PHYSICAL REVIEW VOLUME 167, NUMBER 1 5 MARCH 1968

Stark Effect in the Excited States of Rb, Cs, Cd, and Hg*

ABBAS KHADJAVI† AND ALLEN LURIO
IBM Watson Laboratory, Columbia University, New York, New York

AND

W. HAPPER
Columbia University, New York, New York

(Received 19 September 1967)

Two new experimental techniques have been developed and used to measure the differential Stark shifts between the Zeeman sublevels in excited atomic states. For states whose differential Stark shifts, in uniform electric fields attainable in the laboratory, are comparable to the hfs separation, the method of pure electric-field level crossing may be used. This method has been applied to the $6p\ ^2P_{3/2}$ state of rubidium and the $7p\ ^2P_{3/2}$ state of cesium. The differential shifts are $E(\pm\frac{3}{2})-E(\pm\frac{1}{2})=0.521\pm0.021$ Mc/(kV/cm)^2 in Rb, and 1.077 ± 0.043 Mc/(kV/cm)^2 in Cs. For isotopes with no hyperfine structure $(I=0)$ or states whose Stark shifts are small compared to their hfs, we have used the level-crossing technique with parallel electric and magnetic fields. This technique has been employed to measure the differential shifts in the $5s5p\ ^3P_1$ state of cadmium and the $6s6p\ ^3P_1$ state of mercury. The results are $E(\pm1)-E(0)=-2.550\pm0.105$ kc/(kV/cm)^2 in Cd, and -2.355 ± 0.090 kc/(kV/cm)^2 in Hg. The theory of quadratic Stark shifts in terms of scalar and tensor operators is presented, and the shifts in these four elements are calculated using the Coulomb approximation for the potential of the outer electron. The agreement between the experimental and the theoretical values is satisfactory.

I. INTRODUCTION

THE Stark effect has not been exploited as extensively as the Zeeman effect for the study of atomic structures. This is due to the fact that, except in systems with l degeneracy (Coulomb and harmonic-oscillator potentials), the Stark shift is quadratic in the electric field, and the electric fields necessary to produce measurable changes in the energy of the sublevels of a given J are harder to produce and measure than the corresponding magnetic fields. Further, in order to calculate the Stark shifts, the radial part of the electronic wave function must be known. But precisely for this reason, measurements of the Stark shift offer a convenient test of proposed approximation methods for radial wave functions and radial integrals.

In recent years, considerable progress has been made in theoretical techniques for evaluating the radial integrals and for treating the infinite sums in the perturbation expansion of the Stark effect.[1] Experimentally, the techniques of double resonance, atomic beams, the method of beats, level crossing, and anticrossing have been used to measure Stark shifts.[2] In this paper we present a development of the Stark shift in terms of effective scalar and tensor operators, and give details of the measurement of the tensor Stark operator in the second $^2P_{3/2}$ state of Rb and Cs, and the first $^3P_1$ state of Cd and Hg.

II. THEORY OF THE STARK SHIFTS

A. Scalar and Tensor Stark Operators

The Hamiltonian for an atom in a uniform electric field is given by

$$\mathcal{H}=\mathcal{H}_0-\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,, \tag{1}$$

where $\mathcal{H}_0$ is the Hamiltonian in the absence of the field, $\boldsymbol{\mathcal{E}}$ is the electric field, and $\mathbf{p}=-\sum_i e\mathbf{r}_i$ is the electronic dipole moment. The magnitude of the electronic charge is denoted by e, so that $-e$ is the charge of an electron. For uniform electric fields that are attainable in the laboratory the term $-\boldsymbol{\mathcal{E}}\cdot\mathbf{p}$ can be treated as a perturbation. If we assume the eigenfunctions of $\mathcal{H}_0$ to have definite parity, then the expectation value of the perturbing term $\langle 0|\boldsymbol{\mathcal{E}}\cdot\mathbf{p}|0\rangle$ vanishes since $\boldsymbol{\mathcal{E}}\cdot\mathbf{p}$ has odd parity. Hence, the change in the energy of the state $|0\rangle$, to the lowest order in $\mathcal{E}$, is given by the second-order perturbation formula

$$\Delta E(0)=\sum_i\frac{\langle 0|\boldsymbol{\mathcal{E}}\cdot\mathbf{p}|i\rangle\langle i|\boldsymbol{\mathcal{E}}\cdot\mathbf{p}|0\rangle}{E(0)-E(i)}\,. \tag{2}$$

Since only the even terms are present in the perturbation expansion of $\Delta E(0)$, the ratio of successive nonvanishing terms is of the order of magnitude

$$\epsilon=\frac{(\boldsymbol{\mathcal{E}}\cdot\mathbf{p})^2}{[E(0)-E(i)]^2}\,.$$

This expression can be roughly estimated by substitut-

---

* This work was supported in part by the joint services electronics program (U. S. Army, U. S. Air Force, and U. S. Navy) under contract DA-28-043 AMC-00099(E).

† Submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. Present address: Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235.

[1] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1956); C. Schwartz, Ann. Phys. (N. Y.) **2**, 156 (1959); R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).

[2] J. E. Blamont, Ann. Phys. (Paris) **2**, 55 (1957); R. D. Haun, Jr., and J. R. Zacharias, Phys. Rev. **107**, 107 (1957); E. Lipworth and P. G. H. Sandars, Phys. Rev. Letters **13**, 716 (1964); R. Marrus, D. McColm, and J. Yellin, Phys. Rev. **147**, 55 (1966); E. B. Aleksandrov and V. V. Khromov, Opt. i Spektroskopiya **18**, 545 (1964) [English transl.: Opt. Spectry. (USSR) **18**, 313 (1965)]; B. Budick, S. Marcus, and R. Novick, Phys. Rev. **140**, A1041 (1965); J. J. Forney and E. Geneux, Phys. Letters **20**, 632 (1966); see also Ref. 8.

ing in $\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\sim er\mathcal{E}$ the following values: e is the electronic charge, $r=1$ Å, and $\mathcal{E}=10$ kV/cm. The energy denominator can be taken to be of the order of 1000 cm^{-1}. The result is $\epsilon=6\times10^{-7}$. Hence, the first nonvanishing term gives the change in energy with sufficient accuracy.

