

# **Influence of the Intermolecular Potential Energy Surface on Collisional Energy Transfer in the CO<sub>2</sub>-Ar System**



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# Introduction

How reactant molecules acquire and lose their energy via collisions is of much relevance to the further development of chemical reaction theory. One important, largely unanswered, question is how does *collisional energy transfer (CET)* between a highly vibrationally excited reactant molecule and a thermal medium molecule depend on the nature of the *potential energy surface (PES)*? The PES of a reactant-medium collision system comprises:

- *The intramolecular interaction* within each collision partner (between the component atoms): in general calculations so far indicate that the dependence of CET on the intramolecular PES is weaker than on the intermolecular interaction.
- *The intermolecular interaction* between the collision partners: calculations suggested that the steepness of the wall and the depth of the well play crucial roles on the extent of CET at high and low temperatures respectively.

In the present work, the focus is on  
*how the nature of the intermolecular PES affects CET.*

*Classical molecular dynamics (MD)* is a useful way of studying the detailed mechanisms of CET. To perform these MD simulations a global analytic PES is required. Thus, a series of computational studies of our chosen (CO<sub>2</sub>-Ar) collision system was performed. Results of various *ab initio* and DFT techniques were fitted to yield a range of different models of the intermolecular PES.

MD simulations run on these model surfaces explored the effect of subtle differences in shape of the intermolecular PES on the CET.

A natural question arises: *how good does the fit need to be for the MD simulation to produce meaningful results?*

# The Potential Energy Surface

We have chosen a simple test system, the collisional activation/deactivation of highly rovibrationally excited CO<sub>2</sub> molecule by a thermal Ar atom. This was motivated by the existence of a wide range of experimentally derived intermolecular PESs.

Some previous experimental and computational studies have been performed but they focussed largely on the high energy collisions of Ar with thermal CO<sub>2</sub> or on the effect of anharmonicity and resonances and hence are not closely relevant to the aims of the present study. It would be a natural progression of the present study to include similar systems, such as the collision of thermal noble gas atoms with highly excited molecules of SO<sub>2</sub> or CS<sub>2</sub>, in further shape work, particularly because of the existence of extensive experimental data on CET and the lack of direct experimental or *ab initio* information on the shape of the intermolecular PES.

All of these CO<sub>2</sub>-Ar PESs assumed some functional form for the interaction which was then least-squares fitted to the experimental data. In some cases the functional form of the interaction was based on theoretical or previously calculated data. These PESs as they stand are unsuitable for performing classical MD simulations, as they include no motions of the CO<sub>2</sub> fragment.

In order to add CO<sub>2</sub> motion dependence, we have assumed separation of the PES into **intramolecular** and **intermolecular parts**, as is common in CET studies.

For the internal motions of the CO<sub>2</sub> fragment we have used the potential used previously for CET studies by Suzukawa *et al.* This potential comprises a sum of one Morse function for each C-O bond, a quadratic bending term and a quadratic bond coupling term. For the intermolecular part of the PES we have used a sum of **three pair-wise additive functions**, again a common practice in CET studies. The functional forms used are standard atom-centred radial potential functions, such as the Lennard-Jones n-6, Buckingham exp- :6 and Morse functions.

# ***Ab initio* and DFT calculations**

The parameters for the various radial functions were obtained by fitting to a set of *ab initio* data. Our assumptions about the interaction meant that we could freeze the CO<sub>2</sub> fragment in the linear configuration with a C-O bond length of 1.16 Å. Freezing the CO<sub>2</sub> fragment reduces the number of scanned degrees of freedom in the system from six to two.

Two approaches have been taken to generating the *ab initio* surface in this work. On one hand we have used the [GAUSSIAN 94 suite](#) of programs to generate samplings of the PES within the Møller-Plesset perturbation theory framework up to fourth order. The second approach to generating the PES sample points was to use [density functional theory \(DFT\)](#), implemented in the [Amsterdam Density Functional \(ADF\) package](#). Both approaches used the supermolecule method of generating the interaction energy profile.

