

ARTICLE

Quasi-classical Trajectory Study on the $H^+ + H_2$ Reaction

Hui Song, Xiu-yan Wang, Rex. T. Skodje, Xue-ming Yang*

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

(Dated: Received on October 31, 2005; Accepted on December 2, 2005)

Quasi-classical trajectory (QCT) calculations on the $H^+ + H_2$ reaction system were carried out on a new potential energy surface (PES). Theoretical calculations show that the angular distribution of the forward and backward products is roughly symmetric for the title reaction. The product rotational state distribution was also determined at a few collision energies. In the collision energy range from 0.124 eV to 1.424 eV, the integral cross section for this system monotonically decreases with the collision energy. A comparison with the experimental result of the ion-molecule reaction was also made, the agreement is generally good.

Key words: Ion-molecule, Reaction dynamics, Classical trajectory calculations

I. INTRODUCTION

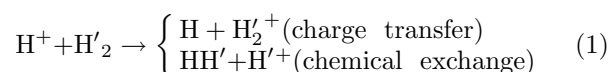
The system H_3^+ , the most simple triatomic system bound by just two electrons, had attracted increasing attentions of both experimentalists and theorists [1-4]. Its importance on the interstellar medium and plasmas has led to a detailed experimental characterization of its spectrum and reaction [5,6]. The potential energy surface for this system has also been obtained using the *ab initio* method [7]. Even though this reaction is the simplest ion-molecule reaction, it has a deep potential well and involves strong nonadiabatic charge-transfer processes at high collision energy. Therefore, fully converged quantum scattering treatment for this ion-molecule reaction is actually very difficult. Recently quantum treatments of this system have been reported [8,9]. Classically treatment of this system is more accessible. Csizmadia *et al.* reported the first classical trajectory calculation for the reaction $D^+ + H_2$ at high collision energies without the nonadiabatic effects [10]. By including the nonadiabatic effects, the original trajectory surface hopping method was performed [11-14]. All these works were performed at relatively higher collision energies and the possibility of strong nonadiabatic effects associated with the charge-transfer process is quite large. Recently, we used the QCT method to investigate the detail dynamics for the $H^+ + D_2$ reaction in the collision energy range of 0.124-1.424 eV [15], which is significantly lower than 1.80 eV where the Born-Oppenheimer approximation breaks down for this reaction. This allows us to look at the complex formation channel in great details without the interference from the charge transfer process.

In this work, we studied the $H^+ + H_2$ reaction using the QCT method at the low collision energies. We

briefly describe the PES that governs the motion of the interacting atoms (ions) and the computed method used for the system.

II. POTENTIAL ENERGY SURFACE AND CALCULATION METHOD

In the $H^+ + H_2$ reaction, the two possible reaction channels can occur,



The charge transfer channel is closed below 1.8 eV. In this study, we only deal with the chemical reaction channel that goes through the complex formation process, all trajectories were run on the lowest potential energy surface only. And the nonadiabatic transfer process is neglected. In the present calculations, a modified DIM PES was used that includes three-body exponential-type correction functions by Ushakov *et al.* [13]. The modified DIM PES was called the KBNN PES.

The methodology of quasiclassical trajectory calculations for atom-diatom reactions is well established [16,17]. Briefly, the classical Hamilton's equations are integrated numerically for motion in three dimensions, that is, trajectories were propagated using a simple Runge-Kutta integration scheme employing a fixed time step size of 3 a.u.. This ensures energy conservation in the calculations in sufficient accuracy. The initial conditions were selected to model the $H^+ + H_2(0,0)$ state using the simplest WKB prescription. The initial separation, $R(H^+ - H_2)$ was set to be $25 a_0$ and the trajectories were propagated until the final product separation again reached $25 a_0$. Because of complex formation, the propagation time required was generally quite long (several ps). The $H^+ + H_2$ reaction at each collision energy was modeled using 100,000 trajectories that randomly sample the vibration-rotational phases and the impact parameter. Total reaction probability at each

* Author to whom correspondence should be addressed. E-mail: xmyang@dicp.ac.cn, Tel: 0411-84379246

collision energy can be determined in this way. The final quantum state of the product diatom was determined in two distinct ways. First, the state distribution was determined using conventional Histogram binning method [18]. In the second approach, the final state was selected using the Gaussian weighting procedure described by Bonnet *et al.* [19,20]. The calculations were carried out at 14 collision energies in the range $E_C=0.124-1.424$ eV for the title reaction. The main focus is on the case $E_C=1.15$ eV where the experimental results have been analyzed. For this case, 500,000 trajectories were used. The complex life-time can also be determined for each reaction trajectory. To perform the life-time analysis on the complex trajectories, we used the dynamical definition of the trapping time of a trajectory which separates out the asymptotic channel motion, as the one used for $H^+ + D_2$ system [15].

