# Supplementary Information: Revisiting the Intricate Photodissociation Mechanism of Ammonia along the Minor $NH + H_2$ Pathway

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# 1 Optimization of critical points on the machine learned potential energy surfaces

The critical points schematically displayed in Section 2.1 Figure 1 in the main text were obtained using the external optimizer feature of ORCA,<sup>1</sup> to which the SHARC package<sup>2,3</sup> is interfaced (a copy of the machine learned potentials and the interface to SHARC, as used in this work is provided at 10.5281/zenodo.14545220). The necessary SHARC scripts were adjusted to allow for the use of the SHARC-NN interface and with this the ammonia potentials to be used for the optimizations. Suitable guess geometries led to the optimized minima and crossing points for the major and minor dissociation channel. The asymptotic energies were obtained via constrained optimizations with an 8 Å distance of the nitrogen atom to the dissociated hydrogen.

### 2 Absorption spectrum and comparison with experiment

Vertical excitation of the 10<sup>5</sup> Wigner distributed geometries (at 297 K) was performed over the whole spectral range – in practice from 0 eV to 10 eV. Out of the 10<sup>5</sup> geometries, 85,578 could be excited. Using these excited points, we computed the absorption spectrum as depicted in Figure S1, employing a Gaussian convolution with 0.1 eV FWHM. The vertical line at 6.41 eV (193 nm) indicates the excitation wavelength of the experimental study<sup>4</sup> targeting to study the rare ammonia dissociation channel, to which comparisons are made in the main text regarding fragmentation quantification. The computed spectrum shows a single, broad peak, with its maximum close to the experimental excitation energy. Moreover, the temperature considered for the Wigner sampling (297 K) also corresponds to the temperature at which the experiment was conducted.



Figure S1 Computed absorption spectrum of ammonia based on Wigner ensemble at 297 K in blue with experimental irradiation energy of 6.41 eV<sup>4</sup> as vertical gray line.

## 3 Nonadiabatic dynamics

The nonadiabatic dynamics using the SHARC program package<sup>2,3</sup> were carried out using the input keywords provided below:

```
nstates 2 0 1
actstates 2 0 1
state 2 mch
coeff auto
ezero 0.00015383
stepsize 0.2
nsubsteps 25
surf diagonal
coupling nacdr
gradcorrect
ekincorrect parallel_nac
```

```
reflect_frustrated parallel_nac
decoherence_scheme edc
decoherence_param 0.1
hopping_procedure sharc
select_directly
```

#### 4 Assessment of trajectories violating energy conservation

91 trajectories leading to the  $NH + H_2$  channel experienced fluctuations in the total energy that were larger than the desired threshold, meaning the deviation from total energy conservation was either larger than 0.1 eV between consecutive time steps or larger than 0.2 eV over the whole trajectory.

Out of all 91 cases, in 29 the energy conservation violation happened after dissociation and thus it was deemed uncritical. In 62, the issue occurred during or before the dissociation concluded (according to our definition), but almost always in close temporal proximity to full fragmentation as indicated in Figure S2. In Figure S2a, we plot the cumulative number of trajectories that do not conserve the total energy as a function of time before the H<sub>2</sub> elimination is complete. The majority of erroneous trajectories, displays large energy fluctuations only 20 fs or less before fully dissociating. This is approximately half of the average time the dissociation itself requires (39 fs, based on the geometric criteria mentioned in the main text).

To complement this analysis, Fig. S2b shows a histogram of the second longest N-H distance recorded at the first occurrence of total energy conservation violation. In most cases, the bonds are quite elongated, indicating that the dissociation is already in progress. None of the 91 trajectories show bond lengths under 2 Å, 2 under 2.5 Å and in total 10 trajectories under 3 Å. For comparison, the N-H equilibrium bond length is 1.05 Å.

Furthermore, if the energy conservation criteria are relaxed by doubling the allowed thresholds (only 36 trajectories still violate them), no trajectory shows a second longest N-H distance below 2.5 Å and only 2 possess one below 3 Å at the time the violation occurs. These findings suggest, that almost all cases of energy conservation issues can be viewed and counted as true rare photodissociations,  $NH + H_2$ . Thus, all the rare channel trajectories were included in the analyses.



**Figure S2** a) Cumulative number of rare photodissociation trajectories exhibiting total energy fluctuations between consecutive time steps of more than 0.1 eV or accumulating a total deviation of over 0.2 eV ordered by the time the fluctuation occurred prior to dissociation. b) Histogram of the second longest N-H bond distances at the point where total energy conservation violation first occurs, distances of 2 Å and 3 Å are indicated by vertical orange and green lines, respectively.

