

straight line. Such plots were linear within experimental error for each concentration. The observed linearity supports the theoretically derived power-law dependence and shows that a high enough value of $q\langle s^2 \rangle^{1/2}$ was obtained to allow observation of the limiting power-law dependence at large q . The slopes were significantly larger than would be obtained for $q\langle s^2 \rangle \ll 1$; for this latter condition, the theoretically predicted slope of 2 is always observed.

The results for all solutions are summarized in Fig. 1, where a is given as a function of concentration. Whereas a power-law dependence of $\Delta\nu$ on q was observed for each concentration, the power a changes significantly with concentration even though the lowest concentrations for which reliable data could be obtained were used. This large concentration dependence increases the difficulty of distinguishing experimentally among the various values predicted by theory. It apparently will be necessary to do future work with solutions even more dilute than those used here, as no reliable means of extrapolating such results to zero concentration is known.

It should be noted that the homodyning spectral

half-widths $\Delta\nu$ reported here are not directly related to the light spectral half-widths predicted by theory, as homodyning spectra are proportional to the convolution of corresponding light spectra. The slopes a would be expected to be somewhat greater than the power dependences with which theory is concerned. Experimental heterodyning spectra or autocorrelation functions would be easier to compare with theory. However, the difficulty in interpreting homodyning data does not obscure the central point of this Communication that a large concentration dependence exists which must be taken into account in the comparison of experimental results and theory.

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Large quantum effects in the collinear $F + H_2 \rightarrow FH + H$ reaction*

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We have performed accurate quantum mechanical calculations of reaction probabilities for the collinear $F + H_2 \rightarrow FH + H$ reaction as well as corresponding quasiclassical trajectory calculations. A comparison of these results shows that very significant quantum mechanical effects are present in this reaction.

The reactions $F + H_2$ and $F + D_2$ have been the subject of several experimental studies^{1,2} which have provided detailed information concerning the distribution of product HF molecules among possible final states. In addition, it is the main pumping reaction in the FH chemical lasers.³ All previous theoretical studies of these reactions have used quasiclassical trajectory methods.^{4,5} Comparison of the results of these quasiclassical calculations with corresponding three dimensional quantum mechanical ones would be very desirable to establish the importance of

quantum effects in this reaction. However, the difficulty in performing such quantum calculations precludes at present such a comparison. For this practical reason we have limited ourselves to a study of the collinear reaction.

For both the quantum and classical calculations, we used the semiempirical potential surface of Muckerman^{4,6} (his surface 5) which has a barrier height of 0.0471 eV (1.09 kcal) and an exothermicity of 1.3767 eV (31.76 kcal). The quantum calculations were done with the close coupling propagation method of Kuppermann.⁷ The range of reagent relative translational energies E_0 was 0.0–0.4 eV and, for most of this range, four vibrational states of HF were open. Between six and nine closed vibrational states were required to ensure adequate unitarity and symmetry of the scattering matrix (conservation of flux to within 0.5% and

