

## THE D+H<sub>2</sub> REACTION: COMPARISON OF EXPERIMENT WITH QUANTUM-MECHANICAL AND QUASICLASSICAL CALCULATIONS

Dahv A.V. KLINER, Klaus-Dieter RINNEN and Richard N. ZARE

*Department of Chemistry, Stanford University, Stanford, CA 94305, USA*

Received 5 December 1989

We have measured the HD( $v' = 1, J'$ ) rotational distribution from the D+H<sub>2</sub> reaction at a center-of-mass collision energy of about 1.05 eV. The experimental data are compared to distributions derived from two quantum-mechanical (QM) calculations and from a quasiclassical trajectory (QCT) calculation. We find essentially perfect agreement between experiment and the QM calculations, while the QCT results are too hot rotationally.

### 1. Introduction

The H+H<sub>2</sub> reaction family [1-4] provides a special opportunity to compare experimental measurements with dynamical calculations performed on "chemically accurate" potential energy surfaces (PESs), which are believed to be in error by less than a few tenths of a kcal/mol [5,6]. Such comparisons allow the validity of various theoretical approaches and approximation methods to be assessed. This information is important in determining the conditions under which these theoretical treatments may be applied to other chemical systems for which the PESs are less accurately determined.

In this Letter, we present data for the D+H<sub>2</sub>( $v=0, J$ )→HD( $v' = 1, J'$ )+H reaction at  $\approx 1.05$  eV center-of-mass collision energy ( $E_{\text{rel}}$ ). We compare the experimental HD( $v' = 1, J'$ ) rotational distribution to those derived from quantum-mechanical (QM) [7,8] and quasiclassical trajectory (QCT) [9] calculations.

Previous experimental work on the H+D<sub>2</sub> system [10-12] has been compared with QCT [13] and distorted-wave Born approximation [14] calculations; QM calculations were not available at the collision energies accessed in these experiments. It was found that the HD( $v', J'$ ) distributions from the H+D<sub>2</sub> reaction at  $E_{\text{rel}} = 1.3$  and 0.55 eV obtained from experiment and QCT calculations were in remarkably good agreement [10,12]. The ability of the

QCT method to model this system successfully was attributed to the fact that the translational energy was substantially in excess of the  $\approx 0.4$  eV (collinear) reaction barrier [15]. Under this condition, classical mechanics may provide a reasonable approximation, even for particles as light as hydrogen atoms. However, a trend was noted for the QCT rotational distributions to be slightly too hot [10,12].

The above reasoning would predict that as the translational energy is increased, the agreement between experiment and QCT calculations will improve (for a given isotopic variant of the H+H<sub>2</sub> reaction). This behavior was indeed observed by Blais and Truhlar [16] for the H+D<sub>2</sub>→HD( $v' = 1, J'$ )+D reaction at  $E_{\text{rel}}$  values of about 2.25 and 1.5 eV [11].

The experimental results of Valentini and coworkers [4] have also been compared to theoretical calculations. There was overall good agreement with QCT calculations, except for D+H<sub>2</sub> at  $E_{\text{rel}} = 0.67$  eV [17]. Phillips, Levene, and Valentini [17] attribute this latter discrepancy to the presence of a reactive scattering resonance. This resonance appears in the lowest partial waves in the QM calculations of Zhang and Miller [7] and of Zhao et al. [18], but disappears in the sum over all partial waves. Nieh and Valentini recently reported further evidence for resonances in the H+para-H<sub>2</sub> reaction [19,20]. Again, these resonances are absent in QM calculations summed over all partial waves [21]. This has

led Nieh and Valentini [20] to suggest that there are errors in the LSTH PES [5] employed in the calculations [21]. However, new QM calculations by Manolopoulos and Wyatt [22] on the DMBE surface [6] confirm the earlier results, and Zhang and Miller state that "it seems unlikely that such errors (in the PES) ... would produce the qualitative changes necessary to reconcile matters" [23].