Additionally, all 111 erroneous trajectories (including the 91 from before, which showed the rare reaction, and those that showed the common or  $N+H+H_2$  and N+H+H+H pathways) were recomputed from the same initial conditions with a smaller nuclear time step of 0.1 fs. Most, namely 93 % (103), of them showed then a dissociation along the frequent channel, while 4.5 % (5) followed the rare pathway. This percentage approximately matches the overall splitting into the two main channels, only slightly favoring the rare fragmentation. Therefore, neither strictly excluding the erroneous trajectories, nor such recomputation can be seen as meaningful for the statistical analysis of the rare channel. Furthermore, this behavior hints at the probabilistic nature of the dissociation channels. While some properties of the initial condition provide certain criteria for the reaction type, such as the minimal total energy requirement for the rare pho-

todissociation, the by far biggest factor is stochasticity. These sizable deviations in total energy discussed above can indicate poorly fitted regions in the PESs or that the time step was too large compared to how rapidly the PES was changing. Regions close to state crossings are prone to sudden changes in potentials and couplings, which can lead to fluctuations in total energy.

Due to the reasonable size and/or region in phase space of the violation of energy conservation, we still believe that the neural network potentials are fitted well enough to establish and analyze the major and minor fragmentation channels of ammonia, but are less confident about the dynamics after the rare dissociation. These doubts are supported by the observation of state orderings where the triplet state is not as expected lowest in energy, but instead in some cases (40 %) the lowest singlet was lower in energy than the triplet state.

Regarding the observed 10 N + H + H<sub>2</sub> and 9 N + H + H + H fragmentations, we are less confident about the fit of the PESs as these regions in phase space were not explicitly considered for the fitting procedure. Moreover, from these,  $6 N + H + H_2$  and 8 N + H + H + H trajectories did not satisfy the overall total energy conservation. We thus refrain from further interpretation of these fragmentation occurrences.

#### 5 Kinetic fit



**Figure S3** Kinetic model of ammonia photodissociation schematically depicted including the reactive ammonia  $NH_3$ , the nonreactive ammonia species  $NH_3^{nr}$ , the frequent  $NH_2 + H$  and rare  $NH + H_2$  dissociation products. The labeled rate constants k and time delays  $\tau^{delay}$  on the arrows indicate the nomenclature for the individual processes used in the discussion.

For the kinetic fit for the species occurring during dissociation, the following differential equations were used according to the kinetic model depicted in Figure 2b of the main text and again in Figure S3:

$$\frac{d[\mathrm{NH}_{3}]}{dt} = \begin{cases}
-k_{\mathrm{nr}}[\mathrm{NH}_{3}] + k_{\mathrm{nr}}^{\mathrm{back}}[\mathrm{NH}_{3}^{\mathrm{nr}}] & \text{for } t \leq \tau_{\mathrm{freq}}^{\mathrm{delay}} \\
k_{\mathrm{nr}}^{\mathrm{back}}[\mathrm{NH}_{3}^{\mathrm{nr}}] + (-k_{\mathrm{nr}} - k_{\mathrm{freq}})[\mathrm{NH}_{3}] & \text{for } \tau_{\mathrm{freq}}^{\mathrm{delay}} < t \leq \tau_{\mathrm{rare}}^{\mathrm{delay}} \\
k_{\mathrm{nr}}^{\mathrm{back}}[\mathrm{NH}_{3}^{\mathrm{nr}}] + (-k_{\mathrm{nr}} - k_{\mathrm{freq}} - k_{\mathrm{rare}})[\mathrm{NH}_{3}] & \text{for } t > \tau_{\mathrm{rare}}^{\mathrm{delay}}
\end{cases} \tag{1}$$

$$\frac{d[\mathrm{NH}_{3}^{\mathrm{nr}}]}{dt} = k_{\mathrm{nr}}[\mathrm{NH}_{3}] - k_{\mathrm{nr}}^{\mathrm{back}}[\mathrm{NH}_{3}^{\mathrm{nr}}]$$
<sup>(2)</sup>

$$\frac{d[\mathrm{NH}_2]}{dt} = \begin{cases} 0 & \text{for } t \le \tau_{\mathrm{freq}}^{\mathrm{delay}} \\ k_{\mathrm{freq}}[\mathrm{NH}_3] & \text{for } t > \tau_{\mathrm{freq}}^{\mathrm{delay}} \end{cases}$$
(3)

$$\frac{d[\mathrm{NH}]}{dt} = \begin{cases} 0 & \text{for } t \le \tau_{\mathrm{rare}}^{\mathrm{delay}} \\ k_{\mathrm{rare}}[\mathrm{NH}_3] & \text{for } t > \tau_{\mathrm{rare}}^{\mathrm{delay}} \end{cases}$$
(4)

