

and fluorescence detection could involve competition between ionization, dissociation, and fluorescence.

In addition to the nitric oxide spectrum we have also recorded the four-photon and three-photon ionization spectrum of benzene up to  $55\,000\text{ cm}^{-1}$  in the second-photon resonance. Above about  $43\,000\text{ cm}^{-1}$  the two-photon resonance does not produce fluorescence. This technique of multiphoton ionization spectroscopy is therefore applicable to molecules which do not fluoresce and extends nonresonant multiphoton gas phase spectroscopy to most molecules. Present laser technology limits four-photon studies to molecules with ionization potentials less than 13.4 eV, but five-photon ionization

may well be observable.

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<sup>1</sup>D. Fröhlich and H. Mahr, *Phys. Rev. Lett.* **19**, 496 (1966).

<sup>2</sup>P. R. Monson and W. M. McClain, *J. Chem. Phys.* **53**, 29 (1970).

<sup>3</sup>I. Webmann and J. Jortner, *J. Chem. Phys.* **50**, 2706 (1969).

<sup>4</sup>R. G. Bray, R. M. Hochstrasser, and J. E. Wessel, *Chem. Phys. Lett.* **27**, 167 (1974).

<sup>5</sup>C. B. Collins, B. W. Johnson, and M. Y. Mirza, *Phys. Rev. A* **10**, 813 (1974).

<sup>6</sup>K. Dressler and E. Miescher, *Astrophys. J.* **141**, 1266 (1965).

<sup>7</sup>R. M. Reese and H. M. Rosenstock, *J. Chem. Phys.* **44**, 2007 (1966).

## Quantum mechanical reactive scattering: An accurate three-dimensional calculation\*

Aron Kuppermann and George C. Schatz<sup>†</sup>

*A. A. Noyes Laboratory of Chemical Physics, Division of Chemistry and Chemical Engineering,<sup>‡</sup> California Institute of Technology, Pasadena, California 91125*

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We have performed accurate three-dimensional (3-D) quantum-mechanical calculations of differential and total cross sections for the  $\text{H} + \text{H}_2$  exchange reaction on the Porter-Karplus<sup>1</sup> potential energy surface. These are the first such calculations that are vibrationally and rotationally converged, and the results are believed to be accurate to 5% or better. They can serve as a comparison standard against which approximate methods can be tested.

To solve the body-fixed 3-D Schrödinger equation for the nuclear motion we perform a partial wave expansion, followed by a close-coupling expansion. For the latter we use variables and basis functions which vary from region to region of configuration space so as to optimize the representation of the wavefunction. This approach, developed previously,<sup>2</sup> has been successfully applied to collinear<sup>3</sup> and coplanar<sup>4</sup> reactions also. The coupled equations are integrated into the interaction region from each of the three arrangement channel regions, using the use of the Gordon method.<sup>5</sup> The solutions are smoothly matched on three appropriately chosen surfaces in internal configuration space by employing the convenient system of coordinates described elsewhere.<sup>6</sup> The full three-body Hamiltonian was used in these calculations, and no approximations were introduced other than those inherent in the numerical methods.

We have performed extensive calculations in the range of total energy  $E = 0.40\text{--}0.70\text{ eV}$  and have found that up to 30 rotational, 4 vibrational, and 100 total basis functions are necessary for convergence of the reaction probabilities to within 5%. The converged results usually satisfy conservation of flux to 1% or better and time reversal invariance to about 6% or better. We found

however that, as for the coplanar reaction,<sup>4</sup> results satisfying flux conservation and time reversal invariance could be obtained before satisfactory convergence was achieved. One cannot, therefore, rely on flux conservation and time reversal invariance as sufficient conditions for convergence. All values of the total angular momentum  $J$  from 0 to about 12 are needed for convergence of the reactive differential cross sections. The angular dependence of the differential cross sections are very sensitive to the magnitudes and phases of the scattering matrix elements. It is of crucial importance to establish the vibrational and rotational convergence of the results for each  $J$ , since otherwise spurious oscillations in the differential cross sections can result. The integral reaction cross sections are much less susceptible to these effects. Computation times on an IBM 370-158 for each  $E$  were 13, 33, 62, and 64 minutes for  $J = 0, 1, 2,$  and  $3$ , respectively, and approximately 75 min for  $J \geq 4$  and 100 basis functions.

