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

Sub-femtosecond quantum dynamics of the strong-field ionization of water to the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states of the cation

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I. HAMILTONIAN AND WAVE FUNCTION

The Hamiltonian $\hat{H}(t)$ is sum of T_N and $V_{X/A}$ operators. The kinetic energy operator is given as

$$T_N = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I}\frac{1}{\sin\gamma}\frac{\partial}{\partial\gamma}(\sin\gamma\frac{\partial}{\partial\gamma}) \tag{1}$$

where $\mu_1 = \frac{2m_{\rm O}m_{\rm H}}{m_{\rm O}+2m_{\rm H}}$ and $\mu_2 = \frac{m_{\rm H}}{2}$. The quantities $m_{\rm O}$, $m_{\rm H}$ and I denote the masses of oxygen and hydrogen atoms, and moment of inertia as defined by $\frac{1}{I} = \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}$. The initial wave function $\Psi(t=0)$, pertinent to the ground electronic state of the neutral H_2O, is taken as a Gaussian wave packet (GWP)

$$\Psi(t=0) = N\exp\left[-\frac{(R-R^0)^2}{2\sigma_R^2} - \frac{(r-r^0)^2}{2\sigma_r^2}\right] \times \left\{\exp\left[\frac{(\gamma-\gamma^0)^2}{2\sigma_\gamma^2}\right] + \exp\left[\frac{(\gamma-\pi+\gamma^0)^2}{2\sigma_\gamma^2}\right]\right\} \tag{2}$$

where R_0, r_0 and γ_0 specify the initial location, while σ_R, σ_r and σ_γ refer to the width parameters of the wave packet along the respective coordinates. While the initial location of the wave packet has been defined from the equilibrium geometry of the neutral, the initial width parameters have been optimized by trial-and-error such as to warrant numerical convergence of the calculated spectra.

II. COMPUTATIONAL DETAILS

Within the Franck-Condon approximation, the initial wave function pertinent to the ground electronic state of the neutral is vertically shifted to the ground- or first-excited state PES of the cation, where it is propagated in time. For this, the time-dependent Schrödinger equation (*c.f.* Eq. (1) in the text) is numerically solved on a grid in the (R,r,γ) space in order to calculate the wavefunction at time t from that at time $t=0$. A $N_R \times N_r$ spatial grid is used in the (R,r) plane defined by $R_{\min} \leq R \leq R_{\max}$ and $r_{\min} \leq r \leq r_{\max}$. The grid along the Jacobi angle γ is chosen as the nodes of a N_γ-point Gauss-Legendre quadrature. The action of the exponential operator on $\Psi(t=0)$ is carried out by dividing the total propagation time into N steps of length Δt. The exponential operator at each Δt is then approximated using the second-order split-operator method [1]. This is used in conjunction with the fast Fourier transform method [2] to evaluate the exponential containing the radial kinetic energy operator and with discrete variable representation method to evaluate the exponential containing the rotational kinetic energy operator [3] on the wave function. The latter is accomplished by transforming the grid wave function to the angular momentum basis (finite basis representation), multiplying it by the diagonal value of the operator $(e^{-ij(j+1)\Delta t\hbar/4I})$ and

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Table I. Grid parameters and initial wavefunction.

Parameter[a)]	value	description
$N_R \times N_r \times N_\gamma$	$128 \times 128 \times 48$	grid size
R_{min}, R_{max}	10^{-6}, 15.34	extension of grid in R
r_{min}, r_{max}	0.5, 15.74	extension of grid in r
ΔR, Δr	0.12, 0.12	grid spacings in R and r
R^0, r^0, γ^0	1.1, 2.86, $\frac{\pi}{2}$	initial location of GWP
σ_R, σ_r, σ_γ	0.3,0.2,0.1	width parameters of GWP
T	1100	total propagation time
Δt	0.135	time step in propagation

a) Bond distances are in a_0, angles in radians, time in fs.

then back transforming it to the grid representation. The initial wave function is propagated for a time T. To avoid unphysical reflections or wraparounds of the high-energy components of the wave function that reach the finite-sized grid boundaries at longer times, the last 20 points of the grid along R and r are multiplied by a damping function [4]. The complete set of numerical parameters utilized in the paper is gathered below in Table I. Due to definition of the Jacobi coordinates, and the poles at $\gamma = 0, \pi$ in the Hamiltonian, such limiting values cannot be reached. This should cause no fundamental limitation, and may be avoided by using, *e.g.*, hypersherical coordinates [5, 6], an issue not pursued in the present work.

