[8]W. D. Rae, A. J. Cole, A. Dacal, R. Legrain, B. G. Harvey, J. Mahoney, M. J. Murphy, R. G. Stokstad, and I. Tserruya, Phys. Lett. 105B, 417 (1981).

[9]See, for example, D. A. Bromley, in *Proceedings of the International Conference on Resonances in Heavy Ion Reactions, Hvar, Yugoslavia, 1977*, edited by N. Cindro (North-Holland, Amsterdam, 1978).

[10]A. Szanto de Toledo, M. Schrader, E. M. Szanto, G. Rosner, and H. V. Klapdor, Phys. Lett. 78B, 58 (1978), and Nucl. Phys. A315, 500 (1979).

Charge Transfer from Atomic Hydrogen to O^{+2} and O^{+3} Ions with Electronvolt Energy

D. A. Church and H. M. Holzscheiter[a]

Physics Department, Texas A&M University, College Station, Texas 77843

(Received 28 May 1982)

The reaction rate constants for charge transfer from atomic hydrogen to O^{+2} and O^{+3} ions have been measured at temperatures near 1.5×10^4 K by using a stored, multicharged ion gas interacting with a hydrogen atomic beam. The results are $k(O^{+2},H) = 1.4(0.6)\times10^{-9}$ cm^3/sec and $k(O^{+3},H) = 10.2(6)\times10^{-9}$ cm^3/sec in agreement with recent theory.

PACS numbers: 34.70.+e, 82.30.Fi

As a result of interest arising from astrophysical processes[1] and applications to magnetically confined fusion plasma research, as well as for basic theoretical reasons, there has been considerable recent theoretical and experimental effort on electron transfer from atomic hydrogen to multicharged ions. We have used a confined, multicharged[2] ion gas[3] with measured temperature and selected mass-to-charge ratio,[2] interacting with a beam of hydrogen atoms, to measure the rate constants for charge transfer from H to O^{+2} and H to O^{+3}. These are the only measurements for mean relative ion energies in the electronvolt range, and the first direct measurements of charge transfer rate constants for multicharged ions interacting with H atoms. Cross-section measurements with energies as low as 11 eV/u have been completed for carbon ions on H by Phaneuf.[4]

The rate-constant calculations of Butler, Heil, and Dalgarno[5] for intermediate charge states of C, N, and O interacting with H extend from 10^3 to 5×10^4 K. The lowest energy to which the calculations for related collisions by Green, Shipsey, and Browne[6] apply is 13 eV, while the unitarized distorted-wave approximation of Ryufuku and Watanabe[7] has a lower energy limit of only 25 eV/u. This energy gap in the theory has recently been bridged by Bottcher and Heil,[8] who have modified the theory of Butler, Heil, and Dalgarno for C^{+4} and C^{+5} on H to extend it beyond the lowest energy of the beam measurements. Otherwise, the rate-constant calculations of Butler, Heil, and Dalgarno, which are potentially highly sensitive to the energy separations of the avoided crossings of the potential energy surfaces,[9] are untested. Questions associated with the necessity of translation factors and switching functions in the general theory have not been wholly settled. Any measurement with relative energy in this range is relevant to the theory.

In the measurements reported here, multicharged ions of oxygen were produced by electron impact ionization of O_2 gas inside a Penning trap, where they were stored for times of the order of seconds.[10] The stored ions move harmonically in the dc electric and magnetic confining fields, with axial angular frequency $\omega_z = (qV/mz_0^2)^{1/2}$ and radial motion angular frequencies $\omega_+ \simeq \omega_c - \omega_-$ and $\omega_- = \omega_z^2/2\omega_c + \omega_z^4/4\omega_c^3$, where $\omega_c = qB/m$ is the cyclotron frequency, V is the relative potential difference between the trap electrodes, and z_0 is a characteristic electrode dimension. The dependence of these frequencies on the charge-to-mass ratio q/m permits selective ion detection, as well as selective ion accumulation by elimination of unwanted ions by resonant excitation during the formation interval.[2] Following formation, the stored ions of interest interact with a neutral beam composed of about 65% H atoms and 35% H_2 molecules, produced in a radio-frequency discharge source. The exponential depletion of the ion number with storage time occurs with a time constant τ which is related to the atomic beam density n and the charge transfer rate constant $k = \int_0^\infty f(v)\sigma(v)v\,dv$ by $k = (n\tau)^{-1}$. The basic measurement consists of determinations of τ, n, the mean relative energy of the ions, and information

about the distribution function $f(v)$.