III. RESULTS AND DISCUSSION

A. Integral cross section

The excitation function, i.e., the integral cross section versus the translational collision energy E_C , was calculated for the $H^+ + H_2$ reaction using the QCT method described above and is shown in Fig.1 over the collision energy range of 0.124-1.424 eV. One can see clearly that the excitation function on the KBNN PES decreases monotonically with increasing collision energy. Since the integral cross section is mostly determined by the dynamics of capture trajectories, the falloff of the ICS with the increasing collision energy is the characteristic of the decrease of the capture radius as collision energy increases. In a simplistic picture, the overall reaction can be viewed as a sequence of two steps: the capture of the projectile to form a complex, and the decay of the complex forward into the reactive channel. An examination of the reactive classical trajectories reveals that the reaction proceeds through a capturing process

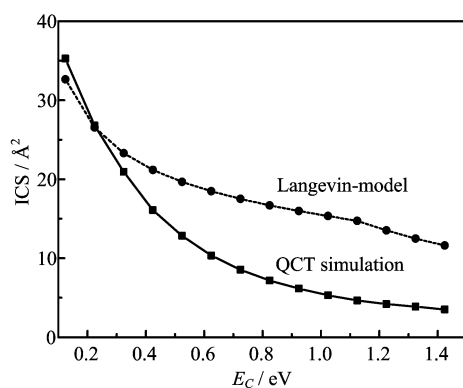


FIG. 1 The total integral cross section (excitation function) for the reaction $H^+ + H_2(v=0, j=0) \rightarrow H_2(v'=all, j'=all) + H^+$ on the KBNN-PES as a function of collision energy.

across the centrifugal barrier into a long lived collision complex. If the reactive cross section (σ_R) is decomposed into a capture cross section (σ_C) and a statistical transmission coefficient (K) into the product channel, $\sigma_R = K\sigma_C$, a Langevin model can be easily constructed based on the KBNN-PES along the reaction path. Using a constant value for the transmission coefficient, K , we see in Fig.1 that a fair model of the $\sigma_R(E_C)$ is obtained using this simple picture.

The product vibrational state-resolved integral cross sections for the reaction $H^+ + H_2(v=0, j=0)$ at 1.15 eV collision energy with the Histogram binning (HB) and Gaussian-weighted binning (GB) methods are shown in Table I. This table shows us the ICSs with the HB method for different vibrational states of the product are much larger than the corresponding value with the GB method. This is mainly because the GB method weighs each final trajectory result by a Gaussian coefficient in which the value of a trajectory close to the nearest integer will be given a larger weight.

TABLE I Integral cross sections (in \AA^2) for the $H^+ + H_2(v=0, j=0)$ reaction at 1.15 eV collision energy.

Method	GB method	HB method
Total	3.07770	4.38389
$V'=0$	1.92628	2.02305
$V'=1$	1.02036	1.71971
$V'=2$	0.13106	0.64113

The comparison with these two binning methods for the ICSs of product rotational state is shown in Fig.2. At $E_C=1.15$ eV for $H^+ + H_2$ reaction, $v'=2$ is already open. Figure 2(a) shows the total product rotational state distribution obtained with the HB method while Fig.2(b) shows the total product rotational state distribution obtained using the GB method. From this figure, the maximum populated rotational state quantum numbers for different vibrational states with the HB method are $j'=14$ ($v'=0$), 12 ($v'=1$) and 9 ($v'=2$), which are significantly larger than those allowed energetically, while corresponding values obtained with the GB method is $j'=13$ ($v'=0$), 10 ($v'=1$) and 5 ($v'=2$). At 1.15 eV collision energy, the maximum allowed rotational quantum numbers should be $j'=12$ ($v'=0$), 9 ($v'=1$) and 4 ($v'=2$). So the results obtained with the GB method are clearly more reasonable.

B. Product differential cross sections

The differential cross sections for the ro-vibrational-state integrated H_2 product were calculated at many collision energies using the QCT method, and three of them are displayed in Fig.3 for the title reaction. The product angular distribution is clearly forward/backward peaking and almost symmetric. This is entirely consistent with the fact that the reaction proceeds through a long-lived complex. At other col-