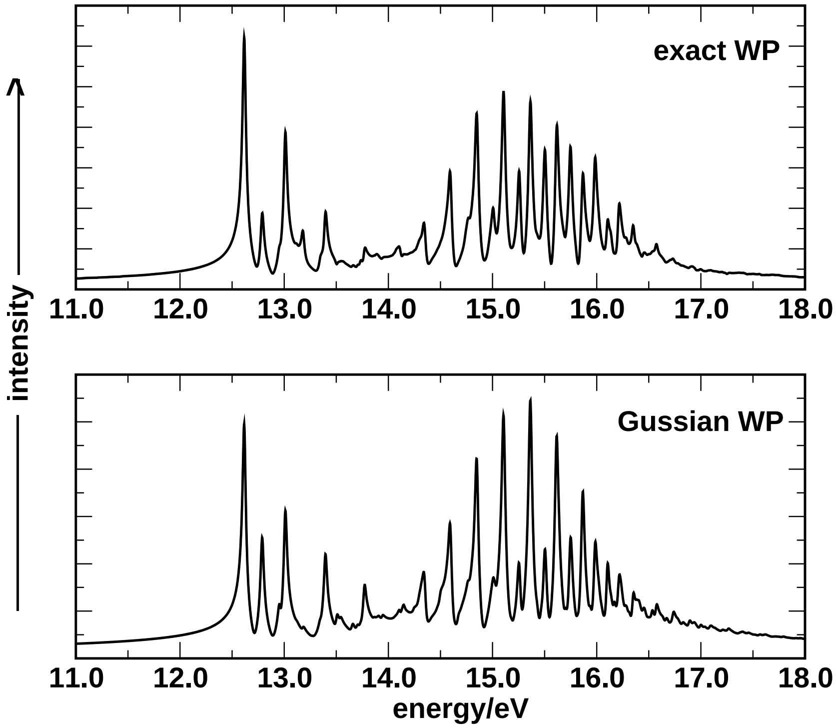

Figure 1. Photoelectron spectrum as calculated from the exact ground-state wave function of H_2O and a suitably chosen Gaussian wave packet; see the text.

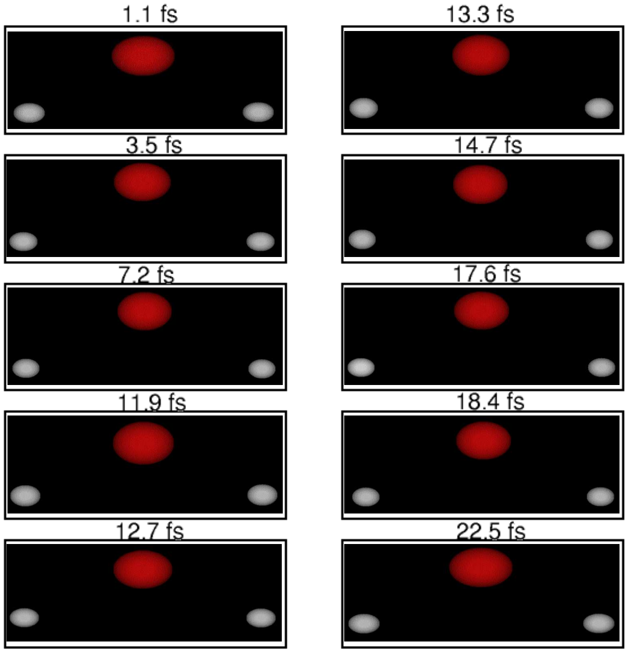

Figure 2. Snapshots of the time-resolved vibronic structures calculated from the expectation values of the positions of the atoms in the H_2O^+ in $^2B_1$ electronic state.

