$ does not depend much upon probe photon energy in the range 1.9–2.4 eV as in Fig. 3(d), whereas $k_2$ and $k_3$ show significant wavelength dependences in Fig. 3(e) and (f), respectively. The $k_2$ spectra in Fig. 3(e) of the OH (black) and OD (red) isotopomers show, respectively, nearly monotonic decrease and a peaked feature, whereas the $k_3$ spectra of both OH and OD in Fig. 3(f) display a local maximum at ~2.4 eV. The remained small isotopic differences in $k_1$ and $k_3$ may be due to numerical errors.

Fig. 3(g) shows absorption spectra of transient components A to D obtained from the $\Delta A(\lambda, t_d)$ map. Again, careful examinations were made to obtain reliable spectra by trying several fitting procedures, i.e., simultaneous global fitting and stepwise iterative fitting with respect to $\varepsilon_i$ and $k_i$, and stepwise subtraction fitting for the $k_1$–$k_3$ components. The absorption spectra in the units of molar absorption coefficients $\varepsilon_A$ to $\varepsilon_D$ in Fig. 3(g) for the OH analogue were obtained from the stepwise independent fitting with three pre-determined rate constants $k_1$–$k_3$. The global fitting leads to essentially similar spectra. But the stepwise independent fitting with fewer fitting parameters would give more reliable $\varepsilon_i$ spectra. Formalisms of fitting functions for obtaining the absorption coefficients are given in the ESI.

Component A involved in the $k_1$ process displays a broad absorption peaking at ~2.3 eV with $\varepsilon_A \approx 1000 – 800$ mol L$^{-1}$cm$^{-1}$ over the range 2.1–2.5 eV, whereas the $\varepsilon_B$, $\varepsilon_C$ and $\varepsilon_D$ spectra appear in higher
energy regions and are smaller than $\varepsilon_A$. The values of $\varepsilon_B$, $\varepsilon_C$, and $\varepsilon_D$ monotonically increase with photon energy and reach 650, 500 and 100 mol$^{-1}$L cm$^{-1}$ respectively at 2.6 eV. The observed abrupt breach over the entire frequency region and subsequent high-energy shifts in Fig. 2(b) are due to $\varepsilon_A$ and other $\varepsilon_j$ components, respectively.

The final component D shows significantly weak absorption in this region, and there is no band in the ground state absorption of trans-$2'$HC [Fig. 1(b)] or cis-$2'$HC. Therefore, component D is not due to the original ground state $S_0$ (component G) but thermally-populated, non-equilibrated ground state $S_0^*$. High vibrational levels are transiently populated in the $S_0$ electronic state after the internal conversion, and they make the absorption red shifted from the stationary $S_1$-$S_0$ absorption in Fig. 1(b). The present multiplex experiments demonstrate the possibility of extracting such non-equilibrium dynamics of high vibrational states.

The other relaxation channel of cis-trans isomerization at the C1’-C9 bond could in principle take place as in Fig. 1(a). However, according to the previous experiments with a UV lamp, the quantum yield to this channel is as small as 1%, compared to the main channel, and their reaction rate is only 0.1 %h$^{-1}$ in methanol. Hence, this channel is negligible under the present experimental condition.

As discussed previously on spectral behaviour (a) and (b), time dependencies are observed differently in the regions above and below 2.25 eV in Fig. 2(c). This is due to the lack of component B in absorption below 2.25 eV as shown in Fig. 3(g). Component B increases with time constant $\tau_1 = 35$ fs and decreases with $\tau_2 = 93$ fs. After the process, component C contributes to the growth at 2.25 and 2.09 eV in Fig. 2(c) due to its broad band tail extending below 2.3 eV after the initial bleach.

The spectral change can be analyzed using the first moment $M_1(t)$, which is defined as the frequency-weighted average of $\Delta A$ given by Eq. (12),

$$M_1(t) = \frac{\int_{\omega_1}^{\omega_2} \omega \Delta A(\omega, t) d\omega}{\int_{\omega_1}^{\omega_2} \Delta A(\omega, t) d\omega}$$

Fig. 2(d) presents the calculated $M_1$ in the region of 2.051–2.337 eV, in which the three time dependences of spectral change are involved. The change of $M_1$ is in parallel with that of $M_0$ in ranges $t_1$, $t_2$ and $t_3$. Namely, the initial blue shift upon excitation towards 2.25 eV in range $t_1$, fast red shift in range $t_2$ and gradual recovery in range $t_3$. Since $\tau_1$ and $\tau_2$ are determined as 35 and 93 fs respectively, these shifts are primarily due to component B which has the absorption coefficient in higher photon energy [Fig. 3(g)]. Note that $M_1$ takes the mid-point value of 2.194 eV if $\Delta A$ is constant over the entire energy range.

