*Supplemental Information for:*

# "Mixed Quantum/Classical Theory (MQCT) Approach to the Dynamics of Molecule-Molecule Collisions in Complex Systems"

by Carolin Joy, Bikramaditya Mandal, Dulat Bostan, Marie-Lise Dubernet[1] and Dmitri Babikov[*]

*Chemistry Department, Marquette University, Milwaukee, Wisconsin 53201-1881, USA*

## I. DETAILED DESCRIPTION OF FULL QUANTUM CALCULATIONS

Quantum state-to-state rate coefficients (Daniel et al. 2011) are available for the rotational quenching of 45 levels of *o/p*-$H_2O$ by *o/p*-$H_2(j)$ for temperature ranging from T = 5-1500K, where the transitions among $H_2$ levels have been considered up to $j(H_2) = 4$ for some water transitions and for some temperatures. These rate coefficients were obtained using a 5D average of the 9D PES of Valiron et. al., 2008 and with quantum calculations for the dynamics of the nuclei. Daniel et al, 2011 calculations extended and completed the previous calculations of Dubernet et al, 2009 and of Daniel et al, 2010 on this system. A summary of the available transitions is given in Table S1, with the full set of calculated rate coefficients available in the BASECOL database (Dubernet et al., 2023).

**Table S1:** A summary of rotational quenching transitions available from full quantum calculations (Daniel et al, 2011). The entries are given in the form: N{ [ $j(H_2)$ transitions], [ ]} where N is the number of the target levels for which there is quenching (target levels are ordered by increasing energies). References are indicated by subscripts *a*, *b*, and *c*. An asterisk (*) marks transitions for which the rate coefficients are calculated between 1000-1500 K.

| Initial level of $H_2$ | *o*-$H_2O$ | *p*-$H_2O$ |
|---|---|---|
| $j_2 = 0$ | $45\{[0 \to 0], [0 \to 2]\}^a$ | $45\{[0 \to 0], [0 \to 2]\}$ |
| $j_2 = 2$ | $45\{[2 \to 0], [2 \to 2]\}^a; 10\{[2 \to 4]\}^{a,*}$ | $20\{[2 \to 0], [2 \to 2]\}$ |
| $j_2 = 4$ | $10\{[4 \to 2]^*, [4 \to 4]\}^a$ | none |
| $j_2 = 1$ | $45\{[1 \to 1]\}^c; 20\{[1 \to 3]\}^c$ | $45\{[1 \to 1]\}^{b,c}; 20\{[1 \to 3]\}^b$ |
| $j_2 = 3$ | $5\{[3 \to 1]\}^c; 5\{[3 \to 3]\}^c$ | $10\{[3 \to 1]\}^b; 10\{[3 \to 3]\}^b$ |

*a)* Dubernet et al, 2009
*b)* Daniel et al, 2010
*c)* Daniel et al, 2011

[1] Observatoire de Paris, PSL University, Sorbonne Université, CNRS, LERMA, Paris, France
[*] Author to whom all correspondence should be addressed; electronic mail: dmitri.babikov@mu.edu
Chemistry Department, Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53201-1881, USA

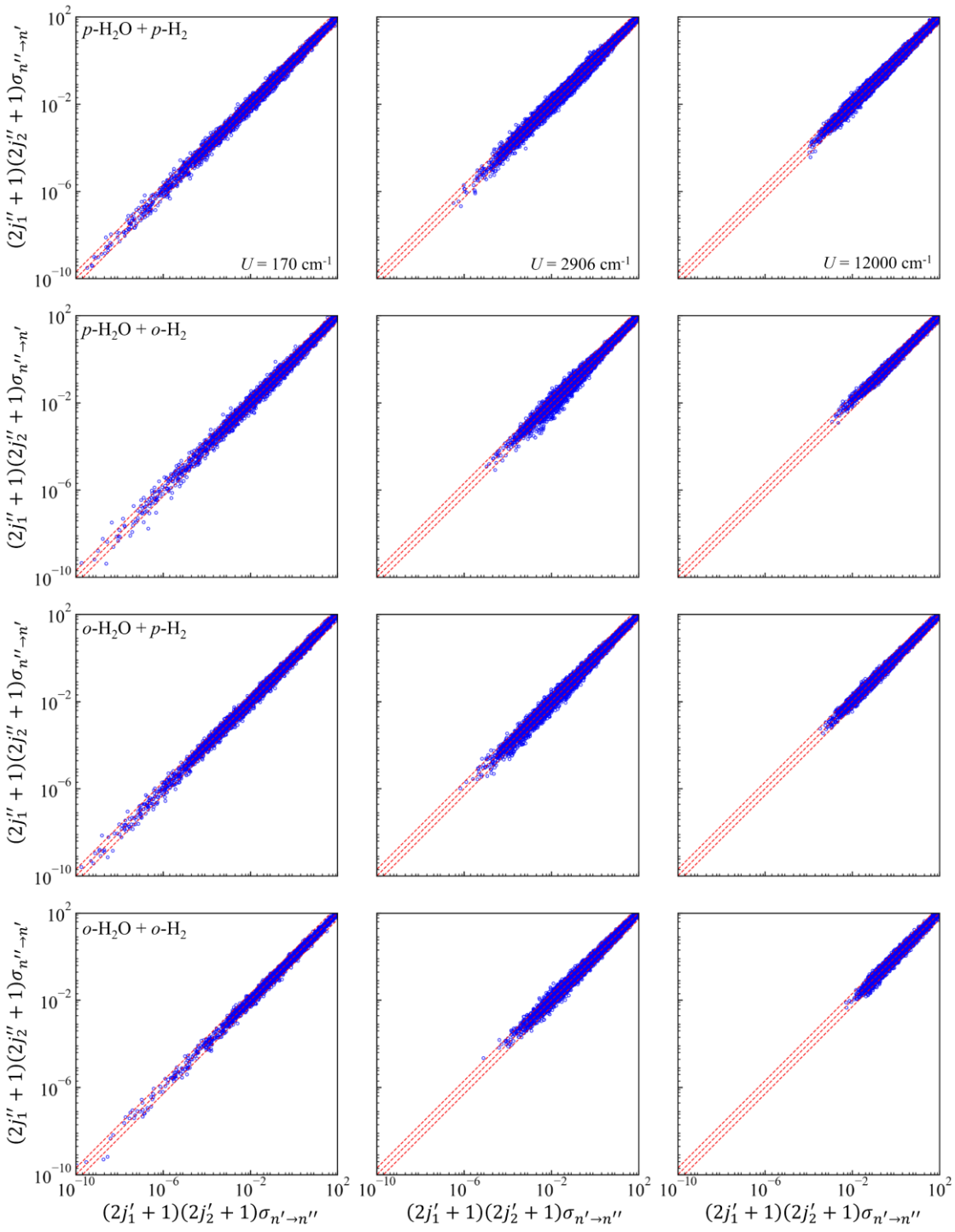


**Figure S1:** The comparison of MQCT state-to-state transition cross sections (in $Å^2$) for quenching and excitation directions of 118838 individual transitions in $H_2O$ + $H_2$ system at three values of collision energy $U$. The deviation of datapoints from the diagonal line indicates the departure from the principle of microscopic reversibility. The factor of 2 difference is shown by red dashed lines. Three columns correspond to three collision energies while four rows correspond to four symmetries of $H_2O$ + $H_2$ as indicated in the figure. In each case, 100 initial states of *o*/*p*-$H_2O$ are combined with two initial states of the projectile, either $j_2 = 0,\ 2, 4$ of *p*-$H_2$ or $j_2 = 1,\ 3$ of *o*-$H_2$.

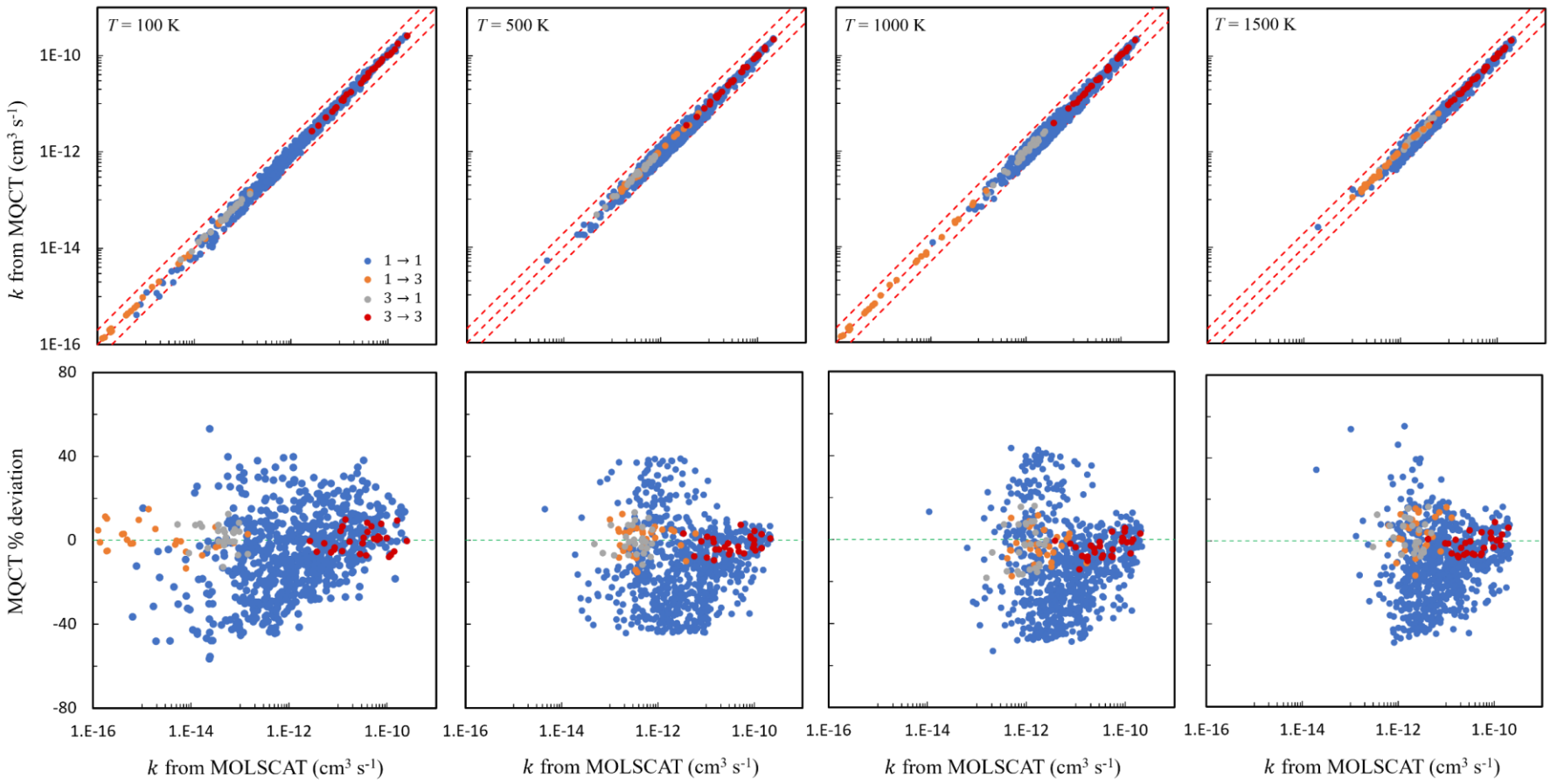


**Figure S2:** Comparison of 1270 state-to-state transition rate coefficients for *p*-$H_2O$ + *o*-$H_2$ collision computed using MQCT (this work) *vs* those predicted by full quantum MOLSCAT calculations (Daniel et al. 2011). Columns correspond to four values of temperature as indicated in the figure. The upper row of frames gives a one-to-one comparison of rate coefficients, while the lower row of frames presents percent deviations of MQCT data relative to MOLSCAT. Color is used to differentiate transitions in the projectile, namely, 1→1, 1→3, 3→1, and 3→3 transitions in $H_2$ are represented by blue, orange, grey and maroon, respectively. Red dashed lines in the upper row represent a factor of 2 difference.