The main PES data used was generated by the GAUSSIAN package and is shown in Figure 1. This *ab initio* surface was calculated at the MP4/6-311+G(2d) level of theory. The 6-311+G(2d) basis is relatively large, with 27 Gaussian basis functions centred on each atom. The DFT surface was calculated using the ADF package with the Vosko, Wilk and Nusair Local Density Approximation (VWN LDA) and Perdew-Wang 91 Generalised Gradient Approximation corrected functional. The basis set used was an ADF type V basis, which is a triple-zeta set of Slater type orbitals with two polarisation functions per atom. The ADF and Gaussian basis sets used are of similar quality. A PES from a lower level MP2/6-311+G(2d) calculation was also used. These surfaces are qualitatively similar to the experimentally derived potentials.

## The intermolecular potential energy surface

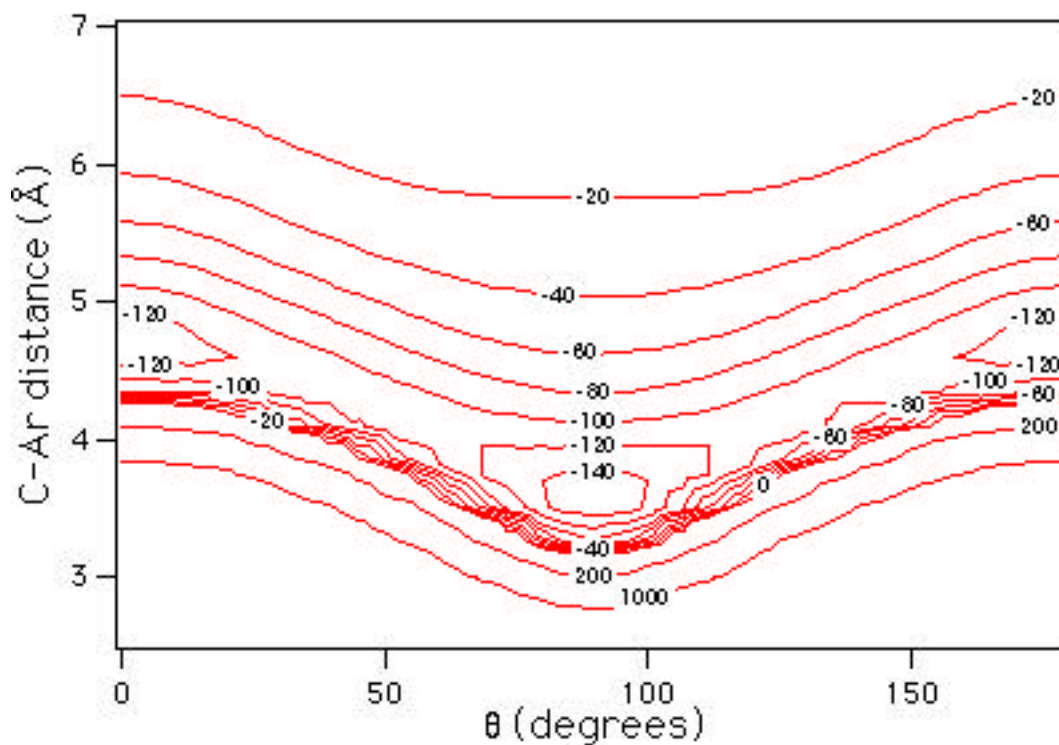


Figure 1. Contour plot of the intermolecular PES of CO<sub>2</sub>-Ar calculated at the MP4/6-311+G(2d) level as a function of C-Ar distance and angle from the linear approach. Contours are in cm<sup>-1</sup>.

# Depth (cm<sup>-1</sup>) of the intermolecular PES (and C-Ar separation (Å)) for T-shaped and linear geometries of CO<sub>2</sub>-Ar

The potential well is 157 cm<sup>-1</sup> deep at the potential minimum for the MP2 and MP4 surfaces (corresponding to the T-shaped complex geometry), and 177 cm<sup>-1</sup> deep for the DFT/PW91 surface. The MP2 and MP4 surfaces vary in the depth of the well in the linear geometry, being 128 cm<sup>-1</sup> and 135 cm<sup>-1</sup> respectively. The corresponding DFT/PW91 surface depth is 137 cm<sup>-1</sup>.

