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Monitoring Non-Adiabatic Dynamics of the RNA Base Uracil by UV-Pump-IR-Probe Spectroscopy

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Abstract

Resolving the excited state dynamics of DNA- and RNA- nucleobases has attracted considerably attention. UV irradiation of the isolated nucleobases leads to the population of an electronic excited state which is quenched by internal conversion mediated by conical intersections on an ultrafast timescale. We present non-adiabatic on-the-fly molecular dynamics simulations of the UV-pump-IR-probe signal of the pyrimidine nucleobase uracil using a novel semiclassical protocol which takes into account the path integral over the excited state vibrational dynamics and properly describes the joint temporal and spectral resolution of the technique. Simulations of vibrational motions of carbonyl fingerprint modes in the electronically excited states reveal clear signatures of different relaxation pathways on a timescale of hundreds of femtoseconds which arise from an ultrafast branching in the excited state. We show that the inherent temporal and spectral resolution of the technique is not purely instrumental but also depends on the vibrational fluctuation timescale.

Keywords

non-adiabatic on-the-fly dynamics; excited states; DNA; time-resolved IR spectroscopy

The strong UV absorption bands of DNA- and RNA- nucleobases lead to the population of bright valence excited states with $\pi\pi^*$ character. The nucleobases have been engineered by nature to be photostable with respect to UV irradiation. At the core of this self-protecting property are few-picosecond excited state deactivation mechanisms involving conical intersections^{1,2} where electronic energy is very rapidly converted into vibrational energy allowing to minimize harmful photochemical processes that can eventually lead to DNA photolesions. These damages can be corrected to some extent in enzymatic repair processes but an accumulation of photolesions leads to genetic mutations and ultimately to diseases like skin cancer. The harmful molecular mechanisms leading to photochemical DNA damage has been shown to occur on the short picosecond timescale³, thus directly competing with photoprotection mechanisms, and are additionally affected by variations of the base sequence and the double helix conformation^{4–7}.

It is well established that the purine nucleobases adenine and guanine decay with a single quenching mechanism^{8–10} which is mediated by the barrierless access to a seam of conical intersections with the electronic ground state^{11–14}. In contrast, the excited state lifetimes of the pyrimidine bases are somewhat longer (with the longest for thymine) and involve several

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Supporting Information Available

Computational details of the non-adiabatic on-the-fly molecular dynamics and mode tracking procedure. Expressions for the Δ -dispersed signal $\tilde{S}(\omega, T; \Delta)$. Discussion of the time evolution of the electronic states and populations. Supporting figures of the Δ -dispersed signal $\tilde{S}(\omega, T; \Delta)$. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

interconnected excited state decay pathways^{15–17}. A direct $\pi\pi^* \rightarrow gs$ channel leads to ultrafast repopulation of the electronic ground state^{9,10,18,19} while an indirect $\pi\pi^* \rightarrow nO\pi^* \rightarrow gs$ channel involves an optical dark $nO\pi^*$ intermediate state with a longer lifetime¹⁹. Dynamical simulations of DNA and RNA bases helped establish the interconnection between the two relaxation mechanisms and additional minor ring-opening pathways but the relative importance of these pathways is still under debate^{20–22}. A clear assignment of spectroscopic signatures of these pathways has only been provided for the earlier stages of the process²⁰.

Commonly applied time resolved techniques such as UV or visible pump-probe or photoelectron spectroscopy offer a high sub-100 fs temporal resolution^{9,10}. The multidimensional optical counterparts of these techniques have been traditionally developed in the 600–800 nm regime limited by laser sources, are now becoming feasible in the UV^{23–28}. The broad bandwidth of the optical or ionizing probe pulses lacks selectivity for the underlying vibrational dynamics. Only the population decay of the bright $\pi\pi^*$ state is captured by probing the system dynamics in the optical regime. These techniques thus fail to directly monitor the population of dark states and to decipher between the particular pathways.

Structural information about the rearrangement of atoms can be derived directly from time- and frequency-resolved vibrational spectroscopy (either with IR- or Raman probes). Unique marker bands (e.g. the IR-intense carbonyl $C=O$ stretch vibrations of the nucleobases) serve as fingerprint of the excited state photoreaction or non-adiabatic relaxation dynamics. This allows to resolve transient reaction intermediates^{29–31}, obtain structural details³² and thus ultimately resolve the reaction mechanism^{3,4,33,34}. The UV-Pump - IR-Probe technique has been proven to be a valuable direct probe for complex photoreactions by allowing to identify the real time reaction mechanism leading to the formation of photolesions in DNA nucleobases^{3,4,34,35} and other photoreactions^{30,31,33,36}.

