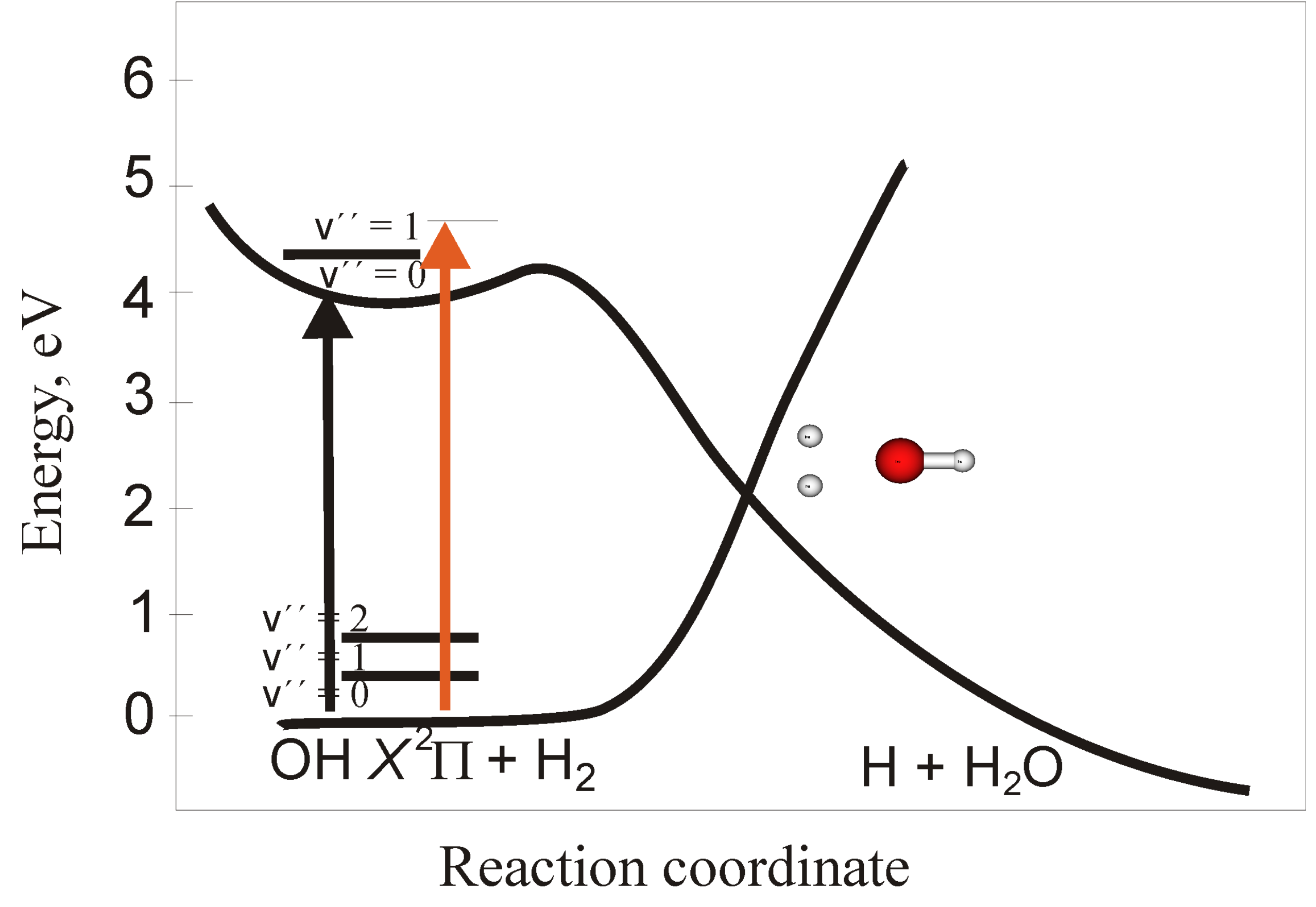
Direct Diabatization and Fitting of Coupled Potential Energy Surfaces for the Reactive Quenching of the Excited $^2\Sigma^+$ state of OH by Molecular Hydrogen

Osanna Tishchenko, Donald G. Truhlar (University of Minnesota and Minnesota Supercomputing Institute), Bina Fu (Dalian Institute of Chemical Physics, Chinese Academy of Sciences), Joel M. Bowman (Emory University), Ahren W. Jasper and Eugene Kamarchik (Sandia National Laboratory)



"Quenching of electronically excited OH radicals proceeds through a conical intersection, leading to H + H2O and X $^2\Pi$ OH + H_2 products. Pump-probe laser methods are used to examine the outcomes of these reactive and non-reactive quenching processes, providing new dynamical signatures of the nonadiabatic process." (Marsha Lester).

