Supplementary Information: The destruction of CH^+ with atomic hydrogen at low temperature understood: a non-adiabatic dynamical study

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1 *Ab initio* grids

The *ab initio* points to generate the fit are computed in two different grids:

For the $CH^+ + H$ system the two C-H distances are scanned together with the H-C-H angle. The angle is scanned from 0° to 180° with steps of 10°. One of the C-H distances changes from 0.6 Å to 2.2 Å and the second C-H distance is scanned from 0.7 Å to 10.0 Å, with steps of 1 and 0.1 Å for distances larger and shorter than 6 Å, respectively.

For the $C^+ + H_2$ system, a set of Jacobi coordinates is defined, with r the H-H distance, and R the distance from C to the H_2 center of mass. In this case the Jacobi angle is scanned from 0° to 90°. R is scanned from 0.7 Å to 10.0 Å, with steps of 1 and 0.1 Å for distances larger and shorter than 6 Å, respectively. r takes values from 0.6 Å to 3.0 Å

2 Diabatic Potential Energy matrix train

The neural net to compute the elements of the diabatic energy matrix is a feed forward neural network with 3 hidden layers and 40 neurons each. Hyperbolic tangent non nonlinearities are employed between the hidden layers, except for the output layer.

The weights are initialized randomly from a normal distribution and the bias are set to zero.

The fundamental invariants are normalized before being inputted into the net:

$$I = \frac{FI - \overline{FI}}{\sigma} \tag{1}$$

with $\overline{FI}$ and σ the mean and standard deviation of each element of the FI vectors in the training dataset.

The output elements of the neural net are linearly scaled prior to the construction of the PEM:

$$V_{NN} = \frac{(O+1)\cdot(E_{max} - E_{min})}{2} + E_{min} \tag{2}$$

where O is an output of the neural net and E_{max} and E_{min} are scalars. In this case $E_{max} = -E_{min}$ with E_{min} being the minimum energy of the fundamental electronic state in the training set.

An AdamW[1] optimizer is employed in the first steps of the training process until the loss gets to 300 meV, where it is changed to a Limited memory Broyden–Fletcher–Goldfarb–Shanno optimizer (L-BFGS)[2]. Once the total loss reaches a value of 150 meV, the regularization term λ_1 (Eq. (6) in the main text) is set to zero, so the training proceeds only on the adiabatic training set.

An in-house Python code is used to train this net with the PyTorch library[3].

3 Long-range

Fig.1 serves to check the accuracy of the long range term included in the diabatic PES, specially in the reactants side.

In the top panel, the *ab initio* energy for the H approaching the CH^+ on the H side is presented together with: 1) the long-range contribution with the scaled $\tilde{R}$ and 2) the unscaled R distances.

As mentioned in the main text $\tilde{R} = R + R_{lim}\cdot\exp(-(R-R_e))$ serves to avoid the divergence of the long-range term as $R \rightarrow 0$. This effect can be clearly seen comparing the solid blue line (which tends to zero as $R \rightarrow 0$) with the dashed black line which diverges as $R \rightarrow 0$.

4 Wave packet calculations

The quantum wave packet calculations are done with the MADWAVE3 program[4,5], in reactant Jacobi coordinates in a body-fixed frame, using grids for the internal coordinates (the distances r and R, associated to the CH internuclear vector, and the vector joining CH^+ center of mass and the H atom), and a basis for the electronic coordinates and total angular momentum $\mathbf{J}$, with modulus J and projections M and Ω, on the z-axis of the space-fixed and body-fixed frames, respectively. The flux on individual final states of the $H_2(v', j')$ products is evaluated by a reactant-to-product coordinate transformation method[6]. The parameters used in the calculations are shown in Table 1, and the meaning of each variable are explained in Ref.[5].

