

Vibrational population inversion in hydrogen iodide from  $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$ 

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(Received 14 April 1972)

A classical trajectory analysis for the reaction  $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$  at 600°K, using trajectories sampled within the transition region, shows vibrational excitation of the HI product molecules, mainly to the  $v=3$  to  $v=5$  levels. The calculated thermal rate is in approximate agreement with measurements by Sullivan. The product angular distribution is peaked at 110–120° relative to the incident atoms as measured for the reaction of D atoms by McDonald, LeBreton, and Herschbach. The translational energy distribution of the products is also similar to that found by McDonald *et al.* for the deuterium analog.

We report here a classical phase space-trajectory study of the reaction  $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$  which leads to a prediction of vibrational population inversion for the HI molecules formed and the possibility of constructing an HI chemical laser utilizing the reaction. Population inversions of the hydrogen halide products from reaction of H atoms with  $\text{F}_2$ ,<sup>1</sup>  $\text{Cl}_2$ ,<sup>2</sup> and  $\text{Br}_2$ <sup>3</sup> have been predicted and observed previously, and from the expected similarity with these systems,<sup>4</sup> the reaction of H atoms with  $\text{I}_2$  may also be expected to yield inversions. Evidence for internal excitation ( $\sim 32$  kcal/mole) of DI from reaction of D with  $\text{I}_2$  in crossed molecular beams has been obtained by McDonald *et al.*<sup>5</sup> Although the energy released in forming HI is less than that for the other hydrogen halides, the energy released plus the

average energy of reactants at room temperature is sufficient to produce HI in the 6th vibrational level.

The potential energy surface used for the calculations is that obtained by Raff *et al.*<sup>6</sup> using the London expression with semiempirical evaluation of the ground state  $^1\Sigma$  potentials for the HI and  $\text{I}_2$  pairs. Reaction is assumed to occur on this single potential energy surface without the possibility of an intersystem crossing to form I atoms in the  $^2P_{1/2}$  state, 21.7 kcal/mole above the lowest state  $^2P_{3/2}$ . The surface is similar in character to those for the other hydrogen-halogen systems in that the elevated entrance valley intersects the side of exit valley for the linear configuration. The barrier to reaction is located in the entrance valley with a height of 0.49 kcal/mole (relative to the minimum for separated H and  $\text{I}_2$ ) for the linear configuration ( $\theta_{\text{HII}} = 180^\circ$ ). The barrier height is insensitive to  $\theta_{\text{HII}}$  for  $180^\circ < \theta_{\text{HII}} < 90^\circ$ , decreasing with decreasing angle to a minimum of 0.47 at  $\theta_{\text{HII}} = 120^\circ$ , then increasing to 0.56 kcal/mole at  $\theta_{\text{HII}} = 90^\circ$ . The net potential energy decrease in passing from reactants to products is 37.8 kcal/mole.

The classical phase space-trajectory techniques for computation were identical to those applied by Jaffe, Henry, and Anderson<sup>7</sup> to study of the reaction  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ . In the 18-dimensional phase space of the momenta and coordinates of the three atoms the flux of points across a surface dividing reactant and product states was determined for equilibrium at 600°K. Sampling of the flux crossing the surface provided the starting points for trajectory calculations forward and backward in time to determine the overall "conversion" coefficient and reactant and product energy distributions.<sup>8</sup> With the dividing surface located at an atom-diatom distance  $R_{\text{H,I}_2} = 4.3 \text{ \AA}$ , 547 starting points were examined for reaction at 600°K. Calculations were terminated in the forward and backward directions when one of the interatomic distances exceeded 10 Å. Computation time required was a total of about 2.5 h on the IBM 7094 system used.

The equilibrium rate constant  $k_e$  for the forward reaction with reactants and products in equilibrium at

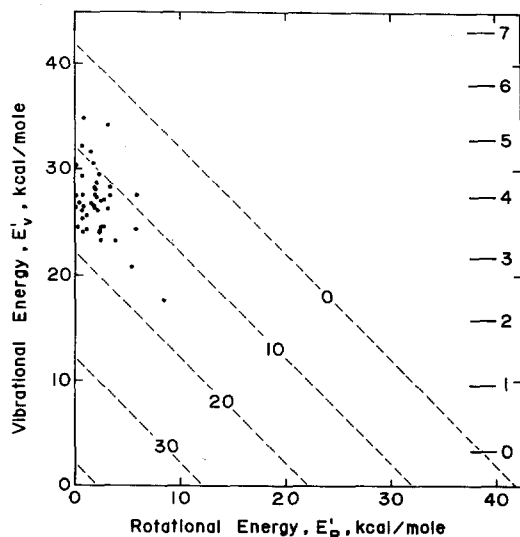


FIG. 1. Distribution of energy among reaction products at 600°K. Each point represents the result for a single trajectory. Vibrational energy levels are indicated at right. Approximate translational energies (kcal/mole) are indicated by the dashed diagonal lines.

