

## CURRENT METHODS FOR THE STUDY OF THE STARK EFFECT IN ATOMS

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## I. INTRODUCTION

IN recent years there has been increasing interest in the experimental study of the Stark effect, connected with the direct effect of electric fields on the electron-density distributions in atoms. This interest has been stimulated by the development of methods for detecting small splittings of atomic levels (of the order of  $10^{-4}$   $\text{cm}^{-1}$  in the optical range, and of the order of  $10^{-7}$   $\text{cm}^{-1}$  in the radiofrequency range), the appearance of possibilities for observing the Stark effect in fields of optical frequency, the development of techniques for calculating atomic wave functions and oscillator strengths by means of computers, which makes it possible in a number of cases to calculate theoretical Stark constants and compare them with experimental values, and, finally, the widespread use of the Stark effect in spectroscopic methods for studying plasmas.\* There are very interesting possibilities for using lasers to observe and study the Stark effect in fields which are so large that the usual perturbation methods for calculating shifts and splittings of atomic levels become unsuitable.

As is well known, the direct classical method for studying the Stark effect is to observe the shifts of the centers of gravity of absorption and emission lines of atoms in an electric field. A detailed discussion of a number of ways of doing this, and of the results on the Stark effect in atoms so obtained, is given in a review article by Stark<sup>[1]</sup> and also in a monograph.<sup>[2]</sup> Under ordinary conditions in an experiment with an atomic vapor the Doppler width of an absorption or emission line is of the order of  $0.1 \text{ cm}^{-1}$ ; for a reliable observa-

tion of a shift of its center of gravity one needs fields of the order of  $10^5$ – $10^6$  V/cm, which are at the limit of practical possibility in an experimental apparatus. This difficulty has been overcome in work in which atomic beams propagated perpendicular to the direction of observation of the absorption or emission are used instead of saturated vapors (Sec. 1 of Chap. III). In this way the widths of the absorption and emission lines were decreased by one to three orders of magnitude, so that fields of  $10^3$ – $10^5$  V/cm could be used and shifts of the centers of gravity of lines by  $10^{-1}$ – $10^{-3}$   $\text{cm}^{-1}$  could be measured with adequate accuracy. For this purpose, besides the usual methods of high-resolution spectroscopy, an original method of comparing the Stark effect with the hyperfine splitting of the levels was used (Sec. 3 of Chap. III), and also a method of observing the double refraction which accompanies the splitting of lines in an electric field (Sec. 2 of Chap. III). These methods have made it possible to observe the Stark shifts of individual sublevels of the hyperfine structure in atoms.

All purely optical methods permit observation of the frequency shifts of transitions associated with two optical terms, the values of the shifts being determined by the shifts of the centers of gravity of both the upper and lower optical terms. New possibilities in regard to this have been opened up by the application to the study of the Stark effect of radiospectroscopic methods, in which one measures the frequency shifts of transitions between sublevels of the ground state of atoms (Sec. 4 of Chap. III). The resolving power of these methods exceeds that of the optical methods by at least three orders of magnitude.

Double radiooptical resonance has made it possible to use the high resolving power of radiospectroscopic methods to study the Stark effect in excited states of atoms (Sec. 5 of Chap. III). In this method the radiofre-

\*Questions connected with the use of the Stark effect in the spectroscopy of plasmas are treated in detail in a recent monograph: H. R. Griem, *Plasma Spectroscopy*, New York, 1964.

quency transitions between the sublevels of an excited state are observed by means of the change of polarization of the scattered resonance light. A number of purely technical difficulties of the method of double radiooptical resonance are eliminated in the methods of level crossing and of beats (Sec. 6 of Chap. III). The basis of the first of these is the change of the angular distribution of the intensity of resonance fluorescence when the levels are split by an amount larger than their natural width; in the method of beats one observes an anomalous increase of the depth of modulation of the resonance fluorescence when it coincides with the frequency of modulation of the exciting term which is split in the electric field.

The limit of the sensitivity of these methods, as also of the method of double radiooptical resonance, is fixed only by the natural widths of the levels.

The methods listed are for the observation of the Stark effect in constant electric fields. A theoretical treatment of the Stark effect in alternating fields indicates a number of distinctive features connected with the inertia of the polarizability of the atom.<sup>[3,4]</sup> These features appear if the frequency of the alternating field is comparable with the distances between the levels corresponding to allowed electric-dipole transitions. Otherwise the Stark shifts of energy levels in an alternating electric field are the same as the shifts in a constant field (cf. Sec. 2 of Chap. I).

In molecules some of the allowed electric-dipole transitions lie in the microwave range, and therefore the study of the Stark effect in this range is of prime interest. The first such study was made in<sup>[5]</sup>, and in particular this work revealed the theoretically predicted conversion of the quadratic Stark effect into a linear effect when the frequency of the field comes close to that of a molecular transition. In atoms the frequencies of electric-dipole transitions as a rule lie in the optical region, and therefore in atomic systems it is interesting in principle to study experimentally the Stark effect in fields of optical frequency.

A possibility for this has appeared in connection with the development of methods of optical orientation (Sec. 1 of Chap. IV) and with the construction of powerful (solid-state) lasers. A field amplitude  $\mathcal{E}_0 = 10^5 - 10^6$  V/cm in a light wave corresponds to a power density in the flux of radiation of about  $10^7 - 10^9$  W/cm<sup>2</sup>, which is easily attained in the unfocused radiation of present ruby and glass lasers containing neodymium and used with single-pulse operation.

In the study of the Stark effect in fields of optical frequency new resonance phenomena that are theoretically predicted (cf. Sec. 2 of Chap. II) can be observed; a resonance Stark effect can be observed in a much weaker field than the ordinary effect in a constant field. This opens up possibilities for studying atomic level shifts which are inaccessible to the constant-field techniques; such studies are especially furthered by the development of powerful lasers with tunable frequencies. Finally, the use of fields of optical frequency allows the field intensity to be raised without breakdown of the gas gap, up to values much larger than the breakdown values for constant fields. Therefore the use of alternating fields extends the experimental possibilities for studying the Stark effect, even if the frequency of the

field is far from the resonance value. Up to now only the very first researches on the shifts and splittings of terms in the electric fields of laser radiation have been carried out (Sec. 2 of Chap. IV). This work has in particular demonstrated the theoretically predicted dependence of the Stark effect on the frequency of the electric field.

It has further been found in<sup>[6,7]</sup> that at field intensities in laser radiation that are comparable with interatomic fields the shifts and broadening of excited atomic levels lead to an effective decrease of the ionization potentials of the atoms.<sup>[8]</sup>

In the present paper we deal with precision methods for observing the Stark effect in atoms (besides the classical spectroscopic method), and compare the experimental results obtained with these methods with the theoretical results. The review includes only papers not included in the previously mentioned review by Stark<sup>[1]</sup> and in the monograph<sup>[2]</sup>.

## II. THEORY OF THE STARK EFFECT

### 1. The Stark Effect in a Constant Electric Field.

Practically all effects of shift and splitting of atomic energy levels in electric fields much weaker than the intraatomic field can be treated with perturbation theory not dependent on the time. Let us consider an atom described by a time-independent Hamiltonian  $\hat{H}_0$  and placed in a uniform electric field  $\mathcal{E}$ . The stationary energy values  $E_n$  of such a system are determined by solving the equation

$$(\hat{H}_0 + \hat{V}) \Psi_n = E_n \Psi_n, \quad (1)$$

where  $\hat{V}$  is the operator for the interaction of the atom with the electric field, and in the electric-dipole approximation can be written in the form  $\hat{V} = -\hat{d}\mathcal{E}$ . Here  $\hat{d}$  is the operator for the dipole moment of the atom. In the perturbation-theory method it is assumed that  $\hat{V}$  is a small correction to the unperturbed operator  $\hat{H}_0$ , for which we know the eigenfunctions  $\psi_n^{(0)}$  and energy eigenvalues  $E_n^{(0)}$ , which are the exact solutions of the equation

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}. \quad (2)$$

The results of the calculation of the stationary energy values  $E_n$  depend on whether the original energy states  $E_n^{(0)}$  are degenerate or nondegenerate.<sup>[9]</sup>

In the case of a nondegenerate initial state, writing  $E_n$  in the form of a series

$$E_n = E_n^{(0)} + \Delta E_n^{(1)} + \Delta E_n^{(2)} + \Delta E_n^{(3)} + \dots, \quad (3)$$

we have

$$\Delta E_n^{(1)} = V_{nn} = \int \psi_n^{(0)*} \hat{V} \psi_n^{(0)} d\tau = -\mathcal{E} Z_{nn}, \quad (4)$$

$$\Delta E_n^{(2)} = \sum_m' \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} = e^2 \mathcal{E}^2 \sum_m' \frac{|Z_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}. \quad (5)$$

Here  $V_{mn}$  is the matrix element of the operator  $\hat{V}$  between the unperturbed states  $m$  and  $n$ , and  $Z_{mn}$  is the matrix element of the coordinate  $Z$  between the states  $m$  and  $n$  (it is assumed that the electric field is directed along the axis of quantization  $z$ );  $e$  is the charge of the electron, and the prime on the sum means that there is no term with  $m = n$ .

The quantity  $\Delta E_n^{(1)}$  is the first-order correction to the energy of the unperturbed level  $n$ ; it is equal to the average value of the energy of perturbation of the atom by the electric field for the state  $\Psi_n^{(0)}$ . This correction is proportional to the electric field strength  $\mathcal{E}$  and describes a linear effect of shifting of the levels in the electric field (linear Stark effect). Owing to the fact that we can have  $Z_{nn} \neq 0$  only if the state  $n$  has no definite parity, there is no linear Stark effect for non-degenerate atomic states. It occurs only for the hydrogen atom, in which there is an accidental degeneracy of terms with different values of the orbital quantum number  $l$ .

The quantity  $\Delta E_n^{(2)}$  is proportional to the square of the electric field strength, i.e., to  $\mathcal{E}^2$ , and describes the quadratic Stark effect. If  $n$  is the ground state of the atom, then  $E_n^{(0)} - E_m^{(0)} < 0$ , and the second-order correction to the energy of the ground state is always negative. Equations (4) and (5), which have been derived on the assumption that there is only a discrete spectrum of unperturbed eigenvalues  $E_n^{(0)}$ , can be easily extended to the case of a continuous spectrum.<sup>[9]</sup>

If the original state  $n$  is degenerate with multiplicity  $s$ , then the first-order correction  $\Delta E^{(1)}$  is determined by solving an equation of the  $s$ -th degree,

$$|V_{nn'} - \Delta E^{(1)}\delta_{nn'}| = 0, \quad (6)$$

where  $n$  and  $n'$  run through all of the  $s$  values which number the degenerate substates. Here  $\delta_{nn'} = 0$  if  $n \neq n'$ , and  $\delta_{nn'} = 1$  if  $n = n'$ . It is easy to see that if the perturbation matrix  $V_{nn'}$  does not connect the degenerate states (i.e., if  $V_{nn'} = 0$  when  $n \neq n'$ ), then the energy corrections  $\Delta E_n^{(1)}$  ( $n = 1, 2, \dots, s$ ) are given by the same formula as for the case of nondegenerate original states Eq. (4). If all  $V_{nn'} = 0$ —a most important case in the study of the Stark effect in atoms—there is no first order correction to the energy.

The second-order correction  $\Delta E_n^{(2)}$  is determined by solving an equation of degree  $s$

$$\left| \sum_m \frac{V_{nm}V_{mn'}}{E_n^{(0)} - E_m^{(0)}} - \Delta E_n^{(2)}\delta_{nn'} \right| = 0. \quad (7)$$

Equation (7) differs from (6) by the replacement of the direct matrix elements  $V_{nn'}$  by the compound matrix elements  $\sum_m V_{nm}V_{mn'}/[E_n^{(0)} - E_m^{(0)}]$ . If the second-order perturbation matrix does not connect the degenerate states by way of one or more states  $m$

[i.e., if  $\sum_m V_{nm}V_{mn'}/[E_n^{(0)} - E_m^{(0)}] = 0$  when  $n \neq n'$ ], then

(7) leads to the same formula for  $\Delta E_n^{(2)}$  as in the quadratic Stark effect for the case of nondegenerate states. If, on the other hand, the second-order perturbation matrix connects the degenerate states through a number of states  $m$ , the formula (5) for the quadratic Stark effect cannot be used [this case is realized when the Stark effect is observed with a magnetic field applied at an angle  $\theta \neq 0, 90^\circ$  with the direction of the electric field (cf. Secs. 5, 6 of Chap. III)].

For an atom containing many electrons the result of the calculation by Eq. (5) depends on the type of coupling between the orbital angular momentum  $L$  and the spin angular momentum  $S$ . Nevertheless, we can draw some general conclusions about the quadratic shift  $\Delta E_n^{(2)}$ . If we describe the state of the atom with quantum numbers

$nJm_J$  (here  $n$  is the principal quantum number,  $J$  is the total angular momentum of the electrons in the atom, and  $m_J$  is its projection in the direction of the electric field), there is a nonzero matrix element  $Z_{mn}$  in only the three following cases<sup>[10]</sup>:

$$\begin{aligned} \langle nJm_J | Z | n'J-1, m_J \rangle &= Z_1 (nJ | n'J-1) \sqrt{J^2 - m_J^2}, \\ \langle nJm_J | Z | n'Jm_J \rangle &= Z_2 (nJ | n'J) m_J, \\ \langle nJm_J | Z | n'J+1, m_J \rangle &= Z_3 (nJ | n'J+1) \sqrt{(J+1)^2 - m_J^2}. \end{aligned} \quad (8)$$

Here  $Z_1, Z_2, Z_3$  are functions of  $J, n, n'$  which do not depend on  $m_J$ . Using (8), we get the classical formula for the quadratic Stark effect, expressing the level shift in terms of  $m_J$ :

$$\Delta E_n^{(2)} = (A + Bm_J^2) \mathcal{E}^2, \quad (9)$$

where

$$\begin{aligned} A &= e^2 \sum_{n'} \left\{ \frac{Z_3^2 (nJ | n'J+1)}{E_{nJ} - E_{n'J+1}} (J+1)^2 + \frac{Z_1^2 (nJ | n'J-1)}{E_{nJ} - E_{n'J-1}} J^2 \right\}, \\ B &= e^2 \sum_{n'} \left\{ \frac{Z_2^2 (nJ | n'J)}{E_{nJ} - E_{n'J}} - \frac{Z_3^2 (nJ | n'J+1)}{E_{nJ} - E_{n'J+1}} - \frac{Z_1^2 (nJ | n'J-1)}{E_{nJ} - E_{n'J-1}} \right\}. \end{aligned} \quad (10)$$

The quadratic Stark shift of a level with a given value of  $m_J$  is determined by the sum of two terms: one of them,  $A \mathcal{E}^2$ , does not depend on  $m_J$  and is the same for all sublevels  $nJm_J$  of a given term; the other,  $B \mathcal{E}^2 m_J^2$ , is proportional to  $m_J^2$  and does not depend on the sign of  $m_J$ .

In experiments on the splitting of terms in an electric field one can measure only the value of the coefficient  $B$ , which determines the difference of the shifts of sublevels with different values of  $m_J$ . The study of the shifts of optical absorption lines allows us to measure both of the quantities  $A$  and  $B$ . In considering these experiments it is convenient to express the shift of a level  $n$  in frequency units, replacing  $Z_{mn}$  by the oscillator strength  $f_{mn}$  of the corresponding transition:

$$f_{mn} = \frac{8\pi^2 m}{h^3} (E_m - E_n) |Z_{mn}|^2. \quad (11)$$

Here  $m$  is the mass of the electron, and  $h$  is Planck's constant. Then the second-order displacement of the level  $n$ , as predicted by perturbation theory, expressed in reciprocal centimeters, is given by the formula

$$\Delta \nu_n = - \frac{e^2 \mathcal{E}^2}{8\pi^2 m h c} \sum_m \frac{f_{nm}}{(\nu_m - \nu_n)^2}. \quad (12)$$

If the energy  $E_m^{(0)}$  for one or more levels  $m$  is close to  $E_n^{(0)}$ , the second-order correction to the energy of the level  $n$  is large, we must not use the relation (5), and the shift of the energy level must be found by exact diagonalization of the matrix of the operator  $\hat{H}_0 + \hat{V}$ . In the case of two closely spaced nondegenerate levels  $E_1^{(0)}$  and  $E_2^{(0)}$  ( $E_1^{(0)} > E_2^{(0)}$ ) this leads to the following stationary values of the energy of the atom in the electric field<sup>[11]</sup>:

$$E_{1,2} = \pm \frac{1}{2} \sqrt{(E_1^{(0)} - E_2^{(0)})^2 + 4|V_{12}|^2}, \quad (13)$$

where the plus sign is for the level  $E_1$  and the minus for  $E_2$  [the origin from which the energy is measured is  $\frac{1}{2}(E_1^{(0)} + E_2^{(0)})$ ]. If  $2|V_{12}| \ll E_1^{(0)} - E_2^{(0)}$ , then the energy values  $E_1 = \frac{1}{2}(E_1^{(0)} - E_2^{(0)}) + |V_{12}|^2/(E_1^{(0)} - E_2^{(0)})$  and  $E_2 = \frac{1}{2}(E_2^{(0)} - E_1^{(0)}) + |V_{12}|^2/(E_2^{(0)} - E_1^{(0)})$  given by (13) are the same as the energies given by second-order perturbation theory for nondegenerate levels (quadratic Stark effect). For  $2|V_{12}| \gg E_1^{(0)} - E_2^{(0)}$  the values  $E_1 = |V_{12}|$  and  $E_2 = -|V_{12}|$  are the same as the energies given by first-order perturbation theory, Eq. (6) (linear Stark effect). Accordingly, in the case of two closely

spaced levels the quadratic Stark effect goes over into the linear effect when the size of the quadratic shift  $|V_{12}|/|E_1^{(0)} - E_2^{(0)}|$  becomes larger than the energy separation between the unperturbed levels  $E_1^{(0)}$  and  $E_2^{(0)}$ .

