

An ab Initio Calculation of the Potential for the Interaction of a Hydrogen Atom with an Ethane Molecule

Paul Blowers and Richard I. Masel*

Department of Chemical Engineering, University of Illinois at Urbana-Champaign,
600 S. Mathews Avenue, Urbana, Illinois 61801-3792

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In this paper ab initio methods including PMP2/aug-cc-pVTZ, CCSD(T)/6-311++G(d,p), and G2 methods are used to calculate the interaction potential for a hydrogen atom approaching ethane along the carbon–carbon axis of ethane. The potential shows a shallow minimum at about 4.0 Å and a strong repulsive core. The position of the minimum moves to smaller distances as the size of the basis set increases. Concurrently, the strength of the core repulsion decreases and the well depth increases. PMP2 calculations show a slightly shallower well than do CCSD(T) calculations, but the repulsive potentials are virtually identical. The potential is well represented by a Morse potential. An exponential-6 potential, a simple exponential, an anti-Morse potential or a Kihara potential fit the data less well. A Lennard-Jones potential and a Mie potential show substantial deviations. A new exponentially damped exponential-6 potential fits the repulsive region slightly better than the Morse exponential-6, anti-Morse, and Lennard-Jones potentials. Potential parameters are included in the paper.

Introduction

In recent papers, our group has been interested in finding some engineering approximations for activation barriers of atom transfer reactions.^{1–4} Generally we are examining reactions where a radical R, reacts with a neutral molecule X–Y, and a ligand is exchanged, i.e.,



Our approach has been to expand V_{RXY} , the potential energy surface for the reaction, as

$$V_{RXY} = V_{RX} + V_{XY} + V_I \quad (2)$$

where V_{RX} is the potential energy surface for an isolated RX molecule as a function of the bond lengths in the molecule, V_{XY} is the potential energy surface for an isolated XY molecule as a function of the bond lengths in the molecule, and V_I is an interaction energy. We then calculate various properties by either finding the saddle point energy analytically or by correlating the terms in the potential to activation energy data.

One of the difficulties at present is that it is difficult to predict V_I without using detailed ab initio calculations. In recent papers, we have been using the approximation

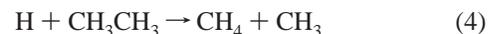
$$V_I = V_i \quad (3)$$

where V_i is the energy to move the reactants close enough to react without distorting any bonds in the reactants. This approximation shows reasonable correlation to rate data.

Unfortunately, V_i is also largely unknown. There are many potentials for the interaction of hydrocarbons with other hydrocarbons,^{5–10} hydrocarbons with solvents,^{11–16} and other species.^{17–23} However, we are not aware of any published

potentials for the interaction of a radical with a hydrocarbon at the distance range of interest during reactions, which is 1 to 2 angstroms.

The purpose of the paper here is to use ab initio methods to calculate V_i for a simple example reaction



The repulsive part of the potential will be fitted to a number of approximate potential functions so we have a function that can be used as described in refs 4 and 29.

Methods

All calculations in this work were done using the GAUSSIAN 94 and GAUSSIAN 98^{24,25} software packages. Calculations were done using a number of basis sets and theoretical methods. All of the calculations were done using a fixed geometry for the ethane with a carbon–carbon bond length of 1.5243 Å and a carbon–hydrogen bond length of 1.0928 Å. The incoming hydrogen was assumed to approach the ethane along the C–C axis since other calculations have shown that that is the optimal reaction pathway. Spin contamination was not a significant problem in the MP2 calculations. Here $\langle s \rangle^2$ was typically between 0.75 and 0.751 except at the closest distances, where $\langle s \rangle^2$ grew to 0.762. Nevertheless, spin projection was used to correct the spin contamination.

The ab initio results were fit to a number of different potentials:^{26–28} a Lennard-Jones potential

$$V_i(r) = 4w \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (5)$$

a Kihara potential

$$V_i(r) = 4w \left(\left(\frac{\sigma - \delta}{r - \delta} \right)^{12} - \left(\frac{\sigma - \delta}{r - \delta} \right)^6 \right) \quad (6)$$

a Mie 9–6 potential

* To whom correspondence should be sent.

