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

ELECTRONIC SUPPLEMENTARY INFORMATION

Uncovering the role of the stationary points in the dynamics of the $F^- + CH_3I$ reaction

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DEFINITION OF THE INTERACTION REGION

The interaction region, where the geometries are assigned to one of the stationary points, is defined by excluding the configurations of the reactant and product channels given below.

Reactant channel

IF $r_{C\text{-}I} < 3.2$ Å AND $r_{CI\text{-}F} > 5.0$ Å AND all $r_{C\text{-}H} < 2.0$ Å,

where $r_{CI\text{-}F}$ is the distance of the middle of the C-I bond to the F atom

S_N2 product channel

IF $r_{C\text{-}I} > 3.2$ Å AND $r_{C\text{-}F} < 2.2$ Å AND $r_{CF\text{-}I} > 5.0$ Å AND all $r_{C\text{-}H} < 2.0$ Å,

where $r_{CF\text{-}I}$ is the distance of the middle of the C-F bond to the I atom

Proton-abstraction product channel

IF $r_{C\text{-}I} < 3.2$ Å AND $r_{C\text{-}F} > 2.2$ Å AND one $r_{F\text{-}H} < 2.0$ Å AND $r_{CI\text{-}HF} > 5.0$ Å,

where $r_{CI\text{-}HF}$ is the distance of the middle of the C-I bond to the middle of the H-F bond

IF^- product channel

IF $r_{C\text{-}I} > 3.2$ Å AND $r_{C\text{-}F} > 2.2$ Å AND $r_{F\text{-}I} < 3.0$ Å AND $r_{FI\text{-}C} > 5.0$ Å AND all $r_{C\text{-}H} < 2.0$ Å,

where $r_{FI\text{-}C}$ is the distance of the middle of the F-I bond to the C atom

IHF^- product channel

IF $r_{C\text{-}I} > 3.2$ Å AND $r_{C\text{-}F} > 2.2$ Å AND one $r_{C\text{-}H} > 2.0$ Å AND $r_{FI\text{-}C} > 5.0$ Å AND $r_{F\text{-}H} < 1.7$ Å AND $r_{I\text{-}H} < 2.8$ Å

$F^- + CH_3 + I$ product channel

IF $r_{C\text{-}I} > 5.0$ Å AND $r_{C\text{-}F} > 5.0$ Å AND $r_{F\text{-}I} > 3.0$ Å AND all $r_{C\text{-}H} < 2.0$ Å

$CH_2 + HF + I^-$ product channel

IF $r_{C\text{-}I} > 5.0$ Å AND $r_{HF\text{-}C} > 5.0$ Å AND one $r_{C\text{-}H} > 2.0$ Å AND $r_{F\text{-}H} < 2.0$ Å,

where $r_{HF\text{-}C}$ is the distance of the middle of the H-F bond to the C atom

Hydrogen-departure product channel

IF not proton-abstraction or not IHF^- or not $CH_2 + HF + I^-$ channel AND there is at least one H atom at ≥5 Å distance from the C atom

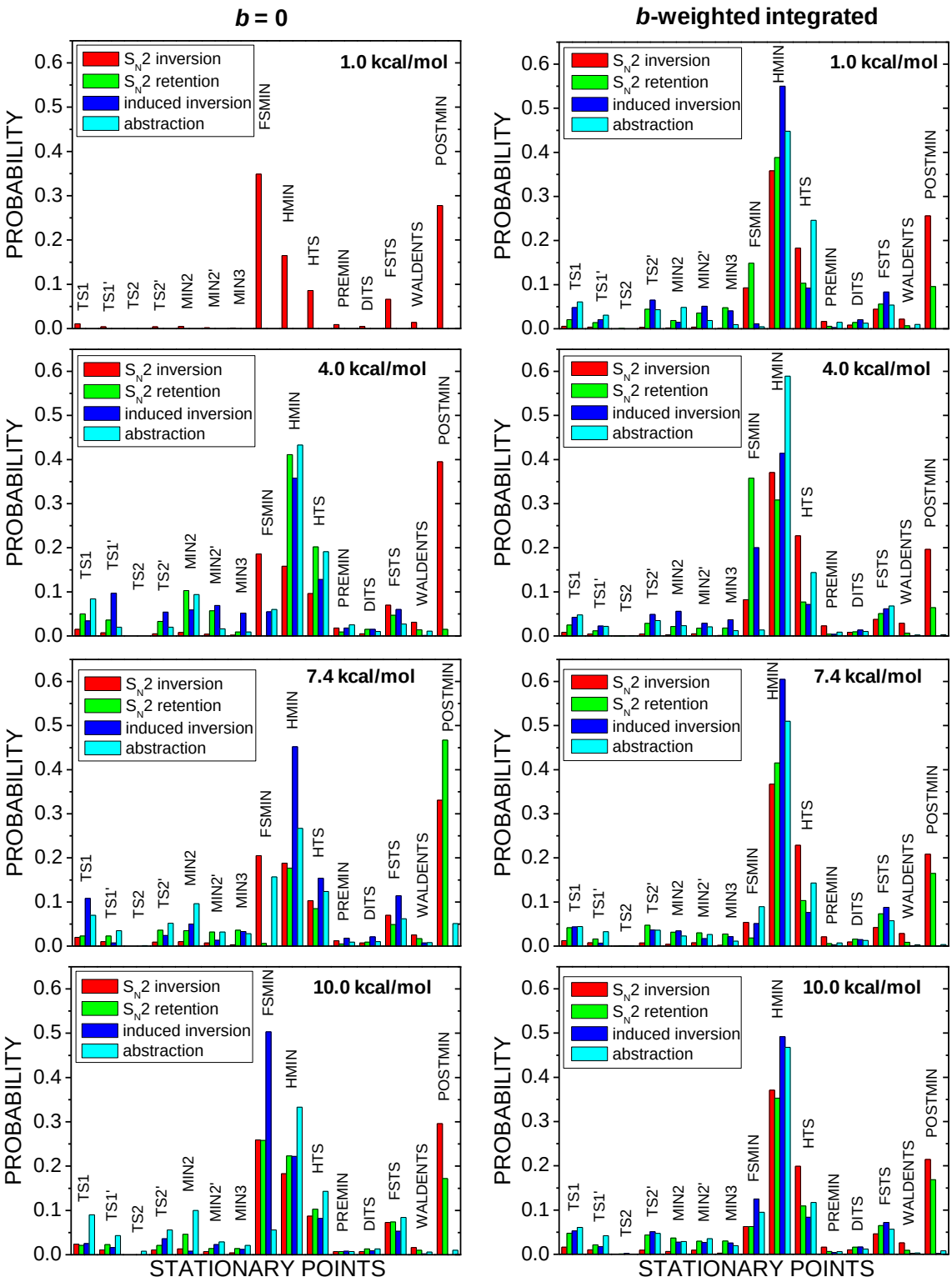

Figure S1 continues on the next page

Figure S1 continues

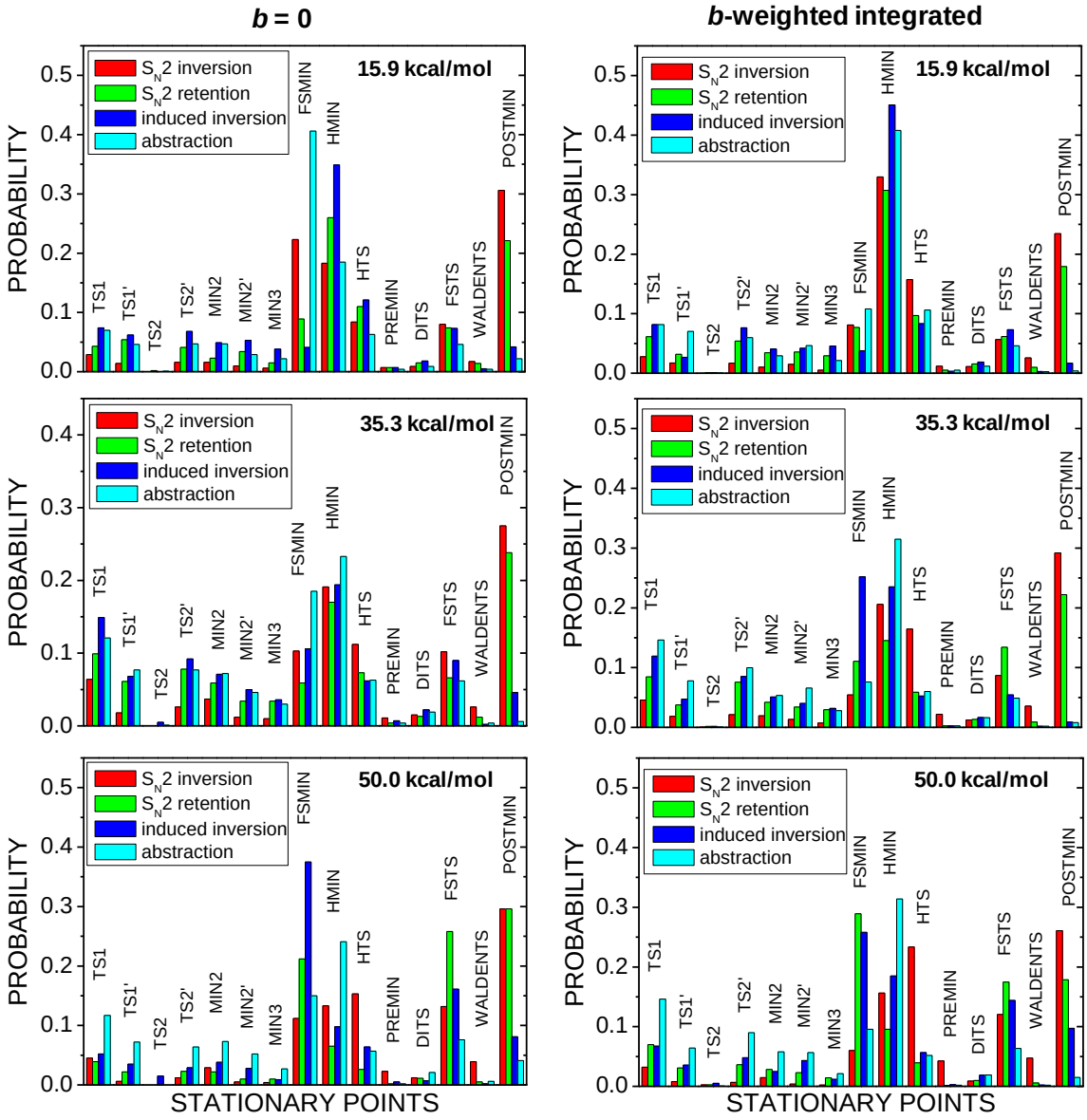

Figure S1. Stationary-point distributions, normalized for each channel, corresponding to $b = 0$ and b-averaged $F^- + CH_3I$ trajectories at collision energies of 1.0, 4.0, 7.4, 10.0, 15.9, 35.3, and 50.0 kcal/mol.

