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Theory of the photodetachment of negative ions in a magnetic field

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The behavior of the photodetachment cross section of the S^- ion near thresholds in a magnetic field is derived. This cross section is shown to have an oscillatory dependence on photon energy. The calculation is based on first-order time-dependent perturbation theory, and final-state interactions are ignored. The weights of individual transitions between the various Zeeman sublevels for different light polarizations are given in terms of the appropriate angular momentum coupling coefficients. Broadening of the features of the cross section due to the motion of the ions is included in the calculation. The Wigner-law behavior known to be valid for zero magnetic field is shown to result from the magnetic field dependent cross section in the limit of low magnetic field. The theory is shown to be in good agreement with experimental results. The extension of the theory to other atomic negative ions is discussed.

I. INTRODUCTION

The cross section for photodetachment of the atomic negative sulfur ion in a magnetic field has been observed to have an oscillatory dependence on the light frequency.[1] This paper presents a theory of such a process whose predictions are in generally good agreement with the experimental data. The theory has been significantly improved over that suggested in Ref. 1 by a more complete treatment of the ionic motion which includes the effects of the motional electric field. The basic element of the theory which is not present in previous zero magnetic field descriptions[2,3] is the confinement of the motion of the detached electron in the directions transverse to the magnetic field. This confinement leads to the quantization of the transverse kinetic energy into the familiar cyclotron or Landau levels.[4] The motion parallel to the field is free and unquantized. Although calculations with significant similarities have been reported for transitions between valence and conduction-band cyclotron states in semiconductors,[5] these concepts have not previously been applied to the photodetachment of negative ions. The present theory predicts the dependence of the photodetachment cross section upon magnetic field strength and upon light frequency and polarization. In addition, it is easily generalized to classes of ions not yet studied and also provides a framework for building an understanding of other processes, such as collisions, which may be important in the experiments.

II. DESCRIPTION OF THE PROBLEM

The process under consideration is the reaction $h\nu + S^- \to S + e^-$. The bound states of S^- consist of a ^2P inverted doublet term formed from a configuration of five equivalent p electrons. The $^2P_{3/2}$ level is the lowest in energy and the fine-structure interval[6] is 482 cm^{-1}. The magnetic quantum oscillations were observed in photodetachment transitions from the $^2P_{3/2}$ level of the S^- ion to the $^3P_2$ level of the S atom in the presence of a magnetic field.

The experiments were performed on ions confined in a trap of the Penning type,[7] in which a uniform magnetic field and a quadrupolar static electric potential are present. Classically, the effect of the electric potential is to cause a charged particle to oscillate harmonically in the axial direction and to cause the center of the cyclotron orbit to precess around the axis of the trap at the magnetron frequency. Quantum mechanically, the energies associated with the axial, cyclotron, and magnetron motions, of both the ion and the electron, are quantized. This leads to additional structure in the cross section over what would be present in a magnetic field alone. However, the experimental resolution was such that only the highest frequency motion, the electron cyclotron motion, could be resolved. Thus we consider only the effect of the magnetic field on the photodetachment process.

Our treatment of the problem of optical transitions between bound and continuum states of a negative ion in a homogeneous magnetic field contains certain simplifying assumptions. We consider electric dipole transitions using first-order time-dependent perturbation theory. We limit our calculation of the dependence of the photodetachment cross section on photon energy to a small region above the threshold. (The experiments probed an interval of 4 cm^{-1} above the threshold.) We consider values of the magnetic field which are low in the sense that the region to which the magnetic field confines an electron is large compared to the dimensions of the S^- ion. This is the case for all fields which presently can be obtained in the laboratory. A measure of this confinement, for an electron of low energy, is the zero-point cyclotron radius, $a_H \equiv (\hbar c/eH)^{1/2}$, where H is the strength of the magnetic field. At a field of 10 kG, a_H is equal to 485 Bohr radii. The calculation will certainly have to be modified at magnetic fields so strong that a_H is comparable to a Bohr radius ($H \approx 2.35 \times 10^9$ G).

Since the wavelength of the detached electron is large compared to the range of the force between electron and neutral atom, we neglect the final-state interactions between the detached electron and the atom. The short range of the interaction is responsible for the qualitative difference between photodetachment and photoionization both at zero magnetic field and at large magnetic field.[8] We expect that the inclusion of final-state interactions would primarily modify the cross section by a multiplicative scale factor, provided we are sufficiently near threshold, as is the case in zero magnetic field.

The negative ion undergoes a periodic cyclotron motion in the magnetic field, which is slow compared to that of a free electron because of its much greater mass. If it were illuminated continuously by monochromatic light, this motion would create discrete sidebands of the light frequency in the frame of the ion. However, in the experiment, the ions were not illuminated continuously for a time which was long compared to the cyclotron period, because their axial motion carried them across the beam of light in a short time. In this case the effect of the motion is to Doppler broaden the features of the cross section rather than to create a discrete sideband structure.

In addition, there is a significant broadening due to the motional electric field. These effects are calculated under the assumption of a Maxwell-Boltzmann velocity distribution. The finite bandwidth of the light and the finite transit time of the ion across the beam of light cause a broadening which is small compared with the motional broadening for the experimental conditions of Ref. 1.

III. THRESHOLD STRUCTURE FOR A STATIONARY ION

We express the electronic wave functions in terms of a coordinate system whose origin is at the nucleus of the ion. The problem of an electron interacting with a heavy neutral core in the presence of a magnetic field is not exactly separable into relative and center-of-mass coordinates.[9] In this section we assume that the Hamiltonian is separable. In Sec. IV we include the effects of the motional electric field, which is the largest of the mixed terms.