The well depths in the T-shaped geometry for the current MP4 calculations are too low (by 25%) when compared to the recent MP4 calculations of Marshall *et al.* They used an extended basis set supplied with bond functions and yielded well depths consistent with the recent experimentally derived surfaces of Hutson *et al.*

Data Source	T-shaped	Linear
<b>this work</b>		
MP2/6-311+G(2d)	157 (3.541)	128
MP4/6-311+G(2d)	157 (3.547)	135
ADF-DFT/PW91	177 (3.721)	137
<b>Marshall <i>et al.</i></b>		
MP4/Sdf(b-ext)	210 (3.456)	117 (4.763)
fitted	210 (3.475)	113 (4.708)
<b>Hutson <i>et al.</i></b>		
single repulsion model	204.16 (3.416)	126.30 (4.572)
split repulsion model	202.57 (3.417)	114.99 (4.589)

## ***Ab initio*, DFT and empirical pair potentials**

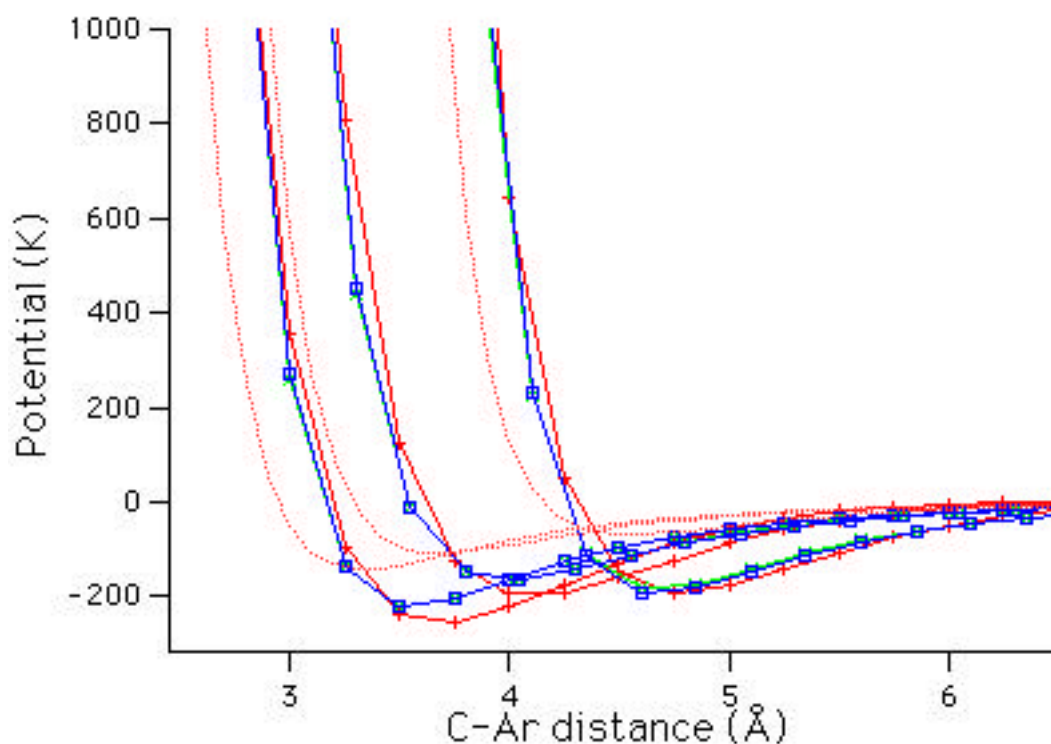


Figure 2. Comparison of 3 slices through the PES originating at the carbon atom at 0, 60 and 90 degrees from the linear approach generated with:

Gaussian 94

MP4/6-311+G(2d)

(blue squares)

MP2/6-311+G(2d)

(green crosses)

ADF

(red plusses)

noble gas Lennard-Jones interaction

(orange dashed)

