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Level-Crossing Spectroscopy with an Electric Field: Stark Shift of the 3^2P Term in Lithium*

B. Budick,† S. Marcus, and R. Novick‡
Columbia Radiation Laboratory, Columbia University, New York, New York

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The method of level-crossing spectroscopy has been extended to a study of the Stark effect on the $3P$ term of lithium. Lithium atoms in a broad atomic beam are subjected to collinear electric and magnetic fields. The field values required to produce a level crossing or degeneracy are determined by observing the change in the angular distribution of the fluorescence resulting from the optical excitation of the $3P$ term. The magnetic field required to produce the crossing is found to shift to higher values as the electric field is applied. The shift increases as the square of the electric field and is given by $\Delta H = +0.056\ (11) E^2$, where ΔH is in gauss and E is in kilovolts per centimeter. The coefficient is in good agreement with the value 0.048 obtained from second-order perturbation theory and the Bates and Damgaard approximation.

HERE we report on a new technique for determining the Stark effect in excited atomic levels with a precision limited only by the natural lifetime of the state. This technique, which exploits level-crossing spectroscopy,[1] can also be applied to molecules. The atoms are optically excited with resonance radiation and are subjected to collinear electric and magnetic fields. The field values required to produce a degeneracy are determined by observing the change in the angular distribution of the fluorescence that occurs at the crossing. In the present method we avoid the difficulties encountered in the optical double-resonance studies of the Stark effect.[2] In particular, the absence of rf fields simplifies the design of the apparatus and permits the use of more homogeneous electric fields. Furthermore, the level-crossing method can be applied to very short-lived states, whereas the rf method could not be used since excessively large rf power levels would be required. A further simplification would be obtained by employing the electric analog of the Hanle effect[3] in which the Stark shifts can be determined in the absence of a magnetic field.

Shifts as small as 1.5 Mc/sec at fields as low as 3 kV/cm have been observed in the 3^2P term of lithium. This extreme sensitivity arises, of course, from the relatively long lifetime of the $3P$ term (about 2×10^{-7} sec) and the proximity of the $3S$ and $3D$ levels. It is clear that this technique can be usefully applied to a large number of atomic and molecular systems with high precision. Recently, precise theoretical methods have been developed for the computation of Stark shifts. These require the numerical solution of a differential equation involving the Hartree-Fock wave function for the state of interest.[4,5] It is expected that further application of the present technique will provide a large body of useful data for testing the predictions of these methods.

As indicated above, we have applied the method to the $(1s^23p)^2P$ term in Li^7. Atoms in an atomic beam are excited by resonance radiation and subjected to a magnetic field of about 915 G. At this field the $^2P_{3/2}$ $(m_J=-\frac{3}{2})$ and $^2P_{1/2}(m_J=\frac{1}{2})$ are known[6] to become degenerate as shown in Fig. 1. A detailed publication on the fine and hyperfine structure of the 3^2P term is in preparation.[7] The apparatus employed here is identical to that used in the fine-structure measurement shown in Fig. 2. The apparatus is placed between the pole faces of a 12-in. Harvey-Wells magnet so that the magnetic field is perpendicular to the plane of the incoming and scattered light, and the Stark plates are oriented so that the applied electric field is collinear with the applied magnetic field. When the levels cross, an interference occurs in the light scattered by the atoms. This results in a detectable change in the angular dis-

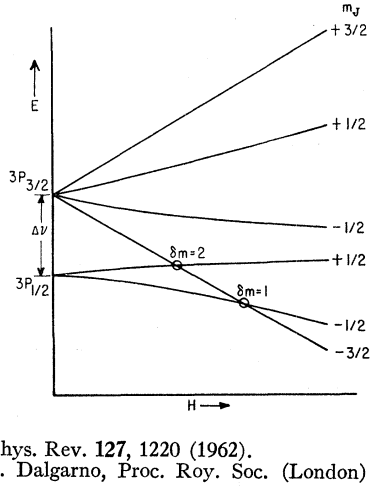

FIG. 1. Zeeman effect on a ^2P term. The observable level crossings are indicated by circles.