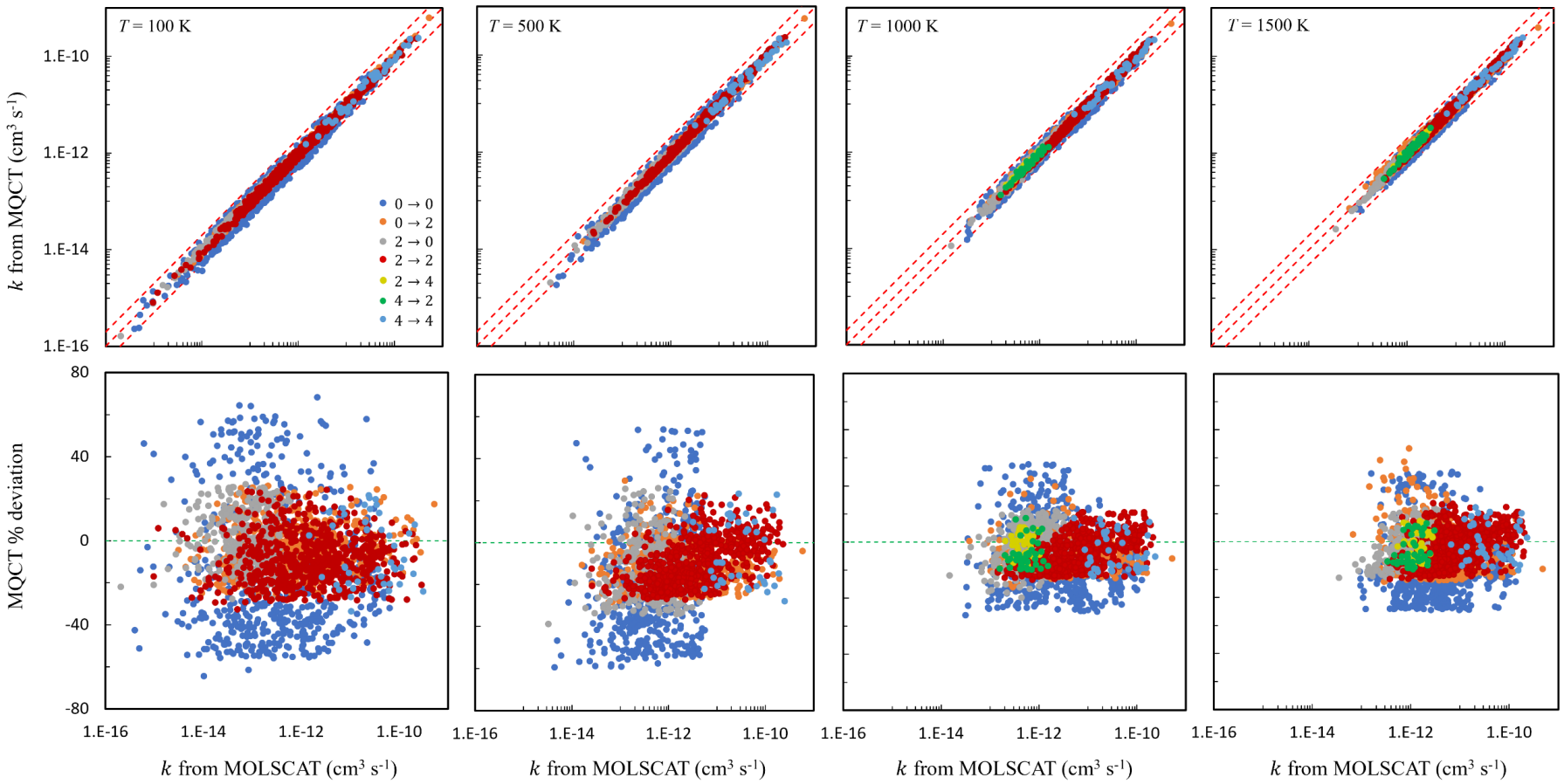


**Figure S3:** Comparison of 4095 state-to-state transition rate coefficients for *o*-$H_2O$ + *p*-$H_2$ collision computed using MQCT (this work) vs those predicted by full quantum MOLSCAT calculations (Daniel et al. 2011). Columns correspond to four values of temperature as indicated in the figure. The upper row of frames gives a one-to-one comparison of rate coefficients, while the lower row of frames presents percent deviations of MQCT data relative to MOLSCAT. Color is used to differentiate transitions in the projectile, namely, 0→0, 0→2, 2→0, 2→2, 2→4, 4→2 and 4→4 transitions in $H_2$ are represented by blue, orange, grey, maroon, yellow, green, and light blue respectively. Red dashed lines in the upper row represent a factor of 2 difference.

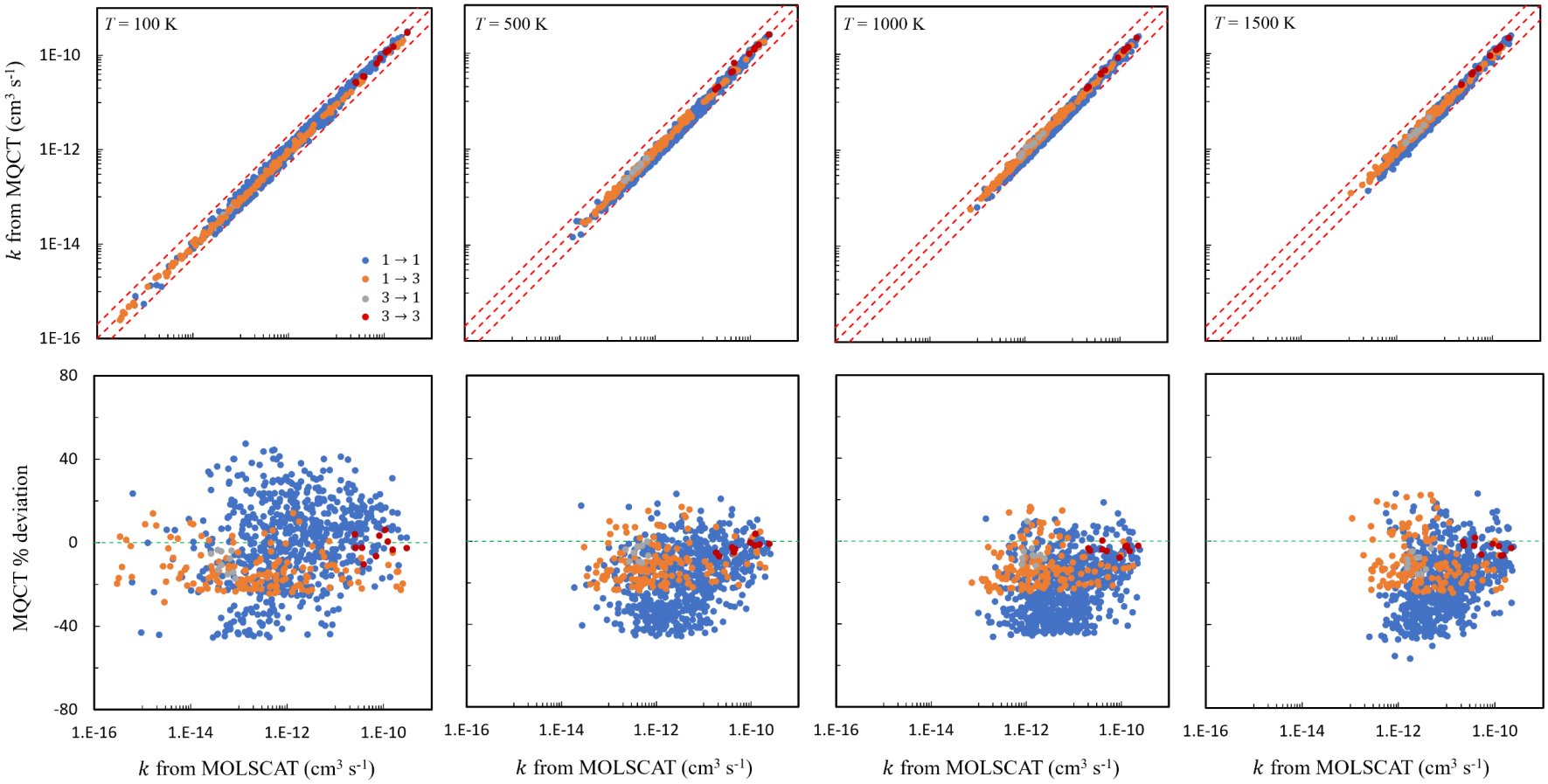


**Figure S4:** Comparison of 1200 state-to-state transition rate coefficients for *o*-$H_2O$ + *o*-$H_2$ collision computed using MQCT (this work) *vs* those predicted by full quantum MOLSCAT calculations (Daniel et al. 2011). Columns correspond to four values of temperature as indicated in the figure. The upper row of frames gives a one-to-one comparison of rate coefficients, while the lower row of frames presents percent deviations of MQCT data relative to MOLSCAT. Color is used to differentiate transitions in the projectile, namely, 1→1, 1→3, 3→1, and 3→3 transitions in $H_2$ are represented by blue, orange, grey and maroon, respectively. Red dashed lines in the upper row represent a factor of 2 difference.

**Table S2:** Average difference and RMS deviation (in %) for the comparisons shown in Fig. S2-S4 at four temperatures and for three symmetries of $H_2O + H_2$, as indicated.

| $p$-$H_2O$ + $o$-$H_2$ | | | |
|---|---|---|---|
| **Transitions in $H_2$** | **T (K)** | **Average difference (%)** | **RMS of % deviation** |
| $1 \rightarrow 1$ | 100 | -15 | 26 |
| | 500 | -12 | 24 |
| | 1000 | -11 | 22 |
| | 1500 | -10 | 20 |
| $1 \rightarrow 3$ | 100 | 4 | 16 |
| | 500 | 3 | 11 |
| | 1000 | -2 | 8 |
| | 1500 | 3 | 9 |
| $3 \rightarrow 1$ | 100 | 4 | 12 |
| | 500 | -2 | 7 |
| | 1000 | -4 | 10 |
| | 1500 | 3 | 8 |
| $3 \rightarrow 3$ | 100 | -0.1 | 6 |
| | 500 | -3 | 5 |
| | 1000 | -4 | 7 |
| | 1500 | -2 | 4 |

| $o$-$H_2O$ + $p$-$H_2$ | | | |
|---|---|---|---|
| **Transitions in $H_2$** | **T (K)** | **Average difference (%)** | **RMS of % deviation** |
| $0 \rightarrow 0$ | 100 | -21 | 32 |
| | 500 | -18 | 30 |
| | 1000 | -17 | 28 |
| | 1500 | -15 | 26 |
| $0 \rightarrow 2$ | 100 | -10 | 14 |
| | 500 | -12 | 16 |
| | 1000 | -11 | 15 |
| | 1500 | -7 | 17 |
| $2 \rightarrow 0$ | 100 | 3 | 15 |
| | 500 | -14 | 20 |
| | 1000 | -0.8 | 13 |
| | 1500 | -8 | 15 |
| $2 \rightarrow 2$ | 100 | -8 | 15 |
| | 500 | -10 | 14 |
| | 1000 | -9 | 13 |
| | 1500 | -4 | 12 |
| $2 \rightarrow 4$ | 1000 | -3 | 10 |
| | 1500 | -5 | 9 |
| $4 \rightarrow 2$ | 1000 | -9 | 13 |
| | 1500 | -7 | 12 |
| $4 \rightarrow 4$ | 100 | -5 | 16 |
| | 500 | -4 | 15 |
| | 1000 | -6 | 14 |
| | 1500 | -1 | 13 |

| $o$-$H_2O$ + $o$-$H_2$ | | | |
|---|---|---|---|
| **Transitions in $H_2$** | **T (K)** | **Average difference (%)** | **RMS of % deviation** |
| $1 \rightarrow 1$ | 100 | -5 | 24 |
| | 500 | -28 | 27 |
| | 1000 | -33 | 25 |
| | 1500 | -25 | 22 |
| $1 \rightarrow 3$ | 100 | -13 | 16 |
| | 500 | -11 | 14 |
| | 1000 | -12 | 15 |
| | 1500 | -10 | 16 |
| $3 \rightarrow 1$ | 100 | -10 | 11 |
| | 500 | -6 | 7 |
| | 1000 | -7 | 9 |
| | 1500 | -10 | 11 |
| $3 \rightarrow 3$ | 100 | -2 | 5 |
| | 500 | -4 | 4 |
| | 1000 | -5 | 6 |
| | 1500 | -4 | 15 |

