Supporting Information for "Correlated Quantum Treatment of the Photodissociation Dynamics of formaldehyde oxide CH$_2$OO"

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S1. QUANTUM DYNAMICAL TREATMENT

The nuclear dynamics is investigated by using the multi-configuration time-dependent Hartree (MCTDH) method[1, 2], which has been developed to solve the time-dependent Schrödinger equation in a highly efficient manner. In this approach, the nuclear wavefunction Ψ describing the nuclear quantum dynamics of a system with several electronic states and f nuclear degrees of freedom is written as follows [3, 4]

$$\Psi(Q_1, Q_2, \cdots, Q_f) = \sum_{\alpha=1}^{\sigma} \Psi^{(\alpha)} |\alpha\rangle$$

$$\Psi^{(\alpha)}(Q_1, Q_2, \cdots, Q_f) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1 \cdots j_f}^{(\alpha)}(t) \prod_{\kappa=1}^{f,\alpha} \phi_{j_\kappa}^{(\kappa,\alpha)}(Q_\kappa, t), \tag{S1}$$

where α numbers the electronic states and $Q_1, Q_2, \cdots, Q_f$ are the nuclear coordinates. The $A_{j_1 \cdots j_f}(t)$ denote the MCTDH expansion coefficients. $\phi_{j_\kappa}^{(\kappa,\alpha)}(Q_\kappa, t)$ are time-dependent basis functions called single-particle functions (SPFs). As Eq. (S1) indicates, the wavefunction Ψ can be expanded in the set $\{|\alpha\rangle\}$ of electronic states, and thus different sets of SPFs can be employed for each electronic state. In the context of MCTDH, this (typical) way of propagating of wavepacket (WP) is called multi-set formulation, which is a particularly suitable method to study non-adiabatic systems [3, 4]. The SPFs, $\phi_{j_\kappa}^{(\kappa,\alpha)}(Q_\kappa, t)$, are expanded in a set of primitive basis functions of the discrete variable representation (DVR) type, which are time-independent basis functions. One needs to choose an appropriate DVR, which yields an efficient and accurate form of the wavefunction Ψ. In this work, we choose the harmonic oscillator (HO) DVR and fast Fourier transform (FFT) in the propagation [3, 4]. In Table S1, we mention the primitive basis and SPF employed in the current work.

When the WP Ψ in Eq.(S1) reaches the end of the grid, it will be reflected or it penetrates the other side of the grid when periodic boundary conditions (*e.g.* FFT) are used. As a result of that, the description of the relevant part of the wavefunction will be depreciated. Since we deal with the photodissociation process along a long range of the $O-O$ stretching coordinate in the current study, we can potentially face the convergence issue in the WP propagation due to this long grid. To circumvent this issue in our calculation, one may annihilate the wavepacket before it reaches the end of the grid. For this purpose Leforestier and Wyatt [5], and later Kosloff[6], established complex absorbing potentials(CAPs). In principle, a CAP creates an artificial change in the Hamiltonian, and one should make

sure that this modification leaves the relevant physics unchanged. In fact, a CAP not only annihilates the wavefunction but also generates (unwanted) reflections. These reflections need to be as small as possible by allowing the CAP to be sufficiently weak and long. In the context of MCTDH, the CAP is usually defined as follows [3]

$$iW(Q) = -i\eta(Q - Q_c)^b\theta(Q - Q_c) \tag{S2}$$

In this equation, Q_c, b and η are the starting point, order, and strength of the CAP, respectively. The symbol $\theta(x)$ denotes Heaviside's step function. The distance between the starting point of the CAP and the end of the grid determines the length of the CAP. We thus modify the potential part of the Hamiltonian in Eq. (2) by adding $iW(Q)$ according to Eq. (S2)

The time-dependent WP introduced in Eq. (S1) is used to calculate an electronic spectrum as described here briefly.