OBJECTIVE: develop a set of coupled full-dimensional analytic potential energy surfaces for dynamics simulations (the three states of interest are $X^2\Pi$ (doubly degenerate at OH + H_2) and $A^2\Sigma^+$).

Adiabatic or diabatic representation?

- ☐ Adiabatic representation

  Advantage: Unique; well defined; provides a good zero-order pictures when the coupling is neglected

  Weaknesses: PESs are not smooth; non-adiabatic coupling is a vector, varying and has singularities

- ☐ Diabatic representation

  Advantage: scalar coupling, smooth surfaces and couplings

  Weaknesses: not unique; neglects some coupling

Strategy:

☐ Calculate 3×3 diabatic potential-energy matrices to represent the three states:

$$\mathbf{U}=\begin{bmatrix} U11(\mathbf{Q}) & U12(\mathbf{Q}) & U13(\mathbf{Q}) \\ U12(\mathbf{Q}) & U22(\mathbf{Q}) & U23(\mathbf{Q}) \\ U13(\mathbf{Q}) & U23(\mathbf{Q}) & U33(\mathbf{Q}) \end{bmatrix} \qquad (1)$$

☐ Fit analytic functional forms to these matrices to obtain global diabatic representations with correct permutation symmetry.

Computational Methods

- ☐ PESs calculations: SA(3)-MCQDPT/aug-cc-pVTZ
- ☐ Active space: *nom*-CPO ≡ {σ,σ*(OH),σ,σ*(HH),2p_y(O),2p_z(O),3p_y(O),3p_z(O)}≡ (8o/7e)
- ☐ Diabatization: The fourfold way

Fourfold-way Diabatization

I. Construct diabatic prototype CSFs lists
II. Determine smooth diabatic MOs (DMOs)
III. Re-express adiabatic state by CI expansions in terms of DMOs
IV. Apply configurational uniformity to get diabats

Diabatic MOs determined by fourfold way

$$D_3(\alpha_N,\alpha_R,\alpha_T)=\underbrace{\alpha_N D^{NO}}_{\text{natural orbital term}} + \underbrace{\alpha_R D^{ON}}_{\text{occupation number term}} + \underbrace{\alpha_T D^{TD}}_{\text{transition density term}}$$

Maximum overlap reference MOs (MORMO) criterion – maximize the reference overlap term $D^{RO} = \sum_{\tau=1}^{\lambda} |\langle u_\tau^{ref}(Q)|u_\tau(Q)\rangle|^2$

$$u_\tau^{ref}(Q) = \sum_i \underbrace{a_i(Q^{ref})}_{\text{MO coefficient of the reference diabatic MO at the reference geometry}} \underbrace{\xi_i(Q)}_{\text{Atomic orbital at the present geometry}}$$

reference diabatic MOs, τ = 1,2,…λ

The diabatic molecular orbitals (DMO) have the following character:

$u_1 \equiv \sigma(OH)|3a_1$, $u_2 \equiv \sigma(HH)|4a_1$, $u_3 \equiv 2p_z(O)|1b_1$,

$u_4 \equiv 2p_y(O)|1b_2$, $u_5 \equiv 3p_y(O)|2b_2$, $u_6 \equiv \sigma^*(OH)|5a_1$,