### 4.3 Potential energy surfaces and decay paths
Fig. 4 presents the calculated potential energy profiles of 2’HC along the decay path after photoexcitation to S_3(π,π*) (a) in methanol and (b) in the vacuum (isolated molecule), and also depicts the molecular orbitals of the π*, π_1, π_2 and n types in Figs. 4(c)–4(f), respectively. The black, red, blue and green lines indicate the potential energy curves of the ground state, excited states of π_1, π*, nπ* and π_2π* characters, respectively. As shown in Fig. 4(a), an ultrafast isomerization pathway in methanol is obtained as S_{3FC} (4.21 eV) → S_{3MIN} (4.03 eV) → S_2/S_1 (4.04 eV) → S_2/S_1 (3.73 eV) → S_{1MIN-trans} (3.6606 eV) → S_{1TS-twist} (3.6634 eV) → S_{1MIN-taut} (3.16 eV) → S_1/S_0 (2.63 eV).

The minimum of S_{3MIN} is significantly close to the intersection of S_3/S_2 in methanol in Fig. 4(a), whereas S_{3MIN} is calculated to be higher than S_3/S_2 in the vacuum in Fig. 4(b). Detailed energies of such critical points are given in Fig. S2 and S3.

After the photoexcitation at geometry S_{3FC}, 2’HC will immediately deform to S_{3MIN} because S_{3FC} and S_{3MIN} are directly connected by the meta-IRC in the S_3 state. At S_{3MIN}, following internal conversion takes place rapidly from the S_3(π,π*) state to the S_2(nπ*) state by passing through the S_2/S_2 region, which is geometrically and energetically close to S_{3MIN} in methanol. Then, 2’HC decays to the S_1 surface via S_2/S_1 since a meta-IRC path directly connects S_2/S_2 and S_2/S_1. Local minimum S_{1MIN-trans} and transition state S_{1TS-taut} are located geometrically and energetically close to S_2/S_1.

Along the reaction path S_{1MIN-trans}→S_{1TS-taut}→S_{1MIN-taut}, proton transfer takes place as depicted in Fig. 4, and the character of the S_1 state changes accordingly from nπ* and π_1,π* since S_{1TS-taut} corresponds to an avoided crossing. Then, 2’HC overcomes the small barrier of S_{1TS-twist} and finally decays to the S_0 electronic ground state surface via the S_2/S_0 region. After the proton transfer, the C1’–C9 bond twisting occurs as depicted in Fig. 4(a), and the dihedral angle C2’–C1’–C9–O10 changes from planar (17°) to perpendicular (89°). This twisting motion is likely to proceed slowly because the distance along the reaction coordinate is substantially long. Also, the motion of heavy atoms is included during the molecular geometry deformation. Based on the present calculations, three experimental decay components can be summarized as follows.

(1) The first experimental decay component A (τ_1 = 35 fs) corresponds to the process of S_{3FC}→S_{3MIN} →S_2/S_2, in which two species S_{3MIN} and S_2/S_2 are involved without clear separation. The small energy difference (0.01 eV) between S_{3MIN} and S_2/S_2 is consistent with the ultrashort lifetime τ_1.

(2) The second component B (τ_2 = 93 fs) corresponds to the proton transfer on the excited state as S_2/S_1→S_{1MIN-trans}→S_{1TS-taut}, in which again two species are involved without clear separation. The proton transfer is undoubtedly supported by the observed deuterium effect, τ_2 = 93 fs (H) → 164 fs (D). As noted above, the electronic configuration of the S_1 state changes from nπ* to π_1,π* during the proton transfer process of S_{1MIN-trans}→S_{1TS-taut}→S_{1MIN-taut}. This change gives rise to the spectral red shift from ε_0 (>2.3 eV) dominant to ε_C dominant (with low energy tail).
The decay of the third component C ($\tau_3 = 690$ fs) is due to the $C'_{1}$–$C9$ bond twisting on the course of $S_{1MIN-taut} \rightarrow S_{1TS-twist} \rightarrow S_{0}/S_{1}$. Conversely, the broad band tail of $\alpha_C$ leads to the $\Delta\alpha$ increase in the energy range lower than 2.25 eV at 150–350 fs in Fig. 2(c).