## Fit of pair potentials to *ab initio* data

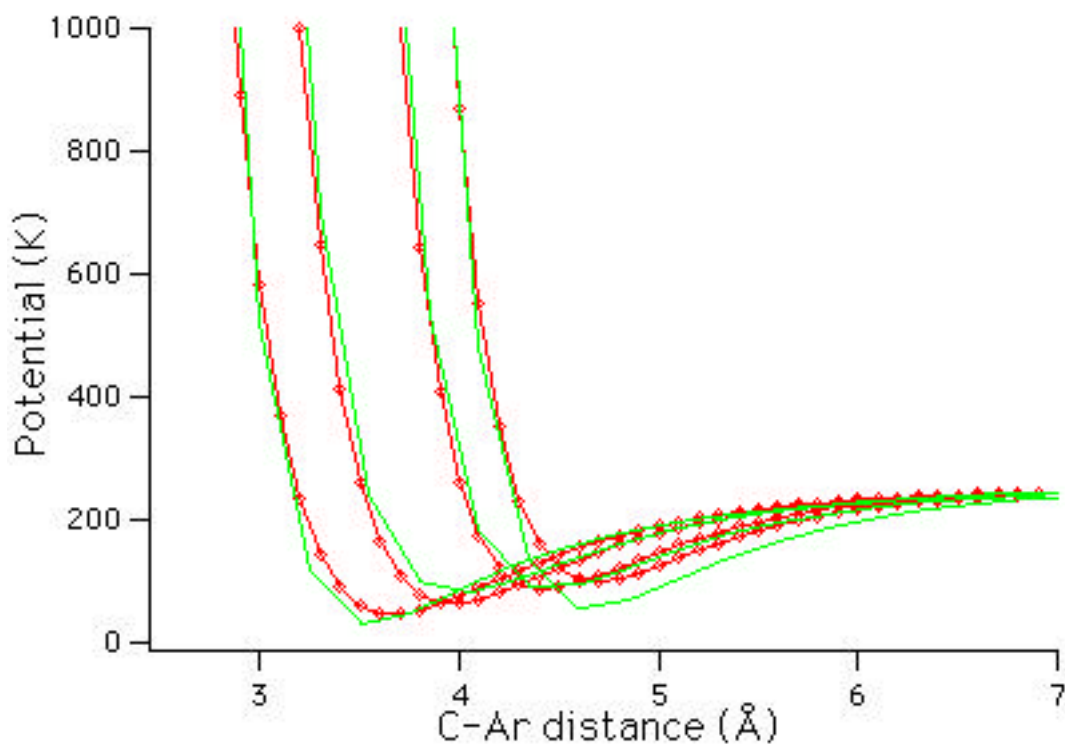


Figure 3. Comparison of:

MP4 data (red diamonds)

Morse fitted potential (green lines)

Four slices through the surface from the carbon atom. Slices at 0, 30, 60 and 90 degrees from the linear approach.

# Molecular dynamics calculations

For each PES a series of MD simulations was performed.

## Initial State Selection

- CO<sub>2</sub> fragment was set up in an initial state selected from the microcanonical ensemble (EMS).
- The argon atom for each trajectory was set up with an initial relative velocity selected from a thermal distribution and an impact parameter selected from a uniform distribution with an upper limit of  $b_{\max} = 15 \text{ \AA}$ .

## Trajectory Integration

The trajectories were integrated using a vectorised Velocity-Verlet integrator until all (or all but a few) of the argon atoms in the batch of trajectories were more than 15 Å from the centre of mass of the CO<sub>2</sub> fragment. This was up to 61 ps of simulation time for some of the systems. We checked that our average energy transfer moments are converged with increasing maximum impact parameter and decreasing integration step size.

## Statistical Analysis

The main quantities used to study the energy transfer as a function of initial internal energy  $E$  and bath temperature  $T$  were the average energy transfer per collision  $\langle E \rangle$  and the average squared energy transfer  $\langle E^2 \rangle$ .

## Conditions Studied

The initial internal energy of the CO<sub>2</sub> fragment was set at five different values from 5 kcal/mol to 100 kcal/mol and the argon bath was sampled at four temperatures from 300 K to 1800 K. This gives a total of 20 batches of 10000 trajectories for each PES.