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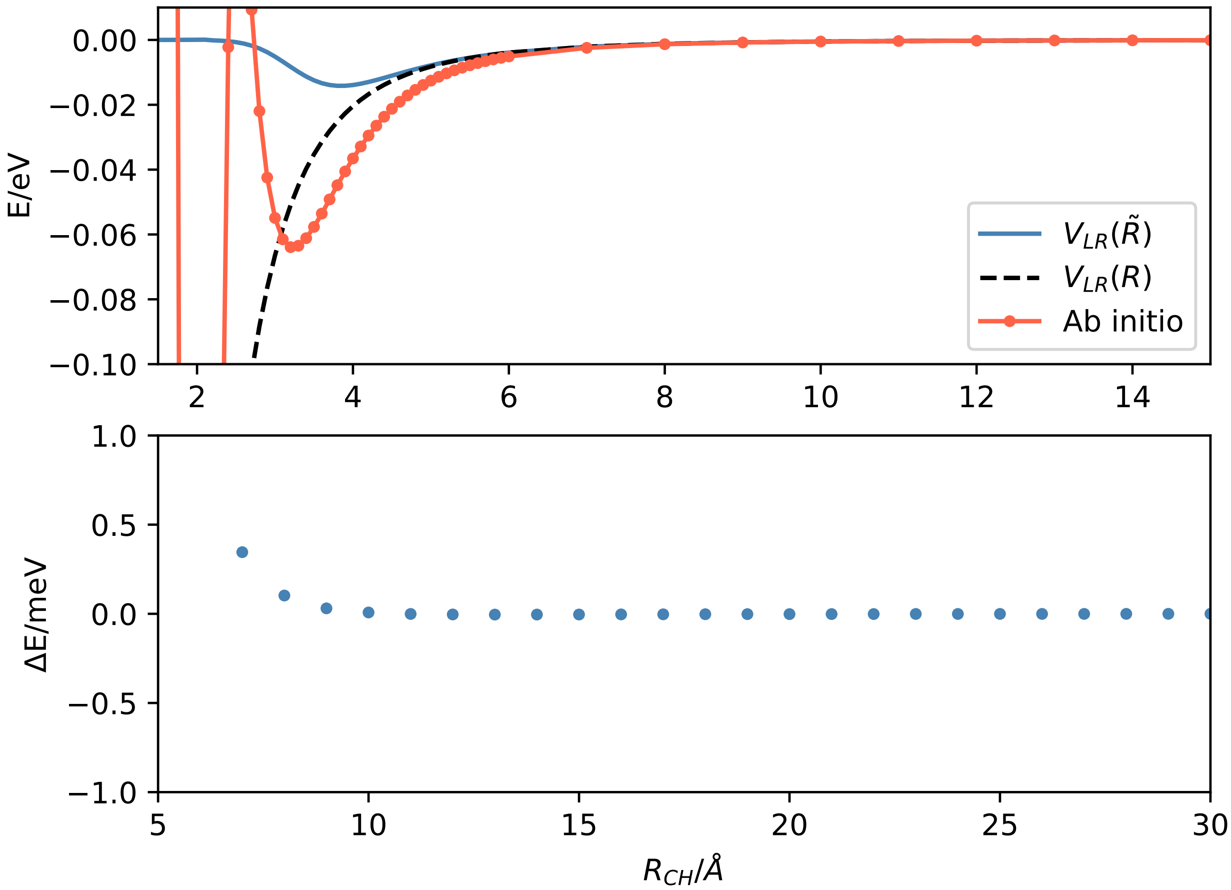

Figure 1 Top panel: With red line-dots the *ab initio* energy for the H approaching the CH^+ from the H side. With dashed black line the long-range energy if computed with the R variable. With solid blue lines the long-range energy if computed with the $\tilde{R}$ variable. Bottom panel: Energy difference between the *ab initio* energy and the $V_{LR}(\tilde{R})$ term.

Table 1 Typical parameters used in the Wave Packet calculations with the MADWAVE3 program. Distances in Å, energies in eV, masses in amu.

$r^{min}, r^{max}, npun_r$	0.1, 25, 448
$R^{min}, R^{max}, npun_R$	0.001, 25, 448
NANGU	240
NELECMAX	3
ABSR1,ABSALP1,N1EXPO	13, 1e-7, 6
ABSR2,ABSALP2,N2EXPO	13, 1e-7, 6
Rcolini$_{ANG}$, Ecol$_{eV}$,deltaE$_{eV}$	12, 0.3, 0.15
nvinipro,nvmaxprod	0,5
jiniprod,jmaxprod	0,15
iommaxprod	min(Jtot,jmaxprod)
xm0,xm1,xm2	1.00783,1.00783,12.
VcutmaxeV	2.5

5 Adiabatic statistical calculations

The adiabatic statistical calculations have been performed using the aZticc.f code described in Ref.[7], using the potential energy surfaces developed in this work. **In Ref.[7] an atom with spin-orbit structure was considered. Here we consider an atom with zero spin and zero orbital angular momentum, having 3 coupled electronic states in the AS3×1 for the channel C$^+$+H$_2$ and only 1 adiabatic state for CH$^+$+H channels. In the AS1×1 case only 1 adiabatic electronic is considered for the two rearrangement channels. The potential matrices are formed following the prescription of Ref.[7] considering L=S=0. These matrices are formed for a grid of npun_R points in R for each J and p and diagonalized to obtain the adiabatic potentials used in the Adiabatic statistical approach. A J_{max}= 80 is considered, including up to Ω_{max}=20. For matrices larger than 2000, a Lanczos method is used to calculate the eigenvalues.** The parameters used are listed in Table 2.