We calculate the cross section by using first-order time-dependent perturbation theory in the form of the golden rule. The perturbation which causes transitions is of the form

$$V \cos\omega t \equiv -\vec{\mathcal{E}}_0 \cdot \vec{\mathrm{P}} \cos\omega t \,, \tag{1}$$

where $\vec{\mathcal{E}}_0$ is the electric-field vector and $\vec{\mathrm{P}}$ is the electric-dipole moment operator. The transition rate from an initial state $|i\rangle$ with energy E_i to a final state $|f\rangle$ with energy E_f, which is part of a continuum, is

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \frac{|\langle f|V|i\rangle|^2}{4} \rho(E_f) \,, \tag{2}$$

where $\rho(E_f)$ is the density of final states, and the energy-conservation condition is $E_i + \hbar\omega = E_f$. The cross section is defined as the transition rate per unit flux of photons, so it is given by

$$\sigma_{i\to f} = (8\pi\hbar\omega/\mathcal{E}_0^2 c)\Gamma_{i\to f} \,. \tag{3}$$

In the absence of the magnetic field, the bound p electron in the negative ion can be promoted to a continuum s or d state. Near threshold the d state is suppressed by the angular momentum barrier. The matrix element for a transition to an s state is independent of the energy in the final state to first order.[2] The density of final states is proportional to k (where k is the momentum in the center-of-mass frame). Thus the cross section is proportional to k, which is proportional to $(\nu - \nu_0)^{1/2}$, where $h\nu$ is the energy of the incident photon and $h\nu_0$ is the threshold energy. This result is in agreement with the prediction of Wigner[10] for production of a pair of particles in an s state with no long-range interaction. Experimentally, the prediction has been found to be valid well beyond the range of energies used in the experiments on magnetic-field-dependent structure.[11] Physically, the result of the detachment process in the magnetic field is to produce an electron which is localized in a region small compared to a cyclotron radius and traveling outward from the neutral atom with equal probability in all directions. The transition matrix element thus involves the evaluation of the final-state wave function at distances small compared to the zero-point cyclotron radius a_H.

If we neglect final-state interactions, we can take the wave function of the detached electron to be that of a free electron in a homogeneous magnetic field. We use the symmetric gauge $\vec{\mathrm{A}} = \frac{1}{2}\vec{\mathrm{H}} \times \vec{\mathrm{r}}$, so that m, the azimuthal component of angular momentum, is preserved as a good quantum number. In cylindrical coordinates the eigenfunctions take the form[4]

$$\psi=(2\pi)^{-1/2}R_{nm}(\rho)e^{im\phi}e^{ik_z z/\hbar}\,, \tag{4}$$

with energies given by

$$E=\hbar\omega_H(n+\tfrac{1}{2}|m|+\tfrac{1}{2}m+\tfrac{1}{2})+k_z^2/2M\,, \tag{5}$$

where $\omega_H=eH/Mc$ is the cyclotron frequency, M is the mass of the electron, and n is the radial quantum number (n_ρ of Ref. 4). The z axis is defined by the direction of the magnetic field, and k_z is the momentum in the z direction.

An alternative formulation of the problem can be made in terms of the quantum numbers n_+ and n_- which take all integer values greater than or equal to zero.[12] They are related to n and m by

$$m=n_+-n_- \tag{6}$$

and

$$\begin{aligned} n&=n_+ \quad \text{if } m\leqslant 0\\ &=n_- \quad \text{if } m\geqslant 0\,. \end{aligned} \tag{7}$$

A virtue of this formulation is the straightforward physical interpretation of n_+ and n_-. Classically, $(2n_+)^{1/2}a_H$ is the radius of the cyclotron orbit and $(2n_-)^{1/2}a_H$ is the distance of the center of the orbit from the z axis. The energy, excluding the motion in the z direction, is simply $\hbar\omega_H(n_++\frac{1}{2})$.

For $\rho\ll a_H$, the normalized radial functions written in terms of n and m have the form

$$R_{nm}(\rho)\cong\frac{1}{a_H|m|!}\left(\frac{(n+|m|)!}{n!}\right)^{1/2}\left(\frac{\rho}{2^{1/2}a_H}\right)^{|m|}\,. \tag{8}$$

We note that the only functions with nonzero probability density at the origin are those with $m=0$, and that this density is independent of n. Since the parity must change in an electric-dipole transition, and since the electron is making a transition from a p state, the final state must have even parity, and is given, in our approximation, by

$$\psi_n=(2\pi)^{-1/2}R_{n0}(\rho)\cos(k_z z/\hbar)\,, \tag{9}$$

with energy

$$E=\hbar\,\omega_H(n+\tfrac{1}{2})+k_z^2/2M\,. \tag{10}$$

It is not at all surprising that $m=0$ states are the ones produced by the photodetachment since these states transform smoothly into the zero field s-wave states as the magnetic field is decreased. Note that these states have $n_+=n_-$. They can be viewed as a superposition of cyclotron orbits for which the radius equals the distance of the center from the origin, i.e., they are composed of cyclotron orbits which intersect the origin.

Since we are considering transitions to cyclotron states, the density-of-states factor in the cross section comes from the one-dimensional continuum in the z direction and is proportional to $1/k_z$ independent of n. For small k_z, the matrix element in Eqs. (2) goes to a constant value so the cross section is proportional to $1/k_z$, independent of n.

The cross section, as a function of the frequency of the light $\nu=\omega/2\pi$, for transitions from a particular magnetic sublevel of the S^- ion to a particular magnetic sublevel of the S atom and spin orientation of the detached electron, has the form

$$\sigma(\nu)=\sum_{n=0}^{n_{\max}}\sigma_n(\nu)=\frac{D\nu}{a_H^2}\sum_{n=0}^{n_{\max}}(\nu-\nu_n)^{-1/2}\,, \tag{11}$$

where

$$\nu_n=\nu_0+(n+\tfrac{1}{2})\hbar\omega_H/2\pi\,, \tag{12}$$

and D is independent of ν and H. The energy of the initial threshold $h\nu_0$ is a function of the magnetic field and the particular levels involved because of the Zeeman effect in the initial and final states. The number $n_{\max}$ is defined as the largest integer n for which $\nu-\nu_n$ is positive. This cross section is graphed in Fig. 1.

