

Charge-transfer cross sections for radiative charge transfer in $\text{Na}+\text{H}^+$ and $\text{K}+\text{H}^+$ collisions at very low energies

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The total cross sections for radiative charge transfer in $\text{H}^+ + \text{Na}(3s) \rightarrow \text{H}(1s) + \text{Na}^+$ and $\text{H}^+ + \text{K}(4s) \rightarrow \text{H}(1s) + \text{K}^+$ collisions at energies below 8 eV have been calculated using an optical potential method. The relevant molecular states and molecular potentials were obtained by full configuration interaction calculations using pseudopotentials for the ion cores of Na and K. From the calculated charge-transfer cross sections, the radiative charge-transfer rate coefficients were obtained for temperatures below 10 000 K. The rate coefficients for both systems are found to have broad maxima around 20 K with values of the order of $10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The rate coefficient for $\text{Na}+\text{H}^+$ remains nearly constant below the maximum, but that for $\text{K}+\text{H}^+$ decreases at lower temperatures. Both the rate coefficients and the differences between them decrease as the temperature increases beyond 20 K.

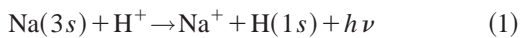
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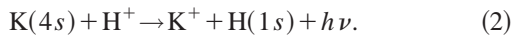
Charge transfer in collisions of neutral sodium and potassium atoms with protons affects the ionization balance in the atmospheres of planets, dwarf stars, and the interstellar medium [1–15]. Nonradiative charge transfer of Na and K to H^+ has been the subject of numerous studies for collision energies ranging from low eV [16,17] to low and high keV [18–32]. However, at low temperatures, such as in ultracold experiments or in interstellar space, collision energies are much less than 1 eV, and radiative charge transfer may become dominant over nonradiative charge transfer.

In this paper, we present a theoretical investigation of the total radiative charge-transfer cross sections in collisions of ground state Na and K atoms with H^+ ions, using an optical potential approach. From the calculated cross sections, we obtained the corresponding rate coefficients in the temperature range of 1–10 000 K.

The collision processes of interest are



and



To calculate the radiative charge-transfer cross sections we use an optical potential method [33–36]. The probability per unit time for radiative neutralization of the H^+ ions is determined by the imaginary part of a complex potential. The scattering wave $F_A(R)$, where R is the internuclear distance and the subscript A denotes the initial upper molecular state ($A^2\Sigma$), is obtained by solving

$$\left[\frac{-1}{2\mu} \nabla_R^2 + V_A(\vec{R}) - E \right] F_A(\vec{R}) = \frac{i}{2} A(R) F_A(\vec{R}), \quad (3)$$

where μ is the reduced mass of the alkali-metal–hydrogen system, and $A(R)$ is the Einstein coefficient given by

$$A(R) = \frac{4}{3c^3} D^2(R) |V_A(R) - V_X(R)|^3. \quad (4)$$

In Eqs. (3) and (4), $V_A(R)$ and $V_X(R)$ are the real parts of the molecular potentials of the upper $A^2\Sigma$ and lower $X^2\Sigma$ states, respectively. The quantity $D(R)$ is the transition dipole matrix element connecting the $A^2\Sigma$ and $X^2\Sigma$ states. For large R values, the $A^2\Sigma$ state separates into the atomic $\text{Na}(3s)$ or $\text{K}(4s)$ state and H^+ , while the $X^2\Sigma$ state separates into the atomic Na^+ or K^+ states and $\text{H}(1s)$.

The scattering wave function $F_A(R)$ is expanded in partial waves. Since the right hand side of Eq. (3) is imaginary, the phase shifts of the partial waves are complex. The imaginary parts represent the neutralization of the protons present in the initial $A^2\Sigma$ state by a radiative charge-transfer process into the $X^2\Sigma$ state.

