PHYSICAL REVIEW A VOLUME 17, NUMBER 6 JUNE 1978

Fine structure of the $1s2s2p\ ^4P^o$ and $1s2p^2\ ^4P$ doubly excited states in lithiumlike carbon, nitrogen, and oxygen

A. E. Livingston
Argonne National Laboratory, Argonne, Illinois 60439

H. G. Berry
Argonne National Laboratory, Argonne, Illinois 60439
and Department of Physics, University of Chicago, Chicago, Illinois 60637

(Received 30 January 1978)

The fine structure of the $1s2s2p\ ^4P^o$-$1s2p^2\ ^4P$ multiplet in the doubly excited quartet system of three-electron C IV, N V, and O VI has been measured using the method of beam-foil spectroscopy. The fine-structure splittings have been determined to within ~ 5 cm^{-1} in both the upper and lower states of each ion, and the absolute transition wavelengths have been measured to within ~ 0.1 Å ($\sim 10^{-3}$ eV). The wavelength results show that existing relativistic and nonrelativistic energy separations calculated for these ^4P states are inaccurate by $\sim 1\%$ for $Z = 6$–8, and that calculations of the fine-structure splittings are inaccurate by (10–20)% for $1s2s2p\ ^4P^o$ and by $\gtrsim 20\%$ for $1s2p^2\ ^4P$. Lifetimes have also been measured for the $J = 5/2$, $3/2$, and $1/2$ levels of $1s2p^2\ ^4P$. Differential metastability is found to be a characteristic feature of these core-excited fine-structure states in all three ions. Comparison with calculated autoionization and K x-ray transition rates for $Z = 7$ and 8 indicates that the $1s2p^2\ ^4P_{5/2}$ lifetime is determined essentially by its autoionization rate to the doublet continuum through magnetic interactions, whereas the $J = 3/2$ and $1/2$ states decay at a slower rate that is more characteristic of the $^4P^o$-^4P radiative transition rate.

I. INTRODUCTION

Doubly excited atomic states often lie energetically far above the first ionization limit of the atom or ion, owing to the promotion in principal quantum number of an inner-shell electron. These states may be depopulated by autoionization to the adjacent continuum, or by radiative deexcitation either to other doubly excited states or to the much lower-lying singly excited states. Doubly excited states in three-electron systems were first detected in laboratory spark sources by Edlén and Tyrén[1] as satellite lines on the long-wavelength side of heliumlike resonances lines in the extreme uv region. They attributed the satellites to $1s^2nl$-$1s2pnl$ transitions, although the first specific term classifications were provided much later by Gabriel and Jordan,[2] using data from laboratory plasmas and the solar spectrum. These classifications have been extended recently by Nicolosi and Tondello.[3] During the past ten years the beam-foil source[4] has proved to be efficient for populating a wide range of multiply excited states in a variety of atomic systems, and both photon and electron spectroscopies have been applied using this method. In particular, virtually all known doubly excited quartet states in lithiumlike systems have been determined using transitions seen only in beam-foil spectra. The field of multiply excited states in beam-foil spectroscopy has been reviewed recently by Berry.[5]

Doubly excited quartet states in three-electron systems represent the simplest cases for which the total spin differs from that of the singly excited (doublet) states. Thus they are metastable with respect to both Coulomb autoionization and electric dipole transitions to singly excited states, so that transitions connecting quartet states are readily observable (though normally weak) in beam-foil spectra. However, the best fractional wavelength precision that has been reported previously is about 10^{-3}, which determines quartet state level energies to within ~100 cm^{-1}. This is superior to the precision normally obtained by electron[6] or x-ray[2,7] spectroscopy (typically $10^3 - 10^4$ cm^{-1}) for quartet state energies. Furthermore, the precision is sufficient to show that existing atomic-structure calculations[8-11] for quartet states in three-electron ions are inaccurate for low Z, but is insufficient to resolve the fine structure or relativistic corrections to the atomic structure. The only previous fine- and hyperfine-structure measurements for three-electron quartet states are in neutral lithium, where Feldman *et al.*[12] have applied a Zeeman-quenching atomic-beam method and Gaupp *et al.*[13] have measured zero-field quantum beats following beam-foil excitation. The hyperfine structure and lifetimes of the $1s2s2p\ ^4P^o$ states in Li I have been calculated by Manson[14] using analytic Hartree-Fock wave functions. In Li I, the relative importance of the spin-spin interaction to the spin-orbit and spin-other-orbit interactions is fundamental to both the energy structure and lifetimes of the $1s2s2p\ ^4P^o$ states, and appears to be the source of some remaining discrepancies between theory and experiment.[12] For these reasons, the measurement of quartet state transition energies and fine structures in multiply ionized three-electron atoms should provide incentive for the improvement of three-electron wave functions in atomic-structure calculations. In addition, such measurements will enable more-reliable peak identifications to be made in the associated high-resolution Auger-electron spectra and laboratory and solar x-ray spectra.

The $\Delta S = 0$ selection rule does not allow doubly excited quartet states to couple with the continuum states via the Coulomb interaction. However, coupling either directly via magnetic interactions (spin-orbit, spin-other-orbit, spin-spin) or indirectly via mixing with autoionizing doublet states may result in differential metastability: different lifetimes for the fine- (and hyperfine-) structure states within a term. There exist no previous measurements of this phenomenon in quartet states of three-electron systems, except for the lowest-lying $1s2s2p\,^4P^o$ term, which is metastable against radiative decay as well as Coulomb autoionization. For this term the lifetimes of the $J=\frac{3}{2}$ and $\frac{1}{2}$ states have been measured unambiguously only in Li I,[12] although the longer-lived $J=\frac{5}{2}$ state has been measured and calculated for nearly all atoms from Li I to Ar XVI.[5] The Hartree-Fock-Slater calculations by Bhalla and Gabriel[15] of total transition rates in three-electron doubly excited states suggest the presence of a Z-dependent differential metastability. Lifetime measurements for individual fine-structure quartet states in lithiumlike ions will thus serve to test the Z-dependent predictions. In particular, the lifetimes are very sensitive to slight deviations from LS coupling which allow mixing with rapidly autoionizing doublet states. In comparisons of prompt and time-delayed autoionization spectra,[6] for example, such lifetime results will enable more-detailed interpretations to be formulated for unresolved spectroscopic features.