The expression for $\Delta E(0)$, given in (2), is formally equivalent to a first-order perturbation if we take the perturbing term to be

$$\mathcal{H}'=\sum_i \frac{\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,|i\rangle\langle i|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}}{E(0)-E(i)}\,. \tag{3}$$

Thus, we take the Hamiltonian to be

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}'\,, \tag{4}$$

with $\mathcal{H}'$, the effective Hamiltonian, given by (3). We shall assume that $\mathcal{H}_0$ represents the usual atomic Hamiltonian including hfs plus the interaction of the atom with an external magnetic field directed along the z axis. Then the states of the atom may be designated by the quantum numbers $i\equiv(\gamma IJFm)$, where I and J are the nuclear and atomic angular momenta, and m is the total z component of angular momentum. The label γ distinguishes between different optical states with the same quantum numbers I, J, and m, and F is an additional label to distinguish between different states with the same values of γ, I, J, and m. When the external magnetic field is zero, F will be the total angular momentum $|\mathbf{I}+\mathbf{J}|$ of the atom, so that we can think of F as labeling the total angular momentum of the state to which the atomic state $|\gamma IJFm\rangle$ would evolve if the magnetic field gradually decreased to zero. For an atom with no nuclear spin we can use a simpler notation $|\gamma Jm\rangle$ to designate the eigenvectors. Since the energies are independent of m in the absence of an external magnetic field, they may be designated by $E(\gamma J)=E(\gamma Jm)$. We take J to be a good quantum number in all calculations: This means that we treat only the cases where the Stark energy is small compared to the fine structure. Using explicit quantum numbers, the effective Hamiltonian of Eq. (3) becomes

$$\mathcal{H}'=\sum_{\substack{Fm\\F''m''\\\gamma'J'F'm'}}\{|\gamma IJFm\rangle\langle\gamma IJFm|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,|\gamma'IJ'F'm'\rangle\langle\gamma'IJ'F'm'|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}$$

$$\times|\gamma IJF''m''\rangle\langle\gamma IJF''m''|\}[E(\gamma IJF''m'')-E(\gamma'IJ'F'm')]^{-1} \tag{5}$$

$$=\sum_{\substack{mm''\\\gamma'J'm'}}\frac{|\gamma Jm\rangle\langle\gamma Jm|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,|\gamma'J'm'\rangle\langle\gamma'J'm'|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,|\gamma Jm''\rangle\langle\gamma Jm''|}{E(\gamma J)-E(\gamma'J')}\Big[\sum_\mu |I\mu\rangle\langle I\mu|\Big]\left\{1+O\left(\frac{\Delta E_{\mathrm{hfs}}}{\Delta E_{\mathrm{opt}}}\right)\right\}\,. \tag{5'}$$

Since the optical energy differences ΔE_{opt} are of the order of 10^4 cm^{-1} while the magnetic and hfs splittings are normally of the order of 10^{-1} cm^{-1} or less, we can neglect the second term in the curly brackets which is at least 10^{-5} times smaller than the first. We can also suppress the unit operators and write the effective Hamiltonian as a purely atomic operator,

$$\mathcal{H}'=\sum_{\gamma'J'm'}\frac{\boldsymbol{\mathcal{E}}\cdot\mathbf{p}\,|\gamma'J'm'\rangle\langle\gamma'J'm'|\,\boldsymbol{\mathcal{E}}\cdot\mathbf{p}}{E(\gamma J)-E(\gamma'J')}\,. \tag{3'}$$

The angular dependence of $\mathcal{H}'$ can be explicitly displayed by expanding $\mathcal{H}'$ in terms of irreducible tensors.[3]

We shall use the spherical basis notation where the components of $\boldsymbol{\mathcal{E}}$ are

$$\mathcal{E}_{\pm1}{}^1=\mp\tfrac{1}{2}\sqrt{2}(\mathcal{E}_x\pm i\mathcal{E}_y),\quad \mathcal{E}_0{}^1=\mathcal{E}_z\,. \tag{6}$$

The components of $\mathbf{p}$ are defined similarly. These components form a tensor of rank one and the scalar product $\boldsymbol{\mathcal{E}}\cdot\mathbf{p}$ is given by the contraction of two tensors $\mathcal{E}_\mu{}^1$ and $p_\mu{}^1$:

$$\boldsymbol{\mathcal{E}}\cdot\mathbf{p}=\sum_\mu(-1)^\mu\mathcal{E}_{-\mu}{}^1p_\mu{}^1,\quad \mu=-1,0,+1\,. \tag{7}$$

It is convenient to define two other tensors to be used in the expansion of $\mathcal{H}'$ as follows:

$$E_M{}^L=\sum_\mu \mathcal{E}_\mu{}^1\mathcal{E}_{M-\mu}{}^1(2L+1)^{1/2}\times(-1)^{M+1}\begin{pmatrix}1 & 1 & L\\ \mu & M-\mu & -M\end{pmatrix} \tag{8}$$

and

$$T_M{}^L=\sum_m |Jm\rangle\langle J,m-M|(-1)^{m-J}\times(2L+1)^{1/2}\begin{pmatrix}J & J & L\\ m & M-m & -M\end{pmatrix}\,. \tag{9}$$

The inverse relations are

$$\mathcal{E}_\mu{}^1\mathcal{E}_\nu{}^1=\sum_L(-1)^{\mu+\nu+1}(2L+1)^{1/2}\times\begin{pmatrix}1 & 1 & L\\ \mu & \nu & -\mu-\nu\end{pmatrix}E_{\mu+\nu}{}^L \tag{10}$$

and

$$|Jm\rangle\langle Jm'|=\sum_L(-1)^{J-m}(2L+1)^{1/2}\times\begin{pmatrix}J & J & L\\ m & -m' & m'-m\end{pmatrix}T_{m-m'}{}^L\,. \tag{11}$$

---

[3] P. G. H. Sandars and J. R. P. Angel [J. R. P. Angel, thesis, University of Oxford, Oxford, England, 1967 (unpublished)]; W. Happer and E. B. Saloman, Phys. Rev. Letters 15, 441 (1965).