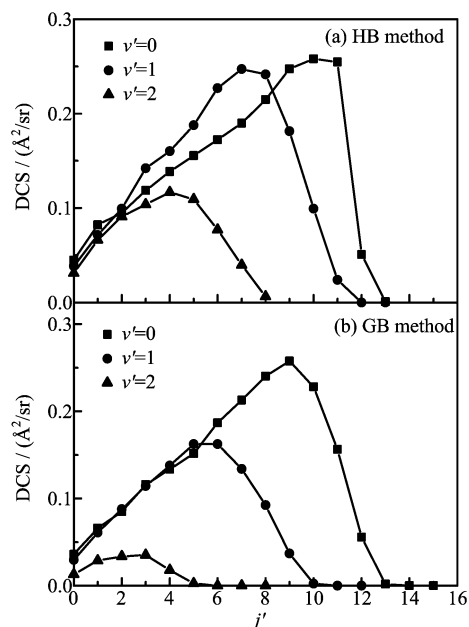


FIG. 2 The vibration and rotational state-resolved integral cross section distributions for the reaction $\text{H}^+ + \text{H}_2(v=0, j=0)$ at 1.15 eV collision energy.

lision energies, the results were very much similar. In addition, the change of the differential cross section with the collision energy is also clear from Fig.3. The higher the collision energy is, the smaller the differential cross section. The forward-backward peaking becomes more pronounced at low collision energies, indicating a trend toward longer complex lifetimes as energy decreases. Furthermore, we have made a direct comparison between the result of an ion beam experiment and the QCT result at a specific scattering angle. The ion beam scattering experiment for the ion-molecule reaction $\text{H}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{H}^+ + \text{H}_2(v'=0, j')$ was carried out by Gerlich [21]. Figure 4 shows the rotational

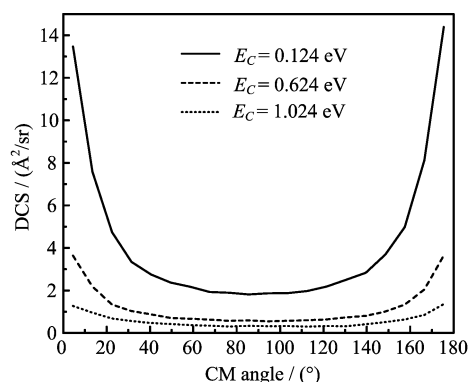


FIG. 3 Center-of-mass total (final-state summed) differential cross-section for $\text{H}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{H}^+ + \text{H}_2$ at 0.124, 0.624 and 1.024 eV. The scattering angle is defined as the angle between the incident H^+ beam and the H^+ product.

state distributions of the H_2 product from the experiment and the QCT calculation with GB method at the scattering angle of 10° . The comparison was made by multiplying a single scale factor to the experimental results. Generally speaking, the agreement between theory and experiment is quite good, suggesting that the QCT picture is quite good to describe the dynamics of this elementary ion-molecule reaction. This also implies that ion-molecule reactions can be generally described semiclassically.

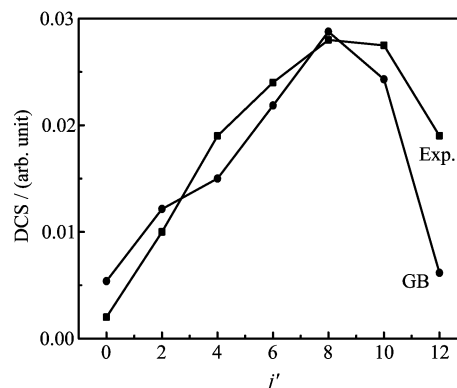


FIG. 4 The product rotational number differential cross section distribution for the reaction $\text{H}^+ + \text{H}_2(v=0, j=0) \rightarrow \text{H}^+ + \text{H}_2(v'=0, j')$ for the experimental and QCT (GB) method, at collision energy $E_C=1.15$ eV and the experiment scattering angle of 10° .

C. The lifetime for the complex

Since this reaction proceeds through the H_3^+ complex, it would be interesting to know the lifetime of the complex. The lifetime for decay of the complex can be obtained by fitting the long time survival probability of an ensemble of orbits to an exponential decay law. The complex lifetime in general depends on both the total energy and the angular momentum of the complex. In Fig.5 we show the lifetime of the complex formed with different impact parameters for the reaction $\text{H}^+ + \text{H}_2$. At a fixed collision energy, the lifetime increases with impact parameter because the centrifugal barriers to decay becomes larger, while the reactive probability goes down with the increasing impact parameter. On the other hand, for collisions with fixed total angular momentum $J=0$, the complex lifetime monotonically decreases with increasing collision energy. For example, the lifetime goes from 1.697 ps at 0.124 eV down to 0.197 ps at 1.424 eV for the $J=0$ collision. The rotational constant for the H_3^+ is about tens of wavenumbers, and the rotational period of the complex is about 0.02 ps at $J=5$. The lifetime of the complex is clearly much longer than the rotational period, therefore, statistical behavior in the product quantum state distribution in this reaction is expected.