In order to follow the change of the spectrum of an atom under the action of an electric field in the case in question, we note that the normalized wave functions for the states with the energies  $E_1$  and  $E_2$  are of the forms<sup>[11]</sup>

$$\begin{aligned}\Psi_1 &= \Psi_1^{(0)} \cos \frac{\beta}{2} + \Psi_2^{(0)} \sin \frac{\beta}{2}, \\ \Psi_2 &= -\Psi_1^{(0)} \sin \frac{\beta}{2} + \Psi_2^{(0)} \cos \frac{\beta}{2},\end{aligned}\quad (14)$$

where  $\tan \beta = 2|V_{12}|/(E_1^{(0)} - E_2^{(0)})$ . Let us further suppose that there is a third (nondegenerate) state  $\Psi_3^{(0)}$  with energy  $E_3^{(0)}$  which is connected only with the state  $\Psi_1^{(0)}$  by an allowed transition. In the absence of the electric field  $\beta = 0$  and  $\Psi_1 = \Psi_1^{(0)}$ ,  $\Psi_2 = \Psi_2^{(0)}$ ; the spectrum consists of a single line with the frequency  $\omega_1^{(0)} = (E_3^{(0)} - E_1^{(0)})/\hbar$ . When the field is applied each of the states  $\Psi_1$  and  $\Psi_2$  becomes a mixture of the unperturbed states  $\Psi_1^{(0)}$  and  $\Psi_2^{(0)}$ . Accordingly there will be two lines in the spectrum, with frequencies  $\omega_1 = (E_3^{(0)} - E_1)/\hbar$  and  $\omega_2 = (E_3^{(0)} - E_2)/\hbar$  and intensity ratio  $I_2/I_1 = \tan^2 \beta/2$ . In a weak electric field, for which  $2|V_{12}| \ll E_1^{(0)} - E_2^{(0)}$ , the intensity of the line  $\omega_1$  is practically independent of the field strength and the intensity of the line  $\omega_2$  is proportional to  $|V_{12}|^2/(E_1^{(0)} - E_2^{(0)})^2$ , i.e., to the square of the field strength. In a strong electric field, when  $2|V_{12}| \gg E_1^{(0)} - E_2^{(0)}$ , the intensities of the lines  $\omega_1$  and  $\omega_2$  become equal. In a weak electric field the frequency  $\omega_1$  is close to  $\omega_1^{(0)}$ , and the frequency  $\omega_2$  is close to  $\omega_2^{(0)} = (E_3^{(0)} - E_2^{(0)})/\hbar$ . Therefore its appearance is regarded as a sign that the forbiddenness of the transition is removed under the influence of the constant electric field.<sup>[12,13]</sup>

## 2. The Stark Effect in Alternating Electric Fields.

The wave function of an atom in an alternating electric field must satisfy the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = (\hat{H}_0 + \hat{V}(t)) \Psi, \quad (15)$$

which does not have any stationary solutions. In the case of a harmonically varying electric field  $\mathcal{E} = \mathcal{E}_0 \cos \omega t$  it is convenient to look for the general integral of (15) in the form

$$\Psi = \sum_n a_n(t) \Psi_n^{(0)}, \quad (16)$$

where  $\Psi_n^{(0)}$  are the eigenfunctions of the time-independent operator  $\hat{H}_0$ . Substitution of (16) in (15) leads to the following system of linear differential equations for the coefficients  $a_n(t)$ :

$$i\hbar \frac{\partial}{\partial t} a_n = E_n^{(0)} a_n + \sum_m V_{nm}(\cos \omega t) a_m, \quad (17)$$

where  $V_{nm}$  is the matrix element of the operator  $\hat{V} = -\hat{d} \mathcal{E}_0$  between the unperturbed states  $m$  and  $n$ , and  $E_n^{(0)}$  are the energy eigenvalues, which are exact solutions of (2). According to Floquet's theorem the solutions of the system (17) can be represented in the form<sup>[12,13]</sup>

$$a_n(t) = e^{i\omega t} \sum_{k=-\infty}^{+\infty} A_k e^{-ik\omega t}, \quad (18)$$

where  $\omega_n$  and  $A_k$  are constant coefficients,  $k = 0, \pm 1, \pm 2, \pm 3, \dots$

These relations allow us to represent the changes of the absorption spectrum of an atom under the action of an alternating electric field. In the absence of the field of frequency  $\omega$  one finds in the absorption spectrum associated with the transition from the state  $n$  to a state  $i$  (which latter we for simplicity regard as unperturbed) a single resonance at the frequency  $\omega_1^{(0)} = \omega_i^{(0)} - \omega_n^{(0)}$  (we assume that the field of frequency  $\omega_1$  is weak enough so that its effect on the states  $n$  and  $i$  of the atom can be neglected). When the field of frequency  $\omega$  is applied the form of the coefficients  $a_n(t)$  shows that a series of resonances with frequencies  $\omega_1 = \omega_i^{(0)} - \omega_n \pm k\omega$  appears in the spectrum. For  $k = 0$  there is only one resonance at the frequency  $\omega_1 = \omega_i^{(0)} - \omega_n$ , corresponding to the absorption of one photon with frequency  $\omega_1$  differing from  $\omega_1^{(0)}$  by the amount  $\Delta\omega = \omega_n - \omega_n^{(0)}$  (we shall call this the one-photon resonance).

For  $k = 1$  there are two resonances with frequencies  $\omega_1' = \omega_i^{(0)} - \omega_n + \omega$  and  $\omega_1'' = \omega_i^{(0)} - \omega_n - \omega$ , which respectively correspond to the absorption of one photon with frequency  $\omega_1$  and the emission or absorption of a photon with frequency  $\omega$  (two-photon resonance). Corresponding to an arbitrary value of  $k$  there are two resonances with frequencies  $\omega_1' = \omega_i^{(0)} - \omega_n - k\omega$  and  $\omega_1'' = \omega_i^{(0)} - \omega_n + k\omega$ , associated with the absorption of a photon of frequency  $\omega_1$  and the simultaneous emission or absorption of  $k$  photons of frequency  $\omega$  [( $k+1$ )-photon resonance]. It is easy to see that all of the polyphoton resonances are shifted relative to their positions for the unperturbed level  $n$  by the same amount  $\Delta\omega = \omega_n - \omega_n^{(0)}$  as the one-photon resonance is shifted. This change of the absorption spectrum of an atom in an alternating electric field of frequency  $\omega$  can be regarded as the result of the shifting of the energy level  $n$  by the amount  $\Delta E_n = \hbar \cdot \Delta\omega = \hbar(\omega_n - \omega_n^{(0)})$  and the occurrence of polyphoton transitions from this shifted level under the action of two harmonic fields.<sup>[14]</sup>

It is possible to calculate the exact value of the shift  $\Delta E_n$  which the level  $n$  undergoes under the action of the electric field by solving Eq. (17) in only a limited number of cases.<sup>[15]</sup> Some general relations showing the nature of the change of  $\Delta E_n$  as compared with the shift of levels in a constant field can be obtained by regarding the combination (atom + electromagnetic field) as a single quantum system.<sup>[15]</sup> The energy of this system is composed of the energy of the field, the energy of the atom, and the energy of their interaction, whose operator  $\hat{V}$  does not depend on the time. If we regard  $\hat{V}$  as a perturbation, the corrections to the energy of the system which are caused by the interaction between the atom and the field can be calculated by the methods of time-independent perturbation theory.

Let us consider the simplest system, consisting of an atom with two nondegenerate energy states  $E_1^{(0)}$  and  $E_2^{(0)}$  ( $E_1^{(0)} > E_2^{(0)}$ ) and  $N$  photons of a definite type  $\lambda$  (the type is fixed by the frequency  $\omega$ , the polarization  $e_\lambda$ , and the wave vector  $k_\lambda$  of the electromagnetic field). The nature of the shift of the levels of the atom in such a system depends essentially on whether or not the field frequency coincides with the frequency  $(E_1^{(0)} - E_2^{(0)})/\hbar$  of the transition. If  $\omega = (E_1^{(0)} - E_2^{(0)})/\hbar$  the system (atom + field) is degenerate. For example, the energy

of the system (atom in state  $E_1^{(0)}$ ,  $N_\lambda$  photons in the field) does not change when the atom makes the transition to the state  $E_2^{(0)}$  and one photon is emitted. The first-order correction  $\Delta E_1^{(1)}$  to the energy of such degenerate states  $E_{N_\lambda, 1}^{(0)} = E_1^{(0)} + N_\lambda \cdot \hbar\omega$  and  $E_{N_\lambda+1, 2}^{(0)} = E_2^{(0)} + (N_\lambda + 1) \cdot \hbar\omega$  is given according to (6) by the solution of the equation

$$\begin{vmatrix} -\Delta E^{(1)} & V_{12} \\ V_{21} & -\Delta E^{(1)} \end{vmatrix} = 0, \quad (19)$$

where  $V_{12}$  is the matrix element of the interaction operator  $\hat{V}$  between the degenerate states  $E_{N_\lambda, 1}$  and  $E_{N_\lambda+1, 2}$ . In the electric-dipole approximation

for  $N_\lambda \gg 1$  the square of the matrix element,  $|V_{12}|^2$ , can be expressed in terms of the amplitude of the electromagnetic field  $\mathcal{E} = \text{Re } e_\lambda \mathcal{E}_0 e^{i(\mathbf{k}_\lambda \mathbf{r} - \omega t)}$  in the form<sup>[11, 15]</sup>

$$|V_{12}|^2 = \frac{\mathcal{E}_0^2 |e_\lambda d|_{12}^2}{4}. \quad (20)$$

It follows from (19) and (20) that for  $V_{12} \neq 0$  the degenerate state of the system (atom + field) splits into two states with energies displaced relative to the original energy by  $\Delta E_1^{(1)} = |V_{12}| = \mathcal{E}_0 |e_\lambda d|_{12}/2$  and  $\Delta E_2^{(1)} = -|V_{12}| = -\mathcal{E}_0 |e_\lambda d|_{12}/2$ .

The normalized wave functions of the system in these two states are<sup>[11, 16]</sup>

$$\left. \begin{aligned} \Psi_1 &= \frac{1}{\sqrt{2}} \{ \Psi_1^{(0)} \Phi_{N_\lambda} + \Psi_2^{(0)} \Phi_{N_\lambda+1} \}, \\ \Psi_2 &= \frac{1}{\sqrt{2}} \{ \Psi_2^{(0)} \Phi_{N_\lambda+1} - \Psi_1^{(0)} \Phi_{N_\lambda} \}. \end{aligned} \right\} \quad (21)$$

Here  $\Phi_{N_\lambda}$  and  $\Phi_{N_\lambda+1}$  are the wave functions of the states of the electromagnetic field with photon numbers  $N_\lambda$  and  $N_\lambda + 1$ . In accordance with the selection rules for polyphoton electric-dipole transitions in systems with a center of symmetry, transitions involving an even number of photons are allowed only between states with the same parity, and transitions involving an odd number of photons, between states with different parities.<sup>[14]</sup> If, for example, in the absence of the field of frequency  $\omega$  a one-photon transition is allowed from the state  $\Psi_1^{(0)}$  to some state  $\Psi_3^{(0)}$  with energy  $E_3^{(0)}$ , then it follows from (21) that when the field of frequency  $\omega$  is present instead of the one resonance  $\omega_1^{(0)} = (E_3^{(0)} - E_1^{(0)})/\hbar$  there will be two groups of resonances: one at the frequencies  $\omega_1 = (E_3^{(0)} - E_1^{(0)} - \Delta E_1^{(1)})/\hbar$ ,  $(E_3^{(0)} - E_1^{(0)} - \Delta E_1^{(1)} \pm 2\hbar\omega)/\hbar$ ,  $(E_3^{(0)} - E_1^{(0)} - \Delta E_1^{(1)} \pm 4\hbar\omega)/\hbar$ , ..., corre-

sponding to one-photon, three-photon, five-photon, and so on, resonances, with frequencies shifted relative to their position for the undisplaced levels by the amount  $\Delta\omega_1 + |V_{12}|/\hbar$ ; and the other group at frequencies  $\omega_1 = (E_3^{(0)} - E_1^{(0)} - \Delta E_2^{(1)})/\hbar$ ,  $(E_3^{(0)} - E_1^{(0)} - \Delta E_2^{(1)} \pm 2\hbar\omega)/\hbar$ ,  $(E_3^{(0)} - E_1^{(0)} - \Delta E_2^{(1)} \pm 4\hbar\omega)/\hbar$ , ..., corresponding to the same resonances except shifted by the amount  $\Delta\omega_1 = -|V_{12}|/\hbar$  (see the general scheme in Fig. 1). Here, as before, we are neglecting resonances associated with polyphoton processes of absorption and emission of photons of the weak field of frequency  $\omega_1$ , and also the displacement of the level  $E_3^{(0)}$  in the alternating electric field of frequency  $\omega$ . According to (21) the intensities are the same for resonances involving the same number of photons.

We note that the effect of a linearly polarized resonance electric field of amplitude  $\mathcal{E}_0$  on nondegenerate states  $E_1^{(0)}$  and  $E_2^{(0)}$  is analogous to the effect of a constant electric field of intensity  $\mathcal{E}_0/2$  on an atomic system with a two-fold degenerate state.

In the case of a nonresonance electric field ( $\hbar\omega \neq E_1^{(0)} - E_2^{(0)}$ ) there are no degenerate states of the system (atom + field), and the corrections to the energies of the unperturbed states  $E_{N_\lambda, 1}$  and  $E_{N_\lambda, 2}$  are given by (4) and (5). Since the states  $E_1^{(0)}$  and  $E_2^{(0)}$  of the atom are nondegenerate, as in the case of the constant electric field there is no first-order correction owing to the parity selection rule (there is no constant dipole moment in nondegenerate states of atoms), and the second-order corrections are of the form

$$\begin{aligned} \Delta E_{N_\lambda, 1}^{(2)} &= \frac{\mathcal{E}_0^2 |e_\lambda d|_{12}^2}{4} \left\{ \frac{1}{E_1^{(0)} - E_2^{(0)} - \hbar\omega} + \frac{1}{E_1^{(0)} - E_2^{(0)} + \hbar\omega} \right\}, \\ \Delta E_{N_\lambda, 2}^{(2)} &= \frac{\mathcal{E}_0^2 |e_\lambda d|_{12}^2}{4} \left\{ \frac{1}{E_2^{(0)} - E_1^{(0)} - \hbar\omega} + \frac{1}{E_2^{(0)} - E_1^{(0)} + \hbar\omega} \right\} = -\Delta E_{N_\lambda, 1}^{(2)}. \end{aligned} \quad (22)$$

The expressions (22) follow directly from (5) when we use the fact that there are two types of intermediate states, one with absorption of a photon  $\hbar\omega$  and one with emission of a photon. It can be seen from (22) that if the frequency  $\omega$  of the linearly polarized electric field approaches zero (more exactly, for  $\hbar\omega \ll E_1^{(0)} - E_2^{(0)}$ ) the quadratic shift of the levels is the same as in a constant field with the same energy density. The sign of the level shift in the alternating electric field is determined by the sign of the difference  $E_1^{(0)} - E_2^{(0)} - \hbar\omega$ . If  $\hbar\omega < E_1^{(0)} - E_2^{(0)}$ , the levels 1 and 2 are displaced so that the distance between them is increased (the effect of "repulsion of the levels"); in the case  $\hbar\omega > E_1^{(0)} - E_2^{(0)}$  the distance between the levels is decreased (an effect of "attraction of levels"). When  $\omega$  approaches the transition frequency  $(E_1^{(0)} - E_2^{(0)})/\hbar$  the shifts  $|\Delta E_{1,2}^{(2)}|$  given by (22) become indefinitely large and are not valid. As in the case of two closely spaced levels in a constant electric field, the correct result in this case can be obtained by exact diagonalization of the matrix of the operator  $\hat{H}_0 + \hat{V}$ .

