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Theoretical study of charge transfer in $He^{+}+H_2$ collisions in the milli-electron-volt regime

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A theoretical investigation of charge transfer in $He^{+}+H_2$ collisions in the ultralow-energy regime (meV) has been conducted. Molecular states have been obtained by using the multiconfiguration self-consistent-field method. The reaction rate constants have been calculated for dissociative and radiative charge-transfer processes. Agreement with the recent measurements of Schauer *et al.* [J. Chem. Phys. **91**, 4593 (1989)] is satisfactory. The present study provides a theoretical rationale for the experimental findings by interpreting the detailed collision dynamics.

I. INTRODUCTION

In addition to the fundamental importance of understanding the collision dynamics of inelastic processes in ultralow-energy ion-molecule collisions, a comprehensive knowledge of dynamical processes in collisions of various combinations of hydrogen atoms and molecules (both neutral and ionic) with helium ions and atoms is also very important. The knowledge can provide theoretical rationales for various phenomena observed in astrophysical atmospheres because hydrogen and helium are the most abundant elements in that environment [1]. Theoretically, the study of the molecular electronic structure and the collision dynamics of the $[HeH_2]^{+}$ system exposes both the charm and the challenge of this simplest many-electron ion-molecule collision system. Hence, a variety of theoretical investigations has been reported relating to one aspect or another of the collision system [2–4]. Unfortunately, rigorous, systematic studies of the collision dynamics of this system are scarce for any regime of collision energies, in contrast to the plentiful quantum-chemical calculations of the molecular potential surfaces [3–7]. Several experimental measurements have determined reaction rates for various exoergic inelastic processes in $He^{+}+H_2$ collisions under conditions that simulate the astrophysical environment [8–10], and Schauer *et al.* [11] recently measured absolute rate constants at ultralow energy in an experiment using a Penning ion trap. Specifically, the reaction rates measured are (i) dissociative charge transfer (DCT)

$$He^{+}(1s)+H_2(X\,^1\Sigma_g^{+};v=0)$$
$$\rightarrow He(1\,^1S)+H^{+}+H(1s)\quad(-6.51\text{ eV})$$

and (ii) radiative charge transfer (RCT)

$$He^{+}(1s)+H_2(X\,^1\Sigma_g^{+};v=0)$$
$$\rightarrow He(1\,^1S)+H_2^{+}(X\,^2\Sigma_g^{+})+h\nu\quad(\geq-9.16\text{ eV})$$

at ultralow energies ($T=15$ K or $E\cong2$ meV).

The experimental findings of Schauer *et al.* [11] suggest that these exoergic inelastic processes are slow compared to most other ion-molecule reactions, the measured rate constants being 3.0×10^{-14} cm^3/s for DCT and 1.0×10^{-14} cm^3/s for RCT at 15 K. Their results also call into question earlier experimental results obtained at somewhat higher temperatures by different groups [8–10].

Earlier studies [2–6] of the adiabatic potential-energy surfaces suggested the presence of an avoided crossing that would constitute a potential barrier between the initial and the final channels for DCT. These studies also indicated that the initial $[He^{+}+H_2]$ channel lies energetically above the final $[He+H_2{}^{+}]$ channel in any configuration and thus has no apparent avoided crossings between the states relevant to RCT. Thus, it was tentatively proposed that exoergic inelastic processes proceed via tunneling for DCT and radiative dipole coupling (rather than nonadiabatic coupling) for RCT. Although we considered these speculations to be qualitatively sound, on the basis of our study of ultralow-energy ion-atom collisions [12], they had not been fully tested by using rigorous theoretical methods.

The present report aims to provide a theoretical rationale for the recent experimental findings by describing the results of a reasonably sophisticated theoretical model, and thereby to shed some light on the general mechanism for charge transfer in ion-molecule collisions in a cold environment.