TABLE 1: V_i , the Energy to Bring the Reactants Together, Calculated at a Variety of Levels of Theory^a

method	V_i , kcal/mol															
	$r=1 \text{ \AA}$	$r=1.25 \text{ \AA}$	$r=1.5 \text{ \AA}$	$r=2.0 \text{ \AA}$	$r=2.25 \text{ \AA}$	$r=2.5 \text{ \AA}$	$r=2.75 \text{ \AA}$	$r=3.0 \text{ \AA}$	$r=3.25 \text{ \AA}$	$r=3.5 \text{ \AA}$	$r=3.75 \text{ \AA}$	$r=4.0 \text{ \AA}$	$r=4.25 \text{ \AA}$	$r=4.5 \text{ \AA}$	$r=4.75 \text{ \AA}$	
PMP2/6-31G*	123.64	72.20	40.216	10.928	5.345	2.50	1.11	0.458	0.029	0.029	-0.018	-0.027	-0.02071	-0.01242	-0.00628	
PMP2/6-311G*	107.05	61.69	34.168	9.562	4.729	2.21	0.973	0.398	0.041	0.041	0.001	-0.012	-0.01406	-0.01268	-0.01023	
PMP2/6-311+G*	104.04	60.99	33.999	9.551	4.733	2.22	0.976	0.397	0.033	0.033	-0.010	-0.023	-0.0246	-0.0219	-0.01801	
PMP2/6-311(2df,p)	106.03	61.25	33.714	9.149	4.491	2.09	0.906	0.359	0.027	0.027	-0.001	-0.017	-0.01669	-0.01406	-0.01098	
PMP2/6-311++G**	102.97	60.79	33.889	9.615	4.682	2.18	0.943	0.371	0.118	0.012	-0.025	-0.035	-0.03257	-0.02717	-0.02146	
PMP2/6-311+G(3df,2p)	101.22	59.51	32.898	8.679	4.082	1.76	0.666	0.193	0.010	-0.047	-0.057	-0.052	-0.04273	-0.03389	-0.02642	
PMP2/aug-cc-pVZT	98.76	57.99	31.785	8.073	3.674	1.50	0.492	0.067	-0.085	-0.121	-0.114	-0.094	-0.07373	-0.05579	-0.04135	
MP4sdtq(fc)/6-311G**	107.51	61.42	33.686	9.289	4.548	2.09	0.900	0.355	0.120	0.026	-0.008	-0.017	-0.01713	-0.01456	-0.01148	
MP4sdtq(fc)/6-311+G**	104.51	60.71	33.516	9.281	4.554	2.10	0.902	0.353	0.114	0.015	-0.022	-0.032	-0.03125	-0.02667	-0.0214	
MP4sdtq(fc)/6-311G(2df,p)	106.73	60.98	33.219	8.845	4.291	1.96	0.827	0.313	0.096	0.012	-0.016	-0.022	-0.01977	-0.01594	-0.01217	
QCISD(t)/6-311G*	107.18	61.11	33.388	9.159	4.481	2.06	0.886	0.349	0.118	0.025	-0.008	-0.017	-0.01701	-0.01437	-0.0113	
CCSD/6-311++G**	104.71	61.04	33.637	9.268	4.531	2.08	0.881	0.332	0.092	-0.005	-0.037	-0.043	-0.03853	-0.03138	-0.02441	
CCSD(T)/6-311++G**	103.32	60.21	33.083	9.080	4.426	2.02	0.847	0.312	0.080	-0.013	-0.043	-0.047	-0.0416	-0.03363	-0.02604	
G2	100.85	60.93	34.459	9.740	4.901	2.37	1.103	0.525	0.258	0.131	0.064	0.008	-0.02471	-0.03881	-0.02973	

^a All calculations were done at $r_{CC} = 1.5243 \text{ \AA}$, $r_{CH} = 1.0928 \text{ \AA}$.

$$V_i(r) = 4w \left(\left(\frac{\sigma}{r} \right)^9 - \left(\frac{\sigma}{r} \right)^6 \right) \quad (7)$$

a Morse potential

$$V_i(r) = w(\exp(-2\alpha(r - \sigma)) - 2\exp(-\alpha(r - \sigma))) \quad (8)$$

an anti-Morse potential

$$V_i(r) = w(\exp(-2\alpha(r - \sigma)) + 2\exp(-\alpha(r - \sigma))) \quad (9)$$

an exponential-6 potential

$$V_i(r) = \left(\frac{w}{1 - (6/\alpha\sigma)} \right) \left(\frac{6}{\alpha\sigma} \exp(\alpha(\sigma - r)) - \left(\frac{\sigma}{r} \right)^6 \right) \quad (10)$$