In the present paper we report the results of our beam-foil measurements of the resolved fine structure of the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition connecting the lowest-lying doubly excited quartet states in lithiumlike C IV, N V, and O VI. These results represent the first measurements of fine structure in three-electron quartet states for ionized systems. We also report the results of our lifetime measurements for the $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ fine-structure states of $1s2p^2\,^4P$ in N V and O VI, and the $J=\frac{5}{2}$ and $\frac{3}{2}$ states in C IV. The lifetimes provide the first experimental evidence for strong differential metastability among these states, which arises from their differing degrees of coupling with the continuum. The precision of the fine-structure energy and lifetime results presented here enables extrapolations of these properties to nearby higher-Z ions along the isoelectronic sequence to be made with some confidence, which will be useful for future identifications of the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition in the spectra of these ions.

II. EXPERIMENT

The Argonne Dynamitron accelerator provided beams of 2.0–4.0 MeV C^+, N^+, and H_2O^+ with ion currents of ~5 μA on target. Standard techniques of beam-foil spectroscopy[4] were used for the wavelength and lifetime measurements. The exciter foil was a $\frac{1}{4}$-in.-diam self-supporting carbon foil of areal density 5 $\mu g/cm^2$, and was preceded by a $\frac{3}{16}$-in.-diam beam collimator. Photons emitted essentially perpendicular to the beam axis by foil-excited ions were dispersed with a 1-m normal-incidence concave-grating monochromator (~8 Å/mm in first order) and were detected by a Channeltron electron multiplier, coupled with standard pulse-counting electronics. Photon emission was accepted from a beam length of ~0.5 mm (~0.08 ns) in order to achieve good spatial resolution along the beam. Doppler broadening of the observed emission was minimized by refocusing the monochromator,[16] enabling linewidths (full width at half maximum) of 0.3 Å to be obtained in first order.

Spectra were recorded by observing the emission directly after the foil and counting pulses for a preset time interval per data channel, while advancing the monochromator wavelength continuously. Good beam current stability was maintained for these scans. Lifetimes were measured by advancing the foil in steps along the beam past the monochromator using a stepping motor connected to a precision screw. The counting period at each foil position was normalized to total ion charge collected in a Faraday cup in order to avoid effects of ion current fluctuations. The stepping commands and data acquisition were performed by an on-line PDP-11 computer.

III. RESULTS

In Fig. 1 we show the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ multiplet in C IV, N V, and O VI as observed during single scans through the respective wavelength regions of the beam-foil spectra. Many such scans at beam energies between 2.0 and 4.0 MeV for each ion were used to obtain the final results. The spectra have been fitted by computer with sums of Gaussians and a constant background. By interval analyses of these lines we have determined the fine structures of the upper and lower terms of each ion.

TABLE I. Observed fine-structure components and multiplet wavelengths for the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition in C IV, N V, and O VI.

Component $J_l \leftarrow J_u$	Wavelength (Å) O VI	N V	C IV
$\frac{3}{2}-\frac{5}{2}$	942.7	1108.4	1342.8
$\frac{1}{2}-\frac{3}{2}$	944.0	1109.3	1343.5
$\frac{3}{2}-\frac{3}{2}$	945.0	1109.8	···
$\frac{5}{2}-\frac{5}{2}$	946.4	1111.0	1344.5
$\frac{1}{2}-\frac{1}{2}$	946.6	···	···
$\frac{3}{2}-\frac{1}{2}$	947.6	1111.8	1344.9
$\frac{5}{2}-\frac{3}{2}$	948.7	1112.4	1345.3
Relative uncertainty	±0.05	±0.05	±0.1
$\bar{\lambda}_{\text{c.g.}}$	946.8	1111.1	1344.2
Absolute uncertainty	±0.1	±0.1	±0.3

In the case of C IV this required the assumption that the unresolved higher-wavelength feature is composed of three Gaussians. (The relative energies of the six fine-structure levels may be determined simply from the five strongest components of the multiplet.) The mean wavelength values of the fine-structure components are listed in Table I. Also listed is the mean multiplet wavelength, representing the energy difference between the $(2J+1)$ statistically weighted centers of gravity of the upper and lower terms. In the oxygen spectrum of Fig. 1 we indicate the presence of a feature at 949.4 ±0.2 Å that we classify as the $n=5$–7 hydrogenic transition complex in heliumlike O VII.

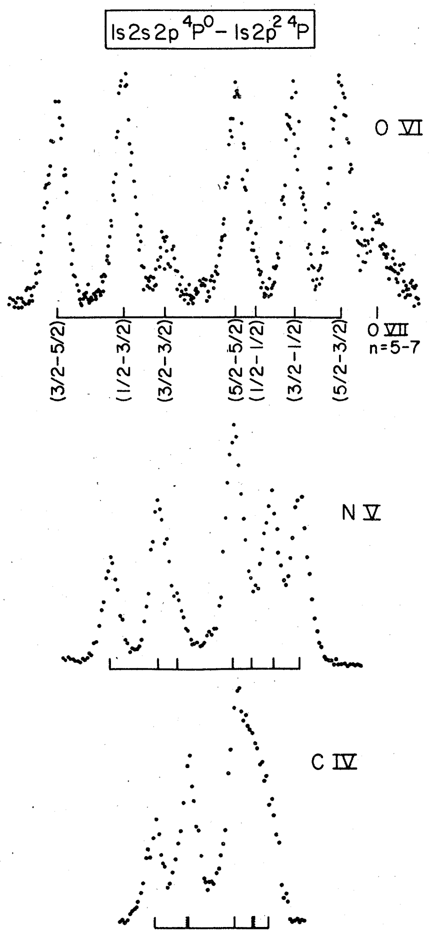

FIG. 1. Wavelength scans showing resolved fine structure of the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition in the beam-foil spectra of C IV, N V, and O VI. The observed linewidth (FWHM) is about 0.3 Å.