II. THEORETICAL METHOD

A. Molecular states

The molecular electronic wave functions and energies of the $[HeH_2]^{+}$ system as functions of the distance between the He^{+} and the center of mass of the H_2 and that between the two H atoms for the molecular symmetries C_{2v} and $C_{\infty v}$, which correspond to the perpendicular and linear geometries, respectively, were obtained by applying the multiconfiguration self-consistent-field plus configuration-interaction (MCSCF-CI) method with a Gaussian basis set. In the present calculation, the level of accuracy is found to be nearly equivalent to that obtained by Hopper [3], who also used the MCSCF-CI method with larger basis sets. Some representative results for the minimum in the He^+-H_2 potential for the perpendicular geometry (C_{2v} symmetry), known as the "polarization well," are given as $(E, R_{\text{He-H}_2}, R_{\text{H}_2}) = (0.003\,27$ eV, $4.437a_0, 1.350a_0)$, which compares favorably with Hopper's results [3] (0.003 34 eV, $4.433a_0$, $1.350a_0$). Since the specific characteristics of the potential surfaces were discussed extensively in a series of papers by Hopper [3], we will restrict our discussion to certain particularly important aspects of the potential surfaces, from both the present study and that of Hopper [3]. The schematic correlation diagram of the $[\text{HeH}_2]^+$ system and representative adiabatic potential curves as a function of reaction coordinate $R_{\text{He-H}_2}$ (with fixed $R_{\text{H-H}} = 1.4a_0$) and $R_{\text{H-H}}$ (with fixed $R_{\text{He-H}_2}$) are displayed in Figs. 1 and 2, respectively, to help illustrate the following points.

(i) The initial $\text{He}^+(1s) + \text{H}_2(X\,^1\Sigma_g^+; v=0)$ channel $(2\,^2A_1)$ potential energy curve in C_{2v} symmetry, which is attractive due to the polarization potential, lies about 9.16 eV above the charge-transferred $\text{He}(1\,^1S) + \text{H}_2^+(X\,^2\Sigma_g^+; v'=0)$ channel, as shown in Fig. 1. Other competing channels not shown here, including $[\text{HeH}^+ + \text{H}]$ and $[\text{HeH}_2^+]$, are well separated in energy from the $[\text{He} + \text{H}_2^+]$ channel. (See Ref. [3] for detailed discussion.)

(ii) Because of an avoided crossing between the $2\,^2A'$ and $3\,^2A'$ states of C_{2v} symmetry, as shown in Fig. 2, a potential barrier is created between the initial $[\text{He}^+(1s) + \text{H}_2(X\,^1\Sigma_g^+)]$ channel and final $[\text{He}(1\,^1S) + \text{H}(1s) + \text{H}^+]$ dissociation channel on a single reactive coordinate. This barrier in H-H coordinate is particularly high and broad when the incoming He^+ ion approaches within $R_{\text{He-H}_2} \cong 4a_0$ of the H_2 molecule. However, as $R_{\text{He-H}_2}$ increases beyond $\sim 5a_0$, the barrier becomes very small and well localized at about $R_{\text{H-H}} \cong 1.7a_0$ (see Fig. 2).

(iii) For both C_{2v} and $C_{\infty v}$ symmetries, the initial $[\text{He}^+(1s) + \text{H}_2(X\,^1\Sigma_g^+)]$ state possesses a minimum, the so-called "polarization well," at $R_{\text{He}^+\text{-H}_2}$ to 4.9–$6.0a_0$ with fixed $R_{\text{H-H}} = 1.4a_0$. This well serves to form a transient collision complex followed either by DCT to the $\text{He}(1\,^1S) + \text{H}(1s) + \text{H}^+$ state through tunneling or by RCT to the $\text{He} + \text{H}_2^+(X\,^2\Sigma_g^+; v') + h\nu$ state.