We present a semiclassical microscopic simulation protocol for the UV-pump - IR-probe signal of uracil which takes into account the entire path integral of the excited state dynamics as well as the temporal and spectral profile of the IR probe pulse. The interpretation of these signals requires a careful analysis of the interplay between spectral and temporal resolution in the excited state since time resolved vibrational spectra^{37–39} may not be simply interpreted as an instantaneous snapshot of the nuclear dynamics⁴⁰; sums over paths smear the temporal and spectral resolutions. The time-dependent vibrational frequencies (subject to non-adiabatic relaxation) introduce a matter-chirp contribution to the signal which affects the effective pulse length for highest temporal resolution. We demonstrate that the resolution in vibrational spectra is governed by both the infrared probe and the underlying matter dynamics and can not be controlled solely by experimental knobs. The present analysis and the conclusions may be readily extended to a stimulated Raman probe⁴¹.

Our simulations employ non-adiabatic on-the-fly molecular dynamics to calculate the vibrational spectra. A small vibrational system is treated quantum mechanically whereas a classical bath causes a time dependent modulation of the system Hamiltonian. The required quantities are directly derived from non-adiabatic mixed quantum-classical dynamics where the excited state vibrational Hamiltonian is reconstructed on-the-fly by block-diagonalization in a mode tracking procedure⁴² which avoids the calculation of the entire excited state Hessian matrix (for details see Sec. Materials and Methods). The numerical algorithm developed for the simulation of the time-evolution of specific “fingerprint” modes (like e.g. $C=O$ modes) scales linearly with the number of vibrations, allowing for

simulations of medium sized molecules in the excited states and numerical effort is decoupled from system size.

We further dissect the contributions of different femtosecond relaxation mechanisms to the signal and predict the signatures of the concurring relaxation pathways, excited state trapping and ultrafast deactivation to the electronic ground state. The spectra show unique signatures from the different deactivation pathways and allow to assess their relative importance in future experiments.

Loop diagram representation of time and frequency resolved pump-probe signals

In the UV-pump - IR-probe technique the pump pulse $\mathcal{E}_1$ centered at time zero promotes the system from its ground electronic state g to the vibrational state a of an excited electronic state (see Scheme 1 (a)) and launches the vibrational dynamics. The IR probe $\mathcal{E}_2$ centered at T can then either stimulate emission that couples the vibrational state a and a lower vibrational state d or absorption to a higher vibrational state c . The complex electric field reads

$$\mathcal{E}(t) = \mathcal{E}_1(t) + \mathcal{E}_2(t - T). \quad (1)$$

The pump-probe signal $S_{pp}(\omega, T)$ is given by the frequency gated change in probe intensity and depends parametrically on T . The relevant loop diagrams shown in Scheme 1 (b) (plus their complex conjugates) contain four field-matter interactions -two with each pulse. Diagrams (i) and (ii) correspond to emission and absorption, respectively of the IR probe pulse. The frequency-gated signal $S_{pp}(\omega, T) = S_{pp}^{(i)}(\omega, T) + S_{pp}^{(ii)}(\omega, T)$ can be directly read off the diagrams and is given by

$$S_{pp}^{(i)}(\omega, T) = \mathcal{I} \left[\frac{2}{\hbar} \int_{-\infty}^{\infty} \frac{d\Delta}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_3 \int_{-\infty}^{\tau_3} d\tau_5 \right. \\ \left. \times \mathcal{E}_2^*(\omega) \mathcal{E}_2(\omega + \Delta) \mathcal{E}_1^*(\tau_5) \mathcal{E}_1(\tau_1) \right. \\ \left. \times \langle V_e G^\dagger(\tau_3, \tau_5) V_n^\dagger G^\dagger(t, \tau_3) V_n G(t, \tau_1) V_e^\dagger \rangle \right] \\ \times e^{i\omega(t - \tau_3) - i\Delta(\tau_3 - T)}, \quad (2)$$

$$S_{pp}^{(ii)}(\omega, T) = \mathcal{I} \left[\frac{2}{\hbar} \int_{-\infty}^{\infty} \frac{d\Delta}{2\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_3 \int_{-\infty}^{\tau_3} d\tau_5 \right. \\ \left. \times \mathcal{E}_2^*(\omega) \mathcal{E}_2(\omega + \Delta) \mathcal{E}_1(\tau_5) \mathcal{E}_1^*(\tau_1) \right. \\ \left. \times \langle V_e G^\dagger(t, \tau_1) V_n G(t, \tau_3) V_n^\dagger G(\tau_3, \tau_5) V_e^\dagger \rangle \right] \\ \times e^{i\omega(t - \tau_3) - i\Delta(\tau_3 - T)}, \quad (3)$$

where $G(t_1, t_2) = (-i/\hbar)\theta(t_1 - t_2)e^{-iH(t_1 - t_2)}$ is the retarded Green's function representing forward propagation from t_1 to t_2 . The advanced Green's function $G^\dagger(t_1, t_2)$ represents backward propagation from t_1 to t_2 , V_e and V_n denote the electronic and vibrational dipole operators, respectively. The two interactions with the probe involve the detection mode ω and another mode $\omega + \Delta$. The relevant range of the τ_3 integration is controlled by the effective bandwidth of the variable Δ . In both diagrams (i) and (ii) the probe is frequency-dispersed in the detection. Since only a single mode is selected for detection one can ask why does the probe duration matter at all? This is apparent from the diagrams which show that the signal involves two interactions with the probe. The frequency dispersed detection only selects the frequency of the last interaction $\mathcal{E}_2^*(\omega)$ whereas the other interaction $\mathcal{E}_2(\omega + \Delta)$ may still involve many other modes, making the signal dependent on the probe

bandwidth and the relative phase of different modes. The time resolution is lost only if the other interaction also selects a single mode and is sharply peaked at $\Delta = 0$. This implies a CW probe. The Δ bandwidth cannot be controlled experimentally since it depends on the system dynamics details.