The following conclusions can be inferred from the results obtained:

(1) Inclusion of closed vibrational channels in the close-coupling expansion is essential, in spite of the fact that this increases the computational time by factors of 10–30. For example, at 0.50 eV the  $J = 0$  distinguishable-atom reaction probability for the  $v = 0, j = 0$  reagent to the  $v' = 0, j' = 1$  product<sup>7</sup> is  $0.71 \times 10^{-3}$  for the vibrationally converged results and  $1.87 \times 10^{-3}$  when using only ground vibrational state basis functions, a difference of a factor of 2.6. Also, at  $E = 0.55\text{ eV}$  the vibrationally converged, orientation-averaged (i.e., summed over  $m'_j$ , and averaged over  $m_j$ ), para-ortho reaction cross section for the same process, is  $0.040\text{ bohr}^2$ .

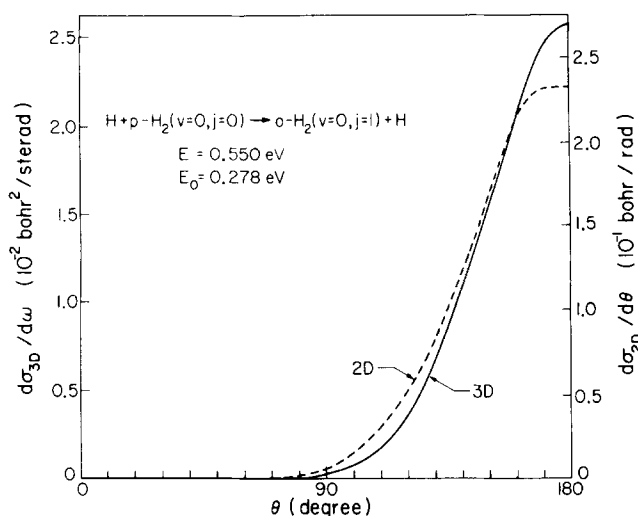


FIG. 1. Three-dimensional ( $d\sigma_{3D}/d\omega$ ) and coplanar ( $d\sigma_{2D}/d\theta$ ) para  $\rightarrow$  ortho differential reactive cross section as a function of the scattering angle  $\theta$  for the  $H + H_2 \rightarrow H_2 + H$  exchange reaction on the Porter-Karplus<sup>1</sup> potential energy surface at a total energy  $E = 0.550$  eV and relative reagent translational energy  $E_0 = 0.278$  eV. The corresponding wave functions have been antisymmetrized with respect to hydrogen atom exchange. The para- $H_2$  reagent is in its ground  $v=0, j=0$  vibrational-rotational state. The ortho- $H_2$  product is in its ground  $v'=0$  vibrational and  $j'=1$  rotational state, the lowest permitted by the Pauli principle. Contributions from all  $m_j$  values of the component of the angular momentum of the diatom product have been included in the cross sections. The solid line represents the three-dimensional results, for which the ordinate scale is at the left of the figure, and the dashed line depicts the coplanar results, for which the ordinate scale is at its right. The corresponding integral reaction cross sections are  $\sigma_{3D} = 0.040$  bohr<sup>2</sup> and  $\sigma_{2D} = 0.36$  bohr, respectively.

Wolken and Karplus,<sup>8</sup> in their pioneering work in which similarly only ground vibrational state basis functions were employed, obtained a value of about 0.43 bohr<sup>2</sup>. This difference of a full order of magnitude between these last two results must be due at least in part to their neglect of closed vibrational channels. Their phenomenological energy threshold is approximately 0.05 eV below our vibrationally converged one.

(2) Because of the much smaller times involved in the  $J=0$  calculations, it would be very helpful if computations of this type, such as those performed by Elkowitz and Wyatt,<sup>9</sup> were representative of the over-all reaction. We do find that at each energy  $E$ , the ratio of two orientation-averaged integral reaction cross sections from the same state of the reagents to different states of the products, usually agrees to within 20% with the corresponding  $J=0$  reaction probability ratio. However, the value of  $J$  which most contributes to the integral reaction cross sections is 2 at 0.40 eV increasing to 4 at 0.70 eV. As a result, the  $J=0$  calculations do not furnish accurate predictions for other appropriate quantities. For example, if we compare the ratio of two orientation-averaged integral reaction cross sections from different states of reagents to the same state of the products, at the same total energy, with the corresponding  $J=0$  reaction probability ratio, these quantities can

differ by a factor of 2 or greater.