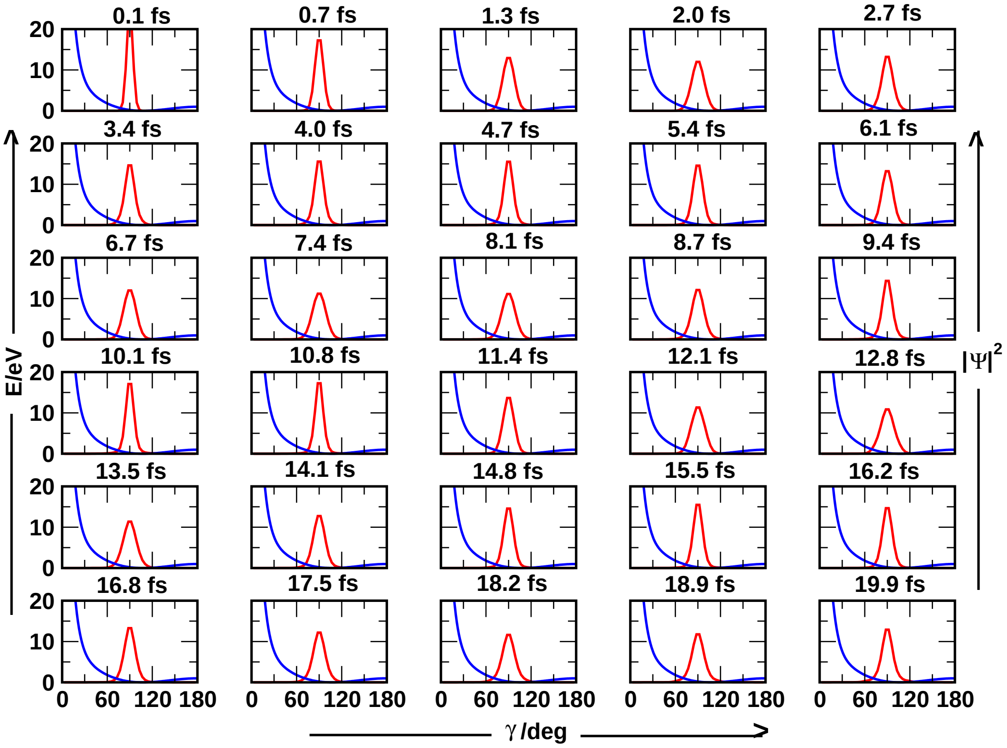

Figure 3. Snapshots of the one-dimensional probability density of the wave packet time evolving on $^2B_1$ as a function of γ at different times. Potential energy curve as a function of γ at the equilibrium geometry of water cation is superimosed.