Semiclassical approach: coupling to a classical bath

Eq. (2) and Eq. (3) may be used for a complete many body propagation of the wavefunction which is exact and numerically expensive. The signal is given by a sum over paths spanning both branches of the loop. We shall employ a simplified protocol by treating some of the bath degrees of freedom as classical while retaining the quantum character of selected vibrations^{40,41} (in our case the IR-intense carbonyl $C=O$ stretch vibrations of the nucleobase). The selected modes are then modulated during the course of the non-adiabatic dynamics of other classical bath degrees of freedom. We further assume that the preparation pump pulse is impulsive setting $\mathcal{E}_1(t) = \mathcal{E}_1 \delta(t)$, and eliminating the τ_1 and τ_5 integrations in Eq. (2) and Eq. (3). The semiclassical signal finally reads

$$S_{pp}(\omega, T) = -\mathcal{J} \left\langle \frac{2i}{\hbar^4} \int_0^\infty d\tau_3 |\mathcal{E}_1|^2 \mathcal{E}_2^*(\omega) \mathcal{E}_2(\tau_3 - T) \times \int_{\tau_3}^\infty dt e^{i\omega(t-T)} \sum_a |\mu_{ag}|^2 e^{-2\gamma_a t} \times \left(\sum_c |\mu_{ac}|^2 e^{-i \int_{\tau_3}^t \omega_{ca}(t') dt'} + \sum_d |\mu_{ad}|^2 e^{i \int_{\tau_3}^t \omega_{ad}(t') dt'} \right) \right\rangle_e, \quad (4)$$

where $\omega_{a\beta} \equiv \omega_a - \omega_\beta$ and γ_a^{-1} is the lifetime of state a . $\langle \dots \rangle_e$ represents the ensemble averaging over a set of classical trajectories. This signal is given by a path integral in the molecule and field space involving the vibrational frequency trajectories $\omega_{ca}(t)$ and $\omega_{ad}(t)$. In addition, the starting point τ_3 is not precisely defined since it is an integration variable. The signal depends not only on the initial and final value of the vibrational frequency $\omega_{ca}(t)$, but rather on the entire pathway from time T to the time when the polarization decays to zero. In time-resolved measurements the probe must have a broader bandwidth than the inverse timescale of the vibrational dynamics. The latter is given by the spread of transition frequencies $\omega_{a'a}$ (decay of a superposition) and by the dephasing rate γ_a . Even if the probe pulse is impulsive and delayed by T , the pulse may not be simply replaced by δ function, since it can be longer than the infrared period. Thus an infrared pulse can be at most “semi impulsive” (i.e. short compared to vibrational relaxation process but not compared to the period of high frequency vibrations $\approx 2000\text{--}3000\text{ cm}^{-1}$). In contrast, the visible pulse used in a stimulated Raman process can be truly impulsive (short compared to the vibrational period)^{41,44–48}.

Electronic Relaxation

UV radiation excites the molecule (Figure 1 (a)) to the bright $\pi\pi^*$ S_2 state which is located 5.07 eV above the S_0 state on MRPT2-CAS(14/10) level of theory and above the dark $nO\pi^*$ state (Figure 1 (b), for a discussion of the electronic excited states and electronic structure methods see Supporting Information (SI)-Table 1). Figure 1 (c) shows the IR stick spectrum of uracil calculated on CAS(14/10) level of theory¹ in the electronic ground state S_0 (bottom), the S_1 minimum with $nO\pi^*$ character (middle) and the S_2 minimum with $\pi\pi^*$ character (top). In S_0 two intense and spectrally isolated $C=O$ stretch vibrations are

¹The $C=O$ vibrational frequencies are calculated on CAS(14/10) level of theory (Basis: 6-31G*). Due to the lack of dynamic electron correlation and the finite basis size vibrational frequencies appear blue shifted compared to experiment, comparison with the experimental vibrational spectrum (recorded at low temperatures in argon matrix)⁴⁹ suggests a scaling factor ≈ 0.86 .