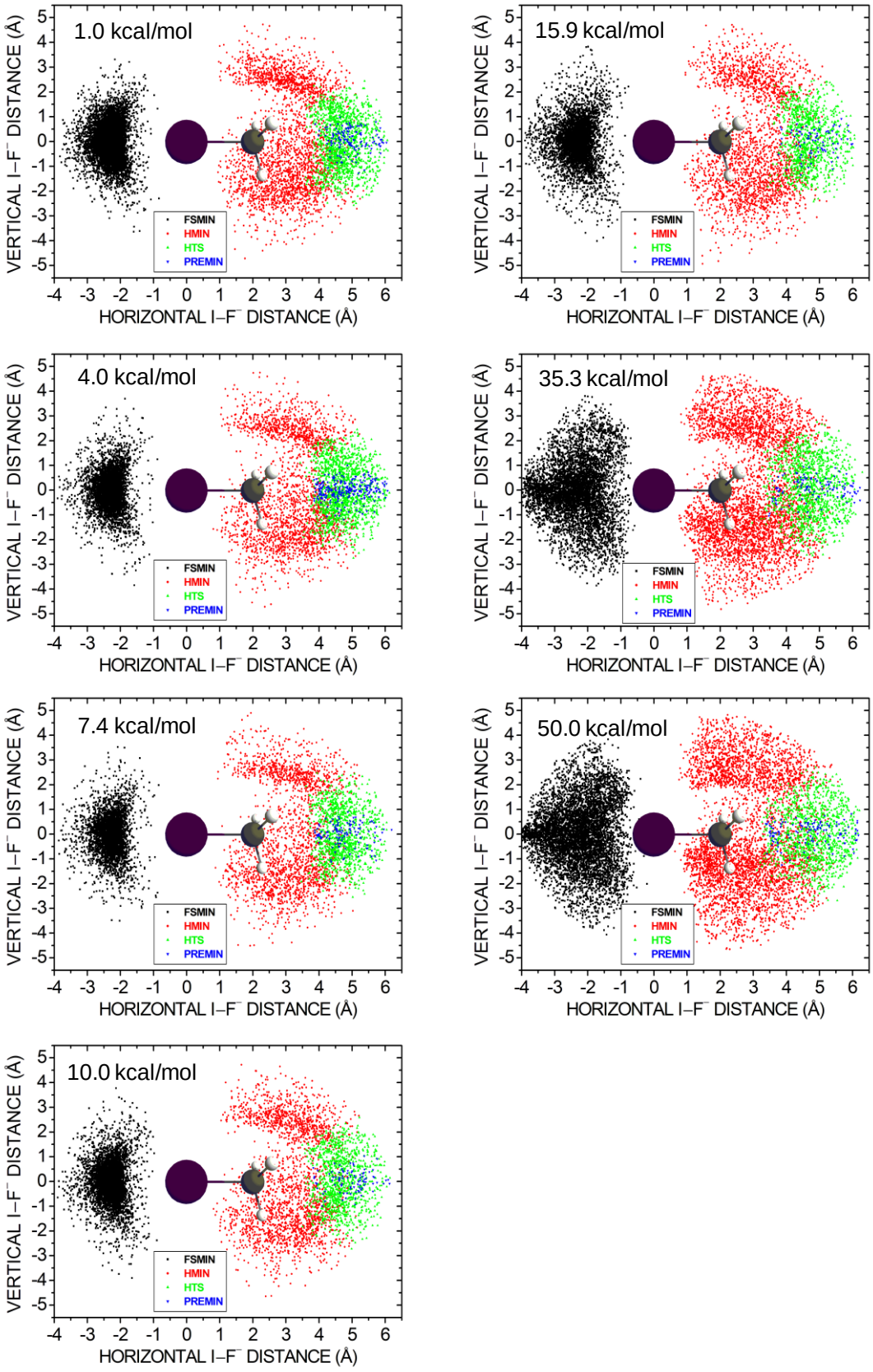

Figure S2. Stationary-point-specific distributions of the positions of F^- in the entrance channel of the $F^- + CH_3I$ reaction obtained by trajectory orthogonal projection onto the I-C-H plane at different collision energies.

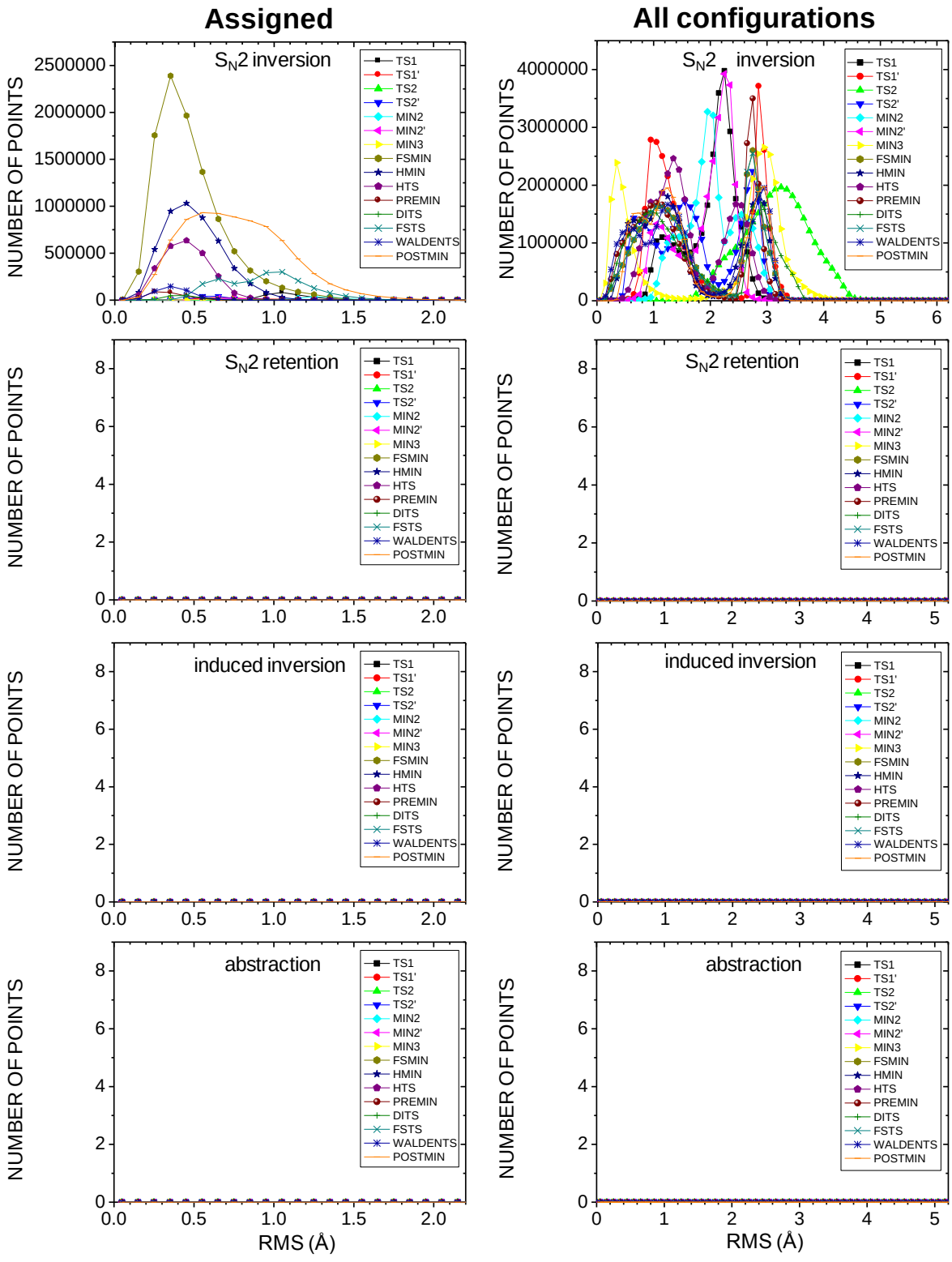

Figure S3. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 1.0 kcal/mol.