and a simple exponential potential

$$V_i(r) = w(\exp(-\alpha r)) \quad (11)$$

In eqs 5 through 11, $V_i(r)$ is the potential, r is the distance from the incoming hydrogen atom to the carbon atom in the ethane, and w , α , δ , and σ are parameters. We also considered our own potential that we will refer to as the BM potential

$$V_i(r) = \left(\frac{w}{1 - (6/\alpha\sigma)} \right) \left(\frac{6}{\alpha\sigma} \exp(\alpha(\sigma - r)) - \left(\frac{\sigma}{r} \right)^6 \left(1 - \exp\left(-\frac{r}{\sigma}\right) \right) \right) \quad (12)$$

Equation 12 is a damped version of the exponential-6 potential. We used the simple exponential damping function suggested by Stone²⁷ rather than the more complex damping function suggested by others because this function fit our data better.

All fitting parameters in the potential models were fit using a search procedure to minimize the sum of the absolute error at each of the ab initio points. This ensured that we followed the potential in the region between 1 and 2 angstroms since most transition state lengths are within this range. We also tried weighting the errors by $\exp(r)$. The latter procedure gave better

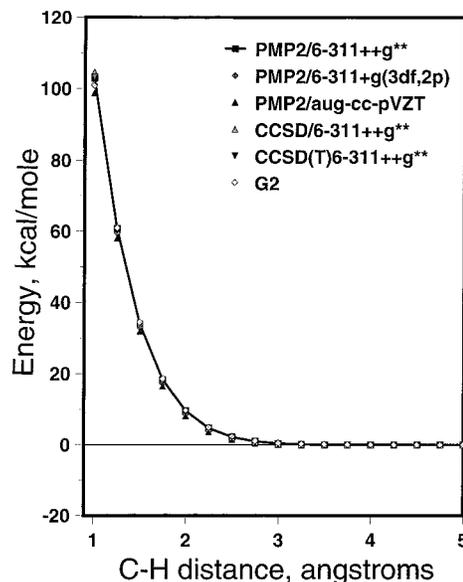


Figure 1. PMP2/6-311++G**, PMP2/6-311+g(3df,2p), PMP2/aug-cc-pVZT, CCSD/6-311++G**, CCSD(T)/6-311++G**, and G2 interaction energy in kcal/mol as a function of the H-C distance in angstroms.

fits in the well region without degrading the performance in the repulsive core.

Results

Table 1 shows the key ab initio results in this paper: $V_i(r)$ calculated at a variety of levels of theory. The energies in the table were scaled to zero energy at infinitely separated hydrogen and ethane. $V_i(r)$ looks qualitatively the same at all of the levels of theory. There is always a shallow well at modest distances and a strong repulsion at shorter distances. Generally, as the size of the basis set is increased, the minimum in the potential moves to shorter distances and the repulsive potential is less

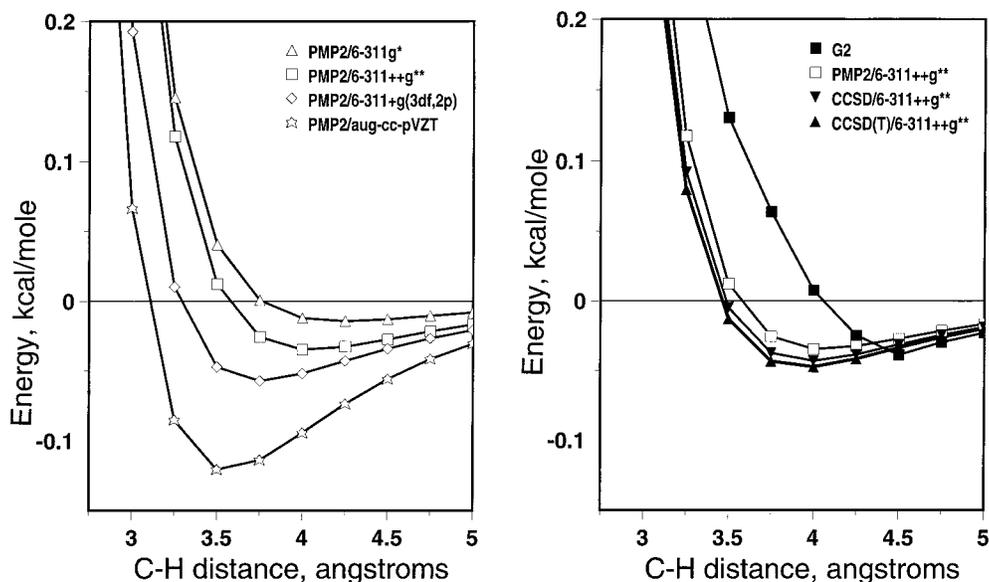


Figure 2. Expanded view of the attractive region in Figure 1. (A) changing basis set; (B) changing method.

