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

Non-adiabatic quantum dynamics of the electronic quenching $OH(A^2\Sigma^+)$+Kr

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Fig. 1S r=1.916 a.u. Π' PES/eV with respect to the reactants. Negative/zero/positive levels in red/black/blue. The Σ^+-Π' diabatic crossing is labeled by a green line.

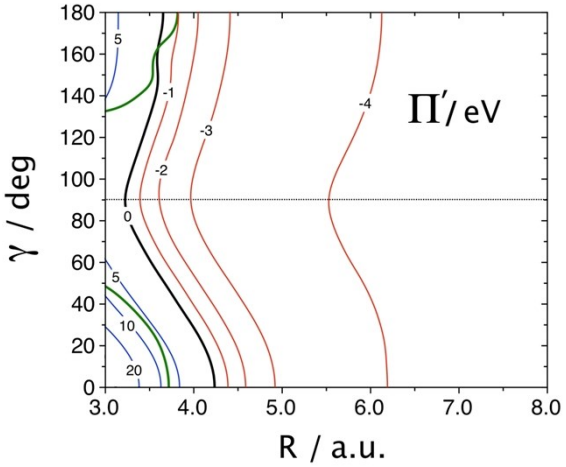
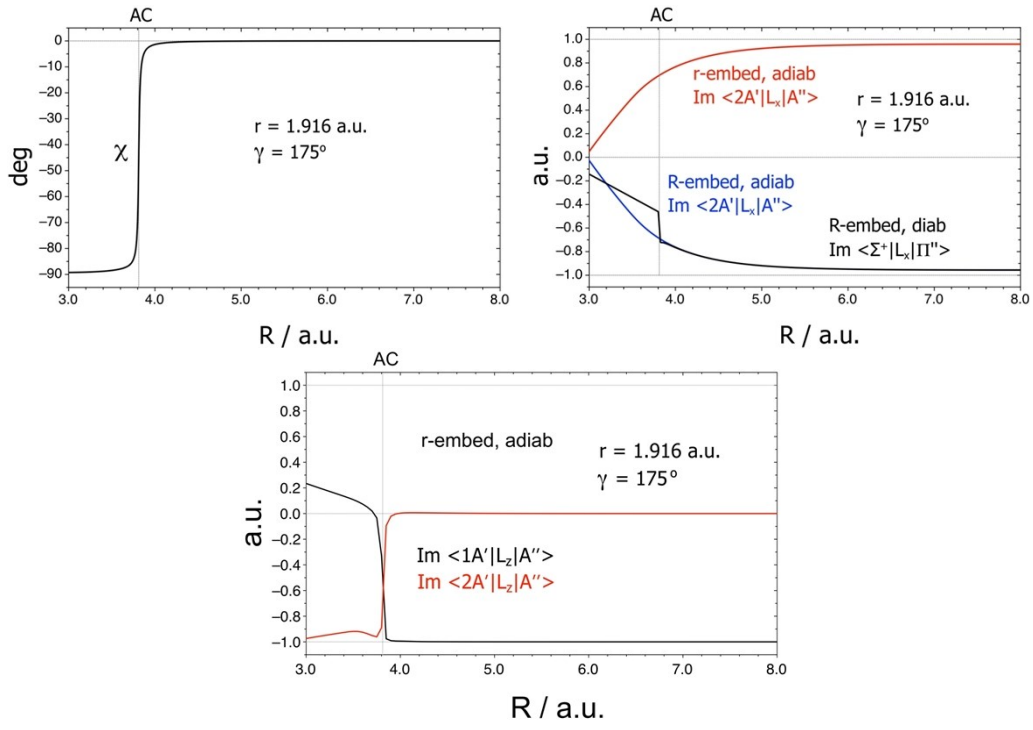


Fig. 2S r=1.916 a.u. and γ=175º. Above: adiabatic-to-diabatic transformation angle χ and $\hat{L}_x$ matrix elements in both embeddings and representations. Below: $\hat{L}_z$ matrix element in the r-embedding and adiabatic representation. AC labels the avoided crossing 1A'-2A' at R_{AC}=3.812 a.u.