identified at $\tilde{\nu} = 2012 \text{ cm}^{-1}$ and $\tilde{\nu} = 1971 \text{ cm}^{-1}$, the splitting is attributed to the different chemical environment in the aromatic π system of uracil. In the $\pi\pi^*$ minimum the higher energy $C = O_7$ mode (where $C = O_n$ is the localized stretch vibration involving atom n) is blue shifted by $\approx 16 \text{ cm}^{-1}$ and the high oscillator strength of this mode is preserved. Due to the broken aromaticity in the $\pi\pi^*$ state, the low-energy $C = O_8$ mode is red shifted by $\approx 41 \text{ cm}^{-1}$ and the oscillator strength is largely diminished, reflecting the population of the anti-bonding π^* orbital of the $C = O_8$ bond. Inspection of the normal mode vector shows that the localized $C = O_8$ mode in S_0 develops into a partially delocalized normal mode whose motion involves the adjacent partial double bond, reflecting the enolat-resonance structure of uracil. Nevertheless both $C = O$ modes remain decoupled. In the S_1 state with $n_{O_8}\pi^*$ character the motion of the $C = O_8$ mode is even more delocalized and the energy is further reduced ($\tilde{\nu} = 1719 \text{ cm}^{-1}$). The oscillator strength is about 33 % of the $C = O_7$ ground state vibration. The high energy $C = O_7$ mode preserves its localized character and shows a blue shift of $\approx 47 \text{ cm}^{-1}$ compared to the S_0 state.

Figure 2 depicts the time evolution of the excited state electronic populations within the first picosecond, averaged over 44 trajectories (electronic structure method CAS(14/10), for details of the non-adiabatic on-the-fly molecular dynamics simulations see Sec. Theoretical Methods). The molecule starts in the bright $\pi\pi^*$ state (47.6 % in S_2 and 52.3 % in S_3), within the first 30 fs the S_2 population is rapidly increased to 86 %, by following the diabatic character of the $\pi\pi^*$ state. This initial $S_3 \rightarrow S_2$ population transfer is accompanied by a partial population of the S_1 state by ≈ 24 % due to $S_2 \rightarrow S_1$ population transfer within the first 50 fs. The S_1 population remains nearly constant until $t = 200$ fs, and then increases to ≈ 57 % at $t = 1$ ps. This increase is fed from the S_2 state whose population is reduced by about ≈ 50 % in the time interval [200; 1000] fs. Accordingly the decay of S_2 occurs by two mechanisms: first due to population of the dark S_1 state with $n_{O_8}\pi^*$ character and second due to population transfer into the electronic ground state S_0 which is populated by about 18 % at $t = 1000$ fs. Additionally a significant fraction of the population (about 24 %) is trapped in the S_2 state at $t = 1000$ fs. Interestingly the S_1 population is not transiently increased by the $S_2 \rightarrow S_0$ relaxation.

The typical trajectories depicted in Figure 2 (b) and (c) demonstrate the two relaxation mechanisms of S_2 (the populated state at time t is highlighted in cyan). Figure 2 (b) shows the population relaxation of the S_2 state leading to a trapped S_1 population. In this trajectory the S_2/S_1 seam of conical intersection is reached at $t = 270$ fs. The energy gap between S_1 and S_0 is then reduced but no hopping event into the ground state occurs and the trajectory evolves on the dark S_1 ($n_{O_8}\pi^*$) state until 1 ps. This relaxation mechanism is denoted as $\pi\pi^* \rightarrow n_{O_8}\pi^*$ trapping. A typical trajectory leading to the repopulation of the electronic ground state S_0 is depicted in Figure 2 (c). Here at $t = 586$ fs $S_2 \rightarrow S_1$ population transfer occurs, followed by $S_1 \rightarrow S_0$ transition at $t = 656$ fs. Subsequent to the initial $S_2 \rightarrow S_1$ hopping event the $\pi\pi^*$ character of the populated state is preserved leading to a S_1/S_0 conical intersection with $\pi\pi^*/gs$ character. Thus the trajectory follows diabatically the $\pi\pi^*$ character in the excited electronic states. Inspection of the complete set of trajectories shows that all observed ground state relaxation events (8 out of 44 trajectories) follow this mechanism. Upon $S_2 \rightarrow S_1$ relaxation the diabatic $\pi\pi^*$ character of the populated state is preserved, followed by relaxation into the S_0 state. The period the system spends in the intermediate S_1 state varies between 8–59 fs which is too short for a transient increase in the S_1 population.

A possible excited state relaxation mechanism is summarized in Figure 1 (b). Subsequent to population of the bright $\pi\pi^*$ state, ultrafast branching of the excited state population takes place. The dominant relaxation channel involves sub-ps population transfer involving the $\pi\pi^*$ and $n_{O_8}\pi^*$ states, followed by trapping of the population in a dark $n_{O_8}\pi^*$ state ($\pi\pi^* \rightarrow$

$n_O\pi^*$ trapping mechanism, right side of Figure 1 (b)), $n_O\pi_{S_1}^* \rightarrow g^s$ relaxation could only be observed as minor channel for propagation times > 1 ps (an elaborate comparison to the relaxation dynamics reported in Refs.^{20,21} and electronic populations until $t = 2$ ps are given in the SI). In a parallel relaxation channel the system relaxes to the S_2 minimum potentially followed by a relaxation into the electronic ground within the first picosecond. The latter is triggered by a crossing of the $n_O\pi^*$ and $\pi\pi^*$ state where the diabatic $\pi\pi^*$ character is preserved in the populated S_1 state, followed by $S_1 \rightarrow S_0$ population transfer (*adiabatic* $\pi\pi_{S_2}^* \rightarrow \pi\pi_{S_1}^* \rightarrow g^s$ relaxation mechanism, left side of Figure 1 (b)).