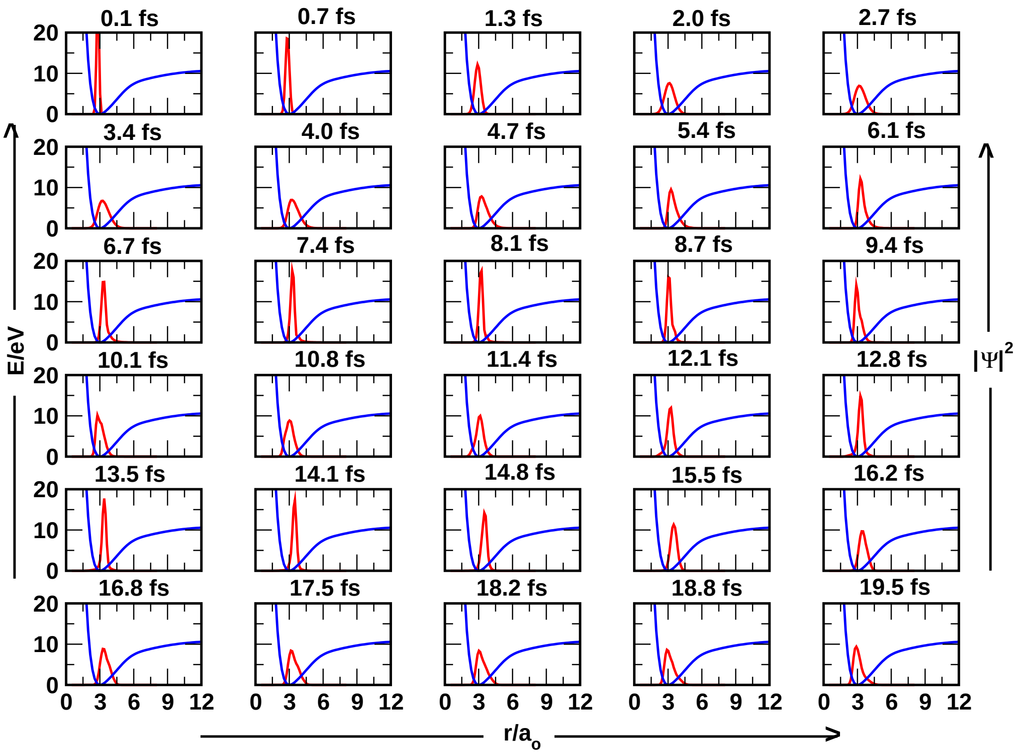

Figure 4. Snapshots of the one-dimensional probability density of the wave packet time evolving on the $^2B_1$ as a function of r at different times. Potential energy curve as a function of r at the equilibrium geometry of water cation is superimposed.

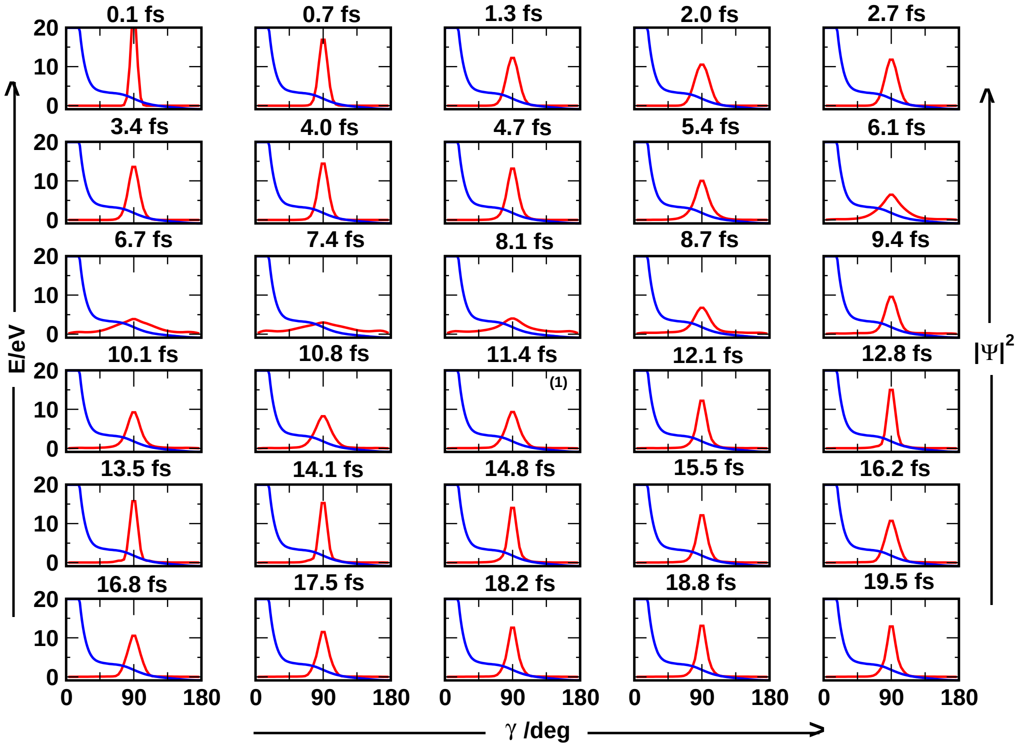

Figure 5. Same as in Fig. 1 for the ${}^2A_1$ state.

