STATISTICAL MODEL FOR H^++D_2 REACTIVE COLLISIONS BASED ON MEAN ISOTROPIC INTERACTION POTENTIAL

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Abstract. The reactive collision process H^++D_2($v= 0$, $j= 0$) $\rightarrow$HD +D^+, for collision energies ranging from the threshold to 1.3 eV, is studied by using a statistical theory based on a mean isotropic potential deduced from a full potential energy surface. Calculated integral cross sections are compared with recent statistical and quantum mechanical calculations performed by using a full potential energy surface. Reasonable agreement between the results obtained by using the two statistical methods is found, both of which however, overestimate quantum mechanical predictions.

1. INTRODUCTION

For the class of reactive collison processes that proceed via formation of the long-lived complexes (due to the existence of the deep potential well at small inter-fragment separations) a simplified theory, exploiting the statistical properties of coupled states of the system, can be used (Light 1967, Miller 1970). If the lifetime of the collision complex is long enough to allow for the randomization of the energy among the internal degrees of freedom, than the decay of the complex into various product channels can be expected to proceed according to their statistical weights.
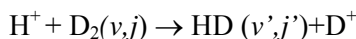
It turns out that the only input that is necessary for the formulation of the theory is the knowledge of the complex formation (or capture) probabilities from reactant and product channels, the decay probabilities being related to them through the microreversibility principle. The simplest (so called Langevin-type) classical models are obtained by assuming an isotropic interaction potential between the fragments which in combination with the centrifugal potential determines, for the given collision energy, the maximum orbital angular momentum (or impact parameter) for which a capture, i.e. complex formation is possible. Mean isotropic potentials can be obtained either by angle-averaging of

the anisotropic asymptotic interactions (for low collision energies) or by angle averaging of (if available) the *ab initio* potential energy surfaces (see Laregaray et al. 2007).

Alternatively, Rackham et al. (2001) calculated capture probabilities by solving the quantum mechanical close-coupled equations in the limited parts of configuration space but employing the *ab initio* potential energy surfaces. Interestingly, the same quality of the results has been obtained based on the definition of the capture probability obtained by running batches of classical trajectories on the limited part of the potential energy surface (so called SQCT method, see Aoiz et al. 2007).

2. THEORY

We start with the formula for the integral, state selective cross section for the process

$$H^+ + D_2(v,j) \rightarrow HD (v',j')+D^+$$

given by

$$\sigma_{vj,v'j'}(E) = \frac{\pi\hbar^2}{(2j+1)2\mu E_c} \sum_{J,\Pi} (2J+1) \frac{p_{vj}(E,J,\Pi)\,p_{v'j'}(E,J,\Pi)}{\sum'_{\widetilde{v}\widetilde{j}} p_{\widetilde{v}\widetilde{j}}(E,J,\Pi) + \sum_{\widetilde{v}'\widetilde{j}'} p_{\widetilde{v}'\widetilde{j}'}(E,J,\Pi)}$$

where (v,j) and (v',j') are vibrational and rotational quantum numbers of the internal motions of the diatomics in the reactant and product arrangements, J is the total motional angular momentum quantum number and $\Pi=\pm 1$ is the total parity quantum number. The collision energy is $E_c = E - E_{vj}$ where E_{vj} is the internal rovibrational energy of D_2. The summations in the denominator are restricted to states that are energetically accessible. In addition, the prime in the first summation symbol indicates that the summation is to be carried out only over the rotational quantum numbers $\widetilde{j}$ of the same parity as the initial quantum number j and this is the direct consequence of the indistinguishability of the two deuterons taking part in the reaction (see Park and Light 2007).

The cumulative complex formation probabilities $p_{vj}(E,J,\Pi)$ can be calculated by summing over all possible quantum numbers l of relative orbital angular momenta:

$$p_{vj}(E,J,\Pi) = \sum_{l=|J-j|}^{J+j} \delta_{\Pi,(-1)^{j+l}}\, p(l,E_c)$$

where the Kronecker delta stands for the conservation of parity and the elementary capture probabilities $p(e,E_c)$ are given by

$$p(l,E_c) = \begin{cases} 1 & l \le l_m(E_c) \\ 0 & l > l_m(E_c) \end{cases}$$

The above expression corresponds to a simple classical Langevin model which assumes that capture (i.e. complex formation) occurs whenever the collision energy is larger than the maximum of an effective isotropic potential. Therefore, the $l_m(E_c)$ is defined as a maximum integer l that satisfies:

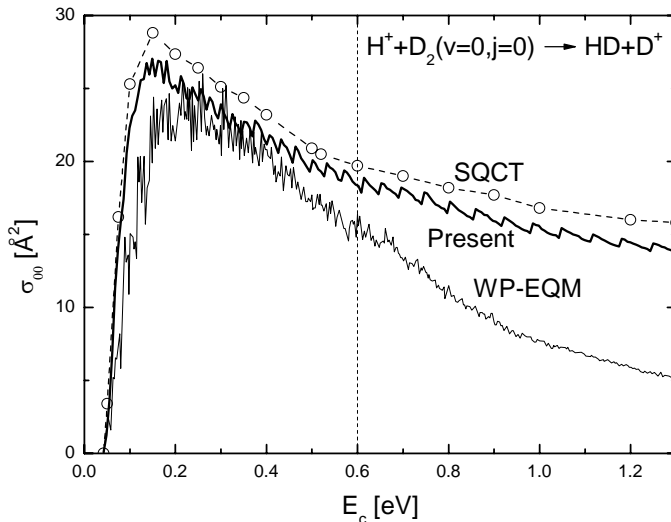$$E_c > \max_R \{\frac{\hbar^2 l(l+1)}{2\mu R^2} + \overline{V}(R)\}$$

Figure 1: Integral cross sections as functions of the collision energy. Thick full line represents present results. Open circles are the results of the statistical SQCT method (Jambrina et al. 2010). Thin full line represents the results of the quantum mechanical WP-EQM method (Jambrina et al. 2010) that are fully converged only below E_c= 0.6 eV (vertical dashed line).

In our calculations we have used as the isotropic interaction potential $\overline{V}(R)$ the mean potential obtained from angle averaging (Laregaray et al. 2007):

$$\overline{V}(R) = \frac{1}{2}\int_0^\pi V(R, r = r_e, \theta)\sin\theta d\theta$$

where $V(R, r, \theta)$ is the potential energy surface of the H$_3^+$ molecule as constructed by Kamisaka et al. (2002). R is the distance between the H$^+$ and center of mass (CM) of H$_2$, r is the bond distance of H$_2$ (r_e=1.40104 a.u. is its equilibrium value) and θ is the angle between the vectors $\vec{R}$ and $\vec{r}$. Different reduced masses μ have been used for the reactant and product channels.

3. RESULTS

Fig. 1 compares integral cross sections for the reaction $H^{+}+D_{2}(v=0, j=0) \rightarrow HD + D^{+}$ calculated by using the present method with those of Jambrina et al. (2010) obtained by using the statistical SQCT method and quantum mechanical WP-EQM method. While our results are slightly lower than SQCT data, both statistical methods are larger than quantum mechanical predictions. The letter are, however, fully converged only for collision energies less then 0.6 eV.

We have also calculated opacity functions and rotational distributions of the product HD molecules and compared them with previous calculations. The effects due to the presence of two indistinguishable deuterons in the reaction have also been investigated.

Acknowledgements

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