Supporting information

The Treatment of Classically Forbidden Electronic Transitions in Semiclassical Trajectory Surface Hopping Calculations

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1. FUNCTIONAL FORM OF THE MODEL YRH POTENTIAL ENERGY MATRICES

The model YRH matrices are formulated in the diabatic representation by defining the matrix elements U_{11}, U_{12} and U_{22}. The adiabatic potential energy surfaces and coupling terms can be obtained analytically from the diabatic matrix elements without approximation. The YRH systems are defined to have no electronic angular momentum.

1.1. U_{11} potential energy surface

The functional form of $U_{11}(\mathbf{R})$ is an extended LEPS (London-Eyring-Polanyi-Sato) function of the form

$$U_{11}(\mathbf{R}) = Q_{\mathrm{RH}}(R_{\mathrm{RH}}) + Q_{\mathrm{YH}}(R_{\mathrm{YH}}) + Q_{\mathrm{YR}}(R_{\mathrm{YR}}) - \sqrt{\frac{1}{2}\left(W(\mathbf{R}) + c(\mathbf{R})^2\right)} + D_{\mathrm{YH}}, \tag{1}$$

where

$$c(\mathbf{R}) = c_a \exp[-c_b W(\mathbf{R}) - c_c(R_{\mathrm{RH}} + R_{\mathrm{YH}} + R_{\mathrm{RY}})], \tag{2}$$

$$W(\mathbf{R}) = (J_{\mathrm{RH}}(R_{\mathrm{RH}}) - J_{\mathrm{YH}}(R_{\mathrm{YH}}))^2 + (J_{\mathrm{YH}}(R_{\mathrm{YH}}) - J_{\mathrm{YR}}(R_{\mathrm{YR}}))^2 + (J_{\mathrm{RH}}(R_{\mathrm{RH}}) - J_{\mathrm{YR}}(R_{\mathrm{YR}}))^2, \tag{3}$$

and $\mathbf{R}$ is the vector of internuclear distances: R_{YH}, R_{RH}, R_{YR}. The exchange $J_\alpha(R_\alpha)$ and Coulomb $Q_\alpha(R_\alpha)$ integrals are given by

$$Q_\alpha(R_\alpha) = \frac{1}{2}\left(S_\alpha(R_\alpha) + w_\alpha T_\alpha(R_\alpha)\right), \tag{5}$$

$$J_\alpha(R_\alpha) = \frac{1}{2}\left(S_\alpha(R_\alpha) - w_\alpha T_\alpha(R_\alpha)\right), \tag{6}$$

where α = RH, YH, and YR. The parameters w_α were introduced to decrease the energy of the system in the interaction region. This treatment is identical to introducing Sato parameters directly into eq. (1). The singlets $S_\alpha(R_\alpha)$ and triplets $T_\alpha(R_\alpha)$ are Morse and anti-Morse curves, respectively, i.e.,

$$S_\alpha(R_\alpha) = D_\alpha\left[1 - \exp\left(-(R_\alpha - R_\alpha^0)\beta_\alpha\right)\right]^2 - D_\alpha, \tag{7}$$

$$T_\alpha(R_\alpha) = \tfrac{1}{2} D_\alpha \left[1 + \exp\left(-(R_\alpha - R_\alpha^0)\beta_\alpha\right)\right]^2 - \tfrac{1}{2} D_\alpha . \tag{8}$$

The values of the parameters used in the representation of $U_{11}(\mathbf{R})$ are listed in Table S1.

1.2. U_{22} potential energy surface

The $U_{22}(\mathbf{R})$ potential energy surface is a weighted sum of diatomic terms

$$U_{22}(\mathbf{R}) = S_{\mathrm{RH}}(R_{\mathrm{RH}}) + \left(T_{\mathrm{YR}}(R_{\mathrm{YR}}) + T_{\mathrm{RH}}(R_{\mathrm{RH}})\right)w_2 + E(\mathrm{Y}^*) + D_{\mathrm{YH}} , \tag{9}$$

where $E(\mathrm{Y}^*)$ can be thought of as the electronic excitation energy of the model Y atom and w_2 is a weighting factor that makes U_{22} more energetically accessible towards smaller R_{YR} and R_{RH}. $S_\alpha(R_\alpha)$ and $T_\alpha(R_\alpha)$ are the same singlets and triplets that appear in the definition of $U_{11}(\mathbf{R})$. The values of the parameters introduced for $U_{22}(\mathbf{R})$ are listed in Table S1.

1.3. U_{12} coupling surface

The potential coupling surface is a rotated two-dimensional Gaussian in the YH and RH bond lengths

$$U_{12}(R_{\mathrm{YH}}, R_{\mathrm{RH}}) = U_{12}^{\max} \exp\left[-\alpha_x G_x(R_{\mathrm{YH}}, R_{\mathrm{RH}})^2 - \alpha_y G_y(R_{\mathrm{YH}}, R_{\mathrm{RH}})^2\right] , \tag{10}$$

where $G_x(R_{\mathrm{YH}},R_{\mathrm{RH}})$ and $G_y(R_{\mathrm{YH}},R_{\mathrm{RH}})$ define the rotated coordinate system

$$G_x(R_{\mathrm{YH}}, R_{\mathrm{RH}}) = \left(R_{\mathrm{RH}} - R_{\mathrm{RH}}^*\right)\cos\theta + \left(R_{\mathrm{YH}} - R_{\mathrm{YH}}^*\right)\sin\theta \tag{11}$$

$$G_y(R_{\mathrm{YH}}, R_{\mathrm{RH}}) = \left(R_{\mathrm{RH}} - R_{\mathrm{RH}}^*\right)\sin\theta - \left(R_{\mathrm{YH}} - R_{\mathrm{YH}}^*\right)\cos\theta . \tag{12}$$

In the preceding set of equations, R_{RH}^* and R_{YH}^* define the location of maximum coupling, and θ is the angle of rotation of the Gaussian axes (G_x, G_y) with respect to the coordinates (R_{RH}, R_{YH}). The Gaussian width parameters are given by α_x and α_y. The values of the parameters used for $U_{12}(R_{\mathrm{YH}},R_{\mathrm{RH}})$ are listed in Table S1. The parameter $U_{12}^{\max}$ defines the maximum potential coupling; this parameter is varied to create the family of matrices used in this study.

Note that the electronic matrix elements of the nuclear momentum vector are assumed to be zero in the diabatic representation. Although the nuclear momentum coupling cannot be strictly vanishing everywhere, is can be neglected in the invariant-space approximation, and we use that approximation here.

Table S1. Model YRH potential energy matrix parameters.

Surface	Parameter	Value		Surface	Parameter	Value	
U_{11}	D_{YH}	4.3	eV		w_{YH}	0.9	
	D_{RH}	3.9	eV		w_{RH}	0.9	
	D_{YR}	0.4	eV		w_{YR}	0.2	
	R^0_{YH}	2.1	a_0	U_{22}	$E(Y^*)$	0.36	eV
	R^0_{RH}	2.1	a_0		w_2	0.2	
	R^0_{YR}	2.5	a_0	U_{12}	θ	$\pi/4$	rad
	β_{YH}	1.0	a_0^{-1}		α_x	0.8	a_0^{-2}
	β_{RH}	1.0	a_0^{-1}		α_y	1.0	a_0^{-2}
	β_{YR}	1.5	a_0^{-1}		R^*_{RH}	2.2	a_0
	C_a	1.5	eV		R^*_{YH}	4.2	a_0
	C_b	1.0	eV^{-2}		U_{12}^{max}	Variable[a]	
	C_c	0.15	a_0^{-1}				

[a]The value of this parameter is varied to create the four different PEMs that are discussed in this paper. It has the values 0.20, 0.10, 0.03, and 0.01 eV.

2. DETAILS OF THE QUANTUM MECHANICAL CALCULATIONS

2.1. QUANTUM MECHANICAL BASIS SETS

Table S2. OWVP basis set parameters.[a]

Parameter	Set I	Set II	Parameter	Set I	Set II
N^{FD}	13	15	$S_{\mathrm{l}}^{\mathrm{G}}(\alpha=1,\chi=1)$	1.64	1.54
N^{asymp}	12	14	$S_{\mathrm{u}}^{\mathrm{G}}(\alpha=1,\chi=1)$	7.910	8.155
N_1^{QV}	10	12	$\Delta^S(\alpha=1,\chi=1)$	0.110	0.105
N_2^{QV}	15	17	$c(\alpha=1,\chi=1)$	0.90	0.95
N_{12}^{QA}	250	270	$m^{\mathrm{g,e}}(\alpha=1,\chi=1)$	58	64
N_1^{QA}	60	70	$N^{\mathrm{o}}(\alpha=1,\chi=1)$	27	27
N_2^{QA}	70	80	$N^{\mathrm{c}}(\alpha=1,\chi=1)$	80	105
$N(\mathrm{HO})$	80	90	$M^{\mathrm{e}}(\alpha=1,\chi=1)$	4640	6720
$J_{\max}(\alpha=1,\chi=1,v=0)$	28	31	$M^{\mathrm{g}}(\alpha=1,\chi=1)$	1566	1728
$J_{\max}(\alpha=1,\chi=1,v=1)$	25	27	$S_{\mathrm{l}}^{\mathrm{G}}(\alpha=1,\chi=2)$	1.58	1.50
$J_{\max}(\alpha=1,\chi=1,v=2)$	21	24	$S_{\mathrm{u}}^{\mathrm{G}}(\alpha=1,\chi=2)$	8.21	8.50
$J_{\max}(\alpha=1,\chi=1,v=3)$	17	20	$\Delta^S(\alpha=1,\chi=2)$	0.130	0.125
$J_{\max}(\alpha=1,\chi=1,v=4)$	11	15	$c(\alpha=1,\chi=2)$	0.90	0.95
$J_{\max}(\alpha=1,\chi=1,v=5)$		9	$m^{\mathrm{g,e}}(\alpha=1,\chi=2)$	52	57
$J_{\max}(\alpha=1,\chi=2,v=0)$	24	27	$N^{\mathrm{o}}(\alpha=1,\chi=2)$	9	9
$J_{\max}(\alpha=1,\chi=2,v=1)$	20	23	$N^{\mathrm{c}}(\alpha=1,\chi=2)$	64	84
$J_{\max}(\alpha=1,\chi=2,v=2)$	16	19	$M^{\mathrm{e}}(\alpha=1,\chi=2)$	3328	4788
$J_{\max}(\alpha=1,\chi=2,v=3)$	9	14	$M^{\mathrm{g}}(\alpha=1,\chi=2)$	468	513
$J_{\max}(\alpha=1,\chi=2,v=4)$		5	$S_{\mathrm{l}}^{\mathrm{G}}(\alpha=2,\chi=1)$	1.64	1.54
$J_{\max}(\alpha=2,\chi=1,v=0)$	33	35	$S_{\mathrm{u}}^{\mathrm{G}}(\alpha=2,\chi=1)$	7.91	8.155
$J_{\max}(\alpha=2,\chi=1,v=1)$	30	32	$\Delta^S(\alpha=2,\chi=1)$	0.110	0.105
$J_{\max}(\alpha=2,\chi=1,v=2)$	27	29	$c(\alpha=2,\chi=1)$	0.90	0.95
$J_{\max}(\alpha=2,\chi=1,v=3)$	23	26	$m^{\mathrm{g,e}}(\alpha=2,\chi=1)$	58	64
$J_{\max}(\alpha=2,\chi=1,v=4)$	19	22	$N^{\mathrm{o}}(\alpha=2,\chi=1)$	52	52
$J_{\max}(\alpha=2,\chi=1,v=5)$	13	17	$N^{\mathrm{c}}(\alpha=2,\chi=1)$	102	128
$J_{\max}(\alpha=2,\chi=1,v=6)$	2	12	$M^{\mathrm{e}}(\alpha=2,\chi=1)$	5916	8192

S_0^{F}	1.0	0.9	M^{g} ($\alpha = 2, \chi = 1$)	3016	3328
$S_{N(\mathrm{F})+1}^{\mathrm{F}}$	20	22	M^{e}	13884	19700
f^{SD}	0.90	0.92	M^{g}	5050	5569
N^{SD}	40	42	M	18934	25269
$S_{\mathrm{l}}^{\mathrm{QR}}$	1.0	0.9	ε_{k}	12	14
$S_{\mathrm{u}}^{\mathrm{QR}}$	15	17	$\varepsilon_{\mathrm{rad}}$	100	120
N^{QS}	170	180	ε_{t}	12	14
N^{QGL}	7	9	ε_{W}	12	14
$N(\mathrm{F})$	1230	1662	ε_{B}	12	14

[a]The definitions of the parameters listed here can be found in Ref. 45 except where noted otherwise.