From Section 3 we have

$$\langle 2\mathrm{A}'|\hat{L}_x|\mathrm{A}''\rangle = -\langle 2\mathrm{A}'|\hat{\mathit{L}}_z|\mathrm{A}''\rangle \sin\gamma + \langle 2\mathrm{A}'|\hat{\mathit{L}}_x|\mathrm{A}''\rangle \cos\gamma$$

$$\langle 1\mathrm{A}'|\hat{L}_x|\mathrm{A}''\rangle = -\langle 1\mathrm{A}'|\hat{\mathit{L}}_z|\mathrm{A}''\rangle \sin\gamma + \langle 1\mathrm{A}'|\hat{\mathit{L}}_x|\mathrm{A}''\rangle \cos\gamma$$

$$\langle \Sigma^+|\hat{L}_x|\Pi''\rangle = \langle 1\mathrm{A}'|\hat{L}_x|\mathrm{A}''\rangle \sin\chi + \langle 2\mathrm{A}'|\hat{L}_x|\mathrm{A}''\rangle \cos\chi ,$$

where $\hat{\mathit{L}}_z$ and $\hat{\mathit{L}}_x$ matrix elements are calculated with MOLPRO. The avoided crossing (AC) is at R_{AC}=3.812 a.u., r=1.916 a.u., and γ=175°, very near to the conical intersection at 180°. Both χ and *Im* $\langle \Sigma^+|\hat{L}_x|\Pi''\rangle$ vary suddenly by traversing the avoided crossing and take their asymptotic values for OH($^2\Pi$)+Kr at large R, the former from –89 to 0° and the latter from –0.121 to –0.955 a.u. Note also that *Im* $\langle 2\mathrm{A}'|\hat{L}_x|\mathrm{A}''\rangle \approx Im\langle \Sigma^+|\hat{L}_x|\Pi''\rangle$ at $R \geq R_{\mathrm{AC}}$, where $2\mathrm{A}' \approx \Sigma^+$ (A"=Π" everywhere) and that all couplings fulfil the C_{s} and $C_{\infty\mathrm{v}}$ selection rules.

Fig. 3S r=1.916 a.u. $\langle \Sigma^+ | \hat{L}_z^2 | \Pi' \rangle$, $\langle \Sigma^+ | \hat{L}_x \hat{L}_z | \Pi' \rangle$, and $Im \langle \Sigma^+ | \hat{L}_y | \Pi' \rangle$. Details as in Fig. 1S.