For the evaluation of the electronic spectrum, one needs to compute the autocorrelation function $C(t) = \langle\Psi(0)|\Psi(t)\rangle$, which is the overlap between the initial and the propagated wavefunctions. If the initial state $\Psi(0)$ is real and the Hamiltonian is symmetric ($H = H^T = H^{\dagger*}$), the autocorrelation function can be computed through [3]

$$C(t) = \langle\Psi(t/2)^*|\Psi(t/2)\rangle \tag{S3}$$

which reduces the propagation time by a factor 2. As usual, the electronic spectrum is evaluated as the Fourier transform of the autocorrelation function $C(t)$ within the framework of Fermi's golden rule,

$$P(E) \propto \int e^{iEt}C(t)dt \tag{S4}$$

In Eq. (S4), it is assumed that a molecule initially in the ground state is excited vertically, $i.e.$ by an ideally short laser pulse, into the manifold of vibronically interacting, final electronic states. The ground state wave function $\Psi(0)$ is obtained by employing a relaxation scheme in imaginary time [3, 7] using the ground state PES of the neutral molecular system. Taking the transition dipole moment to be constant this wave function is subsequently lifted vertically from the ground state X^1A' to the excited state B^1A'. The transition to the C state occurs at higher energy and is ignored, also because the transition dipole is known to be negligibly small (see Table. 2 of Ref. [8])

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TABLE S1. Number of basis functions for the primitive harmonic and SPF basis in the `MCTDH` calculations.

modes	DVR	primitive basis	SPF basis
R_{OO}	FFT	128	9,10,9
R_{CO}	HO	88	9,10,9
θ_{COO}	HO	80	9,10,9

Owing to the finite propagation time T of the wavepacket, the Fourier transformation produces artifacts (so-called Gibbs phenomenon) [3]. In order to reduce this effect, the autocorrelation function is multiplied by some appropriate damping function $\cos^2(\pi t/2T)$ [3]. Furthermore, the autocorrelation function is damped by an additional multiplication with a Gaussian function $e^{-(t/\tau_d)^2}$ for simulating of the experimental line broadening. Here, τ_d is called the damping parameter (dephasing time). This multiplication is equivalent to the convolution of the spectrum with a Gaussian with a full width at half maximum (FWHM) of $4(\ln 2)^{1/2}/\tau_d$ [3]. In this way, the experimental resolution and line broadening effects are simulated.

S2. FITTING POTENTIAL ENERGY SURFACES TO *AB INITIO* DATA POINTS

For using the ab initio data in the nuclear quantum dynamics calculation, we consider the POTFIT approach [9]. Based on this method, one would need to generate a natural potential from the *ab initio* data points. In the next step, this natural potential can be interpolated into a more suitable grid for a MCTDH simulation.

The natural potentials along the O−O, C−O and C−O−O coordinates are generated by employing the POTFIT program in which we use $59, 16$ and 5 grid points, respectively. We then interpolate the natural potential to new primitive grids using the Fast Fourier Transform (FFT) DVR for the O−O stretching mode and harmonic oscillator (HO) DVR for both C−O stretching and C−O−O bending modes. We use a spline function to interpolate the potential along the O−O and C−O stretching modes and a cosine function for interpolating

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the potential energy surfaces along the C−O−O bending mode.