TABLE II. Fine-structure intervals in the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ configurations of C IV, N V, and O VI.

		Interval (cm^{-1})						
		$1s2s2p\,^4P^o$				$1s2p^2\,^4P$		
Ion	Levels	a	b	c	d	a	c	d
O VI	$\frac{5}{2}-\frac{3}{2}$	418 ± 4	374	302	396	252 ± 4	68	232
	$\frac{3}{2}-\frac{1}{2}$	102 ± 5	86	−19	90	295 ± 5	251	292
N V	$\frac{5}{2}-\frac{3}{2}$	212 ± 3	191	133	203	115 ± 3	−24	102
	$\frac{3}{2}-\frac{1}{2}$	35 ± 4	25	−55	29	160 ± 4	126	156
C IV	$\frac{5}{2}-\frac{3}{2}$	100 ± 5	89	40	91	41 ± 5	−59	33
	$\frac{3}{2}-\frac{1}{2}$	0 ± 7	−3	−61	0.9	83 ± 7	53	74

[a] Present work.
[b] Hartree-Fock (Ref. 23).
[c] Relativistic Z-expansion (Ref. 11).
[d] Dirac-Hartree-Fock (Ref. 33, see *Note added)*.

TABLE III. Lifetimes of the fine-structure levels of the $1s2p^2\,^4P$ state in C IV, N V, and O VI.

Ion	J	Lifetime (ns.) a	b	c
O VI	$\frac{5}{2}$	0.10 ± 0.01	0.11	0.10
	$\frac{3}{2}$	1.1 ± 0.1	0.67	0.40
	$\frac{1}{2}$	1.0 ± 0.1	18	0.95
N V	$\frac{5}{2}$	0.30 ± 0.05	0.30	0.24
	$\frac{3}{2}$	1.7 ± 0.1	1.8	0.71
	$\frac{1}{2}$	1.4 ± 0.1	61	1.14
C IV	$\frac{5}{2}$	0.9 ± 0.1		
	$\frac{3}{2}$	2.5 ± 0.3		
	$\frac{1}{2}$	...		

[a] Present work.

[b] Hartree-Fock-Slater (Ref. 15).

[c] Hartree-Fock-Slater including radiative branch (Ref. 30).

The theoretical wavelength of the $5g-7h$ strongest component of this complex is 949.24 Å,[17] in agreement with our observed value. The uncertainties in the absolute wavelength values have been determined by comparison with the wavelengths of nearby well-known lines in each of the spectra. The relative uncertainty of an individual multiplet component represents two standard deviations of its mean wavelength with respect to any other component wavelength. The fine-structure intervals that we derive from our wavelength observations are summarized in Table II, along with theoretical values that will be discussed later in the paper.

We have performed lifetime measurements for the strong components of each multiplet in order to verify our line classifications and to investigate the dependence of lifetime upon fine-structure level in the $1s2p^2\,^4P$ term. Intensity decay measurements were performed at 2.0, 3.0, and 4.0 MeV for C IV, N V, and O VI, respectively. The lifetime results are presented in Table III, along with theoretical values that will be discussed later in the paper. In O VI and N V the $J=\frac{5}{2}$ and $J=\frac{3}{2}$ lifetimes were each measured at two different fine-structure components, and the results were consistent within the quoted uncertainties. The remaining four lifetime results represent measurements at single components. The $J=\frac{1}{2}$ lifetime in C IV could not be extracted from decay measurements performed at various wavelength positions on the unresolved peak. The decay curves for the $J=\frac{5}{2}$ states contained weak, long-lived cascade components, whereas the $J=\frac{3}{2}$ and $\frac{1}{2}$ decays were essentially cascade free.

IV. DISCUSSION

A. Wavelength

The energies of the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ lowest-lying quartet states in three-electron ions have been calculated previously using nonrelativistic variational techniques (Holøien and Geltman[8] and Junker and Bardsley[9]) and using Z-expansion methods (Goldsmith[11] and Summers[10]). Goldsmith's calculations included relativistic contributions due to magnetic interactions of the electrons. Junker and Bardsley[9] employed less-extensive wave functions than Holøien and Geltman[8] and concluded that their variational energy values are less accurate than those of Ref. 8 for low-lying doubly excited states. At low Z, the Z-expansion method is expected to be less accurate than the variational technique owing to the neglect of higher-order electron correlations. With increasing Z, the nonrelativistic Z-expansion energies should improve, but relativistic corrections will also become important. For these reasons, accurate experimental transition energies are essential in assessing the relative accuracies of the Z-expansion and variational techniques for doubly excited states in moderately ionized systems.

The energy separation of the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ terms is determined by our mean wavelength values in Table I with an absolute precision of ~10 cm^{-1} for N V and O VI, and ~20 cm^{-1} for C IV. This represents an order of magnitude improvement over earlier measurements[18-20] of the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition energies. It is instructive to compare our experimental energies for these transitions with available theoretical values in lithiumlike systems. This reveals Z-dependent features and relative accuracies of the various theoretical approaches and also should allow extrapolation to be made to nearby higher-Z ions for future classifications of this transition.

In Fig. 2 we show this comparison by plotting the scaled mean transition energy against inverse nuclear charge, where the screening constant (1.23) has been chosen to approximately eliminate the Z dependence for moderately ionized systems. (The uncertainty in each of the experimental values is less than the size of the symbol.) Our results for C IV, N V, and O VI extend the experimental trend suggested by earlier values at lower Z, and confirm that the nonrelativistic variational calculations of Holøien and Geltman[8] for these ^4P level separations are the most accurate available for $Z=4-8$. In Li I, the superposition-of-configurations result of Weiss[21] is more accurate than the result of Ref. 8. The trend of our results for $Z=6-8$ suggests that the relativistic Z-expansion calculations of Goldsmith[11] are becoming the most