### 4.4 Molecular polarity and solvent effects

Comparisons of calculations between in methanol and in the vacuum would present a general insight about solvent effects. The energies of the crucial points, $S_{2}/S_{1}$, $S_{1MIN-trans}$, $S_{1TS-taut}$, $S_{0}/S_{1}$, are calculated to be similar under the both conditions. The geometrical deformation in the vacuum is also similar to that in methanol along the decay path: in the process from $S_{3FC}$ to $S_{3}/S_{2}$ the O11-H14 bond length increases whereas the O10-H14 distance decreases; in the process from $S_{3}/S_{2}$ to $S_{1MIN-trans}$ both of the O11-H14 bond and the O10-H14 distance become back to the initial values with increase of the $C2'_{1}$-$C1'-C9-O10$ dihedral angle; and in the process from $S_{1MIN-trans}$ to $S_{0}/S_{0}$ the twisting motion of $C'_{1}$–$C9$ bond takes place.

The only significant difference is energy difference 0.42 eV between $S_{3}/S_{2}$ in methanol (4.04 eV) and $S_{3}/S_{2}$ in the vacuum (4.46 eV). This discrepancy can be explained by the molecular polarity. The nπ* state (blue line) has a smaller dipole moment than the ground state or the excited π1π* and π2π* states, and is less stabilized in the polar solvent compared to other π1π* or π2π* states (see Fig. S2 and S3). The calculated dipole moments in the vacuum at the $S_{3FC}$ geometry are 6.63 Debye in $S_{3}(\pi_2\pi^*)$, 4.65 Debye in $S_{2}(\pi_1\pi^*)$, 1.69 Debye in $S_{1}(n\pi^*)$ and 3.99 Debye in $S_{0}$, where 1 Debye $= 3.34 \times 10^{-30}$ Cm.

The nπ state is also less polar i.e. less stabilized along the whole decay path. As a result, the electronic configurations $S_{2}(n\pi^*)$ and $S_{1}(\pi_1\pi^*)$ in methanol are interchanged from $S_{2}(\pi_1\pi^*)$ and $S_{1}(n\pi^*)$ in the vacuum at the $S_{3FC}$ geometry. The ground and ππ* states are more stabilized than the nπ* state during the decay, and the less stabilized nπ* state compared to the ground, π1π* and π2π* states in methanol gives rise to the energy difference.

### 4.5 Ultrafast relaxation processes

Even though the time course of the TRS is analyzed with three components A, B and C, there is no isosbestic points in the TRS [see Fig. 2(b)]. The absence of isosbestic point can be explained by the two types of contributions of spectral change (horizontal change) and intensity change (vertical change). Details are the following.

1. The vibrational distribution in the non-equilibrated state cannot be described by the Boltzmann distribution with any temperature. The ultrafast dynamics takes place so rapidly through the reaction pathway that the spectral change cannot be described by the sum of stationary local structures. Thus, more appropriate descriptions are $A (S_{3FC} \rightarrow S_{3MIN} \rightarrow S_{3}/S_{2}) \rightarrow B (S_{2}/S_{1} \rightarrow S_{1MIN-trans} \rightarrow S_{1TS-taut}) \rightarrow C (S_{1MIN-taut} \rightarrow S_{1TS-twist} \rightarrow S_{0}/S_{0}) \rightarrow D (S_{0}^*),$ rather than $A(S_{3MIN}) \rightarrow B (S_{3MIN}$
trans) → C (S_{1\text{MIN-taut}}) → D (S_0^*). Here, S_0^* means vibrationally non-equilibrated, electronic ground state. Sometimes it is called ‘hot’ ground state but we prefer non-equilibrated or equivalently non-thermal state because ‘hot’ should be related to some defined temperature.

(2) The spectral modulation induced by the wavepacket motion may not be decoupled because of the time-range overlap between ultrafast electronic dynamics and vibrational period. In general, real-time vibrational modulation of electronic states during the electronic relaxation is observed in femtosecond transient absorption kinetics. The present above-mentioned kinetic model involves fast sequential intermediate electronic states A–C and long-lived state D (S_0^*). In such a system, a model based on the static electronic absorption spectra is valid only if the observation is made over a long enough time in which at least several vibrational periods of the coupled modes take place. Otherwise the temporal and spectral overlap of induced absorption the A–C sequential process and coexistence of induced absorption and stimulated emission would make the isosbestic points obscure.