Explicit values of $E_M{}^L$ are the following:

$$
\begin{aligned}
&E_0{}^0=\tfrac{1}{3}\sqrt{3}\,\mathcal{E}^2, && E_{\pm1}{}^1=0,\\
&E_0{}^1=0, && E_{\pm2}{}^2=-(\mathcal{E}_{\pm1}{}^1)^2,\\
&E_{\pm1}{}^2=-\sqrt{2}\,\mathcal{E}_0{}^1\mathcal{E}_{\pm1}{}^1, && E_0{}^2=(\tfrac{1}{6}\sqrt{6})[\mathcal{E}^2-3(\mathcal{E}_0{}^1)^2].
\end{aligned}
\tag{12}
$$

The effective Stark Hamiltonian $\mathcal{H}'$ can now be written as

$$
\mathcal{H}'=\sum_{\substack{J'm'\\ mm''\\ \mu\nu}}\frac{(-1)^{\mu+\nu}}{E(J)-E(J')}|Jm\rangle\langle Jm|\mathcal{E}_{-\mu}{}^1p_\mu{}^1|J'm'\rangle
\times\langle J'm'|\mathcal{E}_{-\nu}{}^1p_\nu{}^1|Jm''\rangle\langle Jm''|\,. \tag{13}
$$

$\sum_m |Jm\rangle\langle Jm|$ is the identity operator in the subspace of a given J and the zero operator elsewhere. Making use of Eqs. (10) and (11) and the relation

$$
\langle Jm|p_\mu|J'm'\rangle=(-1)^{J-m}\begin{pmatrix} J & 1 & J'\\ -m & \mu & m'\end{pmatrix}(J\|p\|J'),
$$

we have

$$
\begin{aligned}
\mathcal{H}'=\sum&\frac{(-1)^{M+2J+J'-m'-2m+1}}{E(J)-E(J')}E_M{}^LT_{M'}{}^{L'}\\
&\times(J\|p\|J')(J'\|p\|J)[(2L+1)(2L'+1)]^{1/2}\\
&\times\begin{pmatrix} 1 & 1 & L\\ -\mu & -\nu & -M\end{pmatrix}\begin{pmatrix} J & 1 & J'\\ -m & \mu & m'\end{pmatrix}\\
&\times\begin{pmatrix} J' & 1 & J\\ -m' & \nu & m''\end{pmatrix}\begin{pmatrix} J & J & L'\\ m & -m'' & M'\end{pmatrix},
\end{aligned}
\tag{14}
$$

where the sum is over the variables μ, ν, m, m', m'', J', L, L', M, and M'. If we use the identities relating the products of $3j$ symbols to the $6j$ symbols we can simplify this expression to

$$
\mathcal{H}'=\sum_L K_L\sum_M(-1)^ME_{-M}{}^LT_M{}^L, \tag{15}
$$

where

$$
K_L=\sum_{J'}\frac{(-1)^{1+J+J'}}{E(J)-E(J')}\begin{Bmatrix} J & J & L\\ 1 & 1 & J'\end{Bmatrix}|(J\|p\|J')|^2. \tag{16}
$$

It is evident from (12) that the expansion of $\mathcal{H}'$ given by (15) consists of only two terms, $\mathcal{H}_0'$ and $\mathcal{H}_2'$, corresponding to $L=0$ and $L=2$. These two terms are referred to as the scalar and tensor interactions.

If we take $\boldsymbol{\mathcal{E}}$ to be in the z direction then $E_M{}^L=\delta_{M,0}E_M{}^L$ [see Eq. (12)] and we need only $T_0{}^0$ and $T_0{}^2$, which are given by the expressions

$$
\begin{aligned}
T_0{}^0&=\sum_m\frac{|Jm\rangle\langle Jm|}{(2J+1)^{1/2}},\\
T_0{}^2&=\sum_m\frac{|Jm\rangle\langle Jm|2(\sqrt{5})[3m^2-J(J+1)]}{[(2J+3)(2J+2)(2J+1)(2J)(2J-1)]^{1/2}}.
\end{aligned}
\tag{17}
$$

We now define the scalar and tensor polarizabilities α_0 and α_2 by the condition that for a uniform electric field $\mathcal{E}$ in the z direction the energy of the $m=J$ state is $-\frac{1}{2}\alpha_0\mathcal{E}^2-\frac{1}{2}\alpha_2\mathcal{E}^2$. Thus

$$
\langle Jm|\mathcal{H}'|Jm\rangle=-\tfrac{1}{2}\alpha_0\mathcal{E}^2-\tfrac{1}{2}\alpha_2\mathcal{E}^2\frac{3m^2-J(J+1)}{J(2J-1)}, \tag{18}
$$

$$
\begin{aligned}
\alpha_0&=-\tfrac{2}{3}\sum_{J'}\frac{|(J\|p\|J')|^2}{(2J+1)[E(J)-E(J')]}=-\frac{2K_0}{[3(2J+1)]^{1/2}}\\
\alpha_2&=2\left[\frac{10J(2J-1)}{3(2J+3)(J+1)(2J+1)}\right]^{1/2}\sum_{J'}\frac{|(J\|p\|J')|^2}{E(J)-E(J')}\\
&\qquad\times(-1)^{J+J'+1}\begin{Bmatrix} J & J' & 1\\ 1 & 2 & J\end{Bmatrix}\\
&=4K_2(\sqrt{\tfrac{5}{6}})\left[\frac{J(2J-1)}{(2J+3)(2J+1)(J+1)}\right]^{1/2}.
\end{aligned}
\tag{19}
$$

Although α_2 is identically zero for $J=\frac{1}{2}$, a small tensor polarizability will still exist when hfs is present due to the higher-order terms which were dropped from Eq. (5').