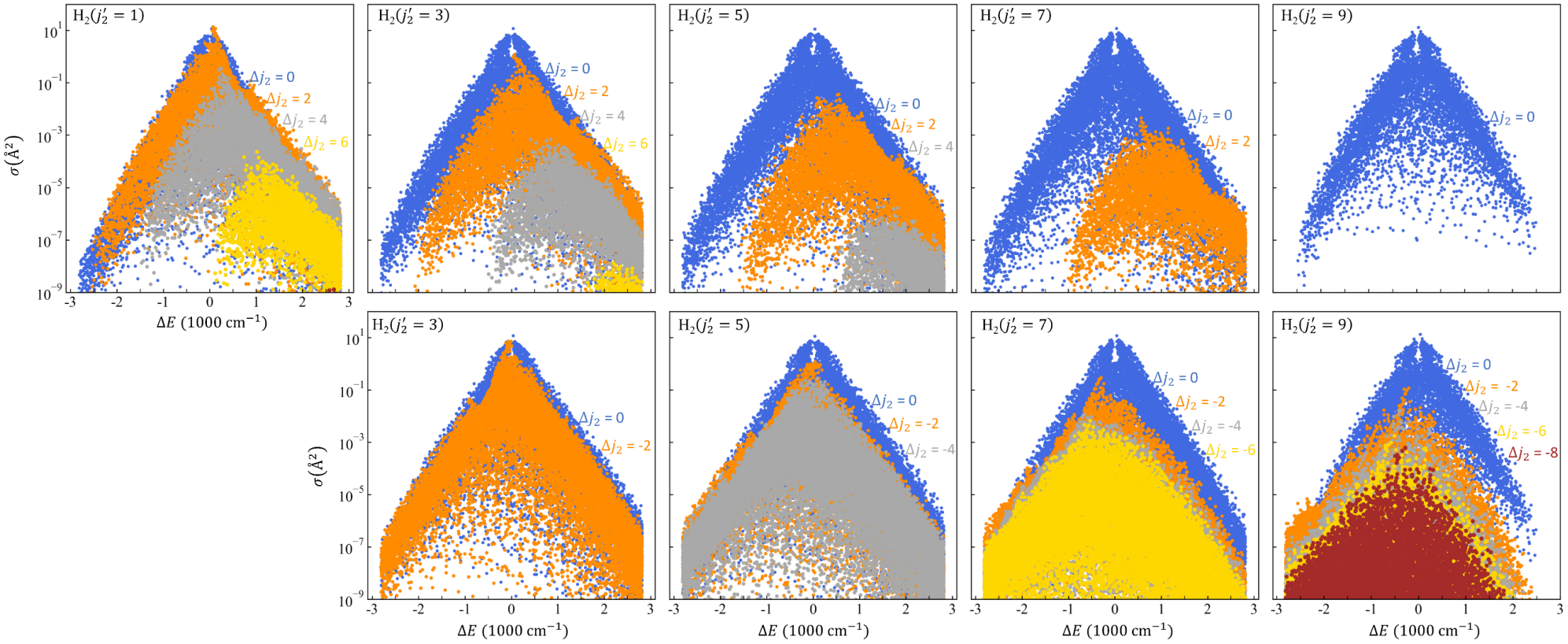


**Figure S5:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall transfer of internal rotational energy, $\Delta E$ in the *p*-$H_2O$ + *o*-$H_2$ system at collision energy $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

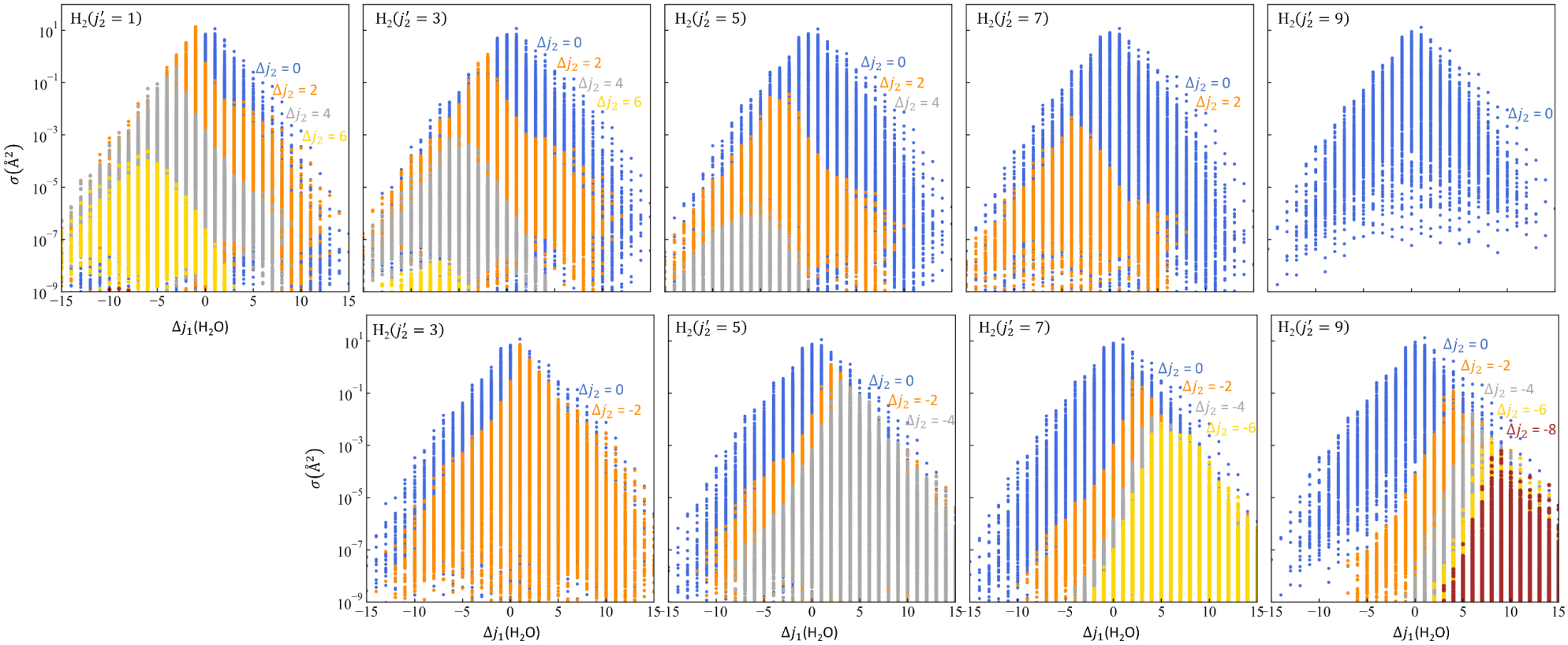


**Figure S6:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *p*-$H_2O$ + *o*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

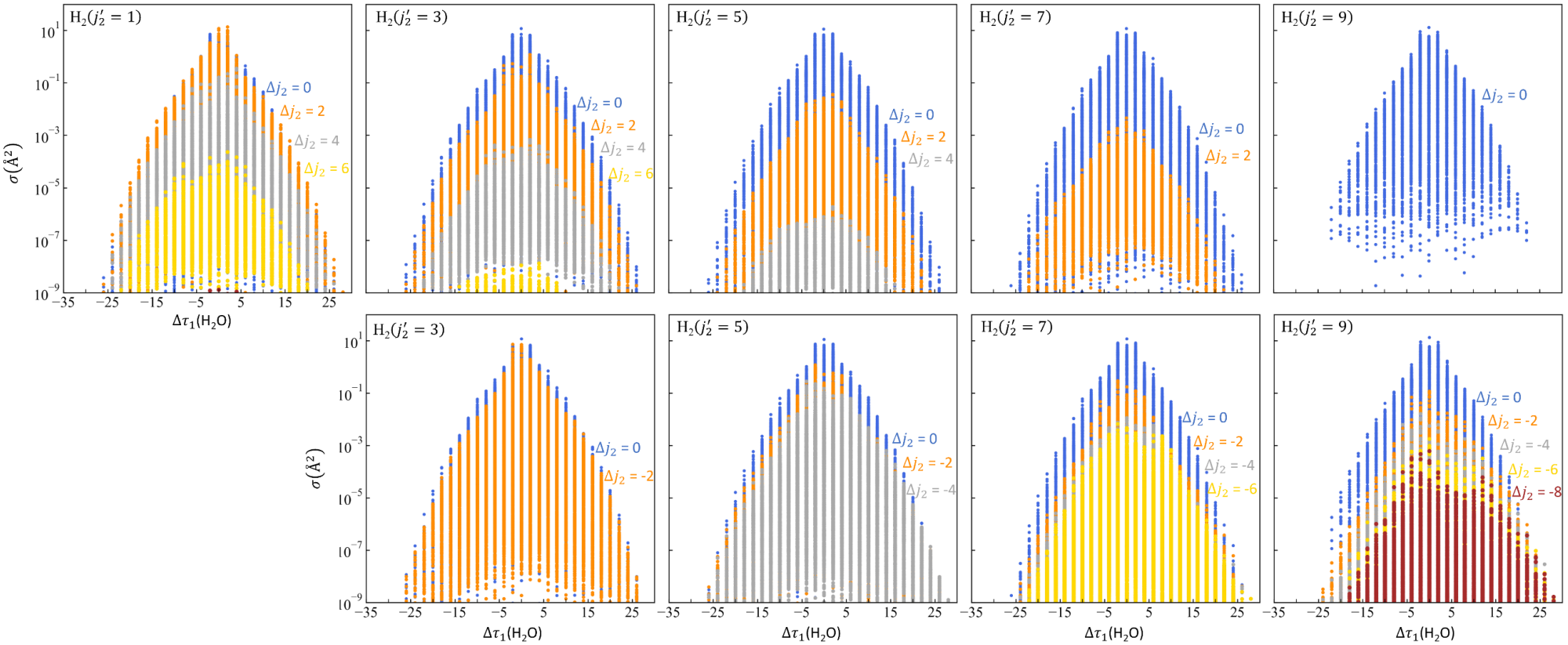


**Figure S7:** Correlation between the values of individual state-to-state cross sections $\sigma_{n' \to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *p*-$H_2O$ + *o*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