In the present work, we used Gaussian-type pseudopotentials [37] for the Na and K ion cores, and treated the systems as one-electron systems. The corresponding molecular potentials $V_X(R)$ and $V_A(R)$ and the molecular orbitals for calculating the dipole moments were obtained by full configuration interaction calculations with Slater-type orbital basis sets, taken from [16]. The molecular interaction potentials should tend at large R to the dispersion potential, which is significant for low energy collisions below 1 eV. The asymptotic dispersion potential can be parametrized as

$$V_{disp}(R) = \frac{-1}{2} \left[\frac{C_4}{R^4} + \frac{C_6}{R^6} + \frac{C_8}{R^8} \right], \quad (5)$$

where C_4 , C_6 , and C_8 are, respectively, the dipole, quadrupole, and octupole polarizabilities of the atoms [38,39], listed in Table I. The calculated potential $V_A(R)$ was smoothly connected to the dispersion potential at the value of R where the two potentials $V_A(R)$ and $V_{disp}(R)$ merge.

TABLE I. Polarizabilities of Na and K atoms. To obtain C_6 , the quadrupole polarizabilities of Na and K, we added estimated values of 24.0 a.u., and 30.0 a.u., respectively, to include small contributions of van der Waals interactions [38,39].

Atom	C_4	C_6	C_8
Na	162.7	1873.0	54139.0
K	322.8	5000.0	55518.0

After obtaining each partial wave $F_{A,J}$ and the corresponding imaginary part of the complex phase shift η_J for the J th partial wave from Eq. (3), the total charge-transfer cross section $\sigma(k_A)$ was calculated using

$$\sigma(k_A) = \frac{\pi}{k_A^2} \sum_{J=0}^{\infty} (2J+1) [1 - \exp(-4\eta_J)], \quad (6)$$

where k_A is the wave number of the incident particle. The calculations employed the program written by Allison [40] for the numerical solutions of Eq. (3) and the evaluation of Eq. (6).

The radiative charge-transfer rate coefficient Γ can be obtained from the calculated cross sections using

$$\Gamma(T) = \int_0^{\infty} v \sigma(v) f(v, T) dv, \quad (7)$$

where v is the velocity of the incident particle, T is the temperature, and $f(v, T)$ is the Maxwell-Boltzmann velocity distribution function.

Figure 1(a) shows the calculated adiabatic potentials V_A and V_X . The two upper curves correspond to the $A^2\Sigma$ states, and the two lower curves to the $X^2\Sigma$ states. The full lines refer to the NaH^+ system, and the dashed lines to the KH^+ system. We will follow this convention in all figures where

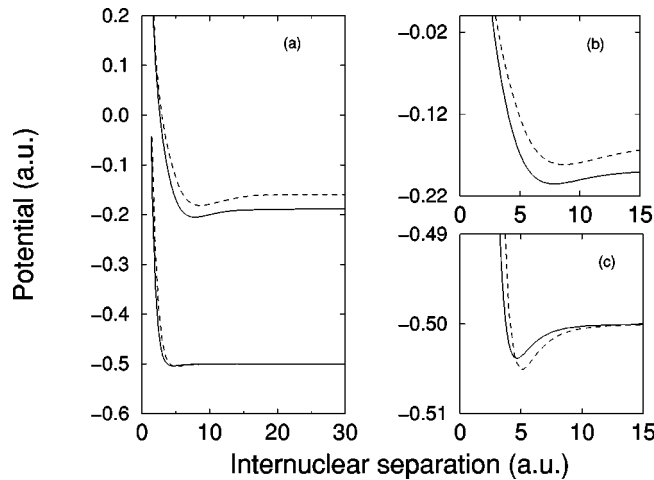


FIG. 1. (a) Adiabatic potentials for HNa^+ , and HK^+ as a function of internuclear distance R . The solid lines are for the HNa^+ system, and the dashed lines correspond to HK^+ . The upper pair is for the $A^2\Sigma$ states, and the lower pair for the $X^2\Sigma$ states. (b) and (c) show the minima of $A^2\Sigma$ and $X^2\Sigma$ of the Na and K potential, respectively.