In many cases the first few radial integrals are more accurately determined from the measured oscillator strengths than from approximate theoretical calculations. To facilitate calculations in these cases we may write K_L in terms of the oscillator strengths to obtain

$$
K_L=\frac{3(2J+1)r_0}{8\pi^2}\sum_{J'}(\lambda_{JJ'})^2f_{J'J}\times\begin{Bmatrix} J & J & L\\ 1 & 1 & J'\end{Bmatrix}(-1)^{J+J'}, \tag{20}
$$

where $r_0=e^2/mc^2$ is the classical electron radius, $(2J+1)f_{J'J}=-(2J'+1)f_{JJ'}$, and $f_{J'J}$ is positive if the J' state lies higher than the J state.[4]

III. APPLICATION TO $^2P_{3/2}$ AND $^3P_1$ STATES

The reduced matrix elements of $\mathbf{p}$ can be simplified by the following equation:

$$
\begin{aligned}
(J\|p\|J')&=(nSLJ\|p\|n'S'L'J')\\
&=(-1)^{S+L'+J+1}[(2J+1)(2J'+1)]^{1/2}\delta_{SS'}\\
&\qquad\times\begin{Bmatrix} L & J & S\\ J' & L' & 1\end{Bmatrix}(L\|p\|L'),
\end{aligned}
\tag{21}
$$

and in the case of a single external electron we have

$$
(l\|p\|l')=e(-1)^{l_>-l}l_>{}^{1/2}\int R_nrR_{n'}dr, \tag{22}
$$

---

[4] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935), Chap. IV.

TABLE I. Experimental and theoretical Stark shifts for Rb and Cs in Mc/(kV/cm)^2.

Nucleus	State	A, B in Mc[a]	α_0(calc)	α_2(calc)	α_2(expt)	Expt crossing fields (kV/cm)
Rb^{85}	$6\,^2P_{3/2}$	8.16, 8.40	3.34	-0.494	-0.521 ± 0.021	8.77 ± 0.18, 10.95
Rb^{87}		27.63, 4.06				14.3
Cs^{133}	$7\,^2P_{3/2}$	16.609, -0.16	9.03	-1.05	-1.077 ± 0.043	11.07 ± 0.2, 13.5

[a] G. zu Putlitz, Ergeb. Exakt. Naturw. **37**, 105 (1965).

where $l_>$ means the greater of l and l'. If there is more than one external electron, then $(L\|p\|L')$ can be expressed as some combination of single electron integrals of the form (22). For the $^3P_1$ state of Hg and Cd one finds that for states J' only one electron has different quantum numbers compared to the state J and this electron is the only one contributing to (21) and (22). Substituting appropriate quantum numbers into Eqs. (19) we have for the $^2P_{3/2}$ state (Rb and Cs) the following values for the polarizabilities:

$$\begin{aligned}\alpha_0&=-(1/45)[9D(\tfrac{5}{2})+D(\tfrac{3}{2})+10S(\tfrac{1}{2})],\\ \alpha_2&=(1/225)[9D(\tfrac{5}{2})-4D(\tfrac{3}{2})+50S(\tfrac{1}{2})],\end{aligned}\tag{23}$$

where the following abbreviations are used:

$$\begin{aligned}D(J')&=2e^2\sum_{n'}\frac{\left(\int_0^\infty R(np)R(n'd)rdr\right)^2}{E(nP_{3/2})-E(n'D_{J'})},\\ S(J')&=2e^2\sum_{n'}\frac{\left(\int_0^\infty R(np)R(n's)rdr\right)^2}{E(nP_{3/2})-E(n'S_{J'})}.\end{aligned}\tag{24}$$

Theoretical values of α_L for the $6p\,^2P_{3/2}$ state of Rb and the $7p\,^2P_{3/2}$ state of Cs are given in Table I. In these calculations we have used the Coulomb approximation for the potential of the outer electron (the method of Bates and Damgaard[5]). Only a finite number of terms are calculated in evaluating the sums $D(J')$ and $S(J')$ and the states near the ionization limit ($E\lesssim0$) and the continuum states ($E>0$) have been neglected. Assuming the Coulomb approximation to be valid otherwise, the errors due to the neglected terms in these sums have been estimated in the Appendix.

For the $nsnp\,^3P_1$ state of cadmium and mercury, the expressions for α_L are

$$\begin{aligned}\alpha_0&=-(1/18)[3D(2)+D(1)+4S(1)],\\ \alpha_2&=-(1/180)[-3D(2)+5D(1)+20S(1)],\end{aligned}\tag{25}$$

where $D(J')$ and $S(J')$ are defined by (24) with the substitution of P_1 for $P_{3/2}$. Calculated values of α_L for the $5s5p\,^3P_1$ state of Cd and the $6s6p\,^3P_1$ state of Hg are given in Table II.

IV. EXPERIMENTAL PROCEDURE

A. Rubidium and Cesium

The theory of interference effects in the resonance fluorescence from "crossing" excited atomic sublevels has been adequately treated in the literature. The scattered intensity is given by the Breit formula[6,7]

$$R(\mathbf{f},\mathbf{g})=C\sum_{\mu\mu'mm'}\frac{f_{\mu m}f_{m\mu'}g_{\mu'm'}g_{m'\mu}}{1+2\pi i\tau\nu(\mu,\mu')}.\tag{26}$$

Here $f_{\mu m}=(\mu|\mathbf{f}\cdot\mathbf{r}|m)$, etc., where $\mathbf{f}$ and $\mathbf{g}$ are the polarization vectors of the exciting light and the fluorescent light, respectively.

