Quantum Mechanical Calculations of Vibrational Population Inversion in Chemical Reactions: Numerically Exact L^2-Amplitude-Density Study of the H_2Br Reactive System

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Numerically exact, fully three-dimensional quantum mechanical reactive scattering calculations are reported for the H_2Br system. Both the exchange ($H+H'Br \rightarrow H'+HBr$) and abstraction ($H+HBR \rightarrow H_2+Br$) reaction channels are included in the calculations. The present results are the first completely converged three-dimensional quantum calculations for a system involving a highly exoergic reaction channel (the abstraction process). It is found that the production of vibrationally hot H_2 in the abstraction reaction, and hence the extent of population inversion in the products, is a sensitive function of initial HBr rotational state and collision energy.

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In this Letter we report the first completely converged, i.e., numerically exact, quantum mechanical calculations of three-dimensional reactive transition probabilities, for a chemical system involving a highly exoergic reaction channel. These results demonstrate a major advance in the capability to provide such converged quantum mechanical reaction probabilities, since the system studies involves large numbers of accessible quantum states and both light and heavy atoms. In fact, the ability to carry out such calculations has been a central goal of chemical dynamicists since the early days of quantum mechanics. The present demonstration of the ability of the L^2-amplitude-density method to treat such problems heralds a new day for molecular-collision dynamics. It is expected that similar methods will be of value for other few-body collision problems. The availability of such exact quantum results provides absolute standards against which approximate methods of reactions producing vibrational population inversion can be tested. Prior to the present calculations, these were unavailable.

The system chosen for this study is

$$H+H'Br \leftrightarrow H'HBr, \tag{1}$$

$$H+H'Br \leftrightarrow H_2+Br, \tag{2}$$

where H and H′ denote hydrogen atoms treated as distinguishable. The H_2+Br arrangement is 0.832 eV exoergic relative to the $H+HBr$ arrangement so that even at the lowest $H+HBr$ collision energies, the $v=0$ and 1 vibrational states of H_2 are energetically accessible. The calculations reported here represent exact quantum dynamics for an assumed realistic potential-energy surface.

The $H+HBr$ system is of interest for several reasons. First, there have been several experimental studies of chemical branching in hydrogen-atom reactions with hydrogen halides,[1,2] and there is considerable interest in the understanding of the potential-energy surface and dynamical effects governing the relative importance of the exchange reaction (1) versus the abstraction reaction (2). The availability of numerically exact three-dimensional quantum reactive scattering calculations should eventually allow for greater understanding of the dynamical aspects of this branching phenomenon.

Second, the $H+HBr$ reaction is considerably more asymmetric than any system yet studied by numerically exact three-dimensional quantum scattering methods, in terms of both the mass of the heavy atom and topology of the potential-energy surface, and thus it provides an extremely challenging test of the method used in the calculations.

Third, the exoergic nature of the $H+HBr \rightarrow H_2+Br$ reaction provides the possibility of the study of vibrational population inversion, which is the phenomenon responsible for most chemical lasers.[3] A particularly interesting aspect of this phenomenon is the dependence of the extent of population inversion on initial state and energy. The dependence of the reaction probability on initial and final quantum states and on energy may also be substantially different from that observed in previous studies of more symmetric systems,[4,5] or in approximate three-dimensional quantal[6] or quasiclassical[7] studies of exoergic systems.

The potential surface we have used in the calculation is due to Last and Baer,[8] as modified by Clary,[9] and is of the type diatomics in molecules plus three center term. This potential was used for an earlier three-dimensional quantum scattering calculation on this system by Clary.[9]

That calculation did not include the exoergic abstraction channel and must, therefore, be considered approximate for the exchange channel as well.

In the present calculations, we employ a recently proposed method[4] which utilizes L^2 expansions of the reactive amplitude density[10] in conjunction with the Fock coupling scheme[11] and a finite-difference boundary-value method[5,12] for a distorted-wave Green's function. In this approach, the solution $\Psi^{\alpha_i n_i}$ of the Schrödinger equation, for a system with three chemical arrangements, is expressed as

$$\Psi^{\alpha_i n_i} = \sum_{\alpha=1}^{3} \Psi_\alpha^{\alpha_i n_i}$$

where α_i is the initial arrangement, n_i represents a complete set of initial quantum numbers, and α labels a general arrangement. In the Fock scheme,[5,11] the $\Psi_\alpha^{\alpha_i n_i}$ for total energy E satisfy the equations

$$(E - H_\alpha^D)\Psi_\alpha^{\alpha_i n_i} = V_\alpha^C \Psi_\alpha^{\alpha_i n_i} + (H - E) \sum_{\alpha' \neq \alpha} \Psi_{\alpha'}^{\alpha_i n_i},$$

where H_α^D is a distortion Hamiltonian describing the arrangement α, V_α^C is the part of the potential not included in H_α^D, and H is the full Hamiltonian. These equations are solved formally by[5]

