Reply to a comment on: Angular momentum relaxation in binary collisions. Comparison of cross sections

Cynthia J. Jameson and A. Keith Jameson

Citation: The Journal of Chemical Physics **94**, 7565 (1991); doi: 10.1063/1.460143
View online: http://dx.doi.org/10.1063/1.460143
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/94/11?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Comment on: Angular momentum relaxation in binary collisions. Comparison of cross sections
J. Chem. Phys. **94**, 7564 (1991); 10.1063/1.460193

Angular momentum relaxation in binary collisions. Comparison of cross sections
J. Chem. Phys. **93**, 3237 (1990); 10.1063/1.458856

Relaxation cross sections for the rotational angular momentum vector in CF4
J. Chem. Phys. **89**, 866 (1988); 10.1063/1.455208

Reply to ‘‘Comment on ‘Zero angular momentum turns’’’
Am. J. Phys. **56**, 81 (1988); 10.1119/1.15438

Reply to ‘‘Comment on ‘Dirac states for unit position and momentum: Phase consistency of their angular momentum representations’ ’’a)
J. Chem. Phys. **78**, 2806 (1983); 10.1063/1.444998

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 35.8.11.3 On: Thu, 28 Jan 2016 07:51:47

Reply to a comment on: Angular momentum relaxation in binary collisions. Comparison of cross sections

Cynthia J. Jameson
Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

A. Keith Jameson
Department of Chemistry, Loyola University, Chicago, Illinois 60626

(Received 28 January 1991; accepted 20 February 1991)

In the cited paper[1] our intention was not to use a model to calculate absolute cross sections, our goal was to find some order in the seventy-odd cross sections that we had measured for linear molecules and spherical tops with various collision partners (other linear molecules, spherical tops, and rare gas atoms). We wanted to use a model without adjustable parameters, which would provide a broad characterization of the relative magnitudes of the cross sections, such as their dependence on moments of inertia, masses, etc. We wanted a model that could be applied to probes and projectiles which were linear molecules and spherical tops and that represents both the probe molecule and the projectile equivalently; we did not want to start out with the assumption that the characteristics of the projectile were less important than the characteristics of the probe. Chandler's model of rough hard spheres provides a correlation time for the angular velocity, which is identical to that for the angular momentum vector in the case of linear molecules and spherical tops.[2] The rare gas atoms cannot be represented appropriately by this model but it allows a representation of all the other projectiles we have used and all of the probe molecules, with no adjustable parameters. Had we used the model in Evans' paper,[3] we could represent only the linear probe molecules and none of the spherical tops. We actually now have data for seven spherical tops rather than the four in Ref. 1. Evans[3] begins with the assumption that the characteristics of the projectile are not as important as the probe molecule in determining the cross sections, so he represents all projectiles as smooth spheres and the moments of inertia of the projectiles do not enter into the picture at all. On the other hand, the rough hard spheres model treats both projectile and probe in the same way, so we could see to what extent the characteristics of the projectile affected the relative values of the cross sections for any given probe molecule.

Our observations are that the σ_J cross sections decrease monotonically with increasing temperature in all cases, contrary to what is indicated in Table I of Ref. 3. Chandler's exponential model[4] for the attractive part gives this qualitative behavior although it does not quite give the observed power law dependence in each case. This is to be expected because it is precisely the differences in the temperature dependences from one collision pair to another that tells us that the anisotropy of the potential is different for each collision pair.

Chandler's model is a simple model but within its limitations it can be applied to all the probe molecules we have studied; it treats both probe and projectile equivalently; there are no adjustable parameters; the exponential approximation incorporates attractive forces in a simple nonadjustable way. The model was very useful in comparing relative magnitudes of cross sections and was not used beyond its capabilities in our paper.

[1] C. J. Jameson and A. K. Jameson, J. Chem. Phys. **93**, 3237 (1990).
[2] D. Chandler, J. Chem. Phys. **60**, 3500, 3508 (1974).
[3] G. T. Evans, J. Chem. Phys. **86**, 3859 (1987).
[4] H. C. Andersen, D. Chandler, and J. D. Weeks, Adv. Chem. Phys. **34**, 105 (1976).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 35.8.11.3 On: Thu, 28 Jan 2016 07:51:47