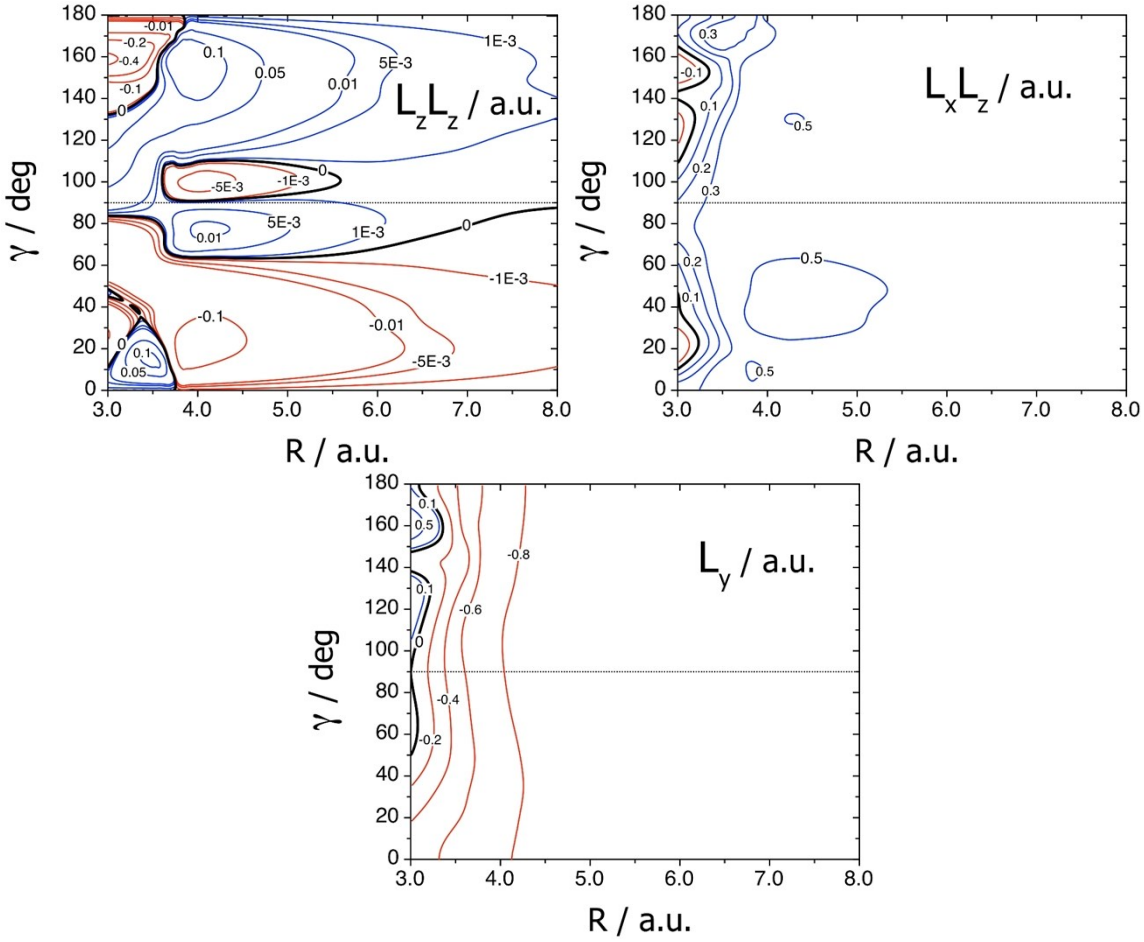


Fig. 4S r=1.916 a.u. *Im*<Σ^+| $\hat{L}_z$ |Π">, *Im*<Σ^+| $\hat{L}_x$ |Π">, *Im*<Π'| $\hat{L}_z$ |Π">, and *Im*<Π'| $\hat{L}_x$ |Π">. Details as in Fig. 1S.

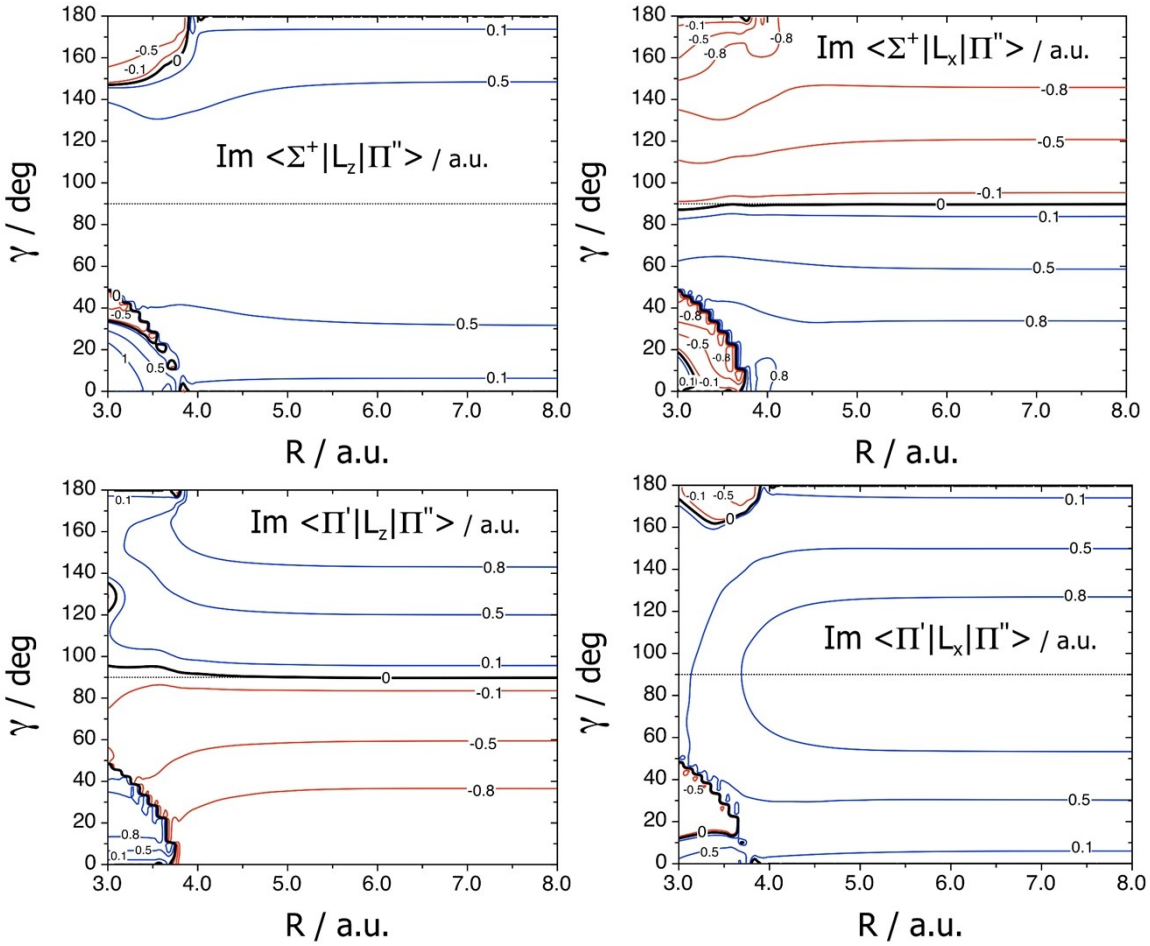


Fig. 5S J=70 and j_0=K_0=0. WP normalized norms and r-summed (R,γ) densities at 5 times.