

elements, characteristic of the irreducible representations spanned by the spin eigenfunctions Θ_s^{SM} , for the permutations \mathcal{L} and (ij) . The evaluation of such matrix elements is less complex than the algebra resulting from an expansion of the wave function Ψ in Slater determinants.

The original derivation of the aforementioned results by the author was awkward. In its stead a different, elegant rederivation by Salmon will be presented elsewhere.¹⁰ Methods for the determination of spin eigenfunctions and their matrix elements⁷ as well as a generalization to more-than-two-electron operators⁵ will also be reported.

*Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

¹J. C. Slater, Phys. Rev. **34**, 1293 (1929); E. V. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge U. Press, Cambridge, England, 1935).

²C. M. Reeves, Commun. ACM (Ass. Comput. Mach.) **9**, 276 (1966); R. McWeeny, in *Encyclopedic Dictionary of Physics*, edited by J. Thewlis (Pergamon, New York, 1962), Vol. 7, p. 568; I. L. Cooper and R. McWeeny, J. Chem. Phys. **45**, 226 (1966); B. Sutcliffe, J. Chem. Phys. **45**, 235 (1966).

³F. E. Harris, J. Chem. Phys. **46**, 2769 (1967).

⁴M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Co. Ltd., Tokyo, 1955).

⁵K. Ruedenberg and R. D. Poshusta, Advan. Quantum Chem. (to be published).

⁶R. Serber, Phys. Rev. **45**, 461 (1934), and J. Chem. Phys. **2**, 697 (1934).

⁷W. I. Salmon, K. Ruedenberg, and L. M. Cheung, to be published; W. I. Salmon, to be published.

⁸E. M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Hafner, New York, 1951); L. F. Mattheiss, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Reports No. 30, 1958 (unpublished), p. 43, and No. 34, 1959 (unpublished), p. 58.

⁹For the Yamanouchi-Kotani functions see, e.g., Ref. 4. The relation to Young's orthogonal representation has been shown by R. Pauncz, *Alternant Molecular Orbital Method* (W. B. Saunders Co., Philadelphia, 1967). As regards Young's representation, see e.g., B. G. Wybourne, *Symmetry Principles and Atomic Spectroscopy* (Wiley, New York, 1970).

¹⁰W. I. Salmon and K. Ruedenberg, to be published.

Spectra of Autoionization Electrons Emitted by Fast, Metastable Beams of Highly Stripped Oxygen and Fluorine Ions*

I. A. Sellin, D. J. Pegg, and Matt Brown

*University of Tennessee, Knoxville, Tennessee 37916, and Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830*

and

Winthrop W. Smith

University of Connecticut, Storrs, Connecticut 06268

and

Bailey Donnally

Lake Forest College, Lake Forest, Illinois 60645

(Received 22 July 1971)

Unidentified metastable autoionizing states of highly stripped and excited oxygen and fluorine ions have been observed and their energies measured. Possible assignments are discussed. Appreciable populations of identifiable lithiumlike states of high electronic spin and high excitation energy have also been observed and their energies compared with the results of variational calculations. The lifetime of a level identifiable as either $1s2p3p^4P^e$ or $1s2s4s^4S^e$ has been measured to be 1.00 ± 0.04 nsec.

The experimental study of states of simple ions (containing a small number of electrons) which are metastable against autoionization by the Coulomb interaction^{1,2} serves several purposes. As

in the case of states metastable against radiative decay, the spin-orbit and spin-spin interactions are much stronger than in isoelectronic states of nearly neutral atoms, leading to rates

for forbidden processes which are sometimes observable experimentally while still very small compared to those for allowed processes. The literature concerning metastable states which decay predominantly by autoionization, or by competition between radiative and radiationless processes, is comparatively sparse. Measurements of the energies of the emitted electrons test variational atomic-structure calculations for these systems. Measurements of emission rates test sensitively the accuracy of wave functions. Measurements of the relative yields of particular metastable states give information concerning the collisional mechanisms governing the state populations. It turns out that relatively long-lived states of high electronic spin and high excitation are produced which are unavailable in other types of collisions experiments.