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† Present address: Physics Department, Hebrew University, Jerusalem, Israel.

‡ Alfred P. Sloan Research Fellow.

[1] P. A. Franken, Phys. Rev. **121**, 508 (1961).

[2] J. E. Blamont, Ann. Phys. (Paris) **2**, 551 (1957).

[3] Peter Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 86; F. Suppe, Z. Physik **113**, 18 (1939).

[4] R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).

[5] A. M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) **275A**, 492 (1963).

[6] B. Budick, H. Bucka, R. Goshen, A. Landman, and R. Novick, Bull. Am. Phys. Soc. **8**, 352 (1963).

[7] B. Budick, H. Bucka, R. Goshen, A. Landman, and R. Novick (to be published).

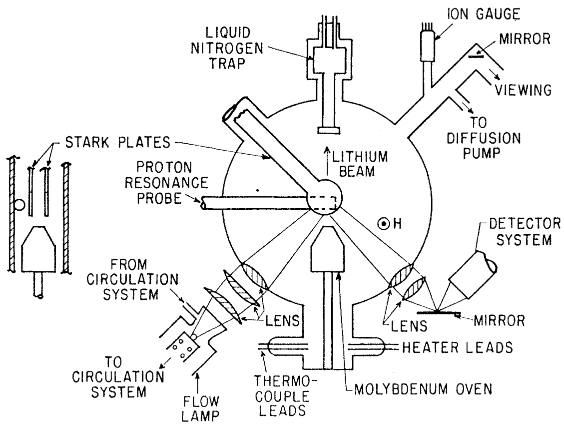

FIG. 2. Apparatus used in level-crossing spectroscopy.

tribution of the resonance fluorescence. An applied electric field shifts one of the levels more than the other, thus lifting the degeneracy. The levels will now cross at a slightly different value of the magnetic field. Detection of shifts in the value of the magnetic field required to produce interference is limited only by the natural width of the excited state. In the case of the $3P$ term of lithium this width is estimated to be 1.5 Mc/sec.

The Li^7 nucleus has a spin of $\frac{3}{2}$. At a magnetic field of 915 G, the electronic and nuclear angular momenta are completely uncoupled so that only their projections on the magnetic field axes m_J and m_I are appropriate quantum numbers. Thus, each of the Zeeman levels consists of four closely spaced sublevels, and sixteen crossings occur. The incident and scattered photon, however, interact only with the electronic structure imposing the selection rule $\Delta m_I=0$ and reducing the number of observable crossings to four. The geometry of our apparatus is arranged so that we can detect the $\Delta m_J=2$ crossing between the ${}^2P_{3/2}(m_J=-\frac{3}{2})$ and ${}^2P_{1/2}(m_J=+\frac{1}{2})$ levels.[1]

Figure 3(a) shows the level-crossing signal obtained in the absence of an electric field. The markers indicate the magnetic field in units of the resonance frequency of protons in a mineral oil sample. Figures 3(b) and 3(c) show the same pattern shifted by electric fields of 3 and 6 kV/cm, respectively.

A plot of the shifts observed in the crossing magnetic field versus the square of the electric field that produces these shifts is shown in Fig. 4. The points lie along a straight line indicating a quadratic Stark shift.

The slope of this line gives the experimental shift in crossing field as $\Delta H=+0.056(11)E^2$, where ΔH is in gauss and E is in kilovolts per centimeter. It is of interest to compare this result with a theoretical estimate based on second-order perturbation theory. The shift in the crossing field is related to the Stark shift of each of the levels by

$$\Delta H=\frac{\Delta W_c(\frac{3}{2},-\frac{3}{2})-\Delta W_c(\frac{1}{2},\frac{1}{2})}{|W_c'(\frac{3}{2},-\frac{3}{2})|+|W_c'(\frac{1}{2},\frac{1}{2})|}, \tag{1}$$