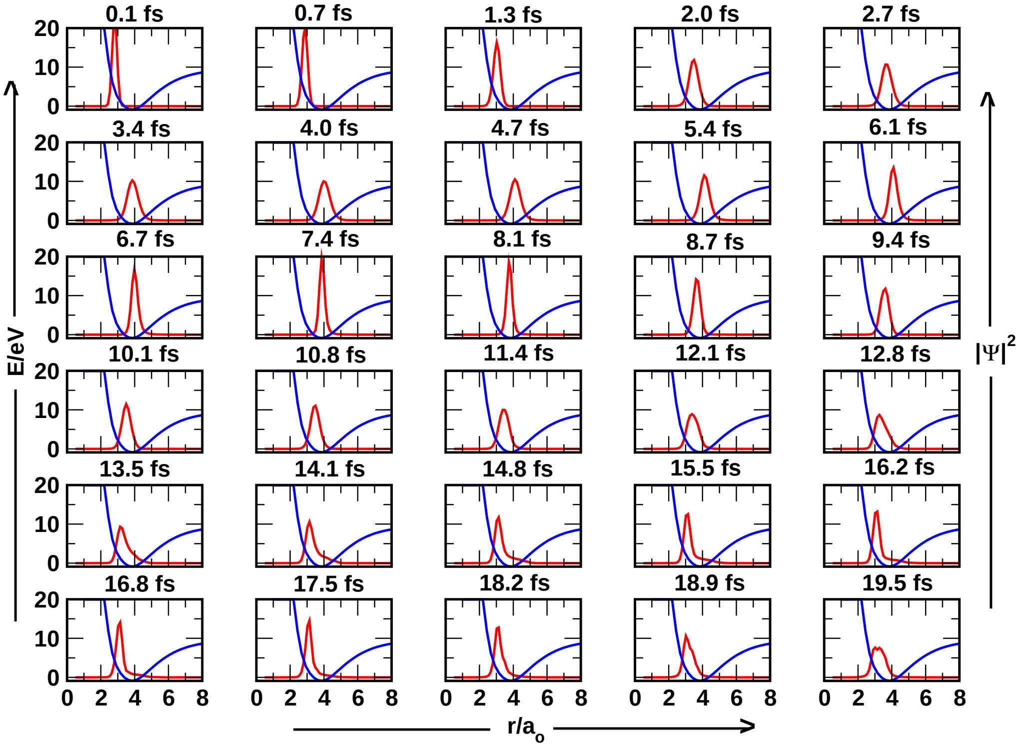

Figure 6. Same as in Fig. 2 for ${}^2A_1$ state.

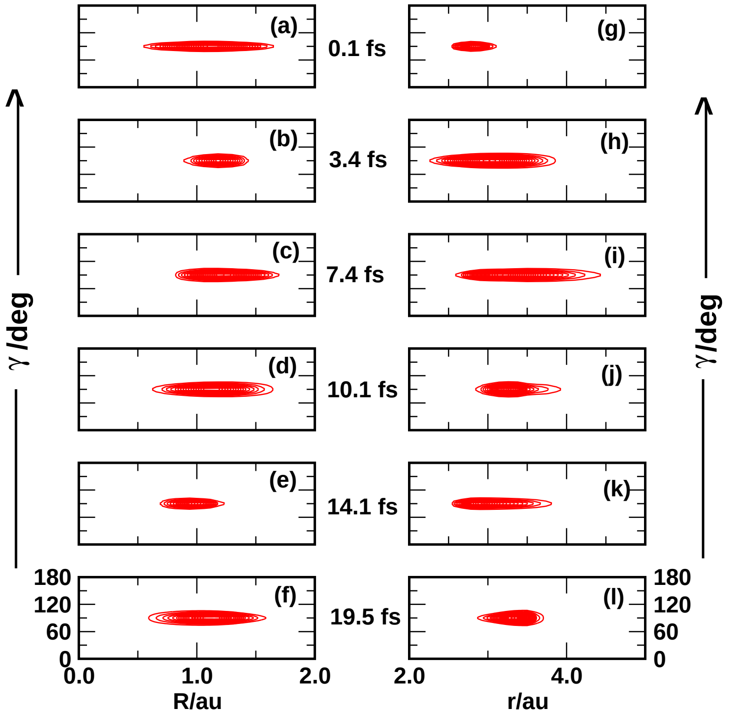

Figure 7. Snapshots of the probability density contours of the wave packet time evolving (in ${}^2B_1$ state) in (R, γ) and (r, γ) planes averaged over r and R, respectively, in the left and right coulms for D_2O^+.

