3D quantum scattering calculations of the reaction $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ for total angular momentum $J=0$

John Z.H. Zhang¹, Danny L. Yeager² and William H. Miller

Department of Chemistry, University of California,

and Materials and Chemical Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

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An improved version of the *S*-matrix Kohn variational method has been applied to calculating 3D quantum reaction probabilities of the ion-molecular reaction $\text{He} + \text{H}_2^+ (\nu) \rightarrow \text{HeH}^+ + \text{H}$. The calculation is carried out for total angular momentum $J=0$ and employs the DIM potential surface of Kuntz. Our results show that vibrational excitation of H_2^+ enhances the reaction probabilities and are in qualitative agreement with early experimental results. The calculated reaction probabilities are found to be highly oscillatory as a function of scattering energy and are associated with resonances of the system.

1. Introduction

Rapid progress has been made in the past few years in the theory of quantum reactive scattering. As a direct result of this progress one can now calculate exact state-to-state reaction cross sections for the simple reaction $\text{H} + \text{H}_2$ [1,2], the isotopically related reaction $\text{D} + \text{H}_2$ [3,4], and most recently for $\text{F} + \text{H}_2$ [5]. However, tremendous difficulties still lie ahead for dynamicists if one wants to calculate cross sections for other systems for a given potential energy surface.

The $\text{H} + \text{H}_2$ reaction family is a light system which interacts on a short-ranged repulsive potential surface, features which make the dynamics calculation relatively easy. While the $\text{H} + \text{H}_2$ reaction is characterized by a high level of vibrational adiabaticity, which implies that the dynamics is "direct" or of a short-time nature, the ion-molecule reaction $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ is quite different from the H_3 family and is a good challenge for application of the *S*-matrix Kohn variation method which has been very successful for treating the $\text{H} + \text{H}_2$ [1], $\text{D} + \text{H}_2$ [3] and $\text{F} + \text{H}_2$ [6] problems.

The experimental work by Chupka [7], Pijkaren [8], and Turner and coworkers [9] on the $\text{He} + \text{H}_2^+$ system shows a strong dependence of the reaction cross section on the initial vibrational state of the reagent over a wide range of energies (1–5 eV). Specifically, the vibrational excitation of the reagent molecule H_2^+ greatly enhances the reactivity. Also, experimentally measured cross sections from highly excited reactant vibrational states ($\nu=2$ and 3) by Chupka and coworkers [7] show a maximum in the energy dependence.

Earlier dynamical studies of this system employed a semi-empirical DIM potential surface [10] fit to *ab initio* points in collinear geometry [11]. The DIM potential surface of the $\text{He} + \text{H}_2^+$ system, for which various dynamics calculations have been carried out, has a well of about 0.2 eV in depth with respect to the reagent and has long-range attractive forces in the exit channel [10,12]. These features make the dynamics considerably more complex than for the simple repulsive H_3 system, and yet offer rich incentive for theoretical investigation.

The collinear quantum-mechanical calculations by Kouri and Baer [13], and subsequently by Adams [14], show no evidence of vibration enhancement in the reaction probabilities on a slightly modified DIM potential surface, but the reaction probabilities in those calculations were found to be strongly oscil-

¹ Current address: Department of Chemistry, New York University, New York, NY 10003, USA.

² Permanent address: Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.

latory as functions of scattering energy. However, a quasiclassical trajectory study by Kuntz and Whitton [12] on the DIM surface yielded reaction cross sections that were considerably enhanced by the vibrational excitation of the reagent molecule H_2^+ , in qualitative agreement with experimental results observed by Chupka and others [7–9]. Based on those calculations, Kuntz [12] argued that collinear calculations for this system are not valid. A recent approximate quantum (RIOS) calculation [15] on the DIM surface yields vibrationally enhanced cross sections and therefore further supports this argument. A new QCT study by Joseph and Sathyamurthy [16] on a new potential surface (MTJS) [17] also yields results in qualitative agreement with those on the DIM surface. It therefore appears clear that the collinear calculations for this system are not useful even in a qualitative sense, and full 3D dynamics calculations are necessary to clarify this argument.

On the other hand, the striking resonance features shown in the collinear quantum calculations [13,14] of the reaction probabilities, which also show up in the experimental observation of the reaction cross sections, strongly suggest that quantum effects for the $\text{He} + \text{H}_2^+$ system may be very important. The existence of strong resonances casts some doubt on whether quasiclassical trajectory (QCT) treatments for this system are fully justified since resonances, which are not detectable by a QCT calculation, could profoundly affect the dynamics. It is desirable to investigate resonance effects in full three-dimensional space.

