Charge transfer of O^{3+} ions in collisions with atomic hydrogen

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Cross sections are calculated for the charge transfer of O^{3+} ions in collisions with hydrogen atoms. The cross sections are in satisfactory agreement with ion-trap measurements at energies near 2.5 eV and with ion-beam measurements between 40 eV and 5 keV. The calculated cross sections uniformly exceed the ion-beam values by about 25%. The discrepancy, if real, may be attributed to the presence of less reactive metastable ions in the beam. The theory demonstrates that the charge-transfer process results in the emission of visible and ultraviolet photons of specific wavelengths whose detection would serve as a diagnostic probe of the detailed mechanism by which charge transfer proceeds.

Charge transfer in collisions of multiply charged ions with hydrogen atoms plays a major role in the determination of the thermal and ionization structure of a wide variety of astrophysical plasmas, in which it competes with radiative and dielectronic recombination as a mechanism for reducing the state of ionization, and with photoionization and electron impact ionization as a mechanism for increasing the state of ionization. The process leads to product ions in excited states and the resulting emissions are a useful diagnostic probe of the plasma environment. Because of applications to magnetically confined fusion plasma research, where it is of particular importance to the formation of neutral beams, to the plasma heating by the beams, and to the transport of impurity ions, charge transfer has been the subject of considerable interest recently, both theoretical and experimental. Measurements of charge-transfer cross sections for O^{3+} ions in collisions with H atoms have been reported by Phaneuf *et al.*[1] at impact energies between 42 and 4915 eV/amu, and Church and Holzscheiter[2] have measured the rate coefficient at a temperature of 2.5×10^4 K. We present here cross sections calculated by *ab initio* quantal methods from energies near thereshold to 5 keV and compare them with the experimental data. Our calculations indicate that charge transfer leads to the emission of spectral lines, whose relative intensities provide a critical measure of the charge-transfer mechanisms.

At low energies, the charge-transfer process may be described as a transition between electronic states of the quasimolecule OH^{3+}. The approach of ground-state O^{3+} ions and ground-state H atoms produces $^1\Sigma^+$, $^1\Pi$, $^3\Sigma^+$, and $^3\Pi$ molecular states which undergo avoided crossings. Using *ab initio* configuration-interaction methods,[3] Dalgarno, Heil, and Butler[4] have calculated the adiabatic interaction potentials $\epsilon_i(R)$, and the matrix elements of the radial-derivative operator $A_{ij}(R)$ which couples the adiabatic molecular states of OH^{3+} for each molecular symmetry. Starting with these potentials and coupling matrix elements, we performed a unitary transformation to a diabatic basis chosen so that the coupling matrix elements of $\underline{C}^{-1}(R)\underline{A}(R)\underline{C}(R)$ vanish.[5] For each molecular symmetry, the diabatic nuclear eigenfunctions satisfy the set of coupled equations[5]

$$\left(\frac{1}{2\mu}\nabla_R^2\underline{I}-\underline{V}(R)+E\underline{I}\right)\underline{F}^d(\vec{R})=\underline{0}\ , \tag{1}$$

where μ is the reduced mass of the colliding system, $\underline{V}(R)=\underline{C}^{-1}(R)\underline{\epsilon}(R)\underline{C}(R)$ is a diabatic potential matrix whose diagonal elements are potential-energy surfaces, and whose off-diagonal elements drive transitions between molecular states of the same symmetry. Equation (1) was solved by expanding $\underline{F}^d(\vec{R})$ in an orthonormal set of total angular momentum eigenfunctions and the resulting coupled differential equations

$$\left(\frac{d^2}{dR^2}+2\mu E-\frac{J(J+1)}{R^2}\right)\underline{I}\,\underline{f}^J(R)-2\mu\underline{V}(R)\underline{f}^J(R)=\underline{0} \tag{2}$$

were integrated numerically from threshold energies to 5 keV.[6,7] For a given value E of the energy of relative motion, close-coupling results were obtained for

low values of the angular momentum J, unitarized second-order distorted-wave Born-approximation results for intermediate J, and first-order distorted-wave Born-approximation results for high J, each method giving way to the simpler approximation as it became sufficiently accurate. The procedure gives results which are identical to those obtained from a complete close-coupled solution of the scattering equations. The total cross section $\sigma(E)$ can be written as the weighted sum

$$\sigma(E)=\frac{1}{12}\sum_{S=0}^{1}(2S+1)(\sigma_S^0+2\sigma_S^1) \ , \tag{3}$$

where σ_S^0 and σ_S^1 are the cross sections for charge transfer in the $^{2S+1}\Sigma^+$ and in the $^{2S+1}\Pi$ molecular symmetries, respectively. The cross sections are expressed as summations

$$\sigma_S(E)=\frac{\pi}{k_i^2}\sum_j\sum_J(2J+1)|S_{ij}^J|^2 \ , \tag{4}$$

where S_{ij}^J is the scattering matrix element connecting the initial state i formed by the approach of O^{3+} and H to a final state j formed by charge transfer and separating to O^{2+} and H^+.