This leads to the following stationary values of the energy of the system atom field<sup>[16]</sup>:

$$\begin{aligned} E_{N_\lambda, 1} &= \frac{(2N_\lambda + 1)\hbar\omega}{2} \pm \frac{1}{2} \sqrt{(E_1^{(0)} - E_2^{(0)} - \hbar\omega)^2 + 4|V_{12}|^2}, \\ E_{N_\lambda, 2} &= \frac{(2N_\lambda - 1)\hbar\omega}{2} \pm \frac{1}{2} \sqrt{(E_2^{(0)} - E_1^{(0)} + \hbar\omega)^2 + 4|V_{12}|^2} \end{aligned} \quad (23)$$

[as before, the origin for measuring energies is  $(E_1^{(0)} + E_2^{(0)})/2$ ]. In addition to the displacements, the expressions (23) also give the splitting of each atomic

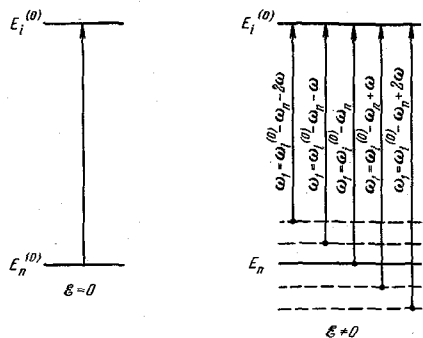


FIG. 1. Change of the absorption spectrum of an atom in an alternating electric field  $\mathcal{E} = \mathcal{E}_0 \cos \omega t$ .

level in a field of nonresonance frequency, unlike Eq. (22), which gives only the shifts of the atomic levels. For  $2|V_{12}| \gg E_1^{(0)} - E_2^{(0)} - \hbar\omega$  we get from (23) the energy values  $E_{N\lambda,1} \approx N\lambda \cdot \hbar\omega + E_1^{(0)} \pm |V_{12}|$ ,  $E_{N\lambda,2} \approx N\lambda \cdot \hbar\omega + E_2^{(0)} \pm |V_{12}|$ , which are the same as the energies given by (19) for the case of a resonance electric field. For  $2|V_{12}| \ll E_1^{(0)} - E_2^{(0)} - \hbar\omega$  the formulas (23) give, besides the two energy values  $E_{N\lambda,1}^{(1)} = E_{N\lambda,1}^{(0)} + |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)$  and  $E_{N\lambda,2}^{(1)} = E_{N\lambda,2}^{(0)} + |V_{12}|^2/(E_2^{(0)} - E_1^{(0)} + \hbar\omega)$ , which agree with the energies given by (22) in second-order perturbation theory (under the condition  $E_1^{(0)} - E_2^{(0)} - \hbar\omega \ll E_1^{(0)} - E_2^{(0)}$ ),\* two further energy values  $E_{N\lambda,1}^{(2)} = E_{N\lambda,1}^{(0)} - E_1^{(0)} \pm E_2^{(0)} + \hbar\omega - |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)$  and  $E_{N\lambda,2}^{(2)} = E_{N\lambda,2}^{(0)} + E_1^{(0)} - E_2^{(0)} - \hbar\omega - |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)$ .

These latter values correspond to resonances associated with shifts of the level  $E_1^{(0)}$  of the atom by the amount  $\Delta E_1^{(2)} = -[E_1^{(0)} - E_2^{(0)} - \hbar\omega + |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)]$  and of the level  $E_2^{(0)}$  by the amount  $\Delta E_2^{(2)} = E_1^{(0)} - E_2^{(0)} - \hbar\omega + |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)$ . In order to find out what sort of changes in the spectrum of the atom are produced by the additional level shifts  $\Delta E_1^{(2)}$  and  $\Delta E_2^{(2)}$ , we must turn to the wave functions of the states corresponding to the energies  $E_{N\lambda,1}^{(1,2)}$  and  $E_{N\lambda,2}^{(1,2)}$ . For simplicity, we confine ourselves to the normalized functions  $\Psi_{N\lambda,1}^{(1)}$  and  $\Psi_{N\lambda,1}^{(2)}$  which correspond to the energies  $E_{N\lambda,1}^{(1)}$  and  $E_{N\lambda,1}^{(2)}$  [12,16].

$$\begin{aligned} \Psi_{N\lambda,1}^{(1)} &= \Psi_1^{(0)} \Phi_{N\lambda} \cos \frac{\beta_\omega}{2} + \Psi_2^{(0)} \Phi_{N\lambda+1} \sin \frac{\beta_\omega}{2}, \\ \Psi_{N\lambda,1}^{(2)} &= -\Psi_1^{(0)} \Phi_{N\lambda} \sin \frac{\beta_\omega}{2} + \Psi_2^{(0)} \Phi_{N\lambda+1} \cos \frac{\beta_\omega}{2}, \end{aligned} \quad (24)$$

where  $\text{tg } \beta_\omega = 2|V_{12}|/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)$ . As in the case of two closely spaced levels in a constant electric field, we trace the change of the one-photon absorption spectrum of the atom from the state  $\Psi_1^{(0)}$  connected by an allowed electric-dipole transition with some third state  $\Psi_3^{(0)}$  (of energy  $E_3^{(0)}$ ), and we shall neglect the perturbation of this latter state by the alternating electric field of frequency  $\omega$ . In the absence of the alternating electric field of frequency  $\omega$  we have  $\beta_\omega = 0$  and  $\Psi_1^{(1)} = \Psi_1^{(0)}$ ,  $\Psi_1^{(2)} = \Psi_2^{(0)}$ ; the absorption spectrum consists of one line with frequency  $\omega_1 = \omega_1^{(0)} = (E_3^{(0)} - E_1^{(0)})/\hbar$ . When the field is applied the states  $\Psi_1^{(0)}$  and  $\Psi_2^{(0)}$  become mixed and two lines appear in the spectrum with frequencies  $\omega_1' = \omega_1^{(0)} - |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)\hbar$  and  $\omega_1'' = \omega_1^{(0)} + \hbar^{-1}[E_1^{(0)} - E_2^{(0)} - \hbar\omega + |V_{12}|^2/(E_1^{(0)} - E_2^{(0)} - \hbar\omega)]$ . The ratio of their intensities is  $I_2/I_1 = \text{tg}^2 \beta_\omega/2$ . In a weak electric field, for which  $2|V_{12}| \ll |E_1^{(0)} - E_2^{(0)} - \hbar\omega|$ , the intensity of the line  $\omega_1'$  is practically independent of the strength of the electric field, and that of the line  $\omega_1''$  is proportional to  $|V_{12}|^2/|E_1^{(0)} - E_2^{(0)} - \hbar\omega|$ , i.e., to the square of the field strength. In a strong electric field, for which  $2|V_{12}| \gg |E_1^{(0)} - E_2^{(0)} - \hbar\omega|$ , the lines  $\omega_1'$  and  $\omega_1''$  are of equal intensity. Accordingly, this pattern of change in the spectrum is entirely analogous to the effect of a constant field, but the criteria for "strong" and "weak"

fields now depends on the frequency of the field. For  $\hbar\omega \ll E_1^{(0)} - E_2^{(0)}$  the difference between the criteria disappears. In a weak electric field and for  $\hbar\omega \ll E_1^{(0)} - E_2^{(0)}$  the frequency  $\omega_1'$  is close to  $\omega_1^{(0)}$  and  $\omega_1''$  is close to the frequency  $\omega_2^{(0)} = (E_3^{(0)} - E_2^{(0)})/\hbar$ , and we can speak of the appearance of forbidden absorption lines under the influence of the alternating electric field.

The most important effect for experiments on the Stark effect in alternating fields is the quadratic effect in a nonresonance harmonic field. In this case, using the relation (5) for the quadratic shift of a nondegenerate level, we can generalize our result (22) for a two-level system to a system with many levels. The result for the shift of an atomic level  $n$  in a nonresonance field  $\mathcal{E} = \text{Re } e_\lambda \mathcal{E}_0 \cdot e^{i(\mathbf{k}_\lambda \mathbf{r} - \omega t)}$  is

$$\Delta E_n^{(2)} = \frac{e^2 \mathcal{E}_0^2}{4} \sum_m \left\{ \frac{|e_\lambda \mathbf{r}|_{mn}^2}{E_n^{(0)} - E_m^{(0)} - \hbar\omega} + \frac{|e_\lambda \mathbf{r}|_{mn}^2}{E_n^{(0)} - E_m^{(0)} + \hbar\omega} \right\}. \quad (25)$$

A rigorous derivation of this formula is given in [3,17], and in [3] the treatment takes into account the finite lifetimes of the atomic states. Comparing (25) and (5), we can easily see that the shift of a level  $n$  in a linearly polarized field with frequency  $\omega \rightarrow 0$  (more exactly, for  $\hbar\omega \ll |E_n^{(0)} - E_m^{(0)}|$ ) is the same as the quadratic shift in a constant field with the same energy density.

The shift  $\Delta E_n^{(2)}$  in an alternating field depends on the polarization  $e$  of the field. In the case of linear polarization, and in the dipole approximation, the distinguished direction is that of the electric vector  $e_\lambda$ . Choosing the  $z$  axis along  $e_\lambda$  and using (8), we get the same dependence of the quadratic Stark shift  $\Delta E_n^{(2)} = (A + Bm_J^2) \mathcal{E}_0$  on  $m_J$  as in the case of a constant electric field [Eq. (9)]. Consequently, in an alternating linearly polarized electric field levels that differ only in the sign of  $m_J$  are not separated. For the case of a circularly polarized alternating electric field, however, with  $e_\lambda = (e_x \pm ie_y)/2^{1/2}$ , the direction of  $\mathbf{k}_\lambda$ , the wave vector of the field, is distinguished. Choosing the  $z$  axis along  $\mathbf{k}_\lambda$  and using the values of the matrix elements in (25) [9]

$$\begin{aligned} \langle nJm_J | \left( \frac{e_x \pm ie_y}{\sqrt{2}} \right) | n'J-1, m_J \pm 1 \rangle &= \mp Z_1 \frac{1}{2} \sqrt{(J \pm m_J + 1)(J \pm m_J + 2)} \frac{e_x \pm ie_y}{\sqrt{2}}, \\ \langle nJm_J | \frac{e_x \pm ie_y}{\sqrt{2}} | n'Jm_J \pm 1 \rangle &= \frac{Z_2}{2} \sqrt{(J \mp m_J)(J \pm m_J + 1)} \frac{e_x \pm ie_y}{\sqrt{2}}, \\ \langle nJm_J | \frac{e_x \pm ie_y}{\sqrt{2}} | n'J+1, m_J \pm 1 \rangle &= \pm \frac{Z_3}{2} \sqrt{(J \mp m_J)(J \mp m_J - 1)} \frac{e_x \pm ie_y}{\sqrt{2}}, \end{aligned} \quad (26)$$

we get the following dependence of the shifts of the levels on  $m_J$ :

$$\Delta E_n^{(2)} = (A_1 \pm A_2 m_J + A_3 m_J^2) \mathcal{E}_0^2. \quad (27)$$

Here  $A_1$ ,  $A_2$ , and  $A_3$  are coefficients which do not depend on  $m_J$ ,\* and the sign in front of  $A_2$  depends on the direction of rotation of the electric vector of the field. It follows from (27) that in circularly polarized light the shift of the levels depends not only on the absolute value of  $m_J$  but also on its sign, and that in the general case

\*That there are no quadratic corrections with nonresonance denominators,  $|V_{12}|^2/(E_1^{(0)} - E_2^{(0)} + \hbar\omega)$ , is due to the fact that in the diagonalization of the operator  $\hat{H}_0 + \hat{V}$  only the resonance terms have been taken into account; this is legitimate for  $E_1^{(0)} - E_2^{(0)} - \hbar\omega \ll E_1^{(0)} - E_2^{(0)}$ .

\*We shall not write these coefficients explicitly because the expressions are cumbersome.

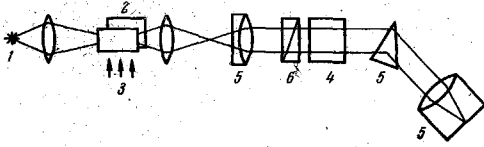


FIG. 2. Scheme of the experimental arrangement for observing the Stark effect in the D lines of Na atoms by the atomic-beam method. 1 – Sodium resonance-radiation lamp; 2 – plates between which the uniform electric field  $\mathcal{E}$  is produced; 3 – beam of Na atoms; 4 – Fabry-Perot etalon; 5 – spectrograph with registration on photographic plate; 6 – polarizing element.

levels that differ only in the sign of  $m_J$  are separated. We note that there will also be such a splitting in elliptically polarized light, which can be represented as a superposition of right and left circular components with different amplitudes. In this case the splitting of levels  $\pm m_J$  will be proportional to the difference of the intensities of the right and left circular components. Accordingly, an elliptically polarized alternating electric field one can observe a Stark splitting of states which are not split in a constant electric field (for example, states with  $J = 1/2$ ) (cf. Sec. 1 of Chap. IV).

### III. THE STUDY OF THE STARK EFFECT IN A CONSTANT ELECTRIC FIELD

1. **Observation of the Shifts of Centers of Gravity of Absorption Lines in Atomic Beams.** In the classical papers on the detection and study of the Stark effect the shifts of absorption lines in atomic vapors were observed.<sup>[1]</sup> Replacement of a saturated vapor by an atomic beam propagated perpendicular to the beam of light makes it possible to reduce the Doppler broadening of the absorption lines by one to three orders of magnitude, and accordingly makes it possible to observe shifts from one to three orders of magnitude smaller than with the saturated vapor. It was in this way that the Stark effect was first successfully studied for the various sublevels of the hyperfine structure of Na atoms.<sup>[18,19]</sup>

Figure 2 shows the scheme of the experimental arrangement for observing the Stark effect in the D lines of Na atoms. Radiation from a resonance sodium lamp passes through a region of uniform electric field, and in this region crosses a beam of Na atoms moving perpendicular to the light beam. The light then goes through a polarizing element, a Fabry-Perot etalon (distance between mirrors 30 mm, resolving power  $2 \times 10^6$ ), and a prism spectrograph, which serves to remove the non-resonance radiation from the sodium lamp, and is then registered on a photographic plate. The sodium lamp was operated in such a way that the intensity of the resonance D lines (transitions  $3^2S_{1/2} - 3^2P_{1/2}$ ,  $\lambda = 5896 \text{ \AA}$ , the  $D_1$  line, and  $3^2S_{1/2} - 3^2P_{3/2}$ ,  $\lambda = 5890 \text{ \AA}$ , the  $D_2$  line) would be as large as possible without self-reversal. Under these conditions the width of the lines was about  $0.1 \text{ \AA}$  and the radiant power in each was of the order of  $10^{-3} \text{ W}$ . The width of the absorption lines of the atomic beam was about  $0.003 \text{ \AA}$ , and over the range of shifts of their centers of gravity that occurred ( $0.03 \text{ \AA}$ ) the resonance lines had practically constant intensity. The apparatus permitted resolution of shifts of the absorption lines of the atomic beam of the order

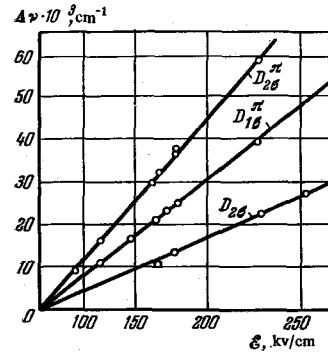


FIG. 3. Dependence of shifts of individual  $\pi$  and  $\sigma$  components of the absorption D lines of Na on the electric field intensity  $\mathcal{E}$ .

of  $10^{-3} \text{ \AA}$  when the electric field was applied. The accuracy of the measurements of shifts by this method was limited by the nonuniformity of illumination of the photographic plate by the radiation passing through the Fabry-Perot etalon when there was no electric field. Although with the large spectral width of the lines in the radiation from the lamp the rings in the intensity distribution should have overlapped to produce a uniform background, the background actually showed a structure.

In the absence of the beam of Na atoms each D line of the absorption of the beam of Na atoms is a doublet owing to the hyperfine splitting of the term  $3^2S_{1/2}$  by  $0.059 \text{ cm}^{-1}$  (the hyperfine splitting of the terms  $3^2P_{1/2}$  and  $3^2P_{3/2}$  is about an order of magnitude smaller and can be neglected). When the electric field was applied the absorption D lines were split into several components and were displaced toward the long-wave end of the spectrum. The displacement was clearly registered at  $\mathcal{E} = 60 \text{ kV/cm}$ , and at  $\mathcal{E} = 280 \text{ kV/cm}$  it was larger than the hyperfine splitting of each individual D line.

Figure 3 shows the experimental dependence of the shifts of individual  $\pi$  and  $\sigma$  components on the field strength  $\mathcal{E}$  ( $\pi$  components correspond to the electric vector  $\mathcal{E}_\parallel$  of the light wave parallel to  $\mathcal{E}$ , and  $\sigma$  components to  $\mathcal{E}_\perp$  perpendicular to  $\mathcal{E}$ ). These displacements are described by formulas  $\Delta\nu = \gamma \mathcal{E}^2$  [where  $\Delta\nu$  is in  $\text{cm}^{-1}$ ,  $\mathcal{E}$  in  $\text{kV/cm}$ , and  $\gamma$  in  $\text{cm}^{-1}/(\text{kV/cm})^2$ ], with the values

$$\left. \begin{aligned} \gamma_{2\sigma}^\pi &= \gamma (P_{3/2, \pm 1/2} - S_{1/2}) = -11.1 \cdot 10^{-7}, \\ \gamma_{1\sigma}^\pi &= \gamma (P_{1/2} - S_{1/2}) = -7.6 \cdot 10^{-7}, \\ \gamma_{2\sigma}^\sigma &= \gamma (P_{3/2, \pm 3/2} - S_{1/2}) = -4.1 \cdot 10^{-7}. \end{aligned} \right\} \quad (28)$$

A negative sign of  $\gamma$  means that the frequency of the corresponding transition decreases with increasing electric field. The measured values of the constants  $\gamma$  for the Stark shifts of the D lines of Na are in good agreement with the values calculated from (12) without inclusion of the spin-orbit interaction<sup>[20]</sup>:

$$\left. \begin{aligned} \gamma_{2\sigma}^\pi &= -10.6 \cdot 10^{-7}, \\ \gamma_{1\sigma}^\pi &= -7.4 \cdot 10^{-7}, \\ \gamma_{2\sigma}^\sigma &= -4.1 \cdot 10^{-7}. \end{aligned} \right\} \quad (29)$$

The shift of the ground  $3^2S_{1/2}$  state of Na is determined by the well known oscillator strength of the basic doublet,  $f \approx 1.0$ , and a calculation by Eq. (12) with  $f_{3S-3P} = 1.0$  gives for all sublevels of this state

$$\gamma_{3S} = -7.3 \cdot 10^{-7} \text{ cm}^{-1}/[\text{kV/cm}]^2. \quad (30)$$

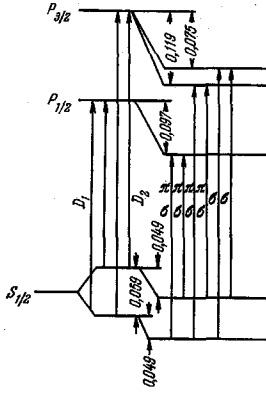


FIG. 4. Scheme of shifts of terms  $P_{3/2, 1/2}$  and  $S_{1/2}$  of the Na atom in an electric field  $\mathcal{E} = 250$  kV/cm. The shifts of the terms are indicated in  $\text{cm}^{-1}$ .