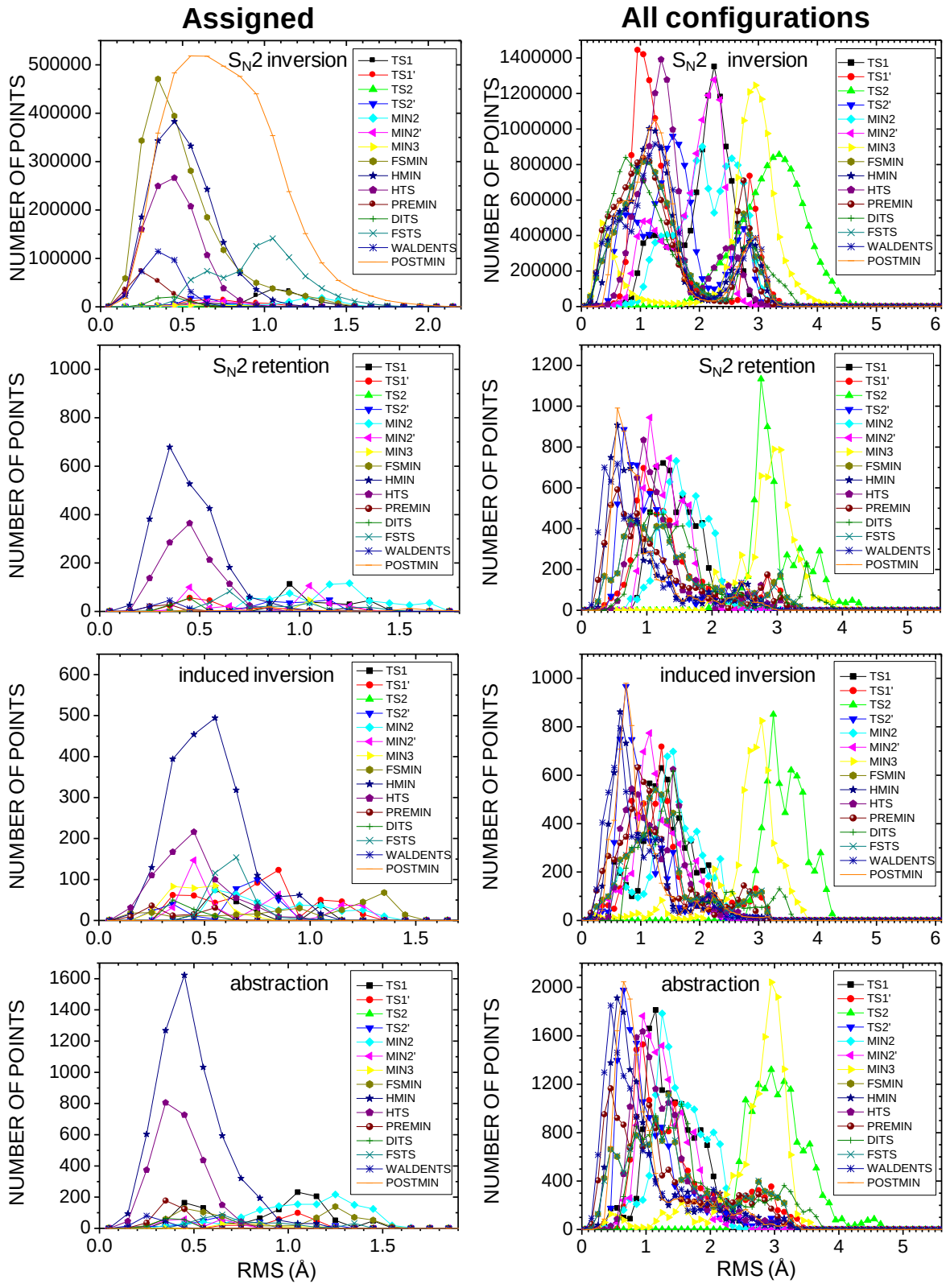

Figure S4. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 4.0 kcal/mol.

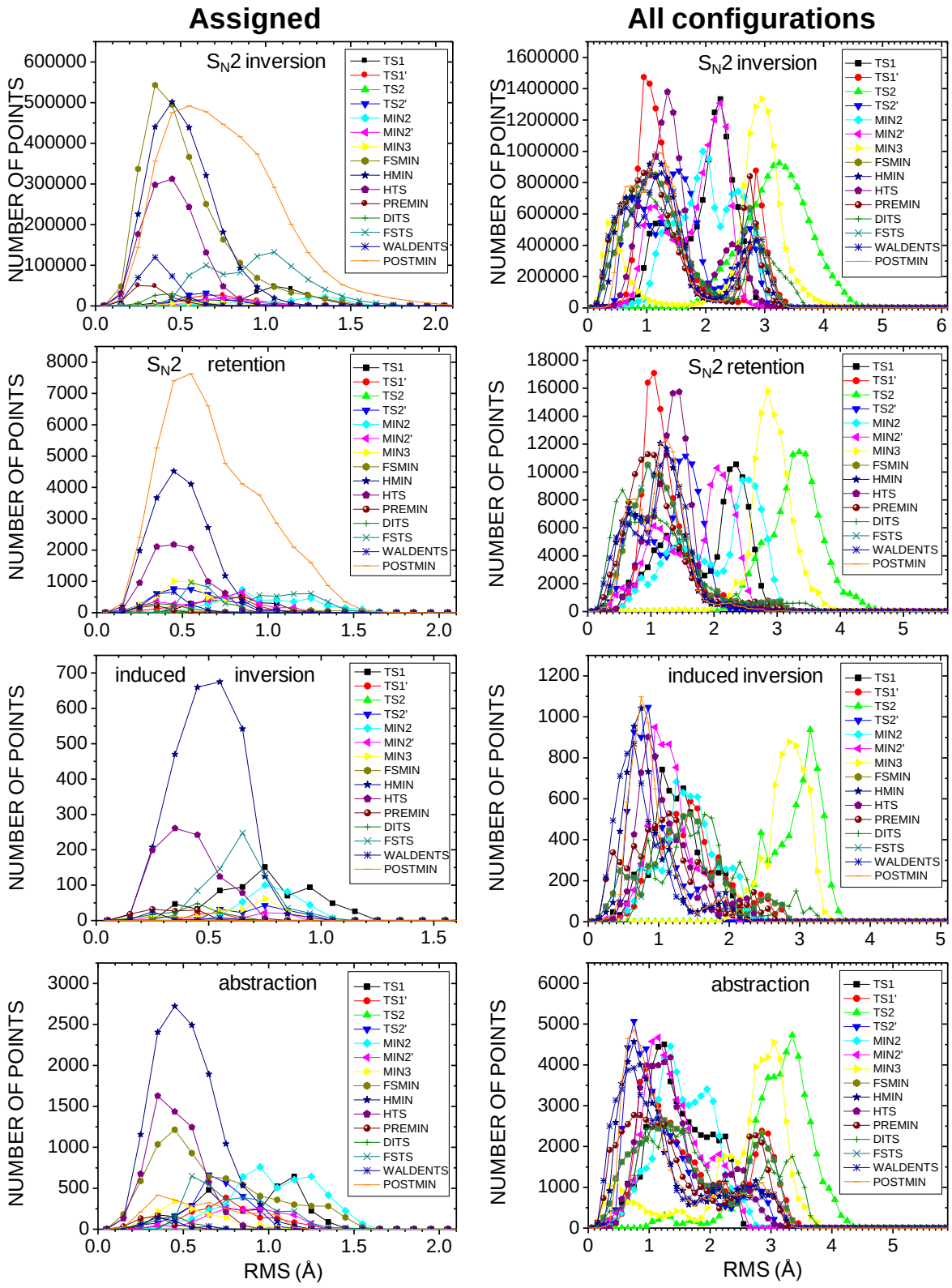

Figure S5. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 7.4 kcal/mol.

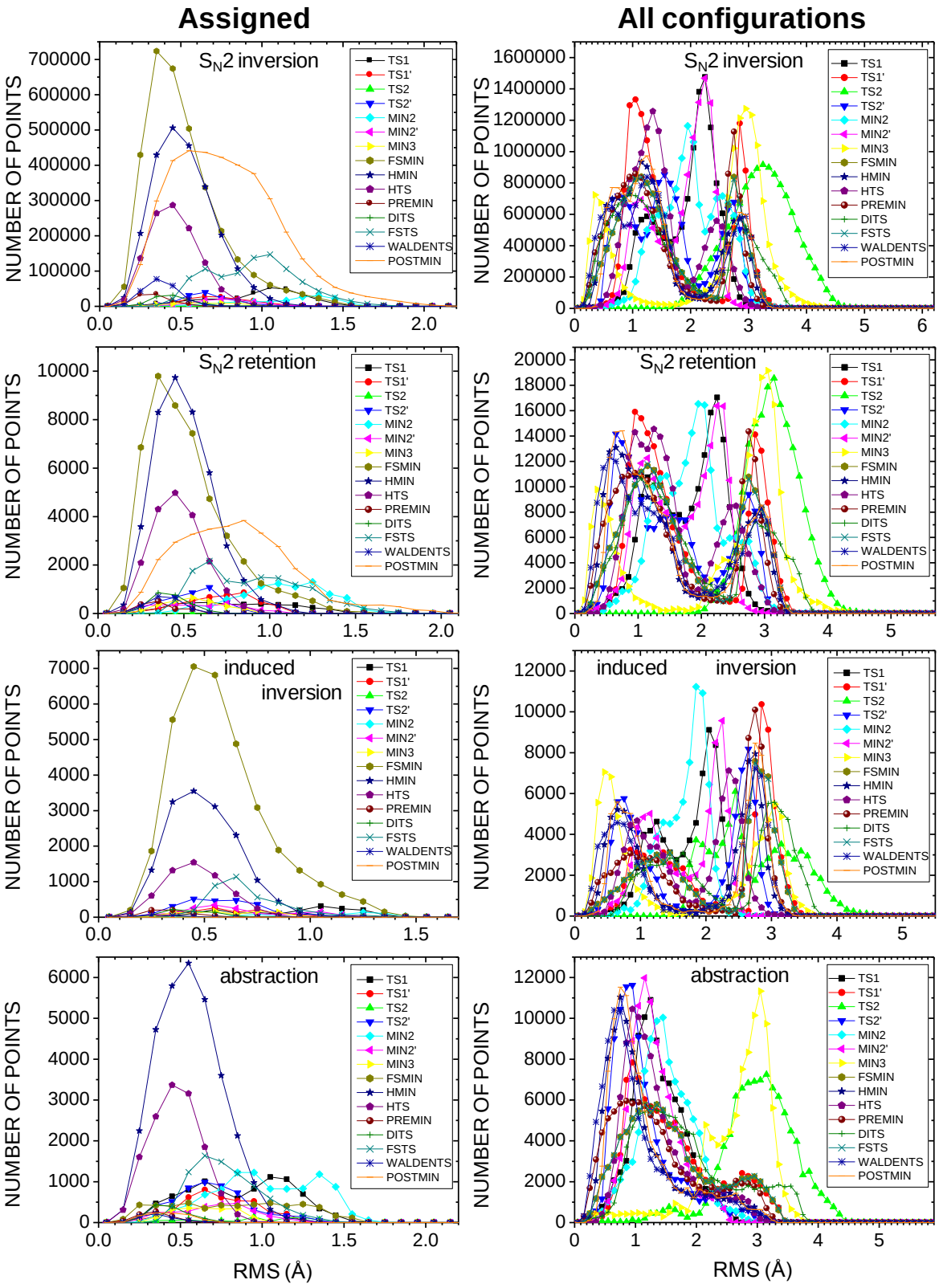

Figure S6. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 10.0 kcal/mol.