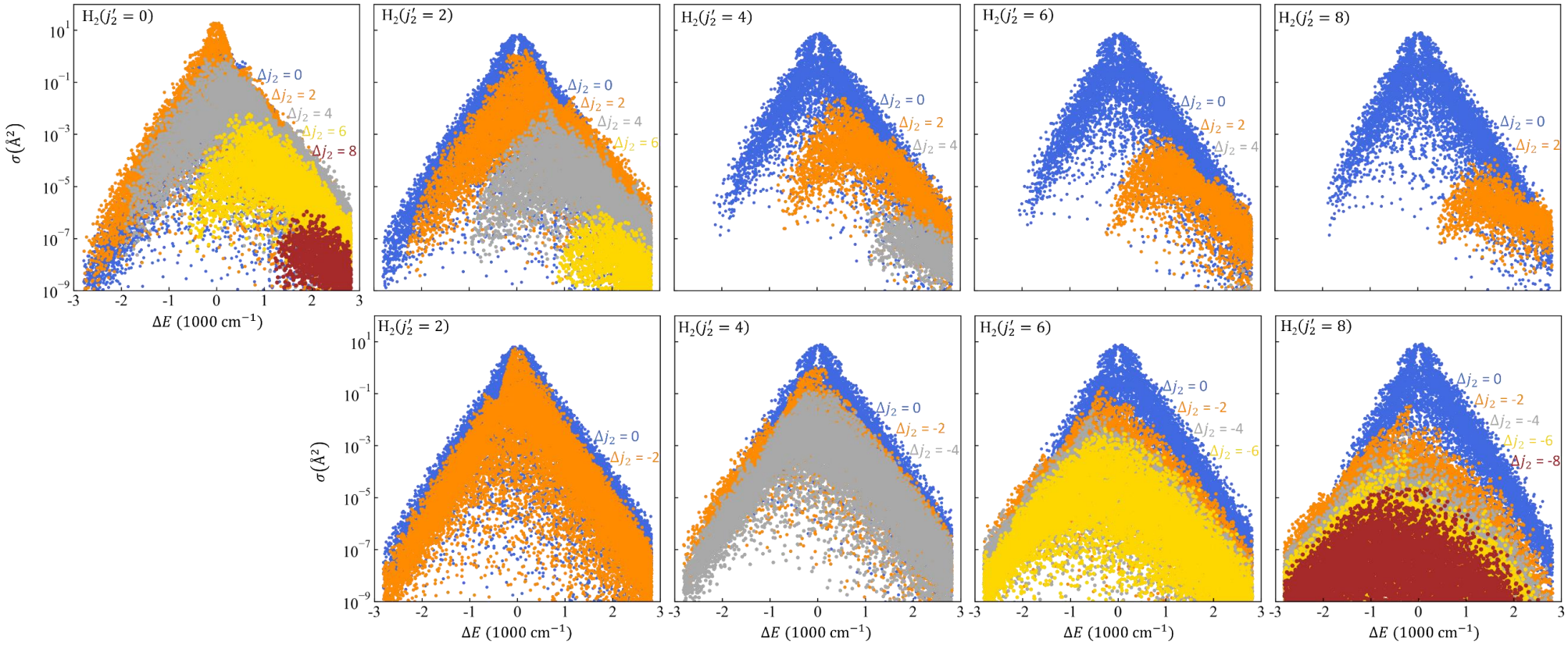


**Figure S8:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall transfer of internal rotational energy, $\Delta E$ in the *o*-$H_2O$ + *p*-$H_2$ system at collision energy $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

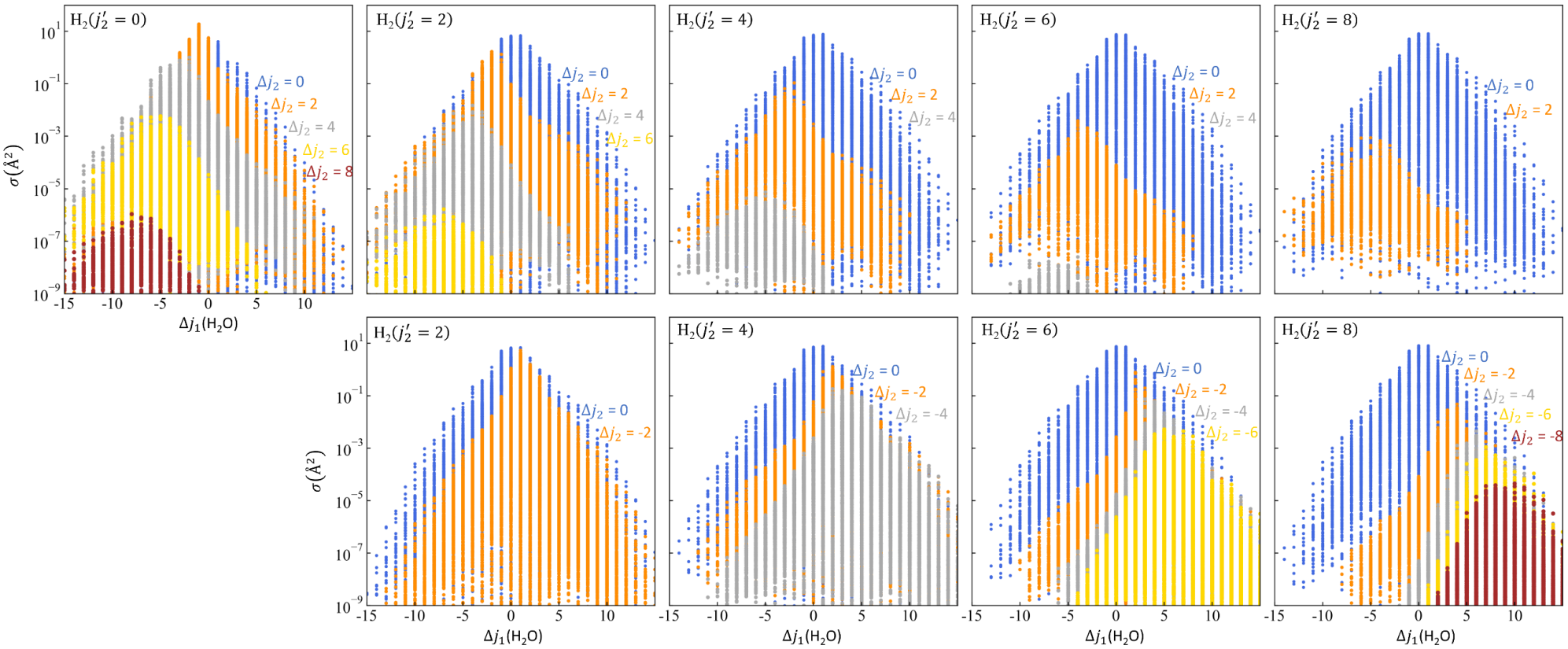


**Figure S9:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *o*-$H_2O$ + *p*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

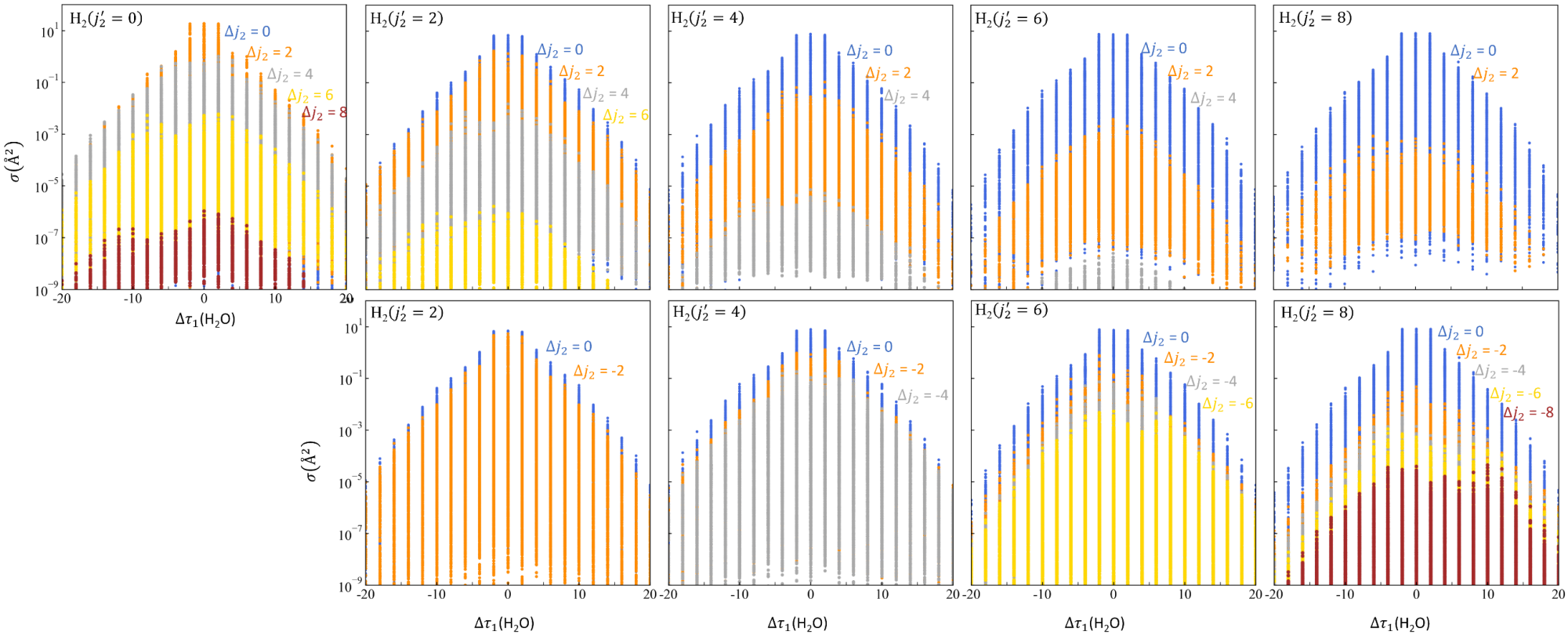


**Figure S10:** The correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *o*-$H_2O$ + *p*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

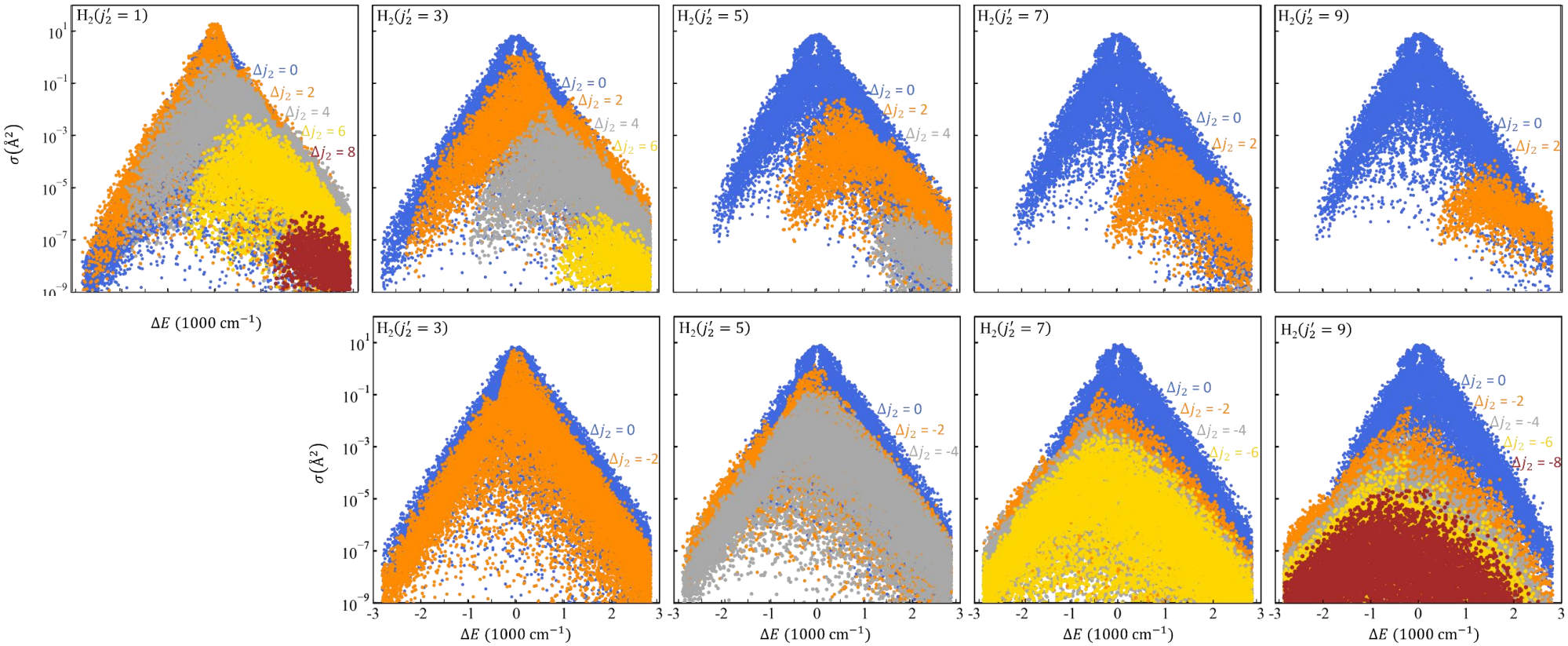


**Figure S11:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall transfer of internal rotational energy, $\Delta E$ in the *o*-$H_2O$ + *o*-$H_2$ system at collision energy $U \sim 704$ $cm^{-1}$ Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

