

convergence is less rapid as l is increased. It is not even obvious that the octupole polarizability coefficients are converging to the true value.

The forms of the proper Padé approximants to be used for calculating the upper and lower bounds to the dispersion forces have been given elsewhere.² In Table II we give the bounds for all the possible multipole interactions that can be obtained with the dipole, quadrupole, and octupole moments. Along with the moments in Table I the appropriate α_{-1}^l are also needed.⁵ In parentheses we give the percent contribution to the dispersion force coefficient arising from the higher frequencies and oscillator strengths [i.e., the lowest state ($2p$, $3d$, or $4f$) is eliminated from the computations and the coefficient recalculated].

The bounds that result from considering the first five Padé approximants give excellent agreement with those obtained by Bell,⁵ Chan and Dalgarno,⁶ and MacQuarrie, Tereby, and Shire.⁷ It should be noticed that the contributions from the higher states are large as $l_a + l_b$ increases. In the dipole-dipole case the first-excited state predominates while in the quadrupole-octupole and octupole-octupole cases the contribution from higher excited states dominate.

From the results in Table I one sees that as l is increased, higher Padé approximants are needed in order to obtain good transition frequencies. In fact the $[5,4]_\alpha$ approximant gives for the first transition frequency 0.3750 ($l=1$), 0.4457

($l=2$), and 0.4763 ($l=3$), whereas the exact frequencies are 0.3750 ($l=1$), 0.4444 ($l=2$), and 0.4688 ($l=3$). Hence, for larger electronic systems where exact wave functions are not known, one might expect even poorer results for the higher multipole properties. However, for dispersion force calculations the Padé method, though not as rapidly convergent as the total multipole ($l_a + l_b$) is increased, still seems capable of giving excellent bounds for all the significant (through C_{10}) dispersion force coefficients.

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⁹The values for C_8 are the same as given in Ref. 2.

¹⁰See Ref. 7.

Fine Structure of the Helium Negative Ion*

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Fine-structure transitions have been observed in the metastable $(1s2s2p)^4P_J$ state of the negative helium ion $^4\text{He}^-$ using an rf resonance technique. Preliminary determinations have been made of the energy separations: $|E_{5/2} - E_{3/2}| = 825.23 \pm 0.2$ MHz and $|E_{5/2} - E_{1/2}| = 8663 \pm 56$ MHz. We have shown that the $J = \frac{3}{2}$ level lies between the $\frac{5}{2}$ and $\frac{1}{2}$ levels. These results are to be compared with the current theoretical estimates of $E_{5/2} - E_{3/2} = -2030$ MHz and $E_{5/2} - E_{1/2} = -9410$ MHz.

The study of fundamental atomic properties has been especially fruitful when high-resolution rf spectroscopy techniques have been applied to simple systems for which accurate wave functions can be calculated. The work of Lamb and others on the fine structure of hydrogen has provided a cornerstone of quantum electrodynamics as well as the first precise value for the Sommer-

feld fine-structure constant α . Theory and experiment agree to within the experimental accuracy of about 10 ppm for the $^2S_{1/2} - ^2P_{3/2}$ interval in this one-electron system. Higher-precision fine-structure measurements to about 1 ppm have been made in the $(1s2s)^3P$ state of helium by Kponou *et al.*¹ These measurements provide an excellent testing ground for the theory of the

two-electron atom. Suitably accurate nonrelativistic wave functions have been provided by Pekeris, Schiff, and Lifson² and by Schwartz.³ Radiative and relativistic corrections to the fine structure are being evaluated. At the present time there are divergence problems with the second-order relativistic operators, but it is felt that these problems can be overcome.⁴ At such time as this is achieved, the calculation of the 3P_0 - 3P_1 interval will attain an accuracy of about 1 ppm. This will provide a critical test of our understanding of the two-electron system and may provide an improved value for α .

The three-electron system He^- is amenable to fine-structure measurements accurate to 1 ppm or better. In view of the success of calculations for He, it seems possible that accurate wave functions can be obtained for He^- and that our understanding of three-electron atomic systems can be tested on a fundamental level, comparable to that obtained in hydrogen and anticipated in helium.

In this Letter we report preliminary fine-structure values for the $(1s2s2p) {}^4P$ state in He^- of sufficient accuracy to provide a critical test of correlation effects in three-electron wave functions currently available for He^- . If correlation can be understood in this weakly bound state (0.08 eV), it should be well understood in similar states of higher Z . It is also possible that unique three-electron effects can be isolated in He^- since it is especially sensitive to correlation. White and Stillinger⁵ have shown analytically that the wave function for three-electron doublet states can contain logarithmic terms. For the quartet state which we have observed, they expect higher-order terms.

The 4P_J states of He^- decay by autoionization to the ground state of He plus a free electron with an energy of 19.7 eV. The ${}^4P_{5/2}$ state decays via only the tensor spin-spin interaction, while the ${}^4P_{3/2}$ and ${}^4P_{1/2}$ states decay via this interaction and spin-orbit coupling with the short-lived doublets of the same configuration. The measured lifetimes of the $J = \frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ states are 500 ± 200 , 10 ± 2 , and 16 ± 4 μsec , respectively.⁶ Previously, the $\frac{5}{2}$ - $\frac{3}{2}$ interval was estimated to be $|\Delta_{53}| = 1080 \pm 270$ MHz with a Zeeman-quenching technique. The $\frac{5}{2}$ - $\frac{1}{2}$ interval, Δ_{51} , was inaccessible to this technique.