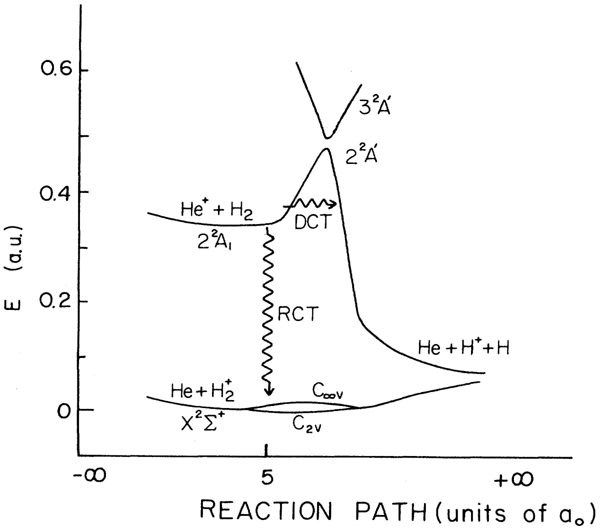

FIG. 1. Schematic correlation diagram of electronic energy for $[\text{HeH}_2]^+$ system as a function of reaction coordinate (with fixed H-H distance).

B. Dissociative charge transfer

As shown in Fig. 1, an avoided crossing between the $2\,^2A'$ and $3\,^2A'$ states creates a potential barrier in the reaction path that the heavy particles need to surmount or tunnel through to reach the final dissociation $(\text{He} + \text{H}^+ + \text{H})$ channel. The height and the width of the barrier are about 0.1 and 0.05 a.u. at $R_{\text{He-H}_2} = 4a_0$, respectively. Hence, in the ultralow-energy collision regime discussed here, tunneling is required for the reaction to occur. (This observation leads to the qualitative conclusion that vibrational excitation of the H_2 molecule will dramatically enhance the reaction rate of DCT because the correspondingly larger internal energy can help compensate for the barrier.)

Although several semiclassical analytical formulas have been developed for describing tunneling in chemical reactions, in the present case, where extremely low-energy collisions are considered, the semiclassical ap-

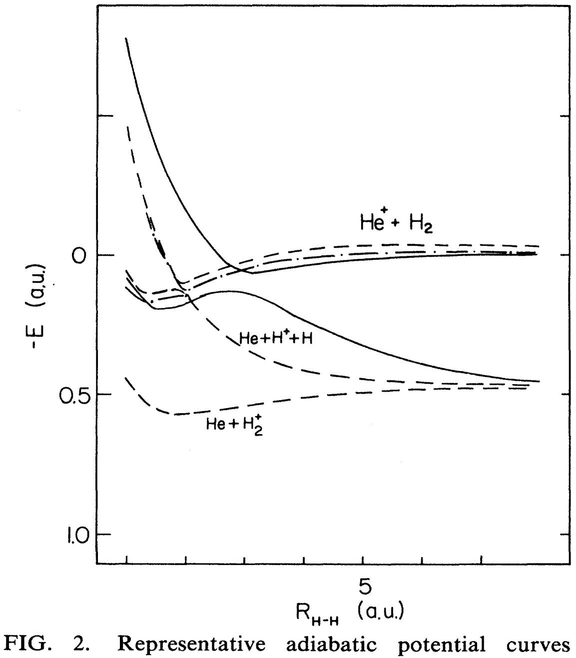

FIG. 2. Representative adiabatic potential curves for $[\text{HeH}_2]^+$ system as a function of $R_{\text{H-H}}$ with fixed $R_{\text{He-H}_2}$ values. Orientation angle of H_2 molecule with respect to He and center of mass of H_2 is 0°. Solid, dash-dotted, and dashed lines correspond to $R_{\text{He-H}_2} = 2.0$, 6.0, and ∞a_0, respectively. Note that all three sets of the adiabatic potentials for $[\text{He}^+ + \text{H}_2]$ and $[\text{He} + \text{H}^+ + \text{H}]$ states possess avoided crossings and dashed-dot and dashed lines become nearly identical at $R_{\text{H-H}} > 2a_0$ for the $[\text{He} + \text{H}^+ + \text{H}]$ state.