Using this value of  $\gamma_{3S}$ , we get for the sublevels of the excited  $P_{1/2}$  and  $P_{3/2}$  states

$$\left. \begin{aligned} \gamma(P_{3/2, \pm 1/2}) &= -18.4 \cdot 10^{-7}, \\ \gamma(P_{1/2, \pm 1/2}) &= -14.9 \cdot 10^{-7}, \\ \gamma(P_{3/2, \pm 3/2}) &= -11.4 \cdot 10^{-7}. \end{aligned} \right\} \quad (31)$$

Figure 4 shows the scheme of displacements and splittings of the  $D_1$  and  $D_2$  lines of Na in a field  $\mathcal{E} = 250$  kV/cm, and indicates the number and polarizations of the absorption components expected by the authors of [19]. It was not possible in [19] to detect the shift of the  $\pi$  component of the  $D_2$  line, and this was regarded as a contradiction with the theory. Actually there is no contradiction here. In order to decide what sorts of transitions ( $\pi$  or  $\sigma$ ) are possible from the state  $S_{1/2}$  to  $P_{1/2, 3/2}$  we must determine the selection rules, i.e., to calculate the nonvanishing matrix elements of the operator  $\hat{d}$  of the dipole moment of the atom:

$$d(S_{1/2} - P_{1/2, 3/2}) = \int \Psi^*(S_{1/2}) | \hat{d} | \Psi(P_{1/2, 3/2}) dq. \quad (32)$$

The sublevels of the ground state of Na correspond to values  $F = 1$  and  $F = 2$  of the total angular momentum of the atom, which result from addition and subtraction of the angular momenta  $J = 1/2$  of the electron shell and  $I = 3/2$  of the nucleus. When the hyperfine interaction is taken into account, the wave function of a sublevel of the ground state,

$$\Psi(S_{1/2}) = \Psi(IJFm_F)$$

can be written [10]

$$\Psi(IJFm_F) = \sum_{m_I m_J} (IJm_I m_J / IJFm_F) \Psi(Jm_J) \Psi(Im_I), \quad (33)$$

where  $\Psi(Jm_J)$  depends only on the quantum numbers of the electron shell and  $\Psi(Im_I)$  only on the quantum numbers of the nucleus, and  $(IJm_I m_J / IJFm_F)$  are Clebsch-Gordan coefficients in the notation of [10]. In the case of large Stark splittings (larger than the magnitude of the hyperfine splitting in the excited states), the wave functions of the sublevels of the excited states  $P_{1/2, 3/2}$  can be represented as products of wave functions for the electrons and the nucleus:

$$\Psi(P_{1/2, 3/2}) = \Psi(J'm_J) \Psi(I'm_I). \quad (34)$$

Then

$$d(S_{1/2} - P_{1/2, 3/2}) = \sum_{m_I m_J} (IJm_I m_J / IJFm_F) \cdot \delta(I, I') \cdot \delta(m_I, m_I') \times \int \Psi^*(Jm_J) | \hat{d} | \Psi(J'm_J) dq. \quad (35)$$

The delta functions:  $\delta(I, I') = \begin{cases} 0 & \text{for } I \neq I' \\ 1 & \text{for } I = I' \end{cases}$  and  $\delta(m_I, m_I') = \begin{cases} 0 & \text{for } m_I \neq m_I' \\ 1 & \text{for } m_I = m_I' \end{cases}$  have appeared because the operator

for the dipole moment of the atom does not act on the wave functions of the nucleus. From (35) there follow the selection rules  $\Delta m_J = 0$  for the  $\pi$  components and  $\Delta m_J = \pm 1$  for the  $\sigma$  components of the absorption lines, and these rules show that only  $\sigma$  transitions are possible between the states  $P_{3/2, \pm 3/2}$  and  $S_{1/2, \pm 1/2}$ . Accordingly, there is a good theoretical explanation for the absence of  $\pi$  transitions in the displaced  $D_2$  line.

The observation of the shifts of centers of gravity of absorption lines of atomic beams has also been used to measure the shift of the frequency of the  $5^1P_1 - 5^1S_0$  ( $\lambda = 4607 \text{ \AA}$ ) transition of strontium atoms in an electric field. [21]

**2. Study of the Stark Effect by Observation of Electric Double Refraction.** The method for studying the Stark effect which we shall now expound is based on the strong dependence of the index of refraction of a medium on the frequency of the light near the maximum of an absorption line. If an absorption line of the atoms is split into  $\pi$  and  $\sigma$  components in an electric field, the index of refraction of light passing through the medium is different for the  $\pi$  and  $\sigma$  components; that is, the medium becomes birefringent.

To make clear the features of the method let us consider an assembly of atoms with density  $N$ , and let the absorption line of each atom have width  $\Gamma$  and frequency  $\omega_0$  at the maximum. The index of refraction  $n(\omega)$  of the assembly at the frequency  $\omega$  is connected with its polarizability  $\bar{\alpha}(\omega)$  by the relation [11]

$$n(\omega) = 1 + 2\pi\bar{\alpha}(\omega). \quad (36)$$

The polarizability  $\bar{\alpha}(\omega) = \int \alpha(\omega) dN$  of the assembly for frequencies  $\omega$  close to  $\omega_0$  can be calculated from the polarizability  $\alpha(\omega)$  of an individual atom by using the well known formula [11]

$$\alpha(\omega) = \frac{|d_0|^2}{\hbar} \frac{1}{\omega_0 - \omega - i\Gamma/2}, \quad (37)$$

where  $d_0$  is the transition matrix element for the absorption line in question. In the case, most important for the experiments, of a Doppler distribution of frequencies  $\omega_0$  with central frequency  $\omega_1$ ,

$$dN = N(\omega_0) d\omega_0 = \frac{N d\omega_0}{\Delta \sqrt{\pi}} \exp\left[-\frac{(\omega_1 - \omega_0)^2}{\Delta^2}\right], \quad (38)$$

and the calculation of  $\bar{\alpha} = \int \alpha dN$  gives [22, 23]

$$n(\omega) = 1 + \frac{2\pi N |d_0|^2}{\hbar \Delta} \text{Re} Z(x, y). \quad (39)$$

Here

$$Z(x, y) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} d\xi \frac{\exp(-\xi^2)}{\xi - x - iy}$$

is the tabulated dispersion function of the plasma, [24]  $\Delta = \Delta\omega_D / 2(\ln 2)^{1/2}$ ,  $x = (\omega - \omega_1) / \Delta$ ,  $y = \Gamma / 2\Delta$ , and  $\omega_D$  is the width of the Doppler contour of the line. Usually



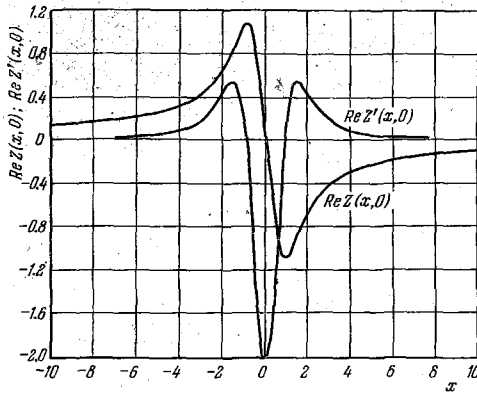


FIG. 5. Curves of the functions  $\text{Re } Z(x,y)$  and  $\text{Re } Z'(x,y)$  for  $y = 0$ .

$y \ll 1$  and  $\text{Re } Z(x, y) = \text{Re } Z(x, 0)$ . Figure 5 shows the dependences on  $x$  of the function  $\text{Re } Z(x, 0)$  and its derivative  $\text{Re} \{ (d/dx)Z(x, 0) \} = \text{Re } Z'(x, 0)$ . The function  $\text{Re } Z(x, 0)$  describes the dependence of the index of refraction on the frequency near the maximum of an absorption line with a Doppler shape. When the contour of the line deviates from the Doppler shape the form of  $n(\omega)$  is changed, but its general character is still the same; for  $\omega = \omega_1$  we have  $n(\omega_1) = 1$ , in the region where  $|\omega - \omega_1|$  is of the order of the half-width of the absorption line  $n(\omega)$  reaches its extreme values, and, finally, for large values of  $|\omega - \omega_1|$  we have  $n(\omega) \rightarrow 1$ .

If the absorption line is split into  $\pi$  and  $\sigma$  components in the electric field, then for all frequencies  $\omega$  we have  $n_\pi - n_\sigma \neq 0$ . Let us consider the cases of small and large splittings ( $\Delta\omega = \omega_1^\pi - \omega_1^\sigma \ll \Delta$  and  $\Delta\omega \gg \Delta$ ), for which there are two different ways of using the effect of electric double refraction for the study of the Stark effect. If  $\Delta\omega \ll \Delta$ , then the difference  $n_\pi(\omega) - n_\sigma(\omega)$  is for practical purposes described by the derivative  $\text{Re } Z'(x, y)$ , and for  $\Delta\omega \ll \omega - \omega_1^{\pi,\sigma}$  it is proportional to

the magnitude of the splitting  $\Delta\omega$  (Fig. 6, a). By measuring the difference  $n_\pi - n_\sigma$  for radiation frequencies near the maximum of the absorption line, one can find the value of the splitting  $\Delta\omega$ . In principle this method allows the detection of extremely small splittings, since a large enough value of  $n_\pi - n_\sigma$  to be detected can be obtained by increasing the atom density  $N$ . At the same time, the application of this method is not without difficulties, since to calculate the value of the splitting from the measured difference  $n_\pi - n_\sigma$  one must know the atom density  $N$ , and the experiment requires the use of a monochromatic source with a radiated line width much smaller than the width of the absorption line. Otherwise the measurement of an average difference  $n_\pi - n_\sigma$  can lead to large errors in the determination of  $\Delta\omega$ .

A determination of the Stark splitting of the D lines of sodium by this method has been made in [25]. The double refraction of saturated Na vapor in an electric field was studied by illumination with the light of a sodium resonance lamp, for which the width of the D lines was of the order of the width of the absorption lines ( $\sim 0.02 \text{ \AA}$ ). The density of the saturated vapor was determined from data on the magnetic rotation of the plane of polarization. The observed splitting of  $D_2^\pi$  and  $D_2^\sigma$ ,  $\Delta\lambda = 0.001 \text{ \AA}$  in a field  $\mathcal{E} = 30 \text{ kV/cm}$ , is about 4 or 5 times the value found later by the atomic-beam method (see Sec. 1 of this chapter), and cannot be regarded as reliable, since the width of the line in the radiation was too large and no account was taken of the hyperfine structure of the absorption line.

Let us go now to the case  $\Delta\omega \gg \Delta$ , in which under the action of the field two resolved dispersion line shapes of  $n(\omega)$  appear near the centers of gravity of the  $\pi$  and  $\sigma$  components of the split line. A measurement of the difference of the frequencies  $\omega$  which correspond to points  $n(\omega) = 1$ , made between the extrema of the dispersion line shapes, gives the value of the splitting  $\omega_1^\pi - \omega_1^\sigma$  directly. Furthermore there is no need to know the atom concentration  $N$ , and there are no very special requirements as to the line width of the radiation. This sort of method has been used in [26] in combination with the atomic-beam technique to study the Stark splitting of the sodium D lines. The scheme of the experiment is shown in principle in Fig. 7. Radiation from a lamp is directed into an electric condenser, through which a beam of Na atoms passes. After going through the condenser the light is focused on the input slit of the spectrograph 7. In front of the spectrograph is a Fabry-Perot etalon. The regions of frequency  $\omega$  near the  $\omega_1^\pi$  and  $\omega_1^\sigma$  of the split  $D_2$  line (see Fig. 4) are easily distinguished through the anomalous variation of the intensity of the light passing through crossed polarizing prisms. The constants so obtained for the shifts of the

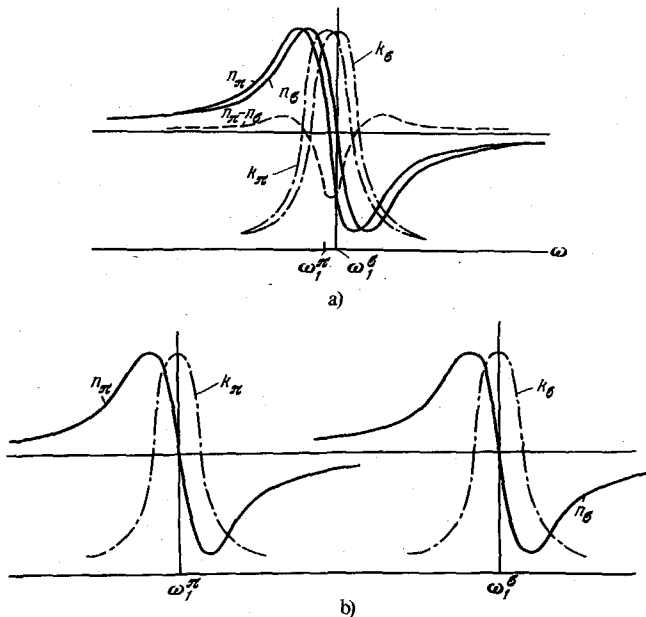


FIG. 6. Dependence of double refraction on frequency near a split absorption line: a) with small splitting; b) with large splitting.  $k_\pi$  and  $k_\sigma$  are the contours of the  $\pi$  and  $\sigma$  component absorption lines.

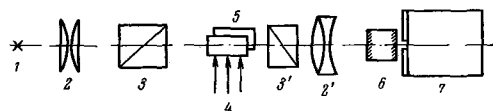


FIG. 7. Scheme of experiment to study the splitting of the sodium D lines by the method of electric double refraction. 1 - Sodium resonance-radiation lamp; 2, 2' - condensing lenses; 3 - crossed polarizing prisms; 4 - beam of Na atoms; 5 - electric condenser; 6 - Fabry-Perot etalon; 7 - spectrograph.

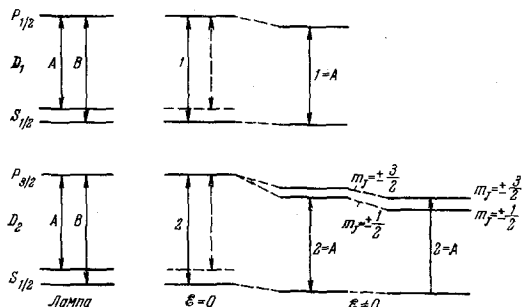


FIG. 8. Diagram of the energy levels of the main doublet of alkali atoms. The two lines A and B are present in the spectrum of the radiation from the lamp. In the absence of an electric field the absorption lines 1 and 2 coincide with the lines B in the radiation from the lamp. With the electric field lines 1 and 2 become resonant with the lines A.

components  $D_{20}^{\pi}$  and  $D_{20}^{\sigma}$  are

$$\gamma_{20}^{\pi} = 11 \cdot 10^{-7} \text{ and } \gamma_{20}^{\sigma} = 4,1 \cdot 10^{-7} \text{ cm}^{-1} / \text{kV/cm}^2 \quad (40)$$

and are in good agreement with the values obtained by the atomic-beam method (see Sec. 1 of this chapter).

3. Study of the Stark Effect by the Method of Comparison with Hyperfine Splitting. An original method for measuring the shifts of atomic absorption lines in an electric field by comparing their magnitudes with the hyperfine splitting of the ground state has been used in [27,28] to study the Stark effect in the  $D_1$  and  $D_2$  lines of the atoms  $\text{Cs}^{133}$  and  $\text{Rb}^{85}$ .

