applied to the system. This wavelength is chosen to exactly connect the 5*s* level of Kr with the 7*s* of Hg. Equation (3) applies, with the quantity $|\gamma|^2$ now given by $(|\mu_{23}{}^A||\mu_{30}{}^A||\mu_{01}{}^B||E|/2\hbar^2\Delta\omega_1)^2$. $\Delta\omega_1 = 4054\ \mathrm{cm}^{-1}$ is the difference between the applied optical frequency and the Hg 7*s*-8*p* transition. At an incident power density of $10^9\ \mathrm{W/cm}^2$, an excited mercury concentration of 10^{17} atoms/cm^3, and $\overline{V} = 5\times10^4$ cm/sec, we find a Kr transition rate of 2.6×10^7 transitions/sec. This transition rate corresponds to an effective cross section for inelastic collision $[W(t) = N_A\sigma_{\mathrm{eff}}\overline{V}]$ of $\sigma_{\mathrm{eff}} = 72\ \text{Å}^2$. This cross section varies linearly with the power density of the applied 5886-Å field. One application of this type of pumping process may be selective rapid ionization of inner-shell electrons, thereby creating an inversion with regard to these levels.[8]

From a somewhat different point of view, we have described a process where by using one or more photons of an external electromagnetic field, large effective cross sections for inelastic collision can be attained without the usual requirement of energy resonance of the atomic species. Experiments to demonstrate these ideas will be undertaken in our laboratory.

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Radiative Decay of the 2^3S_1 and 2^3P_2 States of Heliumlike Vanadium ($Z = 23$) and Iron ($Z = 26$)*

Harvey Gould, Richard Marrus,† and Peter J. Mohr
Department of Physics and Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720

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Lifetimes of the *M*1 decay $2^3S_1 \to 1^1S_0$ and of the decay $2^3P_2 \to 1^1S_0$ have been measured in the two-electron ions V^{+21} and Fe^{+24}. The measured lifetimes are $\tau(2^3S_1) = 16.9(7)$ nsec for V^{+21} and $\tau(2^3S_1) = 4.8(6)$ nsec for Fe^{+24}. The 2^3P_2 lifetimes are compared with a calculation that considers relativistic corrections and hyperfine-structure effects. It is found that for V^{+21}, hyperfine effects contribute appreciably to the lifetime. For Fe^{+24} we obtain $\tau(2^3P_2) = 0.11(2)$ nsec.

The study of radiative decay from the 2^3S_1 and 2^3P_2 levels of the two-electron system offers an opportunity to test the theory of forbidden decay in a system where precise, unambiguous calculations of decay rates can be made. In this paper, we describe some measurements designed to extend existing experimental information on the rates of these decays to the two-electron atoms V^{+21} and Fe^{+24}. We develop a theory for the 2^3P_2 rates which takes into account leading-order relativistic corrections and hyperfine effects. Our results on vanadium show the first evidence for the influence of the hyperfine interaction on the radiative decay of an energy level belonging to the two-electron system.

Experimental work on the 2^3S_1 levels of the two-electron system has established the single-photon nature of the decay in Ar^{+16}[1] and ordinary helium.[2] The theory of this decay has been examined by several authors[3] and detailed calculations of the rates have been made by Drake[4] and by Johnson and Lin[5] using somewhat different starting points. Measurements of this decay rate have been made on Ar^{+16}, Ti^{+20},[6] and Cl^{+15}.[7] The measured rates in Cl and Ar differ from theory by several times the quoted error, whereas the