In zero magnetic field, as noted earlier, the cross section near threshold is proportional to $(\nu-\nu_0)^{1/2}$. The cross section of Eq. (11) must approach this behavior at low magnetic fields. Let us suppose that we can only measure the cross

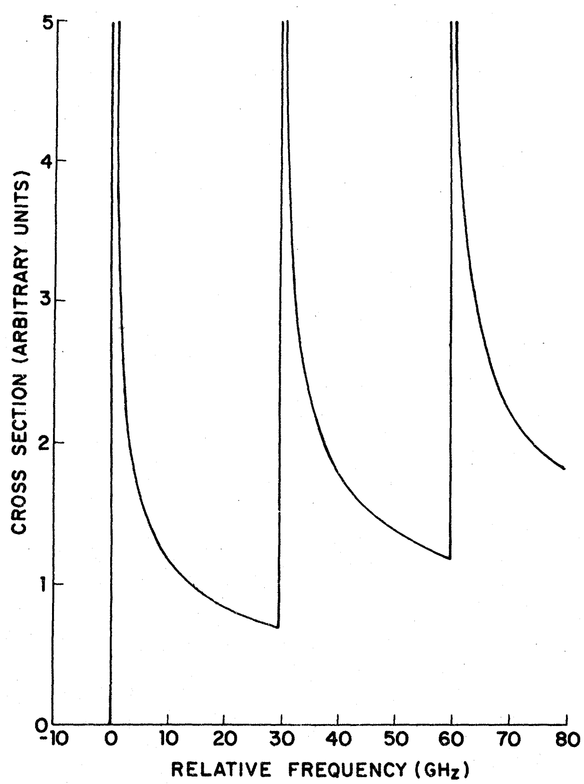

FIG. 1. Photodetachment cross section near threshold in a magnetic field of 10.7 kG described by Eq. (11). The broadening effects due to motion of the ion are not included.

section with a finite experimental resolution $\Delta\nu$, where $\Delta\nu/(\nu-\nu_0)\ll 1$. We decrease the magnetic field so that $\Delta\nu \gg \omega_H/2\pi$, so that we cannot resolve the spikes in the cross section. For a fixed frequency ν, $n_{\max}$ becomes very large, so that we can approximate the sum by an integral in the following way:

$$\sigma(\nu)=\frac{D\nu}{a_H^2}\sum_{n=0}^{n_{\max}}(\nu-\nu_n)^{-1/2}\rightarrow\frac{2\pi MD\nu}{\hbar}\int_{\nu_0}^{\nu}(\nu-\nu')^{-1/2}d\nu$$

$$=\frac{4\pi MD\nu}{\hbar}(\nu-\nu_0)^{1/2}. \quad (13)$$

Thus we recover the Wigner law. Further, we can evaluate the constant factor D in the formula for the cross section in a magnetic field in terms of the cross section in zero field, which may be easier to calculate or measure.

IV. EFFECTS OF THE VELOCITY OF THE ION

The preceeding discussion has neglected effects due to the motion of the negative ion in the magnetic field. We treat this motion classically. For the experimental conditions of Ref. 1 there are two significant effects: the Doppler effect and the motional Stark effect. Only the Doppler effect was considered in the original analysis of Ref. 1. These two effects each cause a broadening of the structure of the cross section of about 1 GHz.

The Doppler effect simply shifts the frequency of the light in the frame of the ion by the amount $(-\vec{v}\cdot\hat{k}\nu/c)$, where $\vec{v}$ is the velocity of the ion, $\hat{k}$ is the unit vector in the direction of propagation of the light, and ν is the frequency of the light in the laboratory frame. In the experiment, the direction of propagation of the light was always perpendicular to the magnetic field.

In a coordinate system moving with the velocity $\vec{v}$ of the center of mass of the ion, which is the most appropriate one for considering the details of the photodetachment process, a motional electric field $\vec{\mathcal{E}}=\vec{v}\times\vec{H}/c$ is present. Therefore, we should use as the final-state wave functions of the detached electron the energy eigenfunctions for an electron in crossed electric and magnetic fields.

We define a coordinate system whose origin is the center of mass of the ion at the moment of detachment and which moves with respect to the laboratory frame at the velocity $\vec{v}$ of the center of mass of the ion at the moment of detachment. The orientation of this frame is such that $v_x>0$, $v_y=0$, and the magnetic field is along the z axis.

For this problem, it is convenient to use the Landau gauge for the vector potential ($A_x=-Hy$, $A_y=A_z=0$).[4] The motional electric field is $\vec{\mathcal{E}}=-(v_x/c)H\hat{y}\equiv-\mathcal{E}\hat{y}$. The Hamiltonian for an electron of charge $-e$ and mass M in this combination of electric and magnetic fields is

$$\mathcal{H}=(1/2M)[(P_x-eHy/c)^2+P_y^2+P_z^2]-e\mathcal{E}y. \quad (14)$$

We can assume a solution of the form

$$\psi=\exp[(i/\hbar)(k_x x+k_z z)]\chi(y). \quad (15)$$

The Schrödinger equation for χ is

$$\frac{-\hbar^2}{2M}\frac{d^2\chi}{dy^2}+[\tfrac{1}{2}M\omega_H^2(y-y_0)^2-e\mathcal{E}y]\chi=(E-k_z^2/2M)\chi, \quad (16)$$

where $y_0=ck_x/eH$ and E is the total energy eigenvalue. This can be rewritten as

$$\frac{-\hbar^2}{2M}\frac{d^2\chi}{dy^2}+\tfrac{1}{2}M\omega_H^2(y-y_0-v_x/\omega_H)^2\chi$$

$$=(E-k_z^2/2M+M\omega_H v_x y_0+\tfrac{1}{2}Mv_x^2)\chi, \quad (17)$$

which is the equation of the simple harmonic oscillator. The energy eigenvalues are

$$E(n,k_z,v_x,k_x)=(n+\tfrac{1}{2})\hbar\omega_H+k_z^2/2M$$
$$-M\omega_H v_x y_0-\tfrac{1}{2}Mv_x^2, \quad (18)$$

and the eigenfunctions are

$$\chi_n(y)=\psi_n(q)=\frac{1}{\pi^{1/4}a_H^{1/2}(2^n n!)^{1/2}}e^{-q^2/2}H_n(q), \quad (19)$$

where $n=0, 1, 2, \ldots$, $q=(y-y_0-v_x/\omega_H)/a_H$, and H_n is the Hermite polynomial of order n.

