Roaming Under the Microscope: Trajectory Study of Formaldehyde Dissocation – Supporting Information

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Table S1: Average values of measured trajectory properties

Line	Property/Energy (k cm^{-1})	34.500	35.000	35.500	36.000	36.223	37.668	38.668	38.814	41.010
1	Photon energy (k cm^{-1})	28.641	29.141	29.641	30.141	30.364	31.829	32.819	32.955	35.151
2	Excitation Band		4^3			$2^1 4^3$	$2^3 4^1$		$2^4 4_1$	$2^6 4^1$
3	TS Fract with 2 bonds*	0.17	0.18	0.19	0.19	0.20	0.22	0.22	0.23	0.24
4	Roam Fract with 2 bonds*	0.73	0.64	0.60	0.54	0..53	0.49	0.45	0.41	0.38
5	TS KE Fract*	0.43	0.43	0.43	0.43	.42	0.42	0.42	0.42	0.41
6	Roam KE Fract*	0.17	0.23	0.25	0.29	.29	0.31	0.34	0.35	0.36
7	TS HHBL $\left(\text{Å}\right)$*	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
8	Roam HHBL $\left(\text{Å}\right)$*	3.0	2.7	2.7	2.5	2.5	2.5	2.4	2.3	2.3
9	TS J(CO)	42.2	42.3	41.6	40.9	41.0	39.0	38.5	38.5	37.6
10	Roam J(CO)	20.2	19.5	19.7	19.7	20.2	18.8	21.5	20.9	22.9
11	TS J(H_2)	4.2	4.3	4.6	4.8	4.9	5.8	6.0	6.1	7.0
12	Roam J(H_2)	7.7	8.4	8.8	9.5	9.9	10.8	11.1	11.6	11.1
13	TSL_{orb}	43.5	43.6	43.0	42.5	42.4	40.5	40.1	40.1	39.2
14	Roam L_{orb}	19.3	19.7	20.0	21.2	22.0	20.8	23.7	24.0	25.4
15	TS r_H $\left(\text{Å}\right)$*	1.89	1.89	1.89	1.89	1.9	1.91	1.91	1.91	1.91
16	Roam r_H $\left(\text{Å}\right)$*	3.19	2.82	2.75	2.54	2.54	2.46	2.29	2.20	2.19
17	TS θ*	0.67	0.67	0.67	0.67	0.67	0.67	0.66	0.67	0.67
18	Roam θ*	0.88	0.87	0.84	0.80	0.78	0.77	0.73	0.71	0.70
19	TS ϕ*	2.62	2.61	2.59	2.58	2.57	2.53	2.53	2.53	2.53
20	Roam ϕ*	1.94	2.08	2.12	2.21	2.19	2.21	2.31	2.35	2.38
21	TS$\beta_0^0(22)$(CO)	-0.5	-0.5	-0.5	-0.5	-0.5	-0.49	-0.49	-0.49	-0.49
22	Roam $\beta_0^0(22)$(CO)	-0.48	-0.47	-0.46	-0.45	-0.45	-0.42	-0.44	-0.44	-0.46
23	TS $\beta_0^0(22)$(H_2)	-0.30	-0.28	-0.27	-0.27	-0.25	-0.22	-0.23	-0.21	-0.22
24	Roam $\beta_0^0(22)$(H_2)	-0.35	-0.37	-0.38	-0.35	-0.40	-0.39	-0.36	-0.38	-0.35
25	*TS* ***J(CO)•J(H$_2$)***	*0.22*	*0.21*	*0.19*	*0.20*	*0.17*	*0.12*	*0.13*	*0.10*	*0.08*
26	*Roam* ***J(CO)•J(H$_2$)***	*-0.35*	*-0.30*	*-0.24*	*-0.13*	*-0.12*	*-0.13*	*-0.09*	*-0.04*	*-0.05*
27	*TS* $A_0^{(2)}$*(CO)*	*0.01*	*0.02*	*0.03*	*0.03*	*0.03*	*0.05*	*0.06*	*0.06*	*0.06*
28	*Roam* $A_0^{(2)}$*(CO)*	*0.01*	*0.*	*0.02*	*0.02*	*0.04*	*0.05*	*0.08*	*0.06*	*0.06*
29	*TS* $A_0^{(2)}$*(H$_2$)*	*0.*	*0.*	*-0.02*	-0.02	-0.03	*-0.04*	*-0.04*	*-0.04*	*-0.05*
30	*Roam* $A_0^{(2)}$*(H$_2$)*	*-0.01*	*-0.02*	*-0.01*	*-0.02*	*0.*	*-0.01*	*-0.01*	*-0.03*	*-0.01*
31	TS β	0.024	0.006	-0.025	-0.025	0.002	-0.044	-0.074	-0.056	-0.065
32	Roam β	-0.073	-0.011	-0.003	-0.085	-0.102	-0.154	-0.194	-0.064	-0.136
33	TS E_{vib}(CO) (cm^{-1})†	**1800**	**1970**	**2040**	**2110**	**2210**	**2460**	**2700**	**2750**	**3350**
34	Roam E_{vib}(CO) (cm^{-1})†	**1560**	**1670**	**1740**	**1890**	**2000**	**2400**	**2480**	**2360**	**2900**
35	TS E_{vib}(H_2) (cm^{-1})†	**6640**	**6850**	**7210**	**7590**	**7530**	**8940**	**8820**	**8970**	**10200**
36	Roam E_{vib}(H_2) (cm^{-1})†	**21500**	**21200**	**21200**	**21200**	**21600**	**23300**	**22400**	**23400**	**22800**
37	TS E_{trans} (cm^{-1})	20500	20700	20700	20700	20800	20600	21300	21000	21200
38	Roam E_{trans} (cm^{-1})	5820	6220	6660	7030	6520	5760	7100	6720	8430
39	TS E_{orb} (cm^{-1})	2	2	1	1	1	1	1	1	1
40	Roam E_{orb} (cm^{-1})	0	0	0	0	0	0	1	1	1