[b]Number of R_i values used in the least squares fit to obtain $\mathbf{K^0}$.

2.2. ENERGY DEPENDENCE OF THE QUANTUM MECHANICAL RESULTS

2.2.1 TABLES

Table S3. Quantum mechanical reaction probability, quenching probability and final vibrational and rotational moments as a function of scattering energy for the initial condition Y + RH(v = 0, j = 0), and centered around 1.10 eV.

System	Energy	P_R	$<v'>$	$<j'>$	P_Q	$<v''>$	$<j''>$
YRH(0.20)	1.07	1.05E-02	1.17	10.9	5.56E-02	0.96	2.88
	1.08	1.27E-02	0.99	11.7	5.44E-02	0.95	2.84
	1.09	1.06E-02	0.86	12.1	5.39E-02	0.92	3.29
	1.10	1.01E-02	0.83	12.4	4.72E-02	0.90	3.35
	1.11	1.36E-02	0.97	12.2	3.82E-02	0.89	3.15
	1.12	1.37E-02	0.90	12.5	3.48E-02	0.84	3.68
	1.13	1.40E-02	0.83	12.9	3.25E-02	0.83	3.95
	Average	1.22E-02	0.93	12.1	4.52E-02	0.90	3.30
YRH(0.10)	1.07	6.98E-03	0.76	12.2	3.85E-02	0.96	1.91
	1.08	8.25E-03	0.81	11.9	3.43E-02	0.95	1.71
	1.09	8.97E-03	0.79	12.0	3.08E-02	0.93	1.60
	1.10	9.12E-03	0.76	12.4	2.95E-02	0.93	1.68
	1.11	9.76E-03	0.80	12.7	2.83E-02	0.93	1.55
	1.12	9.07E-03	0.76	13.1	2.86E-02	0.93	1.62
	1.13	7.67E-03	0.67	13.2	2.98E-02	0.93	1.95
	Average	8.55E-03	0.76	12.5	3.14E-02	0.94	1.72
YRH(0.03)	1.07	7.11E-04	0.93	11.7	2.85E-03	0.97	2.29
	1.08	7.44E-04	0.74	12.5	3.02E-03	0.95	2.62
	1.09	8.68E-04	0.81	12.1	3.24E-03	0.94	3.02
	1.10	1.07E-03	0.86	11.6	3.27E-03	0.93	3.24
	1.11	1.20E-03	0.82	11.9	3.17E-03	0.91	3.44
	1.12	1.20E-03	0.76	12.4	3.11E-03	0.90	3.52
	1.13	1.19E-03	0.76	12.4	3.04E-03	0.90	3.50
	Average	9.98E-04	0.81	12.1	3.10E-03	0.93	3.09
YRH(0.01)	1.07	8.54E-05	1.00	11.4	2.90E-04	0.97	2.24
	1.08	8.58E-05	0.79	12.5	3.04E-04	0.95	2.53
	1.09	9.75E-05	0.85	12.1	3.29E-04	0.93	3.00
	1.10	1.20E-04	0.89	11.6	3.38E-04	0.93	3.28
	1.11	1.32E-04	0.82	11.9	3.35E-04	0.91	3.53
	1.12	1.32E-04	0.77	12.3	3.31E-04	0.90	3.60
	1.13	1.33E-04	0.78	12.4	3.29E-04	0.90	3.59
	Average	1.12E-04	0.84	12.0	3.22E-04	0.93	3.11

Table S4. Quantum mechanical reaction probability, quenching probability and final vibrational and rotational moments as a function of scattering energy for the initial condition Y + RH(v = 0, j = 6), and centered around 1.10 eV.

System	Energy	P_R	$<v'>$	$<j'>$	P_Q	$<v''>$	$<j''>$
YRH(0.20)	1.07	2.71E-02	1.06	11.6	7.71E-02	0.96	4.06
	1.08	2.83E-02	1.06	12.3	1.22E-01	0.97	5.35
	1.09	2.73E-02	1.23	11.3	1.32E-01	0.95	5.01
	1.10	2.43E-02	1.20	11.6	1.39E-01	0.96	4.95
	1.11	2.59E-02	1.11	12.4	1.91E-01	0.96	5.83
	1.12	2.27E-02	0.92	12.8	1.74E-01	0.94	5.61
	1.13	2.45E-02	0.91	12.8	1.20E-01	0.95	4.49
	Average	2.57E-02	1.07	12.1	1.37E-01	0.95	5.04
YRH(0.10)	1.07	2.24E-02	1.42	10.0	4.96E-02	0.94	5.04
	1.08	2.47E-02	1.27	10.9	3.48E-02	0.89	6.13
	1.09	2.63E-02	1.15	11.9	4.07E-02	0.84	5.82
	1.10	2.54E-02	1.06	12.5	6.24E-02	0.89	5.19
	1.11	2.44E-02	0.95	13.4	7.99E-02	0.95	5.15
	1.12	2.69E-02	0.91	13.8	9.49E-02	0.95	5.45
	1.13	2.61E-02	0.77	14.2	9.66E-02	0.96	5.01
	Average	2.52E-02	1.08	12.4	6.56E-02	0.92	5.40
YRH(0.03)	1.07	2.20E-03	1.46	10.1	1.61E-02	0.96	4.56
	1.08	2.81E-03	1.41	10.3	1.01E-02	0.92	4.34
	1.09	3.11E-03	1.27	11.4	8.68E-03	0.89	5.26
	1.10	3.41E-03	1.10	12.6	1.16E-02	0.91	5.51
	1.11	3.29E-03	1.02	13.2	1.31E-02	0.94	5.61
	1.12	3.60E-03	0.99	13.5	1.39E-02	0.97	5.85
	1.13	3.98E-03	0.92	13.8	1.51E-02	0.97	5.98
	Average	3.20E-03	1.17	12.1	1.27E-02	0.94	5.30
YRH(0.01)	1.07	2.55E-04	1.46	10.1	1.67E-03	0.95	4.49
	1.08	3.20E-04	1.43	10.2	1.18E-03	0.92	4.45
	1.09	3.55E-04	1.29	11.3	9.74E-04	0.88	5.27
	1.10	3.92E-04	1.11	12.5	1.38E-03	0.91	5.53
	1.11	3.81E-04	1.04	13.1	1.57E-03	0.94	5.60
	1.12	4.15E-04	1.00	13.5	1.66E-03	0.98	5.90
	1.13	4.62E-04	0.93	13.8	1.78E-03	0.97	6.02
	Average	3.69E-04	1.18	12.1	1.46E-03	0.94	5.32

Table S5. Quantum mechanical reaction probability, quenching probability and final vibrational and rotational moments as a function of scattering energy for the initial condition Y + RH(v = 0, j = 0), and centered around 1.02 eV.

System	Energy	P_R	$<v'>$	$<j'>$	P_Q	$<v''>$	$<j''>$
YRH(0.20)	0.99	1.19E-02	1.28	8.92	5.85E-02	0.96	2.23
	1.00	4.89E-03	1.52	7.59	3.79E-02	0.98	2.10
	1.01	8.28E-03	1.36	8.60	3.31E-02	0.95	2.91
	1.02	1.18E-02	1.51	8.52	4.23E-02	0.97	3.12
	1.03	1.13E-02	1.28	9.42	3.60E-02	0.93	2.84
	1.04	7.98E-03	1.31	10.0	3.33E-02	0.95	2.53
	1.05	6.28E-03	1.19	11.2	4.43E-02	0.94	3.04
	Average	8.92E-03	1.35	9.18	4.08E-02	0.95	2.68
YRH(0.10)	0.99	3.59E-04	1.59	7.31	2.64E-02	1.00	2.00
	1.00	3.73E-04	1.63	6.45	2.49E-02	1.00	1.86
	1.01	1.09E-03	1.59	6.97	2.70E-02	0.99	1.45
	1.02	1.20E-03	1.38	8.72	2.98E-02	0.99	1.49
	1.03	1.72E-03	1.03	10.7	3.64E-02	0.99	1.79
	1.04	3.12E-03	0.89	11.5	4.17E-02	0.99	1.93
	1.05	4.55E-03	0.84	12.0	4.20E-02	0.98	2.10
	Average	1.77E-03	1.28	9.10	3.26E-02	0.99	1.80
YRH(0.03)	0.99	1.25E-05	1.51	7.67	3.83E-03	1.00	2.55
	1.00	1.90E-05	1.54	7.35	3.93E-03	1.00	2.47
	1.01	7.48E-05	1.60	7.22	4.24E-03	1.00	2.67
	1.02	2.15E-04	1.55	7.88	3.83E-03	0.99	2.78
	1.03	2.94E-04	1.47	8.69	3.67E-03	0.99	2.29
	1.04	5.42E-04	1.44	9.20	2.49E-03	0.98	1.66
	1.05	5.77E-04	1.25	10.5	2.22E-03	0.98	1.77
	Average	2.48E-04	1.48	8.37	3.46E-03	0.99	2.31
YRH(0.01)	0.99	1.23E-06	1.51	7.68	4.31E-04	1.00	2.58
	1.00	1.93E-06	1.52	7.47	4.30E-04	1.00	2.55
	1.01	7.46E-06	1.59	7.32	4.78E-04	1.00	2.72
	1.02	2.37E-05	1.55	7.89	4.42E-04	0.99	2.88
	1.03	3.39E-05	1.47	8.69	4.36E-04	0.99	2.43
	1.04	6.54E-05	1.45	9.13	2.97E-04	0.98	1.76
	1.05	7.12E-05	1.29	10.4	2.30E-04	0.98	1.77
	Average	2.92E-05	1.48	8.37	3.92E-04	0.99	2.38

2.2.2 FIGURES

Figure captions:

Figure S1: Variation of quantum mechanical observables as a function of energy for YRH(0.20) and initial condition (1.10, 0).

Figure S2: Same as figure S1, but for YRH(0.10):(1.10, 0).

Figure S3: Same as figure S1, but for YRH(0.03):(1.10, 0).

Figure S4: Same as figure S1, but for YRH(0.01):(1.10, 0).

Figure S5: Same as figure S1, but for YRH(0.20):(1.10, 6).

Figure S6: Same as figure S1, but for YRH(0.10):(1.10, 6).

Figure S7: Same as figure S1, but for YRH(0.03):(1.10, 6).

Figure S8: Same as figure S1, but for YRH(0.01):(1.10, 6).

