Understanding Energy Transfer in Gas-Surface Collisions from Gas-Phase Models

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Supporting Information

Intramolecular potential function for the hydrocarbons

The geometries of the alkanes and alkenes were taken from the Computational Chemistry Comparison and Benchmark Database (http://cccbdb.nist.gov). In particular, the minimum energy geometries at the MP2/cc-pVDZ level of theory were chosen, except for the CH molecule for which the C-H distance was chosen to be 1.10 Å. The conformation selected for each molecule is listed in the next table:

TABLE 1: Conformations the hydrocarbon projectiles studied in this work.

Hydrocarbon	Conformation
$^{15}C^{1}H$	-
CH_4 methane	-
C_2H_6 ethane	staggered
C_4H_{10} n-butane	staggered anti
C_5H_{10} pent-1-ene	linear
c-C_5H_{10} cyclopentane	envelope
C_6H_{12} hex-1-ene	linear
c-C_6H_{12} cyclohexane	twist boat
C_8H_{18} n-octane	linear

The parameters which describe the intramolecular interactions for the alkane and alkene molecules were taken from the force field developed by Pierce *et al.* (*J. Chem. Phys.* 128 (2008) 214903). This force field was parameterized for alkanes and fluoroalkanes so that the potential describes correctly *ab initio* energies and experimental densities and vaporization enthalphies. The intramolecular potential consists of bond, angle and torsion terms:

$$V_{intra} = K_b(r - r_0)^2 + K_a(\theta - \theta_0)^2 + \sum_n \frac{K_{t,n}}{2}\left(1 - cos(n\Phi)\right)$$

The intramolecular parameters are listed in the next table:

TABLE 2: Intramolecular parameters of the hydrocarbons studied in this work.

Bond parameters[a]				
	K_b		r_0	
C-C	309.0		1.53	
C-H	327.5		1.10	
Angle parameters[b]				
	K_a		θ_0	
C_2-C_2-$C_{2/3}$[d]	54.0		112.0	
$C_{2/3}$-C_2-H	43.0		110.0	
H-C_3-C_2	43.0		110.5	
H-C_3-H	38.5		107.7	
H-C_2-H	38.5		108.2	
Torsion parameters[c]				
	$K_{t,1}$	$K_{t,2}$	$K_{t,3}$	$K_{t,4}$
$C_{2/3}$-C_2-C_2-$C_{2/3}$	-0.271	0.152	-0.187	-0.500
H-$C_{2/3}$-$C_{2/3}$-H	0	0	-0.300	0
H-$C_{2/3}$-C_2-$C_{2/3}$	0	0	-0.300	0

[a] Force constants in kcal/mol/Å^2 and distances in Å.
[b] Force constants in kcal/mol/rad^2 and angles in degrees.
[c] Force constants in kcal/mol.
[d] C_3 and C_2 represent C atoms in CH_3 and CH_2 groups respectively.

For the C_5H_{10} and C_6H_{12} alkenes the same set of parameters was used except for the equilibrium angles which involve a sp^2 carbon whose values were changed to 120º.

Interaction potential between the hydrocarbons and the F-SAM

The intermolecular interactions between the projectiles and C and F atoms of the F-SAM surface are described by the potential developed by Wang and Hase (*J. Phys. Chem. B* 109 (2005) 8320) where *ab initio* energies for the CH_4/CF_4 dimer were fitted to a Buckingham exp-5 potential:

$$V_{ij} = A_{ij} exp\left(-B_{ij} r_{ij}\right) + \frac{C_{ij}}{r_{ij}^5}$$

The parameters are listed in the next table:

TABLE 3: Parameters of the C_xH_y + F-SAM intermolecular potential

	A_{ij}	B_{ij}	C_{ij}
C-C	6500.0	6.7422	103.75
C-F	13879	3.0000	756.25
H-C	7514.6	5.1906	1.0937
H-F	7132.7	5.1688	2.3438

A_{ij} in kcal/mol, B_{ij} in Å^{-1} and C_{ij} in kcal·Å^5/mol.