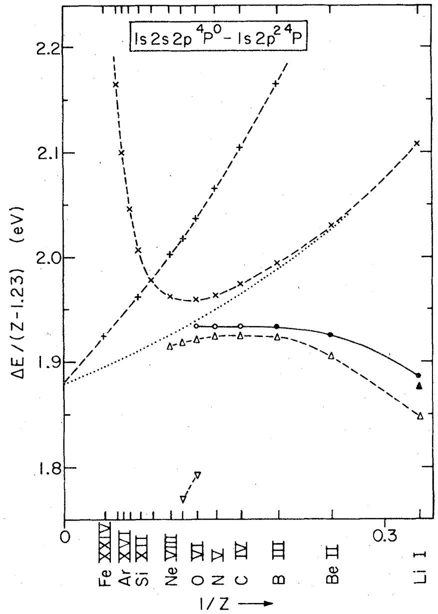

FIG. 2. Scaled mean transition energy vs inverse nuclear charge for the $1s\,2s\,2p\,^4P^o$ - $1s\,2p^2\,^4P$ transition **in lithiumlike systems.** The results of the present work are shown as open circles. The filled circles represent previous experimental results for Li I (Ref. 12), Be II (Ref. 31), and B III (Ref. 32). The theoretical results are from Ref. 8 (△), Ref. 9 (▽), Ref. 10 (+), Ref. 11 (×), and Ref. 21 (▲).

reliable for $Z > 8$. For completeness, the nonrelativistic variational results of Junker and Bardsley[9] and the nonrelativistic Z-expansion values of Summers[10] are also plotted.

At high Z, where departures from LS coupling become important, the results of Goldsmith[11] are very similar to the semiempirical values of Gabriel.[22] These latter were derived by using the Hartree-Fock method, including spin-orbit interaction, to calculate the energy differences between lithiumlike satellite transitions and the heliumlike resonance line for $Z = 6-29$.

The energy matrices presented by Goldsmith[11] allow the isolation of the theoretical contributions due to magnetic interactions in terms of a Z^4-dependent (spin-orbit) and a Z^3-dependent (spin-other-orbit, spin-spin) part. For $Z > 6$, the spin-orbit interaction accounts theoretically for more than 90% of these magnetic corrections. In Fig. 2 we indicate by a dotted line the transition energy values of Goldsmith that result when all the relativistic contributions are excluded. It is evident that our experimental transition energies are sufficiently precise to be sensitive to these relativistic corrections for $Z = 6-8$. However, since the calculated relativistic contributions at low Z are not expected to be highly accurate, we suggest that the departure in the Z-dependent trend of our results from the nonrelativistic values of Holøien and Geltman best displays the effect of these relativistic corrections for $Z = 6-8$. Experimental transition energies for higher-Z systems are needed in order to provide a more-stringent test of the relativistic Z-expansion results.

Previously suggested experimental wavelengths for the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition based upon lower-resolution beam-foil observations in C IV (Ref. 18) and O VI, F VII, and Ne VIII (Ref. 19) all disagree slightly with the present experimental trend. In N V, however, the wavelengths suggested by Knystautas and Drouin[19] (1111 ± 1 Å) and by Berry *et al.*[20] (1112 ± 1 Å) both agree with our result of 1111.1 ± 0.3 Å. We emphasize that the unrecognized presence of measurable fine structure for this multiplet may have affected the wavelength values quoted in Refs. 18–20.

B. Fine structure

The fine-structure energies of three-electron doubly excited states are sensitive to various magnetic interactions involving the spin and orbital angular momenta of the electrons. The spin-orbit and spin-other-orbit interactions between electrons produce level splittings that are described by the Landé interval rule, whereas the spin-spin interaction is largely responsible for deviations from the interval rule and, in extreme cases, abnormal energy ordering of fine-structure levels. The effects of these interactions on level splittings in $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ terms have been observed previously only in neutral lithium.[12,13] Our measurements of resolved fine structure for the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition in C IV, N V, and O VI provide the first experimental data on such relativistic effects for quartet states in three-electron ions.

In Fig. 3 we display our observed relative fine-structure energies for the $J = \frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ levels of the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ terms. The fine structures of both terms are found to have normal energy ordering for $Z = 6-8$, although the ratios of the $\frac{5}{2}-\frac{3}{2}$ to $\frac{3}{2}-\frac{1}{2}$ intervals all deviate considerably from the Landé-rule prediction of 5 : 3. We also show, for comparison, the relative energies of the $J = 2$, 1, and 0 levels of $1s2p\,^3P^o$ in heliumlike C V,[24] N VI,[25] and O VII.[26] The similarity in the fine structures of $1s2s2p\,^4P^o$ and $1s2p\,^3P^o$ is striking. The existence of inverted $J = 0, 1$ levels at higher-Z values than inverted $J = \frac{1}{2}, \frac{3}{2}$ levels suggests that for a given Z the magnitude of the spin-spin interaction may be larger for $1s2p\,^3P^o$ than for $1s2s2p\,^4P^o$.

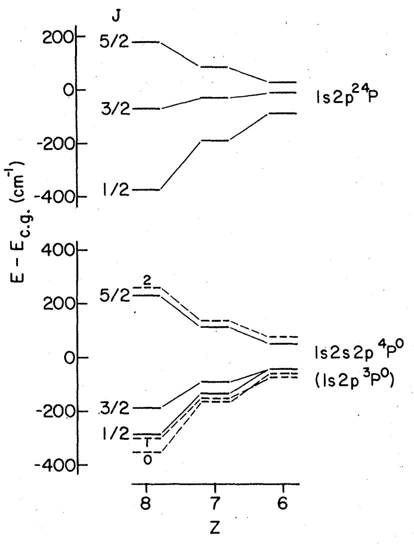

FIG. 3. Experimental relative fine-structure levels of the $1s2s2p\ ^4P^o$ and $1s2p^2\,^4P$ states in C IV, N V, and O VI determined from the present work. Also plotted are the experimental fine structures of the $1s2p\ ^3P^o$ states in C V (Ref. 24), N VI (Ref. 25), and O VII (Ref. 26).