The UV-Pump-IR-Probe signal

In the following we demonstrate how the two non-adiabatic relaxation mechanisms show up in the temporal evolution of the UV-pump - IR-probe signal $S_{PP}(\omega, T)$. Figure 3 (a) depicts the $S_{PP}(\omega, T)$ signal (Eq. (4)) of the $\pi\pi^* \rightarrow n_O\pi^*$ trapping (selected time-slices are given in SI-Figure 6). The calculation is based on a single trajectory and is depicted together with the instantaneous time evolution of the $C = O_7$ and $C = O_8$ stretch vibrations (blue and red line, respectively). These are modulated due to non-adiabatic electronic relaxation in the bath of all remaining vibrational modes. Both modes $C = O_7$ and $C = O_8$ show fast modulations on a 10–20 fs timescale and slower intense modulations on a 50–100 fs timescale. The $C = O_8$ mode is shifted in its center frequency to $\bar{\nu} \approx 1700 \text{ cm}^{-1}$ appearing as new resonance at $t > 270$ fs due to the $\pi\pi^* \rightarrow n_O\pi^*$ population transfer. Detailed comparison of $S_{PP}(\omega, T)$ with the actual time evolution of the $C = O_8$ mode reveals that the new resonance in $S_{PP}(\omega, T)$ slightly precedes $C = O_8$, an intrinsic effect of the path integral expression in Eq. (4) as the signal does not simply represent an instantaneous snapshot of the vibrational frequency at the observation time (represented by the IR probe pulse centered around T). Due to the population of the S_1 state ($n_O\pi^*$) the relative intensity at $\bar{\nu} \approx 1700 \text{ cm}^{-1}$ is reduced compared to the $C = O_7$ mode but still a clear IR signature of the $\pi\pi^* \rightarrow n_O\pi^*$ trapping process is retained in $S_{PP}(\omega, T)$.

The fast frequency fluctuations apparent in $C = O_7$ and $C = O_8$ are not resolved in the pump-probe signal since the IR probe pulse is too long ($t_{FWHM} = 175$ fs), yet the two modes are resolved. Only frequency shifts which capture the average of the $C = O_{7,8}$ modulations can be observed. To examine the effect of the inherent matter chirp on the joint time-frequency resolution we decompose the signal in the form

$$S_{PP}(\omega, T) = \mathcal{J} \int_{-\infty}^{\infty} \frac{d\Delta}{2\pi} \mathcal{E}_2^*(\omega) \bar{S}(\omega, T; \Delta). \quad (5)$$

The Δ -dispersed signal $\bar{S}(\omega, T; \Delta)$ (calculated according to SI-Eq. 5) represents the contribution of the $\omega + \Delta$ mode of the probe to the signal (in addition to the ω mode) and is a joint property of field+ matter which depends on the vibrational dynamics as well as the pump and the probe pulses. The signal (Eq. (4)) is obtained by integrating it over Δ . As is clear from Eq. (5), $\bar{S}$ is not an experimental observable but it allows to visualize the underlying paths in the joint field+matter space that contribute to the signal. If the vibrational dynamics is fast compared to the pulse, the signal will depend on the entire probe bandwidth and the variation of $\bar{S}$ with Δ will resemble the probe envelope. In the opposite limit only a slice of the bandwidth will participate. In the time domain this implies that τ_3 in Eq. (4) will be sharply peaked or diffuse in the two limits, respectively. This will affect the temporal resolution of the technique as will be demonstrated below.

It is our objective to capture the matter dynamics, i.e. the frequency changes of $C = O_{7,8}$ induced by non-adiabatic relaxation in Figure 3 (a). Therefore we consider the effect of a 50

fs probe pulse on $\tilde{S}(\omega, T; \Delta)$ (Figure 3 (b)). As the probe is short compared to the change in vibrational frequency $\omega_2(\tau_3 - T)$ selects limited frequency contributions from the matter chirp in the time domain. Accordingly the dominant contribution in $\tilde{S}(\omega, T; \Delta)$ arises from the broad bandwidth of the pulse itself, and frequency resolution of matter is eroded (see the two unstructured bands along $\omega + \Delta$ in Figure 3 (b)). For a long 400 fs probe pulse (Figure 3 (c)) the induced frequency changes $C = O_{7,8}$ are entirely captured by the probe field and we obtain a high frequency resolution with dominant frequency contributions arising from the matter (at the expense of low temporal resolution). Each resonance along ω can now be decomposed into matter frequency contributions at a given delay T . Figure 3 (d) displays the underlying frequency contributions to a single point in $S_{PF}(\omega, T)$ for different probe durations. For long pulses (300–500 fs) the induced frequency changes $C = O_{7,8}$ are captured by the probe pulse resulting in a double peak structure which correspond to the initial and final frequency of $C = O_8$ due to the non-adiabatic relaxation. The width of $\tilde{S}$ along $\omega + \Delta$ becomes independent of the probe due to the inherent matter chirp contribution (for a comparison with the probe bandwidth see SI-Fig. 5). As the probe is shortened (250–150 fs), $\omega_2(\tau_3 - T)$ selects only limited frequency contributions from the matter chirp. Thus frequency resolution is reduced and non-Gaussian peak shapes appear along $\omega + \Delta$. In the limit when the probe is short compared to the change in the vibrational frequency $C = O_{7,8}$ (20–50 fs) the dominant contribution to $\tilde{S}(t, T; \Delta)$ arises from the pulse itself and frequency resolution is eroded.