These equations were solved using the Python package SymPy<sup>5</sup> with the constraint of initially at time zero having only NH<sub>3</sub> and NH<sub>3</sub><sup>nr</sup> present. From these expressions a fit function was created, fitting the rate constants ( $k_{nr}, k_{nr}^{back}, k_{freq}, k_{rare}$ ), time delays ( $\tau_{freq}^{delay}, \tau_{rare}^{delay}$ ) and relative initial concentration [NH<sub>3</sub>]<sub>0</sub> ([NH<sub>3</sub><sup>nr</sup>]<sub>0</sub> =  $1 - [NH_3]_0$ ). For fitting, the curve\_fit function of the Python package SciPy<sup>6</sup> was used and uncertainties of the species populations over time were provided. The uncertainties were computed as the standard errors of each species population  $SE_i = \sqrt{\frac{p_i(1-p_i)}{N}}$  where N is the total number of trajectories and  $p_i$  are the probabilities, i.e. fractions, of the populations. Note, that for this fit the trajectories categorized as not stable anymore, but still not reacted, were considered as still one of the ammonia species, while few (45 trajectories, 0.09 %) not clearly determinable species trajectories were excluded from the fit. Due to this very low number the fitting should not be significantly impacted by the former.

The nonreactive ammonia species  $NH_3^{nr}$  in the kinetic model is crucial to adequately capture the populations of all species. An equivalent fit without any  $NH_3^{nr}$  present — according to the schematic depiction in Figure S4a — would show a much more rapid decrease in the total ammonia and overall significantly worse agreement with the trajectory data as is depicted in Figure S4b.



**Figure S4** a) Kinetic model of ammonia photodissociation schematically depicted without the nonreactive ammonia species  $NH_3^{nr}$ , only including the reactive ammonia  $NH_3$ , the frequent  $NH_2 + H$  and rare  $NH + H_2$  dissociation products. The labeled rate constants k and time delays  $\tau^{delay}$  on the arrows indicate the nomenclature for the individual processes used in the discussion. b) Relative amounts of ammonia ( $NH_3$ , blue), the frequent ( $NH_2 + H$ , light green) and the rare photodissociation products ( $NH + H_2$ , red) over time. The kinetic fit without a nonreactive ammonia species is indicated by dashed lines. The inset zooms the very small amount of the rare reaction product.

Additionally to fitting the overall reaction, the kinetic model was applied to trajectories excited in different energy windows separately. For this, the observation concluded from the overall fit that only  $NH_3$  is present initially was required. All resulting values are reported in Table S1.

**Table S1** Fitted rate constants  $k_i$  and time delays  $\tau_i^{\text{delay}}$  for the overall reaction and various excitation energy windows according to the kinetic model described in Fig. S3 and eq. 1–4.