## Collisional energy transfer kernel $P(E'|E)$

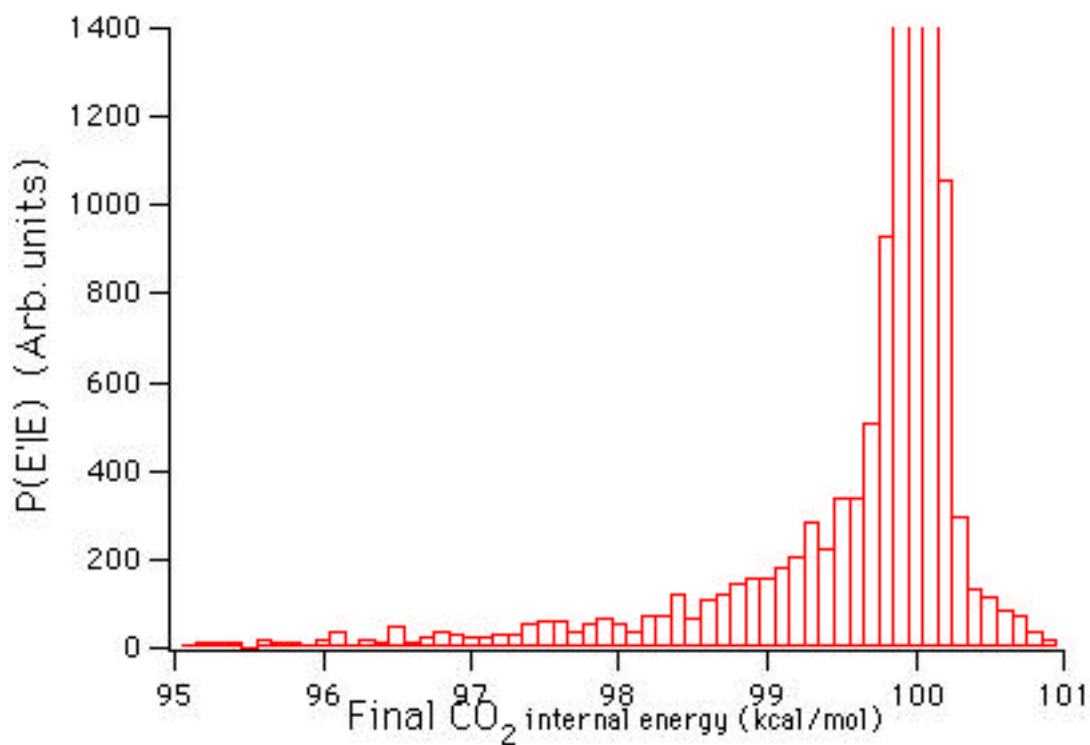


Figure 4.  $P(E'|E)$  for the noble gas Lennard-Jones interaction. Initial internal energy 100 kcal/mol. Bath temperature 300 K.