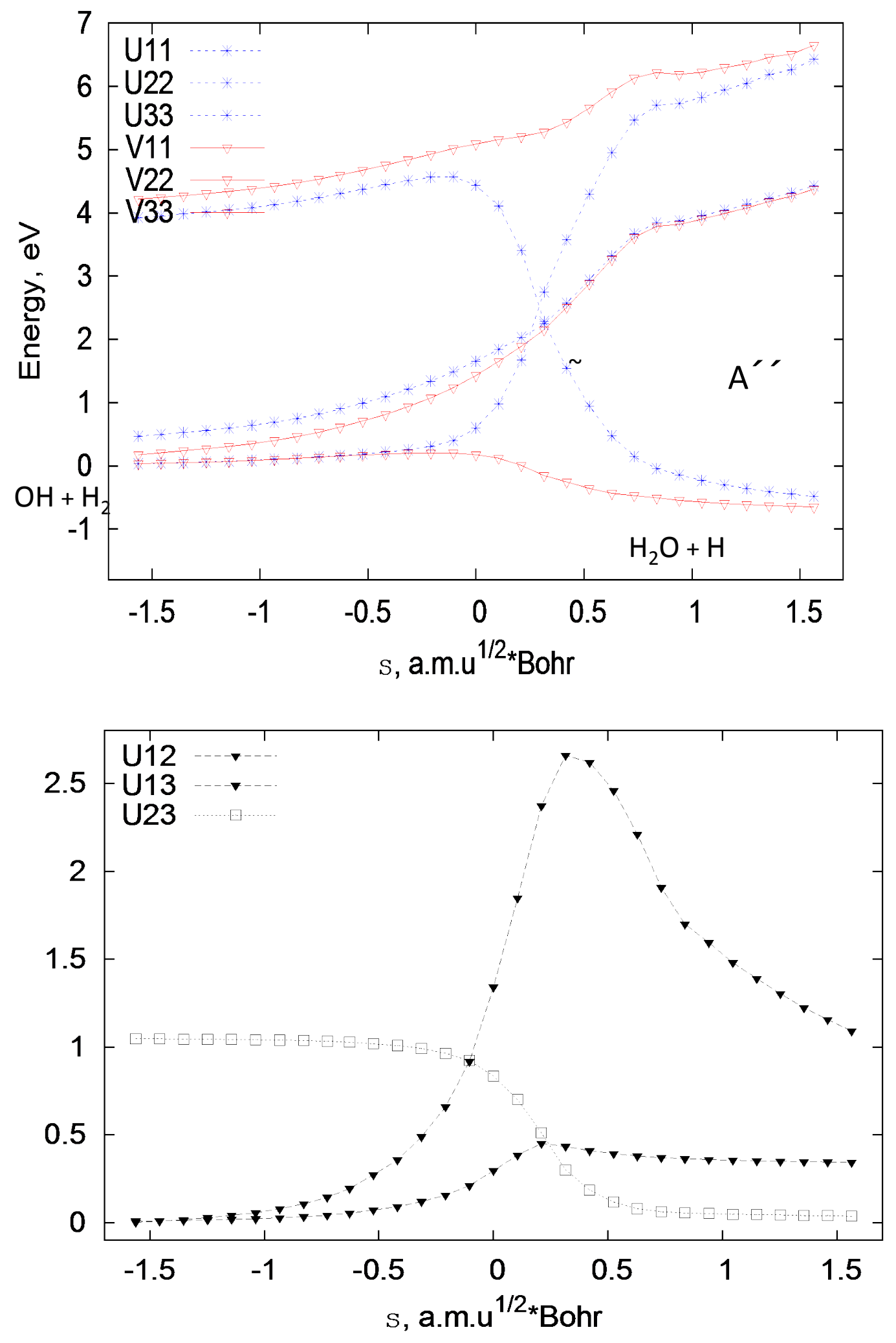
$u_7 \equiv \sigma^*(HH)|3b_2$, $u_8 \equiv 3p_y(O)|2b_1$.

Diabatic prototype CSFs lists

χ_1: 22210000
χ_2: 20210020
χ_3: 20220010
χ_4: 20221000
χ_5: 22120000
χ_6: 21120010
χ_7: 21120010
χ_8: 12220000
χ_9: 21220000