$$\Psi_\alpha^{\alpha_i n_i} = \Psi^{\alpha_i n_i} \delta_{\alpha\alpha_i} + G_\alpha^D \sum_{\alpha'} U_{\alpha\alpha'} \Psi_{\alpha'}^{\alpha_i n_i},$$

where

$$G_\alpha^D = \mathrm{P}(E - H_\alpha^D)^{-1}$$

is a principal-value Green's function, and

$$U = \begin{pmatrix} V_1^C & H-E & H-E \\ H-E & V_2^C & H-E \\ H-E & H-E & V_3^C \end{pmatrix}$$

is the Fock-scheme arrangement-channel generalized coupling matrix. The reactive amplitude density is defined by

$$\zeta_\alpha^{\alpha_i n_i} = \sum_{\alpha'} U_{\alpha\alpha'} \Psi_{\alpha'}^{\alpha_i n_i}.$$

It can be shown that the $\zeta_\alpha^{\alpha_i n_i}$ satisfy

$$\zeta_\alpha^{\alpha_i n_i} = U_{\alpha\alpha_i} \psi^{\alpha_i n_i} + \sum_{\alpha'} U_{\alpha\alpha'} G_{\alpha'}^D \zeta_{\alpha'}^{\alpha_i n_i}, \tag{3}$$

and that they are quadratically integrable (L^2). The solution of Eq. (3) is obtained by L^2 expansion of the $\zeta_\alpha^{\alpha_i n_i}$ in all degrees of freedom, resulting in simultaneous algebraic equations for the expansion coefficients, from which it is straightforward to calculate the reactance matrix and then the transition probabilities. The construction and solution of such equations may be accomplished very efficiently on a class-VI or -VII supercomputer. The expansion coefficients may then be used to calculate the relevant scattering amplitudes. Much of the work is independent of E so that the procedure can be made very efficient.

The calculations reported here were carried out for total angular momentum $J=0$ for several total energies. The basis set used included $v=0$, $j=0$–17; $v=1$, $j=0$–15; $v=2$, $j=0$–13; $v=3$, $j=0$–10 for the HBr molecule; and $v=0$, $j=0$–15; $v=1$, $j=0$–13; $v=2$, $j=0$–11; $v=3$, $j=0$–9; $v=4$, $j=0$–6 for the H_2 molecule, where v denotes the vibrational and j the rotational quantum number. This leads to 177 channels. The radial translational dependences of the reactive amplitude density components in the HBr+H arrangements were expanded in up to 43 distributed Gaussian functions[13] in each channel, while those in the H_2+Br arrangement were expanded with 51 distributed Gaussian functions in each channel, for a grand total of 8083 basis functions. The transition probabilities for initial j less than 10 are stable to better than 1% with respect to further refinement of all basis-set and numerical parameters. For higher initial j values, at the highest energy studied, the results appear converged to better than 5%. Unitarity is satisfied to better than 1% in all cases. The final parameters in the calculation are given in Table I.

In Table II we give the exchange-reaction probabili-

TABLE I. Basis set and Gaussian parameters.

	HBr	H_2
$v=0$, $j_{\max}=$	17	15
$v=1$, $j_{\max}=$	15	13
$v=2$, $j_{\max}=$	13	11
$v=3$, $j_{\max}=$	10	9
$v=4$, $j_{\max}=$	⋯	6
Gaussian width	1.4	1.4
Position of first Gaussian	1.1	1.1
Spacing of Gaussians	0.14	0.14
No. of Gaussians per quantum state	43	51
Position of last Gaussian	6.98	8.10
Step size for integrations over translational coordinates	0.005	0.005

TABLE II. Reaction probabilities for the exchange reaction H′+HBr→H+H′Br for $J=0$, from initial state (v_i, j_i) to all final states as functions of total energy E.

E (eV)[a] / v_i,j_i	0.34	0.38	0.42	0.45
0,0	0.010	0.034	0.059	0.077
0,1	0.025	0.088	0.151	0.191
0,2	0.031	0.108	0.185	0.222
0,3	0.028	0.097	0.166	0.192
0,4	0.019	0.070	0.123	0.149

[a] In this paper, E is defined relative to the H+HBr potential asymptote.

TABLE III. Reaction probabilities for the abstraction reaction $H+HBr \rightarrow H_2+Br$ for $J=0$, from initial state (v_i,j_i) to final vibrational level v_f, summed over final j_f states.