There exist very few calculations of fine-structure energies for doubly excited states of three-electron ions. The relativistic Z-expansion results of Goldsmith[11] may be compared with our measured values for the two lowest ^4P states in C IV, N V, and O VI. In addition, very recent Hartree-Fock calculations by Manson[23] are available for the $1s2s2p\,^4P^o$ state in these ions. The results are summarized in Table II. In Fig. 4 we have plotted a comparison of our measurements with these two calculations for the three ions. The fine-structure level positions are shown relative to their respective (statistically weighted) centers of gravity for each state, and are scaled by an effective nuclear charge $(Z-1.5)$ in order to approximately remove strong Z-dependent effects. For the metastable $1s2s2p\,^4P^o$ state, the Hartree-Fock results[23] agree with our measured values of the level splittings to within (10–20)% for all three ions. On the other hand, the relativistic Z-expansion results[11] are clearly inadequate for describing the fine structure of either the $1s2s2p\,^4P^o$ or $1s2p^2\,^4P$ states for these moderately low charge states. By inspection of Fig. 4 it appears that the major discrepancy between the Z-dependent values and experiment involves only the calculated energies for the $^4P^o_{1/2}$ level and the $^4P_{5/2}$ level.

In order to distinguish the relative contributions of the various magnetic interactions to the fine structure, we follow Refs. 12 and 14 in parametrizing the two fine-structure intervals observed for each state in terms of spin-orbit and spin-spin fine-structure constants. (This approach ignores off-diagonal elements of the spin-orbit interaction, which account for deviations from Landé intervals in very heavy atoms.) Assuming LS coupling, we may express the fine-structure operators for the spin-orbit (SO) and spin-other-orbit (SOO) interactions as

$$H_{SO}+H_{SOO}=C_{SO}\,\vec{L}\cdot\vec{S}, \tag{1}$$

which defines the "spin-orbit" constant C_{SO}. Similarly, the spin-spin operator may be expressed as

$$H_{SS}=C_{SS}[3(\vec{L}\cdot\vec{S})^2+\tfrac{3}{2}(\vec{L}\cdot\vec{S})-L(L+1)S(S+1)]\,. \tag{2}$$

Defining the fine-structure intervals to be E_{53} and E_{31}, we may write these in terms of C_{SO} and C_{SS} for a ^4P state:

$$E_{53}=\tfrac{5}{2}C_{SO}+\tfrac{15}{2}C_{SS},\quad E_{31}=\tfrac{3}{2}C_{SO}-\tfrac{27}{2}C_{SS}. \tag{3}$$

This allows separation of the "spin-orbit" and spin-spin contributions in terms of the level splittings:

$$C_{SO}=\tfrac{1}{30}(9E_{53}+5E_{31}),\quad C_{SS}=\tfrac{1}{90}(3E_{53}-5E_{31}). \tag{4}$$

We have listed in Table IV these fine-structure constants derived from our observed level intervals for the two ^4P states in C IV, N V, and O VI.

The spin-orbit operator H_{SO} scales with effective nuclear charge Z_{eff} as Z^4_{eff}, whereas H_{SOO} and H_{SS} both scale as Z^3_{eff}.[27] Thus, assuming a Z^3_{eff} dependence for the spin-spin constant, we have used our C_{SS} values for C IV, N V, and O VI along with those of Refs. 12 and 13 for Li I to de-

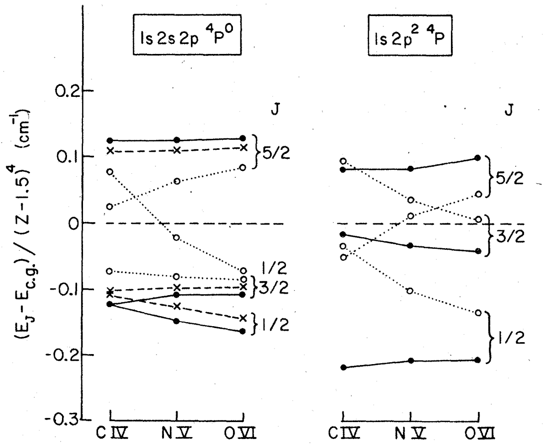

FIG. 4. Scaled fine-structure intervals for the $1s2s2p\ ^4P^o$ and $1s2p^2\,^4P$ states in C IV, N V, and O VI. The results of the present work are shown as filled circles. The theoretical results are from Ref. 11 (○) and Ref. 23 (×).

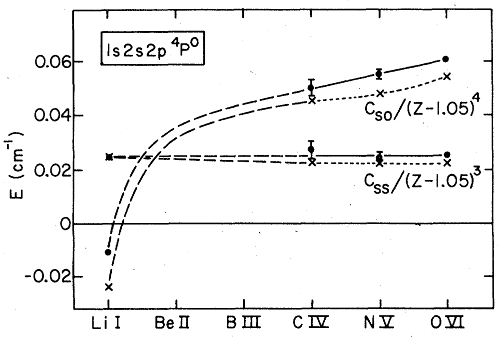

FIG. 5. Scaled fine-structure parameters for the $1s2s2p\,^4P^o$ state **in lithiumlike systems.** The present experimental results for C IV, N V, and O VI and those of Ref. 12 for Li I are shown as filled circles. The theoretical results (**X**) are from Refs. 14 and 23. The dashed lines are drawn to aid the eye.

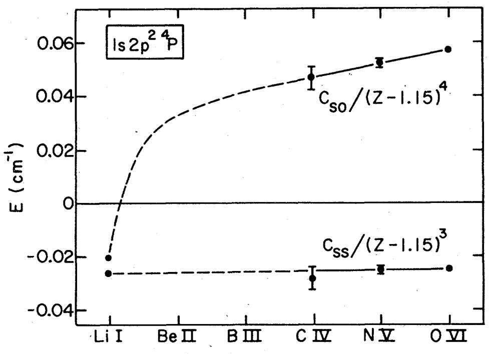

FIG. 6. Scaled fine-structure parameters for the $1s2p^2\,^4P$ state **in lithiumlike systems.** The results for C IV, N V, and O VI are from the present work and those for Li I are from Refs. 12 and 13. The dashed lines are drawn to aid the eye.

