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Measurement of the hyperfine structure of $^{33}S^-$

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A measurement of the hyperfine structure of a stable atomic negative ion has been made using optical probing of microwave transitions. Hyperfine-split Zeeman resonances were observed using state-selective photodetachment to probe the $^2P_{3/2}$ state of $^{33}S^-$ ions which were stored in a Penning ion trap. The results for the dipole and quadrupole hyperfine constants are $a = 91.49(9)$ MHz and $b = 26.24(23)$ MHz. The potential for further application of the technique is discussed.

I. INTRODUCTION

The spectroscopy of negative ions is a relatively young field, largely due to experimental difficulties presented by the negative ions. The first laboratory photodetachment spectroscopy experiments were reported by Branscomb and Fite in 1954.[1] Since that time, information about electron affinities, fine structure, rotational structure, excited states below and above the detachment threshold, as well as about the photodetachment process itself has been obtained from photodetachment experiments of ever increasing precision.[2,3] Such measurements have reached the resolution where even hyperfine structure is observable.[4] However, precise measurements of hyperfine and Zeeman structure require direct observation of the hyperfine and Zeeman splittings.

In the present experiments microwave transitions in negative ions were observed using the technique of state-selective depletion of stored ions by photodetachment with polarized light before and after driving microwave transitions between selected levels.[5] This technique has been applied previously to the measurement of g_J factors in S^- and O^-.[6] A similar technique, based on state-selective photodissociation, was developed by Dehmelt and Jefferts and used in the first experiments on the hyperfine structure of the $H_2{}^+$ ion.[7] The technique can be applied to the measurement of a variety of rf, microwave, or higher-frequency transitions in atomic and molecular negative ions. We have used it to observe the hyperfine split Zeeman transitions in the $^2P_{3/2}$ state of $^{33}S^-$ and have extracted values for the hyperfine constants of this ion. The only other measurements of microwave transitions in a negative ion were done on the ^4P states of the He^- ion in an experiment by Mader and Novick.[8] Those measurements were based on the existence of experimentally suitable, state-dependent autodetachment lifetimes of the ^4P states and produced results for Zeeman and hyperfine structure.

The measurements reported here used a Penning ion trap to store the ions.[9,10] Containment of the ions in an ion trap where the optical and microwave fields can be applied for periods of several seconds or more has significant advantages. A large photodetachment probability per ion can be achieved with readily available cw laser powers. This allows the production of relatively large population differences in the ions that survive illumination and subsequently allows effective probing of those population differences. More fundamentally, the availability of long times for interrogation with the microwaves creates the potential for very precise measurement.[11] Disadvantages of the ion trap include the difficulty of producing some ion species in the trap, and the small state populations, due to a small number of ions in the sample, in systems such as molecular negative ions where a large number of states may be thermally populated. On the other hand, the sensitivity of detection of ions in the trap means that experiments can be performed with small numbers of ions.

II. EXPERIMENTAL TECHNIQUE

A schematic diagram of the apparatus is shown in Fig. 1. The ions were created using dissociative attachment by directing a 200-nA beam of 2-eV electrons into the ion trap at the same time that isotopically enriched carbonyl sulfide (OCS) was leaked into the vacuum system at a pressure of about 10^{-8} Torr. The OCS sample was prepared from 2 mg of elemental sulfur enriched to approximately 70% ^{33}S. The ions were confined by a potential of -1.5 V applied to the trap end caps and by a static axial magnetic field of 0.96 T. The magnetic field was stabilized by means of a magnetic resonance magnetometer. After the electron beam and the OCS leak were turned off, the number of ions in the trap was measured by driving the axial motion of the ions and observing the currents induced on the ring electrode. Photodetachment