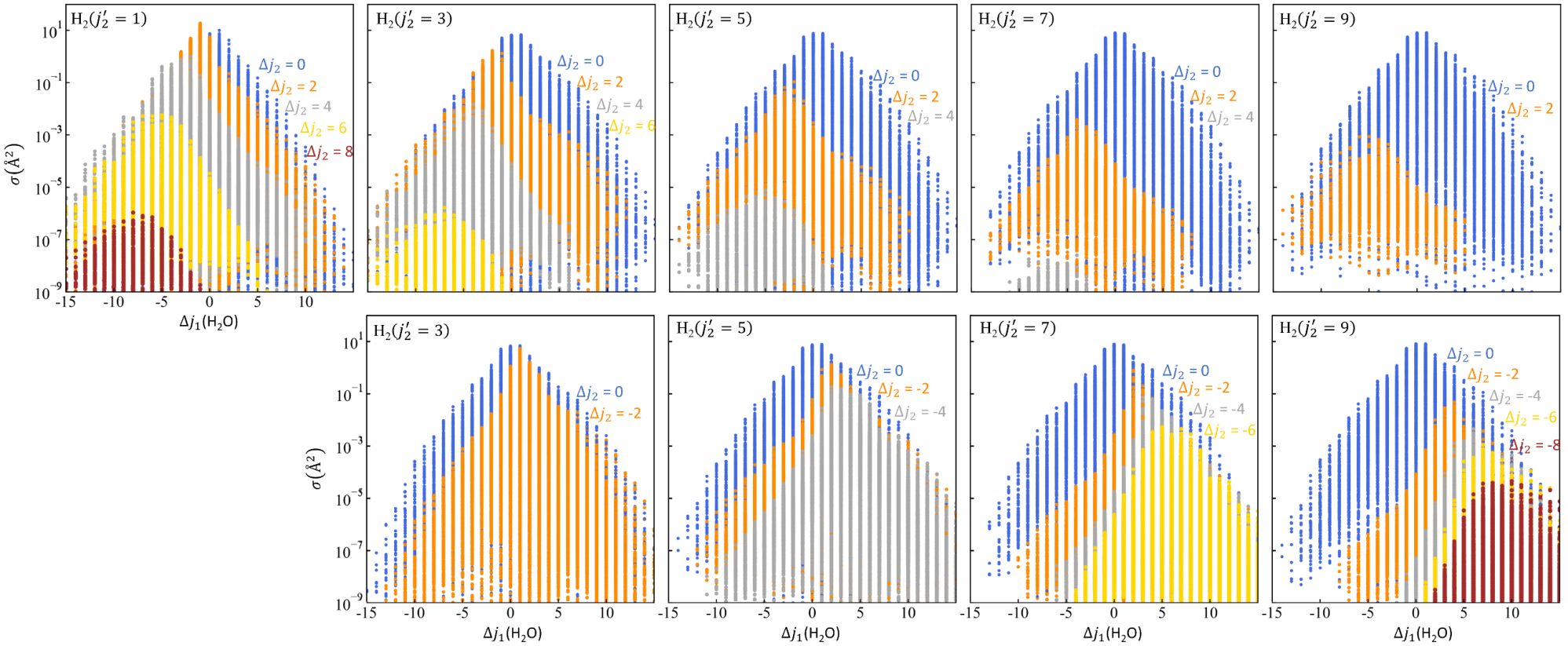


**Figure S12:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *o*-$H_2O$ + *o*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

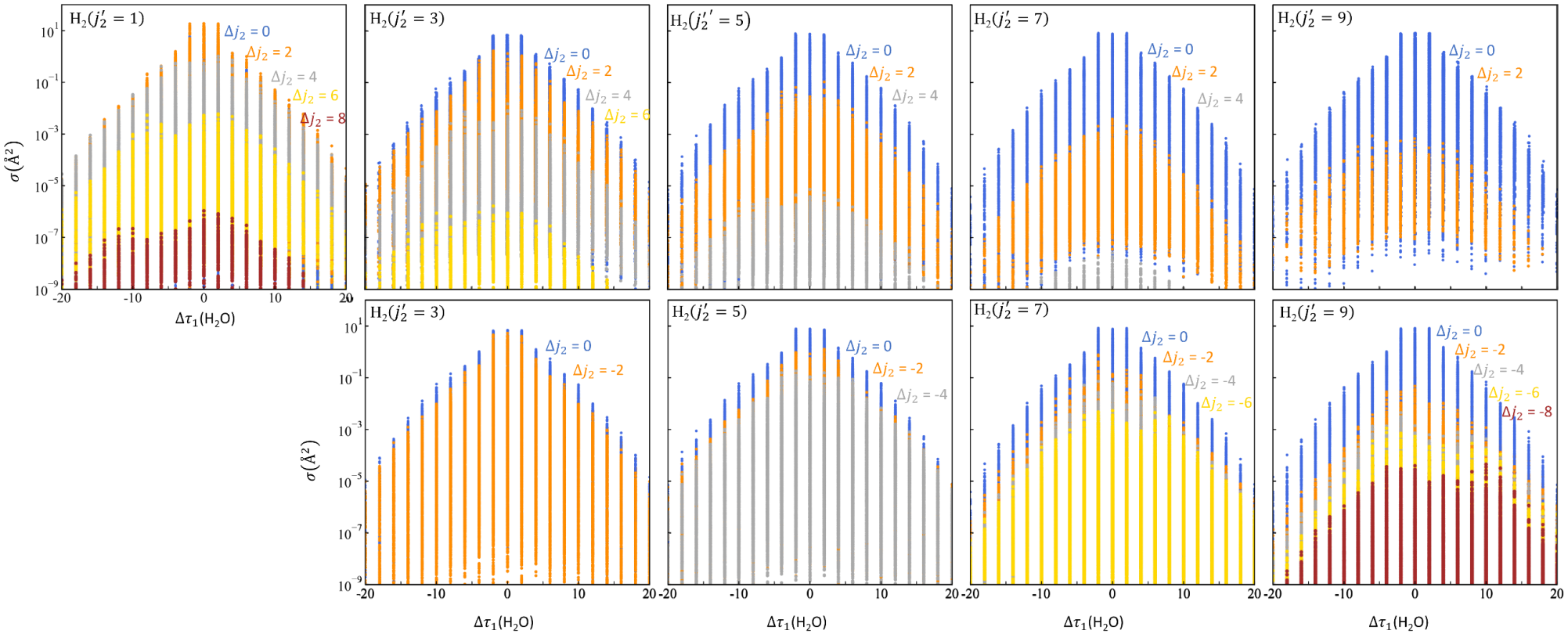


**Figure S13:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n'\to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *o*-$H_2O$ + *o*-$H_2$ system, at $U \sim 704$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

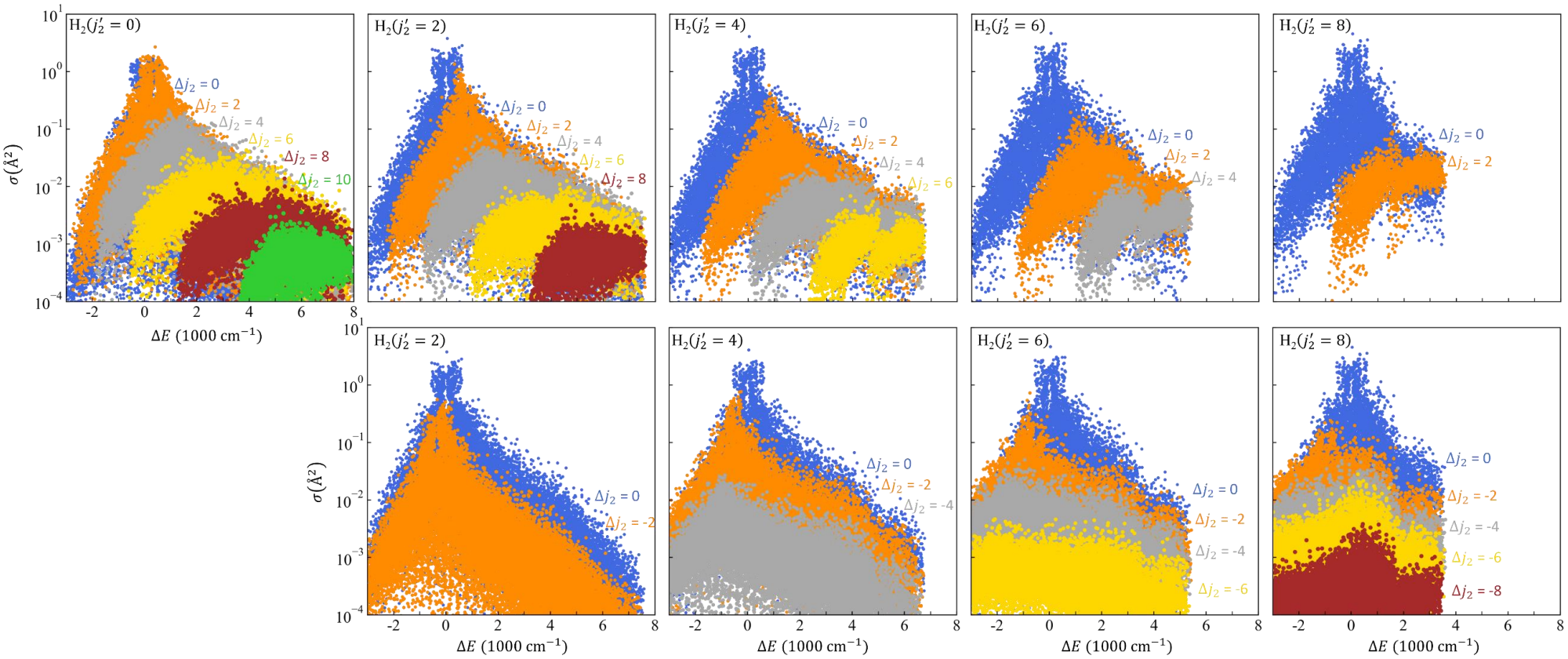


**Figure S14:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall extent of internal rotational energy $\Delta E$ in *p*-$H_2O$ + *p*-$H_2$ system at collision energy $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

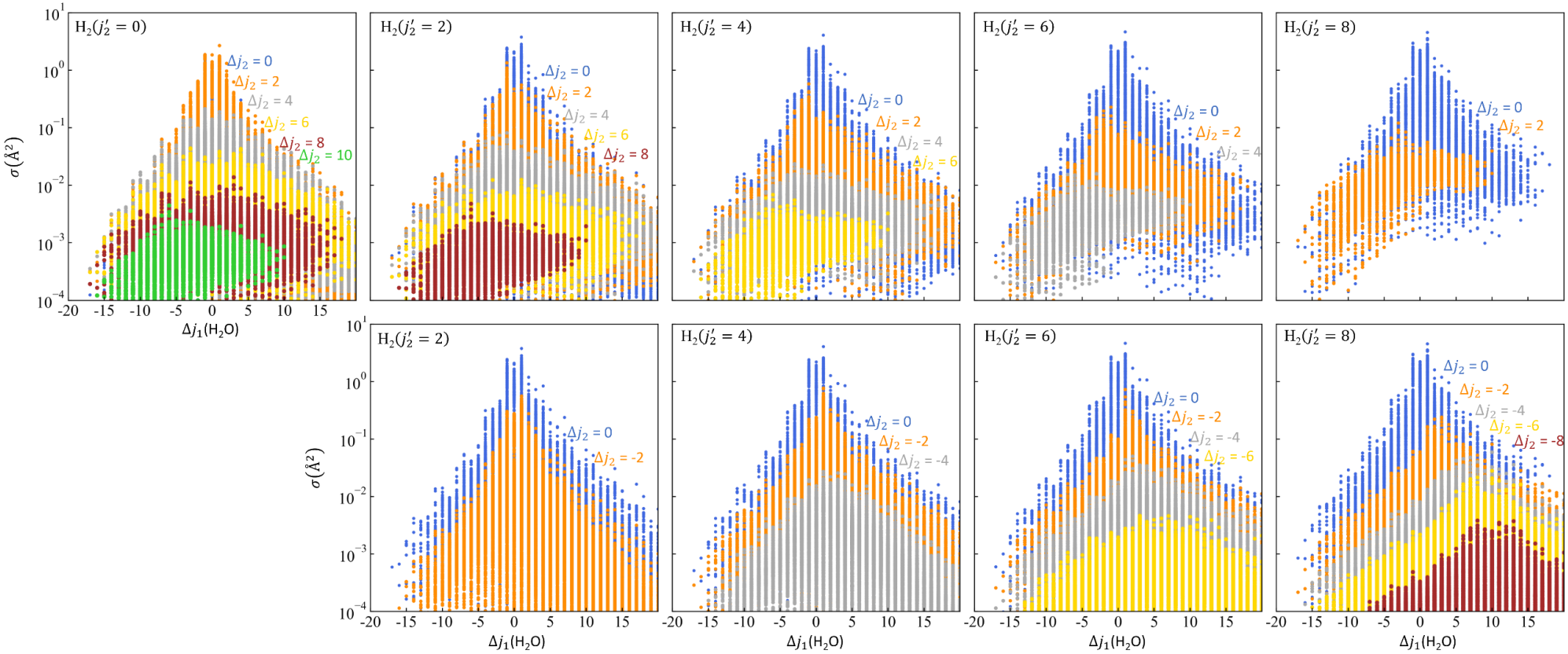


**Figure S15:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *p*-$H_2O$ + *p*-$H_2$ system, at $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