The possibility of a high-precision resonance experiment is suggested by the long lifetimes which would yield a natural resonance width of 10 kHz. State selection, which is needed in order

to detect an rf transition, is provided by the differences in lifetimes.

A beam of He^- , produced from He^+ by double charge exchange in potassium vapor, is directed into a drift tube which contains an rf interaction region and a Faraday-cup ion detector. A population difference evolves between the states both before they enter the rf region and after they leave it. When the $J = \frac{5}{2}$ and $\frac{3}{2}$ states are coupled by an rf field, there is a decrease in the detected ion current. There is a grid in front of the detector held at -20 V to exclude electrons released in flight by autoionization of the ions. The drift tube is wound with a solenoid to provide a static axial magnetic field used to "tune" the transition frequencies via the Zeeman effect. In a search for resonances, the oscillator frequency remains constant and the static magnetic field is swept over a wide range. The rf field can induce a transition between two levels when their separation becomes equal to the applied frequency. Magnetic dipole transitions are allowed between the 4P_J states, with $\Delta J = 0$ (Zeeman transitions) or ± 1 (fine-structure transitions), and $\Delta M = 0$ (axial rf magnetic field) or ± 1 (transverse rf magnetic field).

In Fig. 1, we show the resonant decrease of the ion current as the magnetic field is swept across the $(\frac{5}{2}, -\frac{5}{2})$ to $(\frac{3}{2}, -\frac{3}{2})$ transition. The decrease is 18% of the total current. With 100% square-wave amplitude modulation of the oscillator, a lock-in detector can be used to extract the rf-induced signal from the total ion current. In Fig. 2

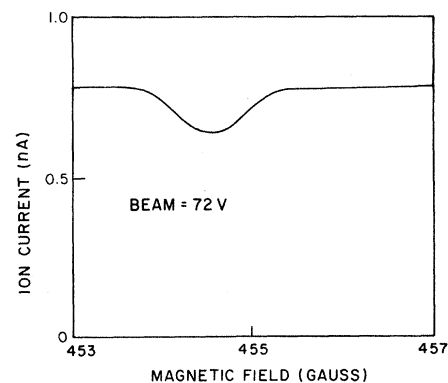


FIG. 1. Resonant decrease in ion current when the $(\frac{5}{2}, -\frac{5}{2})$ to $(\frac{3}{2}, -\frac{3}{2})$ transition is induced by an rf field at 1835 MHz. The rf intensity was adjusted for maximum resonance strength, seen here as 18% of the total current. The transition is tuned through resonance by sweeping the static magnetic field. This transition is labeled D in Fig. 3.

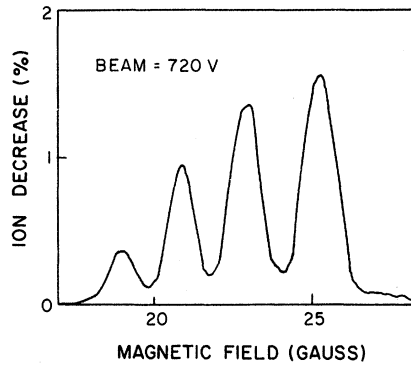


FIG. 2. Fine-structure transitions with $\Delta M = -1$ from $J = \frac{5}{2}$ to $\frac{3}{2}$. They appear at low magnetic field since the oscillator frequency of 777 MHz was only slightly below the zero-field energy separation $|\Delta_{53}| = 825$ MHz.

we show the quartet of $\Delta M = -1$ fine-structure transitions from the $\frac{5}{2}$ to $\frac{3}{2}$ levels. In general, the strength of a resonance is proportional to a product of the transition probability and population differences between the states which are established in the time intervals of flight from the source to the rf region and from the rf region to the detector. The population differences depend on the beam velocity, distances of flight, and lifetimes. The lifetime of most sublevels depends on the magnetic field because it mixes states of the same M that have differing zero-field lifetimes. The transition probability depends on the rf coupling matrix element and is proportional to the square of this element at low rf-field intensities. The resonances seen in Fig. 2 have been observed at low static-magnetic field where the various substates of each J level have nearly the same lifetime. The differing strengths of the resonances is a consequence of differences among the matrix elements since the rf intensity was relatively low. These transitions are indicated by the vertical lines at low field on the energy-level diagram, Fig. 3.