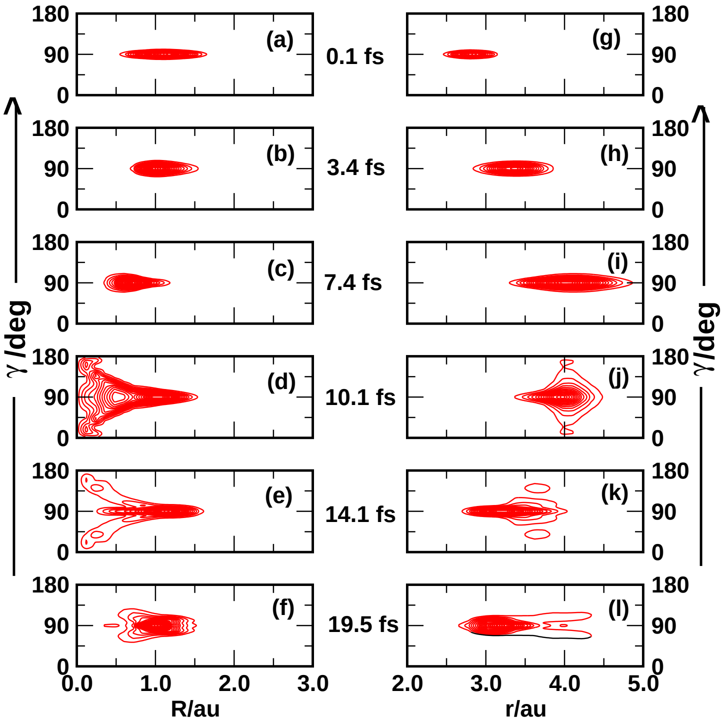

Figure 8. Same as in Fig. 5 for D_2O^+ in $^2A_1$ state.

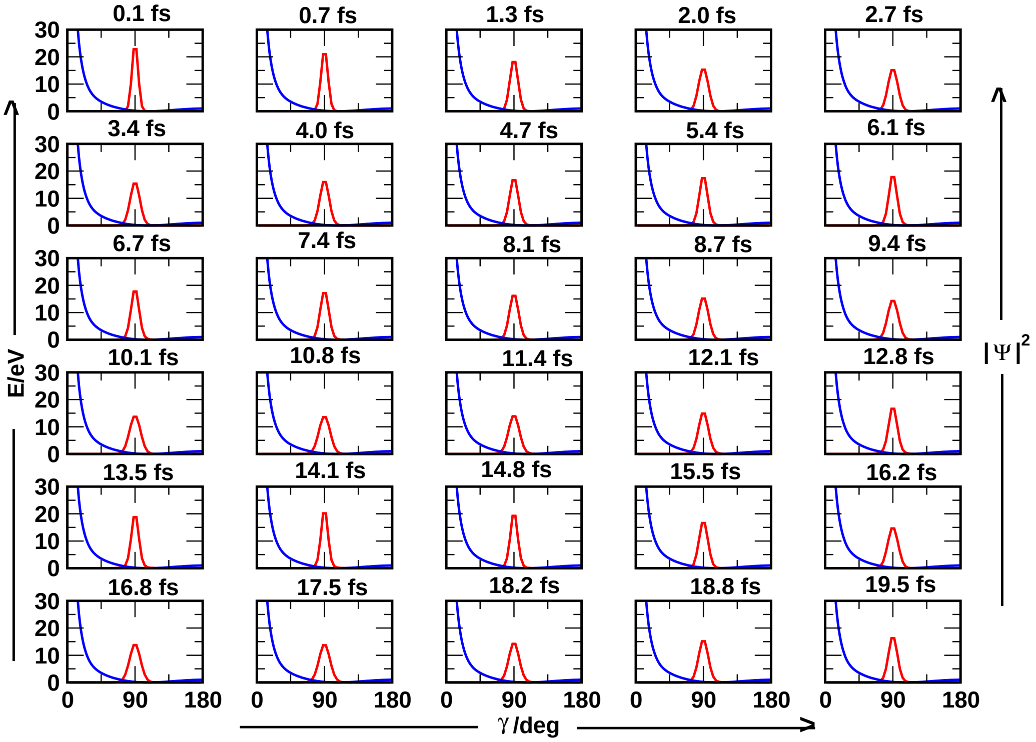

Figure 9. Same as in Fig. 1 for D_2O^+ in ${}^2B_1$ state.