This wave function corresponds to a classical orbit of an electron which is undergoing an $\vec{E}\times\vec{H}$ drift with velocity $-v_x$. In the laboratory frame the neutral atom moves off at velocity $\vec{v}$ and the electron undergoes cyclotron motion around a center whose x and y coordinates are fixed.

We now use the golden rule to calculate the transition rate from the initial bound state $\psi_i(\vec{r})$ to a final state of definite n. As before, we approximate the final-state wave function by its value at the origin for the calculation of the transition matrix element and ignore final-state interactions. The matrix element is

$$\int\psi_i^*(\vec{r})\hat{\epsilon}\cdot\vec{P}\chi_n(y)\exp[(i/\hbar)(k_x x+k_z z)]d^3r$$

$$\cong\chi_n(0)\int\psi_i^*(\vec{r})\hat{\epsilon}\cdot\vec{P}d^3r\equiv\chi_n(0)S, \quad (20)$$

where $\hat{\epsilon}$ is the unit polarization vector. By summing over all final states of different k_x and k_z, we obtain the following expression for the cross section for photodetachment by photons of energy $\hbar\omega=h\nu$:

$$\sigma_{i\to n}=\frac{2\pi\nu|S|^2}{\hbar^2 c}\int\int|\psi_n(q_0)|^2\delta(E_f+E_0-h\nu)dk_x dk_z, \quad (21)$$

where

$$E_f=E(n, k_z, v_x, k_x),\quad q_0=-(y_0+v_x/\omega_H)/a_H, \quad (22)$$

and E_0 is the threshold photodetachment energy.

For the special case $v_x=0$, the integration can be carried out very simply.

$$\sigma_{i\to n}=\frac{2\pi\nu|S|^2}{\hbar^2 c}\left(\frac{2M}{h\nu-E_0-(n+\frac{1}{2})\hbar\omega_H}\right)^{1/2}$$

$$\times\int|\psi_n(q_0)|^2dk_x$$

$$=\frac{2\pi eH\nu|S|^2}{\hbar^2c^2}\left(\frac{2M}{h\nu-E_0-(n+\frac{1}{2})\hbar\omega_H}\right)^{1/2}. \quad (23)$$

This is consistent with Eq. (11), provided we identify E_0 as $h\nu_0$. This energy difference includes the Zeeman shifts of the initial and final states.

For $v_x>0$, the integration is more complicated, but it can still be done analytically. Doing the integration over k_x first, we have

$$\sigma_{i\to n}=\frac{2\pi\nu|S|^2}{\hbar^2cv_x}\int|\psi_n(z+t)|^2dk_z\,, \quad (24)$$

where

$$z\equiv[E_0+(n+\tfrac{1}{2})\hbar\omega_H+\tfrac{1}{2}Mv_x^2-h\nu]/M\omega_Ha_Hv_x\,, \quad (25)$$

$$t\equiv k_z^2/2M^2\omega_Ha_Hv_x\,. \quad (26)$$

Changing the variable of integration to t, we have

$$\sigma_{i\to n}=\frac{2\pi\nu|S|^2M}{\hbar^2c}\left(\frac{2\omega_Ha_H}{v_x}\right)^{1/2}\int_0^\infty t^{-1/2}|\psi_n(z+t)|^2dt\,. \quad (27)$$

This can be reduced to a sum of terms involving parabolic cylinder functions with the aid of the following integral[13]:

$$\int_0^\infty t^{\lambda-1}\exp[-(t^2/2+zt)]dt=e^{z^2/4}\Gamma(\lambda)D_{-\lambda}(z)\,, \quad (28)$$

$$\mathrm{Re}\lambda>0.$$

The parabolic cylinder functions are tabulated in Ref. 14.

Note that the importance of the motional electric field depends upon the ratio of $\frac{1}{2}Mv_x^2$, which is the kinetic energy measured in the lab frame that the electron has when detached at threshold, to the cyclotron energy $\hbar\omega_H$. For the experimental conditions of Ref. 1, $\frac{1}{2}Mv_x^2/h$ was typically 0.3 GHz.

This partial cross section must be averaged over a Maxwell-Boltzmann velocity distribution. The parameter v_x is equal to the projection of the velocity of the ion on the laboratory x-y plane. In the frame of the moving ion, the photons have the Doppler-shifted frequency

$$\nu=\nu_{\mathrm{lab}}(1-\vec{v}\cdot\hat{k}/c) \quad (29)$$

if they have the frequency ν_{lab} in the laboratory frame. The magnitude of the Doppler shift was typically about 1.2 GHz. For light propagating perpendicular to the z axis, the velocity-averaged cross section is

$$\langle\sigma_{i\to n}(\nu_{\mathrm{lab}})\rangle_{\mathrm{av}}=\frac{1}{\pi v_0^2}\int_0^{2\pi}d\theta\int_0^\infty dv\,v\,\exp\left(\frac{-v^2}{v_0^2}\right)\sigma_{i\to n}(\nu,v_x), \quad (30)$$