41	TS final impact param (Å)	0.92	0.92	0.90	0.90	0.89	0.87	0.85	0.85	0.84
42	Roam final impact param (Å)	0.78	0.77	0.77	0.78	0.86	0.88	0.91	0.95	0.93
43	TS r_H, θ, ϕ at rxn frame	2.10	2.10	2.20	2.20	2.20	2.30	2.30	2.30	2.40
		0.83	0.82	0.80	0.79	0.79	0.77	0.73	0.75	0.73
		0.51	0.52	0.54	0.57	0.55	0.58	0.62	0.61	0.61
44	Roam r_H, θ, ϕ at rxn frame	2.80	2.80	2.90	2.90	2.90	3.00	3.10	3.10	3.10
		0.88	0.90	0.90	0.90	0.91	0.90	0.89	0.89	0.83
		0.40	0.38	0.41	0.40	0.41	0.39	0.43	0.41	0.51
45	Dissociation rate constant (ps^{-1})	0.0177	0.0371	0.0638	0.1128	0.1311	0.4092	0.5488	0.6329	1.464
46	Roaming time (ps)†	**0.320**	**0.310**	**0.300**	**0.210**	**0.140**	**0.140**	**0.097**	**0.058**	**0.070**

*Average over the 50 frames preceding the reaction frame

†See text in Section 2 for explaination of boldfaced values, which are based on group a).

Table S2: Explanation of Tabulated Properties

Line(s)	Property	Explanation
1	Photon Energy	Nominal photon excitation energy: Ephoton=Etot-zpe-E(H_2CO)=Etot-5848-10.6
2	Excitation Band	Band of Formaldehyde excited at Photon Energy
3-4	Fract with 2 bonds	Average fraction of 50 frames preceding reaction that have only two bonds for trajectories that produce H2+CO
5-6	KE Fract	Average KE/Etot for 50 frames preceding reaction to H_2+CO
7-8	HHBL	Average HH bond length in Angstroms for 50 frames preceding reaction to H_2+CO
9-10	J(CO)	Average CO angular momentum at end of trajectory (in hbar)
11-12	J(H_2)	Average H2 angular momentum at end of trajectory (in hbar)
13-14	L_{orb}	Average orbital angular momentum of H_2 and CO about their COM at end of trajectory (in hbar)
15-16	r_H	Average value of rH for 50 frames preceding reaction to H_2+CO
17-18	θ	Average value of θ for 50 frames preceding reaction to H_2+CO
19-20	ϕ	Average value of ϕ for 50 frames preceding reaction to H_2+CO
21-22	$\beta_0^0(22)$(CO)	Average correlation of relative velocity and **J(CO), -0.5 corresponds to perpendicular, +1.0 to parallel**
23-24	$\beta_0^0(22)$(H_2)	Average correlation of relative velocity and **J(H2), -0.5 corresponds to perpendicular, +1.0 to parallel**
25-26	**J(CO)•J(H_2)**	Average cosine of angle betwen CO and H_2 rotational vectors
27-28	$A_0^{(2)}$(CO)	$(2/5)P_2(cos\theta_j)$, θ_j =angle between CO rotational vector and transition dipole
29-30	$A_0^{(2)}$(H_2)	$(2/5)P_2(cos\theta_j)$, θ_j =angle between H_2 rotational vector and transition dipole
31-32	β	Average correlation of relative velocity with transition dipole moment, -1.0 correpsonds to perpendicular, +2.0 to parallel
33-34	E_{vib}(CO)	Average vibrational energy of CO at end of trajectory (in cm^{-1})
35-36	E_{vib}(H_2)	Average vibrational energy of H_2 at end of trajcetory (in cm^{-1})
37-38	E_{trans}	Average relative translational energy for CO and H_2 fragments at end of trajectory (in cm^{-1})
39-40	E_{orb}	Average value of orbital angular momentum of CO and H_2 at end of the trajectory (in cm^{-1})
41-42	final impact param	Average value of the impact parameter for departing CO and H_2 fragments, in Å
43-44	r_H, θ, ϕ at rxn	The values of these parameters at the time of reaction (± 1-2 frames)
45	Dissociation rate constant	total rate constant for disappearance of H_2CO from all channels
46	Roaming time	for those trajectories exhibiting roaming before reaction to H_2 + CO, the average time spent roaming