proximation may not be valid, particularly for $k_B T < V_0$ (V_0 = barrier height). Hence, we employ the fully quantal description of the tunneling process. Here, we give only a brief sketch of the theoretical approach used to determine the quantal one-dimensional tunneling probability, since detailed mathematical descriptions are well documented [13]. The Schrödinger equation for a particle moving along a one-dimensional reaction path in a potential V is (in atomic units)

$$\frac{d^2\psi(x)}{dx^2} + 2\mu[E - V(x)]\psi(x) = 0 , \tag{1}$$

where $V(x)$ represents the potential energy as given in Ref. [3] (our result is very similar to that of Ref. [3]), which in practice, is described by a spline fit. The asymptotic form of the solution of Eq. (1) that describes a particle incident from negative values of x is given as

$$\psi(x) \cong \begin{cases} e^{-ikx} + R(E)e^{+ikx}, & x \to -\infty , \\ S(E)e^{ikx}, & x \to +\infty , \end{cases} \tag{2}$$

where

$$k = \sqrt{2\mu E} . \tag{3}$$

$R(E)$ is the reflection amplitude and $S(E)$ is the transmission amplitude for the process in which a "particle" of mass μ of the $[He^+\text{-}H_2]$ incident with energy E will tunnel through the potential $V(x)$. The probability of tunneling is then defined as

$$P_{\text{tun}}(E) = |S(E)|^2 .$$

Equation (1) is solved numerically for several configurations of the molecular orientation subject to the scattering boundary conditions of Eq. (2), to determine $S(E)$ and hence $P_{\text{tun}}(E)$. Predissociation (rotational) resonances that arise from the attractive nature of the initial interaction potential are not included in our DCT calculation; they would increase the theoretical rate.

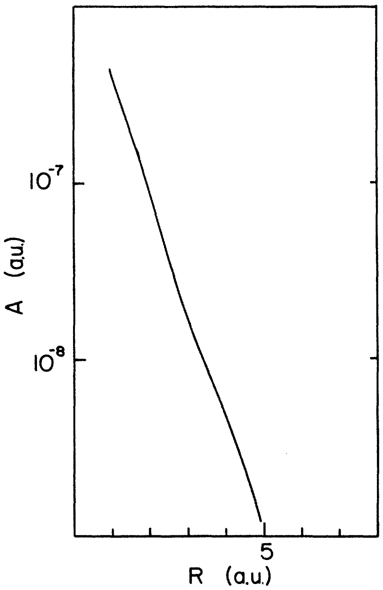

FIG. 3. Einstein A coefficient for the $(He^+ + H_2) \to (He + H_2^+)$ electronic transition in the $[HeH_2]^+$ system in the perpendicular geometry as a function of $R_{\text{He-H}_2}$.

C. Radiative charge transfer

Cross sections due to nonadiabatic coupling in non-radiative-charge-transfer (non-RCT) processes become exceedingly small below a collision energy of several eV, unless there are favorable avoided crossings or accidental energy resonances, while cross sections for RCT rapidly increase in magnitude as the energy is decreased. (A recent theoretical study of radiative and nonradiative charge transfer in $He^+ + H$ collisions [12] illustrates the point.) In the energy regime considered here, it is assumed that the contribution from non-RCT is completely negligible. In the present theoretical model, we have calculated the total reaction rate for the collision-induced radiative "disappearance" of He^+ ion caused by an encounter with a H_2 molecule. Therefore, this rate is actually the sum of RCT and radiative association (RA). However, the contribution to the rate from the RA is estimated to be very small, particularly at higher temperature, as can be understood from the nature of potential surface.

The optical potential method is used to evaluate the transition probabilities. In this phenomenological approach, it is assumed that during a collision, particle flux is lost because of a spontaneous radiative transition from the initial state to a lower-lying HeH_2^+ molecular state that dissociates to a charge-transferred $[He + H_2^+]$ state. Thus, the optical potential-energy function is written

$$W(R) = V(R) - \frac{i}{2}A(R) , \tag{4}$$

where $V(R)$ is the adiabatic potential of the initial channel and $A(R)$ is the transition probability per unit time for the radiative transition. Specifically, $A(R)$ represents the Einstein A coefficient

$$A(R) = \left[\frac{4}{3c^3}\right][\Delta E(R)]^3 |\mu(R)|^2 , \tag{5}$$

where ΔE is the energy separation between the initial and final states and $\mu(R)$ is the transition dipole matrix. The complex phase shift $\eta_l = \eta_l^R + i\eta_l^I$ can be extracted from