Improvements in the apparatus we use to study the electrons emitted by fast beams (2.5–30 MeV) of excited oxygen and fluorine ions have permitted us to examine peaks in the spectrum of emitted electrons in more detail than previously.¹ It is clear that a number of highly energetic states are appreciably populated which are metastable against Coulomb autoionization but not against radiative decay within a given spin system. We have investigated these spectral features with improved resolution to see whether they are all associated with high quartet levels, measured their energies for comparison with atomic-structure calculations, and studied some relative radiative and autoionization rates.

Some results from our most recent experiments are the subject of this Letter. In particular, unidentified metastable autoionizing states have been observed and their energies determined. Theoretical calculations concerning these new states are needed to establish their origin clearly. It appears unlikely that they arise from metastable quartet states of three-electron systems. Their decay in flight has been studied. The $1s2p2p\ ^4P^e(1)$ state which lies just above the lowest quartet state, $1s2s2p\ ^4P^o(1)$, has been observed and its energy, relative population, and decay in flight studied. A number of quartet states of configuration $1s2snl$ and $1s2pnl$ have been identified, including states of such highly excited configurations as $1s2s5s$. Their energies and in a few cases their decays in flight have been studied. A lifetime for one of the highly excited states which appears to be particularly dominant has been measured. Unidentified quartet states of even higher energy

than that of $1s2s5s$ have been observed, all the way up to the ionization limit established by the energies of the parent ion terms (2^3S^e or 2^2P^o). What we find is that appreciable populations of states of high spin and high excitation occur. For example, for 6-MeV O^{5+} ions rough measurements of the $1s2s2p\ ^4P^o$ yield give an occupation probability for this state alone of the order of a few tenths of 1% per emergent lithium-like ion. It is not true that nearly all autoionization electrons are shaken off immediately after leaving the target. This observation is relevant to current investigations of electron shakeoff lifetimes in solid-excited ions.³ The basic reason is that the selection rules for Coulomb autoionization require $\Delta S=0$. The autoionization processes corresponding to spin-orbit and spin-spin interactions permit $\Delta S=1$ (and $\Delta S=2$ transitions in the spin-spin case) but are relatively slow. Since appreciable amounts of relatively long-lived excited states of high spin survive, we suspect that the unidentified states also have high electronic spin.

Our apparatus and techniques are fully described in Ref. 1. The resolution of the spectrometer has since been improved to about 0.8% full width at half-maximum by narrowing its slits. There is a spread in laboratory energies resulting from the transformation from the emitting ions' rest frame to the laboratory frame. Finite slit width naturally contributes to this kinematic spread, as do changes in beam steering (0.5-deg changes in beam direction are observable). Energy loss contributes a slight but measurable shift to each peak energy; all data have been compensated accordingly. We assess our absolute energies to be good to $\pm 0.6\%$, an accuracy comparable to that ascribed by Holøien⁴ for the variational energies of most of the states involved [0.1% for $1s2s2p\ ^4P^o$ and 0.3–0.4% for the higher levels] as calculated by Holøien and Geltman.⁴ The chief contributions to these errors were (1) uncertainties in target thickness, (2) kinematic peak shifts with beam steering, (3) uncertainty in the line shape for kinematically broadened lines. By comparison, errors in the spectrometer calibration (by elastic electron scattering) proved negligible. The use of gas targets to reduce the target-thickness uncertainty was precluded by the nanosecond lifetimes of the weaker spectral features under study. Figures 1 and 2 display segments of electron spectra (in the ionic rest frames) obtained with 6-MeV oxygen and fluorine beams,