Table S3: Parameters for RRKM Calculation

Configuration	Vibrations (cm^{-1})	Reference	Free Rotors (amu-$Å^2$)	H1,O,C,H2 (Å)	Threshold E (cm^{-1})
H_2CO	1164., 1337., 1623., 1806., 2810., 2949.	1	none	{-0.592, 0.949, 0.}, {1.214, 0., 0.}, {0.0028, 0., 0.}, {-0.592, -0.949, 0.}	0
R	**800.,** 1156., 1903., 2815.	2	**15., 15.**	{-1.333, 0.818, 0.}, {0.496, -0.104, 0.}, {-0.699, -0.104, 0.}, {1.780, 2.0824, 0.}	33200
TS for $k_{TS\text{-}Bi}$	589., 652., 1351., 1861., 3039.	3,4	none	{-1.152, 1.461, 0.}, {0.612, -0.062, 0.}, {-0.583,-0.062,0.}, {-1.626,0.261,0.}	30584
TS for k_R	**500., 500.,** 1156., 1903., 2815.	5	none	{-1.309, 0.835, 0.}, {0.521, -0.088, 0.}, {-0.675, -0.088, 0.}, {1.084, 1.606, 0.}	33200
TS for $k_{R\text{-}Rad}$	1156., 1903., 2815.	6	**25., 25.**	{-1.365, 0.797, 0.}, {0.465, -0.126, 0.}, {-0.730, -0.126, 0.}, {2.679, 2.697, 0.}	36178
TS for $K_{R\text{-}Bi}$	**1900., 3800., 100., 300., 300., 400.**		none	{-1.454, -0.400, 1.064}, {0.578, 0.227, -0.084}, {-0.474, -0.244, -0.144}, {-2.073, -0.292, 1.983}	33200

Notes:

General: boldface numbers were adjusted to achieve fit. The structure for TS for $K_{R\text{-}Bi}$is that of Fig. 6, bottom row, center. Vibrations are approximated based on that structure.

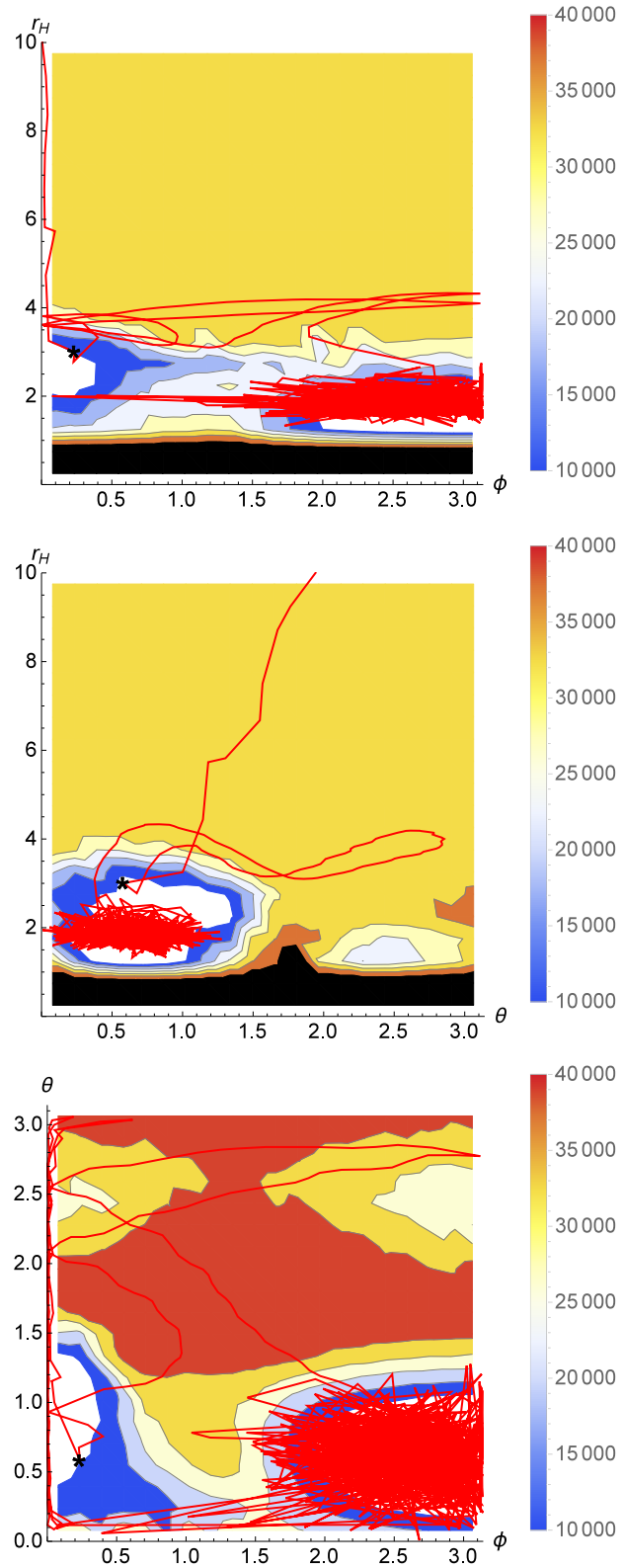

Figure S1: Roaming trajectory at Etot = 36223 cm^{-1}. Formaldehyde almost dissociates via the TS route but eventually roams before reacting at the configuration given by the black *. The nearly straight lines indicate nearly free rotation of the roaming H atom about the CO axis. The units of r_H, ϕ and θ are Å, radians, and radians, respectively.