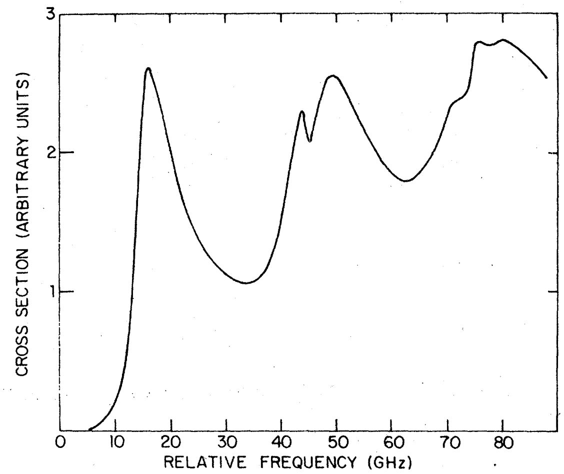

FIG. 2. Photodetachment cross section near threshold in a magnetic field of 10.7 kG as described by Eq. (30), summed over n, for a transition to a final state of a particular m and m_e. The most probable velocity $v_0=7\times10^4$ cm/sec. The broadening effects of the ion motion are clearly present.

where

$$v_0=(2k_BT/M_i)^{1/2}\,,$$

$$\nu=\nu_{\mathrm{lab}}(1-(v/c)\cos\theta)\,,$$

and

$$v_x=v\,. \quad (31)$$

M_i is the mass of the ion, T is the temperature, and k_B is Boltzmann's constant. Figure 2 shows the velocity-averaged cross section for $v_0=7\times10^4$ cm/sec summed over $n=0$, 1, and 2.

V. ANGULAR MOMENTUM WEIGHTING FACTORS

In zero field one would observe a single threshold for transitions from a particular fine-structure level of the S^- ion to a particular fine-structure level of the S atom. The presence of the magnetic field increases the number of thresholds in two different ways. First, the wave function of the detached electron can take values of the cyclotron quantum number $n=0$, 1, 2,... . Second, the fine-structure levels of the S^- ion and the S atom each split up into $2J+1$ magnetic sublevels, where J is the total angular momentum of the ion or atom, and the spin of the detached electron can be parallel or antiparallel to the field.

Orbital angular momentum is not a good quantum number for a free electron in a magnetic field. However, for radial distances much less than a_H from the center of the ion, the wave function of the detached electron is not much affected by the magnetic field. For the calculation of the transi-

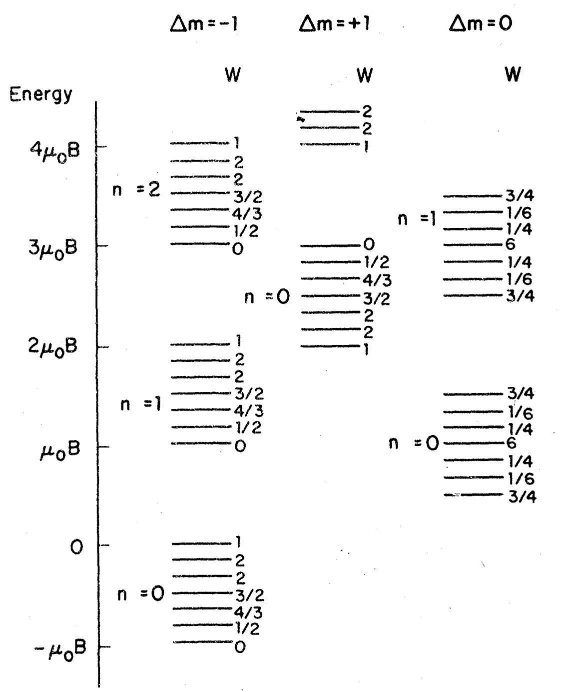

FIG. 3. Energy of onset for each of the Zeeman components of the $^2P_{3/2} \rightarrow {}^3P_2$ photodetachment transition is indicated relative to the location of the threshold at zero magnetic field. Only the electron radial cyclotron quantum number is given for each group of transitions. The weights (W) indicated for each transition are obtained by standard angular momentum coupling techniques appropriate for s electrons in the final state.

tion matrix element, this is the only region that is important, since it is the only region where there is appreciable overlap between the initial- and final-state wave functions. Therefore, for the following discussions, we can treat the wave function of the detached electron as if it were an s wave, just as we would at zero magnetic field.

We wish to calculate the relative weights of transitions between individual magnetic sublevels of the initial and final states. We assume that LS coupling is valid for the S^- ion and the S atom. The initial state is denoted by

$$|i\rangle \equiv |p^5(^2P)JM\rangle\,, \tag{32}$$

where J is the total angular momentum quantum number and is equal to $\frac{1}{2}$ or $\frac{3}{2}$, and M is its z component. In the final state, the atom is in a ^3P_j state, where j can be 0, 1, or 2, and the detached electron is effectively in a $^2S_{1/2}$ state. We denote this state by

$$|f\rangle \equiv |p^4(^3P)jm;(^2S)\tfrac{1}{2}m_e\rangle\,, \tag{33}$$

where j is the total angular momentum of the atom, m is its z component, and m_e is the z component of the free-electron's spin. The relative transition strengths are given by the absolute square of the matrix element of the electric dipole operator $P_q^{(1)}$ between the initial and final states. The polarization index q is equal to 0 for π polarization and to ± 1 for circularly polarized light propagating along the z axis. For σ polarization we sum the contributions from $q=\pm 1$.

In order to calculate the matrix element, we insert a complete set of states $|(L'S')J'M'\rangle$, where the system of the atom and electron is described in terms of LS coupling, and which must then be projected onto the final state, which is described in terms of jj coupling. We have

$$\langle f|P_q^{(1)}|i\rangle = \sum \langle p^4(^3P)jm;(^2S)\tfrac{1}{2}m_e|(j\tfrac{1}{2})J'M'\rangle\langle(j\tfrac{1}{2})J'M'|(L'S')J'M'\rangle\langle(L'S')J'M'|P_q^{(1)}|p^5(^2P)JM\rangle\,. \tag{34}$$

The sum is over all intermediate quantum numbers. By using the Wigner-Eckart theorem and expressing the angular momentum coupling coefficients in terms of Wigner 3-j and 6-j symbols, we obtain

$$\langle f|P_q^{(1)}|i\rangle = (-1)^{j+J-1/2}[2(2j+1)(2J+1)]^{1/2}\langle f\|P^{(1)}\|i\rangle \times \sum_{J'M'}(2J'+1)\begin{pmatrix} J' & 1 & J \\ -M' & q & M\end{pmatrix}\begin{pmatrix} j & \frac{1}{2} & J' \\ m & m_e & -M'\end{pmatrix}\begin{Bmatrix} 1 & 1 & 1 \\ J & \frac{1}{2} & J'\end{Bmatrix}\begin{Bmatrix} 1 & 1 & j \\ \frac{1}{2} & J' & \frac{1}{2}\end{Bmatrix}, \tag{35}$$

where the reduced matrix element $\langle f\|P^{(1)}\|i\rangle$ is independent of J, M, j, m, and m_e.