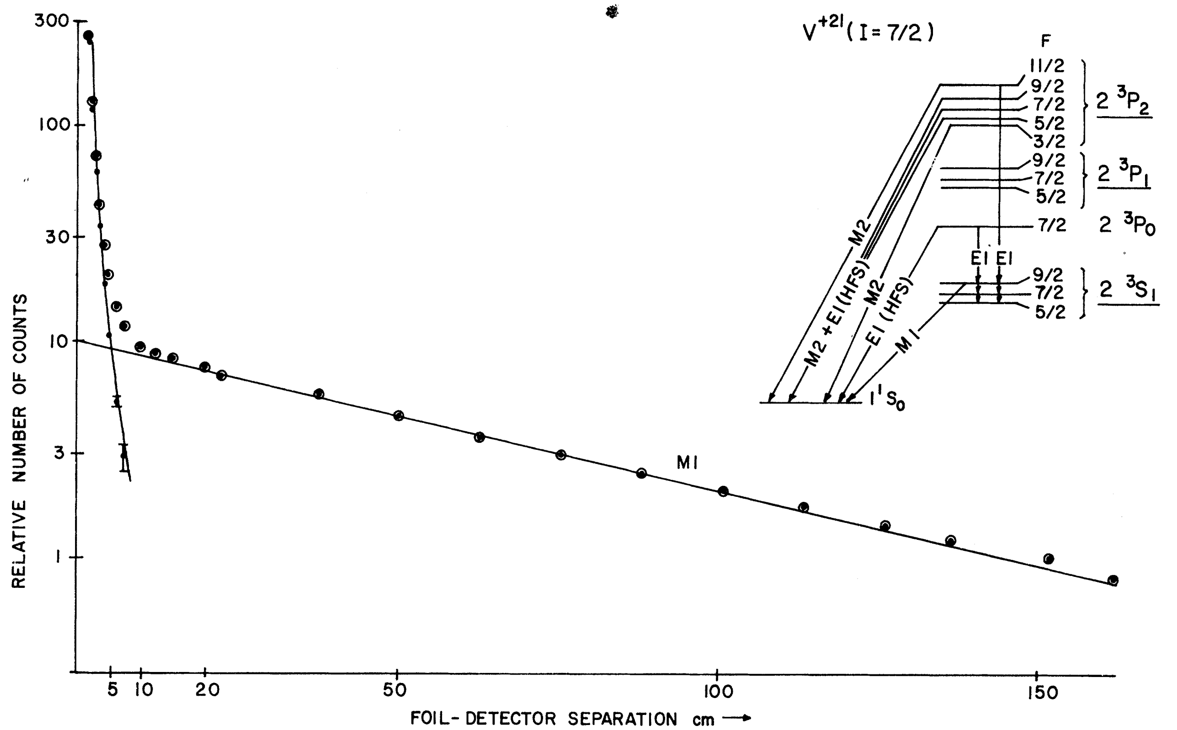

FIG. 1. Sample decay curve obtained with V^{+21} beam. The points beyond 22 cm are fitted by a single exponential and ascribed to decay of the 2^3S_1 level. The small-separation points are fitted by a composite of four exponentials as described in the text and are ascribed to decay of the 2^3P_2 level.

result in Ti is in agreement. In order to establish the Z dependence of this discrepancy we report here measurements on V^{+21} and Fe^{+24}.

Interest in the 2^3P_2 levels centers mainly on the $M2$ decay mode to the 1^1S_0 ground level which has a rate comparable with the $E1$ rate to 2^3S_1 for ions with $Z \simeq 20$. The $M2$ decay was first observed[8] in Ar^{+16} and rates have now been measured in S^{+14},[9] Cl^{+15},[10] and Ar^{+16}.[11] In this paper we present evidence indicating that the decay of this level is strongly influenced by the hyperfine interaction in V^{+21} and give results for Fe^{+24}.

The lifetimes were measured by the beam-foil time-of-flight method. Our apparatus has been described previously[6] and the details are not repeated here. The vanadium ($Z = 23$) and iron ($Z = 26$) ions were obtained from the Lawrence Berkeley Laboratory SuperHILAC at an energy of 7.2 MeV/amu. Excitation of the beams into the metastable states was done with a 50-μg/cm^2 carbon foil. Decay curves are taken by varying the foil-detector separation. The total number of counts under the peak is integrated and normalized to the integrated beam current collected in a Faraday cup. This quantity is plotted as a function of foil-detector separation. A sample decay curve is shown in Fig. 1.

Since the 2^3P_2 and 2^3S_1 energy separations are small compared with the detector resolution, the decay curves are composites, exhibiting fast components and slow components. The slow components are ascribed to the 2^3S_1 decay and the fast components to decay from 2^3P_2. As discussed below, the slow and fast components are probably composites of two or more exponentials as the result of hyperfine effects in V^{+21} and cascading effects in Fe^{+24}.