The interaction between the projectiles and the S atoms of F-SAM were not considered, and a repulsive potential for the projectile/Au interaction is employed to avoid the collapse between the gas and the gold surface at high collision energies,

$$V_{ij} = A_{ij} exp\left(-B_{ij} r_{ij}\right)$$

where A_{ij}= 4185200.0 kcal/mol and B_{ij}= 3.873 Å^{-1}.

Results

TABLE 4: Parameters of the energy transfer model (eqs 10 and 11) for B_2 colliding with the F-SAM as a function of the projectile mass m_g.[a]

m_g	$\langle\Delta E_V\rangle_0$	a_V	b_V	c_V[b]	d_V
4	0.00	16.10	25.45	6.69	2.04
10	0.13	5.93	9.84	3.93	11.73
20	0.15	2.31	8.75	2.54	11.07
40	0.04	0.69	3.41	1.41	12.74
60	0.00	0.80	3.47	1.62	23.48
m_g	$\langle\Delta E_R\rangle_0$	a_R	b_R	c_R[b]	d_R
4	0.05	3.57	8.12	3.73	14.99
10	0.07	3.16	9.16	2.04	11.24
20	0.08	2.40	9.94	1.25	11.34
40	0.05	0.57	5.19	0.98	9.69
60	0.09	0.93	7.68	0.85	18.22
m_g	$\langle E_F\rangle_0$	a_F	b_F	c_F[b]	d_F
4	1.58	41.43	7.53	22.66	9.80
10	1.04	21.22	6.69	10.17	10.42
20	1.25	9.83	7.45	2.75	5.09
40	0.00	2.67	1.78	1.60	18.88
60	0.00	1.40	0.79	17.33	42.71
m_g		a_{VRF}	b_{VRF}	P_∞	d_{VRF}
4		20.13	4.06	58.95	6.51
10		13.47	3.89	80.30	6.46
20		5.43	2.35	90.52	5.37
40		4.04	2.21	95.83	15.29
60		2.88	1.87	84.20	34.25

[a]Units are such that the energy is in eV and m_g in a.m.u.

[b]c is Multiplied by 100 so that it is expressed as a percentage (like P_∞).

TABLE 5: Parameters of the energy transfer model (eqs 10 and 11) for B_2 colliding with the F-SAM as a function of the frequency ω.[a]

ω	$<\Delta E_V>_0$	a_V	b_V	c_V[b]	d_V
300	0.15	2.31	8.75	2.54	11.07
400	0.17	2.65	8.37	3.24	15.74
500	0.14	2.47	7.16	3.85	17.78
600	0.04	2.44	5.75	3.80	18.03
700	0.00	3.20	6.38	4.02	20.68
ω	$<\Delta E_R>_0$	a_R	b_R	c_R[b]	d_R
300	0.08	2.40	9.94	1.25	11.34
400	0.06	1.23	7.08	1.96	10.45
500	0.07	1.51	7.34	2.25	12.18
600	0.11	2.79	9.72	2.42	15.74
700	0.13	2.88	9.86	2.60	16.09
ω	$<E_F>_0$	a_F	b_F	c_F[b]	d_F
300	1.25	9.83	7.45	2.75	5.09
400	1.19	8.60	7.03	3.17	4.88
500	1.21	8.87	7.32	3.05	4.98
600	1.24	8.78	7.48	2.92	5.06
700	1.28	8.81	7.68	2.86	5.09
ω		a_{VRF}	b_{VRF}	P_∞	d_{VRF}
300		5.43	2.35	90.52	5.37
400		5.08	2.21	90.04	5.24
500		4.95	2.15	89.83	5.15
600		4.96	2.16	89.86	5.08
700		5.12	2.24	89.94	5.12

[a]Units are such that the energy is in eV and ω in cm^{-1}.

[b]c is Multiplied by 100 so that it is expressed as a percentage (like P_∞).