TABLE IV. Fine-structure parameters (cm^{-1}) for the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ states in C IV, N V, and O VI

	$1s2s2p\,^4P^o$		$1s2p^2\,^4P$	
Ion	C_{SO}	C_{SS}	C_{SO}	C_{SS}
O VI	142.4 ± 1.5	8.3 ± 0.3	124.8 ± 1.5	−8.0 ± 0.3
N V	69 ± 1	5.0 ± 0.3	61 ± 1	−5.1 ± 0.3
C IV	30 ± 2	3.3 ± 0.4	26 ± 2	−3.2 ± 0.4

termine a screening constant (σ) of 1.05 for $1s2s2p\,^4P^o$ and 1.15 for $1s2p^2\,^4P$. In Figs. 5 and 6 we have plotted our values of the fine-structure constants for these ^4P states, scaled by the appropriate power of effective nuclear charge $(Z-\sigma)$. We have included for completeness the experimental values derived from Levitt and Feldman[12] and Gaupp *et al.*[13] for Li I and, for $1s2s2p\,^4P^o$, the theoretical values of Manson[14,23] for all four ions.

The negative values of C_{SO} in Li I result from the fact that the spin-orbit and spin-other-orbit terms arising from interactions between pairs of electrons are larger than those due to electron-nucleus interactions, as pointed out by Levitt *et al.*[12] By use of observed C_{SO} values for two different ions, we may separate the Z_{eff}^3-dependent and Z_{eff}^4-dependent parts of this parameter, thus isolating the spin-orbit and spin-other-orbit contributions. Our C_{SO} values for O VI in conjunction with those from Refs. 12 and 13 for Li I yield the following partitions of this fine-structure parameter (in cm^{-1}) for the two ^4P states:

$$\begin{aligned} ^4P^o:&\ C_{SO}=0.089Z_{\mathrm{eff}}^4-0.194Z_{\mathrm{eff}}^3\,,\\ ^4P:&\ C_{SO}=0.085Z_{\mathrm{eff}}^4-0.195Z_{\mathrm{eff}}^3\,. \end{aligned} \tag{5}$$

These expressions are also consistent with our C_{SO} values for C IV and N V. The magnitudes of the spin-other-orbit contributions are about eight times larger than the magnitudes of the spin-spin contributions (see Table IV) for all Z. They are slightly larger than the spin-orbit terms for $Z=3$, resulting in the negative C_{SO} values in Li I.[12,13] For $Z>3$, C_{SO} is positive for both states, and the spin-other-orbit contributions are about one-third the values of the spin-orbit terms in O VI.

C. Lifetimes

The lifetime of the $1s2p^2\,^4P$ state in three-electron systems has been measured previously for Li I to C IV using the beam-foil method (see Ref. 5). However, these measurements were all performed by observing the unresolved $1s2s2p\,^4P^o$–$1s2p^2\,^4P$ multiplet, so that the possible fine-structure dependence of lifetimes could not be detected. Comparison of these "multiplet" lifetimes with nonrelativistic single-configuration[28] and multiconfiguration[21] calculations for low Z reveals a slightly more rapid experimental trend towards shorter lifetime with increasing Z than theoretically predicted. This suggests that the opening of (spin-forbidden) decay channels to the continuum via magnetic interactions produces measurable deviations from the radiative transition rates even at low Z. Existing calculations[15,29] of the $1s2p^2\,^4P$ fine-structure lifetimes for $Z\geq 7$ have predicted strong differential metastability among the $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ states. These calculations have included spin-orbit interaction in determining the spin-forbidden x-ray (see Fig. 7) and autoionization transition rates, but have neglected the $1s2s2p\,^4P^o$–$1s2p^2\,^4P$ radiative branch. More recently, Bhalla[30] has included the contribution of this radiative branch in determining the $1s2p^2\,^4P$ lifetimes for

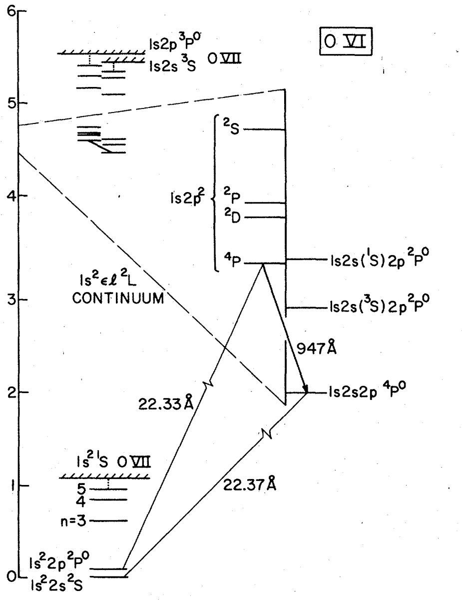

FIG. 7. Energy-level diagram **for lithiumlike** O VI showing the doubly excited level system embedded high in the doublet continuum above the first ionization limit. The wavelengths of x-ray transitions connecting levels of the $1s2s2p$ and $1s2p^2$ configurations to the $2s\ ^2S$ and $2p\ ^2P^o$ states are listed in Refs. 2, 3, and 22 for many **lithiumlike ions.**

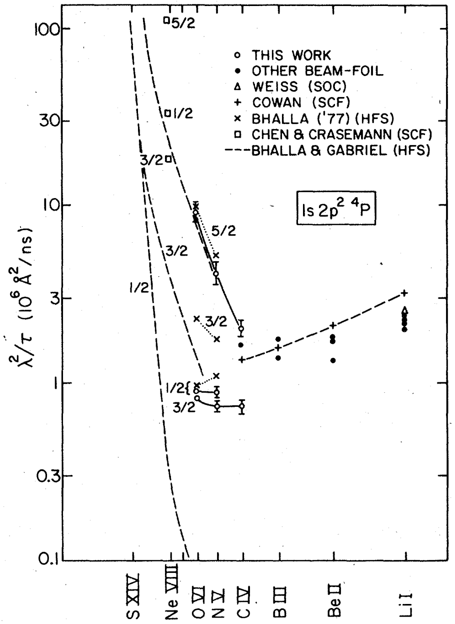

FIG. 8. Scaled inverse lifetime vs inverse nuclear charge for the $1s2p^2\,^4P$ state **in lithiumlike systems.** Previous beam-foil results for Li I - C IV are shown as filled circles, and references to the original work are summarized in Ref. 5. The results of the present work for the resolved fine-structure levels in C IV, N V, and O VI are shown as open circles. The theoretical results are from Ref. 21 ($Z=3$), Ref. 28 ($Z=3$–6), Ref. 29 ($Z=10$), Ref. 30 ($Z=7,8$), and Ref. 15 ($Z\geq 7$).