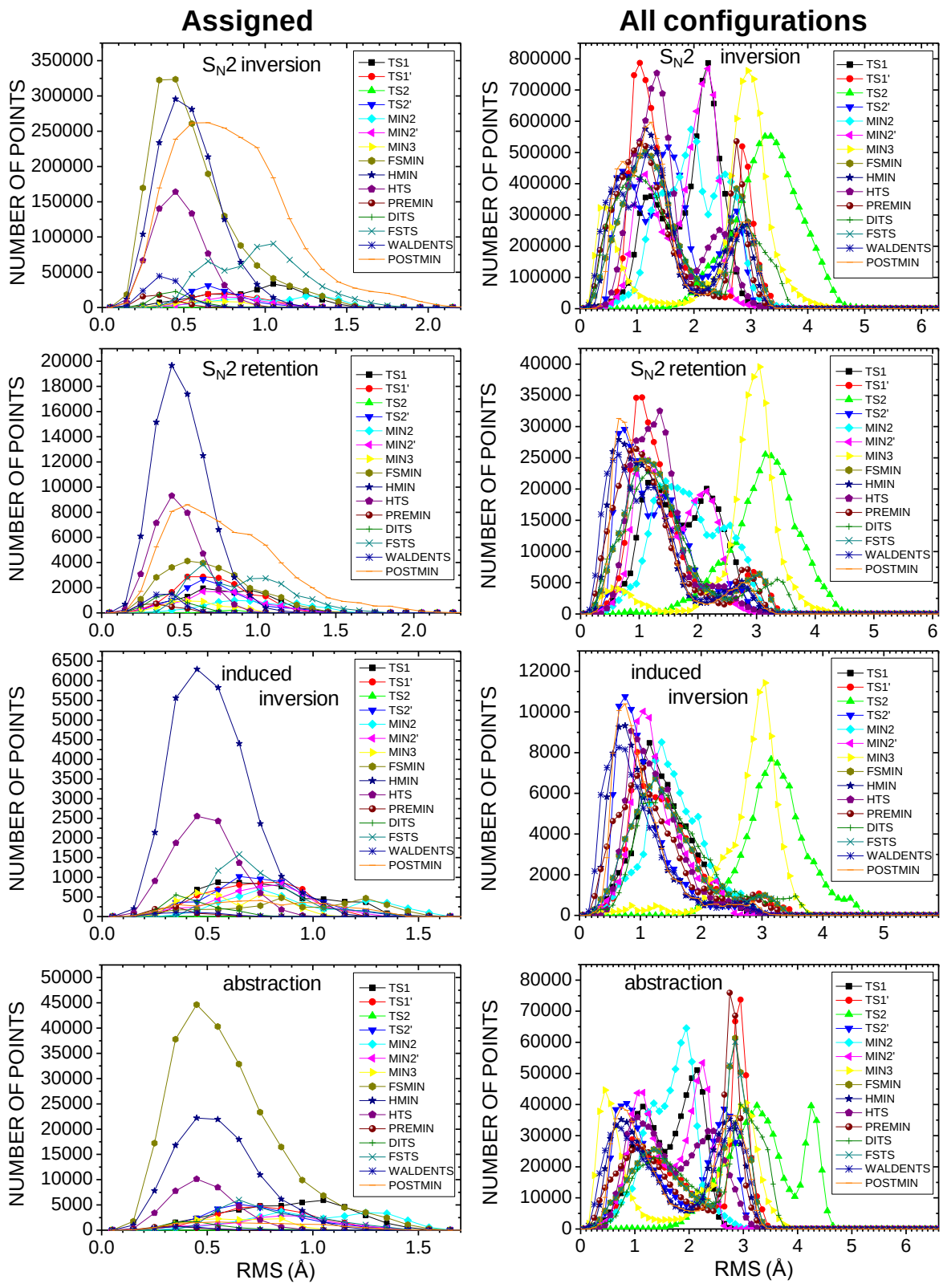

Figure S7. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 15.9 kcal/mol.

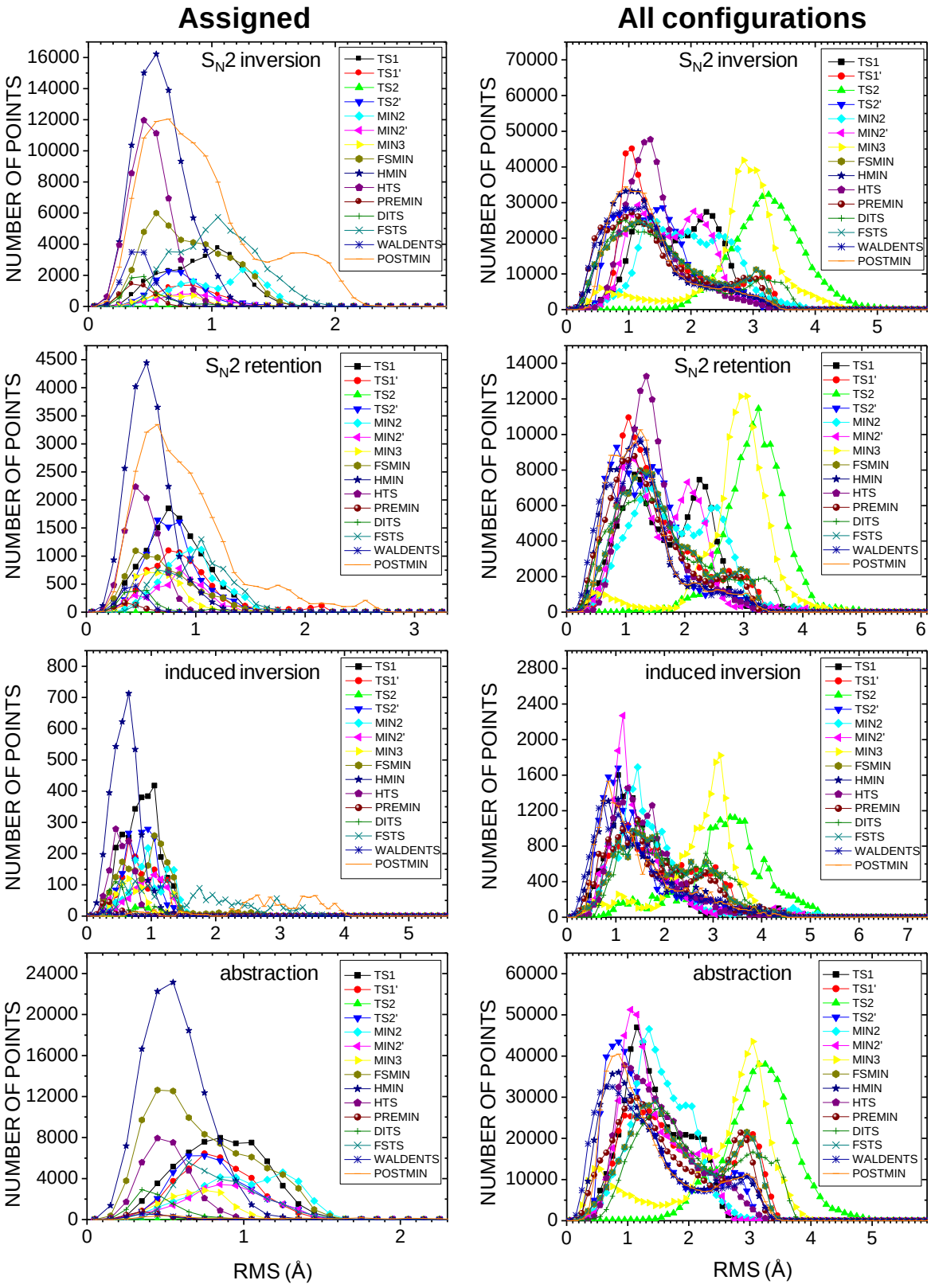

Figure S8. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 35.3 kcal/mol.

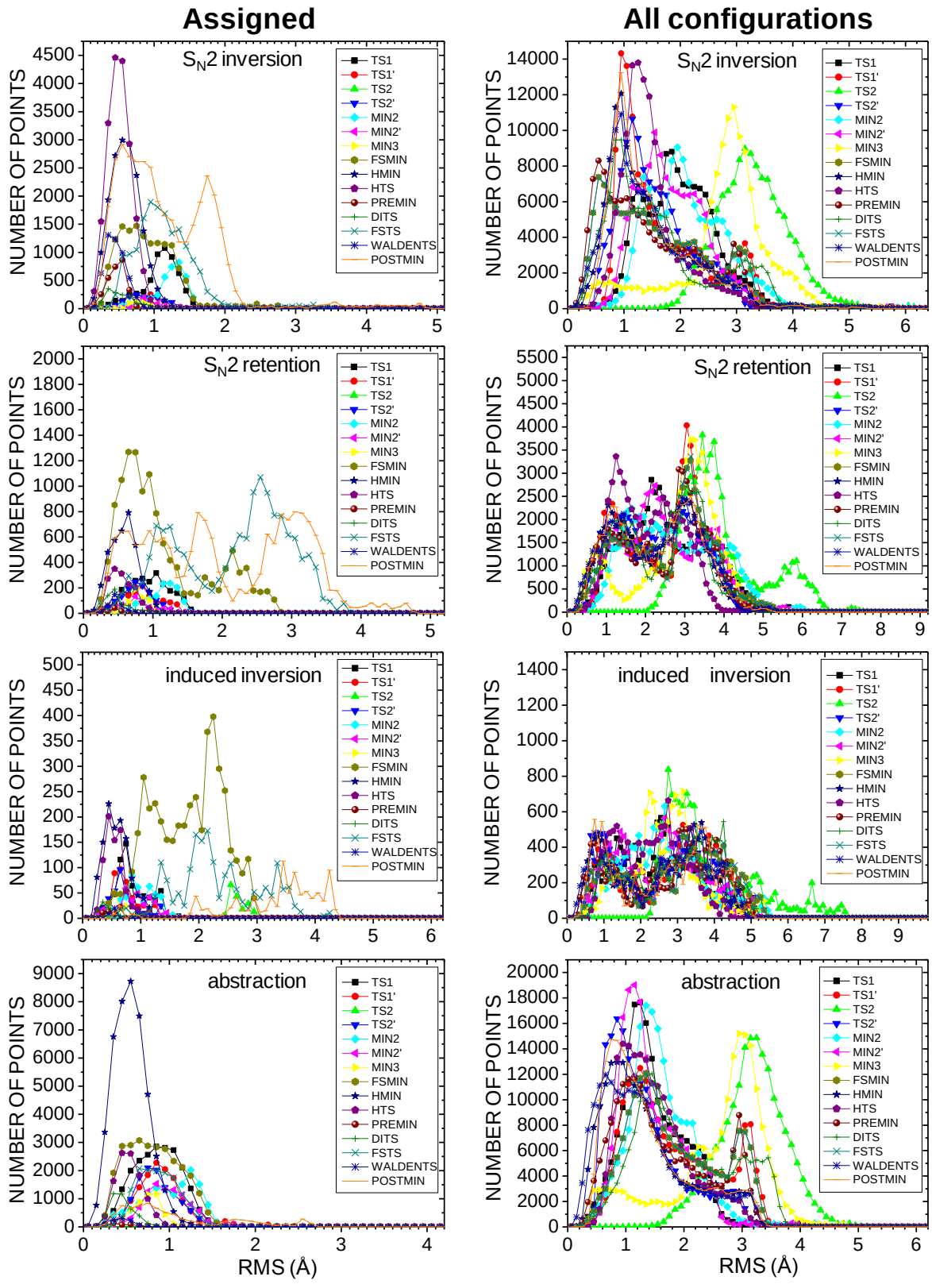

Figure S9. Distributions of the root-mean-square deviations of the actual geometries relative to the assigned and all the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 50.0 kcal/mol.