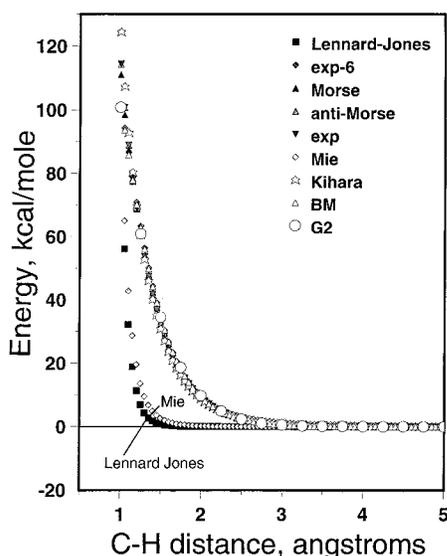


Figure 3. Comparison of the G-2 potential to those calculated from the Lennard-Jones potential, the Mie potential, the Morse potential, the anti-Morse potential, the exponential-6 potential, the BM potential, and an exponential repulsion. Potential parameters are given in Table 2.

stiff. At the PMP2/aug-cc-pVTZ level, the minimum is at 3.5 Å and the well depth is 0.12 kcal/mol.

We have also done MP4, CCSD, and CCSD(T) calculations using moderate sized basis sets. Results are also given in Table 1. If we compare calculations done using the same basis set, we find that the CCSD, CCSD(T), MP4, and PMP2 calculations all give energies within a few percent of each other. The major differences are due to basis set. Larger basis sets give deeper wells and less repulsive cores. There also is a smaller effect of the calculational method. CCSD(T) well depths are slightly larger than MP2 well depths.

We also did G-2 calculations. G-2 calculations are different than the rest in that they add on the zero-point energy. The zero-point energy tends to shift the minimum in the potential to longer distances. At the G-2 level, the well has shifted to 4.5 Å and the well depth has decreased to 0.038 kcal/mol.

Figure 1 shows plots of the CCSD(T)/6-311++G**, G-2, PMP2/6-311G*, PMP2/6-311G* and PMP2/aug-cc-pVTZ po-

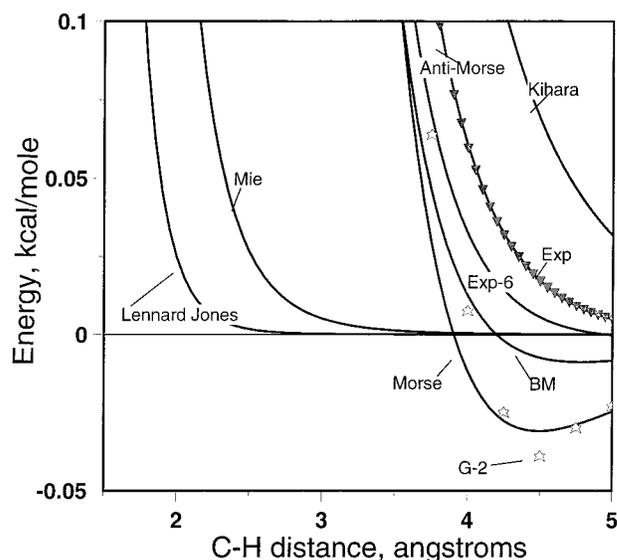


Figure 4. Expanded view of the attractive region in Figure 3 using the second set of parameters in Table 2.

tentials. There are no visible differences between the potentials. All show similar features at the distances shown.

Figure 2 shows an expanded version of the results in Figure 1. Notice that the various methods give different results at long distances. Generally, the well depth in the PMP2 calculation increases as the basis set size increases from 6-311G* to aug-cc-pVTZ. The MP2/6-311++G**, CCSD/6-311++G**, and CCSD(T)/6-311++G** results are all similar, but there is a trend that the well depth increases slightly from MP2 to CCSD(T). The G-2 potential is different than all of the rest. The main difference is associated with the zero-point energy corrections in G-2.