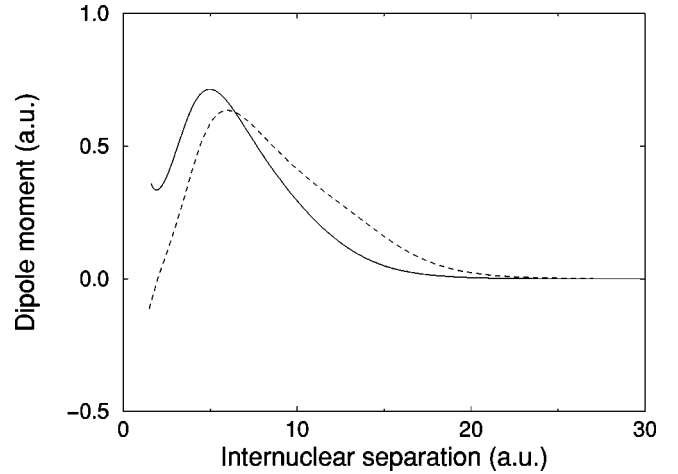


FIG. 2. The calculated dipole moments as a function of internuclear distance R . The solid line is for the HNa^+ system, and the dashed line is for the KH^+ system.

both Na and K results are presented. The potentials have shallow wells. The potential minima of the $A^2\Sigma$ and $X^2\Sigma$ are, respectively, shown in Figs. 1(a) and 1(b). The $A^2\Sigma$ state of KH^+ has a minimum at $R=8.45$ a.u. with a depth of 0.023 a.u., and the $X^2\Sigma$ state has a minimum at $R=5$ a.u. with depth of 0.005 a.u. The $A^2\Sigma$ state of NaH^+ has a well of depth 0.016 a.u. at $R=7.80$ a.u., and the $X^2\Sigma$ state has a well of depth 0.0038 a.u. at $R=4.65$ a.u. These shallow wells may contain quasibound states which cause resonance peaks in the cross sections at low collision energies.

Figure 2 shows the calculated dipole moment $D(R)$. For the transition between two Σ states, only the z component of $D(R)$ is not zero. The peak of the dipole moment for NaH^+ is higher than that for KH^+ , but the dipole moment for NaH^+ vanishes faster than that for KH^+ as R increases. This behavior influences the calculated Einstein coefficients $A(R)$, which are shown in Fig. 3. In both cases, $A(R)$ vanishes exponentially at large R .

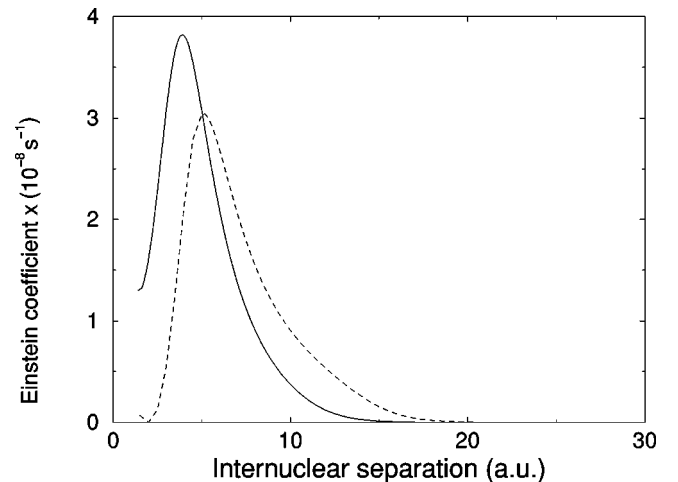


FIG. 3. The calculated Einstein coefficients Eq. (4) as functions of internuclear distance R . The solid line is for the HNa^+ system, and the dashed line is for the HK^+ system.