k <sub>freq</sub> (ps	-1)	k <sub>rare</sub> (ps	-1)	$ au_{ m freq}^{ m delay}$ (	(fs)	$ au_{ m rare}^{ m delay}$ (	fs)	k <sub>nr</sub> (ps	-1)	$k_{\rm nr}^{\rm back}$ (p	$os^{-1}$ )
12.622	$\pm \ 0.004$	0.1814	$\pm 0.0004$	19.12	$\pm \ 0.07$	90.3	$\pm 0.2$	1.642	$\pm \ 0.001$	1.585	$\pm 0.001$
7.93	$\pm \ 0.02$	0.02	$\pm 0.02$	18.68	$\pm \ 0.08$	9×10	$\pm$ 8×10	1.88	$\pm \ 0.01$	0.597	$\pm 0.009$
8.55	$\pm 0.01$	0.0548	$\pm$ 0.0007	1.94	$\pm \ 0.04$	64	$\pm 1$	2.566	$\pm \ 0.007$	1.047	$\pm 0.004$
8.729	$\pm \ 0.007$	0.0839	$\pm 0.0006$	18.07	$\pm \ 0.02$	110.5	$\pm 0.7$	1.895	$\pm \ 0.004$	1.069	$\pm 0.003$
10.455	$\pm \ 0.006$	0.172	$\pm$ 0.008	18.70	$\pm \ 0.02$	112.3	$\pm 0.4$	1.571	$\pm \ 0.003$	1.526	$\pm 0.003$
13.498	$\pm \ 0.008$	0.1927	$\pm 0.0009$	19.83	$\pm \ 0.01$	90.7	$\pm 0.3$	1.297	$\pm \ 0.003$	2.597	$\pm 0.004$
19.99	$\pm 0.02$	0.526	$\pm 0.003$	21.72	$\pm \ 0.02$	96.1	$\pm 0.3$	1.750	$\pm \ 0.005$	4.842	$\pm 0.008$
25.89	$\pm 0.3$	0.838	$\pm$ 0.008	22.41	$\pm \ 0.02$	72.7	$\pm 0.4$	0.964	$\pm \ 0.006$	4.80	$\pm \ 0.02$
34.65	$\pm \ 0.09$	7.3	$\pm 0.1$	23.73	$\pm \ 0.04$	115.7	$\pm 0.7$	0.811	$\pm \ 0.008$	4.00	$\pm \ 0.03$
	k <sub>freq</sub> (ps 12.622 7.93 8.55 8.729 10.455 13.498 19.99 25.89 34.65	$\begin{array}{l} k_{\rm freq} \ ({\rm ps}^{-1}) \\ 12.622 \ \pm \ 0.004 \\ 7.93 \ \pm \ 0.02 \\ 8.55 \ \pm \ 0.01 \\ 8.729 \ \pm \ 0.007 \\ 10.455 \ \pm \ 0.006 \\ 13.498 \ \pm \ 0.008 \\ 19.99 \ \pm \ 0.02 \\ 25.89 \ \pm \ 0.3 \\ 34.65 \ \pm \ 0.09 \end{array}$	$\begin{array}{ll} k_{\rm freq}  ({\rm ps}^{-1}) & k_{\rm rare}  ({\rm ps}^{-1}) \\ 12.622 \ \pm 0.004 & 0.1814 \\ 7.93 \ \pm 0.02 & 0.02 \\ 8.55 \ \pm 0.01 & 0.0548 \\ 8.729 \ \pm 0.007 & 0.0839 \\ 10.455 \ \pm 0.006 & 0.172 \\ 13.498 \ \pm 0.008 & 0.1927 \\ 19.99 \ \pm 0.02 & 0.526 \\ 25.89 \ \pm 0.3 & 0.838 \\ 34.65 \ \pm 0.09 & 7.3 \end{array}$	$\begin{array}{ll} k_{\rm freq} \ ({\rm ps}^{-1}) & k_{\rm rare} \ ({\rm ps}^{-1}) \\ 12.622 \ \pm 0.004 & 0.1814 \ \pm 0.0004 \\ 7.93 \ \pm 0.02 & 0.02 \ \pm 0.02 \\ 8.55 \ \pm 0.01 & 0.0548 \ \pm 0.0007 \\ 8.729 \ \pm 0.007 & 0.0839 \ \pm 0.0006 \\ 10.455 \ \pm 0.006 & 0.172 \ \pm 0.008 \\ 13.498 \ \pm 0.008 & 0.1927 \ \pm 0.009 \\ 19.99 \ \pm 0.02 & 0.526 \ \pm 0.003 \\ 25.89 \ \pm 0.3 & 0.838 \ \pm 0.008 \\ 34.65 \ \pm 0.09 \ 7.3 \ \pm 0.1 \end{array}$	$\begin{array}{ll} k_{\rm freq} \ ({\rm ps}^{-1}) & k_{\rm rare} \ ({\rm ps}^{-1}) & \tau_{\rm freq}^{\rm delay} \ ({\rm ps}^{-1}) & \tau_{\rm freq}^{\rm delay} \ ({\rm ps}^{-1}) & {\rm pt}^{\rm delay} \ ({\rm pt}^{-1}) & {\rm pt}^{-1} \ ({\rm pt}^{-1}) & {\rm pt}^$	$\begin{array}{ll} k_{\rm freq} \ ({\rm ps}^{-1}) & k_{\rm rare} \ ({\rm ps}^{-1}) & \tau_{\rm freq}^{\rm delay} \ ({\rm fs}) \\ 12.622 \ \pm 0.004 & 0.1814 \ \pm 0.0004 & 19.12 \ \pm 0.07 \\ 7.93 \ \pm 0.02 & 0.02 \ \pm 0.02 & 18.68 \ \pm 0.08 \\ 8.55 \ \pm 0.01 & 0.0548 \ \pm 0.0007 & 1.94 \ \pm 0.04 \\ 8.729 \ \pm 0.007 & 0.0839 \ \pm 0.0006 & 18.07 \ \pm 0.02 \\ 10.455 \ \pm 0.006 & 0.172 \ \pm 0.008 & 18.70 \ \pm 0.02 \\ 13.498 \ \pm 0.008 & 0.1927 \ \pm 0.009 & 19.83 \ \pm 0.01 \\ 19.99 \ \pm 0.02 & 0.526 \ \pm 0.003 & 21.72 \ \pm 0.02 \\ 25.89 \ \pm 0.3 & 0.838 \ \pm 0.008 & 22.41 \ \pm 0.02 \\ 34.65 \ \pm 0.09 & 7.3 \ \pm 0.1 & 23.73 \ \pm 0.04 \\ \end{array}$	$ \begin{array}{lll} k_{\rm freq} \ ({\rm ps}^{-1}) & k_{\rm rare} \ ({\rm ps}^{-1}) & \tau_{\rm freq}^{\rm delay} \ ({\rm fs}) & \tau_{\rm rare}^{\rm delay} \ ({\rm fs}) \ ({\rm fs}) & \tau_{\rm rare}^{\rm delay} \ ({\rm fs}) \ ({\rm$	$ \begin{array}{lll} k_{\rm freq}  (\rm ps^{-1}) & k_{\rm rare}  (\rm ps^{-1}) & \tau_{\rm freq}^{\rm delay}  (\rm fs) & \tau_{\rm rare}^{\rm delay}  (\rm fs) \\ 12.622 \ \pm 0.004 & 0.1814 \ \pm 0.0004 & 19.12 \ \pm 0.07 & 90.3 \ \pm 0.2 \\ 7.93 \ \pm 0.02 & 0.02 \ \pm 0.02 & 18.68 \ \pm 0.08 & 9 \times 10 \ \pm 8 \times 10 \\ 8.55 \ \pm 0.01 & 0.0548 \ \pm 0.0007 & 1.94 \ \pm 0.04 & 64 \ \pm 1 \\ 8.729 \ \pm 0.007 & 0.0839 \ \pm 0.0006 & 18.07 \ \pm 0.02 & 110.5 \ \pm 0.7 \\ 10.455 \ \pm 0.006 & 0.172 \ \pm 0.008 & 18.70 \ \pm 0.02 & 112.3 \ \pm 0.4 \\ 13.498 \ \pm 0.008 & 0.1927 \ \pm 0.009 & 19.83 \ \pm 0.01 & 90.7 \ \pm 0.3 \\ 19.99 \ \pm 0.02 & 0.526 \ \pm 0.003 & 21.72 \ \pm 0.02 & 96.1 \ \pm 0.3 \\ 25.89 \ \pm 0.3 & 0.838 \ \pm 0.008 & 22.41 \ \pm 0.02 & 72.7 \ \pm 0.4 \\ 34.65 \ \pm 0.09 & 7.3 \ \pm 0.1 & 23.73 \ \pm 0.04 & 115.7 \ \pm 0.7 \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