As a result of the hyperfine interaction the ground ( $S_{1/2}$ ) and excited ( $P_{1/2}$  and  $P_{3/2}$ ) states of these atoms are split into two components. Since, however, the splitting of the ground state is about an order of magnitude larger, in the absence of an electric field each of the absorption D lines of the vapor, and each of the D lines in the resonance radiation from a lamp containing the same alkali element, can be regarded as consisting of two components. Since the centers of corresponding components in the incident radiation and in the absorption coincide, one observes resonance absorption of the radiation from the lamp by the vapor. An electric field causes a parallel shift of the sublevels of the ground state and an unequal shift of the levels of the excited state. The result is that the centers of gravity of the components of the absorption lines and the lines of the radiation from the lamp no longer coincide and there is a decrease of the absorption. When, however, the difference of the shifts of the excited and ground states becomes equal to the hyperfine splitting, one of the components of the absorption line again comes into coincidence with a component of the line in the radiation from the lamp (Fig. 8) and a maximum of the absorption is observed. By measuring the electric field strength that corresponds to this and knowing the size of the

Table I. Polarizabilities of Cs and Rb (in units  $10^{-24} \text{ cm}^3$ )

|                   |                                  | $\alpha(6P_{1/2})^A$ | $\alpha(6P_{3/2, \pm 3/2})^A$ | $\alpha(6P_{3/2, \pm 1/2})^A$ |
|-------------------|----------------------------------|----------------------|-------------------------------|-------------------------------|
| $\text{Cs}^{133}$ | Measured                         | $187 \pm 29$         | $196 \pm 30$                  | $273 \pm 42$                  |
|                   | Calculated from the data of [31] | 192                  | 191                           | 246                           |
|                   | Calculated from the data of [32] | 187                  | 200                           | 273                           |
| $\text{Rb}^{85}$  | Measured                         | $112 \pm 17$         | $102 \pm 15$                  | $148 \pm 23$                  |
|                   | Calculated from the data of [31] | 116                  | 108                           | 151                           |
|                   |                                  | $\alpha(5P_{1/2})^A$ | $\alpha(5P_{3/2, \pm 3/2})^A$ | $\alpha(5P_{3/2, \pm 1/2})^A$ |

hyperfine splitting, and also the dependence of the shifts of the  $S_{1/2}$  and  $P_{1/2, 3/2}$  levels on  $\mathcal{E}$ , one can determine the constants for the Stark shifts of the  $D_1$  and  $D_2$  lines. It is obvious that for the practical realization of this method the widths of the component lines in the radiation from the resonance lamp must be smaller than the hyperfine splitting of the ground state.

The method used for the registration of the absorption in [27,28] was based on an atomic beam method of Rabi. [29] The experimental arrangement (Fig. 9) differs from Rabi's arrangement, in that the region of constant magnetic field with a radiofrequency alternating magnetic field is here replaced by a region of homogeneous electric field, which is illuminated with light from a resonance lamp containing the alkali element under investigation. As a result of absorption and subsequent spontaneous emission there is a change of the quantum number  $m_j$  of the atoms, and this is accompanied by a corresponding linear change of the intensity of the detected atomic beam. It can be seen from Fig. 8 that one should observe one resonance in the electric field for the  $D_1$  line, and two for the  $D_2$  line. This has been confirmed by the experiments made with  $\text{Cs}^{133}$  and  $\text{Rb}^{85}$ . The width of the resonances was equal to the width of the components of the emission line of the lamp, as measured by an independent method. A check was also made of the quadratic dependence of the shift of the absorption line on the electric field strength.

Table I shows values calculated from the data of these measurements for the polarizabilities  $\alpha$  of the  $\text{Cs}^{133}$  and  $\text{Rb}^{85}$  atoms, as defined by the relation  $\Delta E_n^{(2)} = -\alpha_n \mathcal{E}^2 / 2$  ( $\Delta E_n^{(2)}$  is the quadratic Stark effect corresponding to the level n). In these calculations the shift of the levels of the ground state was determined from the experimental values of the polarizabilities of Cs and Rb atoms in the ground  $S_{1/2}$  state. [30] Within the accuracy of the experiment the values found for  $\alpha$  agree with the values calculated theoretically with the spin-orbit interaction taken into account.

4. Observation of the Stark Effect by Radiospectroscopic Methods. For the successful study of the Stark effect in the ground states of atoms one uses radiospectroscopic methods for determining the absorption of radiofrequency radiation by an assembly of atoms. The resolving power of these methods is at least three orders of magnitude larger than that of optical methods.

The first such work with a radiooptical method was a study of the change produced by an electric field in the frequency of the hyperfine transition  $F = 4, m_F = 0 \rightleftharpoons F = 3, m_F = 0$  in the ground state of  $\text{Cs}^{133}$ . [33] The shift

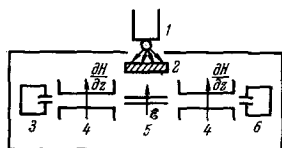


FIG. 9. Scheme of experiment for observing the Stark effect in Cs and Rb. 1 - Resonance lamp; 2 - filters; 3 - source of atomic beam; 4 - region of inhomogeneous magnetic field; 5 - region of constant homogeneous electric field; 6 - detector for atomic beam.

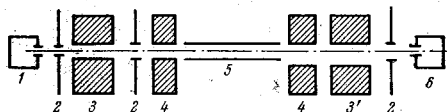


FIG. 10. Scheme of apparatus for measuring the shift of the frequency of the hyperfine transition ( $F = 4, m_F = 0 \leftrightarrow F = 3, m_F = 0$ ) in the ground state of  $\text{Cs}^{133}$  in an electric field. 1 — source of beam of Cs atoms; 2 — diaphragms; 3, 3' — magnets producing inhomogeneous magnetic fields with opposite gradients; 4 — resonator in which an alternating microwave field is produced with a frequency close to that of the hyperfine transition in Cs; 5 — plates between which the electric field is produced; 6 — detector for atomic beam.

of the frequency was measured by means of a Ramsey radiofrequency spectrograph (Fig. 10).<sup>[34-36]</sup> It uses two inhomogeneous magnetic fields 3 and 3' with the same direction and average value of the field strength but with gradients in opposite directions, and two microwave fields 4 before and after the condenser 5 in which the constant electric field  $\mathcal{E}$  is produced. The entire apparatus is adjusted so that only those cesium atoms of the beam reach the detector for which the quantum number  $m_J$  has had the same value throughout. The value of  $m_J$  is changed if the cesium atom absorbs a quantum from the microwave field, and for this to happen the frequency of this field must be the same as that of the hyperfine transition. If the frequencies of the two microwave fields are equal, the apparatus function for this arrangement is of the form shown in Fig. 11.<sup>[34]</sup> To measure the resonance frequency  $\nu_0$  of the transition one uses the main maximum of the resonance curve, whose width is determined by the quantity  $\alpha/L$ , where  $\alpha$  is the most probable speed of the particles in the beam and  $L$  is the distance between the microwave fields, measured along the beam. This distance is made large (of the order of a meter), and thus the spectral width of the resonance curve in this apparatus can be made about an order of magnitude smaller than that of the Rabi spectrograph. In the case considered, at the frequency  $\nu_0 = 9, 192, 631, 830 \pm 10$  cps of the hyperfine transition the width of the resonance curve was 120 cps, and the maximum shift of this frequency in the electric field  $\mathcal{E} \approx 170$  kV/cm was about 4000 cps. An important virtue of this method is that the width of the resonance curve is independent of the uniformity of the electric field along the atomic beam.<sup>[36]</sup> The value of the constant  $\gamma$  for the quadratic Stark shift of the frequency of

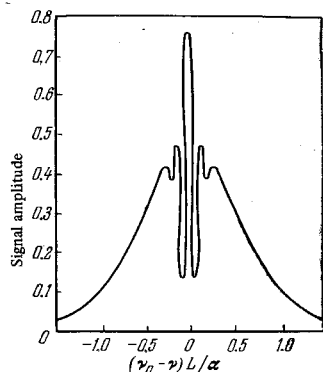


FIG. 11. Theoretical resonance curve of the Ramsey radiofrequency spectrograph.

the hyperfine transition in the  $6 S_{1/2}$  state of  $\text{Cs}^{133}$  found in<sup>[33]</sup> was

$$\gamma = (0.76 \pm 0.04) \cdot 10^{-10} \text{ cm}^{-1} / [\text{kV/cm}]^2.$$

The radiospectroscopic method has also been used successfully to measure the constant for the Stark shift of the frequency of the hyperfine transition ( $F = 2 \leftrightarrow F = 1$ ) in the ground state of  $\text{K}^{39}$ .<sup>[37]</sup> Here the value of  $\gamma$  was smaller than that for Cs by about a factor 30:

$$\gamma = (2.53 \pm 0.25) \cdot 10^{-12} \text{ cm}^{-1} / [\text{kV/cm}]^2.$$

In comparing these experimental results with the expected values of  $\gamma$  [see Eq. (12)] we must keep in mind that the difference of the shifts of the levels of the hyperfine structure is a tiny fraction, of the order  $\Delta\nu_{\text{hf}}/\Delta\nu_{\text{opt}} \approx 10^{-4}$ , of the shift of each of the hyperfine levels taken separately (here  $\Delta\nu_{\text{hf}}$  is the frequency of the hyperfine splitting of the ground state, and  $\Delta\nu_{\text{opt}}$  is the frequency of the optical transition from the ground state to the first excited state). Therefore in the calculations it is necessary to take into account the change of the wave functions of the hyperfine-structure states to terms of order  $\Delta\nu_{\text{hf}}/\Delta\nu_{\text{opt}}$ , which is a matter of considerable difficulty and has been done in<sup>[38]</sup>. On the basis of the results of that paper we have calculated theoretical values of the constant  $\gamma$  for the atoms  $\text{Cs}^{133}$  and  $\text{K}^{39}$  (given in Table IV). A comparison of the theoretical and experimental values of  $\gamma$  shows that the calculation by the method of<sup>[38]</sup> gives values of  $\gamma$  which are too high, and are beyond the limits of experimental error. In<sup>[39]</sup>, with a radiospectroscopic method involving modulation of the electric field and phase detection, extremely small differences could be detected in the shifts of the Zeeman sublevels of the ground state of Cs in an electric field. In a field  $\mathcal{E} = 10^5$  V/cm the difference of the shifts of these sublevels was of the order of 100 cps.\*

**5. Study of the Stark Effect by the Method of Double Radiooptical Resonance.** The method of double radio-optical resonance consists in detecting radiofrequency resonance transitions between the sublevels of an excited state which is split in an electric field by means of the change of polarization of resonance fluorescence. This method was first used to measure the Stark splitting of the  $6^3P_1$  term of mercury by observing the change of the degree of polarization of the resonance fluorescence transition  $6^3P_1 - 6^1S_0$ .<sup>[41]</sup> The idea of the method can be understood easily from an examination of the structure of the splitting of the terms  $6^3P_1$  and  $6^1S_0$  in an electric field (the nuclear spin is not taken into account here—this is permissible only for the even isotopes of mercury) (Fig. 12). Let us suppose that the mercury atoms are in a constant magnetic field and are excited to the level  $6^3P_1$  by polarized resonance radiation with a width of the spectral line which is much larger than the width of the absorption line. Then, if the electric vector of the exciting light is parallel to the magnetic field, only the  $\pi$  component is present in the fluorescence, and there is no scattering of the light in the direction of the magnetic field. The application of

\*The still weaker effect of Stark shift of the frequency of the hyperfine transition in the ground state of the hydrogen atom was detected in<sup>[40]</sup> by the method of comparing the frequencies generated by two hydrogen lasers, one of which was in the electric field.

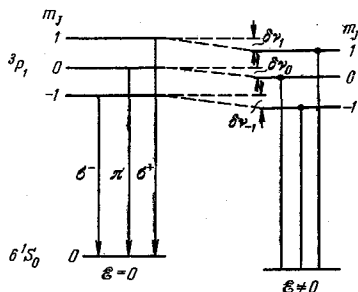
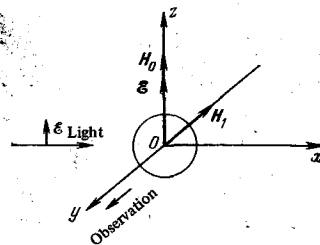


FIG. 12. Splitting of the term  $6^3P_1$  in a magnetic field and in an electric field.

a weak alternating magnetic field at the resonance frequency  $\omega = \Delta E/h$  (where  $\Delta E$  is the splitting of the levels of the term  $6^3P_1$ ) perpendicular to the constant field will induce transitions of atoms between the sublevels with  $m_J = 0$  and  $m_J = \pm 1$ . There will now be  $\pm\sigma$  components in the scattered radiation, and the maximum change of the polarization of the fluorescence corresponds to parametric resonance in the excited state. The action of a constant electric field leads to a shift of the frequency of the resonance transition, and a measurement of this shift gives the magnitude of the Stark shift. With this method one can observe splittings of the order of the natural width of the levels, since their displacement in the electric field does not depend on the Doppler change of frequency of the optical transitions of the atoms. It is easy to fix on the resonance frequency of the magnetic field, because far from resonance there is no  $\sigma$  component of the polarization, so that the change of intensity of the fluorescence with this polarization occurs against a null background.

This method has been used in<sup>[41]</sup> to measure the splittings of the term  $6^3P_1$  in the isotopes of mercury ( $Hg^{196}$ ,  $Hg^{198}$ ,  $Hg^{200}$ ,  $Hg^{202}$ ,  $Hg^{204}$ ,  $Hg^{199}$ , and  $Hg^{201}$ ). A cell containing saturated vapor of the mercury isotope to be studied was placed in parallel constant electric and magnetic fields and was illuminated with linearly polarized resonance light ( $\lambda = 2537 \text{ \AA}$ ) with the electric vector

FIG. 13. Orientations of the fields in the method of double radio-optical resonance.



parallel to  $H_0$  and  $\mathcal{E}$  (Fig. 13). The experiment measured the change of the degree of polarization of the radiation scattered in the direction of the axis Oy on passage through the resonance associated with action of a radio-frequency alternating magnetic field  $H_1$  directed perpendicular to the axis Oz. For this purpose one can either fix the field  $H_0$  and vary the frequency  $\omega$  of the radiofrequency field, or fix  $\omega$  and change the magnitude of  $H_0$ . At high frequencies  $\omega$  and large intensities of the radiofrequency field  $H_1$  the second method is more convenient in practice, and was used for all the measurements.

With the method of double radiooptical resonance one can measure only the difference of the shifts of a pair of corresponding levels. For the even isotopes of mercury this is determined by the size of the coefficient B in Eq. (9):  $h\Delta\nu = |\Delta E_{m_J=\pm 1}^{(2)} - \Delta E_{m_J=0}^{(2)}| = B\mathcal{E}^2$ . The hyperfine structure of the term  $6^3P_1$  must be taken into account in the calculation of the amount the resonances are shifted for odd isotopes. The treatment shows that the shift of the term  $Fm_F$  is given by an expression analogous to (9),  $\Delta E_{Fm_F}^{(2)} = (A' + B'|m_F|^2)E^2$ , where  $A'$  and  $B'$  do not depend on  $m_F$ . Table II shows the results of the calculations of values of  $B'$  and the splittings  $h \cdot \Delta\nu/\mathcal{E}^2$  expressed in terms of the coefficient B for the even isotopes of mercury. A theoretical calculation of the value of the coefficient B (and consequently of the shifts of the resonances) cannot be made at present because there are no theoretical values of the oscillator strengths. A value of the displacement of the sublevels

Table II. Splitting of the Term  $6^3P_1$  of Mercury in an Electric Field

| Hg            | I     | F     | Resonance transition                                | $B'$     | $\frac{h \cdot \Delta\nu}{\mathcal{E}^2}$ |
|---------------|-------|-------|---|----------|---|
| Even isotopes | 0     | 1     | $m_J=0 \rightarrow m_J=\pm 1$                       | B        | B   |
| $Hg^{199}$    | $1/2$ | $1/2$ | $m_F=\frac{1}{2} \rightarrow m_F=-\frac{1}{2}$      | 0        | 0   |
|               |       | $3/2$ | $m_F=\frac{1}{2} \rightarrow m_F=-\frac{1}{2}$      | $B/3$    | 0   |
|               |       | $3/2$ | $m_F=\pm\frac{3}{2} \rightarrow m_F=\pm\frac{1}{2}$ | $B/3$    | $2B/3 (+)$                                |
| $Hg^{201}$    | $3/2$ | $1/2$ | $m_F=\frac{1}{2} \rightarrow m_F=-\frac{1}{2}$      | $B/6$    | 0   |
|               |       | $3/2$ | $m_F=\frac{1}{2} \rightarrow m_F=-\frac{1}{2}$      | $-4B/15$ | 0   |
|               |       | $3/2$ | $m_F=\pm\frac{3}{2} \rightarrow m_F=\pm\frac{1}{2}$ | $-4B/15$ | $-8B/15 (+)$                              |
|               |       | $5/2$ | $m_F=\frac{1}{2} \rightarrow m_F=-\frac{1}{2}$      | $B/10$   | 0   |
|               |       | $5/2$ | $m_F=\pm\frac{3}{2} \rightarrow m_F=\pm\frac{1}{2}$ | $B/10$   | $B/5 (+)$                                 |
|               |       | $5/2$ | $m_F=\pm\frac{5}{2} \rightarrow m_F=\pm\frac{3}{2}$ | $B/10$   | $2B/5 (+)$                                |

Table III. Shift of Sublevels of the Term  $6^3P_1$  in an Electric Field

| Perturbing term | Lifetime of upper state associated with transition to perturbing term from term $6^3P_1$ , sec | Shift of sublevel of term $6^3P_1$ with $m_j = 0$ in field 100 kV/cm, * MHz | Shift of sublevel of term $6^3P_1$ with $m_j = \pm 1$ in field 100 kV/cm, MHz |
|-----------------|--|---|---|
| $6^1S_0$        | $1.2 \cdot 10^{-7}$  | +1.0  | 0   |
| $7^3S_1$        | $1.12 \cdot 10^{-8}$   | 0   | -19.3   |
| $6^3D_1$        | $3 \cdot 10^{-8}$  | 0   | -1.8  |
| $6^3D_2$        | $3 \cdot 10^{-8}$  | -4.4  | -3.3  |

\*The plus sign corresponds to displacement toward higher energy, and the minus sign to displacement toward lower energy of the level.

has been calculated for even isotopes in<sup>[41]</sup> on the basis of experimental data on the probabilities of transitions from the state  $6^3P_1$  to the four states located closest to it,  $6^1S_0$ ,  $7^3S_1$ ,  $6^3D_1$ , and  $6^3D_2$ , which make the main contribution to the splitting of the term  $6^3P_1$ . Table III shows the expected shifts of the states  $m_j = 0$  and  $m_j = \pm 1$  of the term  $6^3P_1$  of even isotopes of mercury in a field  $\mathcal{E} = 100$  kV/cm, owing to the perturbation by these four states. It can be seen from this table that the splitting of the term  $6^3P_1$  in this field should be about 21 MHz.