The eigenvectors of the excited and ground states are $|\mu\rangle$ and $|m\rangle$, respectively; τ is the radiative lifetime of the excited state, and $\nu(\mu,\mu')=(E_\mu-E_{\mu'})/h$ is the difference of excited-state term values. In (26) it is implicitly assumed that the line profile of the excited light is essentially flat over the hyperfine components of the atomic-resonance line. The Hamiltonian for the excited state of an atom with a hfs in an electric field is

$$\mathcal{H}=A\mathbf{I}\cdot\mathbf{J}+B\frac{3(\mathbf{I}\cdot\mathbf{J})^2+\frac{3}{2}\mathbf{I}\cdot\mathbf{J}-I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}+(\beta\mathcal{E}J_z)^2.\tag{27}$$

The first two terms represent the hfs, and the third term is the *m-dependent part only* of the Stark-shift Hamiltonian (18), with

$$\alpha_2=-\tfrac{2}{3}J(2J-1)\beta^2.\tag{28}$$

Expressions (26) and (27) were evaluated using a computer program. The hfs constants A and B, ob-

TABLE II. Experimental and theoretical Stark shifts for Cd and Hg in kc/(kV/cm)^2.

Nucleus	State	g_J[a]	α_0(calc)	α_2(calc)	α_2(expt)
Cd	$5\,^3P_1$	1.4998	8.5	1.3	1.70 ± 0.07
Hg	$6\,^3P_1$	1.479	5.5	0.92	1.57 ± 0.06

[a] R. Kohler and P. Thaddeus, Phys. Rev. **134**, A1204 (1964).

---

[5] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London **242**, 101 (1949).

[6] G. Breit, Rev. Mod. Phys. **5**, 91 (1933); P. A. Franken, Phys. Rev. **121**, 508 (1961); M. E. Rose and R. L. Carovillano, *ibid.* **122**, 1185 (1961). The expression (26) is often quoted in the literature with the sign of i in the denominator incorrect (see, for example, Franken).

[7] U. Fano, Rev. Mod. Phys. **29**, 74 (1957); T. R. Carver and R. B. Partridge, Am. J. Phys. **34**, 339 (1966).

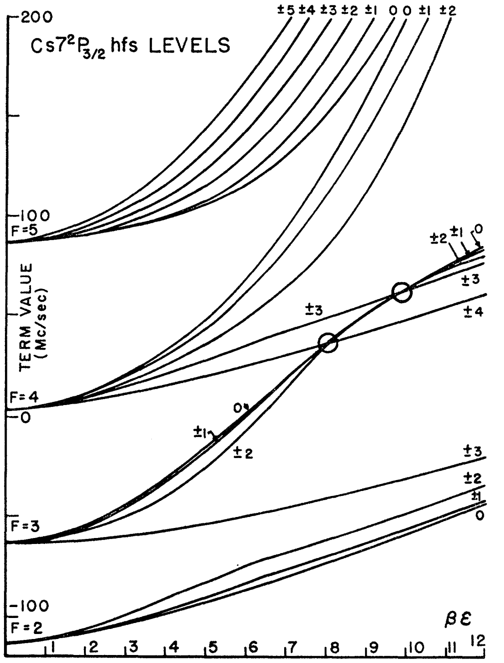


FIG. 1. Dependence of the Cs 7 $^2P_{3/2}$ hfs levels on the applied electric field ℰ. A common downward shift of all levels proportional to $ℰ^2$ has been suppressed.

tained from earlier experiments, I, J, g_J, the lifetime of the excited state τ, and the polarization vectors **f** and **g** formed the input to the program. The output included the term values, the level-crossing signal, and its derivative relative to the electric field. Figure 1 shows the term-value diagram for the 7 $^2P_{3/2}$ state of Cs (the term-value diagram for Rb^{85} 6 $^2P_{3/2}$ was given in a previous paper[8]). Two level crossings occur in passage from a region of low electric field to a region of high electric field. At each crossing there is a change in the angular distribution of the scattered resonance radiation. The tensor Stark shift is obtained from the value of the applied electric field at the crossing.

An atomic-beam apparatus was used in the Rb and Cs experiments. Figure 2 shows the experimental geometry and Fig. 3 gives details of the apparatus. Resonance radiation from a lamp is focused onto an atomic beam in a region near the center of a pair of electric-field plates. The scattered light is detected by a photomultiplier tube. The polarization of the incident and detected beams of radiation were chosen perpendicular to one another and to the electric field. To pass the 4202 Å line of Rb and the 4555 Å line of Cs and exclude the background light, a narrow-band interference filter, appropriate to the wavelength under consideration, was inserted in the output. Initial attempts to carry out the experiment in a glass cell with internal electrodes failed, since the alkali-filled cell would not support an electric field. The electric field was produced by two circular stainless-steel plates 2 in. in diam separated by $\frac{5}{8}$ in. by two quartz rods. In order to increase the signal-to-noise ratio, the applied voltage was modulated at 280 cps and phase-sensitive amplification of the signal was used. The modulation voltage was introduced between ground and the electrode near ground potential. The source of radiation was an Osram lamp. Due to the relatively large Stark shifts in alkalis, a very narrow source of radiation is not advantageous. It was necessary to operate the source at a relatively high frequency (20–40 kc/sec) in order to avoid any interference between the source and the electric-field modulation frequencies.