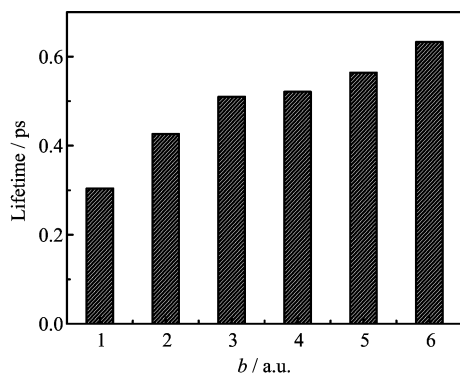


FIG. 5 The impact parameter b fixed (and hence J fixed) collision lifetimes obtained by fitting the lifetime distribution of b =constant classical ensembles.

IV. CONCLUSION

In this work, we have presented the differential cross sections and the integral cross sections for the $\text{H}^+ + \text{H}_2(v=0, j=0)$ reaction at very low collision energies calculated using the QCT method. The calculated product angular distributions are shown to be forward/backward symmetric, which is characteristic of a complex formation reaction. Product ro-vibrational state distributions were also determined. The calculated state resolved DCS is also in agreement with the previous experimental result at a specific scattering angle. The complex lifetime is also determined for different collision energies as well as different impact parameters. The complex lifetime increases with the impact parameter while decreases with collision energy. From the QCT calculations, the complex life is clearly much longer than the rotational period of the reaction complex, suggesting that the statistical model should be good for this elementary ion-molecule chemical reaction. Further analysis shows that the ion-molecule reaction can be viewed as a two step process: capturing and dissociation.

V. ACKNOWLEDGEMENTS

This work was supported by the Chinese Academy of Sciences, the Ministry of Science and Technology and the National Natural Science Foundation of

China (No.20328304, No.10574068, No.20533060 and No.20525313).

- [1] F. O. Ellison, *J. Am. Chem. Soc.* **85**, 3540 (1963).
- [2] G. Ochs and E. Teloy, *J. Chem. Phys.* **61**, 4930 (1974).
- [3] R. K. Preston and J. C. Tully, *J. Chem. Phys.* **54**, 4297 (1971).
- [4] M. Baer and C. Y. Ng, *State-Selected and State-to-State Ion-Molecule Reaction Dynamics*, New York: Wiley, 267 (1992).
- [5] B. J. Mccall, A. J. Huneycutt, R. J. Saykally, T. R. Geballe, N. Djuric, G. H. Dunn, J. Semaniak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, F. Osterdahl and M. Larsson, *Nature* **422**, 500 (2003).
- [6] T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
- [7] A. Ichihara and K. Yokoyama, *J. Chem. Phys.* **103**, 2109 (1995).
- [8] H. Kamisaka, W. Bian, K. Nobusada and H. Nakamura, *J. Chem. Phys.* **116**, 654 (2002).
- [9] I. Last, M. Gilibert and M. A. Baer, *J. Chem. Phys.* **107**, 1451 (1997).
- [10] I. G. Csizmadia, J. C. Ploanyi, A. C. Roach and W. H. Wong, *Can. J. Chem.* **47**, 4097 (1969).
- [11] J. C. Tully and R. K. Preston, *J. Chem. Phys.* **55**, 562 (1971).
- [12] G. Niedner, M. Noll, J. P. Toennies and Ch. Schlier, *J. Chem. Phys.* **87**, 2685 (1987).
- [13] V. G. Ushakov, K. Nobusada and V. I. Osherov, *PCCP* **3**, 63 (2001).
- [14] Ch. Zhu, K. Nobusada and H. Nakamura, *J. Chem. Phys.* **115**, 3031 (2001).
- [15] H. Song, D. Dai, C. C. Wang, G. Wu, S. A. Harich, M. Hayes, X. Wang, D. Gerlich, X. Yang and R. T. Skodje, *J. Chem. Phys.* **123**, 074314 (2005).
- [16] D. L. Bunker, *Methods Comput. Phys.* **10**, 287 (1971).
- [17] D. G. Truhlar and J. T. Muckerman, *Atom-molecule Collision Theory: A Guide for Experimentalists*, New York: Plenum, (1979).
- [18] L. Banares, F. J. Aoiz, P. Honvault, B. B. Honvault and J. M. Launay, *J. Chem. Phys.* **118**, 565 (2003).
- [19] L. Bonnet and J. C. Rayez, *Chem. Phys. Lett.* **277**, 183 (1997).
- [20] L. Bonnet, F. J. Aoiz, P. Honvault, and J. M. Launay, *J. Phys. Chem. A* **108**, 1616 (2004).
- [21] D. Gerlich, *J. Chem. Phys.* **92**, 2377 (1990).