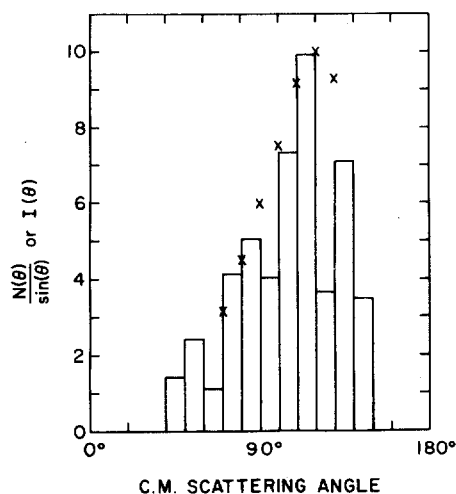


FIG. 2. Reactive scattering distributions as calculated for HI[H(600°K)+I<sub>2</sub>(600°K)] and as measured for DI[H(~350°K)+I<sub>2</sub>(~350°K)] by McDonald *et al.*<sup>5</sup> The direction of the incident atoms is 0°. The experimental distribution is indicated by X's and is normalized to a value of 10 at 120°.

600°K was calculated to be  $8.85 \times 10^{14}$  cm<sup>3</sup> mole<sup>-1</sup>·sec<sup>-1</sup>. Values of the integrals I<sub>1</sub> and I<sub>2</sub> (defined in Ref. 7) were I<sub>1</sub> =  $1.12 \times 10^{-23}$  cm<sup>3</sup> and I<sub>2</sub> =  $1.59 \times 10^{-23}$  cm<sup>3</sup>. The conversion coefficient  $\xi$  determined from the trajectory calculations was  $0.074 \pm 0.011$ . The calculated thermal rate constant  $k = \xi k_e = (6.5 \pm 1) \times 10^{13}$  cm<sup>3</sup> mole<sup>-1</sup>·sec<sup>-1</sup> is in approximate agreement with that determined experimentally by Sullivan,<sup>10</sup>  $1.4 \times 10^{13}$  cm<sup>3</sup> mole<sup>-1</sup>·sec<sup>-1</sup>, independent of temperature in the range 667–800°K.

The procedure for sampling the flux across the phase space dividing surface gave trajectories with equal statistical weights for reactants in thermal equilibrium at the specified temperature. Reactant and product energy distributions were obtained by summations of the results for individual trajectories leading to reaction using the definitions of vibrational and rotational energy given in Ref. 6. Results for the product HI energy distribution are shown by Fig. 1 in which each point represents the outcome of a single trajectory. The distribution is peaked toward the higher vibrational energies and gives relative rate constants  $k(v')$  for production of HI in the interval  $v' - 1/2$  to  $v' + 1/2$ :  $k(0') = 0$ ,  $k(1') = 0$ ,  $k(2') = 1$ ,  $k(3') = 11$ ,  $k(4') = 26$ ,  $k(5') = 5$ ,  $k(6') = 0$ . The average vibrational energy  $\bar{E}_v' = 26.8$  kcal/mole; rotational energy  $\bar{E}_R' = 2.2$  kcal/mole; and translational energy  $\bar{E}_T' = 13.2$  kcal/mole.

The computed fraction of total available energy released to vibration is 64%. For the reactions H+Cl<sub>2</sub> and H+Br<sub>2</sub> Anlauf *et al.*<sup>3b</sup> reported trajectory calculations for LEPS surfaces predicting 56%–59% and 48%–65% of the energy released to vibration. Experimental measurements by the same authors of the infrared chemiluminescence of reaction products gave values

of 45% and 55%, respectively. In trajectory calculations with an LEPS surface adjusted to give results matching those of experiments, Jonathan *et al.*<sup>1b</sup> were able to obtain the experimental value of ~59% of the available energy released to vibration.