## Average energy transfer $\langle E \rangle$ versus $T$ for various pair potentials (original fit)

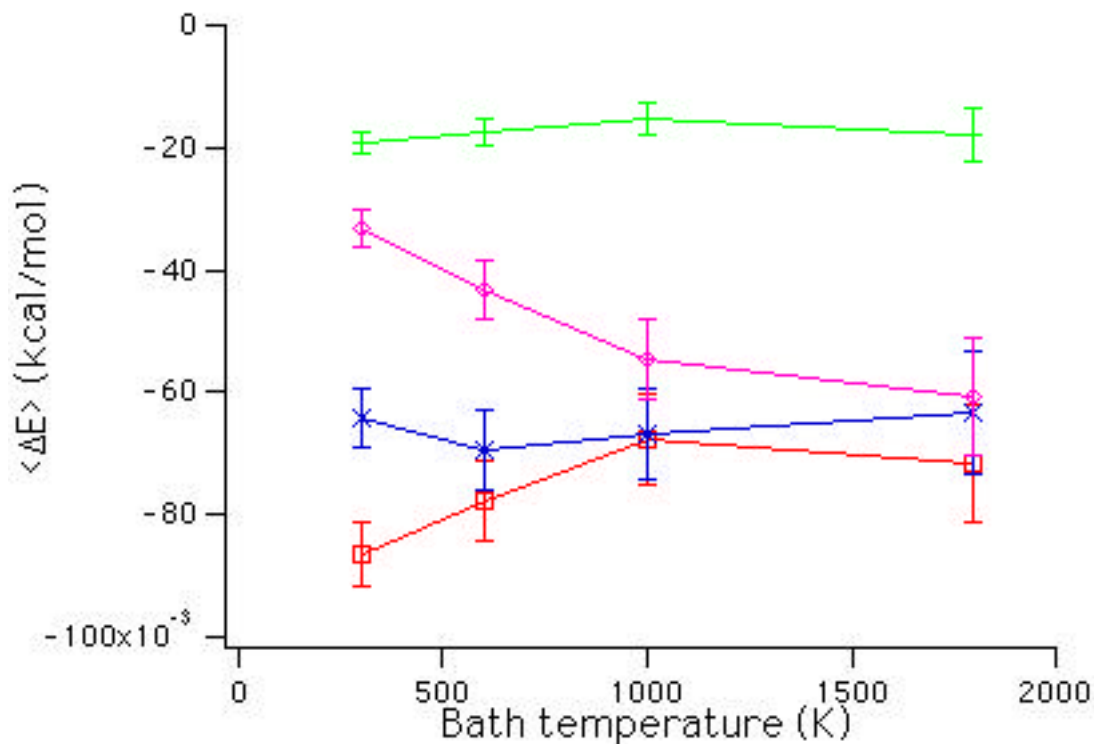


Figure 5. First energy transfer moment as a function of bath temperature. Initial internal carbon dioxide energy 100 kcal/mol.

Original fit potentials of:

exp- :n	(green crosses)
Morse	(purple diamonds)
Lennard-Jones	(blue crosses)
Buckingham exp- :6	(red crosses)

## Average energy transfer $\langle E \rangle$ versus $T$ for a PES using Morse functions

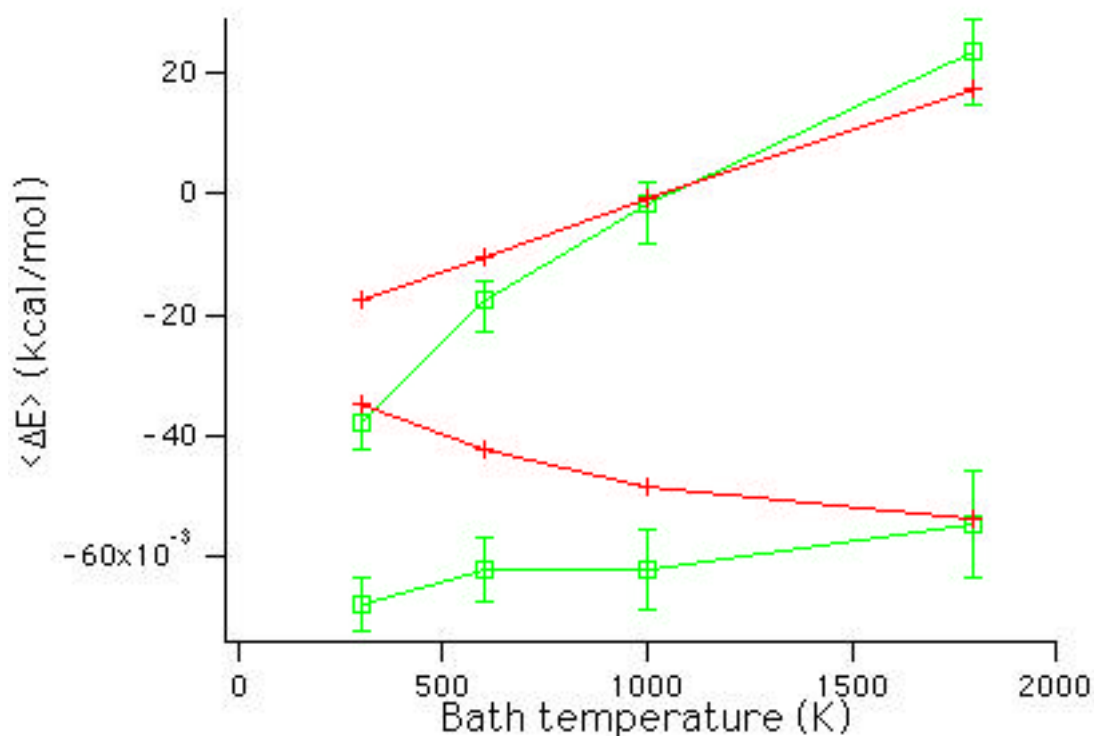


Figure 6. Average energy transfer as a function of bath temperature.