$Z=7$ and 8.

Our lifetime measurements for the fine-structure states of $1s2p^2\,^4P$ in C IV, N V, and O VI provide the first experimental comparisons with the relativistic calculations. In Table III we compare our lifetime values with those Refs. 15 and 30. In Fig. 8 we have plotted our lifetime results along with theoretical and other experimental values for lithiumlike systems. The ordinate of scaled inverse lifetime is proportional to the atomic oscillator strength for the radiative branch, although only in the absence of other decay channels.

Our lifetime results confirm the existence of differential metastability among the fine-structure states of $1s2p^2\,^4P$ for $Z=6$–8. For the $J=\frac{5}{2}$ state we find lifetime values that are close to the results of Bhalla and Gabriel[15,30] for N V and O VI. These lifetimes are nearly an order of magnitude shorter than would be expected in the absence of magnetic interactions. The calculations of Refs. 15 and 30 indicate that the $J=\frac{5}{2}$ lifetime is determined predominantly by its autoionization rate to the doublet continuum, presumably resulting from weak mixing with the rapidly autoionizing $1s2p^2\,^2D_{5/2}$ state (see Fig. 7) via the spin-orbit interaction. In contrast, for the $J=\frac{3}{2}$ and $\frac{1}{2}$ states we find lifetime values that are consistent with the nonrelativistic trend for low Z. This implies that coupling to the continuum is much weaker for these states than for the $J=\frac{5}{2}$ state. The recent calculations of Bhalla[30] verify that the radiative branch we have observed contributes significantly to the lifetimes of the $J=\frac{3}{2}$ and, in particular, the $J=\frac{1}{2}$ state. This is evident in Fig. 8 by comparison with the earlier results of Ref. 15, in which the radiative branch was not considered. Our $J=\frac{1}{2}$ lifetimes are close to the values of Ref. 30, whereas a factor-of-2.5 discrepancy between theory and experiment exists for the $J=\frac{3}{2}$ lifetimes. The experimental results suggest that for the $1s2p^2$ configuration the mixing between the $^4P_{3/2}$ state and the autoionizing $^2D_{3/2}$ state is much weaker than that between the corresponding $J=\frac{5}{2}$ states.

V. CONCLUSION

We have performed the first measurements of fine-structure energies and lifetimes in doubly excited states of lithiumlike ions by observing the resolved fine structure of the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ multiplet in C IV, N V, and O VI. Our wavelength results reveal that existing relativistic calculations of the separations in total term energy of these two lowest-lying ^4P states, as well as of the individual ^4P fine-structure splittings, are inaccurate for moderately ionized three-electron systems. Comparison of our mean transition energies with the Z dependence of elaborate nonrelativistic calculations suggests that the associated relativistic corrections are $\gtrsim 0.1\%$, and that relativistic Z-expansion calculations overestimate these contributions for $Z \sim 8$. It appears that measurements of the transition energies at higher Z are required in order to better determine the accuracy of the relativistic Z-expansion treatment for these three-electron states.

By employing an initial two-component parametrization of the fine-structure intervals under LS-coupling conditions, and by invoking the Z-dependent properties of the various magnetic interactions between electrons, we have obtained Z-dependent parametrizations for the individual contributions of the spin-orbit, spin-other-orbit, and spin-spin interactions for both ^4P states. Although the spin-spin contributions are found to be only ~5% of the spin-orbit contributions for $Z=6-8$, they are responsible for the considerable deviations from Landé-rule level splittings that are observed in both ^4P states. These effects are amplified by the Z-dependent partial cancellation of the spin-orbit terms by spin-other-orbit contributions. The good consistency of these Z-dependent parametrizations with experiment for $Z=3$, 6, 7, and 8 suggests that they should provide reliable estimates of the ^4P fine structures for $Z=4$ and 5, as well as for at least the next few ions ($Z>8$) along the isoelectronic sequence.

Our lifetime results for the fine-structure levels of $1s2p^2\,^4P$ reveal strong differential metastability that results from differing degrees of coupling with the continuum via magnetic interactions for the individual levels. The lifetime of the $J=\frac{5}{2}$ state is much shorter than the $J=\frac{3}{2}$ and $J=\frac{1}{2}$ lifetimes, in agreement with theoretical predictions that the transition rate to the continuum dominates the $J=\frac{5}{2}$ decay. The much weaker autoionization rates predicted for the $J=\frac{3}{2}$ and $\frac{1}{2}$ levels explain the approximate agreement between our measured $J=\frac{3}{2}$ and $\frac{1}{2}$ lifetimes and those extrapolated from nonrelativistic calculations for lower-Z ions. Our results indicate that previous beam-foil lifetime values for the unresolved $1s2p^2\,^4P$ state in BIII and CIV most resemble the $J=\frac{5}{2}$ level lifetime in these ions. Relativistic Hartree-Fock-Slater calculations of total transition rates appear to be reliable for $Z \geqslant 8$ for the $J=\frac{5}{2}$ state and perhaps the $J=\frac{1}{2}$ state, but significant discrepancies remain for the $J=\frac{3}{2}$ state. Lifetime measurements for all three levels in higher-Z systems are desirable in order to test these calculations in more detail, although the radiative decay rate will be increasing more slowly with increasing Z than the autoionization and x-ray rates, making radiative observations more difficult, especially for $J=\frac{5}{2}$.

Finally, we point out that differential metastability among fine-structure levels of weakly autoionizing multiply excited states should be a general phenomenon, even when allowed radiative decay channels exist. As observed in this work for the $1s2p^2\,^4P$ state, coupling of core-excited states to the adjacent continuum by fine-structure interactions may be strongly J selective, so that relative autoionization and radiative decay rates must be considered for individual fine-structure (and, in general, hyperfine-structure) levels when describing the associated lifetimes. These characteristics directly affect time-resolved photon and electron spectroscopies of such states, producing time-dependent relative intensity variations that, for example, may allow the isolation of ions in a particular fine-structure state. Furthermore, the extraction of reliable estimates of relative excited-state populations from line intensities for unresolved fine-structure states in time-resolved Auger-electron spectra demands the recognition of these time-dependent intensity variations.