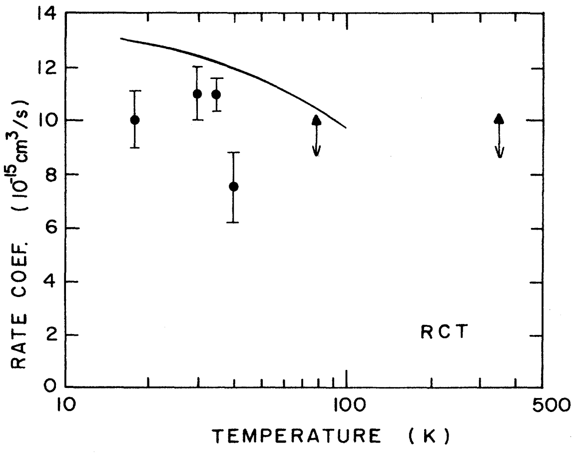

FIG. 4. Radiative charge-transfer rate constant. Theory: solid line, present work. Experiment: (●), Ref. [11]; (▲), Ref. [8]; downward arrows indicate upper limits.

the asymptotic form of the solution that satisfies the radial Schrödinger equation

$$\left[\frac{d^2}{dR^2}+k^2-\frac{l(l+1)}{R^2}-2\mu V(R)\right]F(R)$$
$$=-i\mu A(R)F(R)\ , \qquad (6)$$

where

$$k=\sqrt{2\mu E}\ .$$

The imaginary part of the phase shift reflects the loss of flux from the incoming channel. The total cross section for radiative decay (the sum of the RCT and RA) is then given by

$$\sigma=\frac{\pi}{k^2}\sum_{l}^{\infty}(2l+1)[1-\exp(-4\eta_l^l)]\ , \qquad (7)$$

where η_l^l is the imaginary part of the scattering phase shift, which is calculated exactly in the present study. Because the collision energy is ultralow, a few partial waves l are sufficient to obtain convergence.

Figure 3 shows the Einstein A coefficient used in Eq. (6) for the radiative transition from $[\mathrm{He}^+ + \mathrm{H}_2]$ to $[\mathrm{He}+\mathrm{H}_2^+]$, calculated from the corresponding wave functions, as a function of the $R_{\mathrm{He}\text{-}\mathrm{H}_2}$ separation. (Molecular orientation effects are important at $R \leq 2.5a_0$, the variation of the A value being within 10%.)

III. RESULTS AND DISCUSSIONS

On the basis of the theoretical model described in the previous sections, we have computed the reaction rates for the RCT and DCT processes by integrating the cross sections over Boltzmann distributions appropriate to temperatures in the range $T=15-100$ K. *Ortho*- and *para*-H_2 have a sizable energy difference for rotational transitions and the *ortho*-to-*para* (statistical weights) ratio (3:1) of H_2 has been properly accounted for in the calculation.

The present results are shown in Figs. 4 and 5 for RCT and DCT, respectively, along with the measurements by Schauer *et al.* [11] and others. For RCT, the calculated rates show a monotonically decreasing trend with respect to increasing temperature. The shape and magnitude of the calculated rate constant are in reasonably good agreement with the measurements of Schauer *et al.* [11] and the upper-limit values of Johnsen, Chen, and Biondi [8], and are similar in nature to the results previously obtained for the $\mathrm{He}^+ + \mathrm{H}$ system [12]. In addition, as was found for low-energy ion-atom collisions, the present RCT cross section shows pronounced "predissociation" resonance peaks (not shown) at several characteristic energies, corresponding to transient vibrational and rotational states of the $[\mathrm{HeH}_2]^+$ complex that are temporarily bound by the centrifugal barrier in the effective potential. These resonances are important in enhancing the rate constant. The non-RCT process, which occurs through nonadiabatic coupling, is important only when the collision energy exceeds several eV, and hence the effect of this channel can be safely ignored. The estimate made by Wu and Hopper [9] of direct charge transfer may be too large. Due to the more attractive nature of the respective potential curves, the perpendicular (C_{2v}) geometry is most favorable for the RCT process. Inclusion of the RA in the present result may be responsible partly for a slight overestimation of the RCT rate below 30 K.