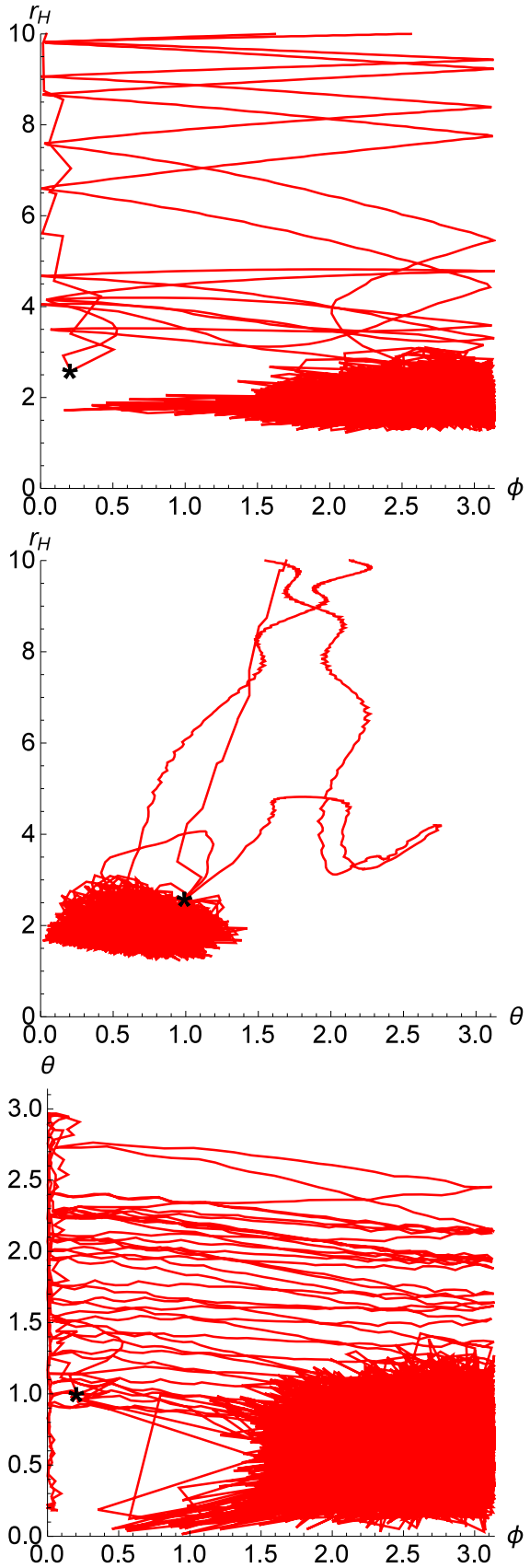

Figure S2: Extreme example of roaming trajectory for Etot=35000 cm^{-1}. The units of r_H, ϕ, and θ are Å, radians, and radians, respectively.