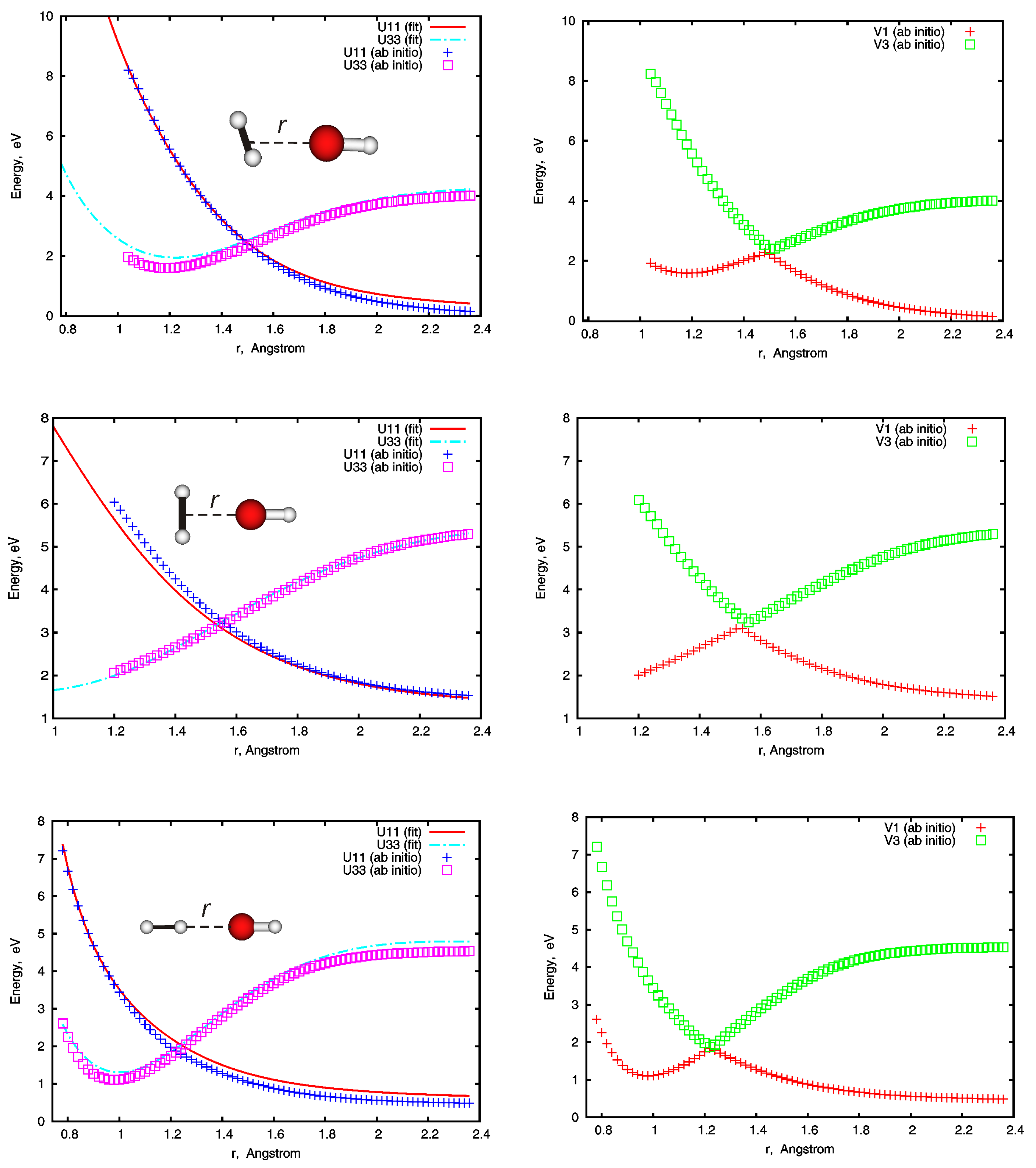
A total of 33,946 calculated data points were used in the fitting of the diagonal and off-diagonal elements of the diabatic potential-energy matrix (1). The fits for U_{11}, U_{22}, and U_{33} have MUEs 0.05, 0.01, and 0.05 eV for energies up to ~5.5 eV relative to the reactant asymptote.