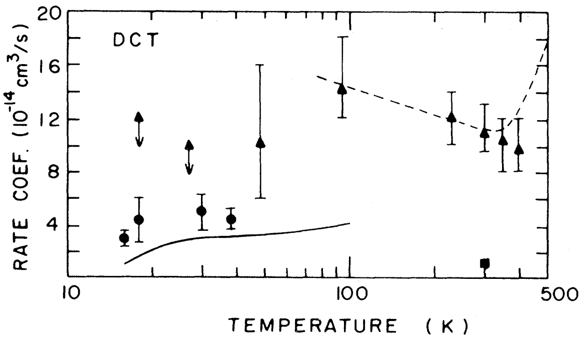

FIG. 5. Dissociative charge-transfer rate constant. Theory: solid line, present work; ■, Ref. [2]. Experiment: (●), Ref. [11]; (▲), Ref. [10]; downward arrows indicate upper limits; (— — —), Ref. [8].

Perhaps we should remark on the role of vibrational excitation of H_2 on the RCT rate. The gain of internal energy in the initial channel due to the vibrational excitation of H_2 molecule has little to do with the collision dynamics of the RCT; i.e., the radiative rate is merely averaged over a different ("excited") distribution of H-H separations. Hence, it can be safely concluded that the effect of vibrational excitation on the RCT rate constant is very weak in contrast to the DCT tunneling process discussed below. An additional remark of resonance effects on the RCT is given later in conjunction with that of DCT.

For DCT, the calculated rate constant is also in reasonable accord with the low-temperature measurements of Schauer *et al.* [11] and compares reasonably well with the earlier high-temperature measurements of Boehringer and Arnold [10] and Wu and Hopper [9]. The measured rates of Johnsen, Chen, and Biondi [8] are consistently higher in magnitude and display an increasing trend below 300 K, in disagreement with the present results. Since at the energies considered here the DCT process proceeds by means of tunneling through the barrier between the $2\,^2A'$ and $3\,^3A'$ states, the trend found by Johnsen, Chen, and Biondi is inconsistent with the present model. The present results do not appear to agree with the one-point theoretical prediction at 300 K by Preston, Thompson, and McLaughlin [2]. Since the semiclassical model used by Preston, Thompson, and McLaughlin [2] does not treat barrier tunneling exactly and includes several simplifying assumptions, the disagreement may not be surprising. In addition, the potentials used by Preston, Thompson, and McLaughlin [2] are less accurate than those used in the present work and those of Hopper [3]; a small difference in the potential translates into a significant difference in the tunneling probability. However, their claim that $v=1$ vibrational excitation enhances the DCT rate constant by a factor of about 100 over that corresponding to H_2 ($v = 0$) is not inconsistent with the tunneling model. The gain of extra (vibrational) internal energy helps to surmount the barrier between the initial and the final channels; hence, the DCT rate is expected to rise rapidly with temperature. As we have said earlier, this is in marked contrast to our finding for RCT. Jones *et al.* [14] have experimentally confirmed this vibrational enhancement effect. Because of the tunneling of a single hydrogen atom, the collinear geometry is favorable for the DCT.

Our treatment of the DCT neglects other, possibly important, resonance effects, such as rotational predissociation. These resonances increase interaction time and hence may help enhance the DCT as well as the RCT. This situation may produce somewhat better agreement in the DCT with the measurement. Moreover, our molecular states and corresponding wave functions may not be sufficiently accurate. Further improvement of the dynamical treatment of the collisions and the quality of the molecular states is called for.

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