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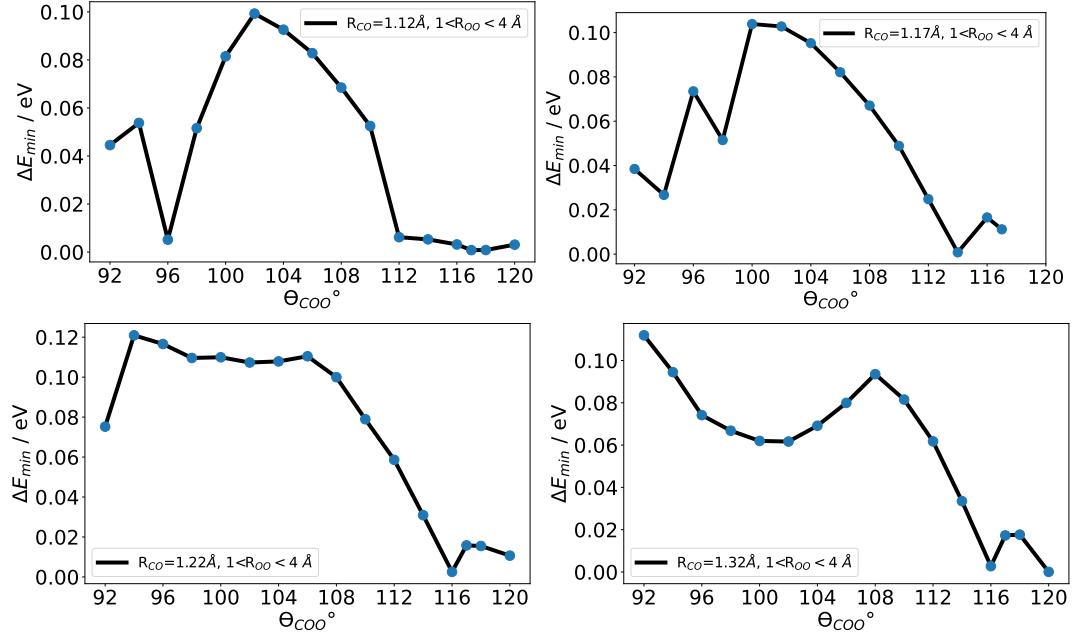
FIG. S1. Minimum energy difference of the r_{OO} PE curves of the B and C states. The (energy difference) dependence on r_{CO} and θ_{COO} is taken into account by carrying out the calculation in the following grids $1.12\mathring{A} < r_{CO} < 1.32\mathring{A}$, $92° < \theta_{COO} < 120°$.
