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The intermolecular potential energy surface of CO₂-Ar and its effect on collisional energy transfer

Terry J. Frankcombe, Rob Stranger, Harold W. Schranz

*Research School of Chemistry
Australian National University
Canberra, ACT, 0200
Australia*

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Abstract:

Classical molecular dynamics (MD) is a useful way of studying intra- and inter-molecular energy transfer in gas-phase collisional processes. However to perform these MD simulations a global analytic potential energy surface (PES), which is not directly experimentally observable, is required to determine the forces on the constituent atoms of the colliding species. Often a functional form of the PES is assumed and the parameters adjusted until the surface reproduces a set of experimental observables.

We have used both conventional ab initio methods and density functional theory methods to generate points on the PES for the carbon dioxide-argon colliding system at different levels of theory. To the intermolecular part of these potential profiles we have fit a variety of simple functional forms. We used MD simulations to look at the effect of the subtle differences in shape of the PES on the average energy transferred per collision ($\langle\Delta E\rangle$) and higher energy transfer moments (such as $\langle\Delta E^2\rangle$). There were found to be significant quantitative differences between the energy transfer moments generated using the different functional forms, even when these forms were fit reasonably well to the same data.