The isotope ^{51}V has a nuclear spin $I = \frac{7}{2}$ and a magnetic moment $\mu = 5.15\mu_N$.[12] The resulting hyperfine structure influences our decay curves by admixing 2^3P_2 with 2^3P_1 and 2^1P_1. The 2^3P_2 level is split into five components with total angular momentum between $F = \frac{3}{2}$ and $F = \frac{11}{2}$ (Fig. 1). Because the hyperfine interaction is diagonal in F, the rates from both $F = \frac{3}{2}$ and $F = \frac{11}{2}$ are unaffected by hyperfine structure. However, the rates from $F = \frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$ will all be altered. Hence, the observed decay curve will be a composite of four exponentials weighted according to the initial populations of each of the hyperfine levels.

The most abundant stable iron isotope has zero spin and hyperfine effects are not present. Hence the decay of 2^3P_2 is exclusively by $E1$ decay to 2^3S_1 and $M2$ to 1^1S_0.

A problem arises in the interpretation of the 2^3S_1 decay because of cascading from 2^3P_0. The lifetime of 2^3P_0 is calculated to be $\tau = 2.7$ nsec which is close to that of 2^3S_1. Hence cascading effects from this level may be important. The shape of the resultant curve will depend upon the relative population $R \equiv N_0(2^3P_0)/N_0(2^3S_1)$ of the two states, and the decay rates. It was found that the data could be fitted by two exponentials for $0 \leqslant R \leqslant 0.8$. Varying the lifetimes of the two exponentials, we find that the "best fit" values for $\tau(2^3S_1)$ vary between 4.2 and 5.3 nsec, where 5.3 nsec results from a single exponential fit ($R = 0$) and, hence, is an upper limit to the 2^3S_1 lifetime. Similarly, the values for $\tau(2^3P_0)$ vary between 1.3 and 3.3 nsec. We note that the theoretical value of $\tau(2^3P_0) = 2.7$ nsec corresponds to $\tau(2^3S_1) = 4.8$ nsec. We have chosen to take the mean value as the experimental value and to take cascading into account by using an increased error.

In Fig. 1, an experimental decay curve is shown for the V^{+21} beam. The decay curve is fitted by identifying the data points beyond 22 cm with the 2^3S_1 decay. These yield a lifetime $\tau(2^3S_1) = 16.9(7)$ nsec. When this decay is subtracted from the experimental data it yields the points for small detector-foil separation as shown. These are fitted by a composite decay curve constructed by assuming that each of the F states associated with 2^3P_2 has the theoretical lifetime shown in Table I. These lifetimes include effects due to hyperfine quenching. Moreover, the initial populations of the F states are taken as proportional to $2F+1$. The resultant fit to the experimental points is as shown and is seen to be quite good.

TABLE I. Theoretical transition rates and lifetimes of the 2^3P_2 state in heliumlike ions.

Z	A_{E1} (nsec^{-1})	A_{M2} (nsec^{-1})	F	$A_{E1}{}^{\text{hfs}}$ (nsec^{-1})	τ (nsec)
16	0.259	0.117	All	< 0.007	2.66
17	0.301	0.194			≃ 2.01
18	0.352	0.312			1.51
22	0.687	1.64			0.429
23	0.820	2.37	3/2	0	0.313
			5/2	0.99	0.239
			7/2	1.75	0.202
			9/2	1.69	0.205
			11/2	0	0.313
26	1.43	6.50			0.126

To calculate accurate theoretical rates for the 2^3P_2 level, the transition matrix elements are evaluated to zeroth and first order in the quantities Z^{-1} and $(Z\alpha)^2$. The zeroth-order term is the nonrelativistic hydrogenic approximation. The term of order Z^{-1} is the first correction in the nonrelativistic Z expansion of the matrix element. The leading relativistic correction, of order $(Z\alpha)^2$, is obtained by evaluating the relativistic transition operator between states formed from properly symmetrized products of hydrogenic Dirac wave functions.