Original (red crosses) and refined (green squares) Morse functional forms.

Initial internal energy of:

15 kcal/mol (upper set)

75 kcal/mol (lower set)

Refined fit excluded *ab initio* points above 0.01 hartree.

## Average energy transfer $\langle E^2 \rangle$ versus T for a PES using Morse functions

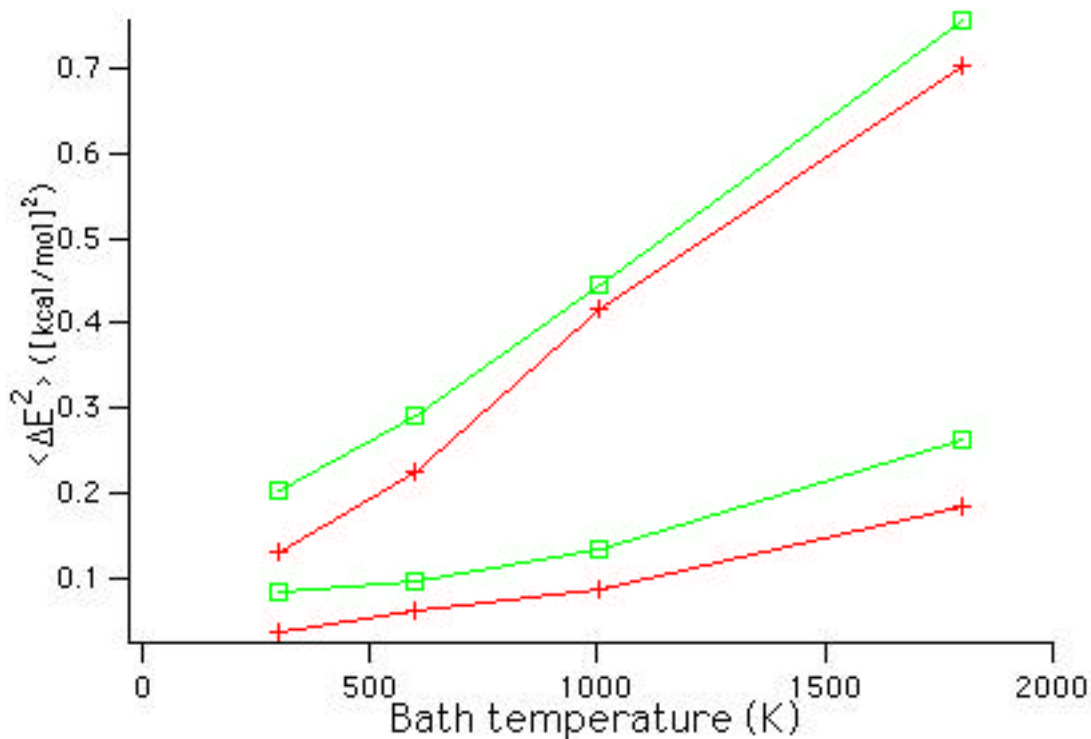


Figure 7. Second moment of energy transfer as a function of bath temperature.

Original (red crosses) and refined (green squares) Morse functional forms.

Initial internal energy of:

15 kcal/mol (upper set)

75 kcal/mol (lower set)

Refined fit excluded *ab initio* points above 0.01 hartree.