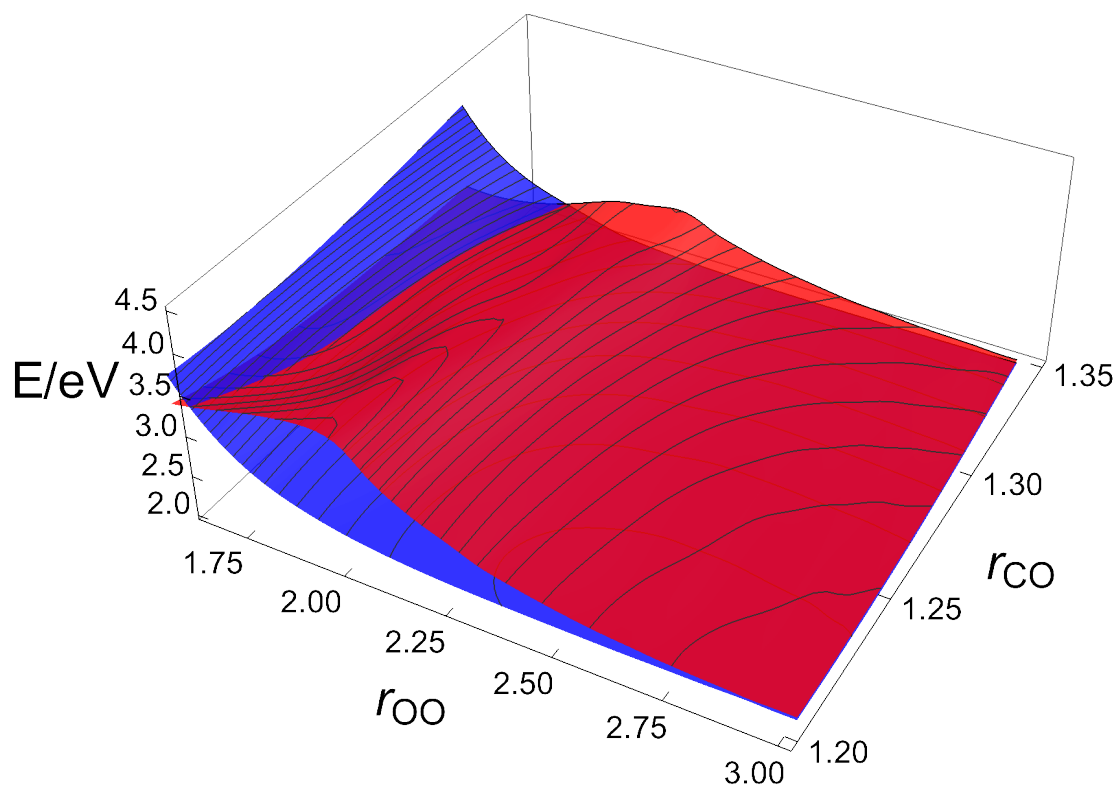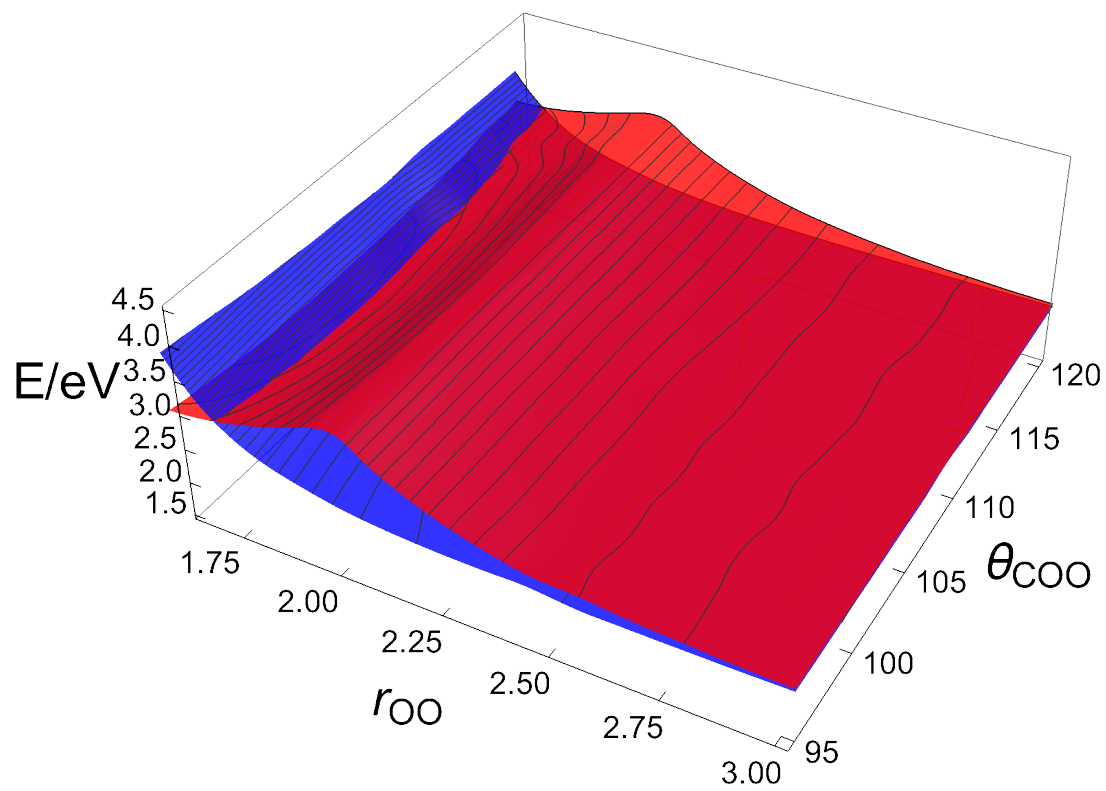
FIG. S2. The diabatic 2D PESs for the B (red) and C (blue) states in the (r_{OO}, θ_{COO}) and (r_{OO}, r_{CO}) coordinate spaces (upper and lower panels, respectively).
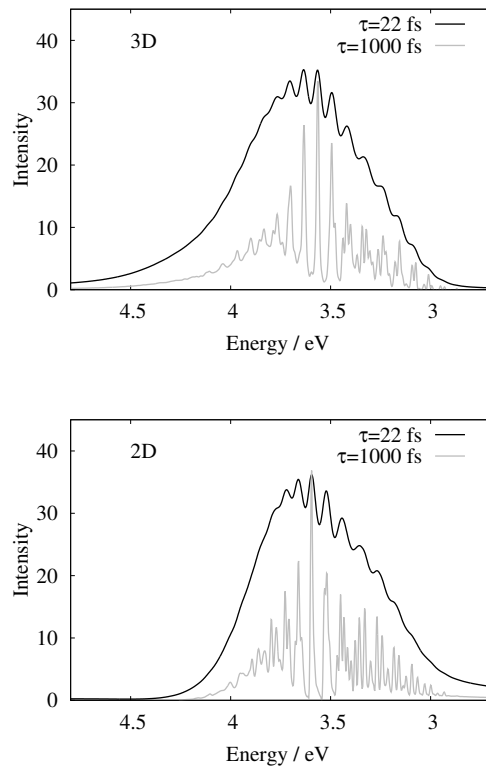
FIG. S3. The computed $B^1A' - X^1A'$ excitation spectrum using the 3D and 2D models in the