LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textural material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1986 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Reactive scattering of H + H₂ and its isotopic analogs

Frank Webster and J. C. Light
The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

(Received 23 July 1986; accepted 7 August 1986)

Although the first accurate close coupling calculations on reactive scattering of H + H₂ were reported nearly a decade ago, the only extensions to isotopic analogs are D + H₂ below 0.55 eV, H + D₂ at 0.74 eV, and Mu + H₂ at six energies including 1.50 eV by Schatz. We present reaction probabilities for J = 0 for H + H₂, D + H₂, and H + D₂, and discover resonance patterns in the energy dependence through 1.50 eV. R matrix propagation techniques successfully applied to H + H₂ are extended to asymmetric systems with modifications of the matching surfaces, propagation in the matching region, and the use of the discrete variable representation (DVR). The accurate LSTH surface as modified by Johnson is used.

The R matrix theory for reactive scattering provides the S matrix for all state-to-state reactive and inelastic processes at fixed total energy E, total angular momentum J, and parity. The close coupled equations are solved separately in each of three arrangement channels described by different sets of Jacobi coordinates. The reactivity is evaluated by matching these solutions on the common boundary. R matrix propagation theory assumes that for sufficiently small volumes of space defined by increments of a scattering coordinate, the R matrix can be diagonalized and the off-diagonal coupling occurs only in matching solutions between sectors. However, the match region cannot be treated exactly in this fashion.

The match region is nearly identical to one described by Schatz et al., and it lies between the isosceles triangle matching surface and an angle independent surface within the arrangement channel. It varies strongly with angle, having zero extent for collinear arrangements. The sector matrices within the match region cannot be diagonal, because this requires that the sector surfaces be defined by constant values of the scattering coordinate and that the scattering coordinate be orthogonal to the internal (surface) coordinates. We choose an orthogonal scattering coordinate and approximately diagonalize the sector R matrices in the match region by finding the expectation value of the sector width for each adiabatic vibration–rotation eigenfunction. The adiabatic energies and the coupling between sectors are calculated within the close coupling approximation. A similar approximation within the match region was introduced in the original H + H₂ work.

Reaction probabilities for five different reactive processes are shown in Fig. 1 every 0.01 eV from 0.50 to 1.50 eV. All show the probability of reaction from the ground state summed over rotational states of the v' product vibrational manifold for v' = 0, 1, and 2. The H + H₂ results of Walker et al. are included at low energy in Fig. 1(a). Figures 1(b) to 1(d) are for the H₂D mass combination. These three processes are coupled in a single S matrix at each energy Figure 1(b) shows the probability of producing HD(ν') from D + H₂. Figure 1(c) shows the H + HD reaction (not inelastic scattering) to HD(ν'). Figure 1(d) presents the back reaction H + HD producing H₂(ν'). Reactions of HD₂ are shown in Figs. 1(e) to 1(g).

Figure 1 shows reaction probabilities which vary smoothly and periodically as a function of energy. The ν' = 0 reactivity in Fig. 1(a) agrees with Schatz below 1.20 eV, but is above the reactivity of Walker et al. The present DVR treatment of the match region should be at least as accurate as Ref. 3, and so the reliability of our results should be better than the differences in Fig. 1(a). The H + H₂ resonance at 0.97 eV is obviously one of a series, presumably associated with Feshbach type resonances in the transition state, and not with specific vibrational thresholds. The other ν' = 0 reactivities also show smooth oscillatory behavior with the period decreasing with increasing mass. Figures 1(a), 1(b), and 1(f) show resonances which are coupled to the ν' = 1 threshold. The reactivity to ν' = 1 and 2 shows wide variation between different systems.

All results use 84 adiabatic vibration–rotation functions per arrangement channel designated by jₘₐₓ(i) = 13, 13, 13, 13, 13, 13, 9, 9, 3 except in an extended match region described by a DVR of dimension 144. The results should be converged. The (probably spurious) rapidly varying structure above 1.30 eV in Fig. 1(e) may indicate problems with the approximate propagation in the match region. We will be interested in comparing the detailed energy dependence of these asymmetric reactions on the LSTH surface with other
independent computational methods.\textsuperscript{16,17} Calculations of cross sections and an examination of the CS approximation are in progress.


\textsuperscript{11}The rotational branching ratios show dramatic energy dependence associated with some but not all of the features in Fig. 1, and these will be discussed in a subsequent publication.

\textsuperscript{12}M. C. Colton and G. C. Schatz, Chem. Phys. Lett. 124, 256 (1986). They observe a narrower resonance at 1.20 eV with 0.04 eV width, and the magnitude of the $v = 0$ reactivity was not reported.


\textsuperscript{14}The symmetric stretch and bending modes at the transition state are nearly degenerate and strongly mixed, and the energies of these modes do not correlate well with the resonance features. The resonance states are mixed with quasibound asymmetric stretch and are described best in other coordinates (see Ref. 13).

\textsuperscript{15}The DVR uses eight vibrational functions at each of 18 angular quadrature points. The vibrational functions are different at each angle.


\textsuperscript{17}R. T Pack, G. A. Parker, and R. B. Walker (private communication).