Comparison of the calculated distributions in angle and translational energy of the HI formed with those obtained by McDonald *et al.*<sup>5</sup> for DI in the crossed beam reaction of D atoms (~350°K) with I<sub>2</sub> (~350°K) indicates approximate agreement. For the DI experiments  $\bar{E}_T'$  was ~9 kcal/mole and the peak of the angular distribution was found at ~120° with respect to the incident D atoms. The corresponding values from the calculations are 13.2 kcal/mole and 110°–120°. The widths of the distributions for both angle and translational energy are similar. Figure 2 shows both angular distributions for comparison.

The energy distribution of reactants (undergoing reaction) showed the reactivity of the I<sub>2</sub> molecules to be insensitive to small changes in vibrational or rotational excitation. The average vibrational, rotational, and translational energies of the reactants were found to be  $\bar{E}_v = 1.1$  kcal/mole,  $\bar{E}_R = 0.8$  kcal/mole, and  $\bar{E}_T = 2.5$  kcal/mole.

The complexity of collisions leading to reaction was similar to that observed by Kuntz *et al.*<sup>11</sup> for reactions of light atoms with heavy diatomic molecules. The duration of collisions leading to reaction was in the range  $5 \times 10^{-13}$  sec to  $7 \times 10^{-13}$  sec. Of the 504 non-reactive trajectories examined, most recrossed the dividing surface in about  $10^{-13}$  sec, but five required more than  $10^{-12}$  sec. The potential energy surface has a well in the exit valley lying 2.8 kcal/mole below the minimum for separated HI+I which together with the masses of the I atoms accounts for the duration of the collisions.

On the basis of the results obtained in this study, which show vibrational population inversions for the HI produced in reaction of H with I<sub>2</sub>, and the success of similar methods in duplicating the energy distributions of products in reactions of H with the other halogen molecules, we predict that laser action can be obtained in a system utilizing the reaction H+I<sub>2</sub>→HI+I.

Support of the National Science Foundation is gratefully acknowledged.

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<sup>5</sup> J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, J. Chem. Phys. **56**, 769 (1972).

<sup>6</sup> L. M. Raff, L. Stivers, R. N. Porter, D. Thompson, and L. B. Sims, J. Chem. Phys. **52**, 3449 (1970).

<sup>7</sup> R. L. Jaffe, J. M. Henry, and J. B. Anderson, "Variation Theory of Reaction Rates: Application to  $F+H_2 \rightleftharpoons HF+H$ ," J. Chem. Phys. (to be published).

<sup>8</sup> The procedure is based on the principle that the distribution in the transition region is identical to an equilibrium distribu-

tion except that states originating from products are missing. Since the principle is of fundamental importance in chemical kinetics and has been questioned by several workers in the field, we have given a full discussion together with demonstrations of its applicability for several simple systems in a separate paper, Ref. 9. However, in the present case, with a low barrier in the entrance valley, dynamic effects are of minor importance in determining the distribution in the region of the dividing surface and the principle is not at issue.

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<sup>11</sup> P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, J. Chem. Phys. **44**, 1168 (1966).

## Erratum: Vibrational population inversion in hydrogen iodide from $H + I_2 \rightarrow HI + I$ [J. Chem. Phys. **58**, 2477 (1973)]

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The agreement between the calculated rate constant and the experimental rate constant at 600 °K is improved by correction of errors in reporting each. The reported values for  $I_1$ ,  $k_0$ , and  $k$  were low by a factor of 2.86 due to omission of a factor of 2 and an integration error. The reported value of the experimental  $k$  was low by a factor of  $T^{1/2}$  omitted from the modified Arrhenius equation. The corrected values for  $k$  are:  $(18.6 \pm 3) \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}$ , calculated;  $(34 \pm 20) \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}$ , experimental.<sup>1</sup> Professor J. D. McDonald has kindly pointed out that the uncertainty in the calculated distribution of scattering angles is very large for angles near 0° and 180° and that the observed agreement

with experiment may well be fortuitous.<sup>2</sup>

<sup>1</sup>J. H. Sullivan, J. Chem. Phys. **36**, 1925 (1962).

<sup>2</sup>Additional calculations by J. D. McDonald [J. Chem. Phys. (to be published)] and by J. C. Polanyi and J. L. Schreiber [Chem. Soc. Faraday Disc. **55** (1973), Comment following Paper D22] show backward scattering for similar potential energy surfaces. R. N. Porter, D. L. Thompson, L. M. Raff, and J. M. White (private communication) using a standard quasiclassical trajectory analysis have found backward scattering and a rate constant at 600 °K of  $(21.4 \pm 0.9) \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}$  for the same potential energy surface used in our calculations.