+H collisions using Eq. (1) and an extension[7] of Eq. (2). At moderate impact parameters [$b=(1-3)a_0$] the charge-transfer probabilities are very close to the 2D results, though they show considerable asymmetry with respect to φ. More detailed information than total-cross sections is probably required to establish effects peculiar to 3D calculations.

Without serous modification the methods used to obtain the present results can be applied to a vast range of problems. In addition to numerical studies, theoretical explanations must be sought for such apparently novel phenomena as the "fingers."

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Isotope-Selective Laser Analysis of the Electron-Impact Excited $6\,^1S_0 \rightarrow 6\,^1P_1$ Transition of Mercury: A Test of the Percival-Seaton Hypothesis

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An isotope-selective technique has been used to measure line polarizations in the range 7.5 to 12.0 eV for the electron-impact–excited 185-nm transition of atomic mercury. Measurements were made on the $I=0$ and $I=\frac{1}{2}$ nuclear-spin isotopes. A stepwise excitation technique was used involving electron excitation followed by single-mode laser excitation. The results obtained indicate a breakdown in the Percival-Seaton hypothesis near threshold.

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In this Letter, we report on results obtained from an experiment in which a low-energy beam of electrons and single-mode laser radiation were used to excite mercury atoms stepwise according to the excitation scheme shown in Fig. 1(a). Fluorescence emitted following the stepwise excitation was analyzed to determine the line polarization of the electron-impact–excited transition. This technique allows several aspects of atomic collision physics to be studied in new detail. The narrow bandwidth of the laser radiation permits the fine and hyperfine structure of atoms to be resolved in the laser-excited transition, thus providing a means of studying the role of spin-orbit

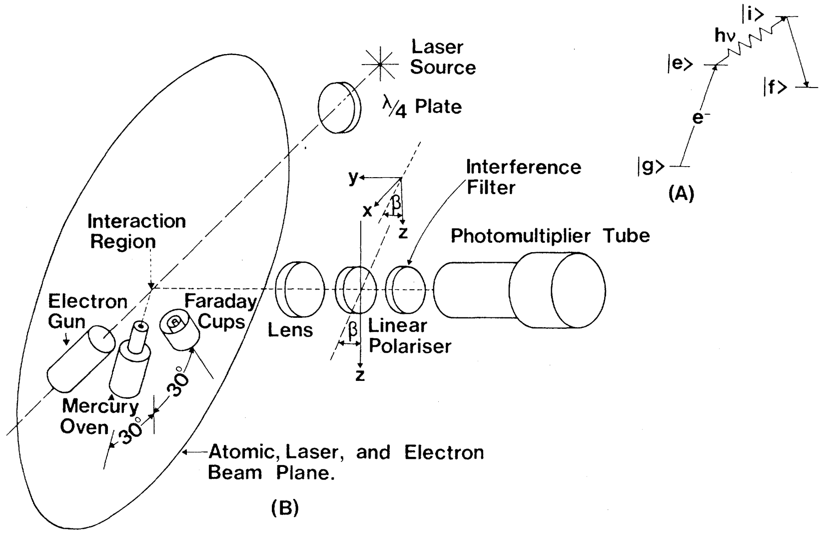

FIG. 1. (a) General stepwise excitation scheme. (b) The geometrical arrangement of the experiment.

interactions in atomic collision processes. The ability to resolve hyperfine structure allows isotope effects to be studied and in suitable cases the validity of the Percival-Seaton hypothesis,[1] that the nuclear spin plays no role in the electron-impact excitation of atoms, may be tested. Stepwise excitation also provides a new means of studying electron-impact–excited vacuum ultraviolet transitions, metastable states, and highly excited states.

The feasibility of this technique was investigated by studying stepwise excitation schemes for the $I=0$ and $I=\frac{1}{2}$ isotopes of mercury in which the $6^1S_0 \rightarrow 6^1P_1$ (185-nm) transition was excited by electron impact followed by single-mode laser excitation of the $6^1P_1 \rightarrow 6^1D_2$ (579-nm) transition. Fluorescence emitted from the $6^1D_2 \rightarrow 6^3P_1$ (313-nm) line was analyzed for line polarization as a function of incident electron energy. The polarization of the 313-nm line depends upon that induced in the electron excitation step and the optical excitation and emission steps. Since the optical processes are theoretically well understood, at least in the limit of weak excitation, it is possible to obtain the electron-impact–induced line polarization of the 185-nm line from measurements made on the 313-nm line.