TABLE 6: Parameters of the energy transfer model (eqs 10 and 11) for B_2 colliding with the F-SAM as a function of the intermolecular parameter L.[a]

Vibration					
L	$\langle\Delta E_V\rangle_0$	a_V	b_V	c_V[b]	d_V
1.00	0.00	0.07	1.02	0.48	31.77
0.83	0.00	0.10	1.56	0.53	16.68
0.67	0.00	0.16	1.78	1.00	11.90
0.50	0.03	0.37	3.29	1.88	10.54
0.33	0.15	2.31	8.75	2.54	11.07
L	$\langle\Delta E_R\rangle_0$	a_R	b_R	c_R[b]	d_R
1.00	0.01	0.49	21.63	0.07	25.30
0.83	0.01	0.53	16.53	0.18	20.32
0.67	0.02	1.10	12.90	0.51	30.28
0.50	0.04	1.43	10.68	0.83	15.41
0.33	0.08	2.40	9.94	1.25	11.34
L	$\langle E_F\rangle_0$	a_F	b_F	c_F[b]	d_F
1.00	0.53	16.40	3.67	71.78	5.74
0.83	1.40	6.29	5.29	61.76	2.69
0.67	0.98	5.17	3.52	48.59	3.06
0.50	1.07	15.12	7.87	23.87	0.18
0.33	1.25	9.83	7.45	2.75	5.09
L		a_{VRF}	b_{VRF}	P_∞	d_{VRF}
1.00		4.18	4.13	26.39	0.00
0.83		12.05	2.83	37.66	5.30
0.67		7.55	2.31	50.13	4.32
0.50		11.61	3.24	71.06	5.98
0.33		5.43	2.35	90.52	5.37

[a]Units are such that the energy is in eV and L in Å.

[b]c is Multiplied by 100 so that it is expressed as a percentage (like P_∞).