(3) Let  $\Omega$  be the angular momentum associated with the tumbling of the triatomic plane around the position vector of the atom with respect to the diatom.<sup>10</sup> For small  $J$ , we observe in each arrangement channel only a weak dynamic coupling between states having different values of  $\Omega$ . This agrees with previous observations by Pack<sup>10</sup> and McGuire and Kouri<sup>11</sup> for nonreactive rotationally inelastic scattering. In addition, for  $J$  less than about 5 or 6, the  $\Omega=0$  reaction probabilities are usually significantly larger, by factors of 2–20, than the others. Neglect of  $\Omega$ -coupling and of unimportant  $\Omega$  contributions can shorten the computation time by one or two orders of magnitude. Preliminary calculations of this type indicate that these approximations can yield results which are quite accurate.

(4) The distribution of products among the several orientation-averaged rotational energy levels is very similar for the 3-D and coplanar reactions. In addition, the angular dependence of the corresponding differential cross sections is also very similar, as shown in Fig. 1.

(5) Over the range of total energies 0.60–0.70 eV, our distinguishable-atom reaction cross section from  $v=j=0$  reagent, summed over all final states of the products, agrees with the quasiclassical trajectory results of Karplus, Porter, and Sharma,<sup>12</sup> within the accuracy of the calculations.

Although Conclusions (1) and (2) indicate that accurate calculations are quite lengthy and can only be done for a small number of benchmark systems, conclusions (3)–(5) indicate that approximate methods that are still very realistic but much faster, might be developed and usefully applied to a significantly larger number of reactions.

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<sup>1</sup>R. N. Porter and M. Karplus, *J. Chem. Phys.* **40**, 1105 (1964).

<sup>2</sup>A. Kuppermann, *Potential Energy Surfaces in Chemistry*, edited by W. Lester (University of California at Santa Cruz, Santa Cruz, 1970) pp. 121–129; *VII International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers* (North-Holland, Amsterdam, 1971), p. 3.

<sup>3</sup>G. C. Schatz and A. Kuppermann, *J. Chem. Phys.* **59**, 964 (1973); G. C. Schatz, J. M. Bowman, and A. Kuppermann, *J. Chem. Phys.* **58**, 4023 (1973).

<sup>4</sup>A. Kuppermann, G. C. Schatz, and M. Baer, *J. Chem. Phys.* **61**, 4362 (1974).

<sup>5</sup>R. G. Gordon, *J. Chem. Phys.* **51**, 14 (1969).

<sup>6</sup>A. Kuppermann, "A Useful Mapping of Triatomic Potential Energy Surfaces," *Chem. Phys. Lett.* (in press).

<sup>7</sup>The unprimed  $v, j$ , and  $m_j$  are the vibrational, rotational and magnetic quantum numbers of the reagent molecule, whereas

the corresponding primed quantities refer to the product molecule.

<sup>8</sup>G. Wolken and M. Karplus, *J. Chem. Phys.* 60, 351 (1974).

<sup>9</sup>A. B. Elkowitz and R. E. Wyatt, "Three-dimensional natural coordinate asymmetric top theory of reactions: Application

to  $H+H_2$ ," *J. Chem. Phys.* (in press).

<sup>10</sup>R. T. Pack, *J. Chem. Phys.* 60, 633 (1974).

<sup>11</sup>P. McGuire and D. J. Kouri, *J. Chem. Phys.* 60, 2488 (1974).

<sup>12</sup>M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* 43, 3259 (1965).