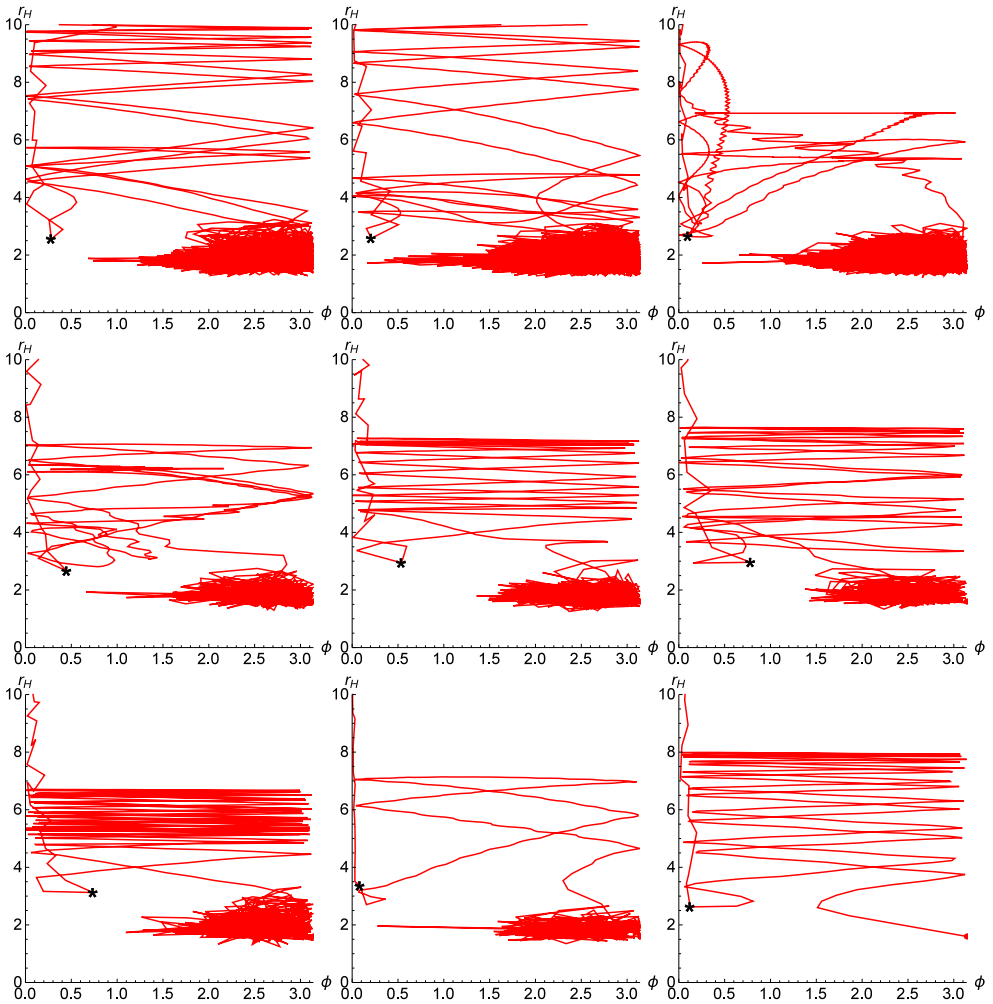

Figure S3: Several trajectories with long roaming times. Reading left to right and top to bottom, the excitation energies in cm^{-1} are 34500, 35000, 35500, 36000, 36223, 37688, 38688, 38814, 41010, respectively. The units of r_H and ϕ are Å and radians, respectively.

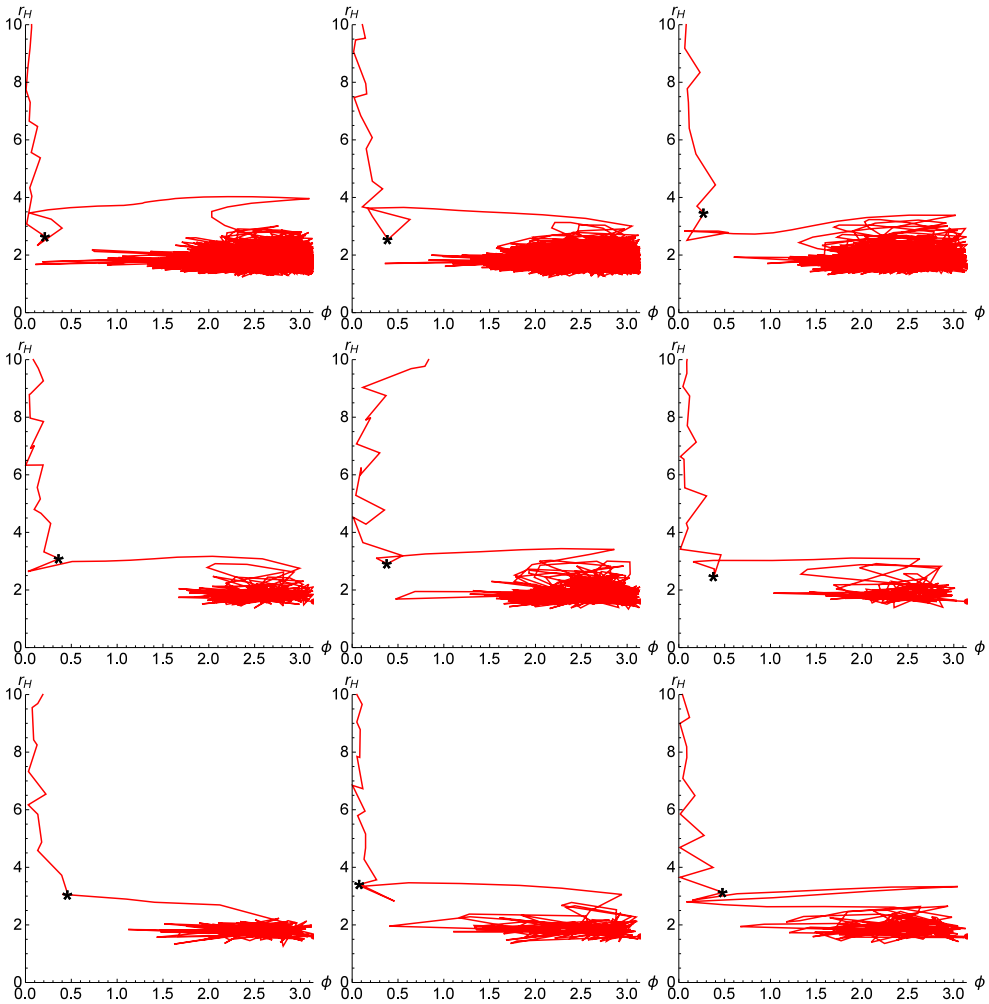

Figure S4: Several trajectories with short roaming times. Reading left to right and top to bottom, the excitation energies in cm^{-1} are 34500, 35000, 35500, 36000, 36223, 37688, 38688, 38814, 41010, respectively. The units of r_H and ϕ are Å and radians, respectively.