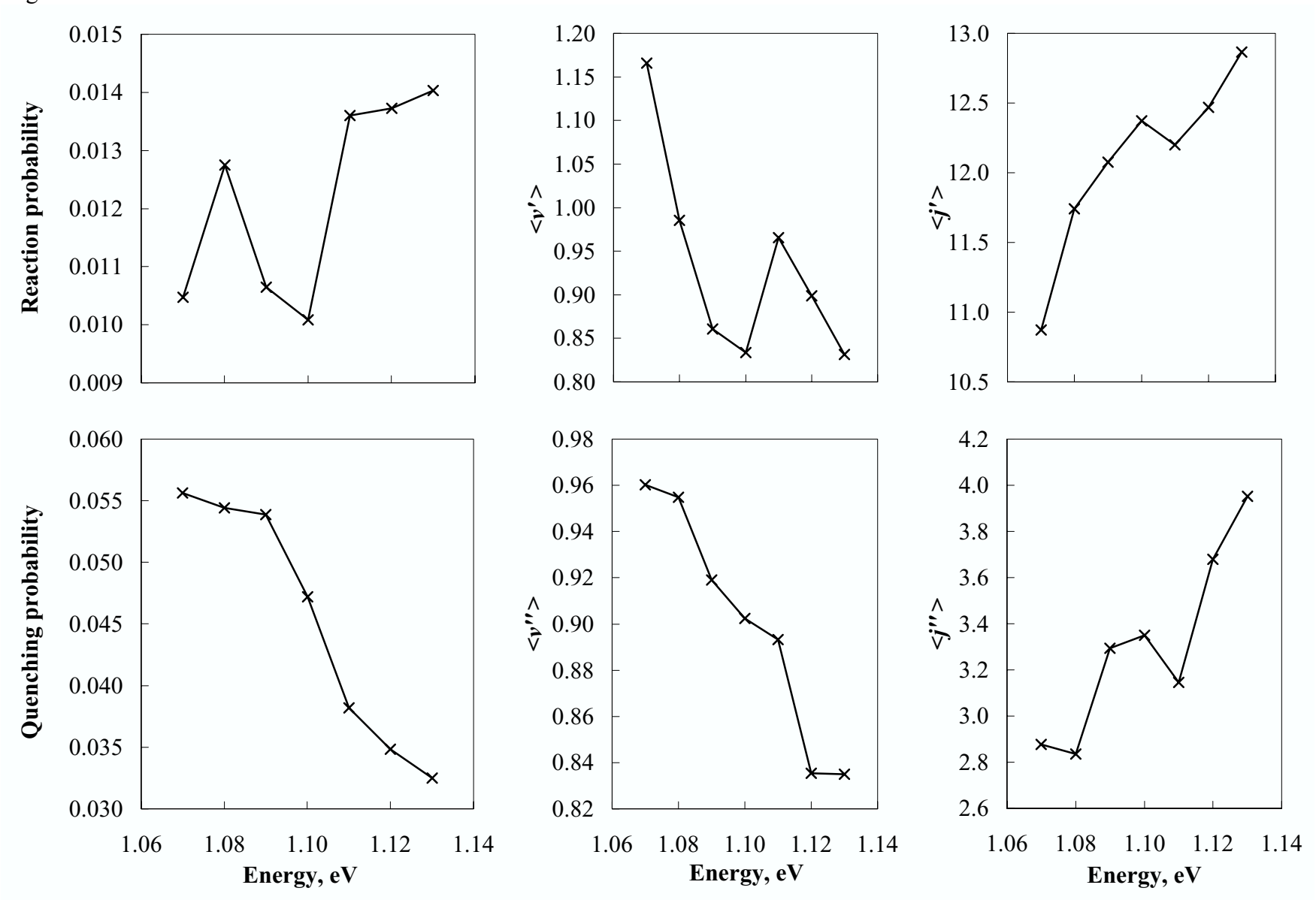
Figure S9: Same as figure S1, but for YRH(0.20):(1.02, 0).

Figure S10: Same as figure S1, but for YRH(0.10):(1.02, 0).

Figure S11: Same as figure S1, but for YRH(0.03):(1.02, 0).

Figure S12: Same as figure S1, but for YRH(0.01):(1.02, 0).

Fig. S1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0.82
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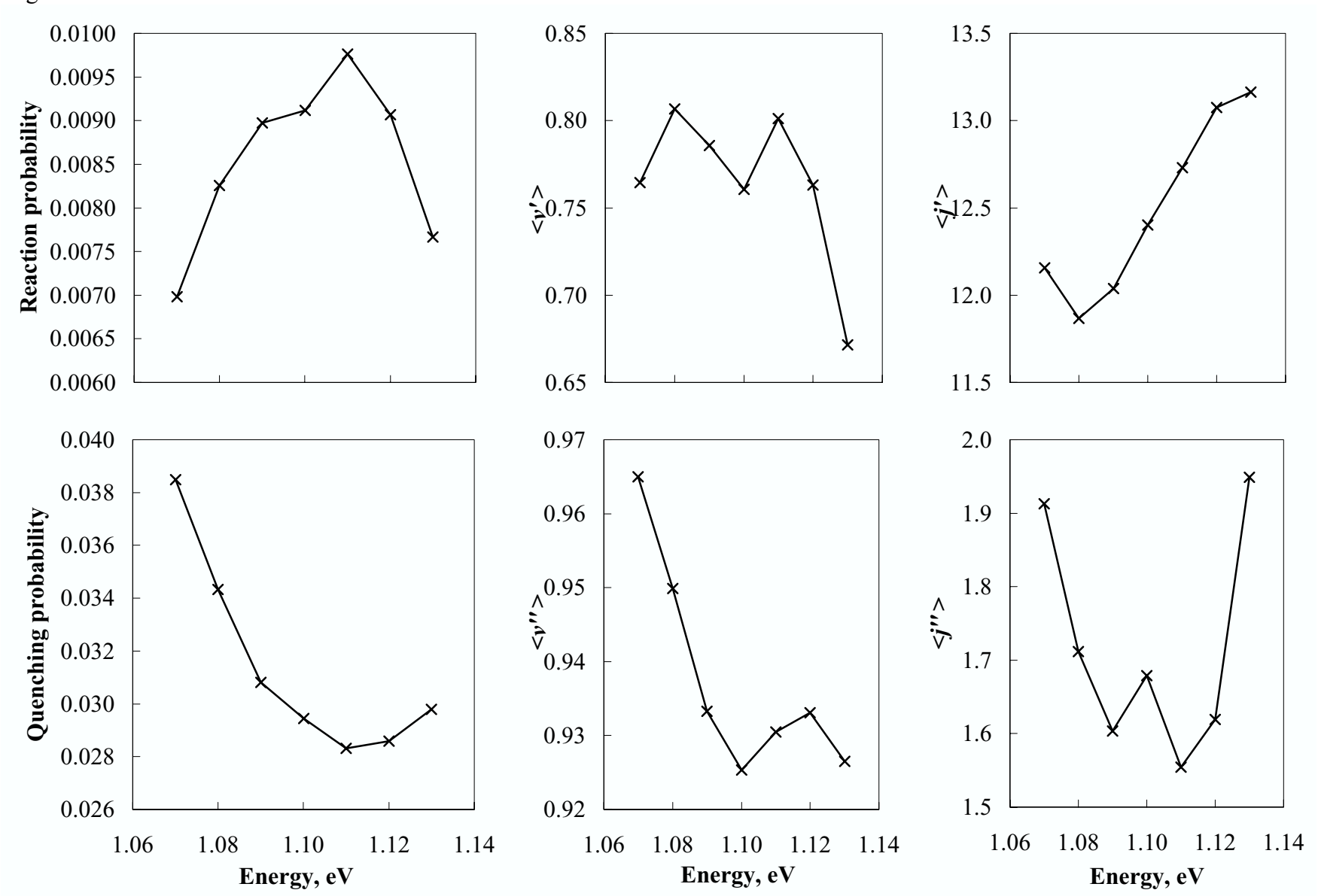
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S2


Reaction probability
0.0100
0.0095
0.0090
0.0085
0.0080
0.0075
0.0070
0.0065
0.0060
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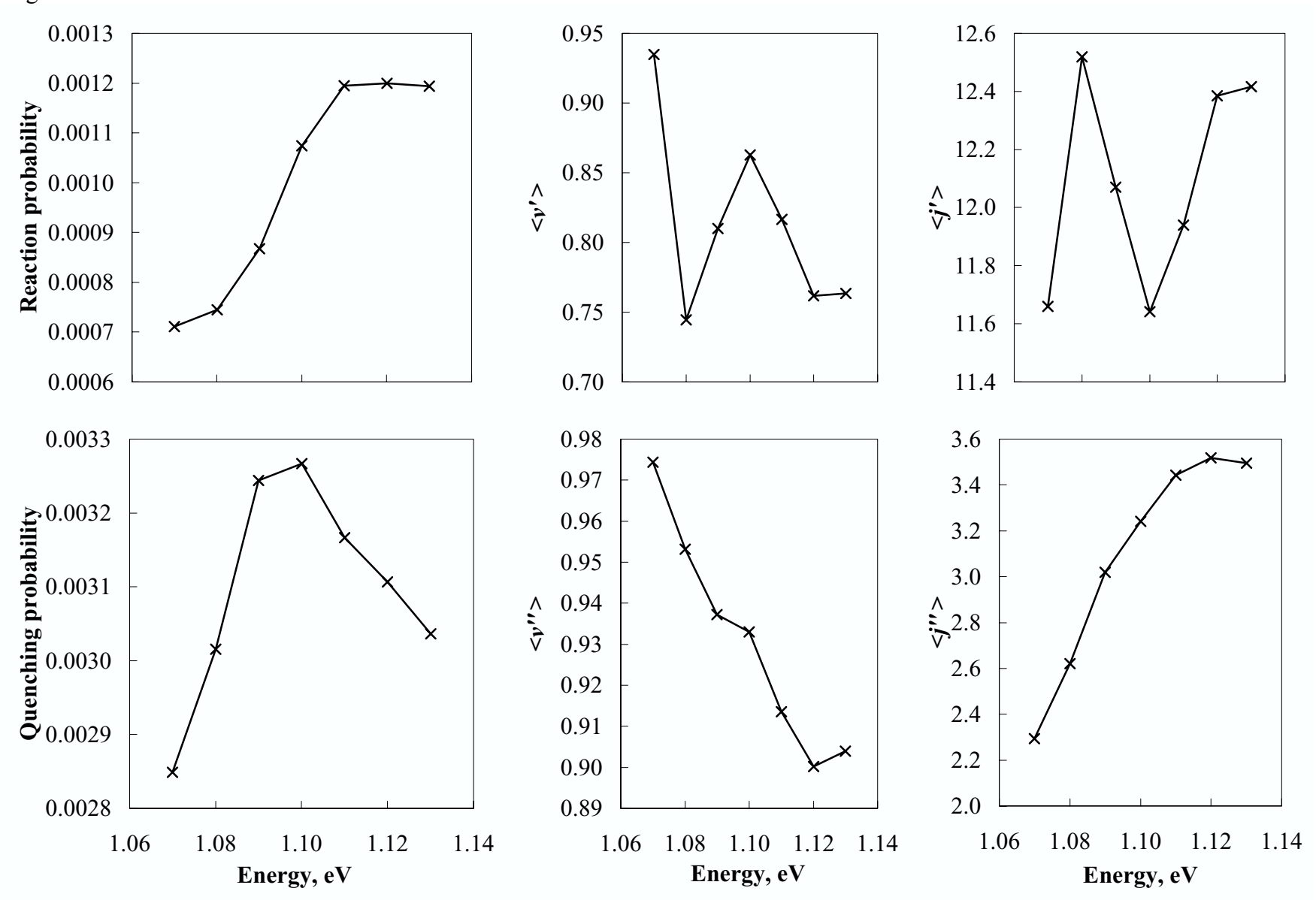
0.85
0.80
0.75
0.70
0.65
<j'>
13.5
13.0
12.5
12.0
11.5
Quenching probability
0.040
0.038
0.036
0.034
0.032
0.030
0.028
0.026
<v''>
0.97
0.96
0.95
0.94
0.93
0.92
<j''>
2.0
1.9
1.8
1.7
1.6
1.5
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S3