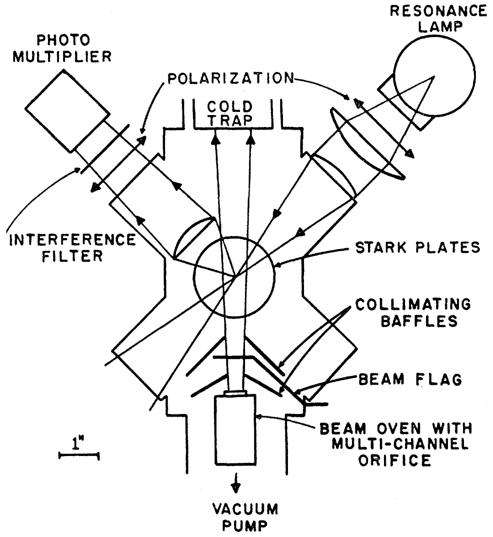
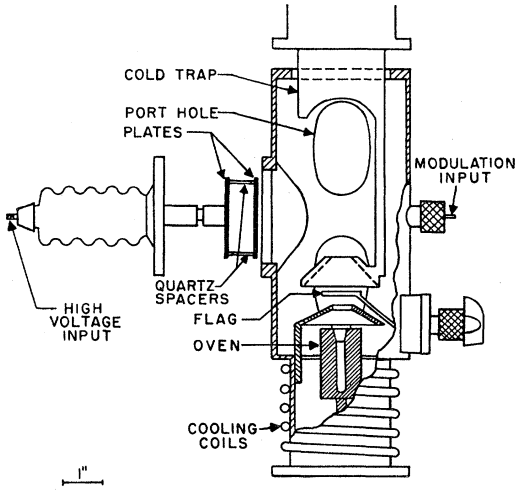


FIG. 2. Schematic diagram of the experimental geometry used in the alkali experiments. The view is in the vertical plane of the incident and detected light paths.



(THE ELECTRIC FIELD PLATES ASSEMBLY IS SHOWN OUTSIDE THE APPARATUS)

FIG. 3. View of the atomic beam apparatus in a vertical plane 90° to that shown in Fig. 2.

---

[8] A. Khadjavi, W. Happer, and A. Lurio, Phys. Rev. Letters **17**, 463 (1966).

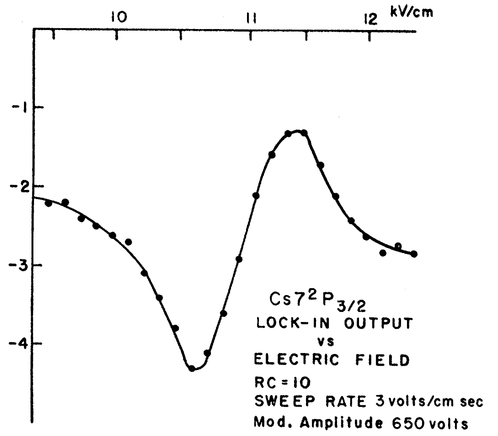


FIG. 4. An experimental curve of the derivative of the level crossing signal versus electric field in Cs.

The experimental derivative signal for Cs, corresponding to the first crossing of Fig. 1, is given in Fig. 4. In addition to broadening due to modulation of the electric field, this curve shows that the total scattered light is decreasing with the electric field, since $dR(\mathbf{f},\mathbf{g})/d\mathcal{E}$ is negative. This is due to scanning of the absorption line through the lamp profile. The experimental and calculated values of the Stark shift for Rb 6 $^2P_{3/2}$ and Cs 7 $^2P_{3/2}$ are given in Table I.

B. Cadmium and Mercury

The even isotopes of cadmium and mercury were chosen for the study of the Stark effect in the *nsnp* $^3P_1$ state. In these isotopes $I=0$ and the hfs vanishes. In the odd isotopes the hfs is present, but since the Stark shifts are relatively small, sublevels belonging to different values of the total angular momentum F cannot be made to cross by applying an electric field. Consequently, for either the odd or the even isotopes only at zero electric field can a level-crossing signal be observed (Hanle effect[9]). The tensor Stark shift can be obtained from the width of the zero-field crossing and the effective lifetime of the excited state. The effective lifetime, however, can be strongly influenced by coherence narrowing and atomic collisions.[10] Furthermore, any stray magnetic fields present change the shape of the crossing signal. In order to avoid such complications, parallel electric and magnetic fields were used to obtain a crossing at a finite electric field.

The Hamiltonian for the *nsnp* $^3P_1$ states of Cd and Hg in parallel electric and magnetic fields is given by

$$\mathcal{H}=g_J\mu_0 mH-\tfrac{1}{2}[\alpha_0+\alpha_2(3m^2-2)]\mathcal{E}^2. \tag{29}$$

The hfs terms are absent, since $I=0$ for the even isotopes. The energy levels corresponding to (29) are shown in Fig. 5. For a constant electric field, three level crossings occur as the magnetic field is swept. One is at zero magnetic field and the other two occur when

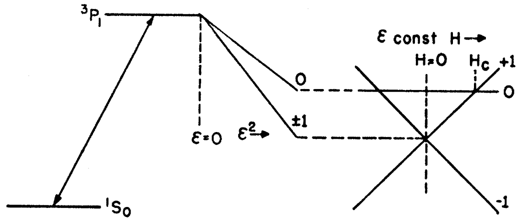


FIG. 5. Dependence of the $^3P_1$ sublevels of Cd and Hg on the applied electric and magnetic fields. On the left is shown the displacement of the magnetic sublevels in a uniform electric field $\mathcal{E}$ at zero magnetic field. On the right is shown the Zeeman effect at constant electric field $\mathcal{E}$.