A similar analysis for the *diabatic* $\pi\pi_{s_2}^* \rightarrow \pi\pi_{s_1}^* \rightarrow gs$ relaxation trajectory is shown in Figure 3 (e–h). In the $S_{PF}(\omega, T)$ signal (Figure 3 (e)) the intensity of the low-energy $C = O_8$ mode is now largely diminished. Only one resonance appears from the $C = O_7$ mode which shows a characteristic blue shift until $t = 500$ fs due to its evolution on the S_2 potential energy surface with $\pi\pi^*$ character. The non-adiabatic relaxation mediated by a $\pi\pi^* \rightarrow gs$ conical intersection shows up in a short spike in the signal due to dramatic red-shift in $C = O_8$ which is already initiated by the $\pi\pi_{s_2}^* \rightarrow \pi\pi_{s_1}^*$ population transfer. Upon relaxation into S_0 the frequency shift is reversed and both modes $C = O_7$ and $C = O_8$ again appear around $\tilde{\nu} = 2000 \text{ cm}^{-1}$. Further on $C = O_8$ and $C = O_7$ appear highly oscillating due to excess vibrational energy in S_0 . The individual modes are not resolved, nevertheless the ground state relaxation is accompanied by a strong increase in intensity showing up in $S_{PF}(\omega, T)$. By examining the Δ -dispersed signal $\tilde{S}(\omega, T = 500 \text{ fs}; \Delta)$ we observe that for a long probe pulse a structured red shifted shoulder along $\omega + \Delta$ can be observed at $\omega = 1856 \text{ cm}^{-1}$ (Figure 3 (g)) which arises from the matter induced changes in vibrational frequency due to non-adiabatic relaxation. An examination of these frequency contributions as a function of pulse duration (Figure 3 (h)) reveals that probe pulses of 150–250 fs are required to resolve this spectral feature. Interestingly the system dynamics induced frequency changes of $C = O_{7,8}$ of both relaxation mechanisms appear on a similar ≈ 100 fs timescale imposing common requirements on the design of probe pulse length and bandwidth. We find that probe pulses of $t_{FWHM} = 150\text{--}250$ fs offer the best compromise of temporal and spectral resolution which allow to resolve spectral features characteristic for the individual relaxation mechanisms (see e.g. the shoulder at $\omega + \Delta \approx 1500\text{--}1600 \text{ cm}^{-1}$ for $t_{FWHM} = 200$ fs in Figure 3 (h)).

The signal $S_{PF}(\omega, T)$ obtained by ensemble averaging $\langle \dots \rangle_e$ over the set of trajectories is depicted in Figure 4 (a). We observe a single intense resonance around $\tilde{\nu} = 2000 \text{ cm}^{-1}$ originating from the time evolution of the $C = O_7$ mode. The frequency and its intensity evolution are depicted in Figure 4 (b) and (c), respectively (blue line). By analyzing the spectral position of the $C = O_7$ mode (Figure 4 (b)) we observe an initial blue shift of the center frequency until $t = 300$ fs due to the initial dynamics in the S_2 and S_1 states, followed by a red shift of $\Delta \tilde{\nu} = 20 \text{ cm}^{-1}$ for $t > 600$ fs. The intensity of the $C = O_7$ mode is initially

diminished until 400–500 fs by about 15 % (Figure 4 (c)). Later on we observe a recovery in the spectral region around $\tilde{\nu} = 2000 \text{ cm}^{-1}$ due to population of the electronic ground state. Both the temporal intensity recovery and red-shift of the center frequency are clear

spectroscopic signatures of the *diabatic* $\pi\pi_{s_2}^* \rightarrow \pi\pi_{s_1}^* \rightarrow g^s$ transition which is responsible for ultrafast photoprotection mechanism of uracil. In the course of the dynamics, ground state relaxation is mediated by the superimposed S_1/S_0 CoIn structures depicted in Figure 4

(d) representing the active part of the $\pi\pi_{s_1}^* \rightarrow g^s$ CoIn seam. They are characterized by a pronounced pyramidalization at C5 accompanied by a out-of-plane displacement of H5 in good agreement with the lowest energy S_1/S_0 CoIn characterized in Refs. ^{16,18,50}. Additionally the dynamically reached CoIn structures show an out-of-plane displacement of N3 and C6, where the degree of C5 pyramidalization can be compensated by a N3 and C6 Dewar-like structure^{34,51}.