Figure 3 compares the G-2 potential to the analytical potentials from eqs 4–11. There are two ways that we have done the fitting, one minimizing $\sum|\text{error}|$, the other minimizing $\sum(\text{exp}(r) \times |\text{error}|)$. Table 2 gives the parameters for each case while Figure 3 plots the results. Generally, the Lennard-Jones and Mie functions are too steep, while the other potentials fit fairly well. There is a small problem with the Kihara potential

TABLE 2: Best Fits to the G-2 Potential

	Lennard-Jones ^a	Mie ^a	Kihara	exp-6	Morse	anti-Morse	exponential	BM
Potential Parameters Calculated by Minimizing $\sum \text{error} $								
w , kcal/mol	2.46×10^{-14}	1.97×10^{-10}	1.87×10^0	2.61×10^{-4}	3.90×10^{-2}	5.82×10^{-4}	$9.58 \times 10^{+2}$	7.35×10^{-3}
α , \AA^{-1}				2.54	1.16	1.13	2.25	2.53
σ , \AA	20	20	3.29	6.37	4.53	6.32		4.89
δ , \AA			-4.58					
$\sum \text{error} $	125.40	116.14	12.38	2.91	9.26	11.24	10.92	2.43
Potential Parameters Calculated by Minimizing $\sum(\exp(r) \times \text{error})$								
w , kcal/mol	2.46×10^{-14}	1.97×10^{-10}	1.46×10^{-5}	1.02×10^{-3}	3.08×10^{-2}	2.01×10^{-7}	$1.42 \times 10^{+3}$	1.98×10^{-2}
α , \AA^{-1}				2.71	1.18	1.26	2.52	2.67
σ , \AA	20	20	12.24	5.54	4.49	9.01		4.34
δ , \AA			-3.04					
$\sum(\exp(r) \times \text{error})$	650.32	613.41	203.95	41.08	56.6	101.9	101.8	28.7

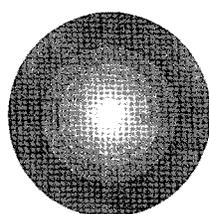
^a Note: σ in the Lennard-Jones and Mie potentials were constrained to be real numbers less than 20. Larger values of σ do not improve the fit. However, one can obtain better fits if one allows σ to be a complex number.

TABLE 3: Best Fits to the PMP2/Aug-cc-pVTZ Potential^a

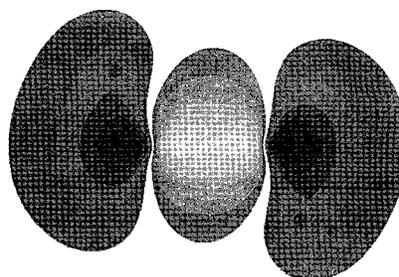
	Lennard-Jones	Mie	Kihara	exp-6	Morse	anti-Morse	exponential	BM
Potential Parameters Calculated by Minimizing $\sum \text{error} $								
w , kcal/mol	2.41×10^{-14}	1.93×10^{-10}	-4.02×10^0	6.10×10^{-4}	3.84×10^{-1}	7.74×10^{-4}	$9.55 \times 10^{+2}$	1.57×10^{-2}
α , \AA^{-1}				2.72	1.18	1.20	2.27	2.73
σ , \AA	20	20	0.802	5.67	6.24	6.88		4.33
δ , \AA			0.52					
$\sum \text{error} $	113.00	103.94	11.73	4.72	12.26	12.57	13.90	4.17
Potential Parameters Calculated by Minimizing $\sum(\exp(r) \times \text{error})$								
w , kcal/mol	2.41×10^{-14}	1.93×10^{-10}	1.46×10^{-5}	2.74×10^{-3}	1.16×10^{-2}	2.59×10^{-7}	$1.59 \times 10^{+3}$	7.63×10^{-2}
α , \AA^{-1}				2.72	1.21	1.34	2.65	2.95
σ , \AA	20	20	12.24	4.85	3.09	9.01		3.54
δ , \AA			-3.40					
$\sum(\exp(r) \times \text{error})$	564.24	533.38	140.42	76.13	67.06	150.96	140.68	56.2

^a Note: σ in the Lennard-Jones and Mie potentials were constrained to be real numbers less than 20. Larger values of σ do not improve the fit. However, one can obtain better fits if one allows the σ parameters to be a complex number.