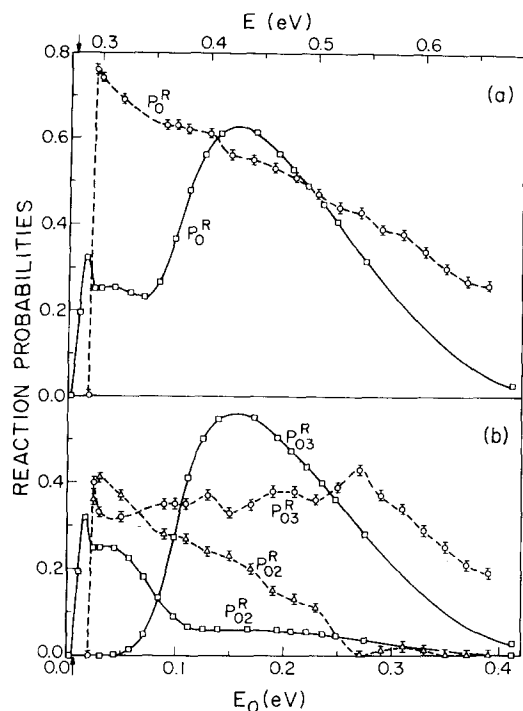


FIG. 1. Reaction probabilities for collinear $F+H_2$ as a function of reagent relative kinetic energy E_0 . (a) Total reaction probability P_0^R from ground vibrational state of reagent. (b) Reaction probabilities P_{02}^R and P_{03}^R (defined in text). Solid lines correspond to quantum calculations and dashed ones to quasi-classical trajectory calculations. The statistical error in the classical results is indicated by the vertical bars. The energy scale at the top of the figure indicates the total energy E of the system relative to the minimum in the isolated H_2 diatomic potential energy curve. The vertical arrow in the abscissa indicates the energy at which the $j=3$ state of HF becomes accessible.

symmetry to within 2.0%). The procedure used to obtain the quasiclassical results is analogous to that used by Bowman and Kuppermann.⁸

The results of some of these calculations are presented in Fig. 1. P_{ij}^R is the reaction probability for reagent H_2 in vibrational state i to form product HF in state j . The total reaction probability P_i^R is the sum of P_{ij}^R over all j . We find that only P_{02}^R and P_{03}^R are significant contributors to P_0^R in the E_0 range investigated.⁹ Figure 1 shows that not only do the P_{02}^R and P_{03}^R quasiclassical results differ rather considerably from the quantum ones, but also the corresponding total reaction probability curves have very different shapes. In the E_0 range 0.025–0.075 eV, the quasiclassical P_0^R is more than 2.5 times greater than the quantum one. This difference between the two P_0^R curves is quite interesting, since they agreed quite well for the $H+H_2$ reaction,⁸ which would have been expected to show greater quantum effects. This indicates the great importance of the nature of the potential energy surface in determining the details of reaction dynamics. The

lack of agreement between the quantum and quasi-classical P_0^R reaction probabilities can be partially explained as arising from the reasonable but nevertheless arbitrary way of assigning a discrete quantum number to a continuous product vibrational energy⁸; however, this problem is not present in the total reaction probabilities P_0^R . Presumably, tunnelling is not very important for this reaction because the zero point vibrational energy of H_2 is sufficient to make the reaction classically allowed even at zero reagent relative translational energy. It is quite possible that the magnitude of these differences between the quantum and classical results in the three dimensional reaction will be significantly attenuated, but to the extent that they may be qualitatively preserved, they could result in large differences in the relative rate constants for the formation of various states of HF.

An interesting feature of the quantum results is the large difference between the energy dependences of P_{02}^R and P_{03}^R . In the $F+D_2$ reaction¹⁰ one finds that P_{04}^R and P_{03}^R show energy dependences similar to P_{03}^R and P_{02}^R , respectively, of $F+H_2$. This similarity appears to be related to the fact that the $j=3$ and 4 levels of DF are very close in total energy to the $j=2$ and 3 levels of HF, respectively.

We are presently conducting semiclassical calculations analogous to those reported for the $H+H_2$ exchange reaction.¹¹ Preliminary uniform semiclassical results are in qualitative agreement with the exact quantum calculations.

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dependence similar to P_{0j}^R with maximum reaction probabilities occurring near $E_0=0.173$ eV. The reaction probabilities at this energy are 3.4×10^{-3} and 1.5×10^{-5} , respectively. No reactive trajectories yielding HF with $j=0$ or $j=1$ were obtained.

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Zubov's construction in the asymptotic stability domain. Applications in the kinetic analysis of open systems

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The study of instabilities in dissipative processes remains of interest to those who are applying the tenets of irreversible thermodynamics to the analysis of open (biological) systems.¹⁻⁷ When such systems are modeled as homogeneous volume elements or cells, their dynamics are usually described by a set of ordinary nonlinear differential equations autonomous in activity variables.⁷ A knowledge of the stability character of the critical points (steady states) is of funda-