The experimentally measured value of the splitting  $\Delta\nu = B\mathcal{E}^2/h = 21.3 \pm 0.5$  MHz agrees with the expected value within the accuracy of the measurements. It was experimentally verified that the splitting of the term  $6^3P_1$  is proportional to the square of the field strength up to  $\mathcal{E} = 70$  kV/cm. The ratios of slopes of plots of the relations  $\Delta\nu = f(\mathcal{E}^2)$  for the odd isotopes  $Hg^{199}$  and  $Hg^{201}$  correspond to the data given in Table II; that is, they are as predicted theoretically.

**6. Observation of the Stark Effect by Level-crossing and Beat Methods.** In level-crossing and beat methods one observes the changes of the angular distribution and polarization of the resonance fluorescence of atoms when there is equality either of the energies of different sublevels of excited states (level-crossing effect) or of the frequency of modulation of the exciting resonance light and the frequency corresponding to the splitting of excited sublevels (beat effect). A complete theory of these methods has been given in<sup>[42-44]</sup>, and we here confine ourselves to a qualitative treatment of the example of a three-level system (Fig. 14).

Resonance scattering of light by such a system can be regarded as the result of the radiation from two oscillators (with natural frequencies  $\omega_{10}$  and  $\omega_{20}$  and dampings  $\Gamma_1/2$  and  $\Gamma_2/2$ ) which execute forced oscillations under the action of exciting resonance radiation. The latter is a sum of harmonics, and each oscillator is intensely pumped only by those harmonics which lie in a spectral range of the order  $\Gamma$  around its resonance frequency.

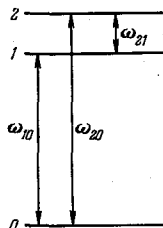


FIG. 14. Three-level scheme for illustrating the interference effects in resonance fluorescence.

Let us first consider the scattering of light of constant frequency. If  $\omega_{21} \gg (\Gamma_1 + \Gamma_2)/2$  the oscillators are excited by different harmonics of the incident light, and these harmonics have independent phases. Therefore the intensity of the scattered light is equal to the sum of the intensities of the radiations of the two oscillators considered separately. If  $\omega_{21} = 0$ , both oscillators are excited by the same harmonics, so that it is not the intensities, but the amplitudes, which add in the scattered light. If  $\omega_{21}$  is of the order of  $(\Gamma_1 + \Gamma_2)/2$ , some of the exciting harmonics will be common to the two oscillators, and for these harmonics the amplitudes add, while for the others the intensities add in the scattered light. Accordingly, as  $\omega_{21}$  is varied the intensity of the scattered light must show a resonance behavior near  $\omega_{21} = 0$ , the width of the resonance being of the order of the natural widths  $\Gamma_{1,2}$ . If the natural widths of the excited sublevels are known, the amount of splitting of the levels 1 and 2 in the electric field can be measured from the change of intensity of the resonance fluorescence.

If the intensity of the exciting light is modulated harmonically at the frequency  $\Omega$ , the phases of its harmonics  $\omega$  and  $\omega' = \omega \pm \Omega$  are correlated.<sup>[42]</sup> Therefore the vibrations of two oscillators will interfere not only when they are excited by the same harmonic, but also when they are excited by harmonics that differ in frequency by the amount  $\Omega$ . This interference of the vibrations of the oscillators is manifested by the appearance of beats of the intensity of the resonance fluorescence at the frequency  $\Omega$ ; the amplitude of the beats depends on the ratio of the frequencies  $\Omega$  and  $\omega_{21}$  and is a maximum for  $\Omega = \omega_{21}$ . The cause of this is the following. The first oscillator is excited by the harmonics in a band of frequencies of order  $\Gamma_1$  around  $\omega_{10}$ . The harmonics correlated with these are in a band shifted by the frequency  $\Omega$ . The interference, and consequently the amplitude of the beats, will be the larger, the greater the extent to which the shifted band overlaps with the absorption band of the second oscillator. As in the method of the intersection of levels, if the natural width of the excited sublevels is known, the frequency by which the levels of the excited state are split can be determined by observing the change of depth of the modulation of the resonance fluorescent light as the frequency of the modulation of the exciting light is varied.

The only limit on the sensitivity of these two methods is the natural width of the excited atomic levels. These methods are related to the method of double radiooptical resonance, but have the advantage over it that in them the broadening and splitting of the levels under the ac-

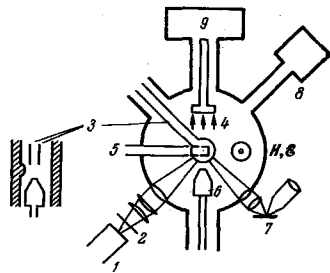


FIG. 15. Scheme of experimental apparatus for the observation of the Stark effect in lithium by the level-crossing method. 1 – Resonance-radiation lamp; 2 – circular polarizer; 3 – electric condenser; 4 – beam of lithium atoms; 5 – device for measuring the magnetic field strength by the proton-resonance method; 6 – furnace; 7 – system for detecting intensity of resonance fluorescence; 8 – vacuum system; 9 – trap cooled with liquid nitrogen.

tion of a powerful radiofrequency magnetic field is avoided. Besides this, the level-crossing method does not require the insertion into the apparatus of elements for producing a powerful radiofrequency field, and owing to this it is possible to increase the uniformity of the electric field. The level-crossing method can be used for the study of the Stark effect in short-lived excited states, where the use of the method of double radio-optical resonance or the beat method is difficult because of the impossibility of producing a sufficiently powerful high-frequency field.

The level-crossing method was first applied to the study of the Stark effect of the  $3^2P$  term of the  $\text{Li}^7$  atom.<sup>[45]</sup> A schematic diagram of the experiment is shown in Fig. 15. The lithium atoms in an atomic beam are excited by resonance radiation (transition  $3P - 2S$ ) and are in a magnetic field. At a field strength of 915 G the sublevels  $^2P_{3/2}$  ( $m_J = -3/2$ ) and  $^2P_{1/2}$  ( $m_J = 1/2$ ) of the term  $3P$  cross, (Fig. 16),<sup>[46]</sup> and this is registered as a resonance behavior of the intensity of the fluorescence at angle  $90^\circ$  with the direction of the exciting radiation. When a constant electric field  $\mathcal{E}$  is applied (parallel to the magnetic field  $H$ ) the sublevels  $^2P_{3/2}$  and  $^2P_{1/2}$  are unequally shifted and cross at a different value of the magnetic field. In the case of the  $3^2P$  term of  $\text{Li}^7$  there are two possible crossings: of the levels with  $m_J = -3/2$  and  $m_J = 1/2$ , and of the levels with  $m_J = -3/2$  and  $m_J = -1/2$ , but the geometry of the observation and the polarizations of the exciting and scattered radiations were chosen in<sup>[45]</sup> so that only the crossing of the levels with  $m_J = -3/2$  and  $m_J = 1/2$  was registered.

Figure 17 shows the relation found experimentally between the relative shift of the levels and the square of

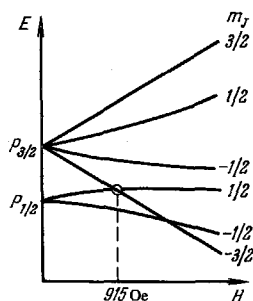


FIG. 16. Scheme of splitting of the  $3P$  term of lithium in a magnetic field ( $^2P_{3/2}$ ,  $^2P_{1/2}$ ).

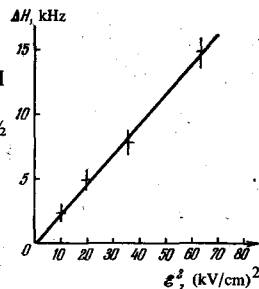


FIG. 17. Dependence of the change  $\Delta H$  of the magnetic field required to produce crossing of the levels  $m_J = -3/2$  and  $m_J = 1/2$  on the square of the electric field.  $\Delta H$  is given in units of the proton resonance frequency.

the electric field. The size of the shift is here expressed in terms of the change  $\Delta H$  of the magnetic field required for crossing of the levels when the electric field is applied. The experimental points are described by the relation  $\Delta H = (0.056 \pm 0.011) \mathcal{E}^2$ , where  $\Delta H$  is in gauss and  $\mathcal{E}$  is in kV/cm. This relation is in good agreement with the theoretical result,  $\Delta H = 0.048 \mathcal{E}^2$ .

A requirement for the applicability of this method to other states or other atoms is that it be possible to produce sufficiently large magnetic field strengths to cause crossing of different sublevels of the hyperfine structure of the term in question,\* and that the different hyperfine sublevels be well enough separated at the crossing point. A shortcoming of the method is the relatively complicated connection between the observed Stark splitting of the levels and atomic constants (oscillator strengths, the fine-structure constant). In<sup>[47]</sup> the level-crossing method has been used to measure the splitting constant of the term  $5^3P_1$  of cadmium:  $\gamma = (8.4 \pm 0.3) \times 10^{-8} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$ .

In<sup>[48]</sup> the level-crossing effect has been used to observe the Stark effect in rubidium  $\text{Rb}^{85}$  (the term  $6^2P_{3/2}$ ) and cesium  $\text{Cs}^{133}$  (the term  $7^2P_{3/2}$ ); the crossing of the levels was produced in the electric field without the application of a magnetic field. The splitting constant  $\gamma = (0.17 \pm 0.01) \times 10^{-4} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$  found in that paper for the term  $6^2P_{3/2}$  of  $\text{Rb}^{85}$  is somewhat smaller than the value  $\gamma = 0.24 \times 10^{-4} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$  obtained in<sup>[49]</sup> by the absorption method, while the splitting constant  $\gamma = (0.36 \pm 0.01) \times 10^{-4} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$  found for the  $7^2P_{3/2}$  of  $\text{Cs}^{133}$  is in good agreement with the theoretical value  $\gamma = 0.34 \times 10^{-4} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$ .<sup>[20]</sup> Requirements for the application of this technique to other states or elements are that there be good resolution of the hyperfine-structure sublevels at the crossing point for the levels in question and that it be possible to produce strong enough electric fields so that the Stark shifts of individual sublevels are comparable with the hyperfine splitting.

It must be especially pointed out that it is possible to use the level-crossing method to study the Stark effect in weak electric fields which correspond to a splitting of excited-state terms by amounts of the order of the natural widths of the levels.<sup>[45]</sup> The splitting of terms in a weak electric field can be regarded as a departure from a coincidence of the levels in zero electric field. Although the change of polarization of resonance fluor-

\*Crossing of the sublevels of the hyperfine structure occurs in fields corresponding to Zeeman splittings of the order of the hyperfine splitting.

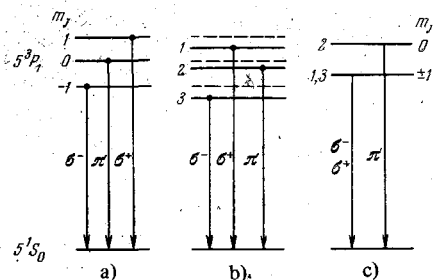


FIG. 18. Schemes of splitting of term  $5^3P_1$  of cadmium: a) in a magnetic field; b) in magnetic and electric fields; c) in an electric field.

escence in a weak electric field was observed soon after the discovery of the Stark effect,<sup>[1,50]</sup> its significance for the study of this effect has come to be understood only recently.

Evidently the level-crossing method will very soon become one of the main precision methods for studying the Stark effect in atoms and molecules.

The method of beats has been used to study the splitting of the term  $5^3P_1$  of cadmium.<sup>[51]</sup> Because of the smallness of the splitting it is not accessible to direct spectroscopic observation by the absorption method. The difficulty of measuring it by the level-crossing method in a weak electric field is due to the small natural width of the levels of the term  $5^3P_1$  of cadmium ( $\Delta\nu = 4.2 \times 10^5 \text{ sec}^{-1}$ ), which makes severe demands for the elimination of stray magnetic fields in the laboratory. Measurements were made in two ways: with magnetic and electric fields acting simultaneously on the cadmium atoms, and with an electric field only.

In a magnetic field  $H$  the term  $5^3P_1$  is split into three equi-distant sublevels  $m_J = 0, \pm 1$  (Fig. 18, a). In such a system beats can occur at the frequencies

$$\omega_H = \gamma_H \cdot H \text{ and } \omega_H = 2\gamma_H \cdot H,$$

where  $\gamma_H$  is the gyromagnetic ratio.

The addition of an electric field of strength  $\mathcal{E}$ , parallel to the magnetic field, leads to a displacement  $\Delta E$  of the levels  $m_J = 1$  and  $m_J = -1$ , both being displaced by the same amount and in the same direction relative to the level  $m_J = 0$  (Fig. 18, b). In this system we can expect beats at the frequency  $2\omega_H$  and at two frequencies located symmetrically relative to  $\omega_H$ :  $\omega_1 = \omega_H + \Delta E/\hbar$  and  $\omega_2 = \omega_H - \Delta E/\hbar$ , so that the difference between the frequencies  $\omega_1$  and  $\omega_2$  is twice the Stark splitting. In the electric field alone (Fig. 18, c) the term  $5^3P_1$  is split

into two levels  $m_J = 0$  and  $m_J = \pm 1$ , separated by the distance  $\Delta E$ . Beats must then occur at the single frequency  $\omega = \Delta E/\hbar$ .

The arrangement for observing the Stark effect by the beat method is closely similar to that for observation with the level-crossing method. Linearly polarized fluorescence from a high-frequency cadmium lamp excited fluorescence ( $\lambda = 3261 \text{ \AA}$ ) of cadmium vapor which was in a vessel of the shape of Wood's fluorescence tube. The power supply of the lamp was modulated at frequencies 436 Hz and 1 MHz. The fluorescence was registered with a FEU-46A photomultiplier. The magnetic field was produced by a system of Helmholtz coils. The electric condenser was formed by two flat electrodes sealed into the resonance vessel.

The results of the experiment confirmed the quadratic relation between the splitting of the levels and the electric field. In the experiments using both electric and magnetic fields the shape of the beat signal agreed with the theoretically calculated curve. Figure 19, a shows the dependence of the splitting on the square of the electric field strength, which is described by the relation  $\Delta\nu = \gamma \mathcal{E}^2$ , where  $\gamma = (6.8 \pm 0.4) \times 10^{-8} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$ . The error of the measurements was mainly a systematic error in the measurement of the electric field strength. The value of  $\gamma$  obtained in this work is somewhat smaller than the value  $\gamma = (8.4 \pm 0.3) \times 10^{-8} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$  obtained by the level-crossing method.<sup>[47]</sup>

In the experiments on beats in an electric field alone the Earth's magnetic field was compensated to an accuracy of  $10^{-2} \text{ G}$ . The beat signal obtained is shown in Fig. 19, b. The symmetry of the curve corresponds to the quadratic character of the effect. The line in Fig. 19, b shows a considerable broadening (by a factor 1.5) in comparison with the resonance line in a magnetic field. The position of the signal maximum, from which the splitting was evaluated in this experiment, corresponds to a value for the constant of  $\gamma = 8.5 \times 10^{-8} \text{ cm}^{-1}/(\text{kV}/\text{cm})^2$ , which agrees with the result of<sup>[47]</sup>.

Since the oscillator strengths for the transitions  $5^3P_1 \rightarrow nS$  and  $5^3P_1 \rightarrow nD$  in cadmium are unknown, it is at present impossible to calculate the Stark splitting of the term  $5^3P_1$  of cadmium.

#### IV. THE STUDY OF THE STARK EFFECT IN FIELDS OF OPTICAL FREQUENCY

1. Observation of Shifts and Splittings of Levels of the Ground State of  $\text{Hg}^{199}$  by Resonance Light. Atoms of  $\text{Hg}^{199}$  in the ground state  $6^1S_0$  have no angular momentum of the electron structure, and since the spin angular momentum of the nucleus is  $I = 1/2$ , in a weak magnetic field the ground state of  $\text{Hg}^{199}$  splits into two sublevels with  $m_I = \pm 1/2$  (Fig. 20), whose energy difference  $\hbar\omega_0$  is proportional to the magnetic field strength. The change of the frequency  $\omega_0$  under the influence of the resonance light of a mercury lamp has been observed in<sup>[52]</sup>.

A detailed theoretical treatment of the effect of the shifting of the frequency  $\omega_0$  by resonance light predicts two types of shifts. First there is a shift owing to the partial mixing of the g-factors of the ground and excited states. It is proportional to the difference  $\omega'_0 - \omega_0$  of the

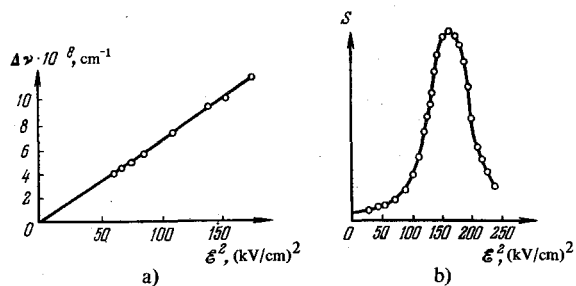


FIG. 19. a) Dependence of the Stark splitting of the levels  $m_J = 0$  and  $m_J = \pm 1$  of the term  $5^3P_1$  of cadmium on the square of the electric field; b) The dependence of the beat signal on the square of the electric field strength.