Minimum-energy reaction path except raise spectator H by 0.3 Å out of plane so C_1 symmetry



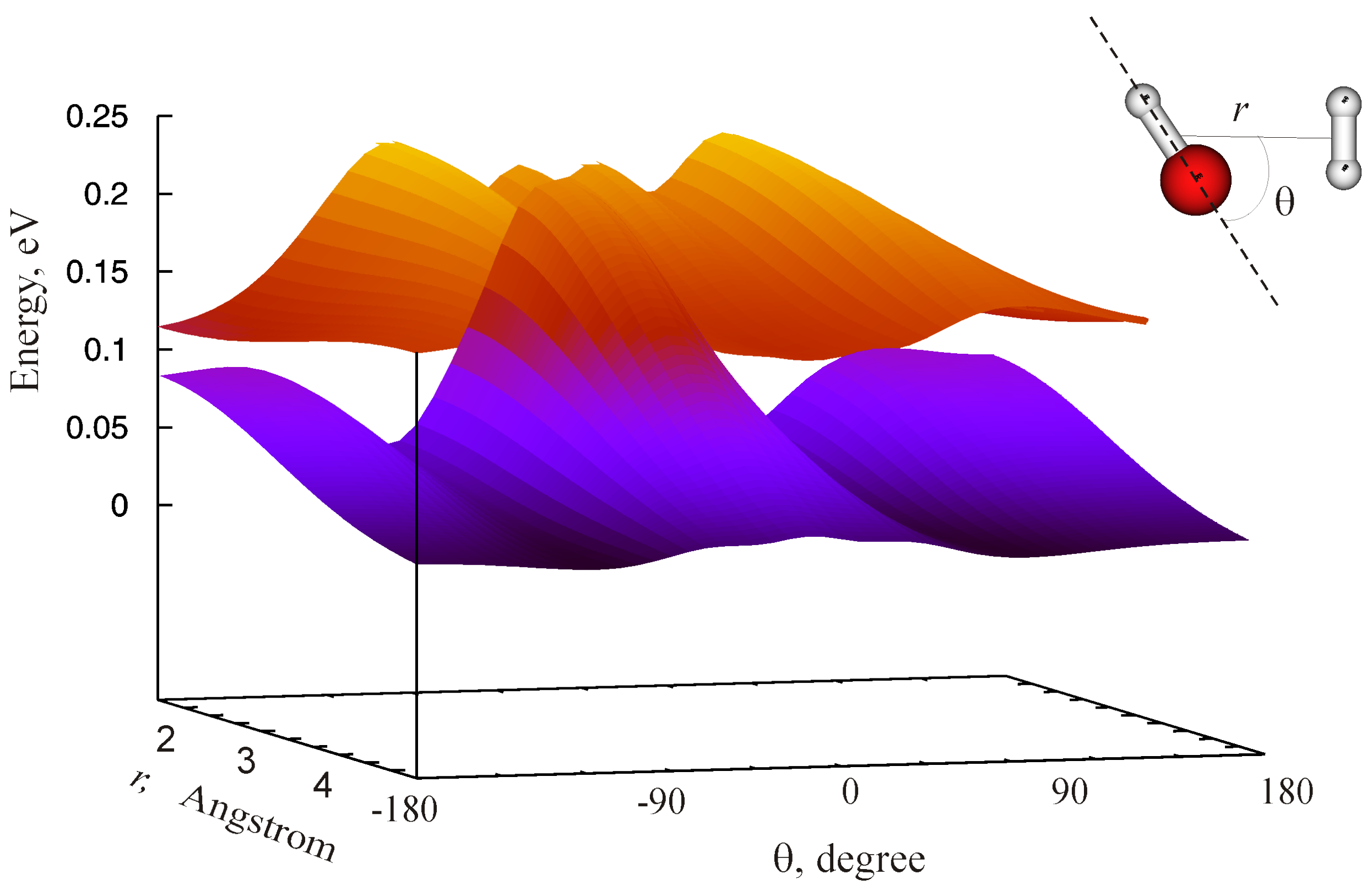
No adiabat equals a diabat;

and all 3 couplings are nonzero.