For the case ($J=\frac{3}{2}$, $j=2$), which was observed in the experiments, the sum reduces to a single term with $J'=\frac{3}{2}$. The relative weights of transitions within this manifold are given by

$$|\langle f|P_q^{(1)}|i\rangle|^2 \propto \left|\begin{pmatrix} \frac{3}{2} & 1 & \frac{3}{2} \\ -M' & q & M\end{pmatrix}\begin{pmatrix} 2 & \frac{1}{2} & \frac{3}{2} \\ m & m_e & -M'\end{pmatrix}\right|^2, \tag{36}$$

where $M'=q+M=m+m_e$, and all irrelevant constant factors have been omitted. The relative weights and Zeeman level structure are illustrated in Fig. 3, where $\Delta M = q$.

The correct weighting of cross sections by the angular momentum coupling coefficients is essential to the prediction of the photodetachment cross section as a function of the light frequency and polarization. For example, in the case of σ polarization, the overlapping of the different partial cross sections would wash out the second bump in the total cross section if all transitions were given equal weight.

VI. COMPARISON OF THE THEORY WITH EXPERIMENT

The experiment of Ref. 1 measures the depletion by photodetachment of a gas of S^- ions. The light frequency is selected to probe the threshold for detachment from the S^- $^2P_{3/2}$ level. At the light intensities used, the depletion of the $^2P_{1/2}$ level is complete. The experimental data is analyzed in terms of the fraction $F(\nu)=N(\nu)/N(\nu')$ where $N(\nu)$ is the total number of ions that survive illumination by light of frequency ν, and ν' is a frequency below the onset of the $^2P_{3/2}$ collection of thresholds. This fraction is related to the photodetachment cross section by

$$F(\nu)=\sum_i f_i \exp[-A\sigma_i(\nu)]\,, \tag{37}$$

where f_i is the initial fraction population of the state $m_j=i$ ($\Sigma f_i=1$), A is proportional to the integrated light intensity, and $\sigma_i(\nu)$ is the total cross section for photodetachment from the state $m_j=i$ at frequency ν. For detachment from the $^2P_{3/2}$ level,

$$\sigma_i(\nu_{\rm lab})\propto\sum_k \langle\sigma_{i\to k}(\nu_{\rm lab})\rangle_{\rm av}\left|\begin{pmatrix}\frac{3}{2} & 1 & \frac{3}{2}\\ -M' & q & M\end{pmatrix}\begin{pmatrix}2 & \frac{1}{2} & \frac{3}{2}\\ m & m_e & -M'\end{pmatrix}\right|^2, \tag{38}$$

where i labels the initial state, k labels the final state, and the other quantum numbers are the same as in Eq. (36). The summation is over all possible final quantum numbers, including the cyclotron quantum number n. For a given set of parameters $\nu_{\rm lab}$, H, and v_0; $\langle\sigma_{i\to k}(\nu_{\rm lab})\rangle_{\rm av}$ is evaluated as follows. The polarization of the light and the value of H determine the relative frequencies of the available thresholds. For each threshold the two-dimensional velocity average, as described in Sec. IV, is computed by a numerical integration. The effect of Doppler and motional-electric-field broadening can be seen by comparing the $v_0=0$ cross section of Fig. 1 with the $v=7\times10^4$ cm/sec cross section shown in Fig. 2. The

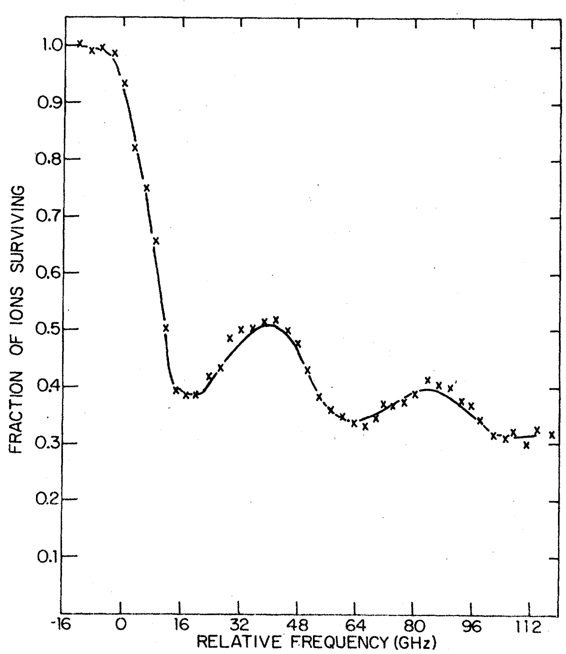

FIG. 4. Photodetachment data near the $^2P_{3/2}\to{}^3P_2$ threshold. The fraction of ions surviving illumination is plotted as a function of light frequency (with an arbitrary zero). The data shown here are for light of π polarization at 15.7 kG. The data points are plotted together with a predicted curve which has three parameters adjusted to give reasonable agreement with the data. The fluctuation in ion number at each point is approximately 1%.