The spectral signature of the $\pi\pi^* \rightarrow n_O\pi^*$ trapping appears red-shifted to the intense $C=O_7$ mode in the ensemble averaged signal $S_{PP}(\omega, T)$ as broad and unstructured plateau with about 15 % intensity compared to the intense $C=O_7$ mode. The plateau like appearance arises from the excess vibrational energy in the $n_O\pi^*$ state populated by non-adiabatic relaxation. The plateau intensity steadily increases from $t > 300$ fs (red line in Figure 4 (c)) providing a unique signature of the dynamics of the optical dark $n_O\pi^*$ state. Similar red-shifted features have been reported for thymine and thymidine but on a slower nanosecond timescale indicative of triplet state formation⁵². As both, the $C=O_8$ carbonyl bond of a $^1n_O\pi^*$ and a $^3\pi\pi^*$ state possess substantial single bond character similar signatures on the respective (femtosecond or nanosecond) timescales are expected.

We have reported simulations of the time resolved UV-pump - IR-probe signal $S_{PP}(\omega, T)$ of the RNA nucleobase uracil undergoing non-adiabatic electronic relaxation. The pump-probe signal should help to unambiguously reveal the interconnected relaxation pathways in future time resolved measurements. We find that both *diabatic* $\pi\pi_{s_2}^* \rightarrow \pi\pi_{s_1}^* \rightarrow g^s$ relaxation and $\pi\pi^* \rightarrow n_O\pi^*$ trapping mechanisms have distinct signatures within the first picosecond in $S_{PP}(\omega, T)$. The system dynamics timescale imposes a lower bound on the probe pulse and defines the actual time resolution which can be observed in the experiment. There are two fundamental reasons why the signal (Eq. (4)) may not be interpreted as snapshots of the instantaneous vibrational frequency: 1. the uncertainty in τ_3 around T limits our ability to initiate the probe process in a sharply defined time. 2. the signal at time T depends on a time integral over the frequency trajectory rather than its value at one time. Both effects preclude the simple interpretation of the signal by inspection. However using modeling, the molecular relaxation parameters may nevertheless be extracted from the signals. Some information of the individual trajectories (i.e. individual non-adiabatic relaxation events) is missed in the ensemble-averaged spectra. Performing nonlinear optical experiments at the single molecule level where individual trajectories can be observed will be an exciting possibility^{53–55}.

Theoretical Methods

The signal is calculated in the semiclassical signal representation (Eq. (4)) where all required molecular quantities are derived from semi-classical non-adiabatic on-the-fly molecular molecular dynamics trajectory calculations. We follow a three step procedure:

1. Non-adiabatic on-the-fly molecular dynamics (NA-O-MD)

NA-O-MD simulations are performed with the *Newton-X* program package⁵⁶ where the nuclei are treated classically and follow Newton's equation of motion. The acceleration on the nuclei is defined by the gradient $E^{Si}(R)/R$ of the respective populated electronic state i . Excited state gradients are evaluated by solving the time-independent Schrödinger equation

for the electrons and a subsequent gradient calculation based on the Ehrenfest theorem^{57,58}. For the integration of the electronic Hamiltonian, the electronic expansion coefficients c_{kj} define the time dependent electronic population, where changes are induced by the quantum chemically derived coupling vector $d_k(R)$, the velocity vector $\dot{R}$ (defined by the PES gradient) and the potential energy matrix V_{kj} which is diagonal in the adiabatic representation. Computational details of the NA-O-MD simulations are given in the SI.

2. Reconstruction of the excited state vibrational Hamiltonian

The NA-O-MD simulations yield trajectories of the electronic state potential energies $E_A(t)$ together with the evolving nuclear geometries $q(t)$ as classical objects. We follow the intramolecular high-frequency spectator modes (i.e. the C=O vibrations) whose frequencies are modulated during the dynamics in the bath of all other nuclear motions in the style of instantaneous normal mode analysis^{59–62} where the spectator modes possess stable (real) eigenvalue during the dynamics. For low frequency skeleton motions the semi-classical signal representation loses validity as the modes can potentially evolve from stable to unstable (and *vice versa*). Here a full quantum propagation of the Green's function according to eq. 2 and 3 is required. The standard approach for the calculation of vibrational frequencies is the diagonalization of the full (mass-weighted) Hessian matrix (within the harmonic approximation) yielding $3N - 6$ vibrational eigenvalues and eigenvectors at time t . To follow the excited state dynamics of the $C=O$ vibrations of nucleobases a block-diagonal Hessian can be constructed in an iterative subspace Davidson procedure⁴², avoiding the calculation of the full excited state Hessian. This mode tracking procedure allows to follow the important modes in the spectrum which are known *a priori* without the need to calculate the full Hessian matrix. Thus, omitting unnecessary modes the numerical effort is decoupled from system size. The computational details of the mode tracking procedure are given in the SI.