Reaction probability
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0.0011
0.0010
0.0009
0.0008
0.0007
0.0006
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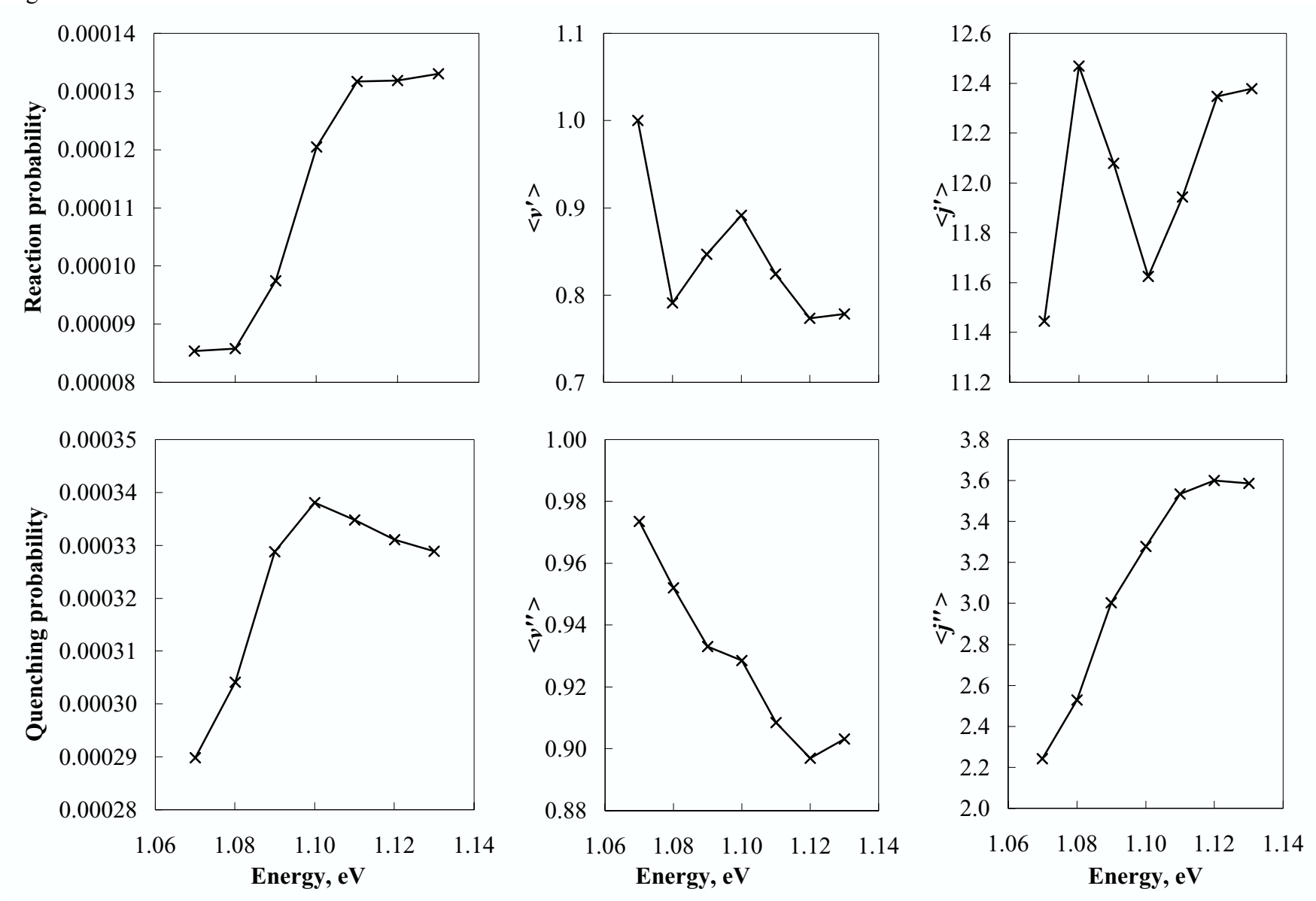
0.85
0.80
0.75
0.70
<j'>
12.6
12.4
12.2
12.0
11.8
11.6
11.4
Quenching probability
0.0033
0.0032
0.0031
0.0030
0.0029
0.0028
<v''>
0.98
0.97
0.96
0.95
0.94
0.93
0.92
0.91
0.90
0.89
<j''>
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S4


Reaction probability
0.00014
0.00013
0.00012
0.00011
0.00010
0.00009
0.00008
<v'>
1.1
1.0
0.9
0.8
0.7
<j'>
12.6
12.4
12.2
12.0
11.8
11.6
11.4
11.2
Quenching probability
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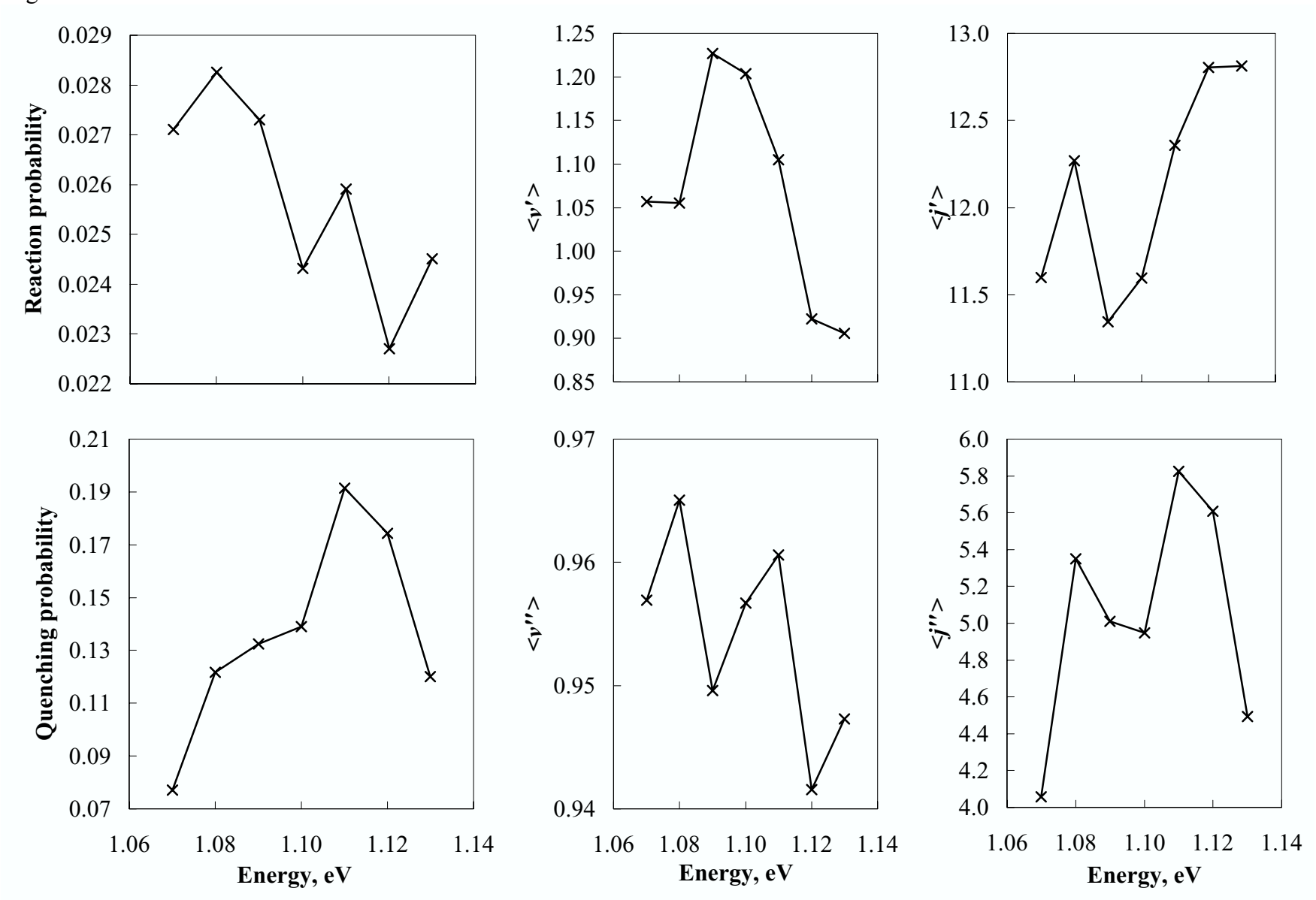
0.00034
0.00033
0.00032
0.00031
0.00030
0.00029
0.00028
<v''>
1.00
0.98
0.96
0.94
0.92
0.90
0.88
<j''>
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S5


Reaction probability
0.029
0.028
0.027
0.026
0.025
0.024
0.023
0.022
<v'>
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
<j'>
13.0
12.5
12.0
11.5
11.0
Quenching probability
0.21
0.19
0.17
0.15
0.13
0.11
0.09
0.07
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0.97
0.96
0.95
0.94
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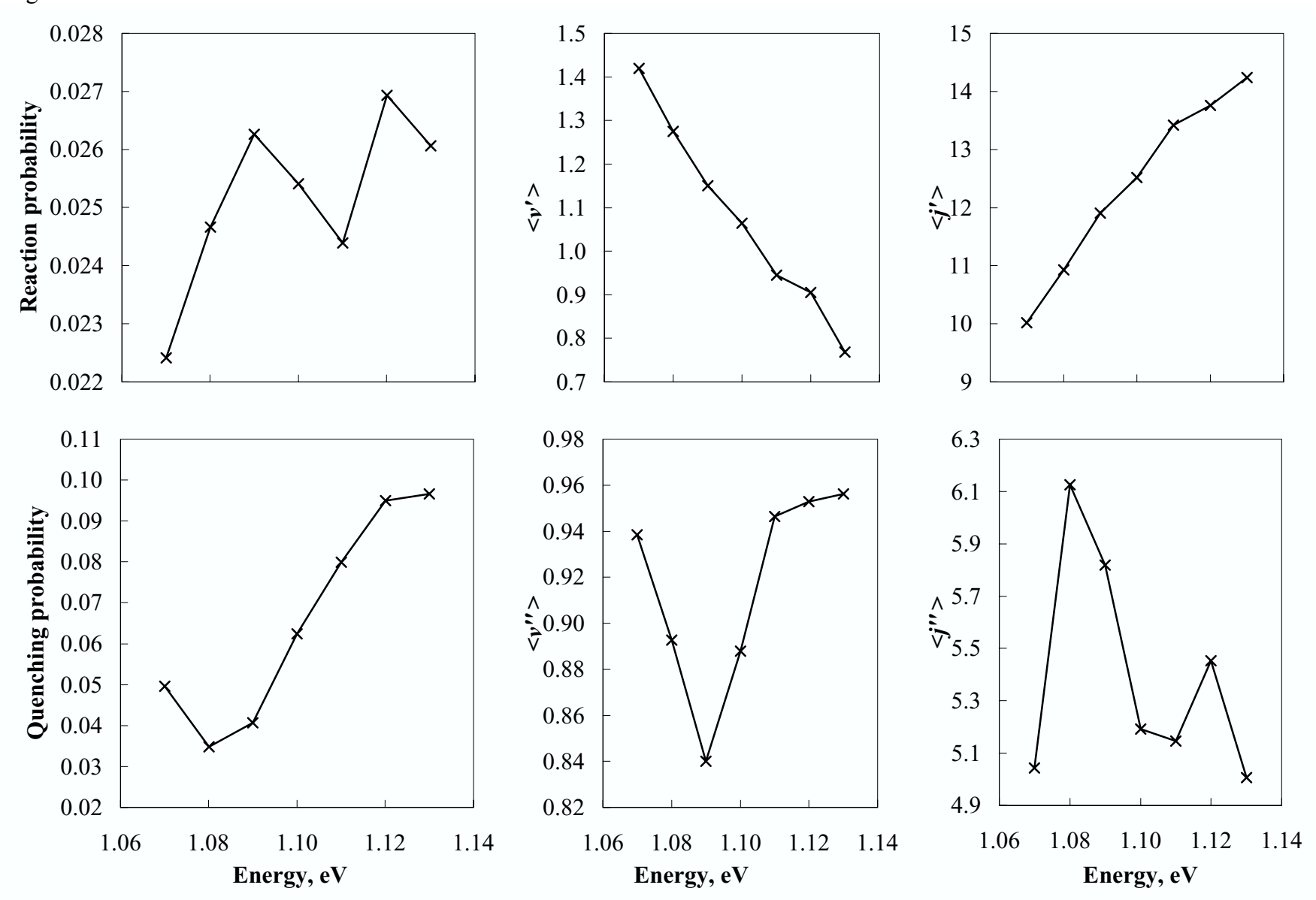
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S6