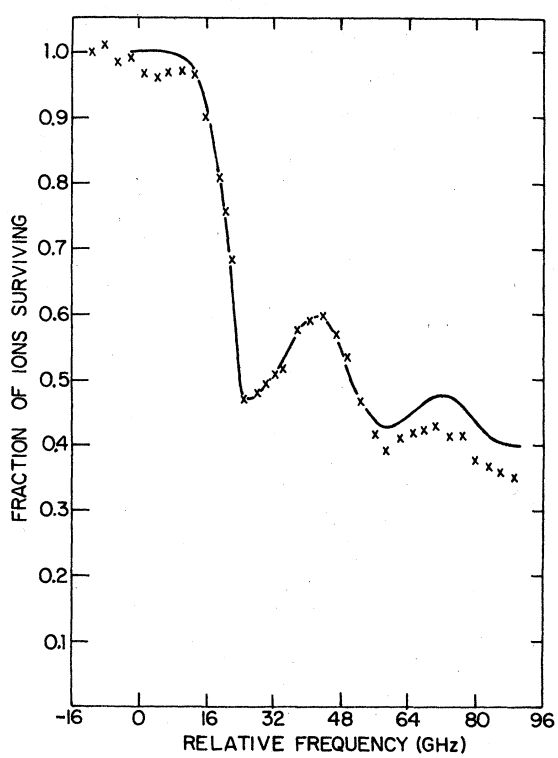

FIG. 5. Photodetachment data at 10.7 kG with π-polarized light (see Fig. 4 caption). The detachment for relative frequencies below 14 GHz could be caused by the admixture of a few percent of σ-polarized light, but the addition of such an admixture to the theoretical prediction does not enhance the overall agreement and, in particular, does not eliminate the discrepancy at the second maximum.

fraction $F(\nu)$ is then computed as a function of $\{f_i\}$ and A.

Measurements were made at magnetic fields ranging from 6 to 15.7 kG, with light of σ and π polarization, and for various levels of integrated light intensity. For each field and polarization the parameters $\{f_i\}$, v_0, and A were adjusted to give the best agreement between the theoretical and experimental $F(\nu)$ curves. Figures 4, 5, and 6 compare the experimental and calculated curves for fields of 15.7, 10.7, and 6 kG and π polarization. Figure 7 shows the experimental and calculated curves for 10.7 kG and σ polarization. The qualitatively different shapes of the π and σ curves for a given H result both from the different available thresholds and from the angular momentum factors assigned to each threshold. In particular the second maximum in the curve for σ polarization, as shown in Fig. 7, would be washed out if each transition were given equal weight. In addition the theory predicts the shift of the onset of the $n=0$ threshold for π and σ polarization. Figures 8 and 9 show the data and the calculated curves at 10.7 kG for both polarizations. The theory predicts a shift of approximately $\frac{2}{3}\nu_H = 20$ GHz. ($\nu_H = \omega_H/2\pi$.) The observed shift is 18.2 GHz. The discrepancy is small compared to the approximately 7-GHz width of the velocity-broadened cross-section peak (Fig. 2) but seems to be outside of statistical errors. The ion temperature which best reproduces the data is 940 °K $=0.08$ eV$/k_B$ which corresponds to $v_0 = 7\times 10^4$ cm/sec. There is no evidence of alignment of the initial ion population, which would result in unequal values of f_i for different $|i|$. It is clear that the theory agrees well with the data.

The theory presented in this paper is an improvement over that of Ref. 1 in that it includes motional-electric-field broadening. With the additional broadening the predictions agree better with the data in three respects: the ion temperature inferred from the data has a value consistent with ion production and trapping conditions; the overall agreement of the prediction with the data is improved; and in particular the predictions reproduce the data better in the vicinity of the $n=0$ cross-section maximum.

In a few data runs the amplitude of the oscillations in ion number is somewhat smaller than the theory predicts (see, for example, Fig. 5). This could possibly be due to collisional effects which are not included in the present theory. Collisions clearly play an important role in the loss of S^- ions from the trap where the dominant process is assumed to be $S^- + OCS \rightarrow S_2^- + CO$. However, attempts to verify the presence of collisional effects in the photodetachment data produced am-

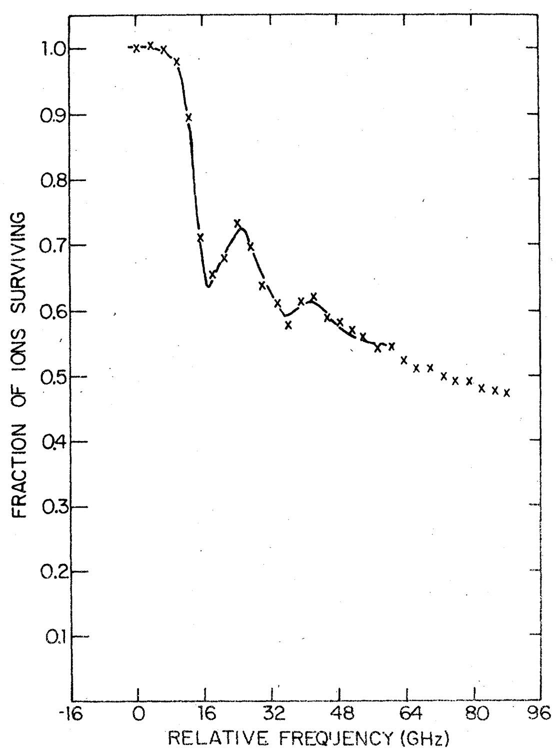

FIG. 6. Photodetachment data at 6 kG with π-polarized light (see Fig. 4 caption).