A theoretical expression for the fluorescence intensity emitted following the stepwise excitation of a single atom is given by[2]

$$I = C \sum_{\substack{mm' \\ uu'}} A_{m'm} E_{uu'} F_{u'u} \times \int_0^{\delta t} \exp[-\Gamma + i(w_{mu} - w_{m'u'})]t\, dt. \quad (1)$$

Γ is the decay constant associated with the fluorescence emission step, the terms $(w_{mu} - w_{m'u'})$ give the sublevel splittings for the laser excited transition, C is a geometrical factor, while δt is the observation time of the detector. It has been assumed that both the electron and laser excitation steps take place in a time short compared with Γ. A and E are excitation operators which describe the electron and laser excitation processes respectively, while F is an emission operator representing the fluorescent emission of the stepwise excited atom. In the limit of weak laser excitation, for which no significant optical pumping of the laser-excited transition occurs, it can be shown that[2]

$$E_{uu'} = \langle u|\vec{e}\cdot\vec{P}|m\rangle\langle m'|\vec{e}^{*}\cdot\vec{P}|u'\rangle$$

and

$$F_{u'u} = \sum_n \langle u'|\vec{f}\cdot\vec{P}|n\rangle\langle n|\vec{f}^{*}\cdot\vec{P}|u\rangle, \quad (2)$$

where $|m\rangle$, $|u\rangle$, and $|n\rangle$ are magnetic sublevels of states $|e\rangle$, $|i\rangle$, and $|f\rangle$ [Fig. 1(a)], $\vec{e}$, and $\vec{f}$ are polarization vectors of the laser field and the scattered fluorescence, and $\vec{P}$ is the electric dipole moment operator. An expression for the intensity emitted from an ensemble of stepwise excited atoms may be obtained by assuming cylindrical symmetry about the electron beam direction. In this case only the diagonal terms of the electron excitation matrix elements $A_{m'm}$ are nonzero, and $A_{11} = A_{-1-1}$. In the notation of Macek and Jaecks $A_{mm} = \langle a_m a_m \rangle$, where a_m is the amplitude for electron excitation from the ground state to the mth sublevel of the first excited state, which may be written as

$$|e(t=0)\rangle = a_1|1\rangle + a_0|0\rangle + a_{-1}|-1\rangle . \quad (3)$$

Integration of A_{mm} over the electron scattering angles yields the partial integral cross sections Q_m.

For the $I=0$, $6^1S_0 \to 6^1P_1 \to 6^1D_2 \to 6^1P_3$ stepwise transition of mercury studied in this work, with the excitation and emission operation matrix elements evaluated for the experimental geometry shown in Fig. 1(b) and with circularly polarized laser excitation, we obtain from Eqs. (1) and (2)

$$I(\beta) \propto 9Q_0(1+\cos^2\beta) + Q_1(38 - 30\cos^2\beta) , \quad (4)$$

where β is the angle the linear polarizer makes with the electron beam direction. The 313-nm line polarization is given by

$$P_0' = \frac{I(0) - I(90)}{I(0) + I(90)} = \frac{9Q_0/Q_1 - 30}{27Q_0/Q_1 + 46} . \quad (5)$$

The electron–impact–excited 185-nm line polarization is given by the expression[4]

$$P_0 = (Q_0/Q_1 - 1)/(Q_0/Q_1 + 1) , \quad (6)$$

where the ratio Q_0/Q_1 is obtained from Eq. (5).