Reaction probability
0.028
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0.026
0.025
0.024
0.023
0.022
<v'>
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
<j'>
15
14
13
12
11
10
9
Quenching probability
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0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
<v''>
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
<j''>
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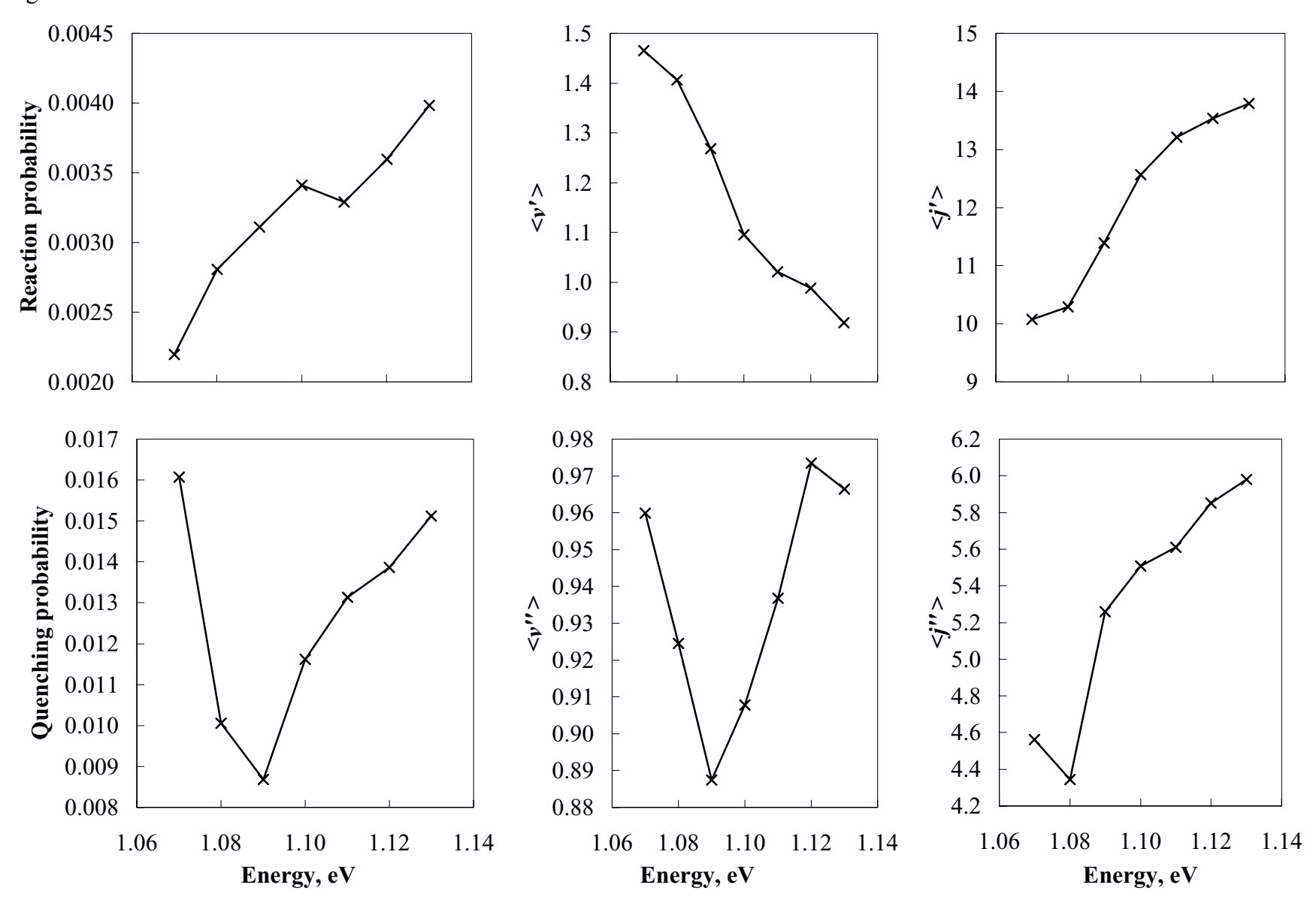
6.1
5.9
5.7
5.5
5.3
5.1
4.9
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S7


Reaction probability
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0.0035
0.0030
0.0025
0.0020
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1.4
1.3
1.2
1.1
1.0
0.9
0.8
<j'>
15
14
13
12
11
10
9
Quenching probability
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0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
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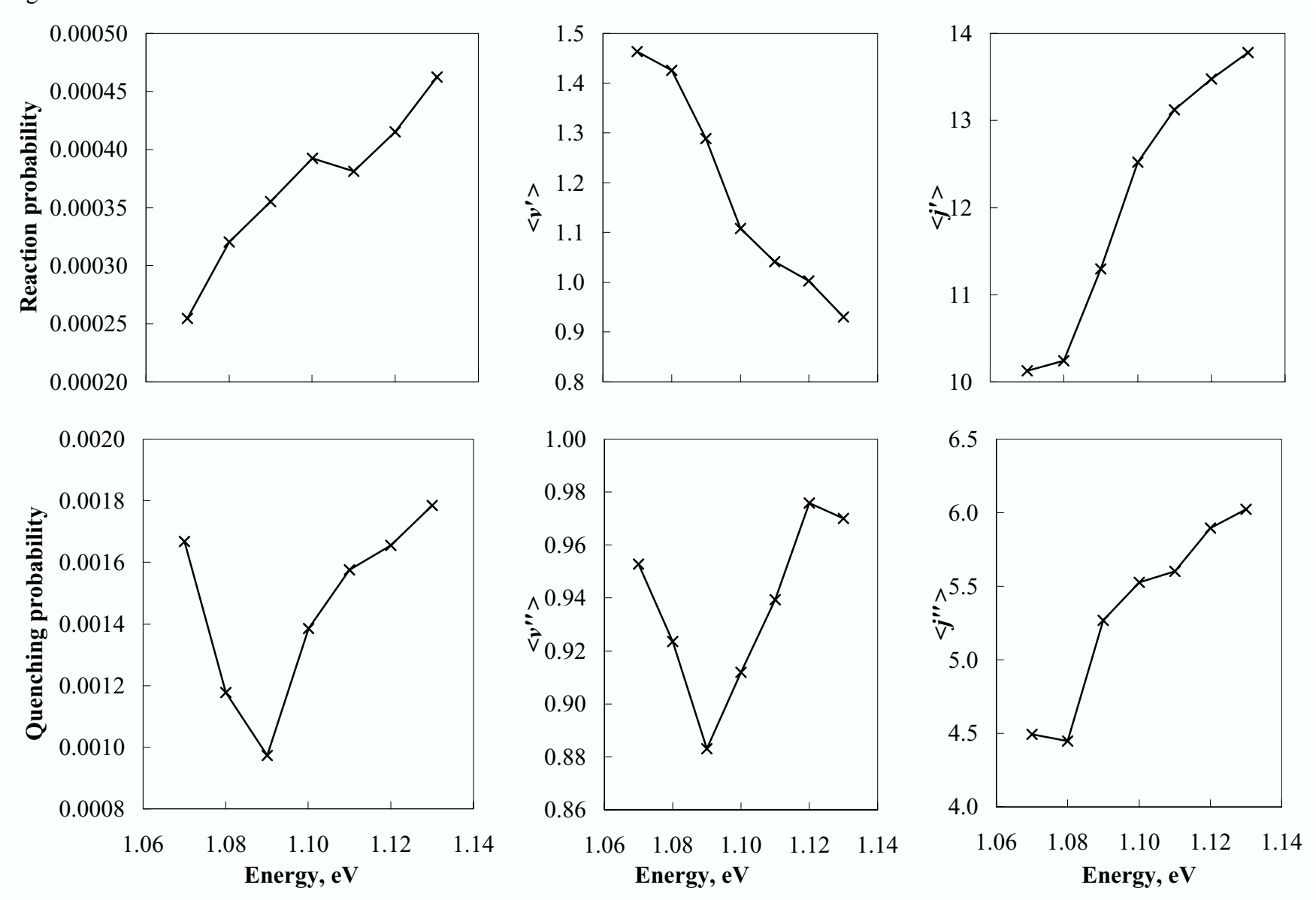
0.97
0.96
0.95
0.94
0.93
0.92
0.91
0.90
0.89
0.88
<j''>
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S8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0.00030
0.00025
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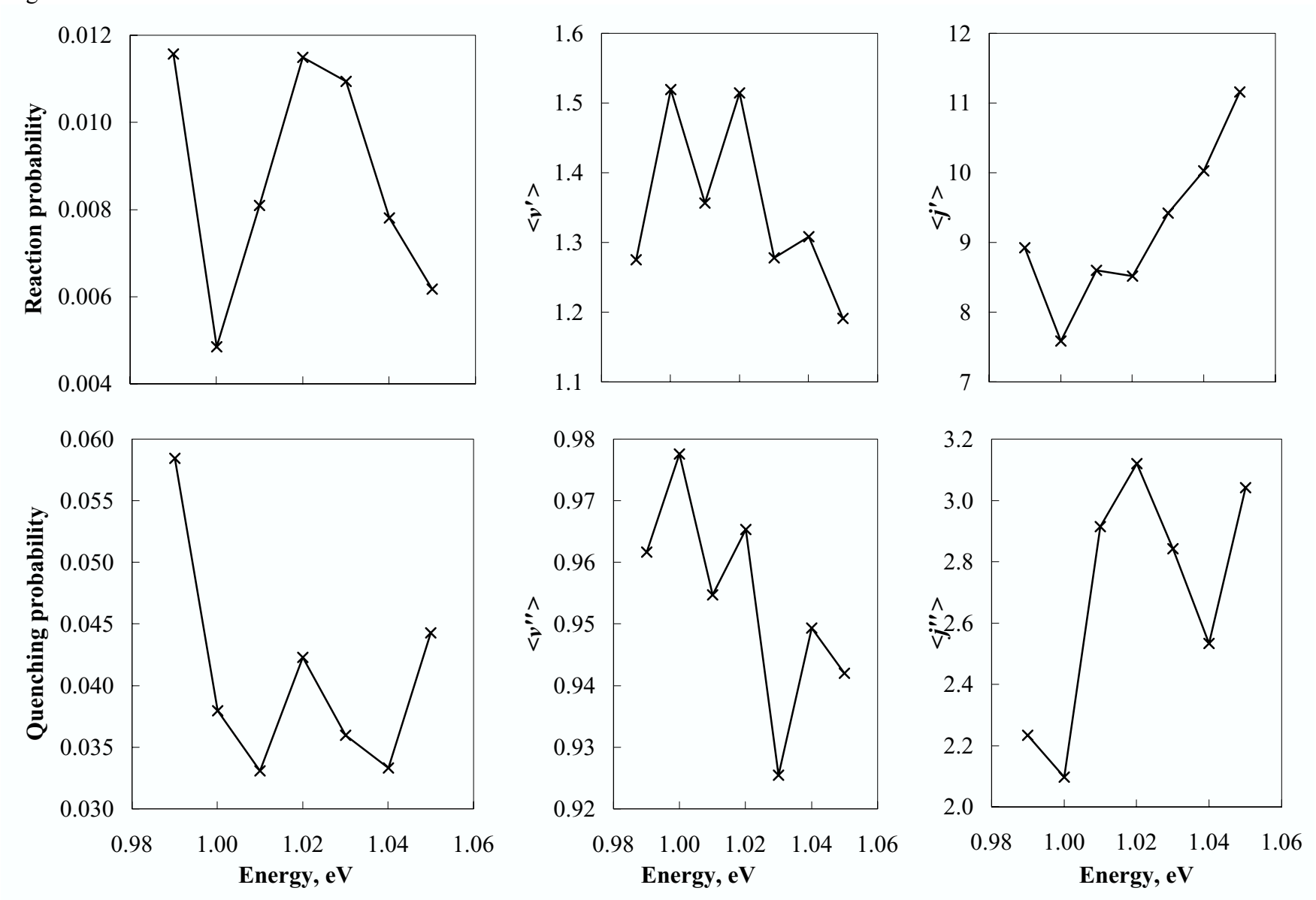
1.4
1.3
1.2
1.1
1.0
0.9
0.8
<j'>
14
13
12
11
10
Quenching probability
0.0020
0.0018
0.0016
0.0014
0.0012
0.0010
0.0008
<v''>
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
<j''>
6.5
6.0
5.5
5.0
4.5
4.0
1.06
1.08
1.10
1.12
1.14
Energy, eV