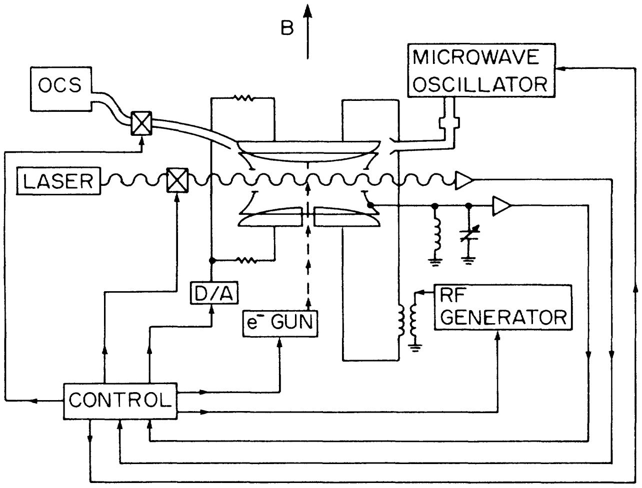

FIG. 1. Schematic diagram of the experimental apparatus. The ion trap is contained in a vacuum system with a base pressure of about 10^{-9} Torr.

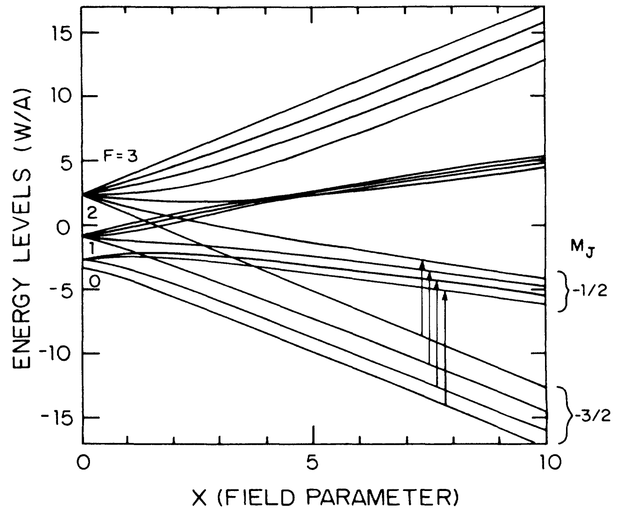

FIG. 2. Energy levels of $^{33}\mathrm{S}^-$ showing the observed transitions. The measurements were carried out at a field of 0.96 T, corresponding to X near 200.

was done using a beam of light from a cw dye laser with linear polarization perpendicular to the magnetic field, an intensity of about 50 mW, and a frequency just above the photodetachment threshold[2,12] near 16 753 cm^{-1}.

From the model of photodetachment in a magnetic field developed by Blumberg, Itano, and Larson,[13] one expects that there should be substantial detachment for all but the $m_J=-\frac{3}{2}$ component of the ground $^2P_{3/2}$ state if the frequency of the light is tuned below the threshold for detachment to the first excited Landau level of the free electron in the magnetic field. This is because the angular momentum selection rules for photodetachment, assuming L-S coupling, result in a probability weighting of zero for a $\Delta m_J=-1$ transition from the $m_J=-\frac{3}{2}$ state of the negative ion. At the laser wavelength below the first excited Landau threshold, the $\Delta m_J=+1$ transition from the $m_J=-\frac{3}{2}$ state is energetically impossible. If the weighting were truly zero, complete polarization of the ions would be possible for cold ions and narrow bandwidth radiation because of the very low rate of collisions in the ion trap. In practice, however, Doppler broadening of the closely spaced Zeeman thresholds and ion collisions with the background gas limit the purity of the state preparation. Furthermore, recent high magnetic field photodetachment experiments on Se^- show significant deviations from the predications of the model of Blumberg *et al.* and, in particular, show a nonzero weighting for the first $m_J=-\frac{3}{2}$ threshold.[14] Nevertheless, for S^-, substantial state selection was achieved by use of the polarization and frequency selective photodetachment scheme.