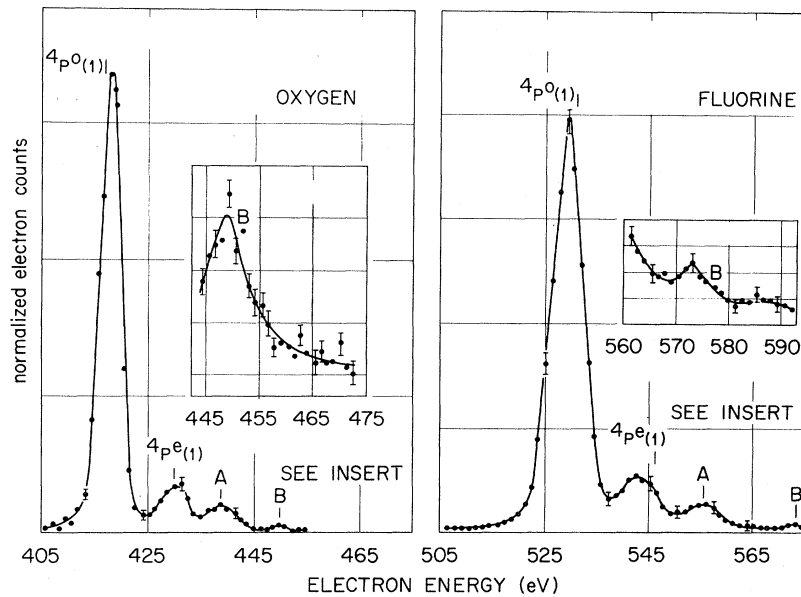


FIG. 1. Spectra of electrons emitted by 6-MeV oxygen and fluorine beams. Features near the lowest three-electron quartet state, in the ionic rest frame.

stripped and excited in an $\sim 20\text{-}\mu\text{g}/\text{cm}^2$ carbon target located approximately 1.5 cm from the spectrometer viewing region. The theoretical kinetic energies for electrons, derived from Ref. 4, are indicated. Within the combined error limits, the agreement between theory and experiment is uniformly excellent. The splitting between the pair of states $4P^e(2)$, $4S^e(2)$ and the $4S^e(3)$ state seems somewhat larger than the theoretically predicted splitting (but still well within the combined error limits). Some possibly relevant level energies, e.g., for $4D$ levels, were not calculated in Ref. 4.

The appearance of the $1s2p2p\ 4P^e(1)$ state in the spectrum is of interest; it can decay radiatively to the $4P^o(1)$ state. Hence a more realistic measure of its relative population is the observed value multiplied by an appropriate branching ratio $(\gamma_{\text{rad}} + \gamma_{\text{auto}})/\gamma_{\text{auto}}$, where γ_{rad} and γ_{auto} are appropriate radiative and autoionizing decay probabilities. Cascades from higher levels contribute appreciably to both the $4P^o(1)$ - and $4P^e(1)$ -state populations. Since the analogous states occur in Li and in He^- , this observation may mean that the role of long-lived cascades into the $4P^o(1)$ and $4P^e(1)$ states in the work of Feldman, Levitt, and Novick⁵ (on Li) and of Blau, Novick, and Weinfeld⁵ (on He^-) needs examination. In their experiments no energy analysis of the emitted electrons was made.

The states (or groups of states) corresponding

to features A and B are unidentified; the variational calculations required to identify them have not been made. They are bound by about 1172 and 1162 eV in O^{5+} , and 1502 and 1484 eV in F^{6+} ($\pm 0.6\%$ peak location accuracy). For previously discussed reasons A and B are likely to contain states of high electronic spin. Lowering the beam energy to 2.5 MeV (shifting the equilibrium charge-state distributions to lower mean

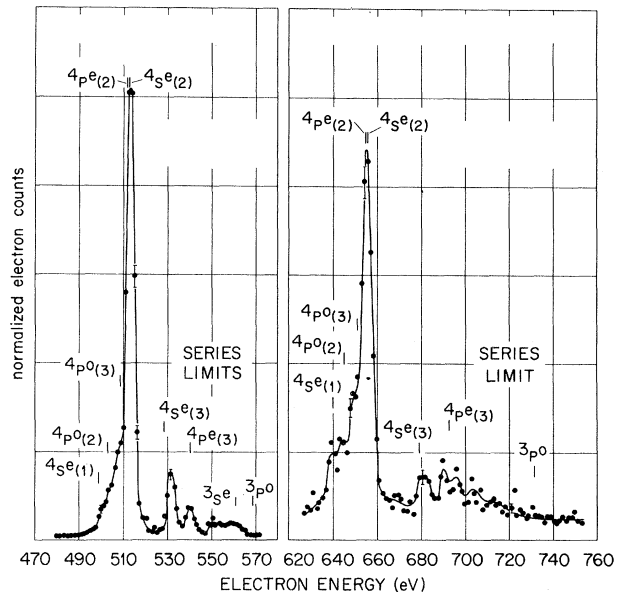


FIG. 2. As in Fig. 1, except the segment shown pertains to the higher three-electron quartet states.

charge) caused these features to become relatively more prominent than at 6 MeV. The presence of highly metastable four-electron systems is therefore suspected. Quintet spin states would be the most metastable. Detailed variational calculations must be made before firm identifications of A and B are possible.