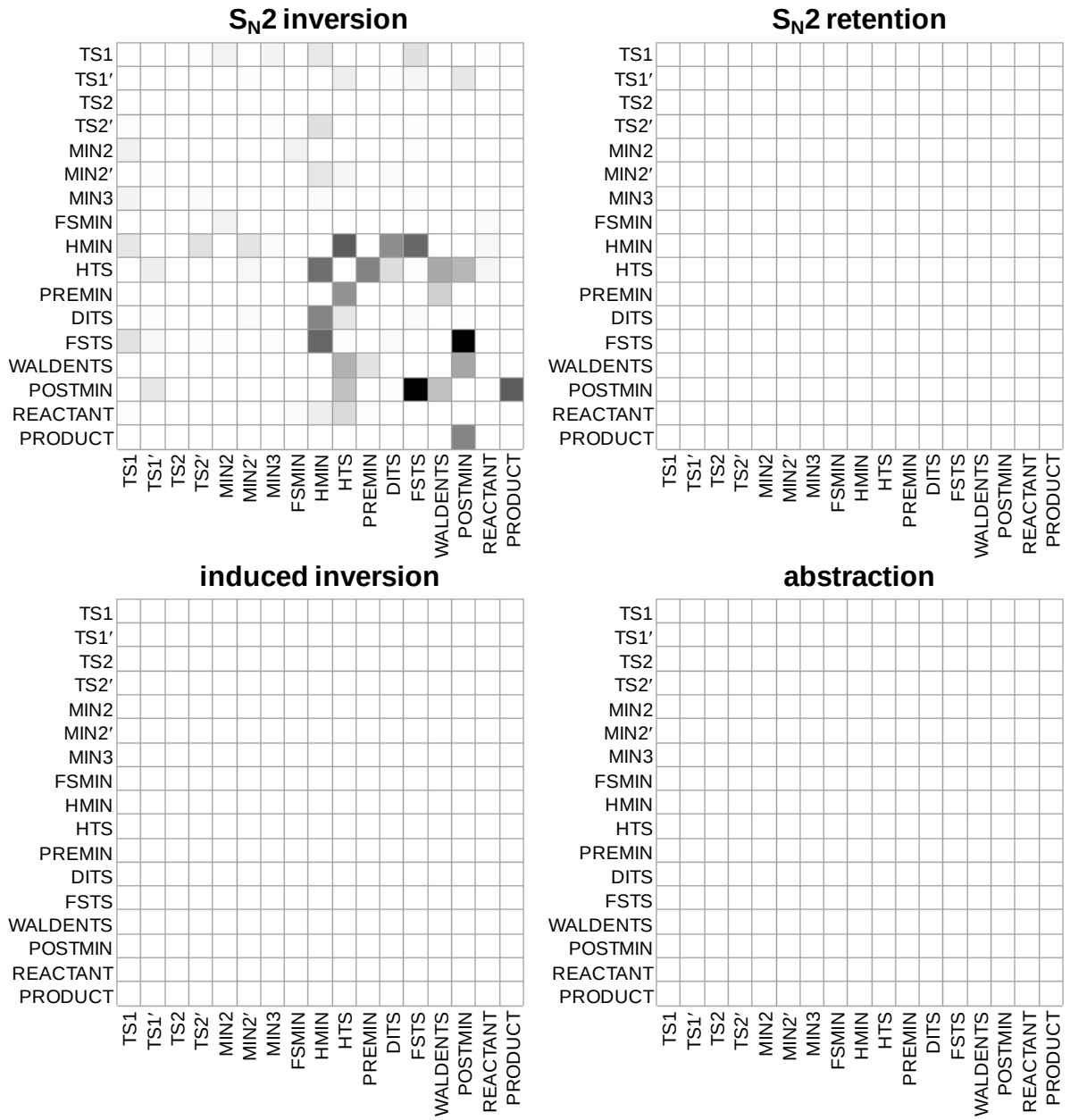

Figure S10. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 1.0 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

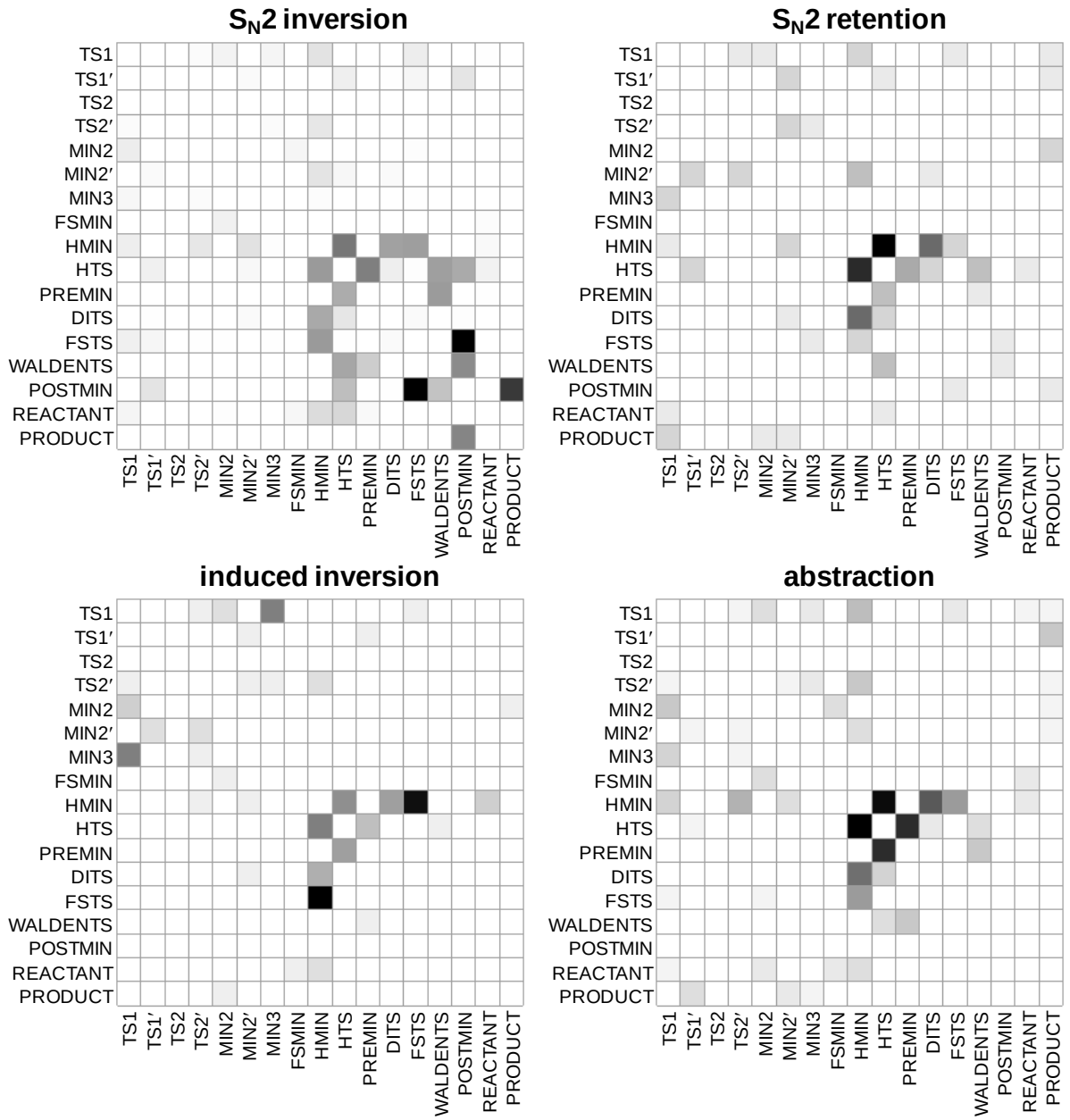

Figure S11. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 4.0 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