upper and lower panels, respectively, for different dephasing times τ. The B and C states are treated as coupled in each panel. In both cases, the RS2-F12 method is used for evaluation of the relevant PESs.
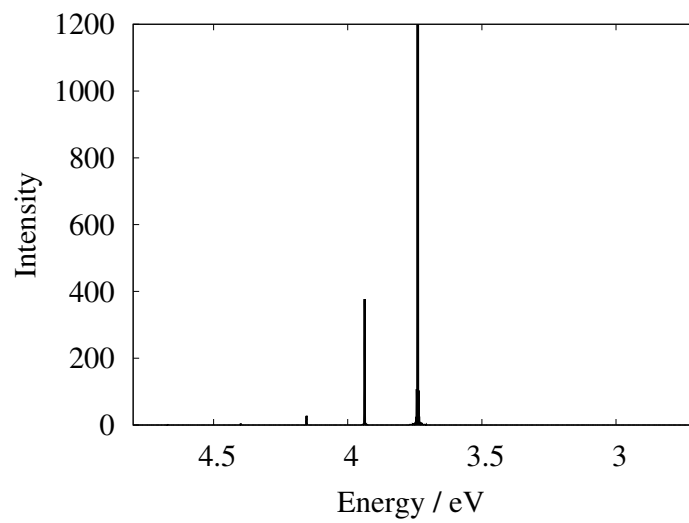
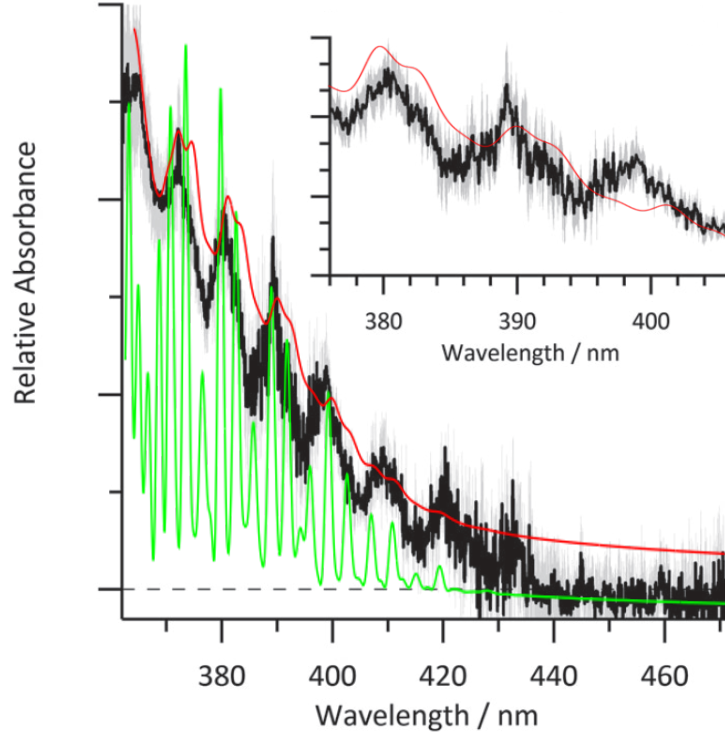FIG. S4. The excitation spectrum using the 1D C−O potential with the uncoupled diabatic B state.