The vacuum apparatus consists of two bakable ultrahigh-vacuum systems connected by a valve, as described in Ref. 2. The Penning trap is mounted in one system with pressure measured by a calibrated nude ion gauge and a quadrupole residual-gas analyzer. The accuracy of the pressure calibration ultimately rests on the agreement of our measurements of singly-charged-ion charge transfer rate constants[10,11] with those of others, made by using different methods at much higher pressures. The second vacuum system, which held the hydrogen discharge source, was connected to the main system through a 0.02-in.-diam orifice and the valve. The passage of the atomic beam from the source through the trap was identified by the increased production of ions during electron impact ionization.

The number of ions stored in the trap was measured by a resonant absorption technique.[2,3] A tuned circuit composed of an external inductance and the capacitance of the trap structure was excited at resonance by a stable oscillator. After the storage interval, the ion axial motion frequency ω_z was swept through resonance by a 100-msec sweep of the trapping potential V. A modulation of the rf amplitude by the excited coherent ion motion, proportional to the ion number, was produced and detected as the ions were driven from the trap. Ion numbers for each q/m were determined from signal amplitudes after integration of a predetermined number of similar signals.

The mean energy was similarly determined with the same circuitry, but with no excitation applied to the tuned circuit. When swept through the tuned-circuit resonance, the incoherent motion of the ions induced a fluctuating potential difference across the tuned circuit in addition to the usual thermal noise. This incoherent signal is proportional to the ion number and to the mean ion energy.[3,12] The magnitude of this signal, scaled relative to the basic tuned-circuit temperature of 350 ± 50 K and to the relative ion number, was used to calibrate the stored-ion mean energies. Ion m/q ratios other than the one desired for study, particularly other charge states of oxygen, were removed from the trap by resonant excitation at the frequencies ω_+ and ω_- during the electron creation pulse. Under these conditions, the O^{+2} mean energy was found to be $(1.45 \pm 0.6) \times 10^4$ K and the O^{+3} mean energy was $(2.5 \pm 0.6) \times 10^4$ K in the 15-V confining dc potential well used. A factor of ≈ 2.5 correction for ion cooling due to the adiabatic decrease of the confining potential before detection is included.

The establishment of the observed mean stored-ion energy, its correspondence to a temperature, and the identification of the form of the distribution function $f(v)$ as a thermal one follow from the rapid relaxation of the stored-ion motional degrees of freedom.

During and shortly after formation, the ions assume a mean temperature proportional to the confining axial potential as a result of the loss of the higher-energy ions axially from the well and the concomitant cooling of the stored remainder.[3] The distribution subsequently remains thermal through continuous relaxation, with an ion-ion collision time constant expected to be the Spitzer self-collision time[13] t_c, suitably scaled for a one-component ion gas. The relaxation time has been directly measured for He^+ ions, as shown in Fig. 1. The ions are brought to resonance with the unexcited tuned circuit, so that their mean axial energy is continuously monitored. Superimposed on the slow temperature decrease due to energy dissipation in the tuned circuit, one sees an increase at time t_0 due to a 1-msec resonant pulse of rf energy into the cyclotron motion. The relaxation from this radial excitation to the axial motion is seen to occur over a time interval of < 30 msec. Scaling this data indicates comparable relaxation times for O^{+2} and O^{+3} ions under measurement conditions. Relaxation rates by other means, e.g., by field inhomogeneities, should be comparable for all q/m ratios. All processes which occur slowly compared with the relaxation time constant, such as the storage-

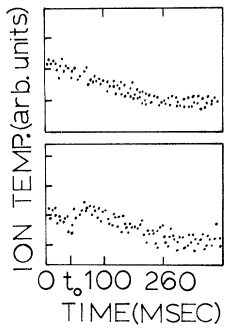

FIG. 1. He^+-ion temperature signals produced by ions at axial resonance with the tuned circuit. Top: The ion temperature decreases slowly as a result of interaction with the circuit. Bottom: At t_0, the radial ion motion is excited by a 1-msec pulse of rf at the cyclotron frequency, resulting in a delayed increase in the mean axial energy.

time measurements, will not significantly alter the thermal character of the ion distribution.