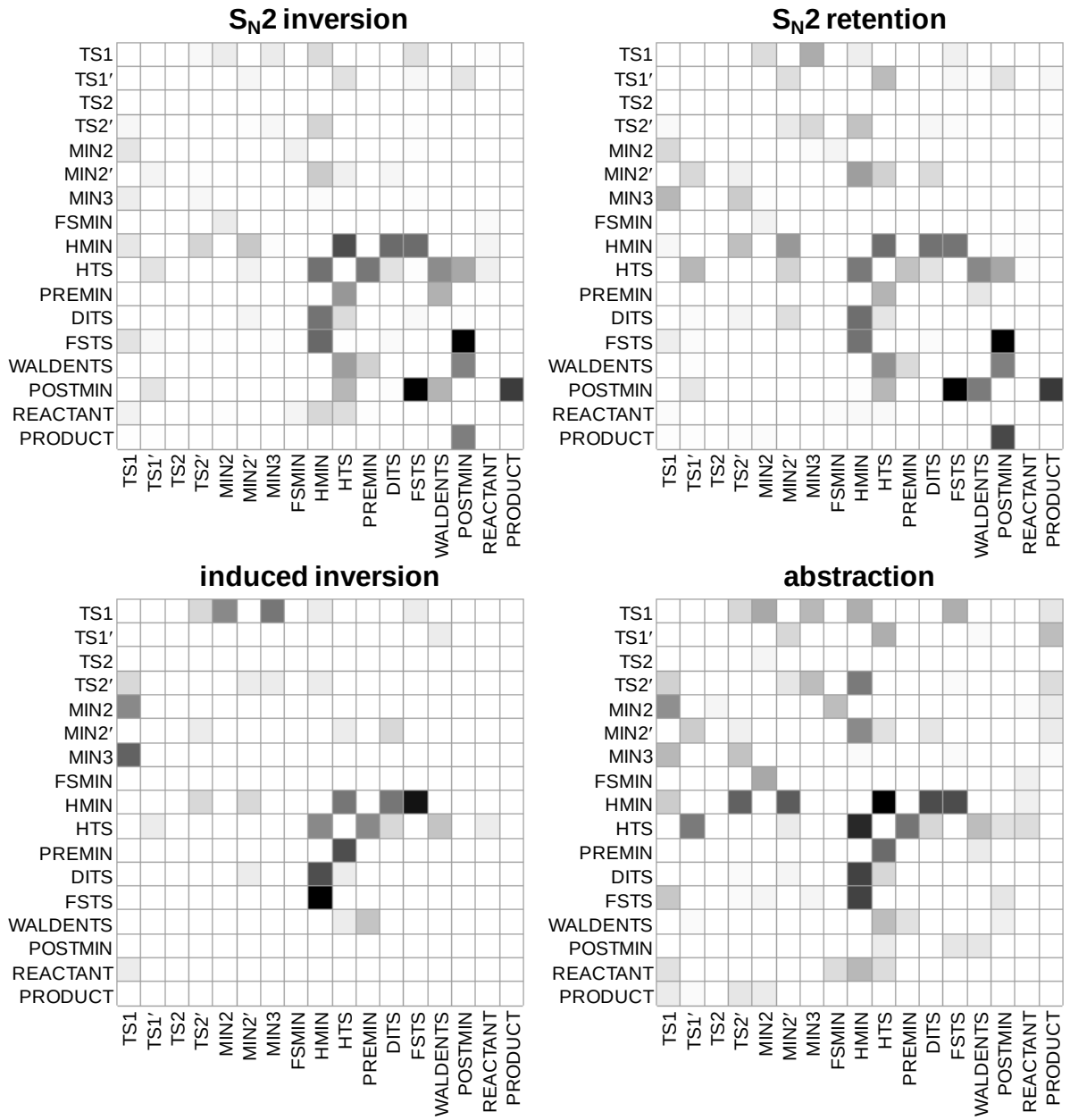

Figure S12. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 7.4 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

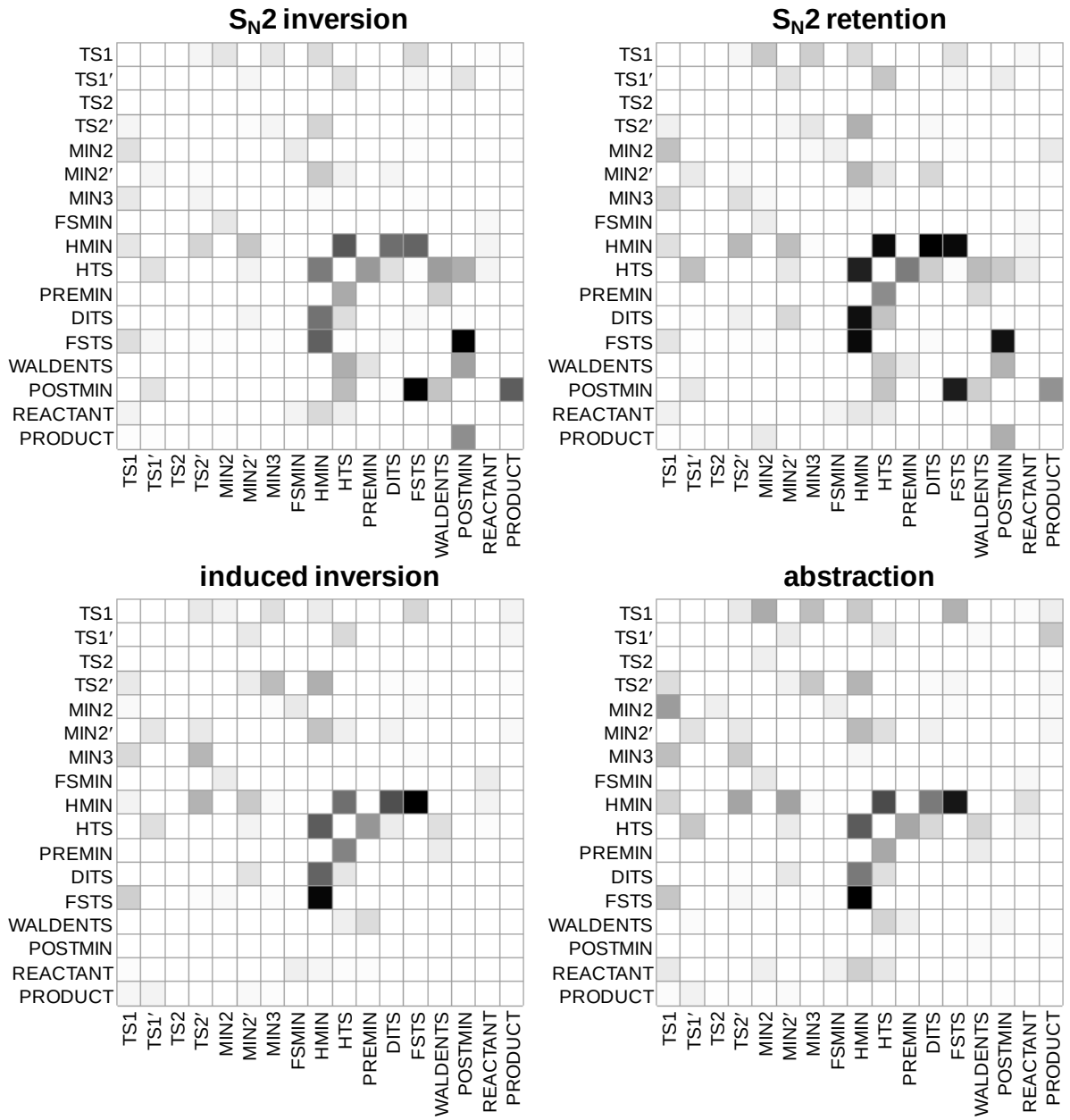

Figure S13. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 10.0 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

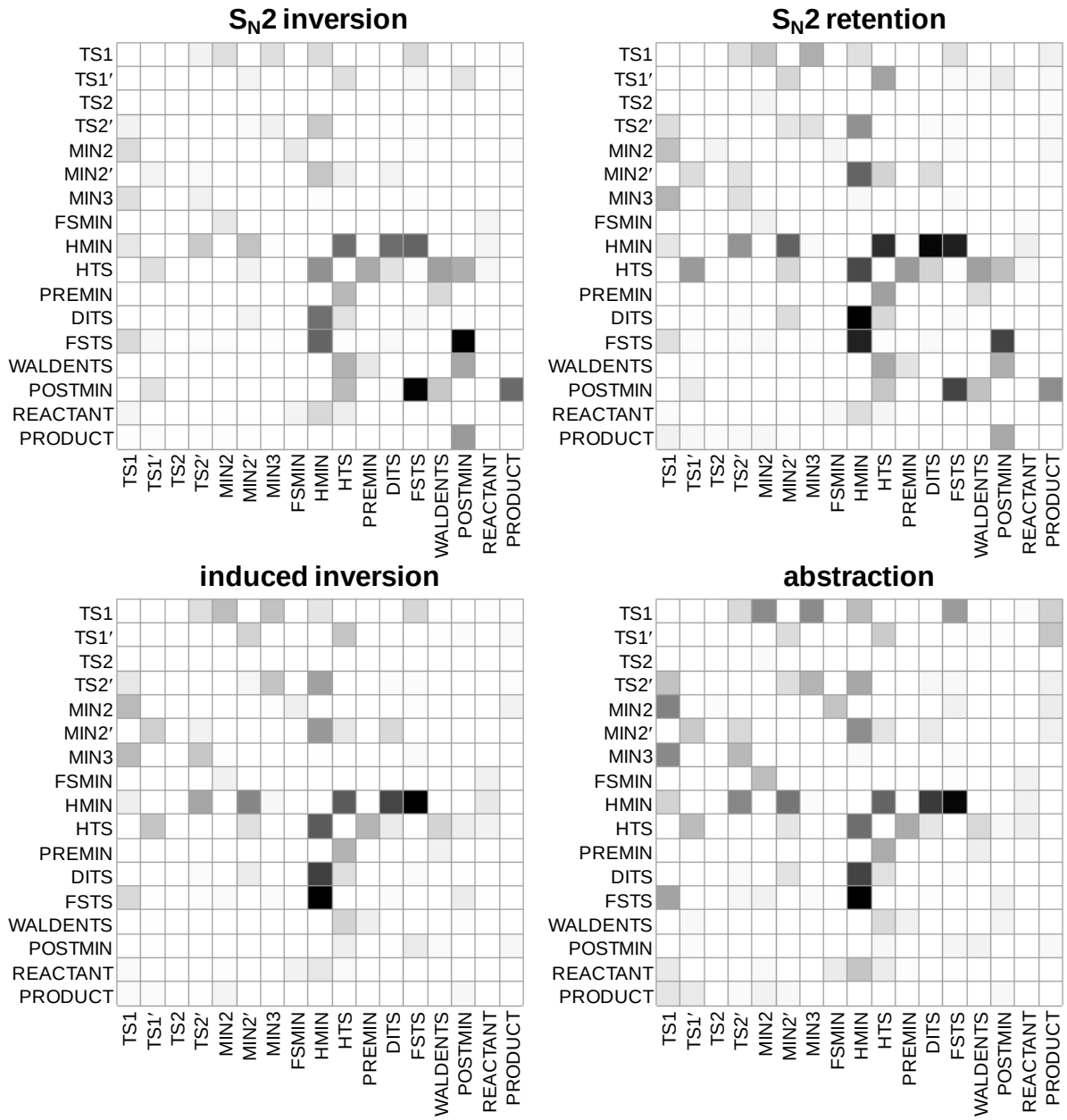

Figure S14. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 15.9 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