Recently, Kress et al. [18] have performed 3D quantum calculation for the $\text{He} + \text{H}_2^+$ system on the MTJS [17] potential surface for total angular momentum $J=0$ using the APH hyperspherical-coordinate method developed by Pack and coworkers [19]. They found numerous resonance peaks in the reaction probabilities and attributed them to the bound states of the shallow well in the entrance channel. Their results also show evidence of vibrational enhancement of the reaction probabilities.

Although the MTJS surface is assumed to be more accurate than the DIM surface because ab initio calculated points at near CI level have been employed in the analytical fitting of MTJS [17] surface while those used in the fitting of DIM surface are at the

SCF level [11], it is still not clear which one would yield results that agree better with experiment [7–9]. We chose the DIM surface to perform our 3D variational calculation since most of the previous dynamics calculations, in particular the collinear quantum calculations [13,14], were carried out on this surface. We used an improved version of the *S*-matrix Kohn variational method to calculate reaction probabilities for total angular momentum $J=0$ on Kuntz's DIM surface [12]. The new version of our method uses an optimized quasi-adiabatic basis representation for the short-range basis functions and multi-channel distorted waves for the asymptotic free functions. We briefly describe these improvements of our method in section 2 and present our numerical results in section 3. Section 4 concludes.

2. Theory

In the *S*-matrix Kohn variational method [3,20], the *S* matrix is given by the matrix equation

$$\mathbf{S} = \frac{i}{\hbar} (\mathbf{B} - \mathbf{C}^T \mathbf{B}^{*-1} \mathbf{C}), \quad (1)$$

where $\mathbf{S}$, $\mathbf{B}$, and $\mathbf{C}$ are matrices of the size of the number of open channels. "T" denotes matrix transpose. $\mathbf{B}$ and $\mathbf{C}$ are given by

$$\mathbf{B} = \mathbf{M}_{00} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0, \quad (2a)$$

$$\mathbf{C} = \mathbf{M}_{10} - \mathbf{M}_0^{*T} \mathbf{M}^{-1} \mathbf{M}_0, \quad (2b)$$

where $\mathbf{M}_{00}$ and $\mathbf{M}_{10}$ are given by

$$(\mathbf{M}_{00})_{nn'} = \langle u_{0n} \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (3a)$$

$$(\mathbf{M}_{10})_{nn'} = \langle u_{1n} \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (3b)$$

where n is a collective index for all the internal quantum numbers, for example, $n = (vjl)$, for the atom-diatom system. Our convention (as always) is that translational functions in the bra are not complex conjugated. $\mathbf{M}$ is a "large $\times$ large" matrix,

$$(\mathbf{M})_{tn,t'n'} = \langle u_t \phi_n | H - E | u_{t'} \phi_{n'} \rangle, \quad (4)$$

$t, t' = 2, \dots, N$; and $\mathbf{M}_0$ is a "large $\times$ small" rectangular matrix,

$$(\mathbf{M}_0)_{tn,n'} = \langle u_t \phi_n | H - E | u_{0n'} \phi_{n'} \rangle, \quad (5)$$

$t = 2, \dots, N$.

In our previous applications, u_i were chosen to be distributed Gaussian functions and u_0 ($u_1 = u_0^*$) incoming (outgoing) spherical Hankel functions multiplied by a cutoff function to regularize its behavior near the origin. ϕ_n are eigenfunctions of the asymptotic arrangement Hamiltonian. In a recent publication [21], we proposed a basis-set contraction scheme in which a linear combination of the primitive basis functions ϕ_n is formed and optimized in a quasi-adiabatic fashion. The quasi-adiabatic basis functions ϕ'_n are optimized basis functions that are obtained by diagonalizing a sub-Hamiltonian matrix for fixed translational coordinate R_i (center of the Gaussian function u_i) for $i=2, \dots, N$. A simple energetic criterion is then imposed to select those functions that are important to the dynamics. Details of this contraction scheme are given in ref. [21].

Another major improvement is the adoption of distorted waves to replace the "free" asymptotic functions $u_{0n}(R)$ used in our earlier applications. This idea has been described in detail previously [3], but the present work is our first implementation of it. The advantage of using distorted waves is that they can describe quite well the long-to-intermediate range potential forces that are inelastic in nature, and thus convergence can be achieved with a much smaller L^2 basis. Since the efficiency of our calculations will ultimately be determined by how large an L^2 basis one must use, use of distorted waves for u_0 (and $u_1 = u_0^*$) can be very helpful. For example, in the $\text{He} + \text{H}_2^+$ case described here, the size of the region which must be covered by the L^2 basis is reduced from about 16 au to about 7 au in the product $\text{HeH}^+ + \text{H}$ arrangement when distorted waves are used; thus, considerable savings can be achieved in the number of L^2 basis functions. The basic idea is to let L^2 basis functions describe the exchange region only, within which chemical reaction occurs.