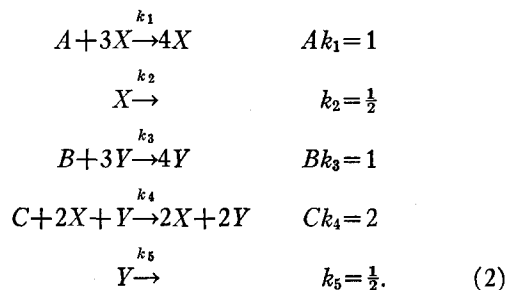
mentally important when one is interested in a system's response to infinitesimal and finite fluctuations from its critical points. Stability in the first approximation is ascertained easily by normal mode analysis⁸ following an expansion of the system about its critical point. Such an analysis gives information only for infinitesimal perturbations⁹ and fails completely in the critical case.^{10,11} It is well known that when normal mode analysis predicts a domain of asymptotic stability, the existence of a Lyapunov function¹² is assured for the system. These Lyapunov functions are easily obtained¹³ but usually give conservative estimates of the asymptotic stability domain.^{14,15}

asymptotically stable has persisted in the field of irreversible thermodynamics.^{16,17} Biologically this is an important question, e.g., in consideration of multiple steady state phenomena.¹⁸⁻²¹ The necessary and sufficient conditions for asymptotic stability were obtained by Zubov²²:

Zubov's Theorem: Our system of interest is given by $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$ and is asymptotically stable in some domain \mathcal{Q} . Let $v(\mathbf{x})$ be a Lyapunov function for the system such that $0 \leq v < 1$ for $\mathbf{x} \in \mathcal{Q}$; $\phi(\mathbf{x})$ is continuous and positive definite but otherwise arbitrary. The surface $v(\mathbf{x}) = 1$ then limitingly contains \mathcal{Q} where \mathcal{Q} is the exact asymptotic stability domain, and is defined by the partial differential equation:

$$\mathbf{f}(\mathbf{x}) \cdot (\partial v / \partial \mathbf{x}) = -\phi(\mathbf{x}) [1 - v(\mathbf{x})] [1 + |\mathbf{f}(\mathbf{x})|^2]^{1/2}. \quad (1)$$

As an example workable in closed form, consider the hypothetical mechanism:



The rate equations are then

$$\begin{aligned} \dot{X} &= -1/2X + X^3, \\ \dot{Y} &= -1/2Y + 2X^2Y + Y^3, \end{aligned} \quad (3)$$

which are seen to have a vanishing asymptotically stable critical point. Such a system might be realized in response to a sudden infusion of X and Y or in response to a pulse of radiation although an actual physical example is not known to us. Inspection of (3) also indicates that the system is unstable for large enough perturbations. In solving for $(X, Y) \in \mathcal{Q}$ we pick $\phi(X, Y) = 2(X^2 + Y^2) / (1 + X^2 + Y^2)^{1/2}$ and obtain $v(X, Y) = 2(X^2 + Y^2)$. The surface $X^2 + Y^2 = \frac{1}{2}$ then determines \mathcal{Q} . Figure 1 illustrates this boundary as well as several orbits resulting from perturbations lying closely adjacent to the boundary.

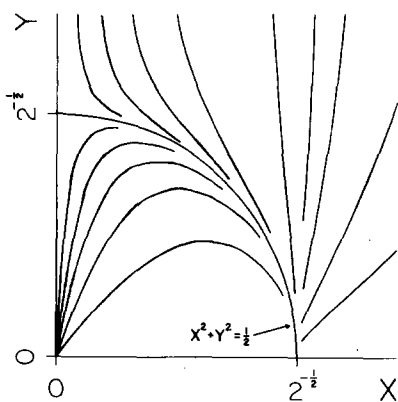


FIG. 1. The asymptotic stability domain of the mechanism (2) as determined by (1) and (3) with $\phi(X, Y) = 2(X^2 + Y^2) / (1 + X^2 + Y^2)^{1/2}$.

mental importance when one is interested in a system's response to infinitesimal and finite fluctuations from its critical points. Stability in the first approximation is ascertained easily by normal mode analysis⁸ following an expansion of the system about its critical point. Such an analysis gives information only for infinitesimal perturbations⁹ and fails completely in the critical case.^{10,11} It is well known that when normal mode analysis predicts a domain of asymptotic stability, the existence of a Lyapunov function¹² is assured for the system. These Lyapunov functions are easily obtained¹³ but usually give conservative estimates of the asymptotic stability domain.^{14,15}

The question of how far a locally asymptotically stable system can be perturbed while remaining