Fig. S9


Reaction probability
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0.006
0.004
<v'>
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1.5
1.4
1.3
1.2
1.1
<j'>
12
11
10
9
8
7
Quenching probability
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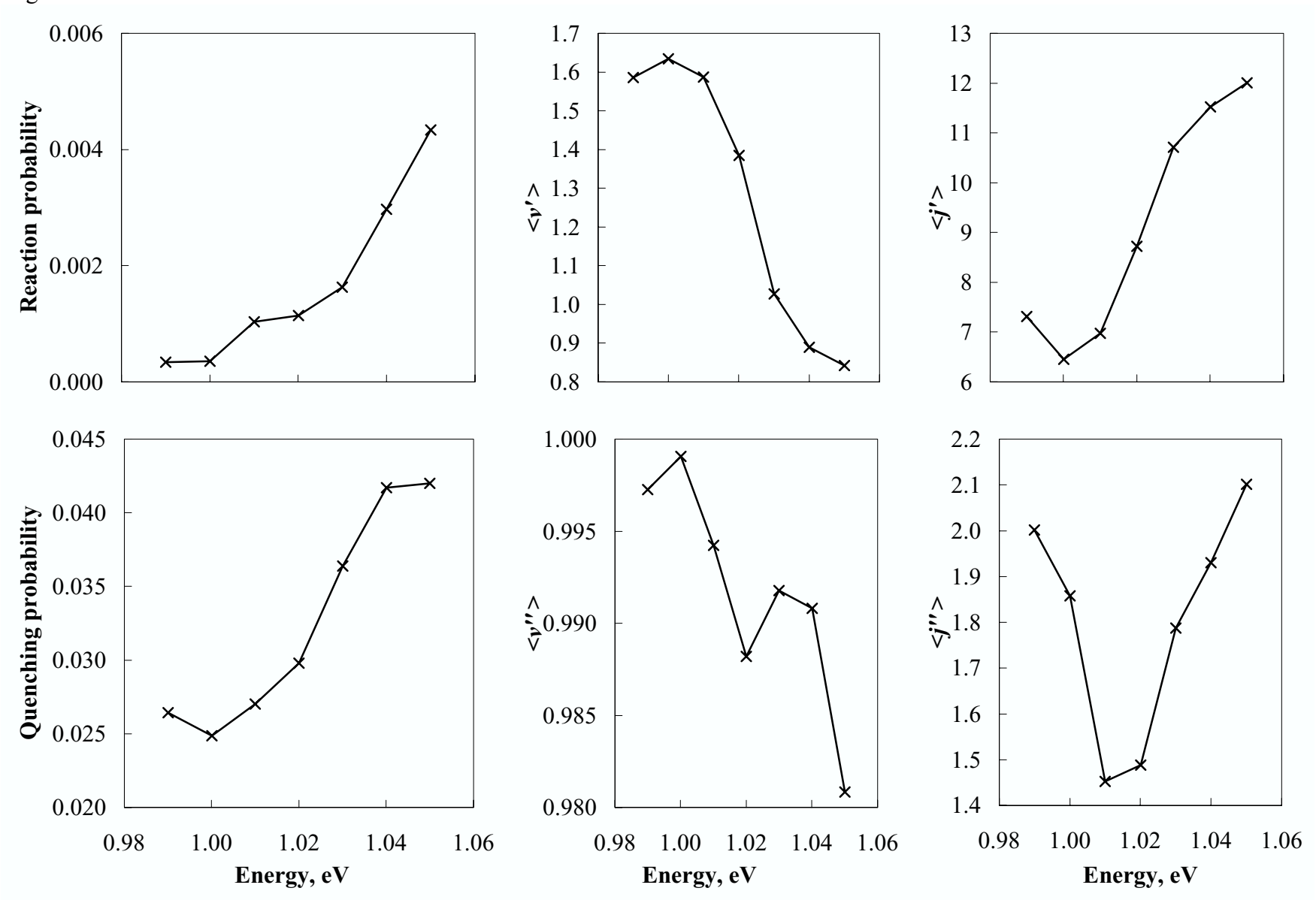
0.055
0.050
0.045
0.040
0.035
0.030
<v''>
0.98
0.97
0.96
0.95
0.94
0.93
0.92
<j''>
3.2
3.0
2.8
2.6
2.4
2.2
2.0
0.98
1.00
1.02
1.04
1.06
Energy, eV

Fig. S10


Reaction probability
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0.002
0.000
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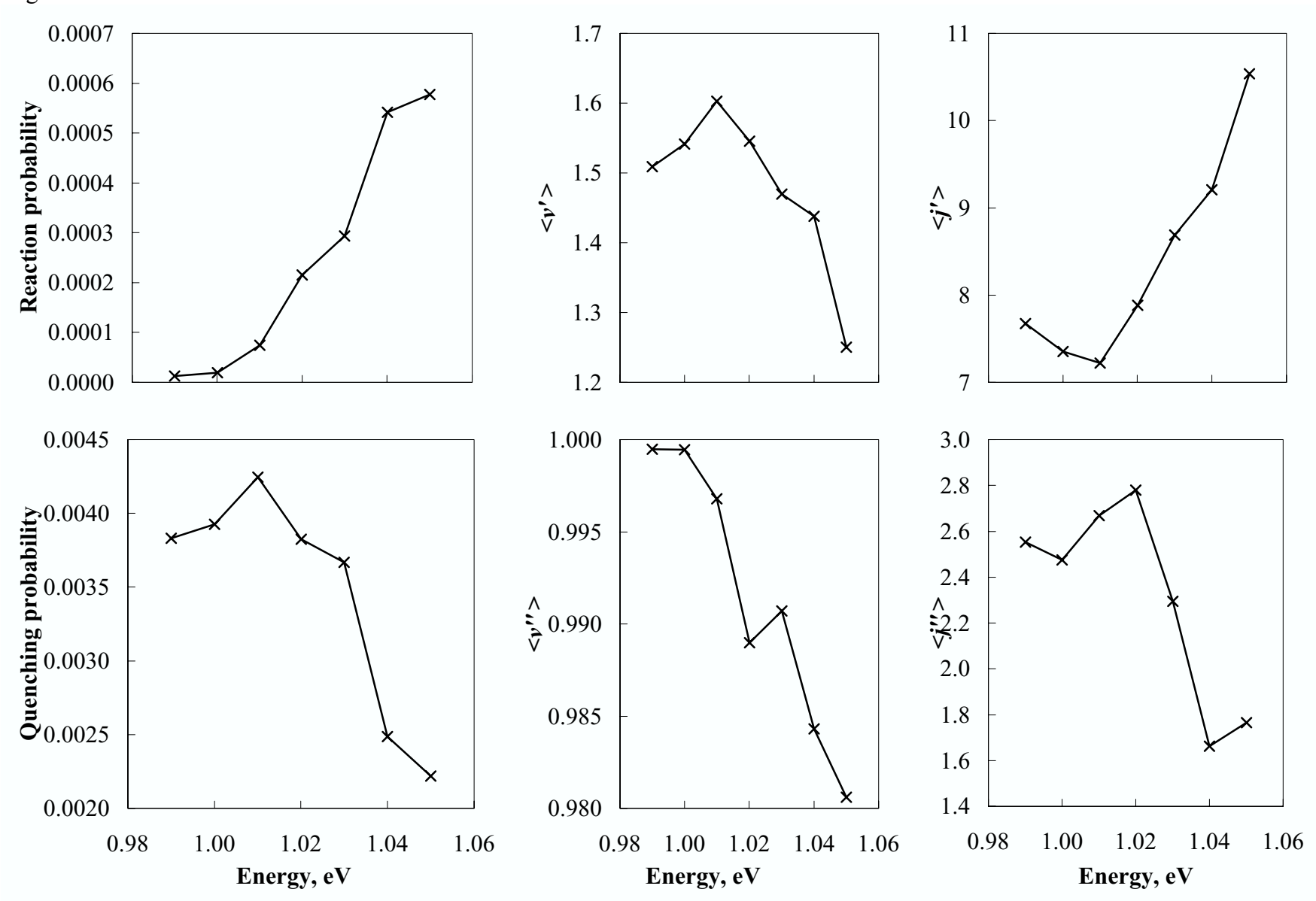
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
<j'>
13
12
11
10
9
8
7
6
Quenching probability
0.045
0.040
0.035
0.030
0.025
0.020
<v''>
1.000
0.995
0.990
0.985
0.980
<j''>
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
0.98
1.00
1.02
1.04
1.06
Energy, eV

Fig. S11


Reaction probability
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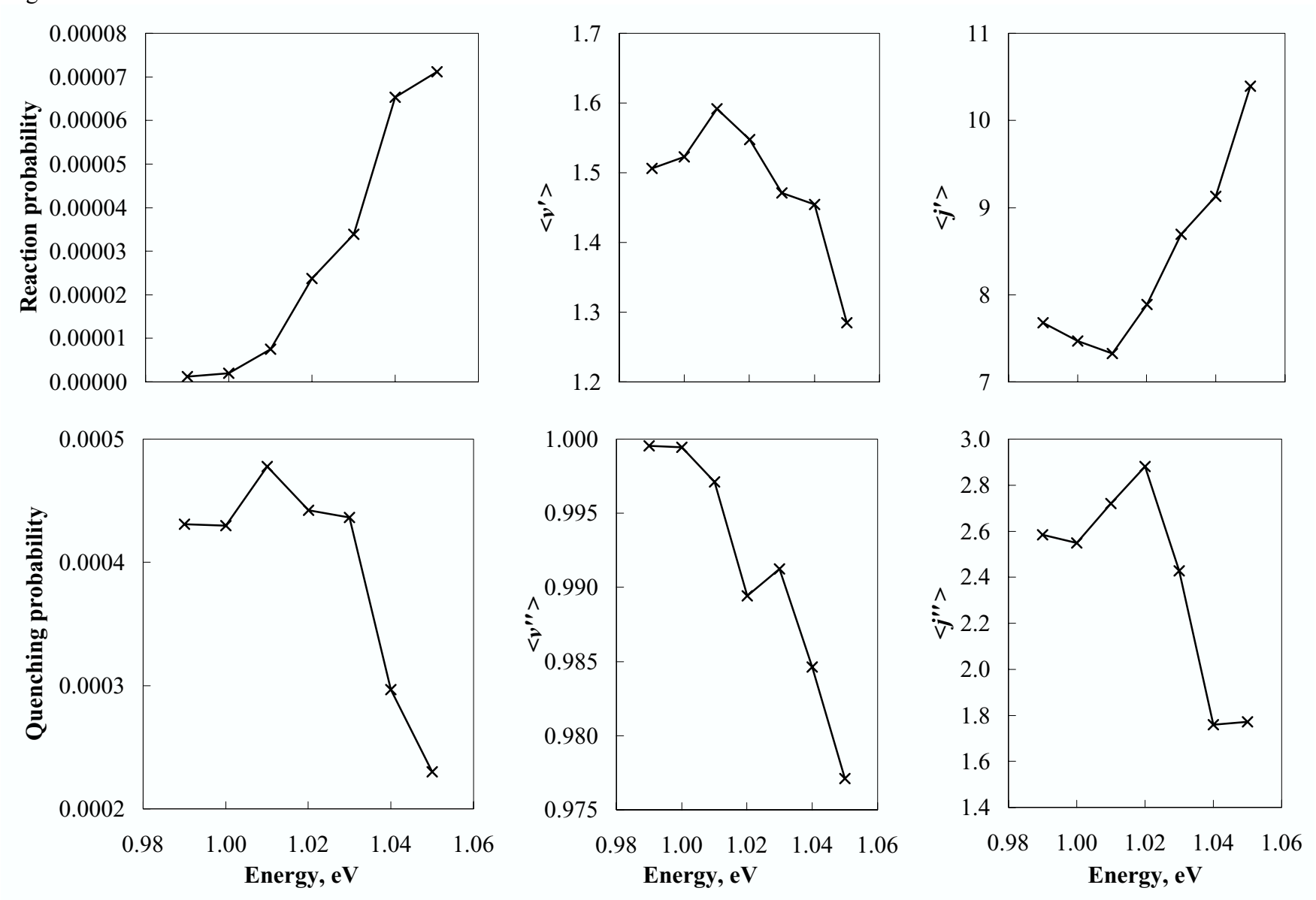
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
<v'>
1.7
1.6
1.5
1.4
1.3
1.2
<j'>
11
10
9
8
7
Quenching probability
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
<v''>
1.000
0.995
0.990
0.985
0.980
<j''>
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.98
1.00
1.02
1.04
1.06
Energy, eV

Fig. S12


Reaction probability
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0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000
<v'>
1.7
1.6
1.5
1.4
1.3
1.2
<j'>
11
10
9
8
7
Quenching probability
0.0005
0.0004
0.0003
0.0002
<v''>
1.000
0.995
0.990
0.985
0.980
0.975
<j''>
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.98
1.00
1.02
1.04
1.06
Energy, eV

3. SEMICLASSICAL TRAJECTORY RESULTS

Table S6. Reaction and quenching probabilities and vibrational and rotational moments for Y* + RH(0,0), 1.10 eV.[a]

