

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

Terry J. Frankcombe  
Department of Chemistry  
Australian National University  
Canberra, ACT 0200, Australia

and

Harold W. Schranz  
Research School of Chemistry  
Australian National University  
Canberra, ACT 0200, Australia

How reactant molecules acquire and lose their energy via collisions is of much relevance to the further development of chemical reaction theory [1]. 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) [2]? The PES of a reactant-medium collision system can be crudely separated into two terms:

- *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 [2,3].
- *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 [2,3].

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 [2]. 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 [4]. 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. Results indicate a significant role in the efficiency of CET is played by the repulsive wall: the average steepness correlates well with the magnitude of the average energy transferred ( $\langle E \rangle$ ) [4,5].

[1] K. A. Holbrook, M. J. Pilling, and S. H. Robertson, *Unimolecular Reactions* (John Wiley & Sons, Chichester, 1996); *Vibrational Energy Transfer Involving Large and Small Molecules*, Vol. 2A, 2B, edited by J. R. Barker (JAI Press, 1995).

[2] S. Nordholm and H. W. Schranz, in *Advances in Chemical Kinetics and Dynamics*, Vol. 2A, edited by J. R. Barker (JAI Press, 1995), pp. 245-281; G. Lendvay and G. C. Schatz, in *Advances in Chemical Kinetics and Dynamics*, Vol. 2B, edited by J. R. Barker (JAI Press, 1995), pp. 481-513.

[3] H. Hippler, H. W. Schranz, and J. Troe, *J. Phys. Chem.* 90, 6158 (1986); H. W. Schranz and J. Troe, *J. Phys. Chem.* 90, 6168 (1986).

[4] T. J. Frankcombe, R. Stranger, and H. W. Schranz, *Internet Journal of Chemistry* 1, 12 (1998).

[5] T. J. Frankcombe and H. W. Schranz, work in progress.