In our measurement, a $\Delta m_I=0$ transition from the $m_J=-\frac{3}{2}$ levels to the $m_J=-\frac{1}{2}$ levels was driven by irradiating the ion trap with a microwave field with a frequency near 18 GHz. These transitions are illustrated in Fig. 2. Concurrent laser photodetachment made the total ion number remaining in the trap a function of the completeness of the microwave transition. After laser and microwave irradiation, the total ion number was measured by driving the axial motion of the ions as before, and the ratio of this number to that obtained before any photodetachment was recorded as a function of microwave frequency. Despite limited mass resolution in the ion number measurement, the presence of significant numbers of $^{32}\mathrm{S}^-$ ions did not present a problem since the microwave resonances in $^{33}\mathrm{S}^-$ were well separated from those in $^{32}\mathrm{S}^-$. The state-selection scheme made the $m_J=-\frac{3}{2}$ to $m_J=-\frac{1}{2}$ transitions, but not the $m_J=+\frac{1}{2}$ to $m_J=+\frac{3}{2}$ transitions observable. An alternative method of state selection, which allows observation of both sets of $|m_J|=\frac{1}{2}$ to $|m_J|=\frac{3}{2}$ transitions, is to detach and probe with π-polarized light, which can be tuned far above threshold.[5,6] This technique produced signals of somewhat smaller size and was not used in the present measurements.

III. RESULTS AND DISCUSSION

Since $^{33}\mathrm{S}$ is an isotope with $I=\frac{3}{2}$, there are four separate $\Delta m_I=0$, $m_J=-\frac{3}{2}$ to $m_J=-\frac{1}{2}$ transitions. Each of these transitions was measured in each of four data sets. The observed linewidth of these transitions was on the order of 1 MHz. The linewidth is apparently due to the large magnetic field dependence of the transitions, and is somewhat larger than might be hoped for based upon estimated magnetic field inhomogeneities, but magnetic field inhomogeneities or instabilities are almost certainly the primary contributors to linewidth. Because the dominant contribution to the linewidth is due to the magnetic field, the line shape cannot be determined *a priori.* In order to extract a line center and to test how sensitive the result was to assumptions about line shape, each of the lines was fit to both Lorentzian and Gaussian curves, with and without a sloping baseline added to allow for imperfect cancellation of possible drifts in the ion signal. Examples of the results of these fits are shown in Fig. 3

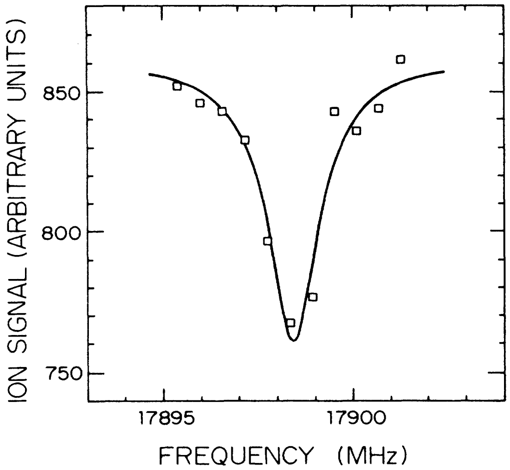

FIG. 3. Example of the data for the $m_I=-\frac{1}{2}$, $m_J=-\frac{3}{2}$ to $m_J=-\frac{1}{2}$ transition in $^{33}\mathrm{S}^-$. The data are shown together with the result of a fit to a Lorentzian curve. Both Lorentzian and Gaussian curves were used as fitting functions in order to extract line centers.

and Fig. 4. The typical uncertainty in a line center obtained in such fits is about 0.1 MHz. This is also the approximate size of the differences in line center produced by the different fitting functions.