4.6 Probe wavelength dependence

If the TR ΔA spectrum is merely a sum of population-weighted static spectra of intermediate species, the rate constants k_1, k_2 and k_3 estimated using Eqs. (7)–(10) should not depend upon the probe wavelength. In fact, k_2 and k_3 depend upon the probe wavelength as in Fig. 3(e) and (f), respectively. Here, let us postulate a model proposed in previous papers^{27,57} that the decay rate constant of k_i is affected by the internal conversion through the conical intersection (CI).

\[ k(E) = k_0 e^{-\frac{|E - E_0|}{\Delta E}}. \]  

(13)

When the electronic wavepacket travels along the decay path around the CI, rate constant k takes the largest value k_0 at the center of the crossing point. Assuming the energy E_0 of absorption from the CI to the final state, the energy level E of any state can be measured with respect to the same final state. As given by Eq. (13), the decay rate constant of k(E) decreases in proportional to exponential of −|E − E_0| at any location above or below the CI due to the standard tunneling probability over an energy gap ΔE. Hence, when the probe wavelength matches transition energy E_0 from the conical intersection to the final excited states, the rate constant k(E) becomes largest.

The local maxima in the k_2 and k_3 spectra in Fig. 3(e) and (f) respectively correspond to the maxima (fitted by blue lines) of the tunneling rate through energy barriers centered at the conical intersections S_2/S_1 and S_1/S_0 in Fig. 4(a), respectively. Table 1 presents estimated energy E_0 and width ΔE. The kinetic deuteration effect is obtained for k_2; i.e., it is 1.9 times larger in the OH analogue than in the OD analogue. In contrast, E_0 and ΔE are similar between the OH and OD analogues at both S_2/S_1 and S_1/S_0.
They essentially reflect the same electronic energy surface provided that the zero-point energy can be neglected. Transition energy $E_0$ from the transient state to higher electronic excited states is estimated to be $\sim 0.1$ eV larger in OD than OH at both $S_2/S_1$ and $S_1/S_0$.

The model makes it possible to discuss the location and width (or shape) of the conical intersection based on experimental evidence. The fact that tunneling width $\Delta E$ at $S_2/S_1$ is larger than that at $S_1/S_0$ indicates that the structural deformation with respect to energy change around $S_2/S_1$ is relatively smaller than around $S_1/S_0$. Furthermore, the $\Delta E$ value is slightly smaller in the OD analogue, in which the vibrational amplitude is smaller. Difference of $E_0 \approx 0.35$ eV between $S_2/S_1$ and $S_1/S_0$ correspond to the calculated energy difference 1.10 eV between 3.73 and 2.63 eV in Fig. 4(a). A possible reason for this discrepancy is difference in the final states of probing transitions $S_m-S_2$ and $S_n-S_1$, where $S_m$ and $S_n$ being higher excited states.

4.7 Equal-pulse-type DUV pump - probe experiments

Fig. 5(a) and (b) present a 2D display of $\Delta A(\omega, t_d)$ and slices of frequency spectra for the equal-pulse-type experiments using DUV pump and DUV probe in the region of 4.43–4.88 eV. Stimulated emission gives negative $\Delta A$ below 4.6 eV in Fig. 5(b) since the DUV probe pulse overlaps the $S_3\leftarrow S_0$ absorption below $\sim 4.6$ eV as shown in Fig. 1(b). The negative $\Delta A$ also means a smaller cross-section of absorption from the photoinduced excited states than that of the stimulated emission to the ground state. On the other hand absorption of transient species are observed as positive $\Delta A$ in the region above 4.6 eV, where the ground state absorption is almost absent in Fig. 1(b) and the transient absorption exceeds the stimulated emission. The shapes of the spectra at various probe delay times in Fig. 5(b) are similar to each other.