Long-lived metastable states can be produced by the electron impact ionization process, which may result in capture rate constants different from those observed for the ground-state ions.[11] The rates $k(O^{+2}, O_2)$, $k(O^{+3}, O_2)$, $k(O^{+2}, H_2)$, and $k(O^{+3}, H_2)$ were independently measured with static gas at several pressures. A single decay constant,[10] in agreement with other measurement methods,[14] was observed for O^{+2} collisions with O_2, but for the O^{+2}-H_2 charge transfer reaction, the ion loss curve required a fit by two exponentials, indicating that the long-lived ^1S or ^1D levels of O^{+2} have a different rate constant for capture from H_2 than does the ^3P ground state. The shorter decay-time-constant component is associated with the metastable states, since it was not observed when 70-eV electrons were used to produce O^{+2} as compared with 400-eV electrons. No metastable-state effects were identified in the H measurement, probably because of the low population of metastable levels with the ionization parameters chosen.

The density $n(H)$ of atomic hydrogen was obtained relative to the calibrated density $n(H_2)$ by a ratio method. With use of a molecular beam (source not discharged) the density of beam plus background relative to background density alone $n'(H_2)/n(H_2)$ was obtained by ionizing H_2 in the trap. The relative fractions of stored H^+ and H_2^+ ions produced by dissociative ionization with 200-eV electrons of the H_2 beam and of the background at the ion trap site are shown in the lower part of Fig. 2. For the background measurement, the valve connecting the source and measurement chambers was partially closed, blocking the direct molecular beam. τ_{H_2} was measured with both valve settings, and $k(O^{+q}, H_2)$ in each case was found to be in excellent agreement with the independent static-gas determination.

With the source discharged, the clearly altered ratio of H^+ and H_2^+ ions produced by ionizing the mixed H and H_2 neutral beam is shown in the upper part of Fig. 2. This unambiguously demonstrates the increased density of H, and decreased density of H_2 in the beam. From this observation, the relative density $n(H)/n''(H_2)$ was obtained. The known cross sections for ionization[15] of H and H_2 were used to correct this neutral-beam density ratio. With use of the relative magnitudes of $n''(H_2)$, $n'(H_2)$, and $n(H_2)$, the density $n(H)$ was obtained relative to the calibrated density $n(H_2)$.

A decay constant τ is measured, where $\tau^{-1} = \tau_{rq}^{-1} + \tau_{H_2}^{-1} + \tau_H^{-1}$. τ_{rq} is the storage time constant for O^{+q} measured in O_2 plus the residual gases, without the neutral beam. τ_{H_2} is the time constant for O^{+q} measured in H_2. It is obtained from separate measurements in background H_2 (beam blocked) and in background H_2 plus an H_2 molecular beam. The final result is corrected for the reduced H_2 density in the dissociated

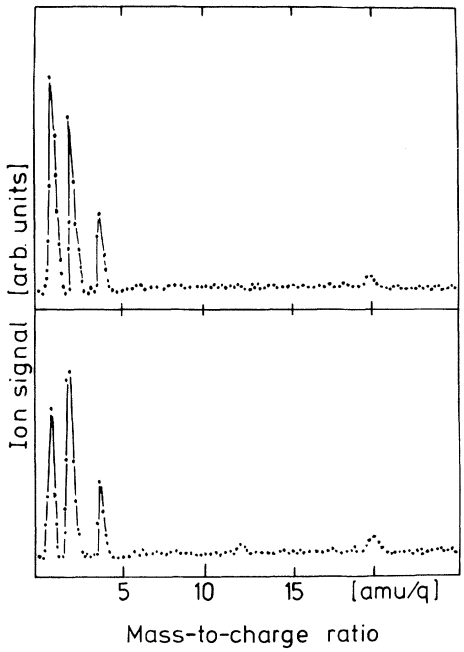

FIG. 2. Stored-ion signals of H^+, H_2^+, and He^+ produced (top) by ionizing residual gas and a 65%-H, 35%-H_2 beam, and (bottom) by ionizing residual gas and a H_2 beam.