For the $M2$ transition, the coefficient of Z^{-1} has been determined by Drake[13] from the Z-expansion calculation of Dalgarno and Parkinson.[14] Taking his result together with the leading relativistic and finite-wavelength (retardation) corrections yields

$$A_{M2}(2^3P_2) = \alpha k^5 (2^{15}/5\times 3^{10})(Z\alpha)^{-2}[1 + 0.147Z^{-1} - 0.640(Z\alpha)^2]^2 \tag{1}$$

(in units where $m_e = c = \hbar = 1$), where k is the transition energy.

Because the nonrelativistic-velocity form of the matrix element for $n \to n$ $E1$ transitions vanishes to lowest order in Z^{-1}, the evaluation of the $E1$ transition rate $2^3P_2 \to 2^3S_1$ is simplified by making the dipole approximation and converting the matrix element to the length form. The error in making this approximation is negligible because of the smallness of the transition energy: $\langle \vec{k} \cdot \vec{r} \rangle = O(\alpha)$. The conversion to length form is valid relativistically and so relativistic corrections may be obtained as described above. For this transition matrix element, the coefficient of Z^{-1} has been obtained by Cohen and Dalgarno.[15] We thus have

$$A_{E1}(2^3P_2) = \alpha k^3 12 (Z\alpha)^{-2}[1 + 0.759Z^{-1} - 0.167(Z\alpha)^2]^2. \tag{2}$$

The transition probability for the $E1$ decay $2^3P_0 \to 2^3S_1$, obtained as for the 2^3P_2 decay, is given by

$$A_{E1}(2^3P_0) = \alpha k^3 12 (Z\alpha)^{-2}[1 + 0.759Z^{-1} - 0.417(Z\alpha)^2]^2. \tag{3}$$

We note that the theoretical uncertainty in the expressions for the transition rates listed above is expected to be of the order of 1% or less for Z in the range 10–40.

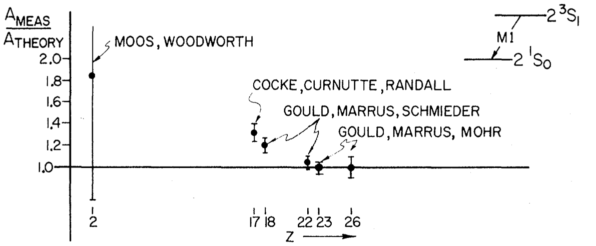

FIG. 2. Comparison between measured and calculated decay rates for the 2^3S_1 level.

In the case of vanadium, which has a nonzero nuclear spin, the 2^3P_2 and 2^3P_0 states undergo an $E1$ transition to the 1^1S_0 state due to hyperfine mixing.[16] An estimate of the transition rate is obtained in the following way. Nonrelativistic intermediate-coupling wave functions are taken as the unperturbed basis. The hyperfine interaction which is diagonal in $F = J + I$, is treated in first-order perturbation theory. Only the effect of mixing of the 2^3P_2 and 2^3P_0 states with the nearby 2^3P_1 and 2^1P_1 states is included. The dipole transition operator then has a nonvanishing matrix element between the perturbed 2^3P_2 and 2^3P_0 states and the 1^1S_0 state which is proportional to the dipole matrix element between the LS coupled 2^1P_1 state and the 1^1S_0 state. The latter is evaluated with the aid of the Z expansion of Dalgarno and Parkinson.[14] The hyperfine matrix elements are approximated by evaluating the contact-interaction term between hydrogenic product wave functions. Energy differences are evaluated by means of the Z expansion of the nonrelativistic energies,[17] together with the Z expansion of the order-α^4 corrections.[18] The transition rates thus obtained are added to the rates discussed above and the resulting values for the lifetime of the 2^3P_2 state are listed in Table I.

In Fig. 2 we compare all of the measured decay rates of 2^3P_2 with the corresponding theoretical rates. Agreement is seen to be very good over a wide range of Z. For vanadium, the theoretical rate includes the contribution from hyperfine quenching. It is seen that the experimental and theoretical rates would be in serious disagreement without contributions from this mechanism. We take this as very strong evidence that hyperfine quenching is indeed present.