$$g_J\mu_0H_c\mp\tfrac{3}{2}\alpha_2\mathcal{E}^2=0, \tag{30}$$

where the subscript c denotes the crossing field. For the case of parallel electric and magnetic fields along the z axis and arbitrary incident and observing directions perpendicular to the z axis we may write exactly the rate of scattering given by Eq. (26). If we define directions as shown in Fig. 6, then we find for $\gamma=0$

$$R(\alpha,\beta)=\tfrac{1}{2}\sin^2\alpha\sin^2\beta+\cos^2\alpha\cos^2\beta-\tfrac{1}{4}\sin 2\alpha\sin 2\beta \times\left[\frac{AH+B\mathcal{E}^2}{1+(AH+B\mathcal{E}^2)^2}+\frac{AH-B\mathcal{E}^2}{1+(AH-B\mathcal{E}^2)^2}\right] -\tfrac{1}{2}\sin^2\alpha\sin^2\beta\left(\frac{1}{1+(2AH)^2}\right), \tag{31}$$

where $AH=g_J\mu_0H\tau/\hbar$ and $B\mathcal{E}^2=-\frac{3}{2}\alpha_2\mathcal{E}^2\tau/\hbar$. The tensor Stark shift is obtained from (30);

$$\alpha_2=\tfrac{2}{3}g_J\mu_0(\pm H_c)/\mathcal{E}^2. \tag{32}$$

In this experiment a cell containing cadmium or mercury was subjected to a constant electric field and the scattered resonance radiation was measured as a function of the applied magnetic field. The incidence and detection directions and the direction of the applied fields were chosen to be mutually perpendicular. The polarizations of the incident and detected lights were

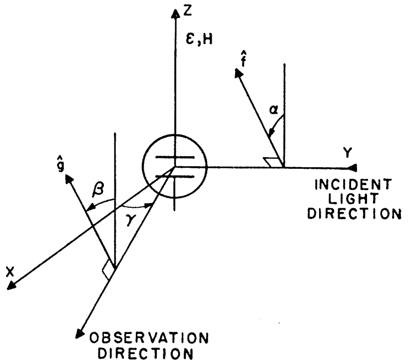


FIG. 6. Light propagation, polarization, and field directions in the Cd and Hg experiments.

---

[9] W. Hanle, Z. Physik 35, 346 (1926).

[10] J. Barrat, J. Phys. Radium 20, 633 (1959).

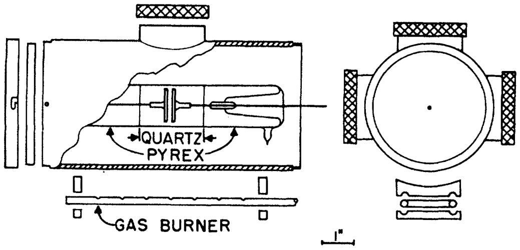


FIG. 7. Basic cell design for Cd and Hg experiments. The gas heating was required for the Cd experiment, while for the Hg experiment a side arm on the cell was maintained at ice temperature.

set at 45° to the field. This choice of polarizations maximizes the level-crossing signal amplitude. The basic cell design and the gas oven used to heat the cell (in case of cadmium) is given in Fig. 7. The central section of the cell was made from quartz to allow the passage of the 3262 Å line of cadmium and the 2537 Å line of mercury. Two 1-in.-diam stainless-steel disks, separated by 4 mm, formed internal electric-field plates. By using appropriate stops, the observed scattering region was limited to the area near the center of the plates at least two plate separations away from the plate edges. The error due to the fringing of the electric field is negligible under these conditions.

A cadmium Osram lamp and a mercury arc discharge tube were used as the source of radiation. A Schott UG-5 filter, UG-11 filter, or an interference filter was placed in the output before the photomultiplier tube. The range of electric-field intensities investigated was up to 50 kV/cm in Cd and 80 kV/cm in Hg. These correspond to crossing magnetic fields of approximately 3 and 8 G, respectively. At higher field values, the cadmium crossing signal could not be observed conveniently. This is due to the "anticrossing"[11] effects of transverse fields when the electric and magnetic fields are not exactly collinear. The order of magnitude of the angle θ between the electric and magnetic fields which can be tolerated may be obtained by equating the radiative width of the levels and the Zeeman energy associated with the transverse magnetic field $H_c \sin\theta$:

$$(1/\hbar)g_J\mu_0 H_c \sin\theta = 1/\tau. \tag{33}$$

Using the experimental value of the lifetime[12] $\tau(\text{Cd}) = 2.4\times10^{-6}$ sec and a typical value of 2.5 G for H_c, we obtain $\theta \approx 40'$.

A comparison of the theoretical curve from Eq. (31) and an experimental curve for Hg is shown in Figs. 8 and 9.

The experimental and theoretical values of the Stark shift for Cd $5s5p\ ^3P_1$ and Hg $6s6p\ ^3P_1$ states are given in Table II.

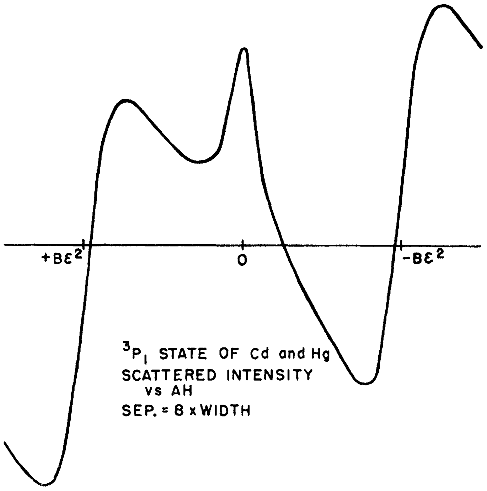


FIG. 8. Theoretical curve of scattered light signal versus H ($\mathcal{E}$=const) for $\gamma=0$ and $\alpha=-\beta=45°$.

V. DISCUSSION

We have demonstrated how the method of level-crossing spectroscopy may be applied to the measurement of the tensor polarizability of an excited atomic state. Although one cannot measure the scalar polarizability by the level-crossing technique, the same atomic-beam equipment in conjunction with a Fabry-Perot interferometer could also be used to measure the scalar and tensor Stark effect.