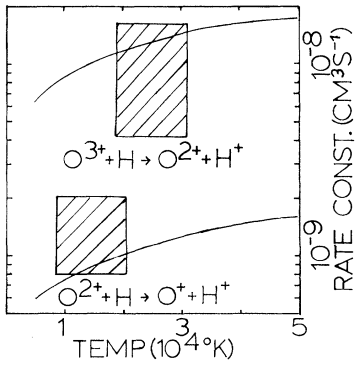

FIG. 3. Theory of Butler, Heil, and Dalgarno (solid line) and experimental results (shaded areas). (The shaded areas represent ± 1 standard deviation uncertainty.)

beam when the source is discharged. Clear differences in τ were obtained when the beam was blocked, or the source not discharged.

τ_H is the effective time constant for O^{+q} to capture an electron from H; it is calculated from the data. Representative time constants are, for O^{+2}, $\tau_{rq} = 16$ sec, $\tau_{H_2} = 38$ sec, and $\tau = 10.6$ sec and for O^{+3}, $\tau_{rq} = 4.5$ sec, $\tau_{H_2} = 4.8$ sec, and $\tau = 2.1$ sec. The results for $k(O^{+q}, H) = [n(H)\tau_H]^{-1}$ are shown in Fig. 3, where they are compared with the calculations of Butler, Heil, and Dalgarno.[5]

Although the precision of the rate constants $k(O^{+q}, H)$ is limited by the precision of the individual component measurements, the data show that $k(O^{+3}, H)$ is significantly larger than $k(O^{+2}, H)$ as Butler, Heil, and Dalgarno predict, and that the two measurements are in good agreement with the theory. No effects associated with hypothetical metastable states in the beam atoms or molecules were identified. In further planned measurements, the density and relative purity of the atomic beam at the trap will be increased to permit measurements with improved precision.

This research was supported by the U. S. Department of Energy, Contract No. DE-AS05-78ER6043, by the Texas A&M Center for Energy and Mineral Resources, and by a National Bureau of Standards/National Science Foundation Precision Measurement Grant.

[a]Now at Institut für Physik, Universität Mainz, D-6500 Mainz, Germany.

[1]A. Dalgarno and S. E. Butler, Comments At. Mol. Phys. 7, 129 (1978).

[2]D. A. Church, in *Physics of Electronic and Atomic Collisions*, edited by S. Datz (North-Holland, Amsterdam, 1982), p. 533.

[3]H. G. Dehmelt, Adv. At. Mol. Phys. 3, 53 (1967), and 5, 109 (1969).

[4]R. A. Phaneuf, Phys. Rev. A 24, 1138 (1981).

[5]S. E. Butler, T. G. Heil, and A. Dalgarno, Astrophys. J. 241, 442 (1980).

[6]T. A. Green, E. J. Shipsey, and J. C. Browne, Phys. Rev. A 25, 1364 (1982), plus earlier articles cited therein.

[7]H. Ryufuku and T. Watanabe, Phys. Rev. A 19, 1538 (1979).

[8]C. Bottcher and T. G. Heil, Chem. Phys. Lett. 86, 506 (1982).

[9]A. Dalgarno, S. E. Butler, and T. G. Heil, J. Geophys. Res. 85, 6047 (1980).

[10]H. M. Holzscheiter and D. A. Church, Phys. Lett. 86A, 25 (1981).

[11]H. M. Holzscheiter and D. A. Church, J. Chem. Phys. 74, 2313 (1981).

[12]D. A. Church and H. G. Dehmelt, J. Appl. Phys. 40, 3127 (1969).

[13]L. Spitzer, Jr., *Physics of Fully Ionized Gases* (Interscience, New York, 1956).

[14]R. Johnsen and M. A. Biondi, J. Chem. Phys. 74, 305 (1981).

[15]L. J. Kieffer and G. H. Dunn, Rev. Mod. Phys. 38, 1 (1966).