Theory, Experiment, and the H + D_2 Reaction

Theofanis N. Kitsopoulos *et al.* (*1*) describe observations on the H + D_2 reaction obtained with the novel experimental technique of reaction product imaging. Experiments such as this are expected to contribute significantly toward our understanding of elementary chemical reactions, especially in cases where direct comparisons with theoretical calculations are possible. The original article shows a comparison of a quasi-classical trajectory (QCT) (*2*) study with the experiment. Here we add to the analysis by comparing our quantum results with the experimental observations.

Our quantum mechanical (QM) calculations were carried out for H + D_2 (*3*) with the use of a variational method for reactive scattering calculations that we have developed over the past several years (*4*). This method can be used to solve the Schrödinger equation for each partial wave of the H + D_2 system, and the resulting scattering matrices can then be combined to give integral and differential cross sections. In our earlier study we reported only integral cross sections (*3*), as no experimental differential cross sections were available. Partial wave scattering matrices were, however, saved from the calculations, and we have used these scattering matrices to reconstruct the present QM differential cross sections.

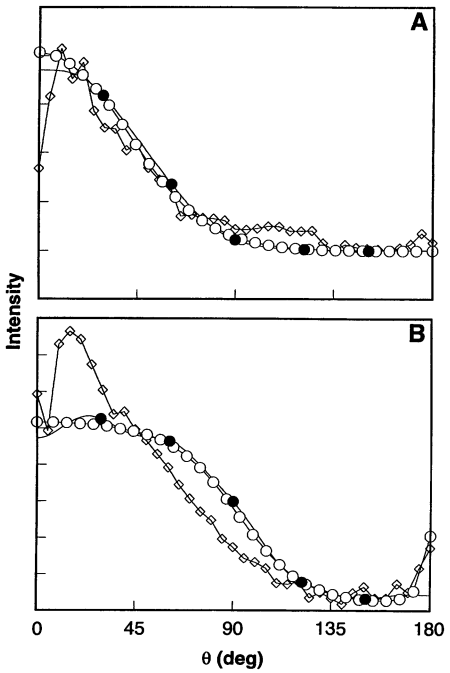

Fig. 1. Differential cross sections as a function of center-of-mass scattering angle for the H + D_2 → HD + D reaction, summed over final HD (v', j') states. (**A**) Collision energy of 0.54 eV. (**B**) Collision energy of 1.29 eV. The experiment in (*1*) is indicated (◇), the quasi-classical results of (*2*) are indicated (●), and the quantum mechanical results of (*3*) are indicated (○).

Our comparison (Fig. 1) includes experimental curves (*1*), QCT curves (*2*), and the present QM results. The QCT calculations were performed with the $D_2(v = 0, j = 0, 1, 2)$ states initially populated, and appropriate thermal averages were taken to simulate the experimental conditions (*2*). The present QM calculations were performed only for $D_2(v = 0, j = 0)$ (*3*) and should be interpreted with this caveat. Nevertheless, because the nuclear spin statistics of D_2 imply a 2 to 1 ratio of even to odd j states, the present $D_2(v = 0, j = 0)$ results should represent a good first approximation to the thermally averaged QM differential cross sections at the (rotationally cold) temperature that exists in a supersonic D_2 molecular beam (*1*).

The QM calculations (Fig. 1) agree remarkably well with the QCT calculations of Aoiz *et al.* (*2*) at both collision energies considered. Thus, the QM calculations do not significantly alter the conclusions of Kitsopoulos *et al.* (*1*). The fact that QCT calculations do so well for these light atom H + D_2 differential cross sections, even though they are averaged over all possible H + D_2 product states, is in itself impressive. Although the calculations agree with the experiment at the lower collision energy (0.54 eV; Fig. 1A), there are significant differences at the higher energy (1.29 eV; Fig. 1B). One possible explanation is that these differences are an artifact of the experiment, as discussed in (*1*).

Another more exotic explanation is that the discrepancy might be a result of the geometric phase associated with the conical intersection between the ground and first excited H + D_2 electronic states (*5*). This geometric phase effect is not included in the calculations (Fig. 1), but Kuppermann and Wu have recently shown that it can have a pronounced influence on differential cross sections for the closely related D + H_2 reaction (*5*). The effect of the geometric phase is expected to be more pronounced for differential than for integral cross sections, and more pronounced the higher the collision energy (*5*). Thus the conclusions of Kuppermann and Wu (*5*) are fully compatible with the discrepancy between theory and experiment (Fig. 1B) being a result of the neglect of the geometric phase in the calculations.

M. J. D'Mello
Thinking Machines Corporation, 245 First Street, Cambridge, MA 02142
D. E. Manolopoulos
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom
R. E. Wyatt
Department of Chemistry, University of Texas, Austin, TX 78712

REFERENCES

1. T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare, D. W. Chandler, *Science* **260**, 1605 (1993).
2. F. J. Aoiz, V. J. Herrero, O. Puentendura, V. Saez Rabanos, *Chem. Phys. Lett.* **198**, 321 (1992).
3. M. J. D'Mello, D. E. Manolopoulos, R. E. Wyatt, *J. Chem. Phys.* **94**, 5985 (1991).
4. D. E. Manolopoulos, M. J. D'Mello, R. E. Wyatt, *ibid.* **91**, 6096 (1989); *ibid.* **93**, 403 (1990).
5. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.* **205**, 577 (1993).

3 August 1993; accepted 20 September 1993

Response: I believe this comment is an important contribution to the discussion of the H + D_2 reaction and its isotopic variants. The point is that exact QM scattering calculations yield the same differential cross section for the H + D_2 reaction as the less precise QCT calculations. Because the QCT calculations showed some discrepancy with the experimental results, this contribution eliminates one possible origin for the discrepancy. Additionally, D'Mello and his coworkers point out a possible important deficiency in the calculation, the absence of the geometric phase correction.

D'Mello *et al.* correctly point out that there may be some problem with extracting a differential cross section of sufficient accuracy to compare with the best calculations from our experimental data. These problems were detailed in our article. We therefore agree with the authors that improvements in both theory experiments are warranted.

David W. Chandler
Combustion Chemistry, 8353, Sandia National Laboratories, Livermore, CA 94551