Table 2 Typical parameters used in the calculations of the adiabatic potentials needed in the Adiabatic statistical calculations. Distances in bohr, energies in eV.

C$^+$ + H$_2$ channel	
$r^{min}, r^{max}, npun_r$	1, 4.5, 600
$R^{min}, R^{max}, npun_R$	1., 40,600
NANGU	50
NELECMAX	1 or 3
J^{max}_{tot}, Ω^{max}	80, min(J_{tot},20)
v_{min},v_{max}	0,7
j_{min}, j_{max}	0,28
CH$^+$ + H channel	
$r^{min}, r^{max}, npun_r$	1, 4.5, 600
$R^{min}, R^{max}, npun_R$	1., 40,600
NANGU	50
NELECMAX	1
J^{max}_{tot}, Ω^{max}	80, min(J_{tot},20)
v_{min},v_{max}	0,5
j_{min}, j_{max}	0,35

The total number of states for reactants (C$^+$+H$_2$) and products (CH$^+$+H) are shown in Fig. 2, for the case AS3×1 , taking CH$^+$(v=0,j=0) eigenvalue as the zero of energy, to illustrate some discussions of the main text.

6 Quasiclassical calculations

Quasiclassical calculations are done with the MDwQT code[8,9], including surface hopping using the fewest switches method of Tully[10]. Initial conditions are set using a Monte-Carlo sampling. For the CH$^+$ vibration, quantum conditions are obtained by the adiabatic switching method[11,12], choosing a single initial trajectory for each v with an energy close to that of the corresponding quantum level, to warranty a stable initial vibrational energy. The initial impact parameter, b, is sampled between 0 and B, according to a quadratic distribution on b, where B is determined for each energy according to a capture model for charge-induced dipole long-range interaction. The initial distance between H and CH$^+$ is set at 100 bohr, and the the trajectories end when any atom-atom distance get longer than 105 bohr. The Hamilton equations are

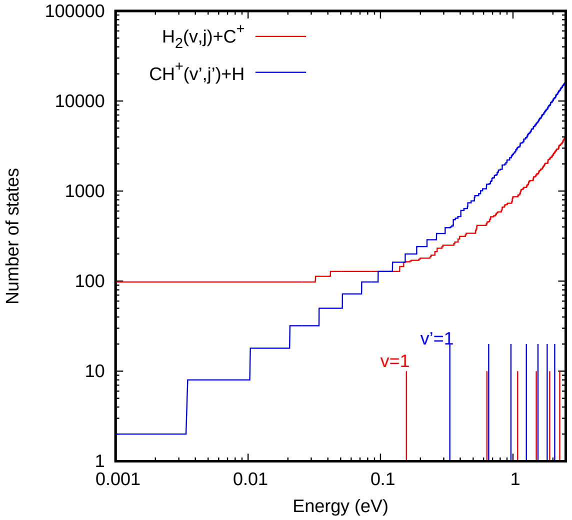

Figure 2 Number of asymptotic states in the CH^++H and C^++H_2 channels, evaluated by counting the number of diatomic rovibrational states below energy E, multiplied by the electronic and rotational degeneracy. The sticks correspond to the (v, j=0) level of H_2 (in red) and CH^+ (in blue), respectively

integrated in time in Cartesian coordinates with the step adaptive Adams-Bashforth-Moulton predictor corrector method[13], using a time step of 1 fs. For each temperature and initial state, $N_{tot} = 10^5$ trajectories are run, and the state-selected rate is computed as:

$$k_{vj}(T) = \sqrt{\frac{8k_BT}{\pi\mu}}\pi b^2_{max}(T)P_r(T), \tag{3}$$

where $\mu = m_H m_{CH^+}/(m_H + m_{CH^+})$, $b_{max}(T)$ is the maximum impact parameter and the reaction probability for each product channel $P_r(T) = N_r/N_{tot}$.

Notes and references

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