In the calculations only those states were retained for which the adiabatic coupling is strong. The $^1\Sigma^+$ symmetry involves two states, the entrance channel and a product channel dissociating to $O^{2+}(2s^22p3s\ ^1P^o)$ and H^+. Each of the $^1\Pi$ and $^3\Pi$ symmetries involves three states. In addition to the entrance channel, the $^1\Pi$ symmetry has states separating to $O^{2+}(2s^22p3p\ ^1P)$ and H^+ and to $O^{2+}(2s^22p3s\ ^1P^o)$ and H^+, and the $^3\Pi$ symmetry has states separating to $O^{2+}(2s^22p3p\ ^3D)$ and H^+ and to $O^{2+}(2s^22p3s\ ^3P^o)$ and H^+. The most complicated is the $^3\Sigma^+$ symmetry with four states. The exit channels dissociate into H^+ and $O^{2+}(2s^22p3s\ ^3P^o)$, $O^{2+}(2s^22p3p\ ^3D)$, and $O^{2+}(2s^22p3p\ ^3S)$. For the $^1\Sigma^+$ symmetry, there is a single crossing of the diabatic curves but several crossings occur for the other symmetries, each of which is associated with a peak in one of the adiabatic coupling elements. The transformation to a diabatic basis maps the complex behavior of the adiabatic coupling elements into a set of simple diabatic coupling functions.[5]

Table I lists the calculated cross sections for the individual molecular symmetries. At low energies charge transfer proceeds largely in the $^3\Pi$, $^3\Sigma^+$, and $^1\Pi$ symmetries in the ratio of 3:2:1; and the principal products are the $O^{2+}(2s^22p3p\ ^3D)$, $O^{2+}(2s^22p3p\ ^3S)$, and $O^{2+}(2s^22p3p\ ^1P)$ states. With increasing energy all states and all four symmetries are significant, although the contribution from the $^1\Sigma^+$ symmetry remains the smallest out to 5 keV.

It is difficult to estimate the possible errors in the calculated cross sections. Below energies of 5 keV, the set of molecular states should be adequate, but errors arising from the limited atomic basis set representation of the molecular states could be substantial. Because the processes are controlled by specific avoided crossings neither rotational couplings nor momentum translation factors are likely to be significant at low energies, though they will have major consequences at higher energies, beyond the range of our calculations.

Figure 1 compares the total calculated cross sections with the data of Church and Holzscheiter,[2] Phaneuf, Meyer, and McKnight,[8] Gardner *et al.*,[9] and Phaneuf *et al.*[1]

The calculated cross sections agree within the probable experimental error with values derived from the ion-trap measurements of Church and Holzscheiter[2] at energies near 2.5 eV. They exceed at all energies

TABLE I. Charge-transfer cross sections $(2S+1)(2-\delta_{o\Lambda})\sigma_{s\Lambda}/12$ and σ in units of 10^{-16} cm^2 for $O^{3+}+H\rightarrow O^{2+}+H^+$ as a function of energy in the center-of-mass system.

Energy E (eV)	$^1\Sigma^+$	$^1\Pi$	$^3\Sigma^+$	$^3\Pi$	Total
0.1	0.008	13.0	25.2	37.1	75.2
1.5	0.142	9.38	19.7	29.7	58.9
10	0.90	8.95	16.7	25.8	52.4
20	1.19	8.88	14.8	24.1	49.0
30	1.45	8.33	14.1	23.0	46.8
50	1.92	6.75	14.0	21.4	44.1
75	2.23	6.03	16.1	19.8	44.2
125	2.38	5.74	19.9	17.4	45.4
250	2.37	3.78	19.1	15.0	40.2
500	2.56	2.83	15.2	12.8	33.4
1000	2.43	4.85	10.5	11.0	28.8
2000	2.34	5.23	7.90	18.6	34.1
5000	2.22	4.05	5.50	19.6	31.4

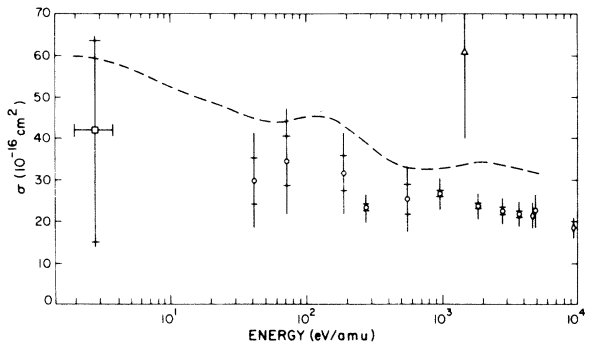

FIG. 1. Cross sections σ for charge transfer of O^{3+} with H as a function of ion impact energy in eV/amu. The dashed curve represents the theoretical results. The measurements are: □, Church and Holzscheiter (Ref. 2); ○, Phaneuf *et al.* (Ref. 1); ◇, Phaneuf *et al.* (Ref. 8); Δ, Gardner *et al.* (Ref. 9).

the cross sections obtained from the ion-beam measurements between 40 eV and 5 keV. The discrepancies are about 25%, which is well within the theoretical uncertainties. If, nevertheless, the discrepancies are real they may arise in part from the presence of less reactive metastable $(1s^2 2s 2p^2)\,^4P$ ions in the beam.[1]

A valuable diagnostic probe of the charge-transfer mechanism and of the possible contribution from metastable species is provided by the spectral lines emitted by the product ions. The singlet and triplet cascades resulting from charge transfer of O^{3+} and H have been worked out.[4,10] Some of the lines are seen in astrophysical sources.[4,10]

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