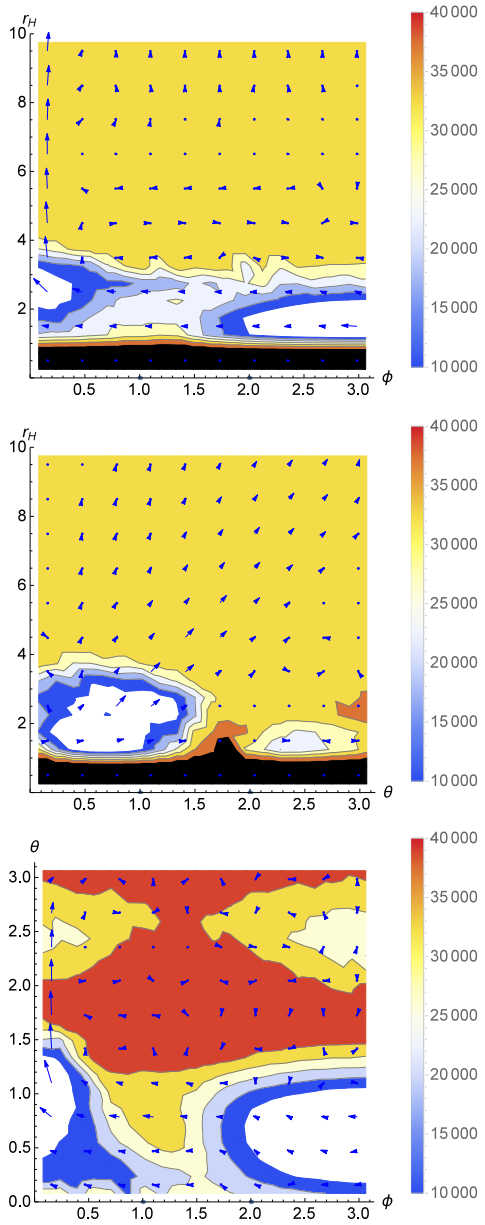

Figure S5: Flux maps for TS reactions to H_2 + CO at an excitation energy of 35000 cm^{-1}. The units of r_H, ϕ, and θ are Å, radians, and radians, respectively.

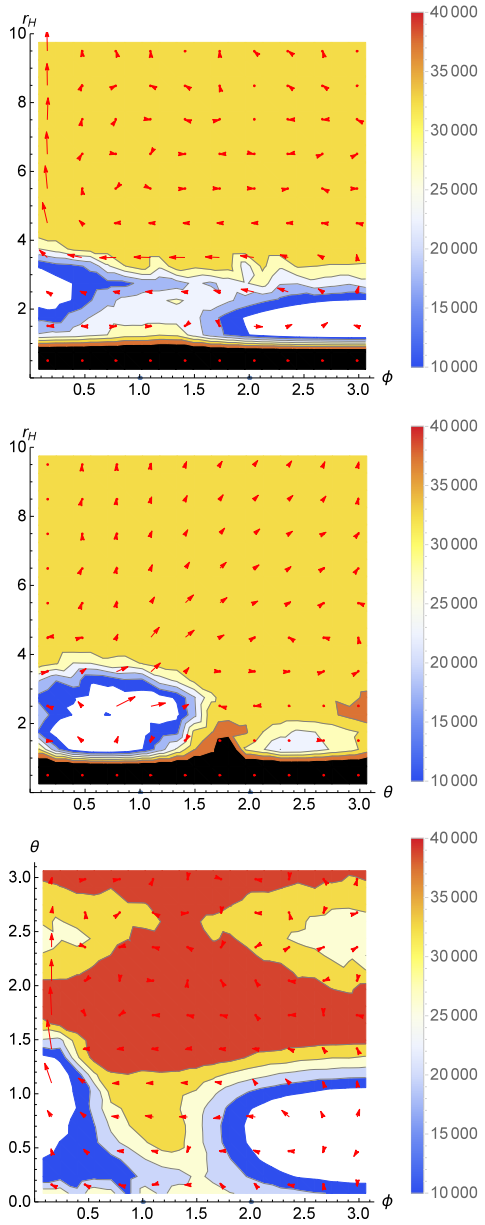

Figure S6: Flux maps for roaming reactions to H_2 + CO at an excitation energy of 35000 cm^{-1}. The units of r_H, ϕ, and θ are Å, radians, and radians, respectively.