The fitted rate constants for the various excitation energy windows are additionally displayed graphically in terms of time constants in Figure S5. This demonstrates, that both reactions proceed faster with higher excitation energy. However, this decrease in time constants is more drastic in the rare case, such that the rare channel becomes less and less rare. Linear fits of the logarithmic data (dotted lines in Figure S5) underline this observation via their differing slopes. Note, that for statistical reasons, the time constant for the minor channel is displayed for excitation energy windows up to 7.25 eV, while there is one more data point shown for the major channel corresponding to the 7.25 eV – 7.50 eV energy window. Extrapolation to higher energies suggests a reversal of the dominant channel at around 9.5 eV. However, at these high excitation energies higher electronic states would most likely be involved, limiting the validity of this extrapolation.



**Figure S5** Fitted time constants for the rare (red) and frequent (green) reaction channels in different excitation energy windows of 0.25 eV width (see Table 1) together with their logarithmic fits (dotted). Note, that the highest shown (7.25 eV-7.50 eV) time constant for the NH + H<sub>2</sub> reaction was not included in the fit.

#### 6 Total energy dependency of reaction outcome

In the main text as well as the section above, the fractions of minor and major dissociation products are analyzed in terms of excitation energy windows. Similarly, the dependence on the total energy of each trajectory can be investigated. Figure S6 shows a somewhat similar picture as the excitation energy dependence examined in Figure 3 in the main text. Here, as displayed in Figure S6a) and b) the trajectories not yet reacted at 1 ps are most dominant at low total energies. In general, the fraction of the minor photoproduct increases with total energy. An outlier is found for the 9.5 eV–10 eV energy window. In addition to product ratios, the overall distribution of total energy is hinted at in Figure S6b), where the maximum is around 7 eV–7.5 eV.



**Figure S6** Analysis of the reaction products (including non-reacted ammonia) found at the end of simulation by total energy. a) Relative amount of observed species in different total energy windows of 0.5 eV width and b) absolute number of occurrences on logarithmic scale for the same energy windows.

The trend of increasing NH +  $H_2$  yields with increasing total energy agrees with the previous study by Wang et al.<sup>7</sup> Table S2 shows fractions of the rare photoproduct for the 4 total energy values investigated in the previous work. While we simulated an ensemble of 50,000 trajectories drawn randomly from a Wigner distribution, Wang et al.<sup>7</sup> only propagated those initial conditions that fell into 4 distinct total energy values (7.4, 7.8, 8.2, and 8.6 eV). They simulated 7500 trajectories for each of these windows, whereas we simulated less trajectories with increasing total energy.

Both studies exhibit the same trend regarding the relative fraction of the rare photoproduct. Although the overall magnitudes are in the same range, we obtain slightly higher  $NH + H_2$  fractions around 7.4 eV

and 7.8 eV, while somewhat lower fractions for 8.2 eV and 8.6 eV compared to the previous work. This means that we see a less pronounced increase in the rare photoproduct with increasing total energy. The differences can be attributed to slightly differing protocols of initial distribution, different time steps used for propagation — 0.2 fs steps instead of the previous 0.5 fs —, and different criteria to determine dissociation. While Wang et al. view a trajectory as terminated when any interatomic distance exceeds 10 Bohr (5.27 Å) or 1 ps is reached, we considered all possible bonding patterns with interatomic distances under 6 Bohr (3.15 Å) counting as bonded and above 8 Bohr (4.23 Å) as dissociated and the necessity of a fragmentation to persist for at least 10 fs, as detailed in Section 2.2 of the main text.

**Table S2** Total number trajectories and ratio of NH + H<sub>2</sub> photoproduct for 4 distinct narrow total energy windows. For comparison, the corresponding values from Ref. 7 for the rare channel are reported for 7500 trajectories and even narrower energy windows of  $E^{tot} \pm 0.05$  eV.

ine E <sub>tot</sub> (eV)	# trajectories	$NH + H_2$ trajectories (%)	Ref. 7 NH + $H_2$ trajectories (%)
ine 7.4 $\pm$ 0.1	7423	0.75	0.29
$7.8\pm0.1$	4599	0.85	0.46
$8.2\pm0.1$	2245	0.94	1.32
$8.6\pm0.1$	850	1.5	2.61
ine			

#### 7 Momenta

Tracking the momenta of the formed fragments throughout the simulation proves to be a reasonable method for detecting not only the type of dissociation, but also the time when the interaction between the formed fragments becomes negligible, i.e. when the momenta become constant. This in general coincides well with the 8 Bohr dissociation criterion and thus serves as a validation of its meaningfulness. The resulting absolute values of the linear and angular momenta of the fragments after the dissociation following the rare channel are visualized in Figure S7. While their averages of 0.23 uÅfs<sup>-1</sup> for the linear and 0.11 uÅ<sup>2</sup>fs<sup>-1</sup> for the angular momentum are provided in the main text, the standard deviations amount to 0.08 uÅfs<sup>-1</sup> and 0.2 uÅ<sup>2</sup>fs<sup>-1</sup> respectively. These standard deviations are very much influenced by the outliers visible in both histograms, especially for the angular momentum. We believe, that reasons for these irregularities can be the occasional lack of conservation of the total energy discussed above in Section S3 or an inadequate fit of the neural network potentials in regions with large distances between the NH and H<sub>2</sub> fragments, which then leads to sudden jumps in the momenta during trajectory propagation in these regions of phase space.



Figure S7 Histograms of a) linear and b) angular momenta after the rare dissociation.

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