Figures

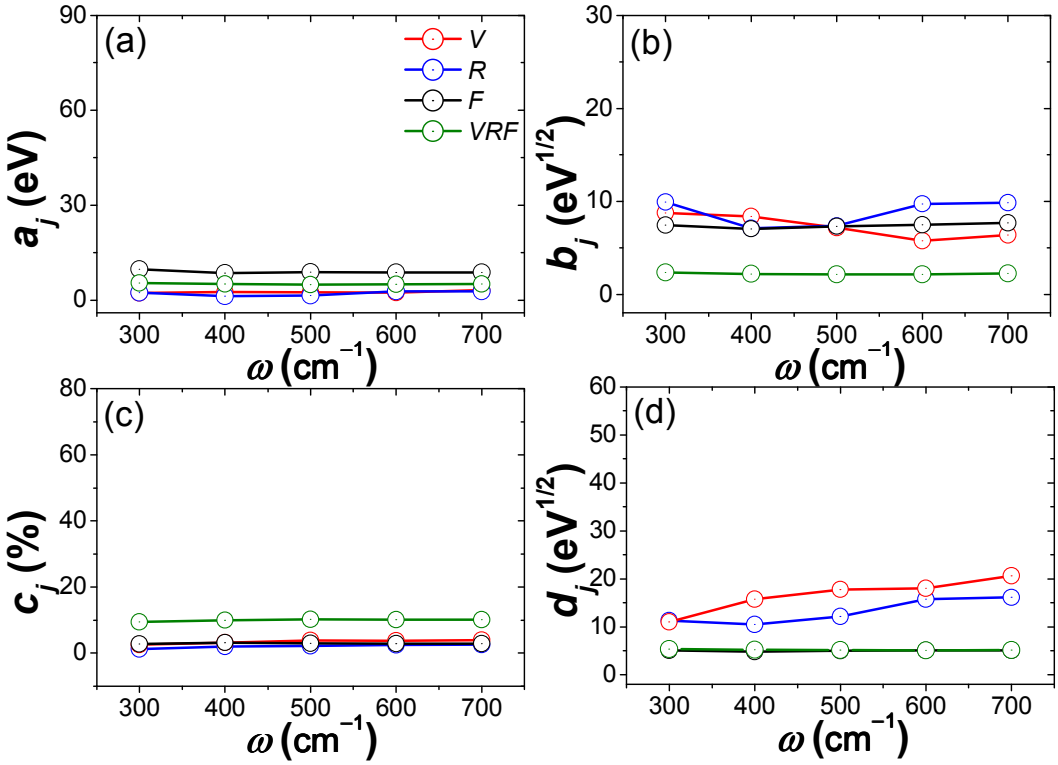

Figure 1. Model parameters of eqs 10 and 11, obtained from fits to the simulation results, as a function of ω. Parameters a_j, b_j, c_j and d_j are displayed in panels a, b, c and d, respectively. The subscript j refers to V (vibration), R (rotation), F (final translation), or VRF (overall energy of the projectile).

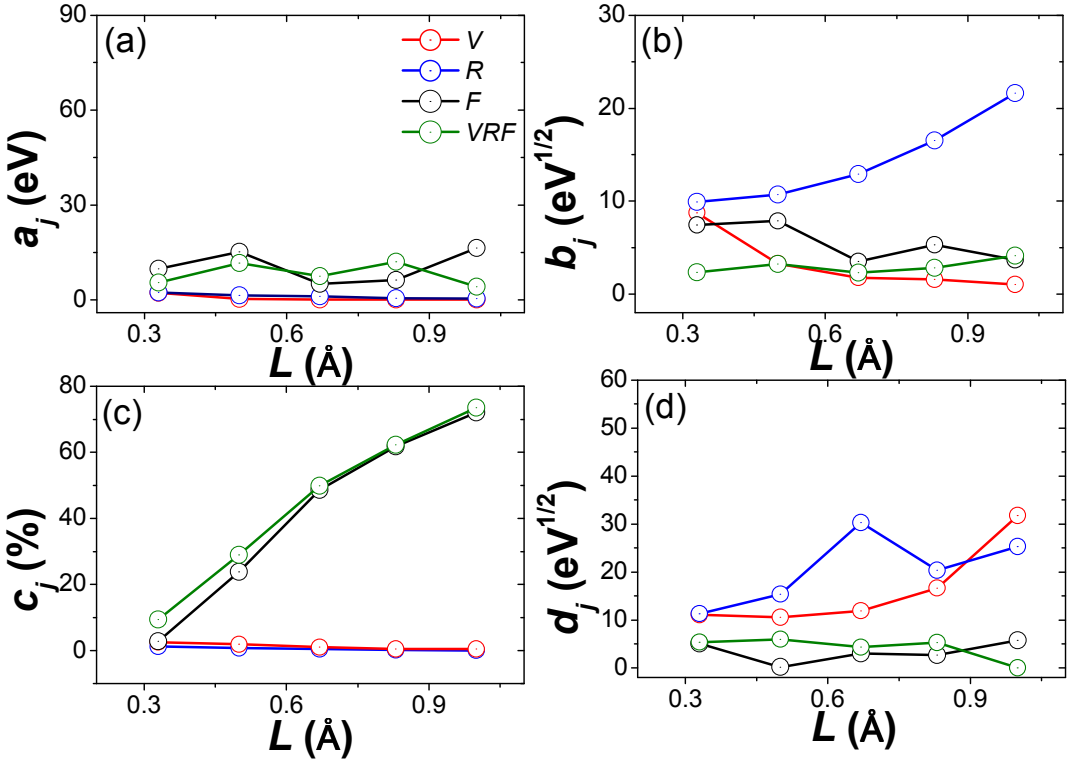

Figure 2. Model parameters of eqs 10 and 11, obtained from fits to the simulation results, as a function of L. Parameters a_j, b_j, c_j and d_j are displayed in panels a, b, c and d, respectively. The subscript j refers to V (vibration), R (rotation), F (final translation), or VRF (overall energy of the projectile).