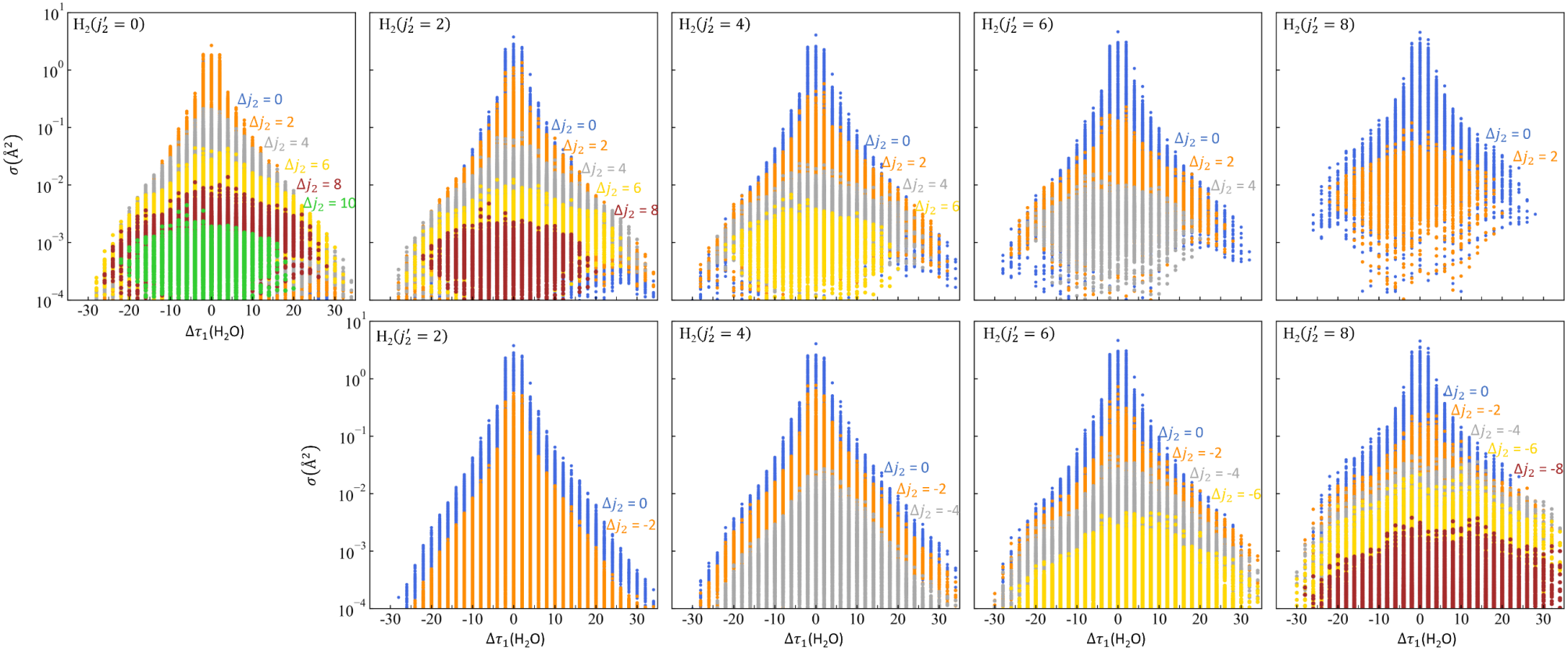


**Figure S16:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *p*-$H_2O$ + *p*-$H_2$ system, at $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

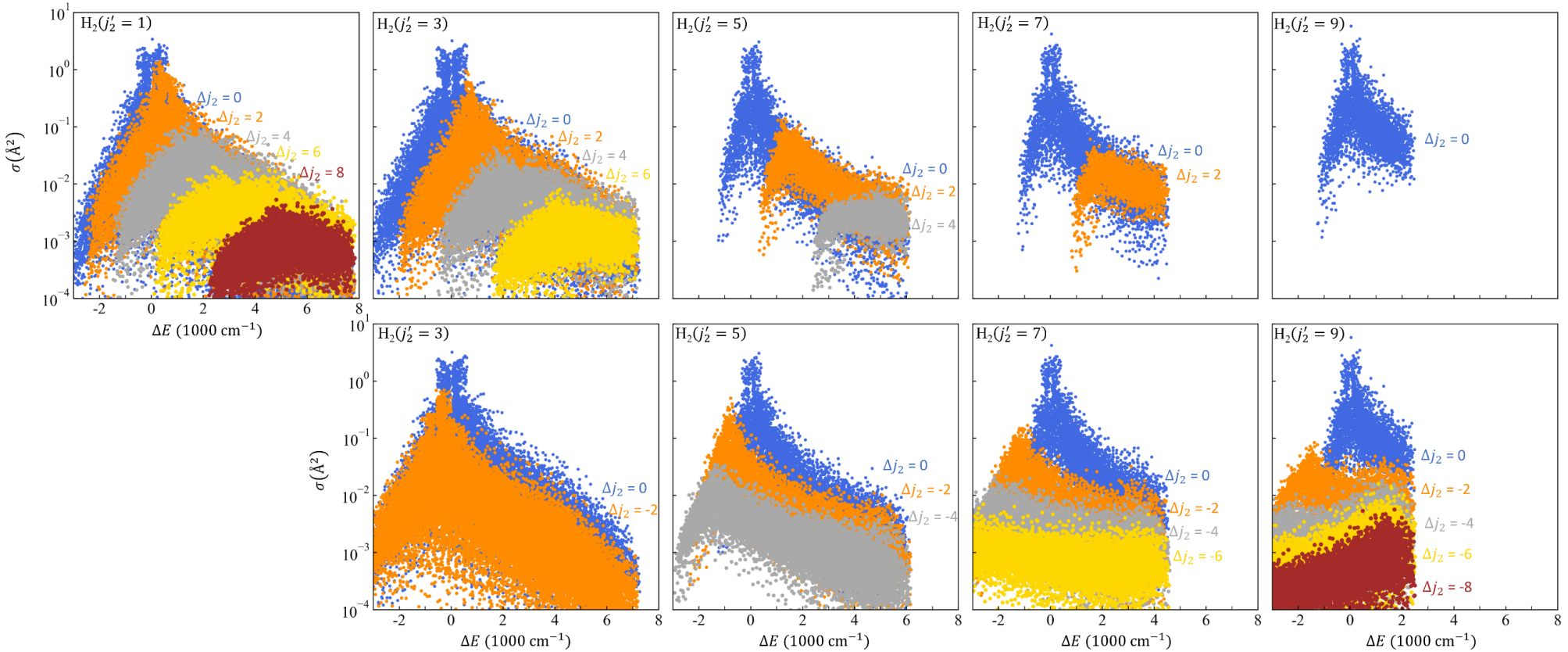


**Figure S17:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall extent of internal rotational energy $\Delta E$ in *p*-$H_2O$ + *o*-$H_2$ system at collision energy $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

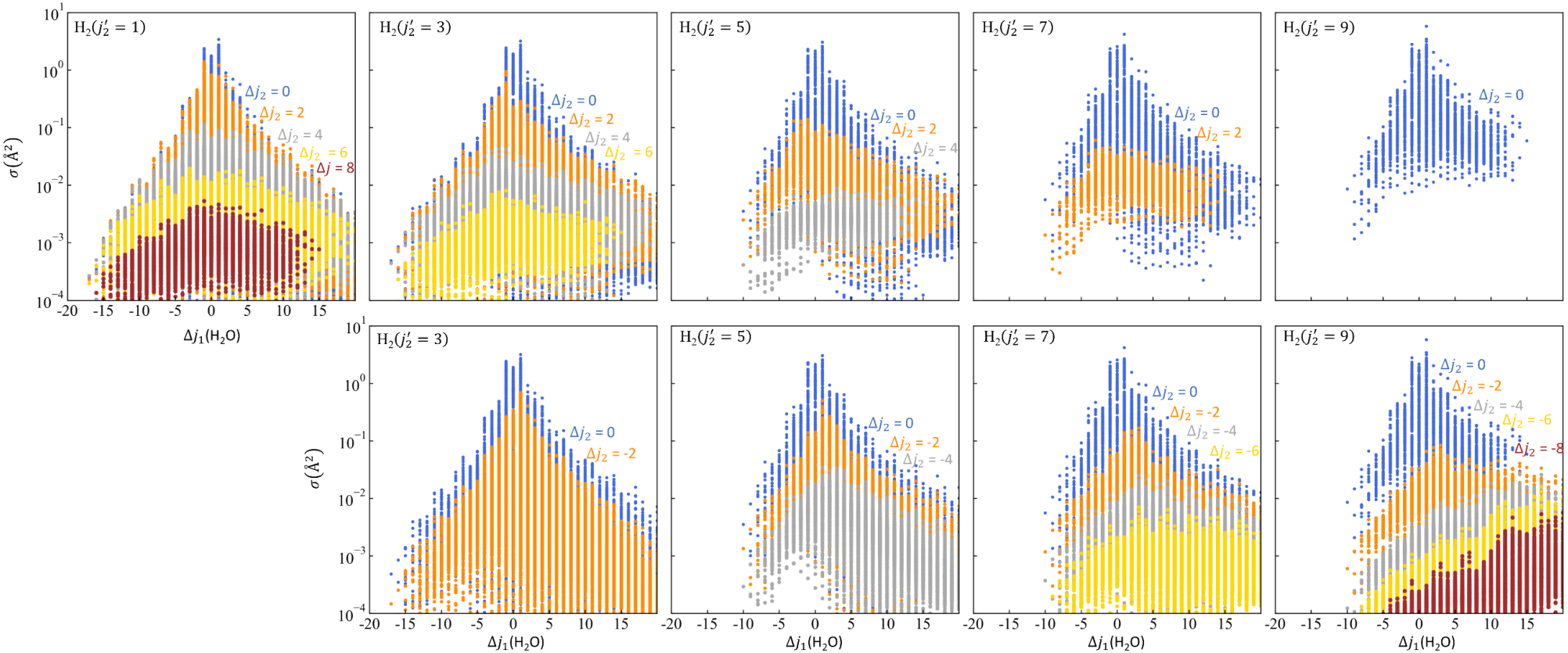


**Figure S18:** Correlation between the values of individual state-to-state cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *p*-$H_2O$ + *o*-$H_2$ system, at $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