One may now ask what we can learn from these measurements beyond the obvious utility of the data to the interpretation of Stark broadening and shift of spectral line arising in plasmas, discharge tubes, stellar media, etc. Since the Stark effect is well understood theoretically, the data provide a test of approximate methods of calculating atomic wave functions or of calculating radial integrals. The only general method for calculating

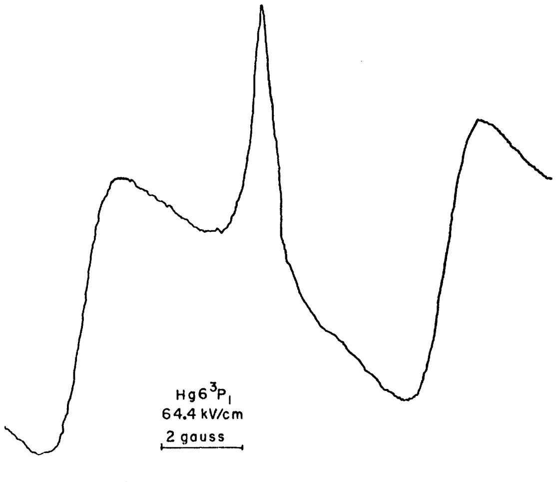


FIG. 9. Experimental curve of scattered light intensity versus magnetic field at a constant electric field of 64.4 kV/cm in the Hg $6s6p\ ^3P_1$ state.

---

[11] T. G. Eck, L. L. Foldy, and H. Wieder, Phys. Rev. Letters **10**, 239 (1963); H. Weider and T. G. Eck, Phys. Rev. **153**, 103 (1967).

[12] F. W. Byron, Jr., M. N. McDermott, and R. Novick, Phys. Rev. **134**, A615 (1964).

radial integrals is that of Bates and Damgaard, which is surprisingly good in view of its simplicity. As yet there are not enough calculations of the polarizabilities by the Sternheimer or Dalgarno[1] method. In view of the number of recent accurate measurements becoming available, we hope someone will be encouraged to carry out these calculations.

In special cases where only one nearby state produces the principal part of the polarizability of the state being investigated, one obtains directly the radial integral between these two states. In other cases where one measures the Stark effect in several members of a fine-structure multiplet we can obtain an estimate of the similarity of their radial wave function. For example, the Stark effect of the $6p\ {}^2P_{1/2,3/2}$ doublet of cesium[13] shows that their radial wave functions differ significantly. Another case of this kind which should be investigated is the Stark effect of the ${}^1P_1$ and ${}^3P_1$ states of the group-II elements.

Finally, these data and this technique may be useful in investigating the buildup of charge layers on transparent insulating surfaces by using level-crossing techniques to measure the electric fields.

APPENDIX

It is convenient to evaluate the error in

$$\Delta E(\pm\tfrac{3}{2}) = -\tfrac{1}{2}(\alpha_0+\alpha_2)\mathcal{E}^2 \tag{34}$$

and

$$\Delta E(\pm\tfrac{1}{2}) = -\tfrac{1}{2}(\alpha_0-\alpha_2)\mathcal{E}^2 \tag{35}$$

separately. We divide the sum in

$$\Delta E(0) = \sum_i \frac{|\langle 0|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2}{E(0)-E(i)} \tag{36}$$

into two parts: $\sum_{i'}+\sum_{i''}$, where $|i'\rangle$ are the states included in calculating the sums $D(J')$ and $S(J')$, and $|i''\rangle$ are those neglected. The sum $\sum_{i''}$ represents the error and satisfies the following inequality:

$$|\sum_{i''}| = \left|\sum_{i''} \frac{|\langle 0|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i''\rangle|^2}{E(0)-E(i'')}\right| < \frac{1}{\Delta}\sum_{i''} |\langle 0|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i''\rangle|^2. \tag{37}$$

Here Δ is the minimum value of $-[E(0)-E(i'')]$. Now using the identity $\sum_b |\langle a|O|b\rangle|^2 = \langle a|O^2|a\rangle$ we obtain

$$|\sum_{i''}| < \frac{e^2\mathcal{E}^2}{\Delta}\{\langle 0|z^2|0\rangle - \sum_{i'} |\langle 0|z|i'\rangle|^2\} \tag{38}$$

for $\boldsymbol{\varepsilon}$ in the z direction. The first term in (34) can be calculated by writing z^2 as

$$r^2\cos^2\theta = \tfrac{2}{3}r^2(4\pi/5)^{1/2}Y_{20} + \tfrac{1}{3}r^2(4\pi)^{1/2}Y_{00} \tag{39}$$

and using the Wigner-Eckart theorem. The result is

$$\begin{aligned} \langle \pm\tfrac{3}{2}|z^2|\pm\tfrac{3}{2}\rangle &= \langle r^2\rangle\tfrac{1}{3}(1-\tfrac{2}{5}),\\ \langle \pm\tfrac{1}{2}|z^2|\pm\tfrac{1}{2}\rangle &= \langle r^2\rangle\tfrac{1}{3}(1+\tfrac{2}{5}), \end{aligned} \tag{40}$$

where $\langle r^2\rangle = (nP_{3/2}|r^2|nP_{3/2})$ can be calculated from the hydrogenic formula.[5] The second term in (38) is identical to the expression for the Stark shifts except for the absence of the energy denominators and can be evaluated similarly. In calculating the Stark shifts in Rb and Cs, the first 16 terms of the sum (36) were taken, although only about eight were significant. The $\Delta E(\pm\tfrac{3}{2})$ error in rubidium turned out to be small but negative. Hence, no definite conclusion can be drawn concerning the α_2 error, except that it should be of the same order of magnitude (about 1% of the calculated value). In cesium both $\Delta E(m)$ errors are positive. Since the neglected states all have higher energies than the perturbed states, the neglected terms all add to $|\Delta E(m)|$. Thus the error in the differential shift, $\alpha_2 = E(\pm\tfrac{1}{2}) - E(\pm\tfrac{3}{2})$, is the larger of the two $\Delta E(m)$ errors. The upper bound of error due to the neglected states were calculated according to (38) and (40) for Cs. The results were about 1% for $\Delta E(m)$ and 4% for α_2.

---

[13] R. Marrus, D. McColm, and J. Yellin, Phys. Rev. **147**, 55 (1966).