In Fig. 3 we compare the measured 2^3S_1 decay rates with the calculated rates. Agreement between theory and experiment is satisfactory for $Z = 22$, 23, and 26, but puzzling discrepancies exist at $Z = 17$ and 18.

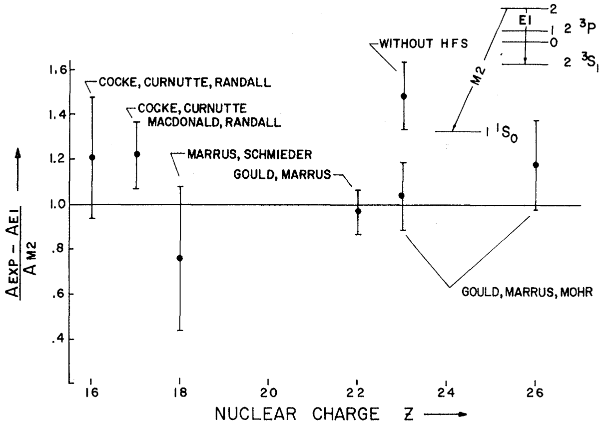

FIG. 3. Comparison between measured and calculated $M2$ rates for decay from the 2^3P_2 level. The point at $Z = 23$ labeled "without HFS" is obtained by making a best fit to our vanadium data using a single exponential.

We are indebted to Al Ghiorso and the staff of the SuperHILAC for their enthusiastic support of this work. The development of the vanadium and iron beams was a vital product of this support. Doug MacDonald gave valuable engineering support. One of us (P.J.M.) gratefully acknowledges helpful conversations with Professor Charles Schwartz and Professor Eyvind H. Wichmann.

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Reverse Temperature Gradient in the Kinetic Theory of Evaporation

J. R. Thomas, Jr.
Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

and

T. S. Chang*
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

C. E. Siewert
Department of Nuclear Engineering, North Carolina State University, Raleigh, North Carolina 27607

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The singular-eigenfunction–expansion method for solving the transport equation is applied to a modeled kinetic-theory Boltzmann equation to solve the problem of evaporation and condensation between parallel surfaces. A remarkable result is obtained for the temperature profile which seems to confirm previous predictions made on the basis of asymptotic approximations.

In a recent paper, Pao[1] suggested that the slope of the temperature profile of a saturated vapor between two parallel surfaces at different temperatures could be in opposition to the imposed gradient for certain values of β, where $\Delta N = \beta \Delta T$ in a saturated liquid-vapor system. Here N represents the molecular density and T the temperature. Pao's prediction was based on an asymptotic analysis for large gap width, and used results obtained for the half-space problem[2] by applying the Wiener-Hopf technique to a modeled Boltzmann equation.

We have approached the same problem through the singular-eigenfunction analysis of Kriese, Chang, and Siewert,[3] also used by Thomas and co-workers,[4-6] and have avoided any asymptotic approximations. Thus for the first time, inverted temperature profiles and critical values of β are calculated explicitly. The surprising result is that our analysis seems to confirm Pao's novel prediction.

We consider the problem of a vapor between two interphase (vapor-liquid or vapor-solid) surfaces maintained at $x = \pm d/2$; we assume that the condensed phase in $x < -d/2$ is kept at temperature $T_0 - \frac{1}{2}\Delta T$ and that the condensed phase in $x > d/2$ is kept at temperature $T_0 + \frac{1}{2}\Delta T$. As a result of evaporation and condensation there is a flow of mass and energy from $x = +d/2$ to $x = -d/2$. Within the vapor, we assume the state of the fluid to be described by the linearized single-relaxation model of the Boltzmann equation[7]:

$$c_x \partial f(x, \vec{c})/\partial x + f(x, \vec{c}) = \pi^{-3/2}[N(x) + (c^2 - \tfrac{3}{2})T(x) + 2c_x U(x)]. \tag{1}$$

Here $f(x, \vec{c})$ is the perturbation of the particle-distribution function, x is the spatial variable, $\vec{c}$ is the molecular velocity, and c_x is the x component of the velocity, all in dimensionless units. In addition, $N(x)$, $T(x)$, and $U(x)$ represent perturbations of the number density, the temperature, and the x com-