Let $\mathbf{V}(R)$ be the full interaction potential matrix (open channels only) in a given arrangement. The distorted wave function, denoted by u_0 , satisfies the radial Schrödinger equation,

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \mathbf{I} - E\mathbf{I} + \boldsymbol{\epsilon} + \mathbf{V} \right) \mathbf{u}_0 = \mathbf{0}, \quad (6)$$

where $\boldsymbol{\epsilon}$ is a diagonal matrix whose elements are eigenvalues of the Hamiltonian for the internal degrees of freedom, and $\mathbf{I}$ is a unit matrix. The asymptotic boundary condition of u_0 is given by the "free" incoming wave,

$$(\mathbf{u}_0)_{nn'}(R \rightarrow \infty) \approx \frac{1}{\sqrt{k_n}} \times \exp \left[-i(k_n R - \frac{1}{2} l_n \pi) \right] \delta_{nn'}. \quad (7)$$

A direct matrix-version Numerov propagator [22] has been selected to perform the numerical integration for efficiency and easy implementation. We integrate the equations inward toward the origin starting with the asymptotic condition in eq. (7).

The modifications to the earlier formulations of S -matrix Kohn variational method (eqs. (3)–(5)) are straightforward and are given by [3]

$$(\mathbf{M}_{00})_{nn'} = \frac{\hbar^2}{2m} \sum_{n''} \langle \mathbf{u}_{0n''n} | f'^2 | \mathbf{u}_{0n''n'} \rangle, \quad (8a)$$

$$(\mathbf{M}_{10})_{nn'} = \frac{1}{2} i \hbar \delta_{nn'} + \frac{\hbar^2}{2m} \sum_{n''} \langle \mathbf{u}_{0n''n}^* | f'^2 | \mathbf{u}_{0n''n'} \rangle, \quad (8b)$$

$$(\mathbf{M}_0)_{in,n'} = \sum_{n''} \langle u_i \phi'_n | H - E | \mathbf{u}_{0n''n} \phi_{n''} \rangle. \quad (9)$$

The cutoff function f is explicitly shown in eqs. (8), and eq. (6) has been used in deriving the simplified expressions for $\mathbf{M}_{00}$ and $\mathbf{M}_{10}$. It is worthwhile to point out that eqs. (8) and (9) involve only "direct" matrix elements (those in the same arrangement channel) because the cutoff function can be chosen to vanish inside the exchange region so that matrix elements of $\mathbf{M}_{00}$, $\mathbf{M}_{10}$, and $\mathbf{M}_0$ between different arrangements are negligible.

3. Results and discussions

The DIM potential surface of Whitton and Kuntz [12] has been employed in our variational calculation for the $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ reaction. The reaction is endothermic by about 0.78 eV on the DIM surface. In the energy range we consider, up to five vibrational states of H_2^+ are open and one vibration for HeH^+ . A detailed description of the potential surface can be found in ref. [12] and, hence, we will not further describe it here. However, we want to point out two main features of the DIM potential surface that are quite different from those of $\text{H} + \text{H}_2$

and other neutral systems which we have encountered previously: First, the DIM potential has a shallow well of about 0.2 eV in the entrance channel which can support bound states. Second, there are long-range attractive forces in the exit channel. These two features are reflected in our dynamics calculation in that more basis functions are required around the region of the well in order to describe the dynamics more accurately, and also long-range forces need to be treated appropriately. The use of quasi-adiabatic basis functions is particularly attractive because these basis functions are optimized locally. The idea of using distorted waves is quite natural in view of the existence of long-range forces in the $\text{He} + \text{H}_2^+$ system.

The dynamics calculation is carried out for this reaction for total angular momentum $J=0$. We used the following basis set in our production runs: $(18, 16, 14, 12, 10, 8, 6) \times 30$ for $\text{He} + \text{H}_2^+$ arrangement and $(13, 11, 9, 7) \times 23$ for $\text{HeH}^+ + \text{H}$ arrangement. This amounts to a total number of 2482 primitive basis functions. The convention of the basis-set notation which we adopt here is the same as our previous conventions and can be found in ref. [3]. These basis functions were contracted to form a smaller op-

timized quasi-adiabatic basis set as described in ref. [21]. We retain only those new basis functions whose eigenvalues are smaller than $\text{ECUT} \cdot E_{\text{tot}}$ where ECUT is a parameter and E_{tot} is the total scattering energy. In our calculations we used a conservative value of 1.4 for ECUT although a value of 1.2 already gives very good results. The actual number of basis functions varies for different scattering energy and ranges from about 1400 to 2000 with the choice of 1.4 for ECUT in our calculations. Choices with smaller values of ECUT result in many fewer basis functions.

