ELECTRONIC AND ATOMIC COLLISIONS

Edited by:
B. C. Čobić and M. V. Kurepa

ABSTRACTS OF PAPERS
VIII ICPEAC
BEOGRAD, 1973

Institute of Physics
Beograd, Yugoslavia

STREAMLINES OF PROBABILITY CURRENT DENSITY AND TUNNELING FRACTIONS FOR THE COLLINEAR $H+H_2 \rightarrow H_2+H$ REACTION

A. KUPPERMANN, J.T.ADAMS and D.G. TRUHLAR *

A.A. Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109, USA
*Dept. of Chemistry, Univ. of Minnesota, Minneapolis, Minn. 55455, USA

Using reactive scattering wave functions for the collinear $H+H_2-H_2+H$ reaction obtained previously /1/, we have calculated the corresponding probability current density vector fields, $\vec{j}=\mathrm{Re}(\Psi^* \vec{v}_{op} \Psi)$, and the associated streamlines. An example of such streamlines is displayed in Figure 1. The abcissa x_1 is the distance from the reagent atom to the center of mass of the reagent molecule, multiplied by the factor $(\mu_{H,H_2}/\mu_{H_2})^{\frac{1}{2}}$, where μ_{H,H_2} is the reduced mass of the $H+H_2$ system and μ_{H_2} that of the H_2 molecule. The ordinate x_2 is the reagent H_2 molecule internuclear distance. The solid lines are equipotentials, whose energies in eV are designated by the numbers at their beginnings and ends. The potential energy surface used was a Wall-Porter fit to the SSMK surface scaled to produce a barrier height of 0.424 eV (9.8 Kcal/mole) /1/. The energy E for the calculation of Figure 1 was 0.430 eV, i.e., 0.006 eV above the energy of the saddle point (represented by a + on the minimum energy path). The 0.430 eV equipotentials are the curves labelled E in the figure. For points in (x_1, x_2) configuration space not in between these two curves, the potential energy of the system exceeds its total energy, and these exterior regions are classically inaccessible. The lines of arrows are the streamlines, which by definition are everywhere tangent to the probability current density vector $\vec{j}$. The length of the arrows are proportional to the magnitude of $\vec{j}$. The spacing between the streamlines in the reagent region of configuration space was made inversely proportional to the magnitude of $\vec{j}$.

An important property of the streamlines is that the normal flux of $\vec{j}$ through a line segment connecting any two streamlines is independent of the shape of this segment or where it is placed: in the reagent, saddle point or product regions. It depends only on which two streamlines it connects. Furthermore, the total normal flux of $\vec{j}$ across a line cutting all streamlines once is also a constant of the motion independent of the position of the cut and equals the product of the initial reagent relative velocity by the total reaction probability from the given initial internal state of the reagent molecule.

It can be seen from Figure 1 that although E is greater than the barrier height, most of the streamlines cut across into the classically inaccessible regions. For this energy of 0.430 eV, 93% of the total flux is associated to such streamlines, and by definition we call this quantity the tunneling fraction γ (in two mathematical dimensions). As a consequence of this definition, γ is a constant of the motion, independent of the position of the cut across which the tunnel

ELECTRONIC AND ATOMIC COLLISIONS

Edited by:
B. C. Čobić and M. V. Kurepa

ABSTRACTS OF PAPERS
VIII ICPEAC
BEOGRAD, 1973

Institute of Physics
Beograd, Yugoslavia

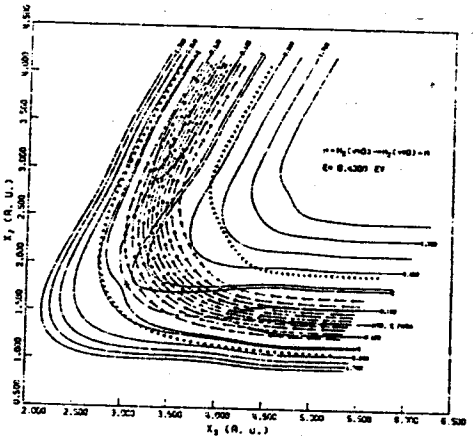

Figure 1

ing flux is calculated, and of any reference reactive scattering model.

From these tunelling fractions as a function of relative collision energy we have calculated the contribution to the collinear rate constant k(T) due to tunneling, as a function of temperature. We find that even for temperature regions in which the Arrhenius plot of k(T) is linear, tunneling contributions can be significant. For example, at 800 K about 27% of the rate constant is due to tunneling.

As the initial relative kinetic energy increases, the streamline plots indicate the development of regions of dynamic inaccessibility for the system. These are associated with the formation of vortices, which constrain the stream lines going from the reagent to the product regions of configuration space to narrower and narrower regions as the energy continues to increase. This correlates well with the decrease of the corresponding total reaction probability with energy.

References.

1. Donald G. Truhlar and Aron Kuppermann, J. Chem. Phys. 56, 2232 (1972).