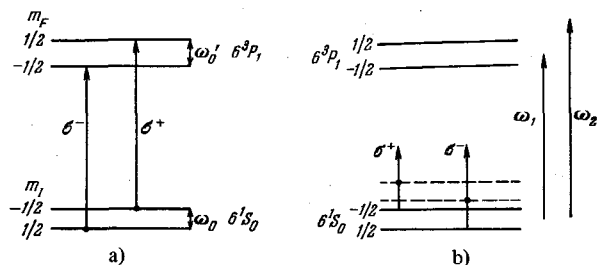


FIG. 20. a) Zeeman structure of the line 2537 Å of Hg<sup>199</sup> [hyperfine component ( $I = 1/2 \leftrightarrow F = 1/2$ )]. b) Displacement of the levels of the ground state of Hg<sup>199</sup> by light.  $\omega_1$  is the frequency of the orienting light;  $\omega_2$  is the frequency of the light causing the shift of the levels of the ground state.

frequencies of the Zeeman splittings of the ground and excited ( $6^3P_1$ ) states, and does not appear for zero magnetic field, nor when the resonance light is circularly polarized. Second there is a shift which occurs owing to the quadratic Stark effect in the electric field of the light.<sup>[54,55]</sup> We shall here consider only the second type of shift of the frequency  $\omega_0$ .

Under conditions of thermodynamic equilibrium the difference of the populations of the sublevels of the ground state is too small for the resonance absorption of a field of frequency  $\omega_0$  to be observed. The well known method of optical orientation, based on the difference of the probabilities of direct and inverse (spontaneous) transitions in atoms,<sup>[53]</sup> was used to produce a substantial difference in the populations. For this purpose a cell containing saturated vapor of Hg<sup>199</sup> was illuminated by a mercury lamp containing the isotope Hg<sup>204</sup>. The frequency of one of the components of the line ( $\lambda = 2537 \text{ Å}$ ) emitted by this lamp coincides with the frequency  $\omega_1$  of the hyperfine component ( $I = 1/2 \rightarrow F = 1/2$ ) of the absorption line  $6^3P_1 - 6^1S_0$  of the isotope Hg<sup>199</sup> (Fig. 20, a). By irradiating Hg<sup>199</sup> vapor with circularly polarized light from such a lamp, when there is a magnetic field one can secure a difference of the order of 60–90 percent in the populations of the Zeeman sublevels of the ground state. With the concentrations of Hg<sup>199</sup> vapor used in the method of optical orientation ( $N \lesssim 10^{12} \text{ cm}^{-3}$ ), however, this difference of the populations is insufficient for the direct observation of the absorption of a radiofrequency field. Nevertheless, the absorption of the energy from the radiofrequency field can be observed through the change of the optical properties of the saturated Hg<sup>199</sup> vapor for the orienting light. In fact, absorption of quanta from the radiofrequency field, leading to a change of the populations of the Zeeman sublevels, is accompanied by a change of the absorption and the intensity of the resonance scattering of the orienting light. With the use of high-sensitivity detectors of optical radiation this method allows the observation of extremely small changes of the absorption of radiofrequency energy (in the limit one transition at the frequency  $\omega_0$  leads to a change of one photon in the registered light flux). In the paper cited the change of the absorption of radiofrequency radiation owing to a shift of the frequency  $\omega_0$  was registered through the change of intensity of the resonance fluorescence light in a direction perpendicular to the orienting beam.

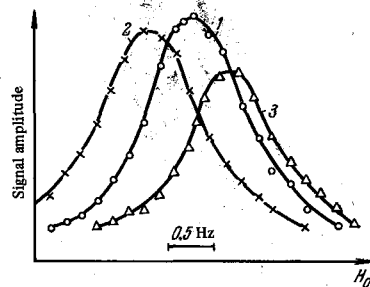


FIG. 21. Displacement of the frequency  $\omega_0$  of the Zeeman splitting in Hg<sup>199</sup> by light (the orienting beam is polarized  $\sigma^+$ ). 1 – without the second beam; 2 – second beam polarized  $\sigma^+$ ; 3 – second beam polarized  $\sigma^-$ .

The experiment was arranged in the following way. A vessel containing Hg<sup>199</sup> vapor was placed in a weak magnetic field and was illuminated by two beams propagated along the magnetic field. A first circularly polarized beam from a lamp containing Hg<sup>204</sup> served for the optical orientation of the Hg<sup>199</sup> atoms. A second beam from a lamp containing Hg<sup>201</sup> produced the shift of the frequency  $\omega_0$  (its frequency  $\omega_2$  could be varied over a range  $\pm 0.03 \text{ cm}^{-1}$  relative to the frequency  $\omega_1$  of the resonance transition  $6^3P_1 - 6^1S_0$ ). A weak radiofrequency field of frequency  $\omega \approx \omega_0$  was also applied to the vessel containing the Hg<sup>199</sup>. The shift of the frequency of the Zeeman splitting caused by the light of the second beam was detected for a fixed frequency  $\omega$  of the radiofrequency field by varying the intensity of the magnetic field  $H_0$  which caused the splitting of the levels by the frequency  $\omega$ . In this case a higher resonance frequency corresponds to a smaller field strength  $H_0$ .

Figure 21 shows the resonance curves of the absorption of the radiofrequency radiation without the second displacing beam, and for two polarizations  $\sigma^+$  and  $\sigma^-$  of this beam. The sign of the displacement of the splitting frequency  $\omega_0$  depends on the polarization of the second beam and corresponds to the predictions of the theory. In fact, since the frequency  $\omega_2$  of the light is larger than the frequency  $\omega_1$  of the transition, according to (22) there is an attraction of the levels  $6^3P_1$  and  $6^1S_0$ ; that is, the energy of the ground state is increased. If the second beam has polarization  $\sigma^+$ , there is resonance perturbation only for the level with  $m_I = -1/2$  and the frequency  $\omega_0$  is increased; on the other hand, for polarization  $\sigma^-$  of the second beam there is resonance perturbation only for the level with  $m_I = +1/2$  and the frequency  $\omega_0$  is decreased. The maximum shift of the frequency  $\omega_0$  in these experiments was about 1 cps, which is of the order of magnitude of the natural width of the levels of the ground state of Hg<sup>199</sup>.

Figure 22 shows a curve of the observed dependence of the shift of the frequency  $\omega_0$  on the frequency difference  $\omega_2 - \omega_1$ . The change of the frequency  $\omega_2$  of the second beam was secured by the use of a lamp containing Hg<sup>199</sup>, which has a broad resonance line in its radiation. The light from this lamp was sent through a filter containing vapor of Hg<sup>198</sup>, and the frequency of the narrow resonance absorption line of this isotope was varied by means of a magnetic field. In accordance with the theory the sign of the frequency shift changes at the resonance point  $\omega_2 = \omega_1$ . An exact treatment taking ac-



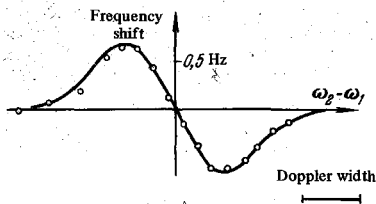


FIG. 22. Dependence of the shift of the frequency  $\omega_0$  on the frequency difference  $\omega_2 - \omega_1$ .

count of the natural widths of the excited levels shows that the quadratic Stark shift is zero for  $\omega_2 = \omega_1$ , and this is also experimentally confirmed. The dispersion shape of the curve of the shift of the frequency  $\omega_0$  is also in good agreement with a theory which takes into account the Doppler broadening of the frequency of the resonance optical transition of the  $\text{Hg}^{199}$  atoms.

## 2. Observations of Shifts and Splittings of Levels of Potassium Atoms in the Radiation Field of a Ruby Laser.

A shift of the frequency of a resonance transition in atoms under the action of a powerful pulse from a ruby laser was first observed in [56]. The object of the study was  $\text{K}^{39}$  vapor (transition  $4S_{1/2} - 4P_{1/2, 3/2}$ ,  $\lambda_2 = 7655 \text{ \AA}$ , line  $D_2$ , and  $\lambda_1 = 7699 \text{ \AA}$ , line  $D_1$  of the principal doublet).  $\text{K}^{39}$  was chosen owing to the relatively large value of the expected shift of the frequency of the absorption line, the large intensity of the resonance-line radiation of the lamp illuminating the vapor, the comparatively large quantum yield of the photoelectric detector for the radiation in the neighborhood of  $0.7 \mu$  (which is especially important with a broad acceptance band of the registering device, which was about 20 MHz), and, finally, the possibility of reliably excluding the background of scattered laser radiation.

The shift which the absorption line associated with the transition  $4S_{1/2} - 4P_{1/2, 3/2}$  of potassium can be expected to undergo in the electric field of the radiation of a ruby laser can be calculated from (22) by using the data on the oscillator strengths in potassium given in [57]. It is mainly due to the shift of the term  $4P_{3/2}$  of the excited state owing to transitions  $4P_{3/2} - 6S_{1/2}$  with oscillator strength  $f = 0.1$ , [58] since the wavelength of this transition,  $6939 \text{ \AA}$ , is close to that of the radiation from the ruby laser,  $6943 \text{ \AA}$  (at room temperature). The calculation with (22) shows that already at a power density of

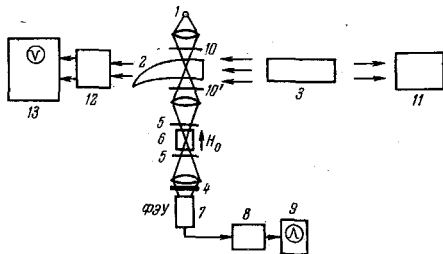


FIG. 23. Scheme of experimental arrangement for observing the shift of the frequency of the transition  $4S_{1/2} - 4P_{1/2, 3/2}$  in potassium in the electric field of a light wave. 1 - potassium lamp; 2 - vessel with potassium vapor; 3 - ruby laser with pulsed figure of merit; 4 - glass light filter FS-7; 5 - crossed polaroids; 6 - auxiliary cell with potassium vapor; 7 - FEU-28 photomultiplier; 8 - amplifier; 9 - pulse oscillograph CI-11; 10 and 10' - crossed polaroids; 11 - spectrograph STE-1; 12 - photoelectric cell F-5; 13 - oscillograph CI-7.

the order of  $1 \text{ MW/cm}^2$  in the radiation from the ruby laser ( $E_0 = 3 \times 10^4 \text{ V/cm}$ ) we can expect the frequency of the transition  $4P_{3/2} - 2S_{1/2}$  to be shifted by  $0.1 \text{ cm}^{-1}$ , which is comparable with the width of the resonance line of the source of radiation. It must be pointed out that for such a frequency shift of the transition  $4S_{1/2} - 4P_{1/2, 3/2}$  in a constant electric field one would need a field strength of the order of  $10^6 \text{ V/cm}$ , which is impossible to use in an experiment.

The scheme of the experiment is shown in Fig. 23. Radiation from the high-frequency potassium lamp 1 goes through the vessel 2 containing saturated  $\text{K}^{39}$  vapor illuminated by pulses from the ruby laser 3, and is registered by the photoelectronic multiplier 7 (FEU-28), the output going to a pulse oscillograph CI-11. At temperature  $100^\circ \text{C}$  the vapor absorbs about 80 percent of the resonance radiation from the lamp, and the Doppler width of the absorption line is about  $0.04 \text{ cm}^{-1}$ . The width of the resonance line in the radiation from the lamp, as measured by means of a scanning Fabry-Perot interferometer, is about  $0.04 \text{ cm}^{-1}$ . In the registration channel the scattered radiation from the laser was cut off with a FS-7 light filter. Besides this, to combat the detection of scattered radiation with spectral components in the neighborhood of the potassium line, a special method of filtration of the resonance radiation line by means of the Faraday effect was used, as described in [59]. This device acts as an optical filter with a pass band of the order of  $0.1 \text{ \AA}$ , allowing the separation of the  $D_1$  and  $D_2$  lines (it weakens the light beam from the lamp by about an order of magnitude, mainly owing to absorption in the polaroid filters).

With this apparatus it was distinctly observed that there was a decrease of the absorption of resonance radiation by the potassium atoms in the vessel 2 during the incidence of a pulse from the laser ( $\Delta t = 20 \text{ nsec}$ ), which was operated to produce single pulses (to modulate the figure of merit a translucent glass light filter KS-19 was introduced into the resonator). The minimal power density of the laser radiation at which the illumination coming through was reliably registered on the oscillograph was about  $10 \text{ MW/cm}^2$  (wave amplitude  $\sim 10^5 \text{ V/cm}$ ). A rough calculation shows that the shift of the absorption line was then of the order of  $0.1 \text{ cm}^{-1}$ , which is somewhat smaller than the expected value. At large intensities the fraction of the light getting through the potassium vapor was some tens of percent; the signal-to-noise ratio was then about 10-20. The comparatively small signal-to-noise ratio (the noise is due to shot-effect fluctuations of the photocurrent from the photomultiplier and cannot be decreased by narrowing the pass band of the registering device because of the small duration of the laser pulse) limited the possibilities of accurate measurement of the frequency shift of the absorption line in the radiation field of the laser, in this experiment.

The best signal-to-noise ratio was achieved in observations of the splitting of the  $D_1$  and  $D_2$  lines of  $\text{K}^{39}$  by the method of electric double refraction (see Sec. 2 of Chapter II). [60] For this purpose crossed polaroids 10 and 10' were inserted in the path of the light beam in the apparatus of Fig. 23, before and after the cell of potassium vapor. In this case the lamp was subjected to forced operation with a line width about  $0.3 \text{ cm}^{-1}$  in

its radiation, and the temperature of the vessel with the potassium vapor was about  $150^{\circ}\text{C}$ . The forced operation of the lamp and the increase of the vapor density made it possible to observe the double-refraction signal with a signal-to-noise ratio of about 50 with much smaller power radiated from the ruby laser. In agreement with the theory the largest signal was observed when the angle between the electric field vector  $\mathcal{E}_L$  of the radiation from the lamp and the electric field vector  $\mathcal{E}_0$  of the laser radiation was  $45^{\circ}$ ; there was no signal when this angle was  $0$  or  $90^{\circ}$ . It was verified that the signal vanished when the crossed polaroids 10 and 10' were removed. This fact, and also the dependence of the signal on the angle between the vectors  $\mathcal{E}_L$  and  $\mathcal{E}_0$  shows that the observed effect is due to double refraction, and not to a shift of the center of gravity of the absorption line of the potassium vapor.

To get reliable quantitative results regarding the Stark splitting of the excited  $4P_{3/2}$  term it is necessary to take into account the dispersion of the double-refraction effect in the region of the absorption line, and also to get a sufficiently reliable value of the concentration of potassium atoms. The dependence of the double-refraction effect on the wavelength of the laser radiation (the dispersion of the splitting of the term  $4^2P_{3/2}$ ) has been measured in<sup>[60]</sup>. According to (12) the splitting of the term  $4^2P_{3/2}$  must show a resonance increase when the frequency  $\omega$  of the laser radiation approaches the frequency of the transition  $4P_{3/2} - 6S_{1/2}$ . The change of wavelength of the laser radiation was produced by varying the temperature of the ruby laser from  $+20^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$ .

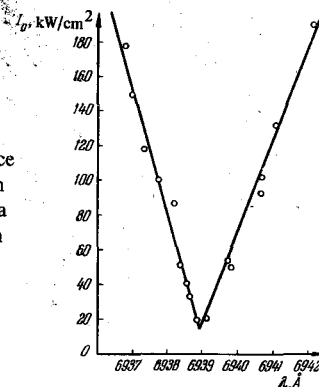
Figure 24 shows the experimental dependence of the intensity  $I_0$  of the laser radiation required to produce a definite value of the double-refraction signal (a transmission of about 10 percent of the light from the potassium lamp that falls on the cell of potassium vapor) on the change of wavelength  $\Delta\lambda = |\lambda - \lambda_0|$  of the laser radiation. According to (12), near resonance the magnitude of the splitting  $\Delta\nu$  of the term  $4P_{3/2}$  is described by the relation  $\text{const} \cdot I_0/\Delta\lambda$ . This dependence is confirmed experimentally. The absence of deviations from linearity in the experimental relation shows that the splitting of the term  $4P_{3/2}$  is in fact due only to the resonance contribution of the transition  $4P_{3/2} - 6S_{1/2}$ .

## V. CONCLUSION

In conclusion, it is interesting to compare the measured constants for the Stark shifts of atomic frequencies with the theoretically calculated values. At present the atomic constants needed for the calculation of Stark shifts of levels can be calculated only for alkali-metal atoms and hydrogenlike atoms. Table IV shows measured and calculated constants for the quadratic Stark effect for alkali-metal atoms. We can draw the following conclusions from a comparison of the experimental and calculated values of the constant  $\gamma$ .

1. The measured frequency shifts of optical transitions in the atoms Li, Na, and K agree within the experimental accuracy with the shifts calculated by methods<sup>[20,57]</sup> which do not take into account the influence of spin-orbit interaction on the atomic wave functions.

FIG. 24. Wavelength dependence of the intensity  $I_0$  of radiation from the ruby laser required to produce a given value of the double-refraction signal.