The corresponding expression for the $I=\frac{1}{2}$ isotope can be obtained in the following way. Assuming that the Percival-Seaton hypothesis holds during the collision process (i.e., the nuclear-spin quantum numbers I and M_I remain unchanged) the first excited state 6^1P_1 ($F=\frac{3}{2}$) can be expressed in terms of the $I=0$ excitation amplitudes as[2]

$$|e(t=0)\rangle = a_1|\tfrac{3}{2}\rangle + [(\sqrt{2}/\sqrt{3})a_0 + (1/\sqrt{3})a_1]|\tfrac{1}{2}\rangle + [(\sqrt{2}/\sqrt{3})a_0 + (1/\sqrt{3})a_{-1}]|-\tfrac{1}{2}\rangle + a_{-1}|-\tfrac{3}{2}\rangle . \quad (7)$$

The hyperfine sublevel excitation amplitudes of Eq. (7) are used to construct electron excitation matrix elements, and the resultant expression for the fluorescent intensity of the $I=\frac{1}{2}$ case is given by

$$I(\beta) \propto Q_0(3\cos^2\beta + 4) + Q_1(10\sin^2\beta + 5) . \quad (8)$$

The corresponding 313-nm line polarization for the $I=\frac{1}{2}$ isotope is given by

$$P_{1/2}' = (3Q_0/Q_1 - 10)/(11Q_0/Q_1 + 20) . \quad (9)$$

Equations (8) and (9) are valid only if the Percival-Seaton hypothesis holds. Under this hypothesis the 185-nm line ($I=\frac{1}{2}$) polarization is given by[4]

$$P_{1/2} = 3(Q_0/Q_1 - 1)/(7Q_0/Q_1 + 11) . \quad (10)$$

For heavy atoms such as mercury, spin-orbit interactions and the breakdown of L-S coupling can play a significant role in the scattering process. However, the predominantly singlet character of the 6^1P_1 state, which only has a small admixture of the 6^3P_1 state, minimizes the effect of spin-orbit interactions in the electron excitation process. It has also been shown recently that the breakdown of L-S coupling affects only the off-diagonal matrix elements of the electron excitation operator $A_{m'm}$.[5]

The experimental geometry is shown in Fig. 1(b). The electron, atom, and laser beams are coplanar and the fluorescence emitted from the stepwise excited atoms was detected perpendicular to this plane. Electrons were produced by an electron gun of an electrostatic-aperture lens design using a tungsten hair-pin filament. The electron-beam current was typically 3 μA with an energy resolution of about 0.3 eV. The mercury-atom beam was produced by an oven with a 2-mm-diam exit nozzle and had a collimation factor of about 3:1. A Spectra-Physics 380 A single-mode ring dye laser was used to provide laser excitation. The vacuum system provided a base pressure of $\sim 1\times 10^{-7}$ Torr and an operating pressure of $\sim 3\times 10^{-6}$ Torr. Helmholtz coils were used to cancel the Earth's magnetic field to less than 20 mG in the interaction region. The absence of any magnetically induced Hanle effects was experimentally verified by monitoring the 313-nm fluorescence as a function of magnetic field.

Radiation trapping effects were investigated by operating over a range of atomic beam pressures. At operating pressures required for a reasonable fluorescence signal, depolarizations of 20% for the $I=0$ and 4% for the $I=\frac{1}{2}$ isotopes were observed. Corrections were made by extrapolating back to zero tank pressure, introducing an uncertainty of 4% and 1.5% in the $I=0$ and $I=\frac{1}{2}$ values.

The weak-excitation description of the stepwise process is applicable provided the Rabi frequencies associated with the laser-excited step are small compared with the decay constant for the electron-excitation step. For the 6^1P_1 case the decay constant for the $6^1P_1 \to 6^1S_0$ transition is