Fig. 5(c) shows the time dependences of $\Delta A(\omega, t_d)$ at probe energy $\hbar \omega = 4.76, 4.70, 4.64$ and 4.59 eV, respectively. The fast $k_1$ and $k_2$ processes cannot be observed due to disturbance by coherent spikes in the region 0–150 fs. Therefore, it is difficult to extract the ultrafast spectral dynamics in this delay time region. In the remaining delay time range $t_d \geq 150$ fs, all of the $\Delta A$ traces display similar monotonic increases. Fitting with two exponential functions plus a constant was found to give either similar relaxation times or significantly unbalanced relaxation times. Therefore, a single exponential function plus a constant in Eq. (14) is employed and the relaxation time $\tau_1' = 647$ fs was obtained as the photon energy average of Fig. 5(d). This value is fairly close to estimated $\tau_1$ of the C=C rotation in Sec. 4.3, i.e., this time dependence corresponds to the formation of the twisted structure after the proton transfer process of $S_{1\text{MIN-taut}} \rightarrow S_{1\text{TS-twist}} \rightarrow S_1/S_0$ in Fig. 4(a).

$$\Delta A = \Delta A_1 e^{-\frac{t}{\tau_1'}} + \Delta A_\infty$$

(14)
Fig. 6(a) presents transient absorption spectra obtained as $\Delta A_1$ and $\Delta A_\infty$ from the 2D $\Delta A$ map of Fig. 5(a) assuming $\tau_1' = 647$ fs in Eq. (14). In particular, $\Delta A_1$ component shows the effect of negative absorption. This bleaching is partly due to population loss of the ground state and to the stimulated emission. The former is estimated to be 4.3 % based on the laser spectrum, laser power, focused spot size and sample concentration. Fig. 6(b) displays the final reconstructed spectra, in which the effects from the population loss, stimulated emission and the ultrafast population decay (vertical change) of the $S_3 \rightarrow S_0$ are excluded.

The contribution from the ultrafast population decay is explained as follows. 2’HC decays nonradiatively to the $S_2$ state within 35 fs after the photoexcitation to $S_3$. The $S_1$-$S_0$ transition is off-resonant with the probe photon energy. Hence, the rapid decay from the $S_3$ state to $S_2$/$S_1$ results in the effective cancellation of the $S_3 \rightarrow S_0$ stimulated emission contribution to the signals. Both of $\Delta A_1$ and $\Delta A_\infty$ display strong absorption at the low energy side in Fig.6(b). This spectral shape corresponds to component D ($S_0^\ast$).

4.8 Coherent dynamics of molecular vibrations

The real-time vibronic modulation can be studied using the spectrogram analysis.\(^{11,59}\) Fig. 7(a) shows a spectrogram $S(\nu, t_d)$ in the region of 200–1000 fs, which is obtained from FT of a time trace of $\Delta A$ in a sliding-time window of the Blackman function with the FWHM of 400 fs. The shape and width of the gate function is determined with special care of avoiding interference with neighbouring modes.\(^{10,11,60}\) The black line in $S(\nu, t_d)$ represents the peak of spectrogram amplitude at each gate delay time, and corresponds to an instantaneous vibrational frequency of the dephasing molecules. This type of modulation can be observed in various molecular systems.\(^{12,61}\)

In Fig. 7(b), similar analyses are applied to a low frequency region, and a frequency peak of 87 cm\(^{-1}\) is clearly obtained along with a peak of 225 cm\(^{-1}\) with a small FT power. Fig. 7(b) corresponds to the Fourier power spectrum of the instantaneous frequency distribution as in Fig. 7(a). The obtained peaks in Fig. 7(a) and (b) are the frequencies of vibrational modes which are vibronically excited by molecular geometry deformation during the decay process after the $S_3$ excitation. In Fig. 7(a), the instantaneous frequency changes in a range 1550–1600 cm\(^{-1}\). The frequency peak firstly decreases from 1650 cm\(^{-1}\) at 200 fs to 1530 cm\(^{-1}\) at 450 fs, and increases again to 1620 cm\(^{-1}\) at 650 fs. It should be reminded that the time scale of the spectrogram in Fig. 7(a) is restricted by the averaging time window of 400 fs in this analysis. These modes are coupled to the molecular deformations and impulsively excited along the decay path.

The fact that the lifetime of the vibrational modulation is less than 800 fs in Fig. 7(a) is consistent with those in the transient absorption spectra, $\tau_1 = 35$ fs, $\tau_2 = 93$ fs and $\tau_3 = 690$ fs. The vibrational
modulation is understood based on the molecular geometry deformations in the process from $S_{3FC}$ to $S_{1MIN-taut}$ shown in Fig. 4(a).