The resonances which were analyzed to provide the fine-structure results of this Letter are shown in Fig. 4. They are identified by the transitions labeled A, B, C, and D on the energy-level diagram, Fig. 3. These resonances are observed at relatively high static magnetic field, where appreciable mixing of states with the same magnetic quantum number M occurs. The transition D is the strongest because it has the largest rf matrix element and because the $M = -\frac{5}{2}$ sublevel retains its zero-field lifetime. The three smaller resonances have smaller matrix ele-

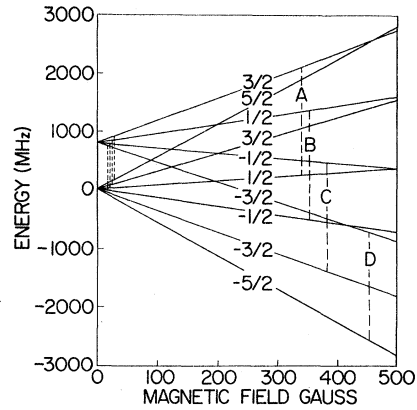


FIG. 3. Energy sublevels as a function of magnetic field for the $J = \frac{5}{2}$ and $\frac{3}{2}$ levels. The $J = \frac{1}{2}$ level lies above these two with a zero-field energy of 8663 MHz. The energy ordering of the levels shown here is that found theoretically by Manson, while the numerical values are those measured in the present work. Transitions which have been observed are indicated by vertical dashed lines.

ments and the $J = \frac{5}{2}$ sublevels involved have lifetimes shortened from their zero-field values because of mixing with the short-lived J states, leading to smaller population differences.

For the transition D, neither of the participating sublevels has $M = \pm \frac{1}{2}$, and the transition frequency depends solely on Δ_{53} . However, the remaining three resonances do involve $M = \pm \frac{1}{2}$ sublevels and have transition frequencies which depend slightly on Δ_{51} . At the magnetic fields where they were observed, the calculated transition frequency for each of the resonances A, B, C, and D

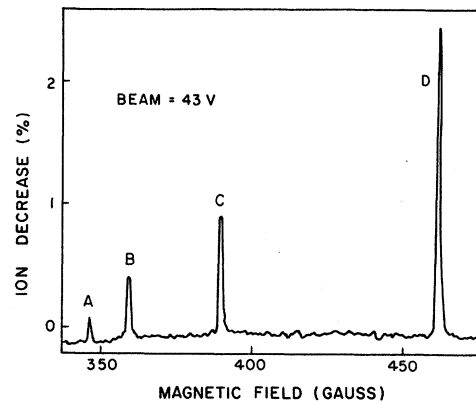


FIG. 4. With an oscillator frequency of 1835 MHz, the $\Delta M = +1$ transitions from $J = \frac{5}{2}$ to $\frac{3}{2}$ are observed at high field. Coupling with the distant $J = \frac{1}{2}$ levels shifts the three small resonances A, B, and C enough to estimate Δ_{51} . Since the large resonance D does not involve $M = \pm \frac{1}{2}$ sublevels, its position depends solely on Δ_{53} .

changes by -0.2 , 1.8 , 2.4 , and 0 MHz, respectively, if the value of Δ_{51} assumed in the calculation is changed from 8 to 9 GHz, with Δ_{53} fixed at 825 MHz. Thus, A and D serve primarily to establish Δ_{53} . The separation of B and C from these resonances serves primarily to establish Δ_{51} .

Although the rf technique employed here does not establish the sign of the fine-structure intervals, it was shown that they have the same sign. Transition frequencies for A , B , and C were calculated as a function of Δ_{51} at the fields where they were observed, with a positive value assumed for Δ_{53} . There was a unique positive value of Δ_{51} for which all three calculated transition frequencies agreed with the oscillator frequency. Since the intervals have the same sign and $|\Delta_{51}|$ is greater than $|\Delta_{53}|$, we conclude that the $J = \frac{3}{2}$ level lies between the other two. Consequently, the ordering is either the normal structure or fully inverted structure. Manson⁷ predicts the fully inverted structure; with increasing energy the order of the states is $\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$. The ordering in He^- is therefore different from that in the analogous state in excited lithium where it has been shown from studies of the optical quartet spectrum that with increasing energy the order of the states is $\frac{3}{2}$, $\frac{5}{2}$, and $\frac{1}{2}$.⁸

Data were taken on each of the resonances A , B , C , and D under a variety of experimental conditions. No significant shifts with rf power level, beam energy, or background pressure were found. The major source of uncertainty is due to gradients in the static magnetic field. The fine-structure results are

$$|\Delta_{53}| = 825.23 \pm 0.82 \text{ MHz},$$

$$|\Delta_{51}| = 8663 \pm 56 \text{ MHz}.$$

These uncertainties are felt to represent a 68% level of confidence (1σ). We note again that these intervals have the same sign.

Using simple three-electron wave functions,

Manson⁷ has calculated fine-structure intervals of

$$\Delta_{53} = -2030 \text{ MHz}, \quad \Delta_{51} = -9410 \text{ MHz}.$$

If we adopt the signs found by Manson, the difference between theory and experiment is about 1 GHz in each case and is within the uncertainty in this simple calculation.

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Note added in proof.—Recently, Douglas, Hambro, and Kroll [Phys. Rev. Lett. **29**, 12 (1972)] published new theoretical values for the 2^3P fine-structure splittings in helium. These calculations remove most of the outstanding discrepancies between theory and experiment.

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