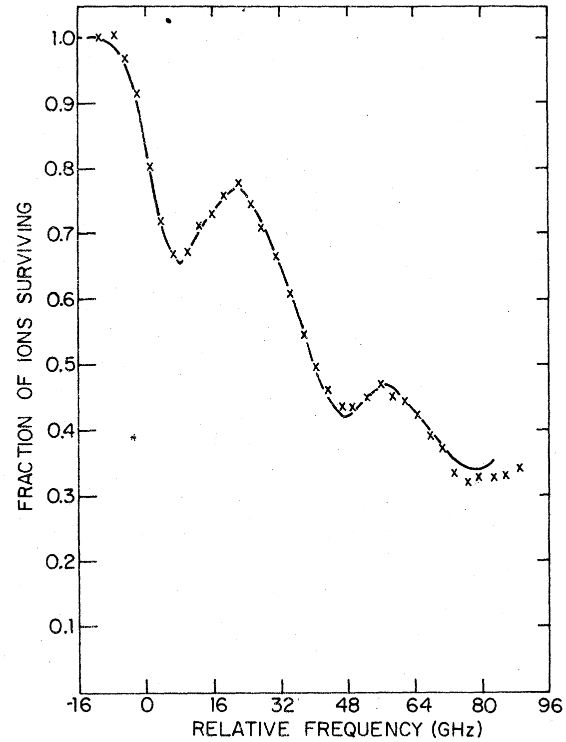

FIG. 7. Photodetachment data at 10.7 kG with σ-polarized light (see Fig. 4 caption).

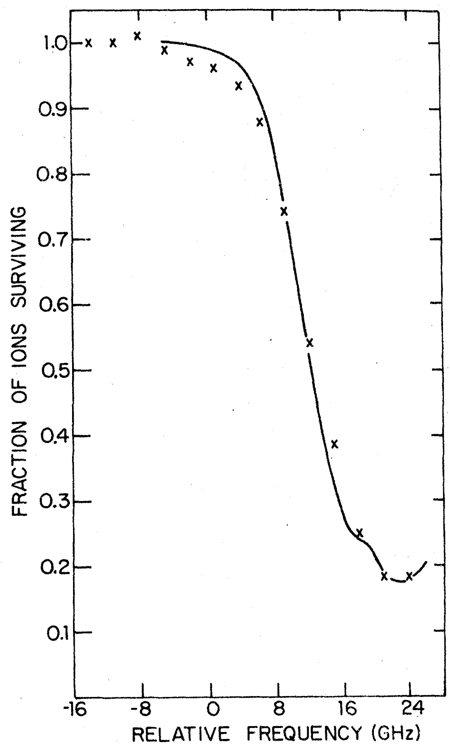

FIG. 8. Photodetachment data at 10.7 kG with π-polarized light. The possible admixture of a few percent of σ-polarized light producing detachment at relative frequencies less than 7 GHz does not significantly affect the location of the features from 14 to 26 GHz.

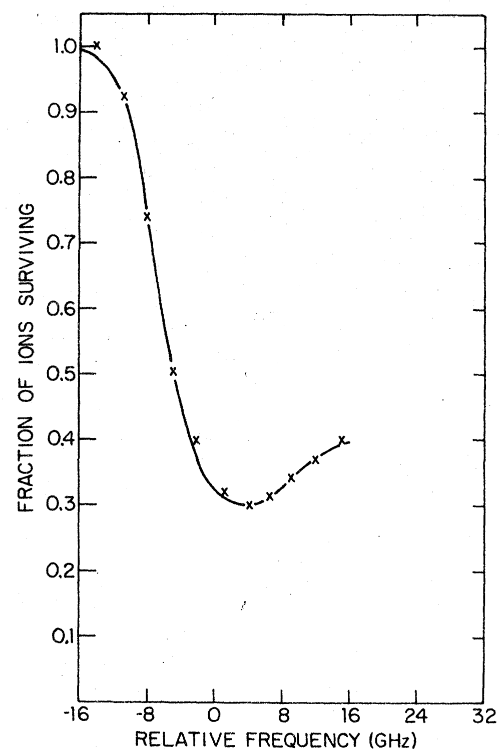

FIG. 9. Photodetachment data at 10.7 kG with σ-polarized light with the same frequency scale as in Fig. 8. These data, together with those shown in Fig. 8 show the polarization dependence of the $n=0$ thresholds.

biguous results. It is clear that not all the relevant parameters are carefully controlled in the experiments. In a few data runs illumination of the ions at a frequency below the $^2P_{3/2}$ threshold produced more ions than were lost through photodetachment of ions in the $^2P_{1/2}$ state. These excess ions were present in some of the 10.7-kG data runs including those presented in Figs. 5 and 7. We do not have a detailed explanation of this effect.

VII. EXTENSION OF THE THEORY TO OTHER NEGATIVE IONS

Our theory, which was developed for S^-, should be equally valid for O^- and Se^-, which are similar in structure. More generally, a cross section with the form of Eq. (11) should be valid whenever we consider the photodetachment of a p electron, although the details of the angular momentum coupling may vary.

We can generalize our result to cases where, in zero magnetic field, the detached electron is in a state of arbitrary orbital angular momentum l. The square of the transition matrix element of Eq. (2) in zero magnetic field is proportional to $(\nu-\nu_0)^l$, as a consequence of the Wigner law. This is still true in the presence of a weak enough magnetic field, since the final-state wave function is not modified very much in the region of space where it overlaps the initial-state wave function. However, the density-of-states factor depends upon the behavior of the wave function at large distances. In zero magnetic field it is proportional to $(\nu-\nu_0)^{1/2}$, while in a finite magnetic field it is proportional to the function of Eq. (11). Therefore, for transitions between particular magnetic sublevels, we have

$$\sigma(\nu) \propto \nu(\nu-\nu_0)^l \sum_{n=0}^{n_{\max}} (\nu-\nu_n)^{-1/2} . \qquad (39)$$

The factor of ν comes from Eq. (3). For example, the photodetachment of an s electron, as in the case of photodetachment of the alkali negative ions, corresponds to the case $l=1$, since the zero field the detached electron is in a p wave. This description does not include the effects of motional broadening.

VIII. CONCLUSIONS

An experiment on the detachment of electrons from negative sulfur ions has motivated the present calculation of the effect of a magnetic field on the photodetachment cross section. It is clear that the agreement between the present theory and experiment is better than that achieved by the simpler description used in Ref. 1. The theory takes into account more fully the broadening of the features of the cross section due to ionic motion. The connection to the zero magnetic field cross section is made explicit. The extension of the theory to the other atomic negative ions is discussed.

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