3. IR intensities

We approximate the IR intensities by neglecting the nuclear coordinate dependence but taking into account the relative intensity of vibrational modes in the different electronic excited states (Frank-Condon approximation). Non-Condon effects can be incorporated by numerical differentiation of the excited state dipole moment with respect to the “fingerprint” normal modes q_i .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Chemical structure of uracil. (b) Schematic of the femtosecond excited state relaxation mechanisms. (c) Carbonyl stretch vibrations: frequencies and relative intensities of the carbonyl marker bands in the electronic ground state S_0 ($\tilde{\nu}_{\text{C=O}_7} = 2012 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{C=O}_8} = 1971 \text{ cm}^{-1}$), and the excited states S_1 ($n\pi^*$; $\tilde{\nu}_{\text{C=O}_7} = 2059 \text{ cm}^{-1}$, $\nu_{\text{C=O}_8} = 1706 \text{ cm}^{-1}$) and S_2 ($\pi\pi^*$; $\tilde{\nu}_{\text{C=O}_7} = 2028 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{C=O}_8} = 1929 \text{ cm}^{-1}$).

Figure 2.

Time evolution of electronic populations and sample trajectories: (a) Mean adiabatic electronic state population averaged over 44 trajectories starting in the bright $\pi_O\pi^*$ state. Depending on the initial geometry the initial state is either S_2 (47.7 %) or S_3 (52.3 %); (b) time-evolution of the electronic states for a prototype trajectory showing $\pi\pi^* \rightarrow n_O\pi^*$ relaxation ($S_2 \rightarrow S_1$ population transfer at $t = 270$ fs). (c) time-evolution of the electronic states for a prototype trajectory showing $\pi\pi^* \rightarrow gs$ relaxation ($S_2 \rightarrow S_1$ population transfer at $t = 586$ fs, $S_1 \rightarrow S_0$ population transfer at $t = 645$ fs).

Figure 3.

(a) $S_{PP}(\omega, T)$ signal of the $C=O_7$ and $C=O_8$ modes of uracil (Gaussian probe $\mathcal{E}$ with $t_{FWHM} = 175$ fs, centered at $\omega_0 = 2000$ cm^{-1} ; $\Delta T = 25$ fs) for the prototype trajectory of $\pi\pi^* \rightarrow n_O\pi^*$ trapping ($S_2 \rightarrow S_1$ population transfer at $t = 270$ fs). Also shown are the instantaneous $C=O$ stretch vibrational frequencies. (b) The Δ -dispersed signal $\bar{S}(\omega, T = 270 \text{ fs}; \Delta)$ (Eq. (5)) for a probe pulse characterized by t_{FWHM} and ω_{FWHM} as indicated. (c) same as (b) but for $t_{FWHM} = 400$ fs and $\omega_{FWHM} = 74$ cm^{-1} . The $\mathcal{E}$ temporal and spectral widths are marked in panels (b) and (d). (d) $\bar{S}(\omega = 1678 \text{ cm}^{-1}, T = 270 \text{ fs}; \Delta)$ for various probe durations. (e–h) same as (a–d) but for a trajectory of diabatic $\pi\pi^*_{S_2} \rightarrow \pi\pi^*_{S_1} \rightarrow gs$

relaxation ($S_2 \rightarrow S_1$ population transfer at $t = 586$ fs; $S_1 \rightarrow S_0$ population transfer at $t = 645$ fs); the Δ -dispersed signal (f-h) is evaluated at $T = 500$ fs.

Figure 4.

(a) Signal $S_{PP}(\omega, T)$ of $C=O_7$ and $C=O_8$ modes averaged over 44 trajectories - δ_2 pulse parameters: $t_{FWHM} = 175$ fs, $\omega_0 = 2000$ cm⁻¹; $\Delta T = 25$ fs; (b) Peak shift of $C=O_7$ vibrational frequency as indicated by black dots in (a). (c) Time evolution of $C=O_7$ and $C=O_8$ vibrational frequency. (d) Overlay of S_1/S_0 CoIn structures reached during the dynamics.

Scheme 1.

Time-resolved frequency-dispersed pump-probe spectroscopy: (a) schematic of ground and excited states accessed by the pump-probe pulse sequence; solid arrows represent intervals with forward time propagation, dashed lines represent backward time propagation. (b) closed-time path-loop diagrams which together with their complex conjugates represent the pump-probe signal. Diagram (i) stimulated emission and (ii) absorption contribution to the signal, diagram rules are given in Ref. ⁴³. ω_1 and ω_1' denote interactions with the pump, the corresponding times τ_1 and τ_5 are centered around zero. $\omega + \Delta$ represents an interaction with the probe at time ω^3 which is centered around the pump-probe delay T . Time translational invariance of the matter correlation functions implies that the sum of frequencies in each diagram must be zero, i.e. $\omega_1 - \omega_1' + \omega - (\omega + \Delta) = 0$.