The normal modes that are relevant to the decay path can be determined by comparing them with the molecular geometry deformations along $S_{3FC}$, $S_{3MIN}$, $S_3/S_2$, $S_2/S_1$, $S_{1MIN-trans}$, $S_{1TS-taut}$, and $S_{1MIN-taut}$. As shown in Fig. 4(a), the molecular geometry significantly changes in the C7-C8 bond length ($1.344 \text{ Å} - 1.383 \text{ Å}$) and the dihedral angle of C2′-C1′-C9-O10 ($0° - 40°$). It follows that the C7-C8 bond stretching motion and the C1′-C9 bond twisting motion are enhanced during the decay path from $S_{3FC}$ to $S_{1MIN-taut}$.

The distance of O11-H14 and O10-H14 also change significantly in connection with the proton transfer. However, the vibrational frequency of OH stretch $\sim 3000 \text{ cm}^{-1}$ is out of the spectrogram, and we do not discuss here. The reason for the missing of the frequency range higher than $2000 \text{ cm}^{-1}$ is insensitivity of if any frequency modulation due to the ir short vibrational periods ($<15 \text{ fs}$) which are close to the experimental time resolution of $12 \text{ fs}$.

4.9 Normal mode analyses

Normal mode analyses are carried out on the three minima, $S_{3MIN}$, $S_{1MIN-trans}$ and $S_{1MIN-taut}$, at the TDDFT level of theory with CPCM (methanol). There are several normal modes in the range from $1500 \text{ cm}^{-1}$ to $1700 \text{ cm}^{-1}$ at $S_{3MIN}$, $S_{1MIN-trans}$ and $S_{1MIN-taut}$. The most relevant normal modes which have the largest contribution to the C7-C8 bond stretching motion are chosen by a normal-mode displacement analysis. They possess vibrational frequencies of $1647 \text{ cm}^{-1}$ ($S_{3MIN}$, $\tau_1 = 35 \text{ fs}$), $1591 \text{ cm}^{-1}$ ($S_{1MIN-trans}$, $\tau_2 = 93 \text{ fs}$) and $1623 \text{ cm}^{-1}$ ($S_{1MIN-taut}$, $\tau_3 = 690 \text{ fs}$). The normal mode displacements are depicted in Fig. S4(a), (b) and (c), respectively. In the previous paper, the vibrational frequency of C7-C8 stretch has been calculated around $1550 \text{ cm}^{-1}$ and $1600 \text{ cm}^{-1}$, which is consistent with the present results.

Although the calculated vibrational frequencies are slightly higher than observation due to the lack of anharmonic effect in the calculations, the trend of the vibrational modulation is successfully reproduced; e.g., the peak frequency decreases first and increases again. Also, the time dependence of the vibrational modulation in Fig. 7 (a) is consistent with the determined lifetimes $\tau_1 - \tau_3$. Therefore, it is concluded that the observed spectrogram peak modulation in Fig. 7(a) corresponds to the vibrational modulation of C7-C8 stretch, which is enhanced during the decay process.

In a low-frequency range $70-150 \text{ cm}^{-1}$, only two normal modes are obtained on $S_{3MIN}$, $S_{1MIN-trans}$ and $S_{1MIN-taut}$. Their vibrational frequencies are 89 and $122 \text{ cm}^{-1}$ at $S_{3MIN}$, 93 and $107 \text{ cm}^{-1}$ at $S_{1MIN-trans}$ and 84 and $110 \text{ cm}^{-1}$ at $S_{1MIN-taut}$. Their normal-mode displacements include the twisting motion of the C1′-C9 bond, as depicted in Fig. S4(d), (e) and (f), respectively. These results explain satisfactorily the observed spectrogram peak of $87 \text{ cm}^{-1}$ shown in Fig. 7(b).

In a range $220-290 \text{ cm}^{-1}$, two normal modes are also obtained on $S_{3MIN}$, $S_{1MIN-trans}$ and $S_{1MIN-taut}$. These normal modes involve bending motion of the molecular plane, as depicted in Fig. S4(g), (h) and (i),
respectively. Therefore, the spectrogram peak at 225 cm\(^{-1}\) with a small FT power corresponds to the bending modes which are weakly enhanced by the twisting motion along the decay path.