The line centers produced by each of the fitting functions were fit to a hyperfine Hamiltonian which included dipole and quadrupole hyperfine structure and nuclear and electronic Zeeman terms. The nuclear g factor was put into the Hamiltonian as a fixed constant. For each set of data, the magnetic field was determined by measuring either the electron cyclotron frequency or the $^{32}\mathrm{S}^-$ Zeeman frequency, or both. These frequencies were also used in the numerical fit. Thus the fit produced a value for either g_J directly or for the ratio $g_J(^{33}\mathrm{S}^-)/g_J(^{32}\mathrm{S}^-)$, as well as values for the magnetic dipole and electric quadrupole hyperfine structure constants. The values obtained for all of these quantities were consistent from run to run within the errors obtained from the fitting program. The average results are $a=91.55(9)$ MHz, $b=26.26(23)$ MHz, and $g_J(^{33}\mathrm{S}^-)/g_J(^{32}\mathrm{S}^-)=1.000\,002(2)$. All of these quantities should be first order insensitive to errors associated with magnetic field inhomogeneities, which were identified as the principle potential source of systematic errors in the measurements[6] of the g_J factor in $^{32}\mathrm{S}^-$. Thus the quoted statistical errors, which are approximately twice the standard deviations obtained from the fits, are reasonable estimates of the total experimental errors. However, the results for the dipole and quadrupole hyperfine constants must be corrected for a small change in apparent size due to the mixing of the fine-structure states in the magnetic field. In the present case, this correction can be obtained simply from second-order perturbation theory if we assume that L-S coupling is valid, and yields the corrected values, $a=91.49(9)$ MHz and $b=26.24(23)$ MHz.

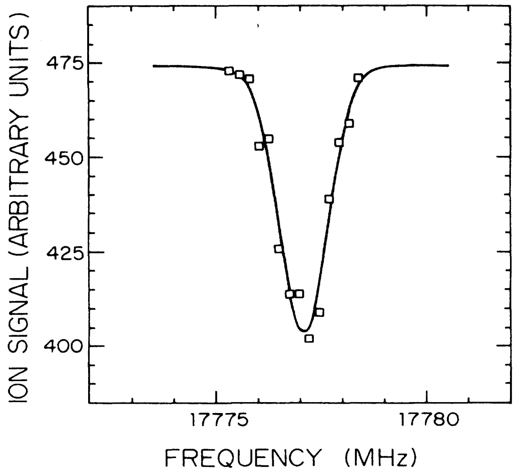

FIG. 4. Example of the data for the $m_I=-\frac{3}{2}$, $m_J=-\frac{3}{2}$ to $m_J=-\frac{1}{2}$ transition. The data are shown with the result of a fit to a Gaussian curve.

The precision of the results for the hyperfine structure constants, while limited by the inhomogeneities and instabilities in the magnetic field, is sufficient to provide meaningful information about the structure of the S^- ion. In the absence of *ab initio* calculations with which to compare, some information about the structure of the S^- ion can be obtained by comparing the hyperfine constants to the constants obtained in measurements on other systems. From an analysis of the quadrupole coupling constants of several molecules containing sulfur, Bird and Townes[15] deduced a quadrupole coupling per p electron for atomic $^{33}\mathrm{S}$ of $-2b=-55$ MHz, with an estimated error or 15% or $b=27.5(41)$ MHz. The agreement of this value with the present result for b in $^{33}\mathrm{S}^-$ suggests that there is no large change in structure between S and S^-. A similar conclusion can be drawn by comparing the measured dipole coupling constant with the value $a=87.9$ MHz estimated for $^{33}\mathrm{S}^-$ by extrapolating from hyperfine measurements on neutral chlorine using the values of the nuclear magnetic moments and using the measured fine-structure constants in S^- and Cl as a measure of the relative sizes of $\langle r^{-3}\rangle$ for the electrons. The closeness of the extrapolated and measured values for the dipole constant demonstrates that any major differences between the structure of the S^- ion and the isoelectronic, neutral Cl atom are reflected as much in the fine structure as in the hyperfine structure.