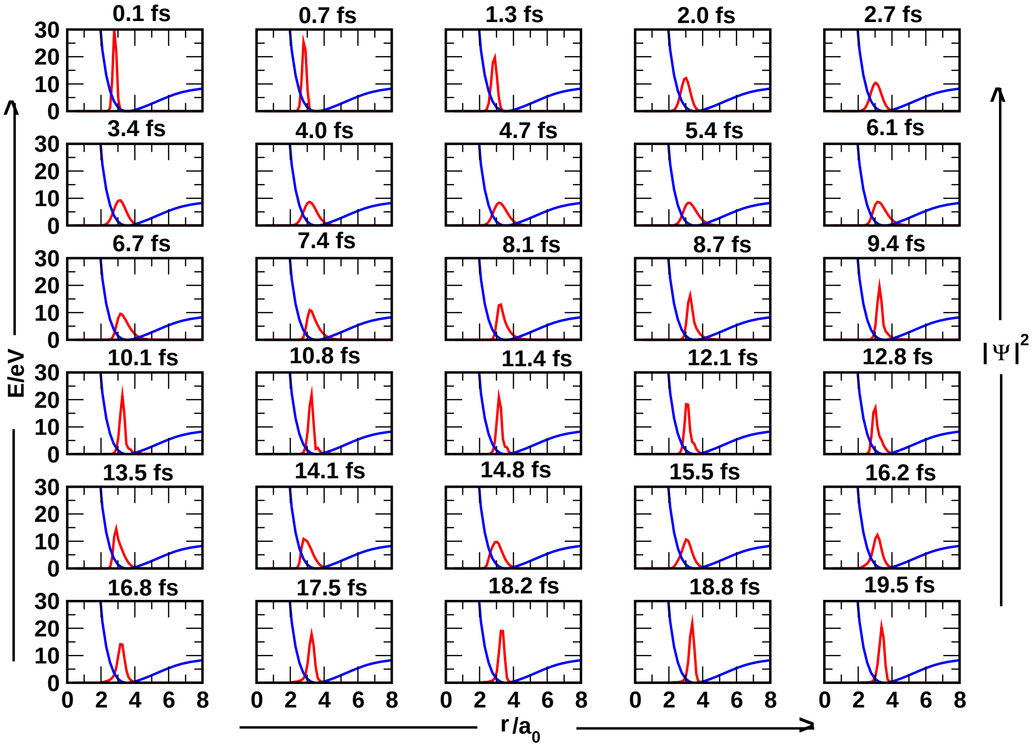

Figure 10. Same as in Fig. 2 for D_2O^+ in $^2B_1$ state.