Reactants far apart

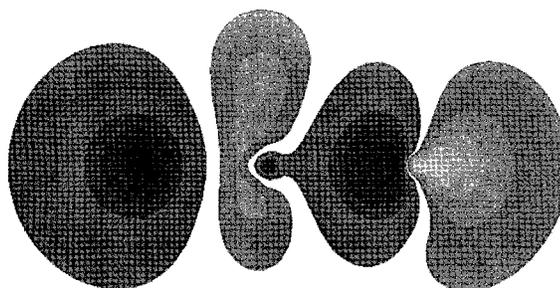


hydrogen



ethane

$$r_{\text{CH}} = 1.5 \text{ \AA}$$

**Figure 5.** Changes in the HOMO as the hydrogen atom approaches the ethane.

in that a negative value of δ is found from the fit. However, even the Kihara potential fits the ab initio results reasonably well.

Table 2 shows the absolute errors with each potential. It happens that the BM potential fits slightly better than the rest, at least in the repulsive region.

We have also fit the PMP2/aug-cc-pVTZ potential with each of the potentials, and the results are given in Table 3. Generally, the Lennard-Jones and Mie functions are too steep, while the other potentials fit fairly well. Again, there is a small problem with the Kihara potential in that a negative value of δ is found. The Kihara potential still fits the ab initio reasonably well.

Table 3 also shows the absolute errors with each potential. Once again, the BM potential fits slightly better than the others, at least in the repulsive part of the potential.

Figure 4 shows a blowup of the attractive region of the potential. Notice that the Morse potential fits reasonably in the attractive part of the potential, even though the parameters in the potentials were optimized to the repulsive core. The BM potential shows a well at the right distance, but the well depth is too shallow. None of the other potentials can simultaneously fit in the well and in the repulsive core.

Once can of course fit each of the potentials in the attractive region, but then the potentials do not fit the repulsive core.

Discussion

The results here were basically as expected. One can calculate a potential with ab initio methods. MP2 and CCSD(T) results are within a few percent of each other at the same basis sets but the results are basis set dependent. The aug-cc-pVTZ results are below the 6-11++G(3df,2p) results. Generally, we find that the calculated well depth increases as we add more polarization functions to the basis set. This result suggests that polarization forces are controlling the well. In contrast, in the region from 1 to 2 Å the results are largely independent of the basis set. Consequently polarization forces are less important at short distances.

We also found that the repulsive parts of the ab initio potentials are easily fit with the exponential-6, the Morse, and the BM potentials. The Kihara potential also fit the ab initio data, but the Lennard-Jones and Mie potentials did not fit as well. Surprisingly, only the Morse potential fit accurately in both the attractive region and the repulsive core. We were expecting other potentials to fit too, but the results do not show good agreement.

Another surprise was that the BM potential fit the repulsive part of the potential slightly better than the other potentials examined here. It is well known that damped exponential-6 potentials fit better than simple exponential-6 potentials at short distances. However, we have found that we need to damp the dispersive potential out to substantially longer distances than had previously been supposed.

Physically, the current generation of damping factors is calculated assuming that the wave function of the reactants is hardly perturbed. However, in our calculations we are getting to short enough distances that diffuse and polarization functions mix into the ground-state wave function. This produces substantial distortions of the electron clouds and a reduction in the dispersive interaction.

For example, Figure 5 shows how the HOMO changes as the reactants come together. One should not put too much faith in these pictures since orbital pictures are not unique. Still, one finds that the MOs of the system are substantially changed at the distances in our calculations.

Conclusions

In summary, in this paper we have used a variety of ab initio methods to calculate the potential for the interaction of a hydrogen atom with an ethane molecule when the hydrogen approaches the ethane along the ethane's C–C axis. At the distances of interest, the computations quickly converged with increasing basis set size and with the complexity of the computational procedure. However, at longer distances, giant basis sets were needed to get reasonable results. The results

were well fit with a Morse potential. The exponential-6 and Kihara potential also fit the ab initio data, but the Lennard-Jones and Mie potentials did not fit as well. We also found that damping the exponential-6 potential gave an even better fit in the repulsive region. The Morse potential is still best overall. These results provide potentials which can be used to estimate activation barriers as described in refs 4 and 29.

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