PEM	Method	N_{traj} (thousands)	P_R	$<v'>$	$<j'>$	P_Q	$<v''>$	$<j''>$
YRH(0.20)	Quantum		1.22×10^{-2}	0.93	12.1	4.52×10^{-2}	0.90	3.30
	TFS-(–,+)	100	$(3.40 \pm 0.01) \times 10^{-2}$	0.77 ± 0.01	13.1 ± 0.1	$(6.82 \pm 0.08) \times 10^{-2}$	0.47 ± 0.01	5.57 ± 0.05
	TFS-AFH	100	$(6.81 \pm 0.01) \times 10^{-3}$	0.81 ± 0.03	13.9 ± 0.2	$(1.98 \pm 0.04) \times 10^{-2}$	0.35 ± 0.01	7.92 ± 0.10
	TFS-(+,+)	100	$(3.52 \pm 0.06) \times 10^{-2}$	0.90 ± 0.01	12.7 ± 0.1	$(6.56 \pm 0.08) \times 10^{-2}$	0.65 ± 0.01	5.12 ± 0.06
	TFS-(–,–)	100	$(2.73 \pm 0.05) \times 10^{-2}$	0.81 ± 0.01	12.7 ± 0.1	$(7.32 \pm 0.08) \times 10^{-2}$	0.45 ± 0.01	5.77 ± 0.05
	TFS-(R,+)	100	$(2.00 \pm 0.04) \times 10^{-2}$	0.84 ± 0.02	13.5 ± 0.1	$(3.54 \pm 0.06) \times 10^{-2}$	0.56 ± 0.01	5.95 ± 0.08
	GS(½)≡MDQT*	10	$(5.67 \pm 0.23) \times 10^{-2}$	0.85 ± 0.03	13.1 ± 0.2	$(1.09 \pm 0.03) \times 10^{-1}$	0.62 ± 0.01	5.67 ± 0.15
	GC(½)	10	$(9.65 \pm 0.30) \times 10^{-2}$	0.95 ± 0.03	12.3 ± 0.1	$(1.65 \pm 0.04) \times 10^{-1}$	0.66 ± 0.01	5.41 ± 0.12
	AS(½)	10	$(1.33 \pm 0.03) \times 10^{-1}$	0.97 ± 0.02	12.2 ± 0.1	$(2.34 \pm 0.04) \times 10^{-1}$	0.66 ± 0.01	5.22 ± 0.10
	AC(½)	10	$(6.21 \pm 0.24) \times 10^{-2}$	0.86 ± 0.03	13.0 ± 0.2	$(1.16 \pm 0.03) \times 10^{-1}$	0.65 ± 0.01	5.14 ± 0.14
	GS(n_χ)	100	$(3.76 \pm 0.06) \times 10^{-2}$	0.87 ± 0.01	12.8 ± 0.1	$(6.71 \pm 0.08) \times 10^{-2}$	0.62 ± 0.01	5.74 ± 0.06
	GC(n_χ)	100	$(3.97 \pm 0.07) \times 10^{-2}$	0.89 ± 0.01	12.8 ± 0.1	$(7.52 \pm 0.08) \times 10^{-2}$	0.63 ± 0.01	5.61 ± 0.06
	AS(n_χ)	100	$(4.00 \pm 0.06) \times 10^{-2}$	0.86 ± 0.01	12.9 ± 0.1	$(6.98 \pm 0.08) \times 10^{-2}$	0.59 ± 0.01	6.03 ± 0.06
	AC(n_χ)	100	$(3.53 \pm 0.06) \times 10^{-2}$	0.85 ± 0.01	13.0 ± 0.1	$(6.28 \pm 0.08) \times 10^{-2}$	0.59 ± 0.01	5.90 ± 0.06
	TFS-(–,+)-di	5	$(3.31 \pm 0.07) \times 10^{-1}$	0.54 ± 0.02	12.5 ± 0.1	$(2.69 \pm 0.06) \times 10^{-1}$	0.40 ± 0.01	5.50 ± 0.12
	TFS-AFH-di	5	$(1.20 \pm 0.49) \times 10^{-3}$	1.00 ± 0.33	14.0 ± 1.3	$(1.48 \pm 0.17) \times 10^{-2}$	0.14 ± 0.04	5.26 ± 0.44
YRH(0.10)	Quantum		8.55×10^{-3}	0.76	12.5	3.14×10^{-3}	0.94	1.72
	TFS-(–,+)	100	$(1.48 \pm 0.04) \times 10^{-2}$	0.79 ± 0.02	13.0 ± 0.1	$(3.45 \pm 0.06) \times 10^{-2}$	0.47 ± 0.01	5.51 ± 0.07
	TFS-AFH	100	$(4.81 \pm 0.22) \times 10^{-3}$	0.88 ± 0.03	13.2 ± 0.2	$(1.22 \pm 0.03) \times 10^{-2}$	0.38 ± 0.01	7.50 ± 0.12
	TFS-(+,+)	100	$(1.49 \pm 0.04) \times 10^{-2}$	0.89 ± 0.02	12.9 ± 0.1	$(3.22 \pm 0.06) \times 10^{-2}$	0.66 ± 0.01	5.04 ± 0.08
	TFS-(–,–)	100	$(1.27 \pm 0.04) \times 10^{-2}$	0.87 ± 0.02	12.7 ± 0.1	$(3.46 \pm 0.06) \times 10^{-2}$	0.46 ± 0.01	5.71 ± 0.07
	TFS-(R,+)	100	$(1.01 \pm 0.03) \times 10^{-2}$	0.81 ± 0.02	13.5 ± 0.1	$(1.92 \pm 0.04) \times 10^{-2}$	0.53 ± 0.01	6.24 ± 0.11
	GC(n_χ)	100	$(1.62 \pm 0.04) \times 10^{-2}$	0.91 ± 0.02	12.7 ± 0.1	$(3.61 \pm 0.06) \times 10^{-2}$	0.62 ± 0.01	5.51 ± 0.08

YRH(0.03)	Quantum		9.98×10^{-4}	0.81	12.1	3.10×10^{-3}	0.93	3.09
	TFS-(–,+)	200	$(1.89 \pm 0.10) \times 10^{-3}$	0.82 ± 0.04	13.0 ± 0.2	$(4.09 \pm 0.14) \times 10^{-3}$	0.50 ± 0.02	5.39 ± 0.14
	TFS-AFH	200	$(6.70 \pm 0.58) \times 10^{-4}$	0.97 ± 0.06	12.4 ± 0.3	$(1.60 \pm 0.09) \times 10^{-3}$	0.51 ± 0.03	6.28 ± 0.26
	TFS-(+,+)	200	$(1.95 \pm 0.10) \times 10^{-3}$	0.84 ± 0.04	12.8 ± 0.2	$(4.15 \pm 0.14) \times 10^{-3}$	0.64 ± 0.02	4.98 ± 0.16
	TFS-(–,–)	200	$(1.44 \pm 0.08) \times 10^{-3}$	0.89 ± 0.04	12.6 ± 0.3	$(4.45 \pm 0.15) \times 10^{-3}$	0.49 ± 0.02	5.53 ± 0.14
	TFS-(R,+)	200	$(1.36 \pm 0.08) \times 10^{-3}$	0.84 ± 0.05	13.3 ± 0.3	$(2.38 \pm 0.11) \times 10^{-3}$	0.60 ± 0.02	5.45 ± 0.21
	GC(n_χ)	200	$(2.02 \pm 0.10) \times 10^{-3}$	0.86 ± 0.04	13.2 ± 0.2	$(4.29 \pm 0.15) \times 10^{-3}$	0.67 ± 0.04	4.99 ± 0.15
YRH(0.01)	Quantum		1.12×10^{-4}	0.84	12.0	3.22×10^{-4}	0.93	3.11
	TFS-(–,+)	300	$(2.57 \pm 0.29) \times 10^{-4}$	0.83 ± 0.09	12.6 ± 0.5	$(4.50 \pm 0.39) \times 10^{-4}$	0.56 ± 0.04	4.90 ± 0.35
	TFS-AFH	300	$(1.00 \pm 0.18) \times 10^{-4}$	0.97 ± 0.13	12.4 ± 0.7	$(1.70 \pm 0.24) \times 10^{-4}$	0.51 ± 0.07	5.76 ± 0.65
	TFS-(+,+)	300	$(1.83 \pm 0.25) \times 10^{-4}$	0.87 ± 0.10	12.3 ± 0.6	$(4.40 \pm 0.38) \times 10^{-4}$	0.64 ± 0.04	4.97 ± 0.39
	TFS-(–,–)	300	$(1.73 \pm 0.24) \times 10^{-4}$	0.90 ± 0.11	12.6 ± 0.6	$(5.67 \pm 0.43) \times 10^{-4}$	0.48 ± 0.04	5.49 ± 0.33
	TFS-(R,+)	300	$(1.23 \pm 0.20) \times 10^{-4}$	0.73 ± 0.13	13.1 ± 0.8	$(2.33 \pm 0.28) \times 10^{-4}$	0.66 ± 0.05	4.27 ± 0.45
	GC(n_χ)	300	$(2.43 \pm 0.28) \times 10^{-4}$	0.81 ± 0.08	13.0 ± 0.6	$(5.47 \pm 0.43) \times 10^{-4}$	0.62 ± 0.04	5.15 ± 0.36

[a]The values after the ± sign are the 1σ statistical uncertainties due to the finite number of trajectories, computed by the method of Ref. 25.

Table S7. Reaction and quenching probabilities and vibrational and rotational moments for Y* + RH(0,6), 1.10 eV.

PEM	Method	N_{traj} (thousands)	P_R	$\langle v' \rangle$	$\langle j' \rangle$	P_Q	$\langle v'' \rangle$	$\langle j'' \rangle$
YRH(0.20)	Quantum		2.57×10^{-2}	1.07	12.1	1.37×10^{-1}	0.95	5.04
	TFS-(–,+)	50	$(2.57 \pm 0.07) \times 10^{-2}$	0.81 ± 0.02	12.0 ± 0.1	$(1.74 \pm 0.02) \times 10^{-1}$	0.71 ± 0.00	5.90 ± 0.04
	TFS-AFH	50	$(2.14 \pm 0.21) \times 10^{-3}$	1.33 ± 0.07	11.9 ± 0.4	$(1.20 \pm 0.01) \times 10^{-1}$	0.79 ± 0.01	5.62 ± 0.05
	TFS-(+,+)	50	$(1.58 \pm 0.06) \times 10^{-2}$	0.99 ± 0.03	12.6 ± 0.0	$(1.71 \pm 0.02) \times 10^{-1}$	0.78 ± 0.00	6.03 ± 0.05
	TFS-(–,–)	50	$(2.51 \pm 0.07) \times 10^{-2}$	0.90 ± 0.02	11.7 ± 0.1	$(1.76 \pm 0.02) \times 10^{-1}$	0.70 ± 0.00	5.89 ± 0.04
	TFS-(R,+)	50	$(7.42 \pm 0.38) \times 10^{-3}$	1.13 ± 0.04	12.2 ± 0.3	$(1.37 \pm 0.02) \times 10^{-1}$	0.79 ± 0.00	5.77 ± 0.05
	GC(n_χ)	50	$(1.85 \pm 0.06) \times 10^{-2}$	0.97 ± 0.03	12.8 ± 0.1	$(2.08 \pm 0.02) \times 10^{-1}$	0.78 ± 0.00	6.03 ± 0.04
YRH(0.10)	Quantum		2.52×10^{-2}	1.08	12.4	6.56×10^{-2}	0.92	5.40
	TFS-(–,+)	75	$(1.40 \pm 0.04) \times 10^{-2}$	0.98 ± 0.02	11.8 ± 0.1	$(1.15 \pm 0.01) \times 10^{-1}$	0.77 ± 0.00	6.14 ± 0.04
	TFS-AFH	75	$(2.65 \pm 0.19) \times 10^{-3}$	1.25 ± 0.05	11.9 ± 0.3	$(8.87 \pm 0.10) \times 10^{-2}$	0.82 ± 0.00	5.91 ± 0.05
	TFS-(+,+)	75	$(1.37 \pm 0.04) \times 10^{-2}$	0.98 ± 0.03	12.8 ± 0.1	$(1.14 \pm 0.01) \times 10^{-1}$	0.80 ± 0.00	6.45 ± 0.04
	TFS-(–,–)	75	$(1.44 \pm 0.04) \times 10^{-2}$	0.97 ± 0.02	11.9 ± 0.1	$(1.17 \pm 0.01) \times 10^{-1}$	0.76 ± 0.00	6.02 ± 0.04
	TFS-(R,+)	75	$(6.48 \pm 0.29) \times 10^{-3}$	1.15 ± 0.04	11.9 ± 0.2	$(1.03 \pm 0.01) \times 10^{-1}$	0.82 ± 0.00	6.09 ± 0.04
	GC(n_χ)	75	$(1.56 \pm 0.05) \times 10^{-2}$	1.04 ± 0.02	12.6 ± 0.1	$(1.29 \pm 0.01) \times 10^{-1}$	0.79 ± 0.00	6.57 ± 0.04
YRH(0.03)	Quantum		3.20×10^{-3}	1.17	12.1	12.7×10^{-2}	0.94	5.30
	TFS-(–,+)	100	$(2.33 \pm 0.15) \times 10^{-3}$	1.00 ± 0.05	12.4 ± 0.3	$(1.41 \pm 0.04) \times 10^{-2}$	0.76 ± 0.01	6.72 ± 0.10
	TFS-AFH	100	$(6.30 \pm 0.79) \times 10^{-4}$	1.32 ± 0.09	12.1 ± 0.5	$(1.09 \pm 0.03) \times 10^{-2}$	0.82 ± 0.01	6.64 ± 0.11
	TFS-(+,+)	100	$(2.04 \pm 0.14) \times 10^{-3}$	1.09 ± 0.06	12.9 ± 0.3	$(1.46 \pm 0.04) \times 10^{-2}$	0.78 ± 0.01	7.17 ± 0.10
	TFS-(–,–)	100	$(1.83 \pm 0.14) \times 10^{-3}$	1.08 ± 0.06	12.2 ± 0.4	$(1.44 \pm 0.04) \times 10^{-2}$	0.75 ± 0.01	6.56 ± 0.10
	TFS-(R,+)	100	$(1.44 \pm 0.12) \times 10^{-3}$	1.15 ± 0.06	12.4 ± 0.4	$(1.22 \pm 0.03) \times 10^{-2}$	0.81 ± 0.01	6.65 ± 0.10
	GC(n_χ)	100	$(2.35 \pm 0.15) \times 10^{-3}$	1.12 ± 0.05	12.4 ± 0.3	$(1.40 \pm 0.04) \times 10^{-2}$	0.74 ± 0.01	7.62 ± 0.10
YRH(0.01)	Quantum		3.69×10^{-4}	1.18	12.1	1.46×10^{-3}	0.94	5.32
	TFS-(–,+)	200	$(1.90 \pm 0.31) \times 10^{-4}$	1.03 ± 0.14	12.0 ± 0.9	$(1.75 \pm 0.09) \times 10^{-3}$	0.73 ± 0.02	7.11 ± 0.20
	TFS-AFH	200	$(6.00 \pm 1.73) \times 10^{-5}$	1.17 ± 0.23	12.7 ± 1.4	$(1.40 \pm 0.08) \times 10^{-3}$	0.78 ± 0.02	7.07 ± 0.21