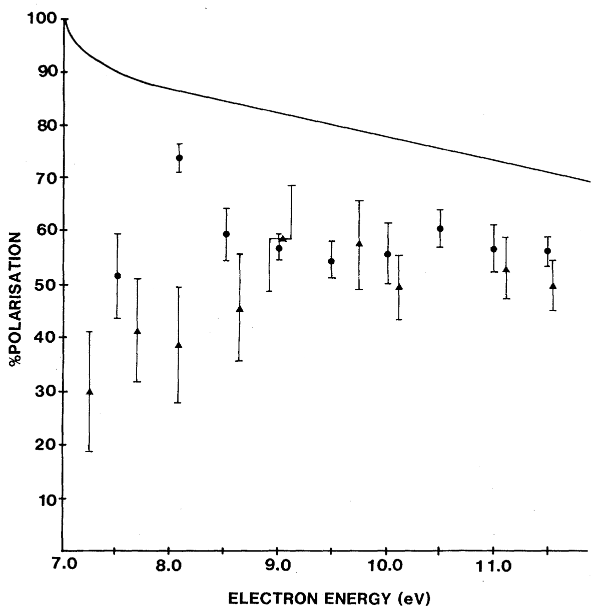

FIG. 2. Experimental and theoretical polarization values for the 185-nm line. Experimental uncertainties are 90% confidence limits. Circles, $I = 0$ isotope data. Triangles, Ottley *et al.* data. Solid line, theoretical values from McConnell and Moiseiwitsch (Ref. 4) for $I = 0$. All measured values are for circularly polarized laser radiation at 40 mW/mm^2 peak intensity.

approximately 1 GHz compared with estimated maximum Rabi frequencies for the laser-excited transition of about 100 MHz. Experimental verification was obtained by carrying out polarization measurements for a range of laser powers from 5 to 50 mW/mm^2. No significant variations were observed. Theoretical calculations[2] confirm that no significant optical pumping should occur under the experimental conditions used in this work. Circularly polarized rather than linearly polarized laser excitation was used because it was found both theoretically and experimentally that greater sensitivity for the polarization measurements was obtained.

The strength of the stepwise-excited signal relative to the direct-excitation signal was typically 50% at 9 eV and increased at lower energies as the direct signal diminished. Measurements were performed by taking repeated runs as a function of polarizer angle with the laser tuned and detuned to eliminate the signal from direct electron excitation of the $6^{1,3}\mathfrak{D}$ levels. Four measurements, at polarizer angles separated by 90° to eliminate small instrumental asymmetries, were used for each polarization measurement. Each datum point shown in Fig. 2 is the average of up to 20 independent measurements.

TABLE I. Ratio of partial total cross sections Q_0/Q_1 for $I = 0$ and $I = \frac{1}{2}$ isotopes. Experimental uncertainties are 90% confidence limits.

Incident electron energy	$Q_0/Q_1(I = 0)$	$Q_0/Q_1(I = \frac{1}{2})$
8.0	$5.60^{+0.62}_{-0.52}$	$3.05^{+0.42}_{-0.36}$
8.5	$3.90^{+0.70}_{-0.54}$	$2.43^{+0.15}_{-0.14}$
9.0	$3.64^{+0.26}_{-0.23}$	$3.36^{+0.23}_{-0.21}$
9.5	$3.38^{+0.34}_{-0.30}$	$3.54^{+0.58}_{-0.45}$
10.0	$3.51^{+0.67}_{-0.51}$	$3.52^{+0.66}_{-0.51}$
10.5	$4.01^{+0.44}_{-0.37}$	$3.42^{+0.50}_{-0.41}$

Figure 2 shows theoretical and experimental polarization values of the 185-nm line for the $I=0$ isotopes. Comparison with the theoretical predictions of McConnell and Moiseiwitsch[4] is made by using the predicted values for the Q_0 and Q_1 in Eq. (6).

The $I=0$ experimental data exhibit a decrease in polarization towards threshold in contrast to their theoretical predictions. These experimental results confirm the behavior near threshold observed by Skinner and Appleyard[6] and Ottley *et al.*[7] using direct electron excitation on the naturally occurring isotope mixture. Comparison with polarization data obtained by Ottley *et al.*[7] for the direct excitation of the naturally occurring isotope mixture is in reasonable agreement with our $I=0$ data, except around 8 eV, once allowance is made for the depolarization due to the nonzero nuclear-spin isotopes and for the larger experimental uncertainties present in their data. A test of the Percival-Seaton hypothesis can be made by comparing the ratio of partial total cross sections Q_0/Q_1 obtained from the polarization data by use of Eqs. (5) and (9). Equation (9) depends explicitly on the Percival-Seaton hypothesis. A comparison of Q_0/Q_1 data is shown in Table I. At higher energies the agreement is good, but at 8.0 and 8.5 eV a marked discrepancy exists which lies well outside 90% confidence limits for the data.

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