## Average energy transfer $\langle E \rangle$ versus $T$ for various pair potentials (refined fit)

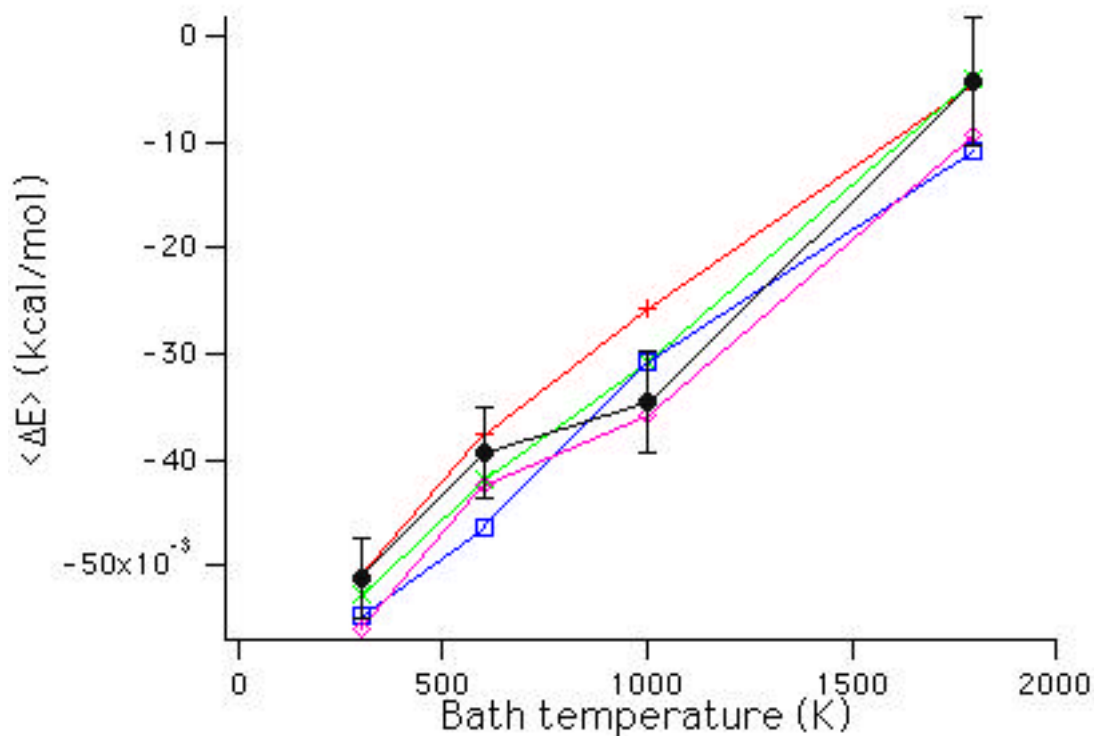


Figure 8. Average energy transfer as a function of bath temperature. Initial internal energy 30 kcal/mol.

Intermolecular potentials:

- Noble gas Lennard-Jones (grey circles)
- ADF Lennard-Jones (red plusses)
- MP4 Lennard-Jones (green crosses)
- MP4 Morse (blue squares)
- MP2 Lennard-Jones (purple diamonds)

Refined fit excluded *ab initio* points above 0.01 hartree.

# Summary of Results

• **The pair potential approximation:** The energy transfer moments converge when the different pairwise functional forms are fitted well to the important regions of the potential.

• **DFT vs *ab initio*:** The energy transfer moments calculated from the DFT/PW91 potential (Figure 8) are in excellent agreement with the results using *ab initio* potentials.

It is clear that DFT does not give reliable results for properties such as intermolecular well depths (e.g. see Table 1) due to the poor handling of the dispersion energy in current functionals. The consensus view is that DFT is of little practical use for the calculation of intermolecular potentials.

However, in further studies, we have noted that, at typical temperatures ( $T > 300$  K) the repulsive wall of the intermolecular potential generally plays a much larger role in the efficiency of CET than the well. Initial trends shown in the present and further calculations indicate that DFT methods may be suitable for approximate/inexpensive estimation of CET.

• **Quality of fit:** The energy transfer results are sensitive to the quality of the fit of the functional forms to the *ab initio* data. With this in mind, the success of the noble gas-based Lennard-Jones interactions is remarkable given that it is markedly different from the other PESs.

• **Well effects:** The lower temperature energy transfer results are sensitive to the potential well region, as expected. The data has not been analysed for the dependence on the angle- and time-averaged steepness of the repulsive wall, or the curvature of the wall.

• **Further calculations:** have revealed a strong correlation of energy transfer with the steepness of the repulsive wall. We also plan to further investigate the pair-wise potential approximation and determine whether the experimentally derived potentials can be suitably expanded in terms of computationally inexpensive radially symmetric potentials.