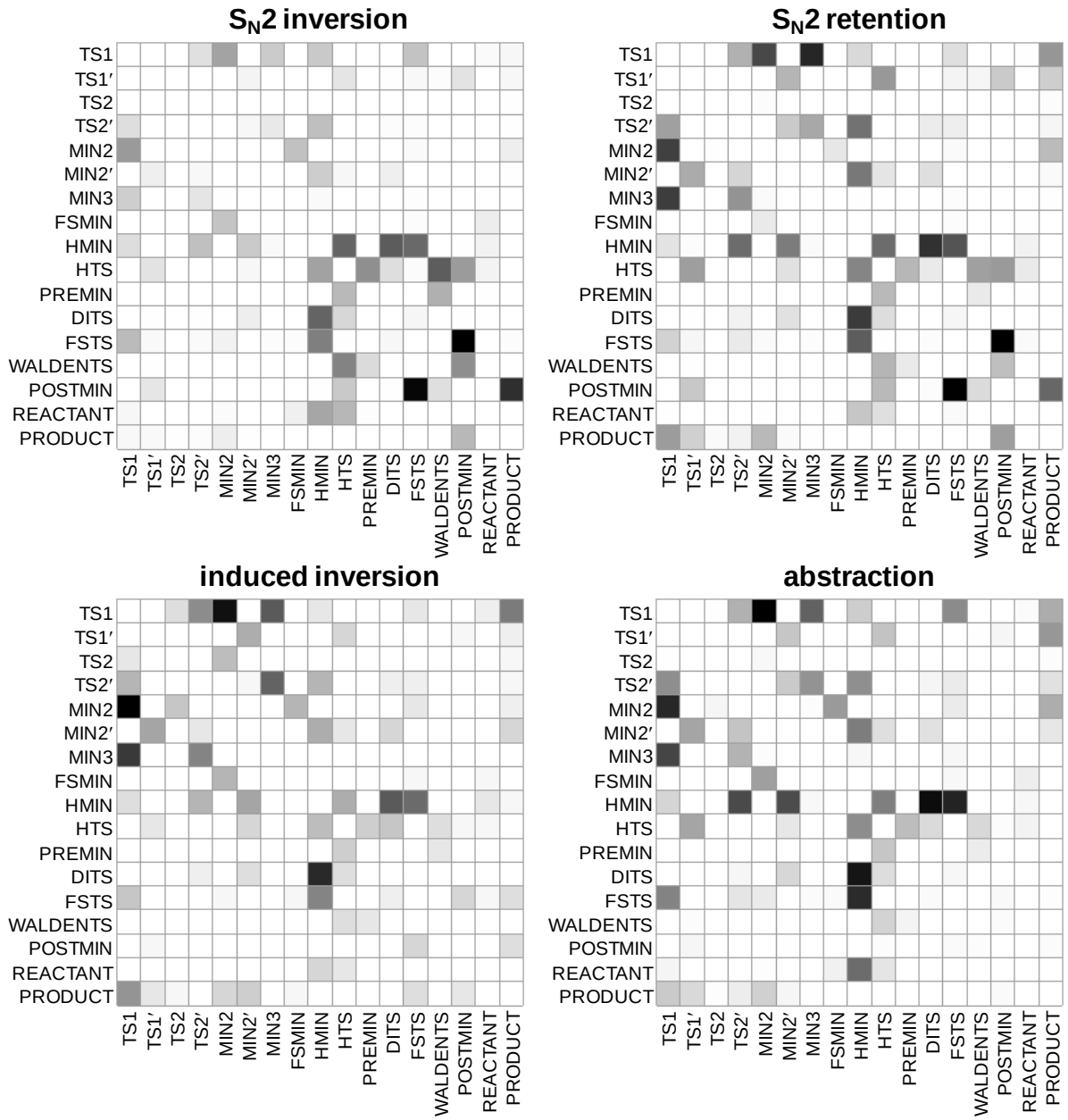

Figure S15. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 35.3 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

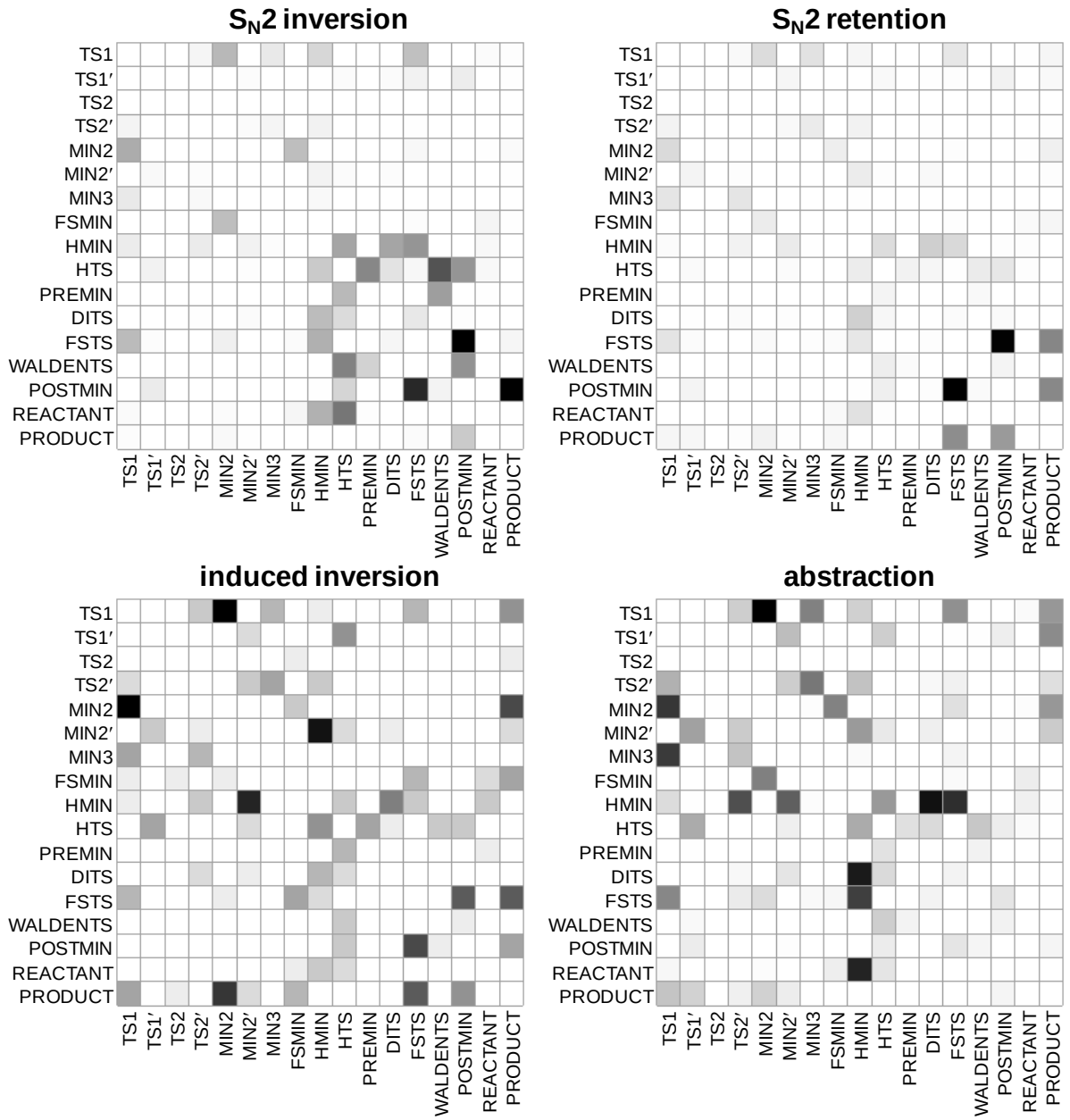

Figure S16. Transition probability matrices for the stationary points of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 50.0 kcal/mol. Darker matrix elements mean higher probabilities for row → column transitions between stationary points.