E (eV)[a] v_i,j_i v_f	0.34	0.38	0.42	0.45
0,0 0	0.014	0.015	0.018	0.023
0,0 1	0.038	0.035	0.028	0.022
0,1 0	0.033	0.036	0.043	0.057
0,1 1	0.108	0.099	0.080	0.064
0,2 0	0.034	0.039	0.045	0.060
0,2 1	0.158	0.146	0.121	0.096
0,3 0	0.019	0.024	0.027	0.036
0,3 1	0.171	0.162	0.142	0.115
0,4 0	0.007	0.009	0.010	0.012
0,4 1	0.149	0.146	0.138	0.117

[a] E is the total energy relative to the $H+HBr$ potential asymptote.

ties, summed over all final states of H′Br, from some initial states, (v_i,j_i), of HBr. We see that the probabilities increase with increasing translational energy. As the initial rotor state is increased, the reaction probabilities at first increase and then decrease. This is analogous to the behavior of the exchange-reaction probability in the completely hydrogenic systems.[4,5] In Table III, we give reactive probabilities for the abstraction reaction $H+HBr \rightarrow H_2(v_f)+Br$, again for various initial states of HBr and summed over final H_2 rotor states. Especially at low initial translational energy, as the initial rotor state j_i increases, the $v=1$ product states of H_2 become greatly favored in the abstraction reaction. Thus, one observes that the exoergic reaction pathway produces a substantial vibrational population inversion. However, as the translational energy increases, the $v_f=1$ probabilities decrease and those for $v_f=0$ increase. As expected from the difference in barrier heights for the two processes on the diatomics in molecules plus three center term surface (0.081 eV for abstraction and 0.238 eV for exchange), at low initial translational energy, the abstraction reaction is very dominant over the exchange process.

In Table IV, we give an explicit comparison of the $J=0$ reaction probabilities for exchange and abstraction for a range of energies and several initial HBr rotor states. At the highest energies studied, the exchange-reaction probabilities are larger than the abstraction-reaction probabilities. The results of recent experimental measurements by Aker, Germann, and Valentini[2] of the branching between the abstraction and exchange-reaction channels, carried out at even higher total energy than the present calculations, also show a larger cross section for the exchange reaction compared to abstraction. However, at lower energies the theoretical abstraction-reaciton probabilities are larger than the theoretical exchange-reaction probabilities, and the dominance increases as the initial HBr rotor state increases. The results at 0.42 eV show that a transition is occurring from abstraction domination to exchange domination. Indeed, for the lowest three HBr rotor states, the exchange probability is somewhat *larger* than the abstraction probability. However, the $j_i=3$ and 4 results at 0.42 eV show that abstraction is still dominant. At the highest energy of 0.45 eV, the exchange probability is largest for *all* initial j states, and the margin is larger than at 0.42 eV. It is interesting to note that the recent experimental measurements of the cross sections for exchange and abstraction by Aker, Germann, and Valentini[2] show that the exchange is favored by a factor of about 3 over abstraction. Our results for $J=0$ are in qualitative agreement with this.

The results show that the inverted product population distributions are sensitive to small differences in the rotational energy of the reactants. Because the rotational spacings of the reactant HBr are small and yet produce large effects on the product-state distributions, it is an interesting question, but doubtful, whether quasiclassical methods will be reliable for describing such effects. Our results provide an absolute standard with which to test such approximate methods.

In summary, the quantum dynamics of the type of reaction which involves a vibrational population inversion is difficult to treat accurately because of the large number of quantum states involved. The ability to treat such systems has been a goal of collision dynamicists for the

TABLE IV. Reactive probabilities for the exchange reaction $H'+HBr \rightarrow H'Br+H$ (all final states) and the abstraction reaction $H+HBr \rightarrow H_2+Br$ (all final states) for $J=0$ and various initial HBr states (v_i,j_i).

E (eV)[a]	0.34		0.38		0.42		0.45	
v_i,j_i	Exch.	Abst.	Exch.	Abst.	Exch.	Abst.	Exch.	Abst.
0,0	0.010	0.052	0.034	0.050	0.059	0.046	0.077	0.046
0,1	0.025	0.141	0.088	0.136	0.151	0.123	0.191	0.121
0,2	0.031	0.191	0.108	0.185	0.185	0.166	0.222	0.156
0,3	0.028	0.189	0.097	0.186	0.166	0.169	0.192	0.151
0,4	0.019	0.156	0.070	0.155	0.123	0.147	0.149	0.129

[a] Total energy relative to the $H+HBr$ potential asymptote.

past 50 years. The present convergence of fully three-dimensional quantal reaction probabilities for the present highly asymmetric reaction having a large exoergicity is a very encouraging benchmark in the quantum theory of reactive scattering. It demonstrates clearly the ability of L^2 methods employing the Fock-scheme amplitude density to calculate state-to-state reaction probabilities for very challenging systems. Of course, it is desirable next to carry out complete cross-section calculations for the H_2Br system. This involves calculations for total angular momentum quantum number $J > 0$, and as J increases, the number of quantum states entering will also increase. We have recently carried out studies[14,15] on more symmetric systems which indicate that more difficult systems and higher total angular momenta can be treated by the combination of a variational principle with the amplitude-density approach. These combinations of techniques should allow for very detailed comparisons of theory and experiment for state-to-state reaction dynamics and, in particular, for further studies of quantal effects on the initial-state dependence of product population inversion.

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