Continetti, Balko, and Lee [24] recently measured vibrational state resolved differential cross sections for the reaction  $D+H_2 \rightarrow HD+H$  at  $E_{rel}=0.53$  and 1.01 eV. They have also noted some discrepancies between their results and the QM calculations of Zhang and Miller [7]. Clearly, more comparisons between QM theory and experiment are needed.

## 2. Present results

We have measured the  $HD(v'=1, J')$  rotational distribution for the  $D+H_2$  reaction at  $E_{rel} \approx 1.05$  eV

using the method described in ref. [11]. Briefly, DBr is purified and mixed with  $H_2$ . This reagent mixture effusively flows [12] from a capillary nozzle ( $T \approx 294$  K) into a high vacuum chamber, where the reagent beam is crossed by a focused, pulsed laser beam ( $\approx 210$  nm). The laser both photodissociates DBr, yielding fast D atoms<sup>#1</sup>, and ionizes the HD product of the reaction via (2+1) resonance-enhanced multiphoton ionization (REMPI) [26]. The  $HD^+$  ions are detected with a computer-interfaced, shuttered, time-of-flight mass spectrometer (TOF/MS) [27]. The (2+1) REMPI detection procedure has been calibrated against a high-temperature, effusive nozzle source of HD [26]. The measured rotational distribution is shown in fig. 1 (solid curve), where the error bars represent one standard deviation.

Because the DBr is photolyzed by the tunable probe laser, the photolysis wavelength and therefore the collision energy is varied as different rotational lev-

<sup>#1</sup> At 210 nm, the production of slow D atoms and  $Br(^2P_{1/2})$  is negligible. See ref. [25].

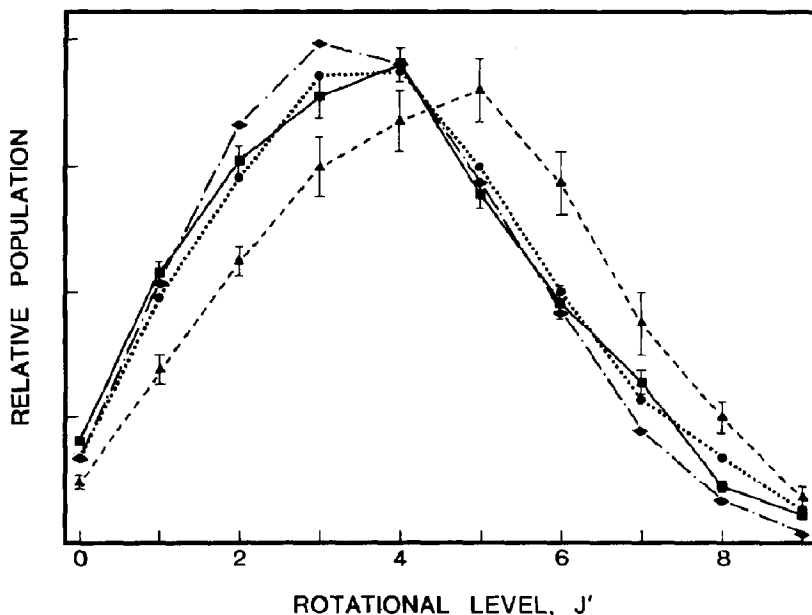


Fig. 1.  $HD(v'=1, J')$  rotational distributions from the  $D+H_2$  reaction at a center-of-mass collision energy of about 1.05 eV; experiment (solid curve), where the error bars represent one standard deviation; QM calculations (dotted curve [7] and dash-dotted curve [8]), given without error estimates; and QCT calculations (dashed curve [9]), where the error bars represent one standard deviation in the sampling statistics. All four distributions have been normalized to the sum of the common populations.

els are detected. This is a minor complication. In the present experiment,  $E_{\text{rel}}$  is 1.07 eV for  $J' = 0$  and 1.02 eV for  $J' = 9$  (average  $E_{\text{rel}} = 1.05$  eV). This variation is well within the thermal spread in  $E_{\text{rel}}$ .