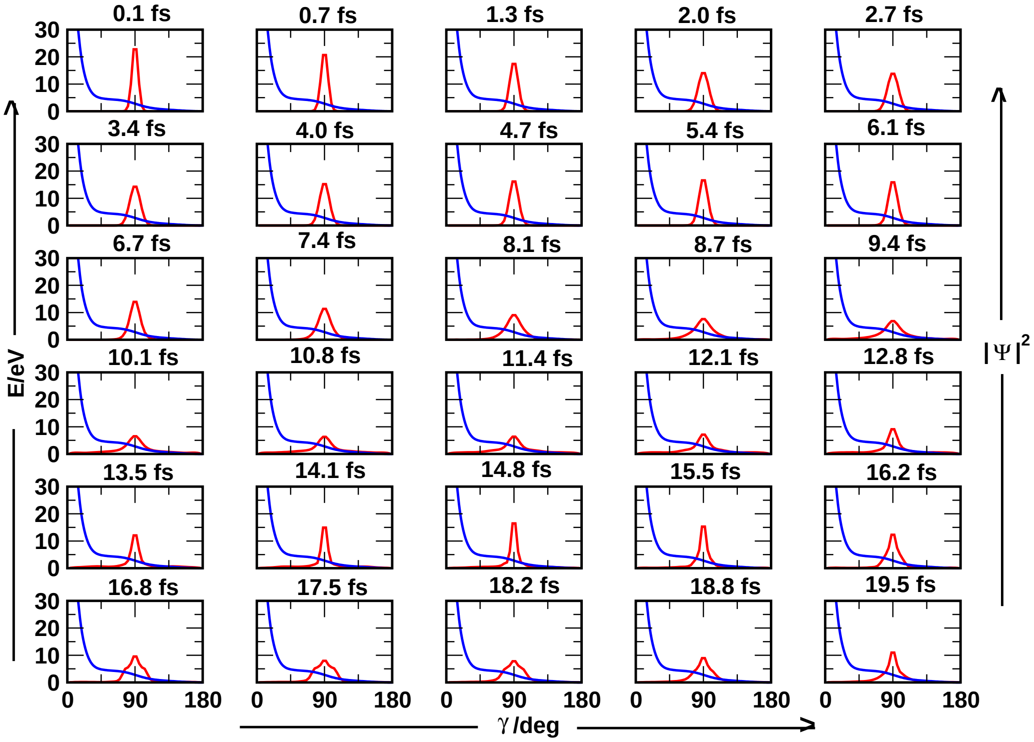

Figure 11. Same as in Fig. 3 for D_2O^+in $^2A_1$.

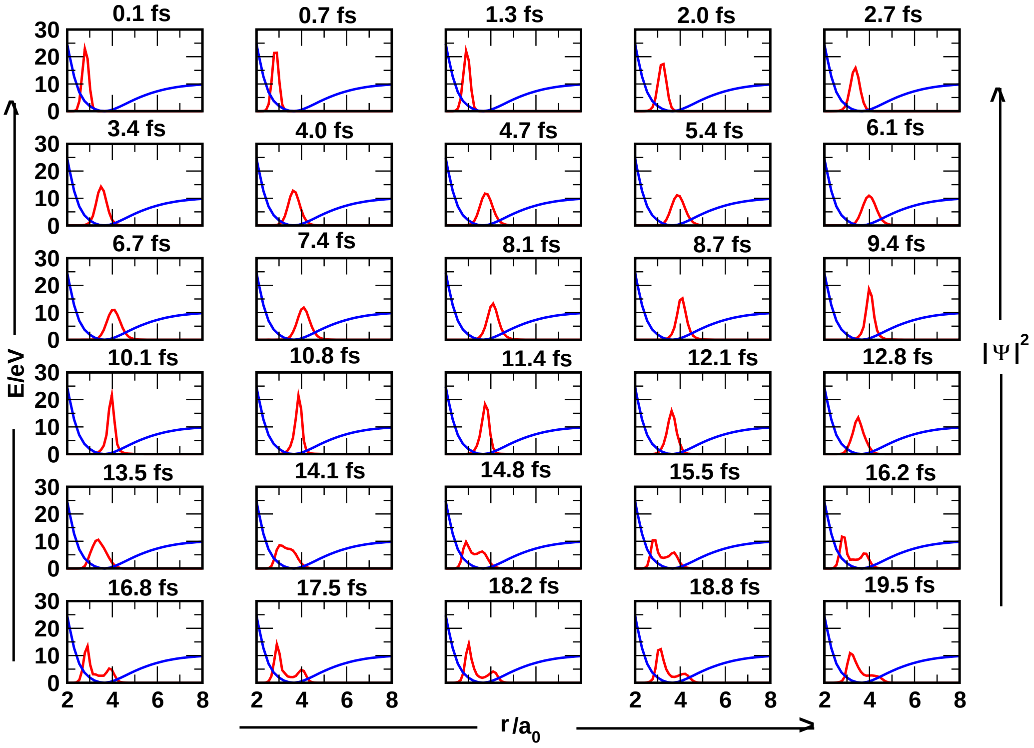

Figure 12. Same as in Fig. 4 for D_2O^+in ${}^2A_1$.

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