Since both the quadrupole and dipole hyperfine interactions involve $\langle r^{-3}\rangle$, a value for the quadrupole moment of the $^{33}\mathrm{S}$ nucleus can be obtained from the ratio b/a.[16] The result, without taking into account quadrupole shielding, is $Q=6.62(6)\times10^{-26}$ cm^2, where the error is given includes only the experimental errors in a and b. The relativistic correction included in this number (assumed to be the same as for the neutral atom) is at the same level as the experimental error, about 1%. Sternheimer[17] has estimated a quadrupole shielding factor of 1.052 for neutral S, which suggests that the actual value of Q might be five percent higher or close to 7.0×10^{-26} cm^2. The uncertainty in this number is mainly due to the uncertainty in the shielding correction. An accurate calculation of the electronic structure of S^- would produce a more accurate value for Q. In any case, the presently reported value for the quadrupole hyperfine interaction is the best value for extraction of the nuclear quadrupole moment of ^{33}S.

IV. EXTENSIONS OF THE TECHNIQUE

As discussed above, the resolution of the measurements was limited by the linewidth due to the large and imperfect magnetic field. With or without a better field, it should be possible to measure hyperfine structure with greater resolution in the Penning trap by using an rf triple resonance scheme to make the much less field-dependent $\Delta m_I = \pm 1$, $\Delta m_J = 0$ transitions visible. Alternatively, it is clear that while a large field is necessary for the Penning ion trap and a reasonable field is necessary for g_J-factor measurements, it is clearly not necessary for hyperfine structure measurements. The modest size of the hyperfine structure makes it impossible to use values of the magnetic field corresponding to field-independent transition frequencies in the Penning trap.[11] However, it may be possible to improve the accuracy of the measurements dramatically by using an rf (or Paul) trap for hyperfine structure measurements at low magnetic fields. The polarization dependence of the photodetachment cross section in a modest magnetic field can be used to provide and probe population differences.

Direct hyperfine structure measurements should also be possible in experiments on beams of negative ions. The precision of rf measurements on fast ion beams (with energies of a few keV) will generally be limited by transit time linewidths on the order of 1 MHz. However, ion beams appear to offer at least one significant advantage in such experiments, that advantage being the relative ease of production of a wide number of negative ion species in a discharge source.[18] On the other hand, the limited interaction time with th photodetaching light is potentially a major difficulty in considering rf measurements of negative ions in beams. The photodetachment cross sections can be several orders of magnitude smaller than the resonant excitation cross sections used in rf-optical double resonance experiments on positive ions in beams.[19] The rf signals will be quadratic in the ion detachment fraction, usually a very small quantity. The best geometry for such experiments appears to be that of colinear ion and laser beams. The reduced Doppler widths present in such a geometry would not be significant for state selection based on the polarization dependence of the detachment, but the larger achievable detachment fractions would. Given interaction lengths of 1 m and laser powers of a few watts, detachment fractions on the order of a few tenths of a percent to 1% should be achievable in many circumstances. The cross sections for photodetachment by a transition to an autodetaching state are generally orders of magnitude larger than those for a transition directly to the continuum, and much larger detachment fractions can be readily achieved. Indeed, optical pumping dips due to saturation of an autodetachment transition have been observed.[4] Even without the large transition rates available in this special case, the detachment fractions attainable with a colinear geometry should produce reasonable signals. Thus rf experiments, such as the present hyperfine measurements, can be performed with ease for an appropriate species in an ion trap, and ion traps offer the potential for extremely high precision measurements. However, it also should be possible to carry out such experiments on beams of negative ions. The use of ion beams for rf experiments may make it possible to study species which would be difficult to produce in a trap.

V. CONCLUSIONS

The technique of state-selective photodetachment for probing of microwave transitions has been extended to the measurement of hyperfine structure in a negative ion. The dipole and quadrupole hyperfine structure of the $^{33}S^-$ ion were measured. These constants provide information about the structure of the S^- ion and about the ^{33}S nuclear quadrupole moment. It should be possible to extend the technique to use in measurements on a variety of negative ions, perhaps in ion beams as well as ion traps.

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