where $\Delta W_c(J,m_J)$ and $W_c'(J,m_J)$ are the Stark shift and Zeeman slope, respectively, of the level (J,m_J) at the crossing field. The Zeeman slopes are given by

$$\begin{aligned} W_c'(\tfrac{1}{2},\tfrac{1}{2})&=(2/11)\mu_0,\\ W_c'(\tfrac{3}{2},-\tfrac{3}{2})&=-(22/11)\mu_0, \end{aligned} \tag{2}$$

where μ_0 is the Bohr magneton. The Stark effect in alkali spectra for zero magnetic field is discussed extensively by Condon and Shortley.[8] Their formulas must be modified, however, since the applied magnetic field mixes fine structure states of the same m_J. In our

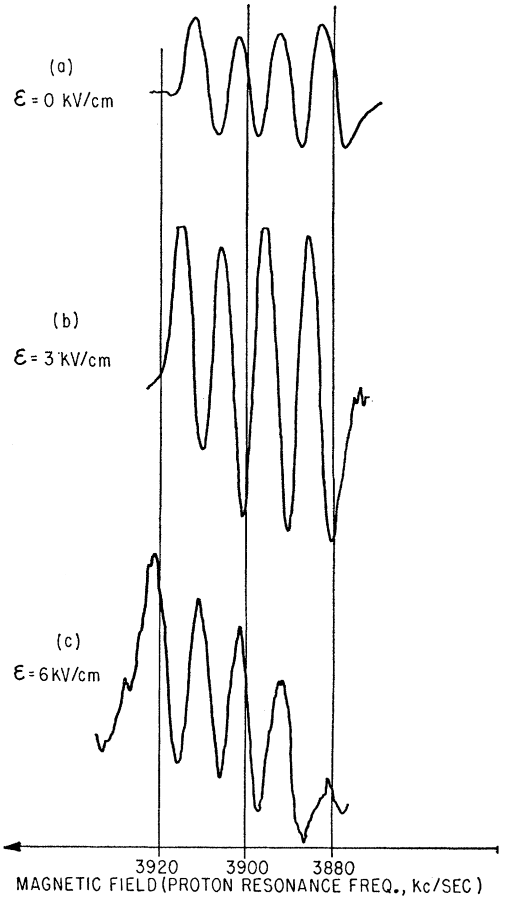

FIG. 3. Figure 3(a) shows the hyperfine level-crossing pattern at zero electric field. Figures 3(b) and 3(c) show the pattern shifted when electric fields of 3 and 6 kV/cm are applied. The vertical bars in the figures refer to proton NMR magnetometer readings.

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[8] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1957), p. 415.

case, the mixing of the states in question is given by

$$|^2P,\tfrac{1}{2},\tfrac{1}{2},H_c\rangle=(32/33)^{1/2}|^2P,\tfrac{1}{2},\tfrac{1}{2}\rangle-(1/33)^{1/2}|^2P,\tfrac{3}{2},\tfrac{1}{2}\rangle,$$
$$|^2P,\tfrac{3}{2},-\tfrac{3}{2},H_c\rangle=|^2P,\tfrac{3}{2},-\tfrac{3}{2}\rangle, \tag{3}$$

where the designation H_c indicates that the wave function is valid at the crossing field and that J is only approximately a good quantum number. It is well known that any convenient coupling representation of the S and D states may be used if the hyperfine structure of the S states and the fine structure of the D states are ignored in the energy denominator occurring in the perturbation calculation. Thus, for convenience, we used the zero field ^2D and ^2S wave functions.

Using the wave function given in Eq. (3), we find that the Stark shifts of the states of interest are

$$\begin{aligned}\Delta W_c(\tfrac{3}{2},-\tfrac{3}{2})&=3A_d,\\ \Delta W_c(\tfrac{1}{2},\tfrac{1}{2})&=(2/11)A_s+(35/11)A_d,\end{aligned} \tag{4}$$

where

$$\begin{aligned}A_s&=E^2\sum_{n'}\frac{|(3^2P\|P\|n'^2S)|^2}{E_{3p}-E_{n's}},\\ A_d&=E^2\sum_{n'}\frac{|(3^2P\|P\|n'^2D)|^2}{E_{3p}-E_{n'd}},\end{aligned} \tag{5}$$

and where E is the electric field.