TFS-(+,+)	200	$(2.30 \pm 0.34) \times 10^{-4}$	1.04 ± 0.12	13.2 ± 0.8	$(1.70 \pm 0.09) \times 10^{-3}$	0.79 ± 0.02	7.29 ± 0.20
TFS-(–,–)	200	$(2.05 \pm 0.32) \times 10^{-4}$	1.22 ± 0.13	11.2 ± 0.8	$(1.79 \pm 0.09) \times 10^{-3}$	0.73 ± 0.02	6.96 ± 0.20
TFS-(R,+)	200	$(1.85 \pm 0.30) \times 10^{-4}$	1.14 ± 0.12	11.9 ± 0.7	$(1.33 \pm 0.08) \times 10^{-3}$	0.85 ± 0.02	6.72 ± 0.20
GC(n_χ)	200	$(2.45 \pm 0.35) \times 10^{-4}$	0.96 ± 0.11	13.9 ± 0.5	$(1.72 \pm 0.09) \times 10^{-3}$	0.74 ± 0.02	7.79 ± 0.21

Table S8. Reaction and quenching probabilities and vibrational and rotational moments for Y* + RH(0,0), 1.02 eV.

PEM	Method	N_{traj} (thousands)	P_R	$\langle v' \rangle$	$\langle j' \rangle$	P_Q	$\langle v'' \rangle$	$\langle j'' \rangle$
YRH(0.20)	Quantum		8.92×10^{-3}	1.35	9.18	4.08×10^{-2}	0.95	2.68
	TFS-(–,+)	100	$(2.29 \pm 0.05) \times 10^{-2}$	0.87 ± 0.02	11.9 ± 0.1	$(7.60 \pm 0.08) \times 10^{-2}$	0.54 ± 0.01	4.73 ± 0.04
	TFS-AFH	100	$(3.28 \pm 0.18) \times 10^{-3}$	1.05 ± 0.04	11.7 ± 0.2	$(3.11 \pm 0.05) \times 10^{-2}$	0.72 ± 0.01	4.54 ± 0.06
	TFS-(+,+)	100	$(2.24 \pm 0.05) \times 10^{-2}$	1.09 ± 0.02	11.3 ± 0.1	$(7.24 \pm 0.08) \times 10^{-2}$	0.80 ± 0.00	3.82 ± 0.04
	TFS-(–,–)	100	$(1.74 \pm 0.04) \times 10^{-2}$	0.80 ± 0.02	11.8 ± 0.1	$(8.19 \pm 0.09) \times 10^{-2}$	0.53 ± 0.01	4.60 ± 0.04
	TFS-(R,+)	100	$(1.48 \pm 0.04) \times 10^{-2}$	1.02 ± 0.02	11.7 ± 0.1	$(4.53 \pm 0.07) \times 10^{-2}$	0.74 ± 0.01	4.38 ± 0.05
	GC(n_χ)	100	$(2.51 \pm 0.05) \times 10^{-2}$	1.04 ± 0.02	11.5 ± 0.1	$(8.08 \pm 0.09) \times 10^{-2}$	0.80 ± 0.00	4.05 ± 0.04
YRH(0.10)	Quantum		1.77×10^{-3}	1.28	9.10	3.26×10^{-2}	0.99	1.80
	TFS-(–,+)	100	$(8.35 \pm 0.29) \times 10^{-3}$	0.87 ± 0.03	12.0 ± 0.2	$(3.08 \pm 0.05) \times 10^{-2}$	0.51 ± 0.01	4.97 ± 0.06
	TFS-AFH	100	$(2.03 \pm 0.14) \times 10^{-3}$	1.02 ± 0.05	11.8 ± 0.3	$(1.37 \pm 0.04) \times 10^{-2}$	0.63 ± 0.01	5.19 ± 0.09
	TFS-(+,+)	100	$(8.28 \pm 0.29) \times 10^{-3}$	1.03 ± 0.03	11.7 ± 0.2	$(2.97 \pm 0.05) \times 10^{-2}$	0.76 ± 0.01	4.20 ± 0.07
	TFS-(–,–)	100	$(6.70 \pm 0.26) \times 10^{-3}$	0.84 ± 0.03	11.8 ± 0.2	$(3.04 \pm 0.05) \times 10^{-2}$	0.51 ± 0.01	4.76 ± 0.06
	TFS-(R,+)	100	$(5.39 \pm 0.23) \times 10^{-3}$	0.98 ± 0.03	12.0 ± 0.2	$(1.88 \pm 0.04) \times 10^{-2}$	0.68 ± 0.01	4.86 ± 0.08
	GC(n_χ)	100	$(8.96 \pm 0.30) \times 10^{-3}$	1.08 ± 0.03	11.5 ± 0.1	$(3.16 \pm 0.06) \times 10^{-2}$	0.73 ± 0.01	4.53 ± 0.07
YRH(0.03)	Quantum		2.48×10^{-4}	1.48	8.37	3.46×10^{-3}	0.99	2.31
	TFS-(–,+)	200	$(1.05 \pm 0.07) \times 10^{-3}$	0.89 ± 0.05	12.0 ± 0.3	$(3.41 \pm 0.13) \times 10^{-3}$	0.53 ± 0.02	5.17 ± 0.13
	TFS-AFH	200	$(3.05 \pm 0.39) \times 10^{-4}$	0.93 ± 0.09	11.9 ± 0.5	$(1.62 \pm 0.09) \times 10^{-3}$	0.62 ± 0.03	5.28 ± 0.20
	TFS-(+,+)	200	$(8.80 \pm 0.66) \times 10^{-4}$	1.06 ± 0.06	11.7 ± 0.3	$(3.62 \pm 0.13) \times 10^{-3}$	0.70 ± 0.02	4.93 ± 0.14
	TFS-(–,–)	200	$(7.40 \pm 0.61) \times 10^{-4}$	0.85 ± 0.07	12.0 ± 0.3	$(3.84 \pm 0.14) \times 10^{-3}$	0.51 ± 0.02	5.13 ± 0.13
	TFS-(R,+)	200	$(7.25 \pm 0.60) \times 10^{-4}$	1.05 ± 0.06	11.6 ± 0.3	$(2.29 \pm 0.11) \times 10^{-3}$	0.58 ± 0.02	5.57 ± 0.17
	GC(n_χ)	200	$(1.05 \pm 0.07) \times 10^{-3}$	1.01 ± 0.05	11.8 ± 0.3	$(3.61 \pm 0.13) \times 10^{-3}$	0.69 ± 0.02	4.79 ± 0.14
YRH(0.01)	Quantum		2.92×10^{-5}	1.48	8.37	3.92×10^{-4}	0.99	2.38
	TFS-(–,+)	500	$(1.16 \pm 0.15) \times 10^{-4}$	0.83 ± 0.10	12.0 ± 0.5	$(4.16 \pm 0.29) \times 10^{-4}$	0.47 ± 0.03	5.64 ± 0.24
	TFS-AFH	500	$(4.00 \pm 0.89) \times 10^{-5}$	1.25 ± 0.15	10.9 ± 0.9	$(1.96 \pm 0.20) \times 10^{-4}$	0.51 ± 0.05	6.39 ± 0.35

TFS-(+,+)	500	$(9.00 \pm 2.12) \times 10^{-5}$	1.56 ± 0.14	8.9 ± 0.9	$(4.05 \pm 0.45) \times 10^{-4}$	0.75 ± 0.05	4.41 ± 0.40
TFS-(–,–)	500	$(8.50 \pm 2.06) \times 10^{-5}$	0.82 ± 0.13	12.7 ± 0.6	$(4.60 \pm 0.48) \times 10^{-4}$	0.39 ± 0.05	5.30 ± 0.36
TFS-(R,+)	500	$(4.50 \pm 1.50) \times 10^{-5}$	1.22 ± 0.21	11.8 ± 0.9	$(2.25 \pm 0.34) \times 10^{-4}$	0.71 ± 0.07	5.20 ± 0.53
GC(n_χ)	500	$(1.14 \pm 0.15) \times 10^{-4}$	0.96 ± 0.10	12.3 ± 0.6	$(4.10 \pm 0.29) \times 10^{-4}$	0.75 ± 0.03	4.48 ± 0.26

Table S9. Reaction and quenching probabilities and vibrational and rotational moments for the MXH systems with the (1.10, 0) initial conditions.[a]

PEM	Method	P_R	$<v'>$	$<j'>$	P_Q	$<v''>$	$<j''>$
MXH(SB)	Quantum[b]	0.15	0.26	7.76	0.32	0.82	3.64
	TFS-(–,+)[b]	0.45	0.26	6.49	0.35	0.73	3.42
	TFS-AFH	0.21	0.25	6.60	0.14	0.97	3.69
	TFS-(+,+)	0.47	0.23	6.74	0.32	0.82	3.36
	TFS-(–,–)	0.35	0.25	6.72	0.42	0.70	3.22
	TFS-(R,+)	0.45	0.24	6.42	0.27	0.88	3.18
	GC(n_χ)	0.53	0.23	6.52	0.37	0.84	3.53
MXH(SL)	Quantum[b]	0.20	0.23	8.11	0.49	0.57	3.56
	TFS-(–,+)[b]	0.53	0.33	6.89	0.35	0.60	3.07
	TFS-AFH	0.37	0.32	7.15	0.13	0.65	2.82
	TFS-(+,+)	0.54	0.32	7.14	0.34	0.56	3.00
	TFS-(–,–)	0.49	0.34	6.77	0.37	0.61	2.98
	TFS-(R,+)	0.53	0.33	6.79	0.38	0.66	2.93
	GC(n_χ)	0.52	0.33	6.69	0.40	0.52	3.23
MXH(WL)	Quantum[b]	0.37	0.28	8.34	0.17	0.49	3.19
	TFS-(–,+)[b]	0.61	0.35	7.21	0.14	0.58	2.68
	TFS-AFH	0.53	0.35	7.33	0.07	0.50	2.80
	TFS-(+,+)	0.57	0.39	6.98	0.17	0.34	2.87
	TFS-(–,–)	0.60	0.39	6.90	0.15	0.53	2.67
	TFS-(R,+)	0.59	0.36	7.01	0.12	0.49	2.47
	GC(n_χ)	0.51	0.38	7.32	0.30	0.37	2.82

[a]The Monte Carlo errors for P_R, P_Q, and $<v'>$ are no greater than 0.01, for $<v''>$ are no greater than 0.02, and for $<j'>$ and $<j''>$ are no greater than 0.2.

[b]The quantum and TFS-(–,+) results are taken from Ref. 15.