Note added: Upon completion of this manuscript we learned of new calculations of the ^4P fine structure in three-electron systems by Cheng *et al.*[33] Using Dirac-Hartree-Fock methods, they have obtained fine-structure intervals for both the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ states of CIV, NV, and OVI that differ from our experimental values by typically ~10 cm^{-1}, and are thus the most accurate calculations available for these states. These new results have been included in Table II.

In addition, new nonrelativistic calculations of energies and hyperfine constants for quartet states of three-electron systems ($Z=3-9$) have just been published by Lunell and Beebe.[34] By employing configuration-interaction wave functions, they have obtained energies for the $1s2s2p\,^4P^o$-$1s2p^2\,^4P$ transition that show slightly better agreement with experiment than do the results of Holøien and Geltman,[8] especially for the lower-Z systems.

ACKNOWLEDGMENTS

We are grateful to Dr. Steven T. Manson, Dr. Chandra P. Bhalla, Dr. Kwok-Tsang Cheng, and Dr. Samuel Goldsmith for permission to quote their unpublished results and for helpful comments. We wish to thank Gerald Gabrielse for stimulating discussions on the data analysis. This work was supported under the auspices of the Division of Basic Energy Sciences of the D.O.E.

[1] B. Edlén and F. Tyrén, Nature 143, 940 (1939); earlier observations of x-ray satellites in heavier atoms are discussed by H. E. White [*Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934)].

[2] A. H. Gabriel and C. Jordan, Nature 221, 947 (1969).

[3] P. Nicolosi and G. Tondello, J. Opt. Soc. Am. 67, 1033 (1977).

[4] H. G. Berry, Rep. Prog. Phys. 40, 155 (1977).

[5] H. G. Berry, Phys. Scr. 12, 5 (1975).

[6] R. Bruch, M. Rødbro, P. Bisgaard, and P. Dahl, Phys. Rev. Lett. 39, 801 (1977); D. Schneider, R. Bruch, W. H. E. Schwarz, T. C. Chang, and C. F. Moore, Phys. Rev. A 15, 926 (1977); S. Schumann, K. O. Groenevald, K. D. Sevier, and B. Fricke, Phys. Lett. 60A, 289 (1977).

[7] D. L. Matthews, B. Johnson, G. Hoffman, and C. F. Moore, Phys. Lett. 49A, 195 (1974); P. Richard, R. L. Kauffman, F. F. Hopkins, C. W. Woods, and K. A. Jamison, Phys. Rev. Lett. 30, 888 (1973); and Phys. Rev. A 8, 2187 (1973).

[8] E. Holøien and S. Geltman, Phys. Rev. 153, 81 (1967).

[9] B. R. Junker and J. N. Bardsley, Phys. Rev. A 8, 1345 (1973).

[10] H. P. Summers, Astrophys. J. 179, L45 (1973).

[11] S. Goldsmith, J. Phys. B 7, 2315 (1974). We have been informed by S. Goldsmith of a printing error in his expression for the energy of the $1s2s2p\,^4P^o_{5/2}$ state. The coefficient for the $\alpha^2 Z^4$ term should read $-0.171\,875$ instead of $-0.140\,625$. The corrected expression has been used for determining the results of Goldsmith quoted in the present paper.

[12] P. Feldman, M. Levitt, and R. Novick, Phys. Rev. Lett. 21, 331 (1968); M. Levitt and P. D. Feldman, Phys. Rev. 180, 48 (1969); M. Levitt, R. Novick, and P. Feldman, Phys. Rev. A 3, 130 (1971).

[13] A. Gaupp, M. Dufay, and J. L. Subtil, J. Phys. B 9, 2365 (1976).

[14] S. T. Manson, Phys. Rev. A 3, 147 (1971).

[15] C. P. Bhalla and A. H. Gabriel, *Beam-Foil Spectroscopy*, edited by I. A. Sellin and D. J. Pegg (Plenum, New York, 1976), p. 121.

[16] J. O. Stoner, Jr., and J. A. Leavitt, Appl. Phys. Lett. 18, 477 (1971).

[17] J. D. Garcia and J. E. Mack, J. Opt. Soc. Am. 55, 654 (1965).

[18] I. Martinson, Nucl. Instrum. Methods 90, 81 (1970).

[19] E. J. Knystautas and R. Drouin, in Ref. 15, p. 393.

[20] H. G. Berry, W. S. Bickel, S. Bashkin, J. Désesquelles, and R. M. Schectman, J. Opt. Soc. Am. 61, 947 (1971).

[21] A. W. Weiss (unpublished), quoted in Ref. 18.

[22] A. H. Gabriel, Mon. Not. R. Astron. Soc. 160, 99 (1972).

[23] S. T. Manson (private communication).

[24] B. Edlén and B. Löfstrand, J. Phys. B 3, 1380 (1970).

[25] K. Bockasten, R. Hallin, K. B. Johansson, and P. Tsui, Phys. Lett. 8, 181 (1964).

[26] R. C. Elton, Astrophys. J. 148, 573 (1967).

[27] R. H. Garstang, Mon. Not. R. Astron. Soc. 111, 115 (1951).

[28] R. D. Cowan (unpublished), quoted in Ref. 18.

[29] M. H. Chen and B. Crasemann, Phys. Rev. A 12, 959 (1975).

[30] C. P. Bhalla (private communication).

[31] H. G. Berry, J. Bromander, I. Martinson, and R. Buchta, Phys. Scr. 3, 63 (1971).

[32] I. Martinson, W. S. Bickel, and A. Ölme, J. Opt. Soc. Am. 60, 1213 (1970).

[33] K. T. Cheng, J. P. Desclaux, and Y.-K. Kim (to be published).

[34] S. Lunell and N. H. F. Beebe, Phys. Scr. 15, 268 (1977).