Using the results obtained above, we find that the shift in the crossing field is given by

$$\Delta H=-(A_s+A_d)/12\,\mu_0. \tag{6}$$

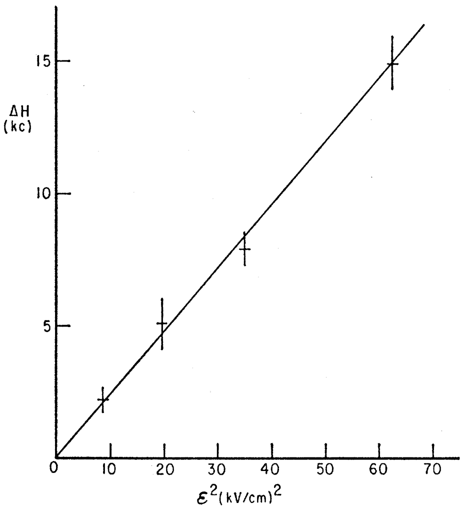

FIG. 4. Shifts in magnetic field required to produce degeneracies as a function of the square of the applied electric field. ΔH is in units of the proton magnetometer frequency.

TABLE I. Electric-dipole reduced matrix elements for hydrogen and for lithium.[a]

	Hydrogen	Lithium (Bates & Damgaard approximation)
$\|(2S\|r\|3P)\|^2$	3.13	0.018
$\|(3S\|r\|3P)\|^2$	54.0	35.5
$\|(4S\|r\|3P)\|^2$	2.0	17.9
$\|(5S\|r\|3P)\|^2$	0.3	1.12
$\|(6S\|r\|3P)\|^2$	0.11	0.314
$\|(3D\|r\|3P)\|^2$	6.74	6.65
$\|(4D\|r\|3P)\|^2$	3.82	3.10
$\|(5D\|r\|3P)\|^2$	0.587	0.513
$\|(6D\|r\|3P)\|^2$	0.200	0.189

[a] The matrix elements are given in the units of the first Bohr radius of hydrogen.

In calculating the theoretical shift in the crossing field due to the Stark effect, contributions from the nS and nD states up to and including $n=6$ were considered. It was thus necessary to calculate the reduced matrix elements of the electric dipole operator between each of of these states and the $3P$ state. Table I gives these elements as calculated for the hydrogen atom, as well as those calculated by the Bates and Damgaard[9] method as applied to lithium. The matrix elements involving the D states are essentially the same for lithium and hydrogen indicating negligible shielding effects. The S-state matrix elements, however, are in very poor agreement, as expected, since the S electrons exhibit a marked core penetration.

Using the Bates and Damgaard matrix elements given in Table I, we find that the shift in the crossing field is $\Delta H=+0.048E^2$. This agrees to within the stated precision with the experimental result and provides further evidence for the adequacy of the Bates and Damgaard approximation method.[10,11]

In the procedure reported here, level degeneracies were produced by both electric and magnetic fields. It is well known that zero-field Zeeman level crossings can be effectively used for determining the lifetimes of excited states. We would like to propose that an analogous technique with electric fields can be used to determine the Stark effect for many elements whose high magnetic-field level crossings are impossible to observe. Interference signals produced in this way would have a line shape determined by the Stark effect and lifetime parameters. Alternatively, previous experimental or theoretical knowledge of the Stark effect in the excited state under study could yield values for its lifetime.

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

[10] A. Lurio, R. L. de Zafra, and R. J. Goshen, Phys. Rev. **134**, A1198 (1964).

[11] A. Lurio and R. Novick, Phys. Rev. **134**, A608 (1964).