### 3. Comparisons with theory

#### 3.1. Quantum-mechanical calculations

Zhang and Miller [7] recently reported fully converged (32 partial waves), three-dimensional QM calculations on the LSTH PES [5] for the  $\text{D} + \text{H}_2$  reaction in the energy range accessed in the present experiment.  $E_{\text{rel}} = 1.05$  eV corresponds to a total energy,  $E$  ( $E_{\text{rel}}$  plus  $\text{H}_2$  zero-point energy), of 1.32 eV. Zhang and Miller calculated product internal-state distributions at  $E = 1.35$  and 1.25 eV. We have taken a weighted average of the  $\text{HD}(v' = 1, J')$  rotational distributions at these two energies to obtain a distribution corresponding to that measured in the experiment. This procedure appears justified since the calculated distributions change smoothly with increasing translational energy [28,29]. In the QM calculations, the  $\text{H}_2$  reagent was restricted to be in the  $(v=0, J=0)$  state, while in the experiment the reagent beam was effusive ( $(v=0, J)$  thermal). Again, this is expected to have a negligible impact on the comparison because the reactivity is not strongly dependent on  $J$  at the energies used in the present experiment [30] (also see below), and very few  $\text{H}_2$  rotational states are populated at room temperature. Zhang and Miller's QM rotational distribution is shown as the dotted curve in fig. 1. Because the experiment measures relative populations (not absolute cross sections), the QM and experimental distributions have been normalized to the sum of the common populations [10,12,16].

Zhao et al. [8] have also performed QM calculations that can be compared to the present experiment. Aside from employing a different computational method, these calculations differed from those of Zhang and Miller in three respects: (i) the DMBE PES [6] was used; (ii) calculations were performed with the  $\text{H}_2$  reagent in both  $J=0$  and  $J=1$ ; and (iii) 34 partial waves were included. The results of these two QM calculations differ slightly. The major difference is thought to be the use of different surfaces

[29]. The predicted  $\text{HD}(v' = 1, J')$  rotational distributions from the reaction  $\text{D} + \text{H}_2(v=0, J)$  are nearly identical for  $J=0$  and  $J=1$  (at both  $E = 1.25$  and 1.35 eV), further supporting the above claim that the various initial conditions for the  $\text{H}_2$  rotational state do not greatly affect the current comparison between experiment and theory. Zhao et al.'s QM rotational distribution is shown as the dash-dotted curve in fig. 1<sup>#2</sup>. Again, we have taken a weighted average of the distributions computed at  $E = 1.25$  and 1.35 eV. We have also weighted the  $J=0$  and  $J=1$  contributions according to their respective populations at  $T = 294$  K, a procedure that has a negligible effect on the calculated distribution. Finally, this QM distribution has been normalized to the sum of the populations common to the experimental distribution.

*The agreement between the distributions derived from experiment and from the two QM calculations is nearly perfect.* This agreement is especially meaningful in light of the relatively small error bars on the experimental points. The QM distribution of Zhang and Miller (dotted curve) [7] is perhaps in better accord with experiment than that of Zhao et al. (dash-dotted curve) [8], though the difference is barely at the level of statistical significance.

While it cannot yet be claimed that the quantitative agreement between QM calculations and experiment demonstrated in fig. 1 is general, the initial success reported here is very encouraging. It suggests that the present level of theory is adequate to describe fully quantitatively some features of the  $\text{H} + \text{H}_2$  reaction dynamics.

#### 3.2. Quasiclassical trajectory calculations

The fully converged, three-dimensional QM calculations are very computationally intensive. There is great interest in much simpler treatments of the dynamics that can be applied to more complicated

<sup>#2</sup> The QM and QCT distributions shown in fig. 1 should not be directly compared as they have all been normalized to the experimental distribution. For comparison, the calculated partial cross sections into  $\text{HD}(v' = 1)$  are  $0.220 \text{ \AA}^2$  for Zhang and Miller (QM) [7],  $0.211 \text{ \AA}^2$  for Zhao et al. (QM) [8], and  $0.259 \pm 0.004 \text{ \AA}^2$  for Blais and Truhlar (QCT) [9].

systems. QCT calculations are the primary such method. Recently, Blais and Truhlar [9] have presented QCT calculations for the  $D+H_2$  reaction, again on the LSTH PES [5]. They reported  $HD(v', J')$  product distributions at several values of  $E_{rel}$ , including 1.05 eV. The initial state of the  $H_2$  reagent was taken as  $(v=0, J=1)$ . At room temperature, 66% of the  $H_2$  occupies this quantum state. Thus, comparison between this calculation and the experiment is appropriate.