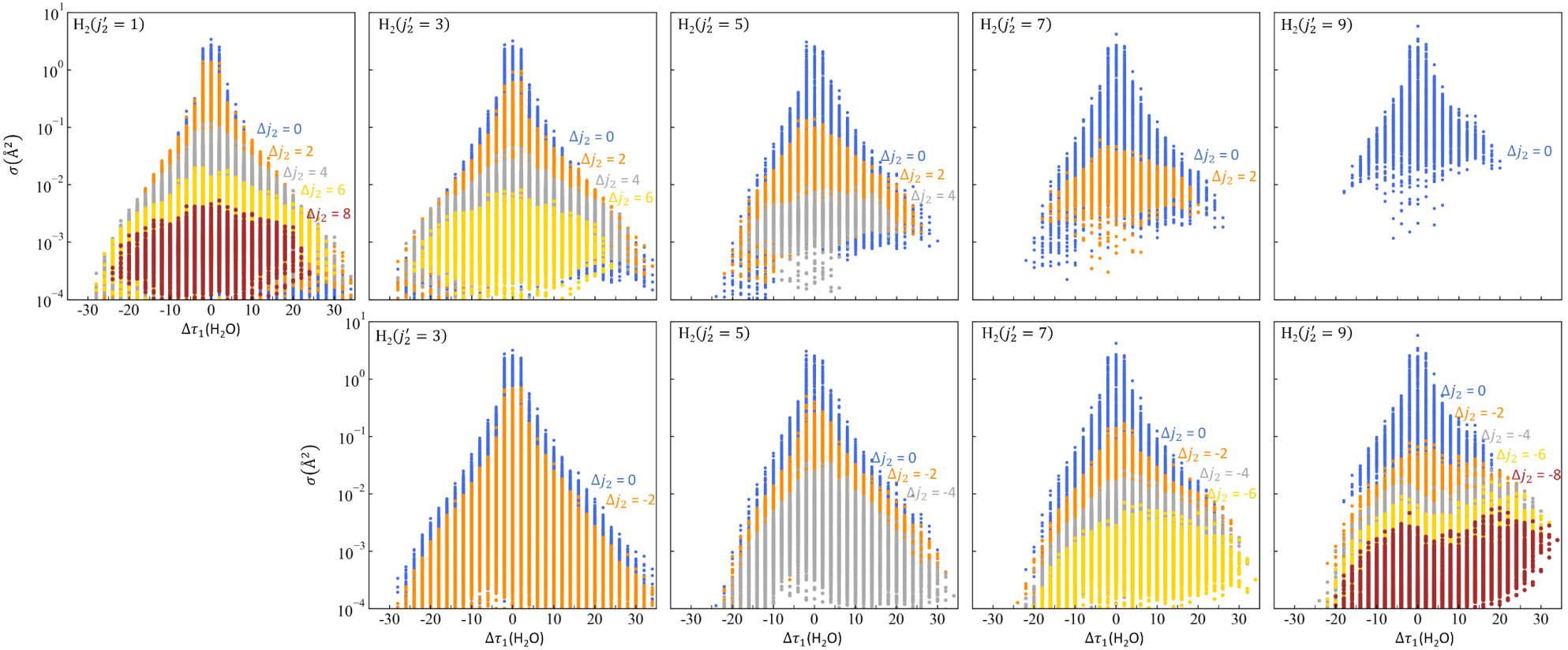


**Figure S19:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *p*-$H_2O$ + *o*-$H_2$ system, at $U$ = 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

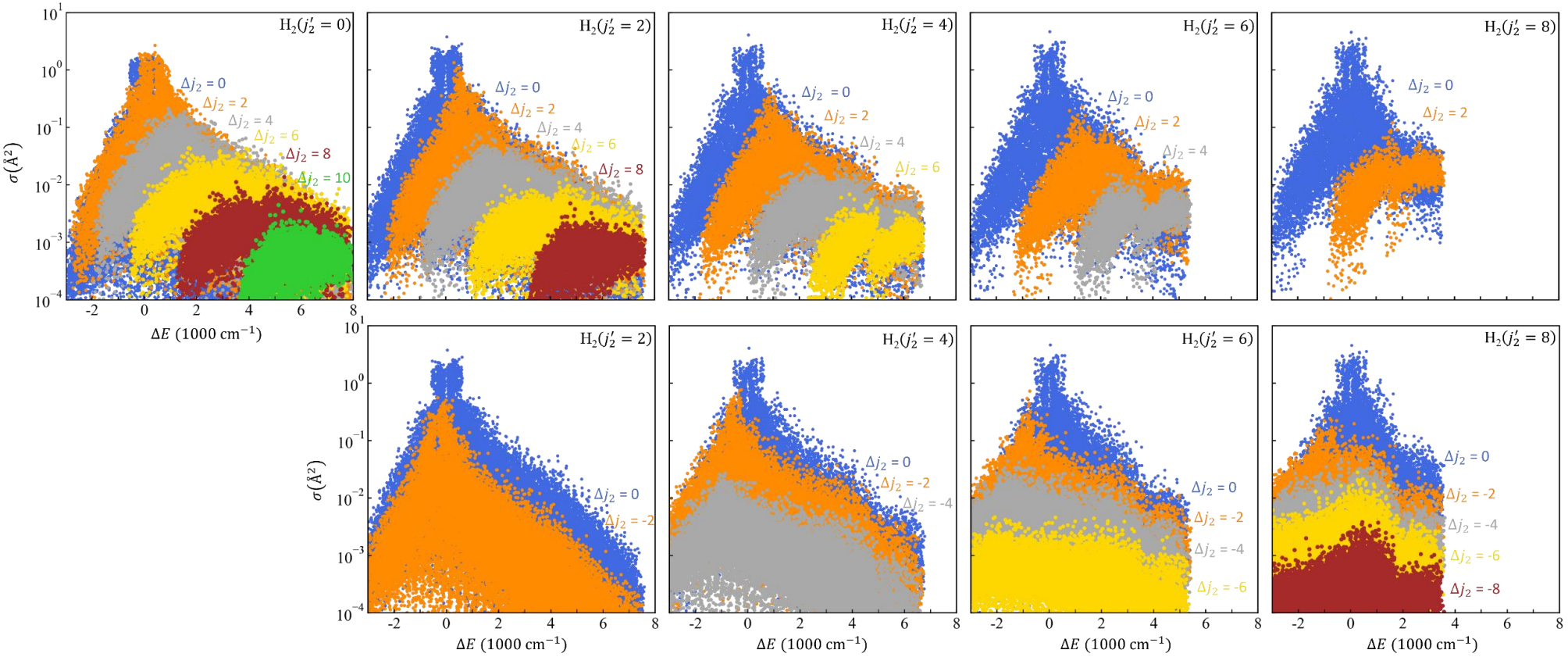


**Figure S20:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall transfer of internal rotational energy, $\Delta E$ in the *o*-$H_2O$ + *p*-$H_2$ system at collision energy $U \sim 12000$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper right corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

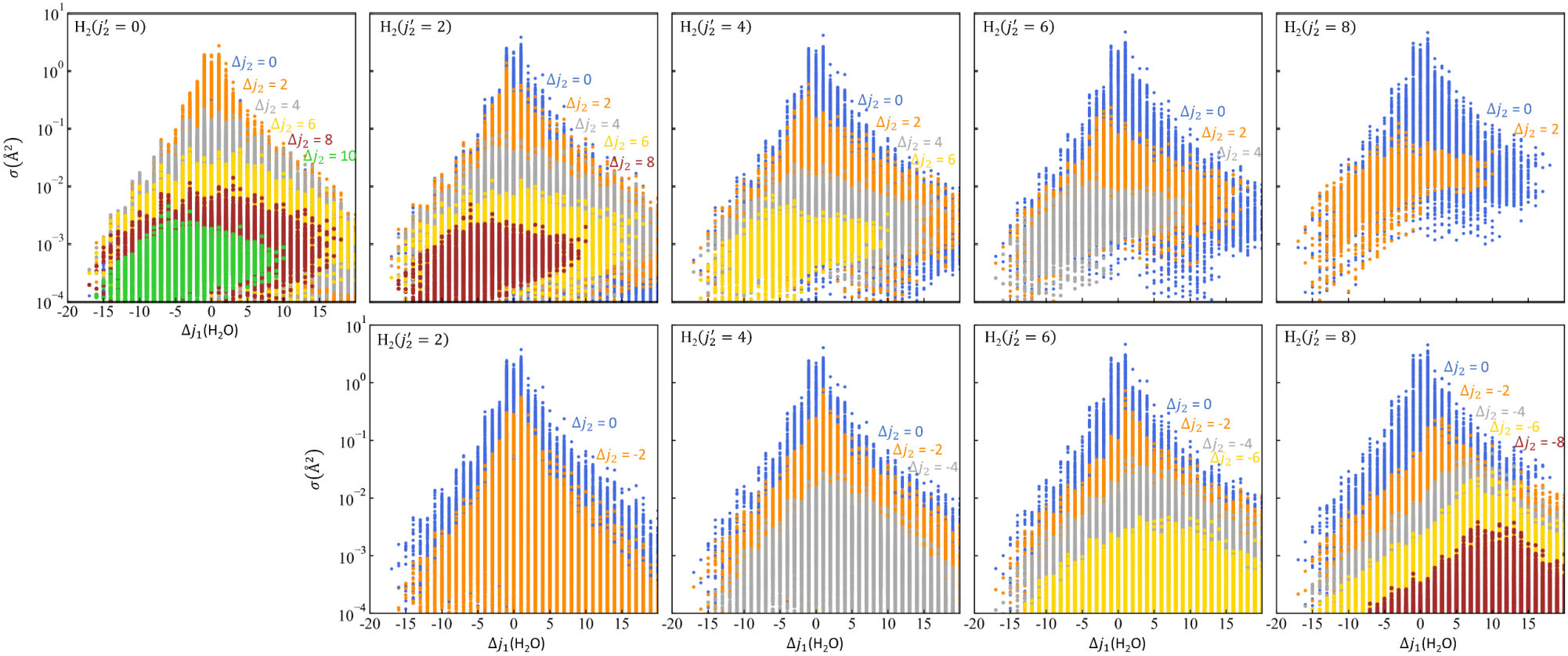


**Figure S21:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *o*-$H_2O$ + *p*-$H_2$ system at collision energy $U \sim 12000$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper right corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

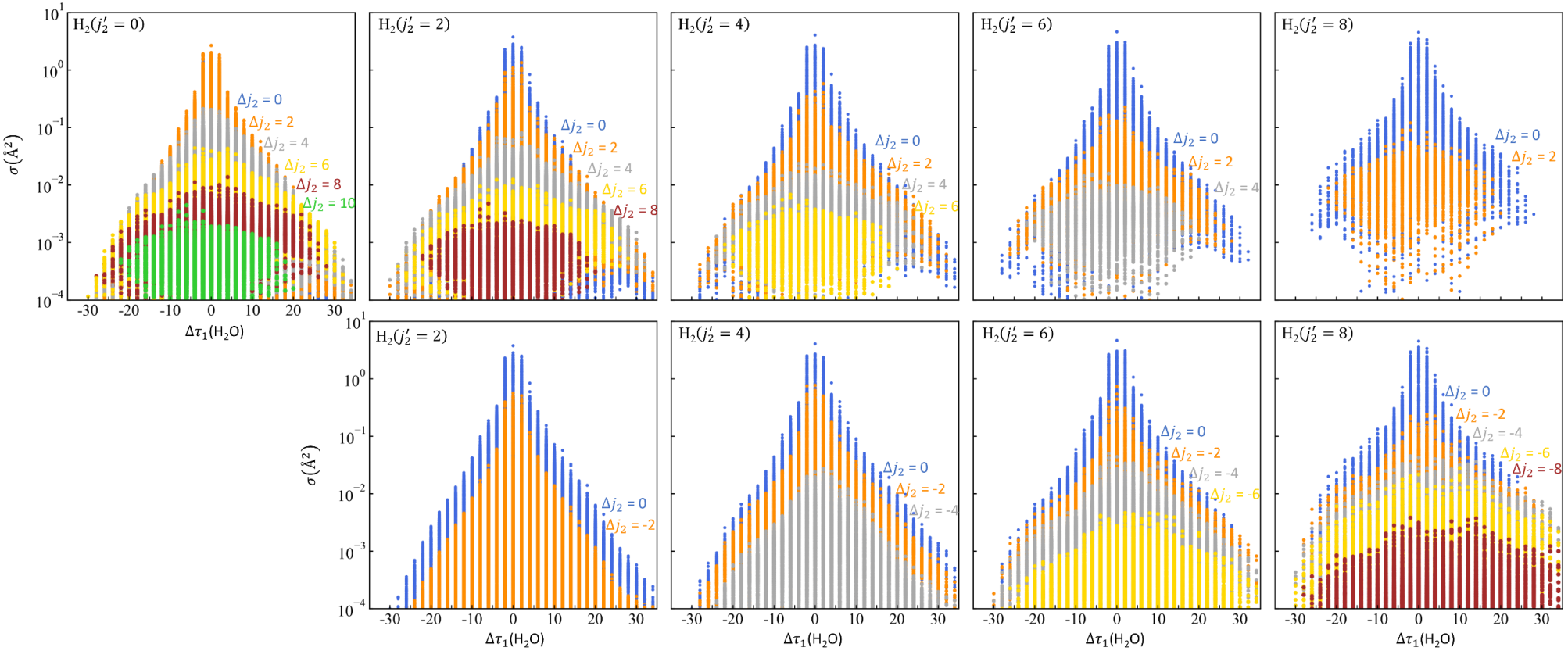


**Figure S22:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *o*-$H_2O$ + *p*-$H_2$ system at collision energy $U \sim 12000$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