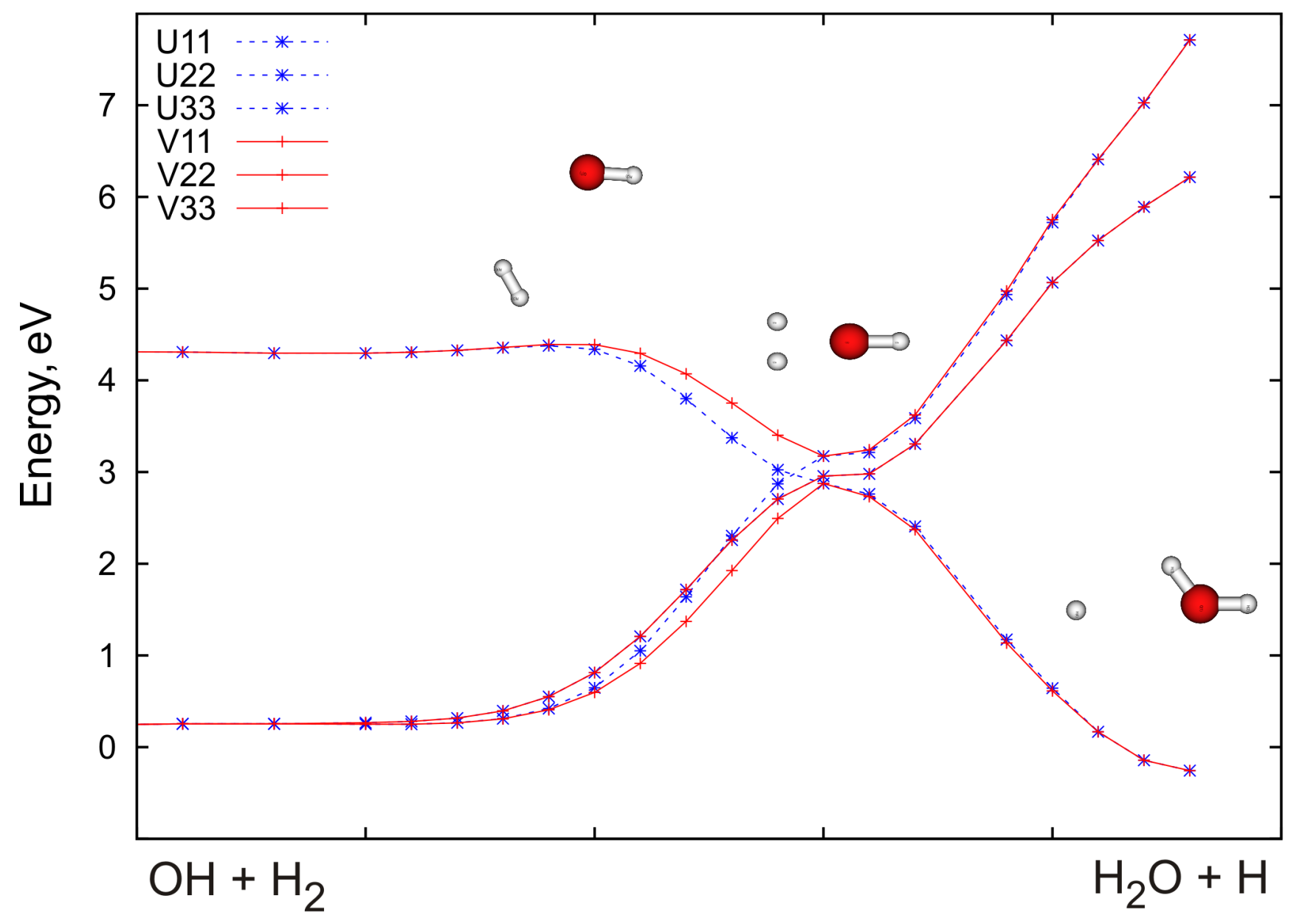
1D-cuts through our fitted and calculated PESs as functions of the distance between the centers of mass of OH and H_2 illustrating conical intersections at C_s (top), C_{2v} (middle), and $C_{\infty v}$ (bottom) geometries.