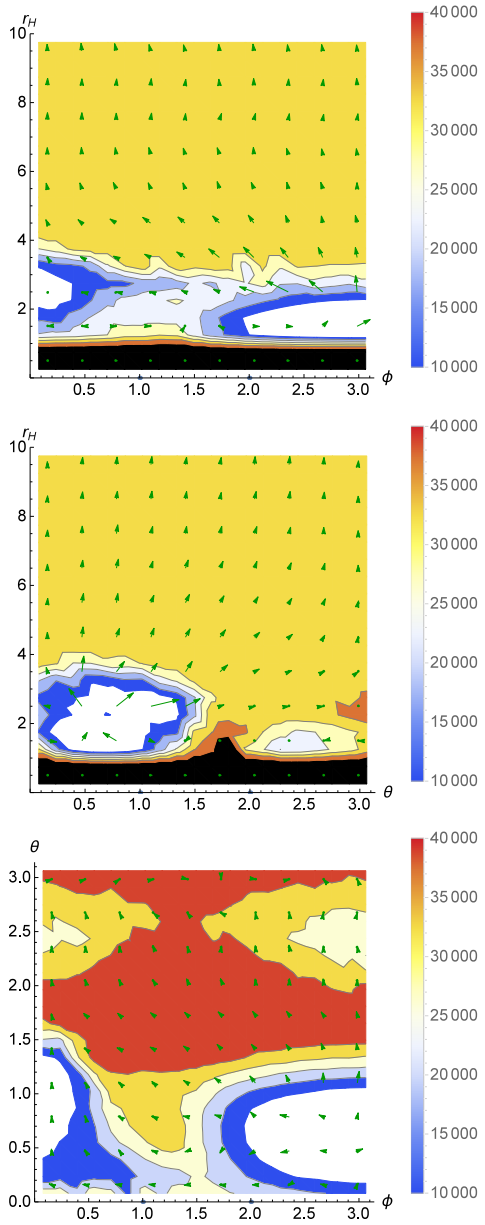

Figure S7: Flux maps for TS reactions to H + HCO at an excitation energy of 35000 cm^{-1}. The units of r_H, ϕ, and θ are Å, radians, and radians, respectively.

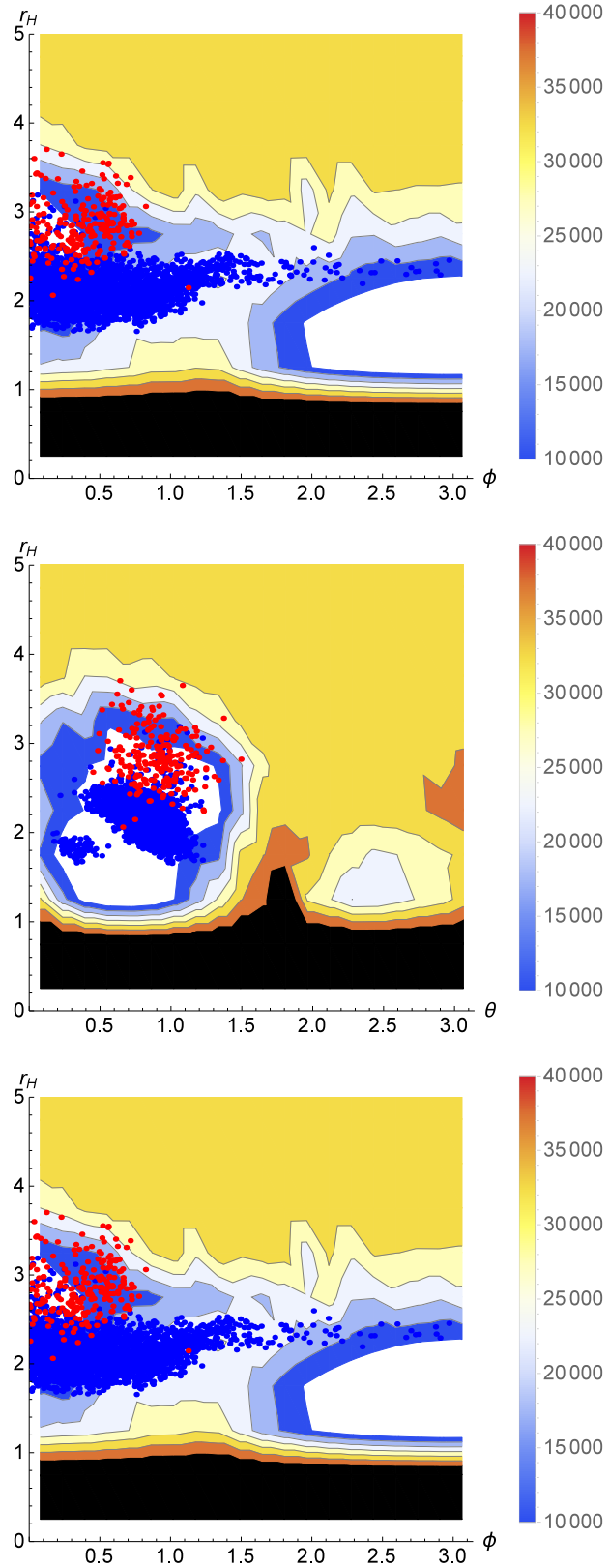

Figure S8: Reaction configuration plots for TS (blue, n=2643) and roaming (red, n=233) reactions at E_{tot}=35000 cm^{-1} projected onto the ϕ, r_H, θ, r_H, and ϕ, θ planes, superimposed on the minimum energy potential surface contour plot. The units of r_H, ϕ, and θ are Å, radians, and radians, respectively.