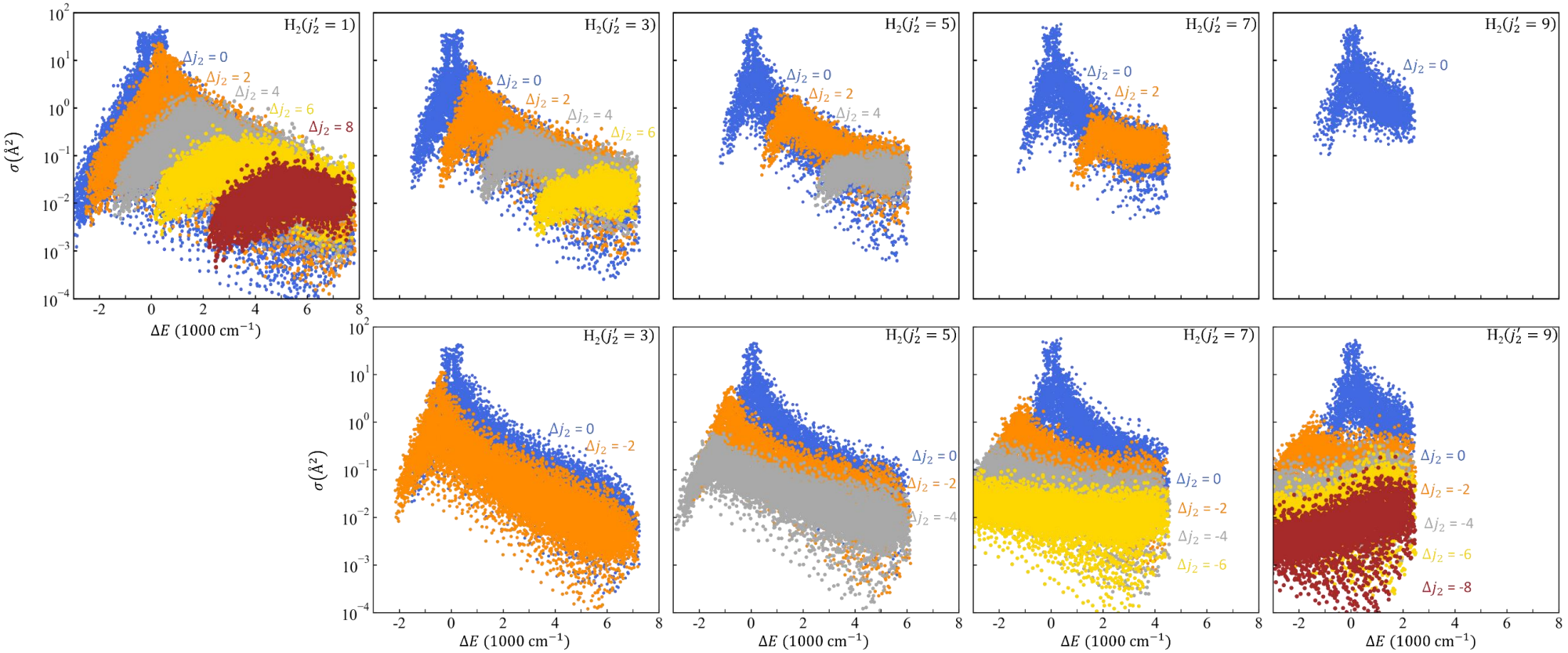


**Figure S23:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n' \to n''}$ and the overall transfer of internal rotational energy, $\Delta E$ in the *o*-$H_2O$ + *o*-$H_2$ system at collision energy $U \sim 12000$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper right corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

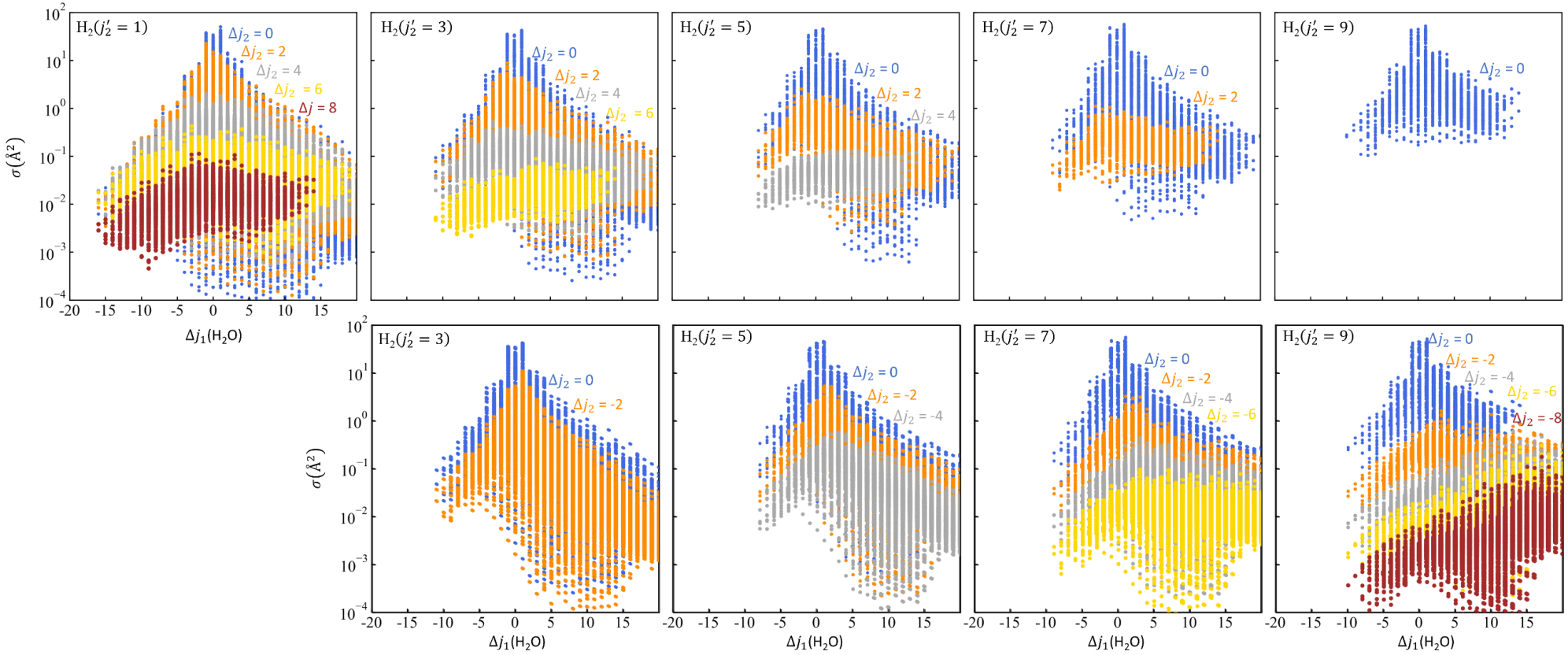


**Figure S24:** Correlation between the values of individual state-to-state transition cross sections $\sigma_{n'\to n''}$ and change in the rotational state of $H_2O$ ($\Delta j_1$) in the *o*-$H_2O$ + *o*-$H_2$ system at collision energy $U \sim 12000$ cm$^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

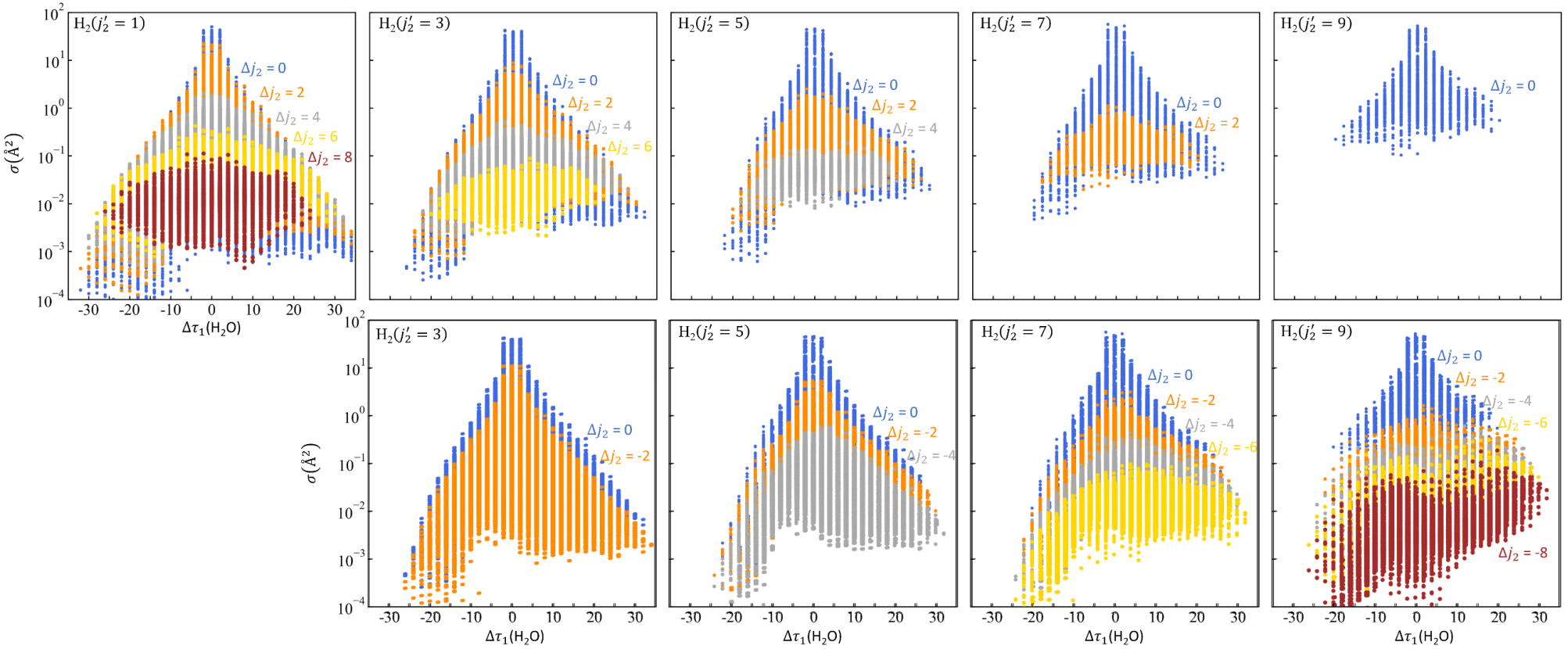


**Figure S25:** Correlation between the values of individual state-to-state cross sections $\sigma_{n'\to n''}$ and change in the $\tau_1$ of $H_2O$ ($\Delta\tau_1$) in the *o*-$H_2O$ + *o*-$H_2$ system at collision energy $U$ ~ 12000 $cm^{-1}$. Here 100 initial states of water are considered. The initial state of $H_2$ molecule is given in the upper left corner of each frame. Top and bottom rows of frames correspond to excitation and quenching of $H_2$. Colors represent different transitions in $H_2$: $\Delta j_2 = 0, \pm 2, \pm 4, \pm 6, \pm 8$ are shown by blue, orange, grey, yellow, and maroon symbols, respectively.

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