2. For the Rb and Cs atoms a method for calculating Stark shifts which does not include the spin-orbit interaction leads to values appreciably different from the experimental results. There are especially large discrepancies for the calculations of frequency shifts of transitions associated with shifts of the first excited P terms, which have relatively large values of the spin-orbit (fine-structure) splitting. Inclusion of the spin-orbit interaction for Rb and Cs atoms leads to values of the shifts which agree with the experimental results to within the accuracy of the measurements.<sup>[28,32]</sup>

3. The theoretical method for calculating the frequency shifts of transitions between hyperfine levels of the ground states of alkali-metal atoms<sup>[38]</sup> leads to values of the shifts which are too large, beyond the limits of error of the experiments. This discrepancy is evidently due to insufficient accuracy in the calculation of polarizabilities of alkali-metal atoms in the ground state. The polarizability occurs linearly in the formula for the frequency shift of a hyperfine transition,<sup>[38]</sup> and the theoretical methods for calculating it give values larger than experimental results.<sup>[66]</sup>

Experimental data on frequency shifts of atomic transitions in electric fields can be used to calculate oscillator strengths in atoms. The observation of the Stark effect in fields of optical frequency is especially interesting in this connection. By varying the frequency of the optical radiation one can separate out the contribution of only one term or a few terms to the Stark shift. Unfortunately, it is at present difficult to make reliable quantitative studies in this region because of the lack of frequency-tunable continuous-wave lasers and the insufficient stability of existing powerful pulsed lasers. We give here the results of a treatment of the data obtained in a study of the shift of the frequency of the  $3P - 2S$  transition in Na by the atomic-beam method (see Sec. 1 of Chap. II),<sup>[67]</sup> and compare the values of oscillator strengths obtained from these data with the values obtained by other experimental methods. To do this it is necessary to calculate the relative shift of the sublevels of the  $3P$  term, after determining which intermediate states ( $nS$  or  $nD$ ) make the larger contribution to the shift given by the relation (12). The relative shifts of the sublevel states  $P_{1/2, 3/2}$  for perturbation by only the  $nS$  terms or only the  $nD$  terms, without inclusion of the spin-orbit interaction, have been calculated and tabulated in<sup>[68]</sup>. According to this paper for the pure S perturbation  $\Delta\nu P_{3/2, m_J = \pm 1/2}$ ;  $\Delta\nu P_{1/2, m_J = \pm 1/2}$ :

Table IV. Comparison of Observed and Calculated Constants for the Quadratic Stark Shifts  $\Delta\nu$  of Frequencies of Transitions in Alkali-metal Atoms. The constant  $\gamma$  is defined by the relation  $\Delta\nu = \gamma\mathcal{E}^2$ , where  $\Delta\nu$  is in  $\text{cm}^{-1}$ ,  $\mathcal{E}$  in  $\text{kV/cm}$ , and  $\gamma$  in  $\text{cm}^{-1}/(\text{kV/cm})^2$

| Atom                        | Transition                     | obs*                           | Method of Observation                         | calc                     |
|-----------------------------|--------------------------------|--------------------------------|---|--------------------------|
| Li <sup>7</sup>             | 2P-2S                          | $+(4 \pm 2) 10^{-7} 61$        | Shift of center of gravity of absorption line | $2.7 10^{-7} 20$         |
|                             | 3P-2S                          | $-(1.4 \pm 0.3) 10^{-4} 61$    |   | $-1.1 10^{-4} 20$        |
|                             | 2P-4S                          | $-(1.9 \pm 0.4) 10^{-4} 61$    |   | $-1.5 10^{-4} 20$        |
| Na <sup>23</sup>            | 3P <sub>1/2</sub> -3S          | $-7.6 10^{-7} 19$              | Atomic-beam method                            | $-7.4 10^{-7} 20$        |
|                             | 3P <sub>3/2</sub> -3S          | $-4.1 10^{-7} 19$              |   | $-4.1 10^{-7} 20$        |
|                             | 3P <sub>3/2, ±1/2</sub> -3S    | $-11.1 10^{-7} 19$             | Double-refraction method                      | $-10.6 10^{-7} 20$       |
|                             | 3P <sub>3/2, ±1/2</sub> -3S    | $-4.1 10^{-7} 28$              |   | $-4.1 10^{-7} 20$        |
|                             | 3P <sub>3/2, ±1/2</sub> -3S    | $-11.0 10^{-7} 26$             |   | $-10.6 10^{-7} 20$       |
|                             | 3P <sub>3/2, ±1/2</sub> -3S    |                                |   |                          |
| K <sup>39</sup>             | 5P-4S                          | $-3.4 10^{-5} 62$              | Shift of center of gravity of absorption line | $-3.3 10^{-5} 57 **$     |
|                             | 6P-4S                          | $-1.6 10^{-4} 62$              |   | $-1.8 10^{-4} 57 **$     |
|                             | 4S (F=2)-                      | $-(2.53 \pm 0.25) 10^{-12} 37$ |   | $-3.1 10^{-12} 20.38 **$ |
|                             | 4S (F=1)-                      | $-(2.21 \pm 0.17) 10^{-12} 63$ |   | $-3.0 10^{-12} 38.64 **$ |
|                             |                                |                                |   | $-3.3 10^{-12} 38.65 **$ |
| Rb <sup>85</sup>            | 5P-5S                          | $-(2.0 \pm 0.2) 10^{-6} 28$    | Radiospectroscopic method                     | $-0.9 10^{-6} 20$        |
|                             | 5P <sub>3/2, ±1/2</sub> -5S    | $-(1.8 \pm 0.2) 10^{-6} 28$    |   | $-2.0 10^{-6} 28.31$     |
|                             | 5P <sub>3/2, ±1/2</sub> -5S    |                                |   | $-0.6 10^{-6} 20$        |
|                             | 5P <sub>3/2, ±1/2</sub> -5S    | $-(3.0 \pm 0.4) 10^{-6} 28$    |   | $-1.8 10^{-6} 28.31$     |
|                             |                                |                                |   | $-1.9 10^{-6} 20$        |
|                             |                                |                                |   | $-2.9 10^{-6} 28.31$     |
| Cs <sup>133</sup>           | 7P-6S                          | $-1.18 10^{-4} 49$             | Comparison with hyperfine-structure splitting | $-1.17 10^{-4} 20$       |
|                             | 7P <sub>3/2, ±1/2</sub> -6S    | $-1.46 10^{-4} 48$             |   | $-1.63 10^{-4} 20$       |
|                             | 7P <sub>3/2, ±1/2</sub> -6S    | $+(0.36 \pm 0.01) 10^{-4} 48$  | Shift of center of gravity of absorption line | $+0.34 10^{-4} 20$       |
|                             | -7P <sub>3/2, ±1/2</sub> -6S   |                                |   |                          |
|                             | 6P <sub>1/2, ±1/2</sub> -6S    | $-(3.8 \pm 0.6) 10^{-6} 28$    | Level-crossing method                         | $-3.1 10^{-6} 20$        |
|                             | 6P <sub>1/2, ±1/2</sub> -6S    |                                |   | $-3.8 10^{-6} 28.31$     |
|                             |                                |                                |   | $-3.4 10^{-6} 28.32$     |
|                             | 6P <sub>3/2, ±1/2</sub> -6S    | $-(4.0 \pm 0.8) 10^{-6} 28$    | Comparison with hyperfine-structure splitting | $-2.3 10^{-6} 20$        |
|                             | 6P <sub>3/2, ±1/2</sub> -6S    |                                |   | $-4.0 10^{-6} 28.31$     |
|                             | 6P <sub>3/2, ±1/2</sub> -6S    | $-(6.2 \pm 1) 10^{-6} 28$      |   | $-3.8 10^{-6} 28.32$     |
| 6P <sub>3/2, ±1/2</sub> -6S |                                | $-4.9 10^{-6} 20$              |   |                          |
|                             |                                |                                | $-5.4 10^{-6} 28.31$                          |                          |
|                             |                                |                                | $-6.0 10^{-6} 28.32$                          |                          |
| 6S (F=4)-                   | $-(0.76 \pm 0.01) 10^{-10} 33$ | Radiospectroscopic method      | $-0.82 10^{-10} 20.38 **$                     |                          |
| 6S (F=3)-                   |                                |                                | $-0.79 10^{-10} 38.64 **$                     |                          |
|                             |                                |                                | $-0.99 10^{-10} 38.65 **$                     |                          |

\*The positive sign of  $\gamma$  means that the frequency of the transition is increased in the electric field.

\*\*Calculated by us on the basis of data in the papers cited.

$\Delta\nu_{P_{3/2, m_J = \pm 3/2}} = 2 : 1 : 0$ , and for the pure D perturbation we have  $\Delta\nu_{P_{3/2, m_J = \pm 1/2}} : \Delta\nu_{P_{1/2, m_J = \pm 1/2}}$ :

$\Delta\nu_{P_{3/2, m_J = \pm 3/2}} = 55 : 50 : 45$ . The experimental ratios

of the shifts are<sup>[31]</sup>:  $\Delta\nu_{P_{3/2, m_J = \pm 1/2}} : \Delta\nu_{P_{1/2, m_J = \pm 1/2}}$ :

$\Delta\nu_{P_{3/2, m_J = \pm 3/2}} = 18.4 : 14.9 : 11.4$ . First it is necessary to calculate from the experimental pattern of the splitting and the data on the pure S and D perturbations<sup>[68]</sup> the relative weights of the S and D perturbations:

$$Z = \frac{\sum_{n=3}^{\infty} \frac{f_{3P-ns}}{(\nu_{nS} - \nu_{3P})^2}}{\sum_{n=3}^{\infty} \frac{f_{3P-nd}}{(\nu_{nD} - \nu_{3P})^2}} \quad (41)$$

If for the pure S perturbation  $\Delta\nu_{3/2, \pm 1/2} : \Delta\nu_{1/2, \pm 1/2} : \Delta\nu_{3/2, \pm 3/2} = a_S : b_S : c_S$ , for the pure D perturbation

$\Delta\nu_{3/2, \pm 1/2} : \Delta\nu_{1/2, \pm 1/2} : \Delta\nu_{3/2, \pm 3/2} = a_D : b_D : c_D$ , and for the actual mixed perturbation (from experiment)

$\Delta\nu_{3/2, \pm 1/2} : \Delta\nu_{1/2, \pm 1/2} : \Delta\nu_{3/2, \pm 3/2} = a_{SD} : b_{SD} : c_{SD}$ , then some simple algebraic calculations lead to the following formula for  $Z$ <sup>[68]</sup>:

$$Z = \frac{a_S + b_S + c_S}{a_D + b_D + c_D}, \quad \frac{b_D a_{SD} - a_D b_{SD}}{a_S b_{SD} - b_S a_{SD}} = 0.176. \quad (42)$$

To begin with let us assume that the shifts of the terms 3P<sub>1/2, 3/2</sub> are due to only the nearest terms 3S, 4S, and 3D. Then by (12) the shift of the center of gravity of the term 3P is

$$\Delta\nu_{3P}^{\text{theor}} = \frac{1}{3} (\Delta\nu_{3/2, \pm 1/2} + \Delta\nu_{1/2, \pm 1/2} + \Delta\nu_{3/2, \pm 3/2}) = 203 \mathcal{E}^2 \left[ \frac{f_{3P-3D}}{(\nu_{3D} - \nu_{3P})^2} + \frac{f_{3P-3S}}{(\nu_{3S} - \nu_{3P})^2} + \frac{f_{3P-4S}}{(\nu_{4S} - \nu_{3P})^2} \right], \quad (43)$$

where  $\Delta\nu_{3P}$  is in  $\text{cm}^{-1}$ , the field  $\mathcal{E}$  in  $\text{kV/cm}$ , and the frequency differences  $(\nu_{3D} - \nu_{3P})$ ,  $(\nu_{3S} - \nu_{3P})$ , and  $(\nu_{4S} - \nu_{3P})$  are in  $\text{cm}^{-1}$ . The actual shift of the center

of gravity of the term 3P as measured experimentally is

$$\Delta v_{3P}^{\text{exp}} = 14.9 \cdot 10^{-7} \text{ cm}^{-1} \quad (44)$$

Using the value  $f_{3P-3S} = -(\epsilon_{3S}/\epsilon_{3P})f_{3S-3P} = -f_{3S-3P}/3 = -0.33$ , we get from (41)–(44)

$$f_{3P-3D} = 0.93, \quad f_{3P-4S} = 0.17. \quad (45)$$

Since it was assumed that the shift of the term 3P is due to the perturbations by only the 3S, 4S, and 3D terms, the values of  $f_{3P-3D}$  and  $f_{3P-4S}$  obtained in this way are larger than the true values.

In order to take into account the perturbation by the other terms, we must introduce into (43) the sums

$$\sum_{n=5}^{\infty} f_{3P-nS}/(\nu_{nS} - \nu_{3P})^2 \quad \text{and} \quad \sum_{n=4}^{\infty} f_{3P-nD}/(\nu_{nD} - \nu_{3P})^2.$$

Then instead of (42) and (43) we have

$$\frac{f_{3P-3S}}{(\nu_{3S} - \nu_{3P})^2} + \frac{f_{3P-4S}}{(\nu_{4S} - \nu_{3P})^2} + \sum_{n=5}^{\infty} \frac{f_{3P-nS}}{(\nu_{nS} - \nu_{3P})^2} = 0.176 \left( \frac{f_{3P-3D}}{(\nu_{3D} - \nu_{3P})^2} + \sum_{n=4}^{\infty} \frac{f_{3P-nD}}{(\nu_{nD} - \nu_{3P})^2} \right), \quad (46)$$

$$\Delta v_{3P}^{\text{theor}} = 203 \text{ cm}^{-1} \left[ \frac{f_{3P-3D}}{(\nu_{3D} - \nu_{3P})^2} + \sum_{n=4}^{\infty} \frac{f_{3P-nD}}{(\nu_{nD} - \nu_{3P})^2} + \frac{f_{3P-3S}}{(\nu_{3S} - \nu_{3P})^2} + \frac{f_{3P-4S}}{(\nu_{4S} - \nu_{3P})^2} + \sum_{n=5}^{\infty} \frac{f_{3P-nS}}{(\nu_{nS} - \nu_{3P})^2} \right]. \quad (47)$$

A further relation between the desired oscillator strengths is provided by the sum rule, which for the 3P term gives us

$$\sum_{n=3}^{\infty} f_{3P-nS} + \sum_{n=3}^{\infty} f_{3P-nD} = 1. \quad (48)$$

We have three equations for four unknown quantities:

$$f_{3P-4S}, \quad f_{3P-3D}, \quad \sum_{n=5}^{\infty} f_{3P-nS}, \quad \text{and} \quad \sum_{n=5}^{\infty} f_{3P-nD}.$$

A lower limit for  $f_{3P-4S}$  and  $f_{3P-3D}$  can be obtained

if a relation is established between  $\sum_{n=5}^{\infty} f_{3P-nS}$  and  $\sum_{n=4}^{\infty} f_{3P-nD}$ . In the absence of such a relation a limit can be fixed in the following way.

1) Let us set  $\sum_{n=5}^{\infty} f_{3P-nS} = 0$ . Then from (46), (47), and (48) we have<sup>[68]</sup>

$$f_{3P-3D} = 0.85, \quad f_{3P-4S} = 0.17, \quad \sum_{n=4}^{\infty} f_{nD} = 0.31. \quad (49)$$

Here  $f_{3P-4S} = 0.17$  is the maximum possible value of  $f_{3P-4S}$  (since it was assumed that  $\sum_{n=5}^{\infty} f_{3P-nS} = 0$ ); on the other hand, according to the sum rule (48) this value  $f_{3P-3D} = 0.85$  is the smallest possible value of  $f_{3P-3D}$ , since  $\sum_{n=4}^{\infty} f_{3P-nD} = 0.31$  is the largest possible value of the sum.

2) Let us set  $\sum_{n=4}^{\infty} f_{3P-nD} = 0$ . Then, in analogy with case 1), we get

$$f_{3P-3D} = 0.93, \quad f_{3P-4S} = 0.14, \quad \sum_{n=5}^{\infty} f_{3P-nS} = 0.26. \quad (50)$$

Now  $f_{3P-3D}^{(\text{max})} = 0.93$ ,  $f_{3P-3S}^{(\text{min})} = 0.14$ , and  $\sum_{n=5}^{\infty} f_{3P-nS}^{(\text{max})} = 0.26$ . Accordingly,

$$\left. \begin{aligned} 0.85 < f_{3P-3D} < 0.93, \\ 0.14 < f_{3P-4S} < 0.17, \\ 0 < \sum_{n=4}^{\infty} f_{3P-nD} < 0.31, \\ 0 < \sum_{n=5}^{\infty} f_{3P-nS} < 0.26. \end{aligned} \right\} \quad (51)$$

A comparison with the values given in<sup>[60]</sup>,  $f_{3P-3D} = 0.83$  and  $f_{3P-4S} = 0.16$ , shows that the experimental and calculated values are rather close together. A comparison

with the theoretical estimates  $\sum_{n=4}^{\infty} f_{3P-nD} = 0.175$  and

$\sum_{n=5}^{\infty} f_{3P-nS} = 0.023$  shows<sup>[57]</sup> that the approximation

$\sum_{n=5}^{\infty} f_{3P-nS} = 0$  is satisfactory and gives a reasonable

limit on the quantity  $\sum_{n=4}^{\infty} f_{3P-nS}$ , whereas the approxi-

mation  $\sum_{n=4}^{\infty} f_{3P-nD} = 0$  is excessively crude. For a

more accurate estimate of the sums  $\sum_{n=4}^{\infty} f_{3P-nD}$  and

$\sum_{n=5}^{\infty} f_{3P-nS}$  we need an additional relation connecting

these quantities.

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