Calculations using our old computer code, which does not utilize multi-channel distorted waves, requires us to place distributed Gaussians as far out as 16 au in the $\text{HeH}^+ + \text{H}$ arrangement. However, use of multi-channel distorted waves reduces the distance from 16 au to about 7 au, and therefore reduces the number of Gaussians by more than a factor of two. Various convergence tests indicate that reaction probabilities are converged to within a few percent.

The transition probabilities from $\text{H}_2^+(v, j=0)$ to $\text{HeH}^+(v'=0)$ are plotted as a function of scattering energy, in fig. 1 for $v=0, 1$, and in fig. 2 for $v=2, 3$.

Fig. 1. Transition probabilities for the reaction $\text{He} + \text{H}_2^+(v, j=0) \rightarrow \text{HeH}^+(v'=0, \text{all } j') + \text{H}$ for total angular momentum $J=0$. The solid curve is for $v=0$ and dashed curve is for $v=1$.

Fig. 2. Same as fig. 1, except the solid curve is for $v=2$ and dashed one for $v=3$.

A total number of 127 energies from 0.98 to 1.26 eV are plotted in order to map out the resonance features. It is clear from these two figures that: reaction probabilities are enhanced by vibrational excitation of the reagent H_2^+ with dominant transitions from initial $v=2$ and 3 states; and second, transition probabilities have numerous resonance peaks as a function of energy for all values of the initial vibration v . In particular, many resonances have very narrow width in energy space, and this implies long-lived metastable states with lifetime on the order of picoseconds. These findings indicate that the DIM surface of Kuntz [12] can indeed produce vibrational enhancement in full 3D quantum calculations for the reaction $\text{He} + \text{H}_2^+$, and further confirm the argument that collinear calculations are not valid for this system.

In order to further investigate the role of initial rotation we also report reaction probabilities from the initial $j=2$ state of H_2^+ . Fig. 3 shows reaction probabilities from the initial reactant state H_2^+ ($v=0, 1, j=2$) and those from H_2^+ ($v=2, 3, j=2$) are shown in fig. 4. It appears that rotational excitation enhances the reaction for H_2^+ in state $v=0$ or 1, but slightly decreases the reaction when H_2^+ is in state

$v=2$ or 3. On the other hand, the level of vibrational enhancement of the reaction is decreased for the initial state $j=2$.

4. Conclusions

The ion-molecule reaction $\text{He} + \text{H}_2^+$ exhibits rich resonance structure, with resonance lifetimes being considerably longer than those in neutral systems such as $\text{H} + \text{H}_2$ or even $\text{F} + \text{H}_2$ in 3D quantum calculations for $J=0$. The narrow resonances are mostly likely due to wells in the potential surface that are deep enough to support bound states. The strong quantum effects in the $\text{He} + \text{H}_2^+$ system make it important to study the reaction quantum mechanically. Our results essentially reach the same conclusions as those by Kress and coworkers [18] about the role of vibrational excitation and the richness of resonances for the $\text{He} + \text{H}_2^+$ reaction, although the two calculations are done on two quite different potential surfaces. Since reaction probabilities for $J=0$ are not experimentally observable in scattering experiments, it will be desirable to compute the cross sections in order to compare directly with experiments. An im-

Fig. 3. Same as fig. 1, except for initial $j=2$.

Fig. 4. Same as fig. 2, except for initial $j=2$.

portant question is, however, whether this resonance structure will survive the partial-wave averaging in the calculation of integral cross sections, because resonance energies shift as J increases so that structure tends to be washed out when summed over J . Based on our early calculations for the $H+H_2$ and $D+H_2$ systems, we expect that resonances in the $He+H_2^+$ system will be broadened considerably, if they are not completely quenched, in the integral cross sections. However, the resonances should show up more clearly in the *differential* cross sections and particularly for those cross sections whose final rotational states are resolved [23]. Another very attractive alternative is to observe resonances in photodetachment experiments [24], for which reactive scattering calculations for $J=0$ can be directly observed and compared with the photoelectron spectrum [25,26].

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