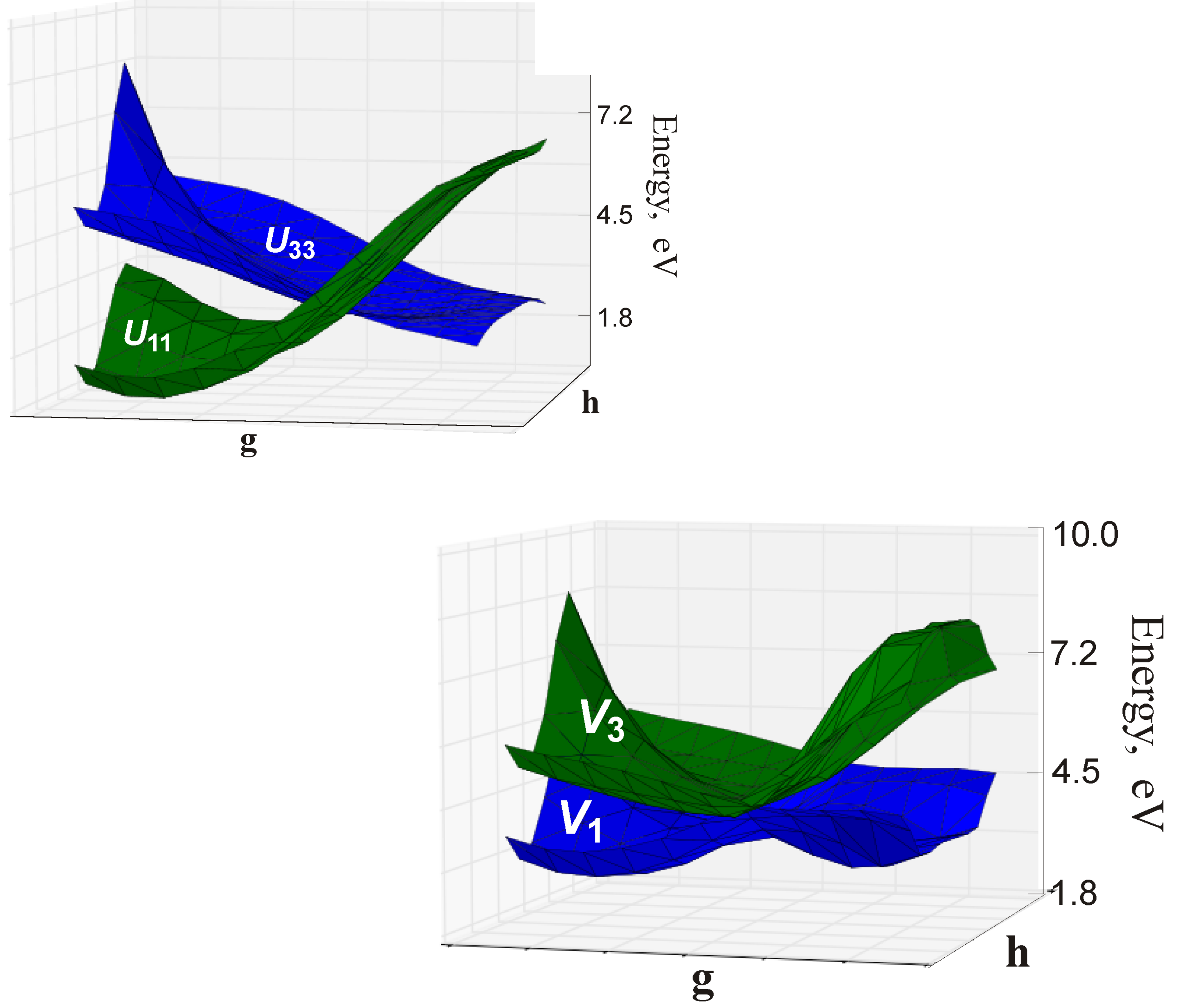
This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under grant no. DE-SC0008666.



The 1 *A´* and 2 *A´´* PESs correlating with $X\,^2\Pi + H_2$ and $A\,^2\Sigma+ + H_2$, respectively, displayed as a function of a distance between the centers of mass *r* and the OH orientation angle *θ*.

Linear synchronous path from reactants to products via conical intersection





2-Dimensional views of our fitted diabatic (top) and adiabatic (bottom) PESs as functions of the gradient difference (**g**) and the derivative coupling (**h**) vectors near a point on the C_{2v} seam of conical intersections. The Cartesian coordinates for **g** and **h** vectors are taken from a previous study by Yarkony (J. Chem. Phys. 113, 22, 10093) and scaled by factors of 1.5 and 0.35, respectively. The analytic representation of the adiabatic potential-energy surface is obtained by diagonalizing the diabatic potential energy matrix (1).

ACCOMPLISHMENTS: Global full-dimensional analytic diabatic representations of the potential energy surfaces for OH (2Σ+) + H2 reaction have been developed from electronic structure calculations and will be used in dynamics calculations.