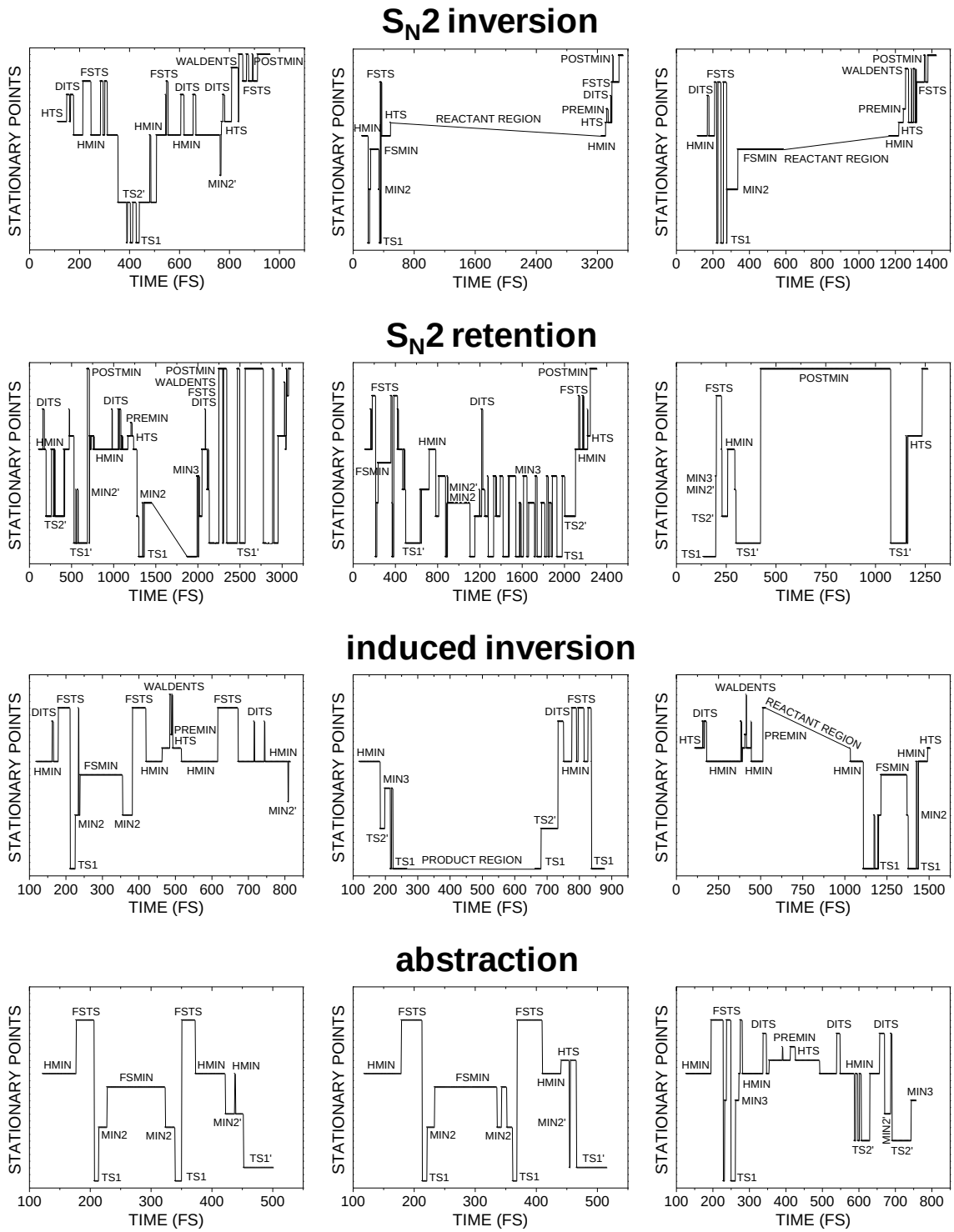

Figure S17. Assigned stationary points as a function of integration time for selected trajectories of the $F^- + CH_3I$ reaction at $b = 0$ and collision energy of 35.3 kcal/mol. (All the three S_N2 retention trajectories proceed with double inversion.)

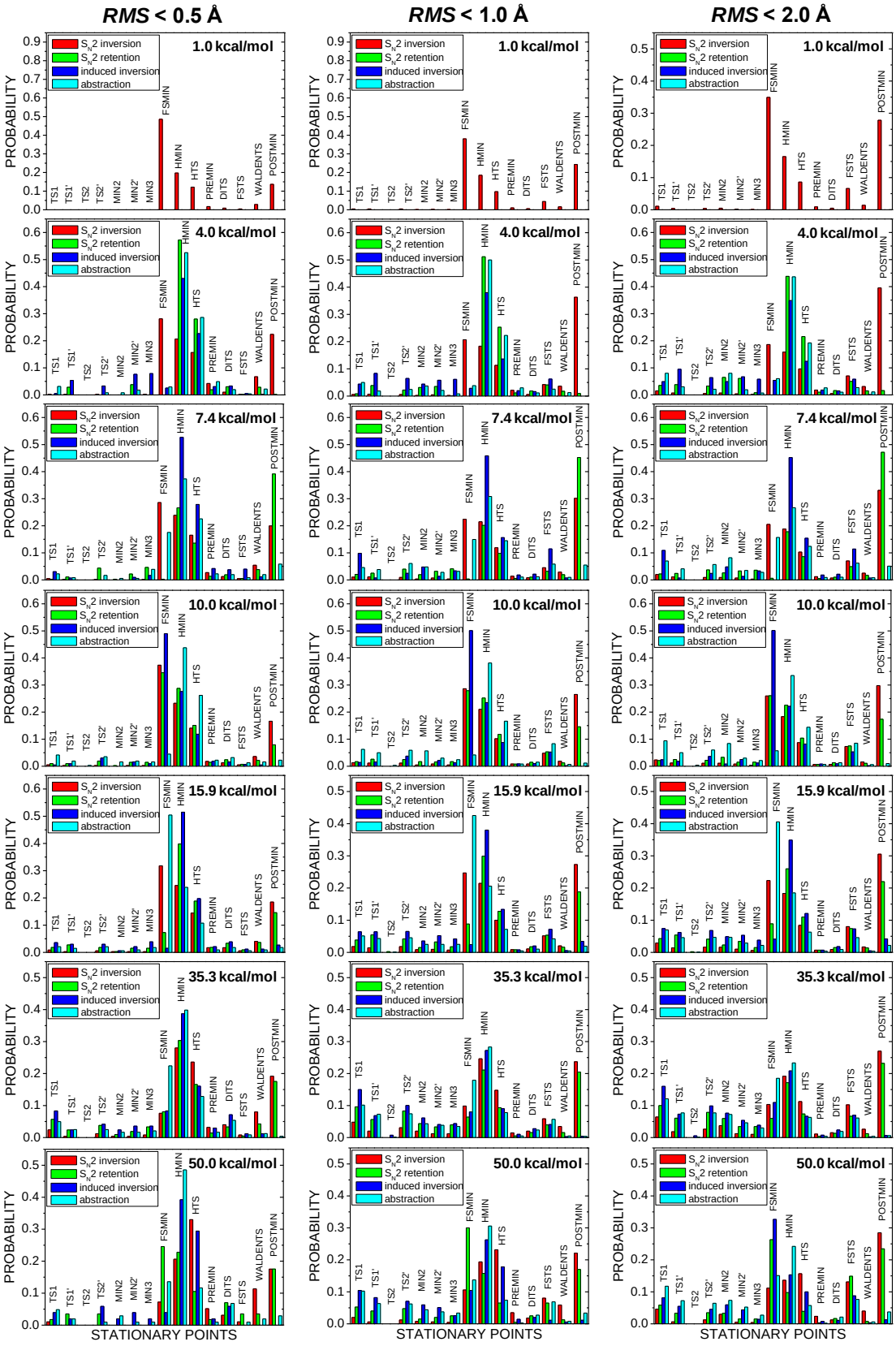

Figure S18. Distance-constrained stationary-point distributions, normalized for each channel, corresponding to $b = 0$ $F^- + CH_3I$ trajectories at collision energies of 1.0, 4.0, 7.4, 10.0, 15.9, 35.3, and 50.0 kcal/mol.

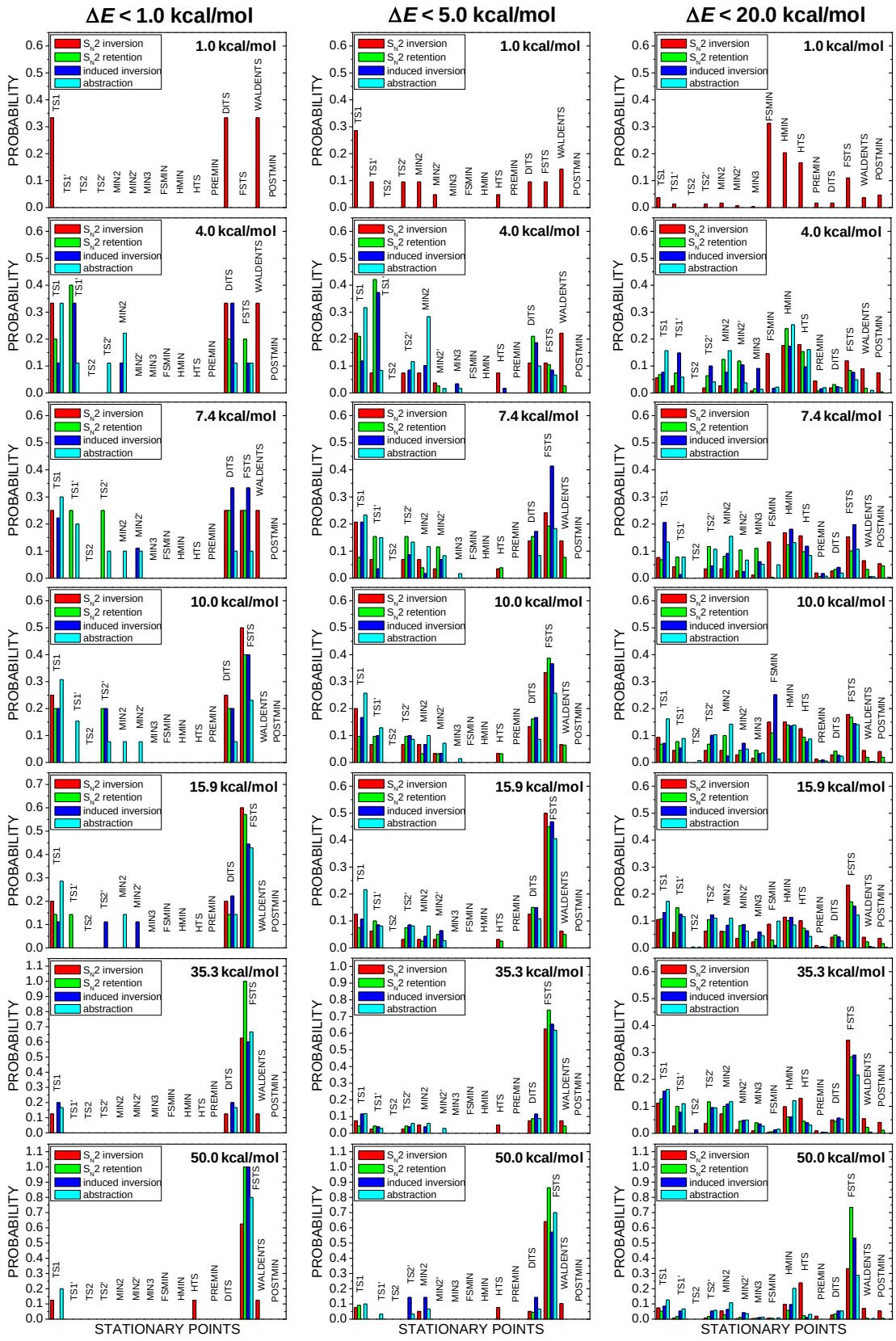

Figure S19. Energy-constrained stationary-point distributions, normalized for each channel, corresponding to $b = 0$ $F^- + CH_3I$ trajectories at collision energies of 1.0, 4.0, 7.4, 10.0, 15.9, 35.3, and 50.0 kcal/mol.