Supplementary Information

Gas-Surface Energy Exchange and Thermal Accommodation in Collisions of CO_2 and Ar with Methyl, Hydroxyl, and Perfluorinated Self-Assembled Monolayers

Jessica W. Lu, William A. Alexander and John R. Morris

Department of Chemistry, Virginia Tech, Blacksburg Virginia, 24060

Potential Energy Wells Depths. Determination of the minimum energy on the gas/surface potential energy surface can aid in understanding of energy exchange and accommodation and can be facilitated through *ab initio* electronic structure calculations. In place of a simulated surface, the calculations here used CO_2 and Ar and CH_4, CH_3OH, and CF_4 in an effort to approximately evaluate a trend for minimum well depths for Ar and CO_2 at a distance from the CH_3-, OH-, and F-SAM surface.

Second-order Möller-Plesset perturbation theory (MP2) combined with Dunning's double-ξ correlation-consistent basis set augmented with diffuse functions (aug-cc-pVDZ) was used to calculate minimum energy wells for Ar and CO_2 interacting with CH_4, CH_3OH, and CF_4, small molecule analogues of the terminal groups of the CH_3-SAM, OH-SAM, and F-SAM, respectively. Similar calculations have been previously performed for Ar with CH_4,[1] CF_4,[1] and CH_3OH,[2] and CO_2 with CF_4.[3] The motivation for the basic reproduction of these calculations here is two-fold: to compute similar values for CO_2, and to focus on the trends rather than absolute values. Corrections for basis-set superposition error (BSSE) were done by applying the counterpoise method.[4] The Gaussian03 suite of programs was used to perform all calculations for depths of potential wells and well-minimum approach distances.[5] The minimum well depth of the approach calculated for Ar-CH_4 is found to be -1.18 kJ/mol, when Ar approaches the carbon on the face of the methane molecule along one of the C-H bonds. CO_2 interactions were

calculated for the molecule approaching the methane face with its CO bonds perpendicular to the C-H bond. The interactions of Ar and CO_2 with CF_4 were calculated with analogous approach geometries to those of methane.

The geometry used for the Ar – CH_3OH calculations involves Ar approaching methanol at the O-atom at an angle that bisects the H-O-C angle. The minimum well depth for CO_2 and CH_3OH shows the C-atom approaching the O-atom as to bisect the H-O-C angle, with each of the C-O bonds on CO_2 positioned perpendicular to the axis that intersects the C-atom of CO_2 and O-atom of CH_3OH; here, CO_2 is coplanar to H-O-C on CH_3OH. The calculated well depths are listed in Table 3 of the article.

Ar interaction with the CF_4 molecule results in a well depth of -1.41 kJ/mol. Well depths for Ar with CH_4 and CH_3OH are -1.18 and -1.08 kJ/mol, making all Ar wells at these approaches approximately the same. CO_2, in contrast, forms deeper wells with CH_4 and CH_3OH at these approach geometries, -2.90 kJ/mol and -11.95 kJ/mol respectively. As approximated by the potential well depth formed between CO_2 and CF_4, the strength of the CO_2 interaction with the F-SAM is about as strong as the well depth formed between CO_2 and CH_4, as approximated by the potential well depth formed between CO_2 and CF_4.

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TABLE S1.

Molecule/Monolayer		BC Fraction	Percent Energy Transferred $(E_i-\langle E_f\rangle)/E_i*100$	Final Energy IS $\langle E_{IS}\rangle$
50 kJ/mol	Ar, CH_3-SAM	0.75 +/- 0.01	86.3 +/- 0.3 %	10.1 +/- 0.3
	Ar, OH-SAM	0.61 +/- 0.01	83.9 +/- 1.0 %	11.7 +/- 0.7
	Ar, F-SAM	0.39 +/- 0.01	74.6 +/- 0.8%	15.2 +/- 0.2
	CO_2, CH_3-SAM	0.82 +/- 0.01	88.5 +/- 0.4 %	10.4 +/- 0.2
	CO_2, OH-SAM	0.81 +/- 0.03	88.2 +/- 0.9%	11.5 +/- 0.2
	CO_2, F-SAM	0.45 +/- 0.01	78.0 +/- 0.4 %	14.8 +/- 0.6
78 kJ/mol	Ar, CH_3-SAM	0.67 +/- 0.01	90.8 +/- 0.1 %	11.2 +/- 0.1
	Ar, OH-SAM	0.55 +/- 0.01	88.0 +/- 0.8 %	14.1 +/- 0.1
	Ar, F-SAM	0.32 +/- 0.01	79.7 +/- 0.4 %	19.5 +/- 0.4
	CO_2, CH_3-SAM	0.74 +/- 0.03	91.5 +/- 0.7 %	12.3 +/- 1.1
	CO_2, OH-SAM	0.67 +/- 0.02	90.5 +/- 0.9 %	13.3 +/- 0.8
	CO_2, F-SAM	0.36 +/- 0.01	82.7 +/- 0.2%	17.5 +/- 0.4
106 kJ/mol	Ar, CH_3-SAM	0.62 +/- 0.02	92.5 +/- 0.4 %	12.1 +/- 0.4
	Ar, OH-SAM	0.45 +/- 0.02	89.6 +/- 0.4 %	14.8 +/- 0.5
	Ar, F-SAM	0.26 +/- 0.01	83.7 +/- 0.1 %	23.0 +/- 0.2
	CO_2, CH_3-SAM	0.68 +/- 0.02	93.0 +/- 0.2 %	11.9 +/- 0.1
	CO_2, OH-SAM	0.61 +/- 0.02	92.3 +/- 0.4 %	14.4 +/- 0.2
	CO_2, F-SAM	0.28 +/- 0.02	83.7 +/- 0.1 %	20.4 +/- 0.5
130 kJ/mol	Ar, CH_3-SAM	0.59 +/- 0.01	93.9 +/- 0.2 %	12.0 +/- 0.1
	Ar, OH-SAM	0.44 +/- 0.01	91.0 +/- 0.1 %	16.2 +/- 0.3
	Ar, F-SAM	0.25 +/- 0.02	84.4 +/- 0.5 %	23.9 +/- 0.3
	CO_2, CH_3-SAM	0.65 +/- 0.01	93.9 +/- 0.1 %	12.9 +/- 0.1
	CO_2, OH-SAM	0.63 +/- 0.05	92.8 +/- 0.1 %	16.4 +/- 1.0
	CO_2, F-SAM	0.27 +/- 0.03	85.8 +/- 0.6%	21.9 +/- 0.3