The QCT rotational distribution is shown as the dashed curve in fig. 1 (see footnote 2). Again, the theoretical data are normalized to the sum of the populations common with the experimental distribution. *The QCT calculation reproduces the form of the rotational distribution, but is too hot by about one rotational quantum.*

For the  $H+D_2$  experiment discussed in section 1 ( $E_{rel}=1.3$  eV) [10,12], the total energy  $E$  was 1.49 eV. In the present  $D+H_2$  experiment,  $E$  is 1.32 eV. Although the total energies are similar, the difference between the QCT and experimental distributions is significantly more pronounced for  $D+H_2$ . Two possible contributions to this discrepancy were discussed in the analysis of the  $H+D_2$  results [12]: (i) binning errors in the assignment of reactive trajectories to product quantum states, and (ii) the incomplete cancellation [31] of two opposing quantum-mechanical effects, tunneling and changes in zero-point energy (ZPE) in going from reactants to products. The effects of point (ii) are mass dependent. They are most important for trajectories that pass close to the reaction barrier. An additional contribution to the trend of QCT rotational distributions to be too hot has been suggested by Blais [32]. The quantum  $H_2(v=0)$  reagent is confined primarily to the center of the potential well, while the classical oscillator with the corresponding ZPE is found preferentially at the inner and outer classical turning points. This improper weighting of the  $H_2$  internuclear distance may result in enhanced rotational excitation of the reaction product because the cone of acceptance is a sensitive function of reagent bond length [33]. This explanation is consistent with the fact that there is a greater discrepancy between QCT and experimental product distributions for  $D+H_2$  than for  $H+D_2$  [10,12] because the ZPE of  $H_2$  is larger than that of  $D_2$ .

Further comparisons of experimental measurements to QM calculations are required in order to assess the generality of the quantitative agreement between QM calculations and experiment presented here and to determine the source of the outstanding discrepancies [17,20,24]. Similar comparisons to QCT calculations are necessary in order to ascertain the conditions for which such calculations provide an accurate description of the reaction dynamics.

### Acknowledgement

We are grateful to N.C. Blais, W.H. Miller, and D.G. Truhlar for valuable discussions. We thank D.G. Truhlar for providing his data prior to publication. DAVK acknowledges the National Science Foundation for a predoctoral fellowship. This work is supported by the National Science Foundation under NSF CHE 87-05131.

### References

- [1] D.G. Truhlar and R.E. Wyatt, *Ann. Rev. Phys. Chem.* 27 (1976) 1.
- [2] *Intern. J. Chem. Kinetics* 18, No. 9 (1986).
- [3] R.D. Levine and R.B. Bernstein, *Molecular reaction dynamics and chemical reactivity* (Oxford Univ. Press, New York, 1987).
- [4] J.J. Valentini and D.L. Phillips, in: *Advances in gas phase photochemistry and kinetics*, Vol. 2. Bimolecular reactions, eds. M.N.R. Ashfold and J.E. Baggott (Roy. Soc., London, 1989) p. 1, and references therein.
- [5] B. Liu, *J. Chem. Phys.* 68 (1973) 1925; P. Siegbahn and B. Liu, *J. Chem. Phys.* 68 (1978) 2457; D.G. Truhlar and C.J. Horowitz, *J. Chem. Phys.* 68 (1978) 2466; 71 (1978) 1514.
- [6] A.J.C. Varandas, F.B. Brown, C.A. Mead, D.G. Truhlar and N.C. Blais, *J. Chem. Phys.* 86 (1987) 6258.
- [7] J.Z.H. Zhang and W.H. Miller, *J. Chem. Phys.* 91 (1989) 1528.
- [8] M. Zhao, D.G. Truhlar, D.W. Schwenke and D.J. Kouri, to be published.
- [9] N.C. Blais and D.G. Truhlar, *J. Chem. Phys.* 88 (1988) 5457.
- [10] R.S. Blake, K.-D. Rinnen, D.A.V. Kliner and R.N. Zare, *Chem. Phys. Letters* 153 (1988) 365.
- [11] K.-D. Rinnen, D.A.V. Kliner, R.S. Blake and R.N. Zare, *Chem. Phys. Letters* 153 (1988) 371.