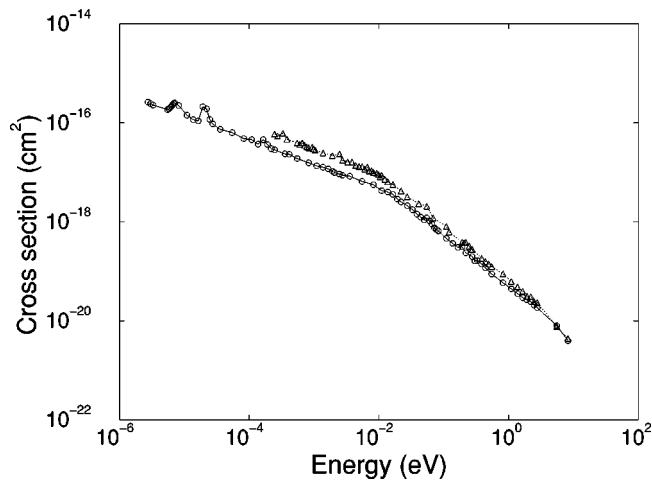


FIG. 4. The total radiative charge transfer cross sections for HNa^+ (solid line) and HK^+ (dashed line). The circles and triangles indicate the computed energy points.

The calculated radiative charge-transfer cross sections are shown in Fig. 4. The numerical integration of the Schrödinger equation was carried out with convergence criteria for the phase shift of the real part of the wave function. The phase shift is calculated each time the wave function changes sign. When the difference of successive phase shifts became less than a predetermined value ϵ_{phase} , the integration was terminated. As has been argued [40], this approach is valid only if the real part of the potential has a range comparable to or greater than the imaginary part. In the present cases, this condition is satisfied. When the contribution from the l partial wave became less than a percentage ϵ_{cross} of the total cross section, the l expansion was terminated. We chose ϵ_{cross} to be 5%. The value of ϵ_{phase} was 10^{-5} in the higher energy range, but for lower energies the convergence of the phase was relaxed to 10^{-4} for $\text{Na}+\text{H}^+$. For $\text{K}+\text{H}^+$, ϵ_{phase} above 0.2 eV was taken to be 10^{-4} , but it was increased as the energy decreased, and for energies up to 0.003 eV ϵ_{phase} ranged over $1 \times 10^{-3} - 7 \times 10^{-3}$, and for the lowest three energies ϵ_{phase} was 9×10^{-2} .

As the collision energy decreases, interactions at large R values become more important. Because of the $1/k_A^2$ factor in Eq. (6), the corresponding cross sections increase. The cross

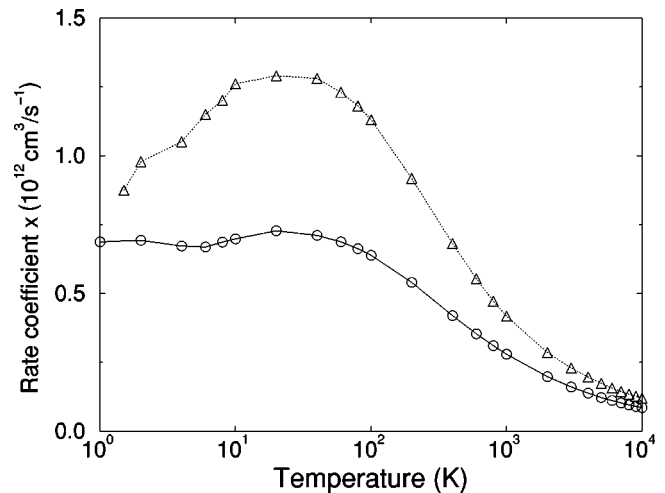


FIG. 5. The rate coefficients for HNa^+ (solid line) and HK^+ (dashed line). The circles and triangles indicate the computed temperature points.

sections for $\text{K}+\text{H}^+$ are larger than those for $\text{Na}+\text{H}^+$ at lower energies, but the difference decreases at higher energies. The structure in the cross sections reflects contributions from shape resonances. Figure 5 shows the calculated rate coefficients. Because the cross sections for $\text{K}+\text{H}^+$ are larger overall than those for $\text{Na}+\text{H}^+$, so are the rate coefficients, but the difference decreases as the temperature increases. This is because, at high temperatures, the main contributions to the rate coefficients come from energies where the cross sections are of comparable magnitudes in both systems. Although the cross sections for $\text{K}+\text{H}^+$ were not calculated below 10^{-5} a.u., we can obtain the rate coefficient at 2 K, since the Maxwell velocity distribution function at 2 K is narrowly peaked at 8×10^{-5} and the contribution from v less than 10^{-5} is of the order of 10^{-17} cm^3/s .

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