## Quantum mechanical reaction cross sections for the three-dimensional hydrogen exchange reaction\*

Allan B. Elkowitz<sup>†</sup>

*Department of Physics, University of Texas, Austin, Texas 78712*

Robert E. Wyatt<sup>‡</sup>

*Department of Chemistry, University of Texas, Austin, Texas 78712*

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For the past several years, great effort has been devoted to obtaining accurate reaction probabilities for dimensionally restricted collinear<sup>1</sup> and coplanar<sup>2,3</sup> reactions.<sup>4</sup> Quantum studies of three dimensional reactions are much less numerous. Even though approximate DWBA studies of  $H+H_2$  appeared a decade ago,<sup>5,6</sup> it has only been within the past year that the first close coupling study of a three-dimensional reaction has been reported. Wolken and Karplus<sup>7</sup> computed the  $j=0$  to  $j'=1$  reaction cross section by integrating a system of coupled *integro-differential* equations for several values of  $J$  (total angular momentum quantum number). Their vibrationally adiabatic basis was limited to several rotational channels in the lowest ( $n=0$ ) vibrational manifold.

In this Communication, we report the results of extensive multichannel quantum mechanical studies of the three-dimensional hydrogen exchange reaction. Reaction cross sections were obtained for both the Porter-Karplus<sup>8</sup> potential surface (collinear barrier height 0.396 eV) and the Yates-Lester-Liu surface<sup>9</sup> (collinear barrier 0.424 eV). In our formulation of the scattering problem,<sup>10,11</sup> we first express the Hamiltonian operator in natural coordinates<sup>12</sup> and then partition it into a translational Hamiltonian for motion along a reaction coordinate, a vibrational Hamiltonian containing a local Morse potential, and a hindered asymmetric top Hamiltonian. The last term describes both free or hindered internal rotation of the system in addition to the free tumbling of the three particle triangle.<sup>13-15</sup> As a result of this partitioning of the total Hamiltonian, we expand the scattering wavefunction in local bases consisting of products of Morse oscillator and hindered asymmetric top states. Both the Morse and internal rotor components of the asymmetric top functions depend parametrically on the atom-molecule separation. The close coupled *differential* equations for the translational wavefunctions were then solved repeatedly using the Magnus method<sup>16</sup> at many values of  $E$  (total energy) and  $J$  on both potential surfaces.

Large basis sets designed to allow for both vibrational and rotational nonadiabaticity were employed. On the Porter-Karplus surface, a typical basis at low energy ( $E \lesssim 0.60$ ), included 22 channels, with 12 in the  $n=0$  vibrational manifold, 6 in  $n=1$ , and 4 in  $n=2$ . At higher energies, 50 channels (distributed 30/16/4) were employed. On the Yates-Lester surface, most calculations employed a 46 channel basis (distributed 30/16). On each surface the  $S$ -matrix was calculated at eight energies for each value of  $J$ , for  $J$  as high as 14. Altogether, about 100 production calculations were run<sup>17</sup>; the average computation time per  $(E, J)$  was about 1200 sec on the CDC 6600.

The energy dependence of reaction cross sections for  $j=0 \rightarrow j'=1, 3, 5$  para to ortho rotational transitions<sup>18</sup> for the two potential surfaces we show in Fig. 1. These cross sections include the appropriate factor for nuclear spin statistics for an even  $j$  to odd  $j$  transition.<sup>19</sup> Also shown is the  $j=0 \rightarrow$  all  $j'$  reaction cross section—without nuclear spin factors.<sup>20</sup> Figure 1 (a) compares our results with other three-dimensional cross sections on the same potential surface. These are the  $0 \rightarrow$  all cross section computed by Karplus, Porter, and Sharma<sup>21</sup> from classical mechanics; the  $0 \rightarrow 1$  cross section at one energy computed by Choi and Tang<sup>22</sup> with the DWBA formalism; and the Wolken-Karplus  $0 \rightarrow 1$  reaction cross section.<sup>7</sup> Our  $0 \rightarrow$  all reaction cross section is in much closer agreement with classical mechanics than would be expected by inspection of low energy *collinear* reaction probabilities.<sup>23</sup> In the collinear case, the classical threshold<sup>24</sup> is about 0.06 eV higher than the quantum result<sup>25</sup>; in 3-D, the threshold difference has narrowed to about 0.02 eV. We also note from the figure that the single DWBA result is in excellent agreement (at least for this one energy) with the full close coupling result. Also, the Wolken-Karplus cross section is very similar in shape to our result, but their threshold is shifted to lower energy by about 0.06 eV. This shift may be due in part to their use of a vibrationally adiabatic basis.<sup>26</sup>

The quantum reaction thresholds on either surface