- [12] K.-D. Rinnen, D.A.V. Kliner and R.N. Zare, *J. Chem. Phys.* 91 (1989) 7514.
- [13] N.C. Blais and D.G. Truhlar, *Chem. Phys. Letters* 102 (1983) 120.
- [14] S.H. Suck Salk, C.R. Klein and C.K. Lutrus, *Chem. Phys. Letters* 110 (1984) 112;  
M.S. Bowers, B.H. Choi, R.T. Poe and K.T. Tang, *Chem. Phys. Letters* 116 (1985) 239;  
J.N.L. Connor and W.J.E. Southall, *Chem. Phys. Letters* 123 (1986) 139.
- [15] B. Liu, *J. Chem. Phys.* 80 (1984) 581;  
D.M. Ceperley and B.J. Alder, *J. Chem. Phys.* 81 (1984) 5833;  
R.N. Barnett, P.J. Reynolds and W.A. Lester Jr., *J. Chem. Phys.* 82 (1985) 2700.
- [16] N.C. Blais and D.G. Truhlar, *Chem. Phys. Letters* 162 (1989) 503.
- [17] D.L. Phillips, H.B. Levene and J.J. Valentini, *J. Chem. Phys.* 90 (1989) 1600.
- [18] M. Zhao, D.G. Truhlar, D.J. Kouri, Y. Sun and D.W. Schwenke, *Chem. Phys. Letters* 156 (1989) 281.
- [19] J.-C. Nieh and J.J. Valentini, *Phys. Rev. Letters* 60 (1988) 519.
- [20] J.-C. Nieh and J.J. Valentini, *J. Chem. Phys.*, in press.
- [21] J.Z.H. Zhang and W.H. Miller, *Chem. Phys. Letters* 153 (1988) 465;  
D.E. Manolopoulos and R.E. Wyatt, *Chem. Phys. Letters* 159 (1989) 123.
- [22] D.E. Manolopoulos and R.E. Wyatt, submitted for publication.
- [23] J.Z.H. Zhang and W.H. Miller, *Chem. Phys. Letters* 159 (1989) 130.
- [24] R.E. Continetti, B.A. Balko and Y.T. Lee, in: 1989 Conference on the Dynamics of Molecular Collisions, Asilomar, California (July 16-21, 1989) p. B9;  
R.E. Continetti, B.A. Balko and Y.T. Lee, to be published.
- [25] R. Magnotta, D.J. Nesbitt and S.R. Leone, *Chem. Phys. Letters* 83 (1981) 21;  
K. Kleiner, E. Linnebach and M. Pohl, *J. Chem. Phys.* 91 (1989) 2181.
- [26] K.-D. Rinnen, D.A.V. Kliner, R.N. Zare and W.M. Huo, *Israel J. Chem.* 29 (1989) 369.
- [27] K.-D. Rinnen, D.A.V. Kliner, R.S. Blake and R.N. Zare, *Rev. Sci. Instr.* 60 (1989) 717.
- [28] W.H. Miller, private communication.
- [29] D.G. Truhlar, private communication.
- [30] C.A. Boonenberg and H.R. Mayne, *Chem. Phys. Letters* 108 (1984) 67.
- [31] G.C. Schatz, private communication;  
D.G. Truhlar, A.D. Isaacson and B.C. Garrett, in: Theory of chemical reaction dynamics, ed. M. Baer (CRC Press, Boca Raton, 1985) p. 64.
- [32] N.C. Blais, private communication
- [33] I. Schechter, R. Kosloff and R.D. Levine, *Chem. Phys. Letters* 121 (1985) 297.