5. Conclusions

The ultrafast dynamics of DUV photoexcited 2’HC has been determined for the first time. The ultrafast processes are summarized as follows. The first spectral changes take place due to the internal conversion through conical interactions \(S_3/S_2\) and \(S_2/S_1\), and explained by lifetime \(\tau_1 = 35\) fs. The proton transfer occurs subsequently, as confirmed by the experimental evidence of kinetic deuteration effects on the dynamics. The internal conversion \(S_3/S_2\) and \(S_2/S_1\) are strongly expected from the DFT calculations in Fig. 4. Otherwise the \(S_1\) state cannot undergo the proton transfer that takes place only on the \(S_1\) state. 2’HC undergoes the proton transfer before C1’-C9 rotation with time constant \(\tau_2 = 93\) fs before \textit{cis-trans} isomerization at the ring. The last process is the C=C twist with \(\tau_3 = 690\) fs. Even after the relaxation to the ground electronic state, isomerization towards flavanone in the time range longer than 1.6 ps has not been observed in the present experimental time scale. The real-time vibronic motion has been observed as the spectrogram. The observed instantaneous frequency modulation has been successfully reproduced by normal-mode analyses along the decay path.

Conflicts of interest

There are no conflicts to declare.

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Table 1. Experimentally-determined rate constant $k_i$ and energy width $\Delta E$ at conical intersections $S_2/S_1$ and $S_1/S_0$, respectively.

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<td>2.42</td>
</tr>
<tr>
<td>$\Delta E$ / eV</td>
<td>0.83</td>
<td>0.65</td>
<td>0.52</td>
<td>0.43</td>
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Fig. 1  (a) Photochemistry of trans-2’-hydroxychalcone (2’HC). (b) Electronic absorption spectra of trans-2’HC in methanol.
Fig. 2  (a) Two-dimensional difference absorption spectrum $\Delta A(\omega, t_d)$ with pump on and off for trans-2'-hydroxychalcone (2'H'C) in methanol. (b) Spectral change of $\Delta A$ at nine delay times. (c) Time dependence of $\Delta A$. (d) Temporal change of 0th and 1st order moment $M_0$ and $M_1$ in the region of 2.051–2.337eV. (e) Spectrogram $S(\nu, t)$ in a sliding-time window of 400 fs.
Fig. 3  (a)–(f) Experimentally determined lifetimes $\tau_1 - \tau_3$ and rate constants $k_1 - k_3$ assuming sequential processes for $\Delta A(\omega, t_d)$. Black and red symbols correspond to OH and OD analogues, respectively. (g) Determined molar absorption coefficients $\varepsilon_A - \varepsilon_D$ (see text for A–D).
Fig. 4  Schematic potential energy profile of the decay path after photoexcitation to $S_3$ state for 2'-hydroxychalcone (2'HC) (a) in methanol and (b) in the vacuum. Red, blue and green lines correspond to the electronic configurations of $\pi_1\pi^*$, $n\pi^*$ and $\pi_2\pi^*$, respectively. The potential energy curves around $S_2/S_1$ and $S_{1\text{TS-lacl}}$ are avoided crossing, and depicted by blue and red mixed lines. $S_1/S_0$ were computed at the SF-TDDFT/BHHLYP/6-31G(d) level, whereas the other geometries were at the $\omega$B97XD/6-31G(d) level. The key geometrical parameters are indicated. Optimized geometries and variation of energies at the crucial points in methanol and in the vacuum are given in Table S1, S2 and Fig. S2, S3, respectively. (c)–(f) Molecular orbitals of $\pi^*$, $\pi_1$, $\pi_2$ and $n$ at the $S_{0\text{MIN}}$ geometry, respectively.
Fig. 5 (a) Two-dimensional difference absorption spectrum $\Delta A(\omega, t_d)$ with pump on and minus off for \textit{trans}-2’-hydroxychalcone (2’HC) in methanol. (b) Spectral change of $\Delta A$ at eight delay times. (c) Delay time dependence of $\Delta A$. (d) Experimentally determined lifetimes $t_1'$. 
**Fig. 6** Absorption components $\Delta A_1$ and $\Delta A_\infty$ estimated using Eq. (14). The effects from population loss, stimulated emission and ultrafast population decay are excluded from (a) and resultant spectra is (b).
**Fig. 7** Spectrogram $S(v, t)$ showing real-time vibrational frequency dynamics in *trans*-2′-hydroxychalcone (2′HC).