FIG. S5. The computed low-energy part of the RS2-F12 excitation spectrum using the 2D model (r_{OO} and θ_{COO}), compared with the experimental spectrum from Ref. [10]. The spectrum with green color has no dephasing, while the spectrum depicted in red has a dephasing time $\tau = 40$ fs (also in the inset), which depicts the spectrum on an expanded scale.
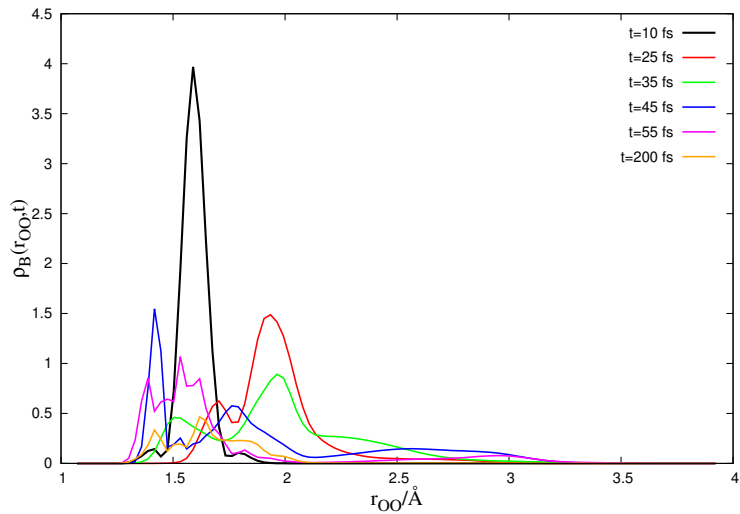
FIG. S6. Snapshots of the one-dimensional reduced densities along r_{OO} for the B state for different propagation times (see Ref. [3]).
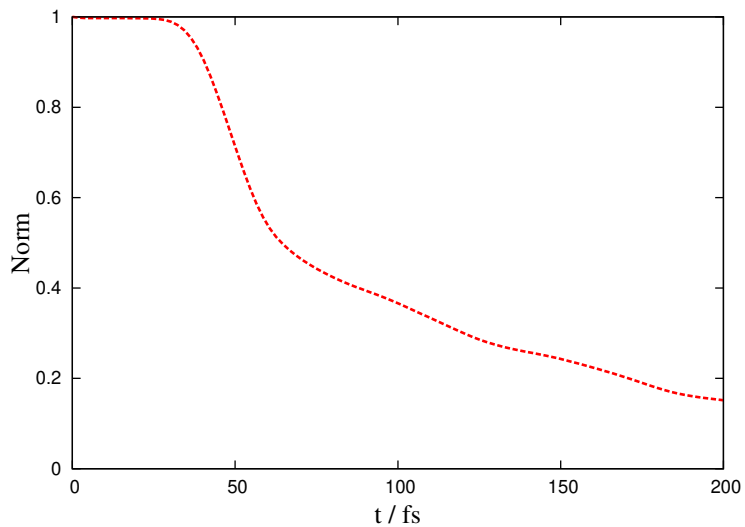

FIG. S7. The norm of the wavefunction computed by using the 3D model with the coupled B and C states.