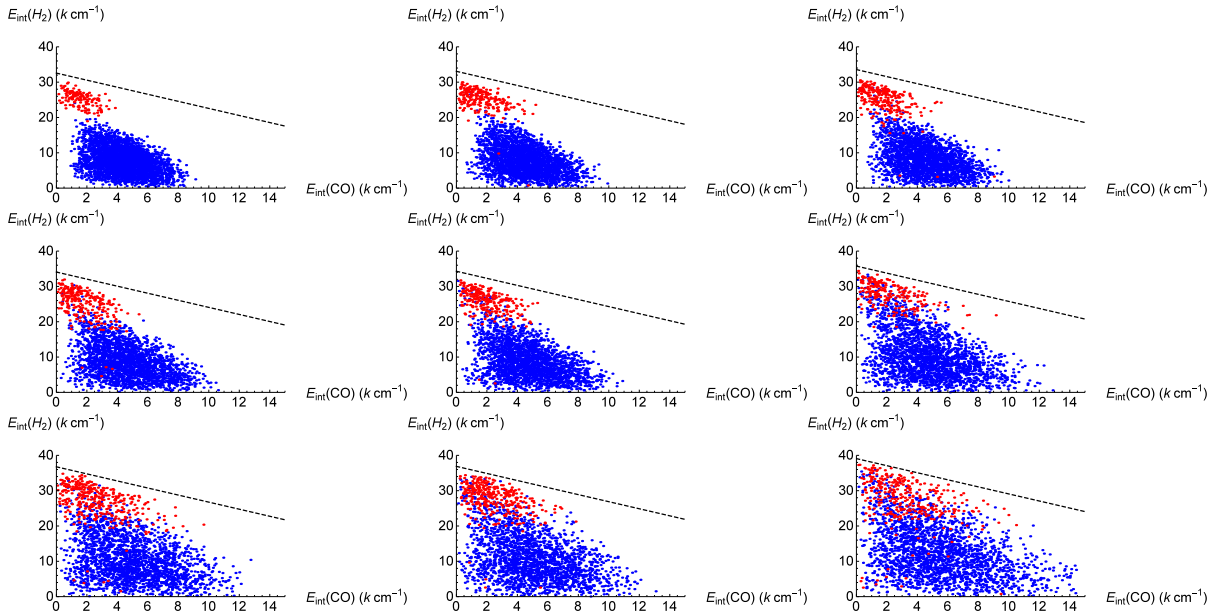

Figure S9: Correlation between $E_{int}(H_2)$ and $E_{int}(CO)$. The distance between any point and the dashed line gives the sum of the energy associated with orbital motion of the CO and H_2 and the energy associated with relative translation of these fragments. Red points are for roaming trajectories, whereas blue points are for TS trajectories. Reading left to right and top to bottom, the excitation energies in cm^{-1} are 34500, 35000, 35500, 36000, 36223, 37688, 38688, 38814, 41010, respectively.

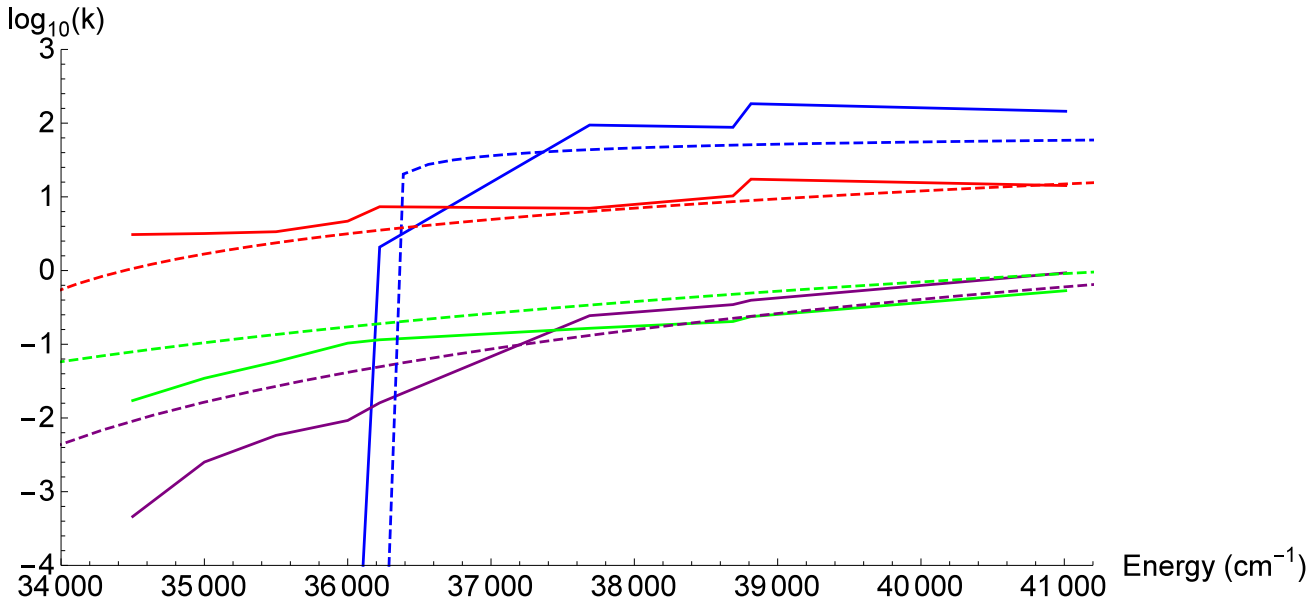

Figure S10: Comparison of rate constants that fit the trajectory data (solid lines) with RRKM rate constants (dashed lines) calculated using the parameters listed in Table S-3. RRKM rate constants were calculated using "A General RRKM Program", W. L. Hase and L. Zhu.

References

(1) Zhang, X.; Bowman, J. M., New Insights on Reaction Dynamics form Formaldehyde Phototissociation. *Phys. Chem. Chem. Phys.* **2006**, *8*, 321-332.

(2) Bowman, J. M.; Bittman, J. S.; Hardy, L. B., Ab Initio Calculations of Electronic and Vibrational Energies of HCO and HOC. *J. Chem. Phys.* **1986**, *85*, 911-921.

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