The decays in flight of several states in the spectrum were studied by the standard method of measuring the counting rate (per unit beam current) as a function of target position, over a range of 15 cm. The features marked ${}^4P^e(1)$, A , B , and ${}^4P^e(2)$, ${}^4S^e(2)$ were studied [notation: ${}^4P^e(2) - 1s2p3p {}^4P^e$; ${}^4S^e(2) - 1s2s4s {}^4S^e$]. Complete spectra at selected downstream target positions were also accumulated. All but one feature had complex decay curves in the sense that more than one exponential was clearly needed to fit the data. (In each case fast components of order 1 nsec or less were present.) Only the decay curve for the feature corresponding to the pair of states ${}^4P^e(2)$, ${}^4S^e(2)$ contained an appreciable interval (~ 3 decay lengths) in which a single exponential was dominant. Since equal state lifetimes are unexpected, it is likely that one state predominates. A small, long-lived tail on this decay curve extending out to 15 cm was attributable to two sources of background: detector noise, and the wing of the peak corresponding to a substantially longer-lasting ${}^4P^o(2)$ feature, to which either of the ${}^4P^e(2)$ or ${}^4S^e(2)$ states (as well as other states) can cascade. Since the more energetic states in the spectrum give rise to substantially smaller features than that for the ${}^4P^e(2)$ - ${}^4S^e(2)$ pair, and since the largest of these also have even parity, it appears very likely that the decay curve in question is negligibly contaminated by cascades. Since the relative slopes of signal and background were $> 10:1$, and since the zero intercept of the extrapolated background was about 3% of that for the signal, a clear separation of the signal was possible. We measure a value of $(1.00 \pm 0.04) \times 10^{-9}$ sec (3σ counting error) for the lifetime of the state in question, a value determined by the sum of all radiative and autoionization decay channels. Which of the two states is associated with the

measured lifetime of $(1.00 \pm 0.04) \times 10^{-9}$ sec is not known. The possibility that two state lifetimes differing by $\leq 10\%$ are being observed cannot be excluded experimentally. A paper by Garcia and Mack⁶ is helpful insofar as it gives approximate radiative rates for several of the states in lithium whose isoelectronic analogs appear here. It happens that the smallest rate among those calculated by them (two to four orders of magnitude smaller than for other transitions of similar ν^3) pertains to the transition ${}^4P^o(1)$ - ${}^4P^e(2)$ because of a small radial transition moment for this process. Transitions to the ${}^4P^o(3)$ and ${}^4P^o(2)$ levels would then dominate, a situation consistent with the observed survival of the ${}^4P^o(2)$ state. Although Garcia and Mack did not calculate the relevant radiative rates for the ${}^4S^e(2)$ state, the corresponding moment is not expected to be small.⁶ It is plausible but not certain that the ${}^4P^e(2)$ level is the one observed.

The existence of appreciable populations of long-lived autoionizing states of high spin and high average excitation in highly stripped ion beams may be a general phenomenon, i.e., not restricted to these particular systems. Clearly, other systems of appreciably different Z merit investigation.

*Research sponsored in part by Union Carbide Corporation and by Oak Ridge Associated Universities under contract with the U. S. Atomic Energy Commission.

¹B. Donnally, W. W. Smith, D. J. Pegg, M. Brown, and I. A. Sellin, *Phys. Rev. A* **4**, 122 (1971); this paper includes a number of references to earlier work.

²I. S. Dmitriev, V. S. Nikolaev, and Y. A. Teplova, *Phys. Lett.* **26A**, 122 (1968); I. S. Dmitriev, L. I. Vinogradova, V. S. Nikolaev, and B. M. Popov, *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **3**, 35 (1966) [*JETP Lett.* **3**, 20 (1966)], and to be published.

³H. D. Betz, *Phys. Rev. Lett.* **25**, 903 (1970).

⁴E. Holøien and S. Geltman, *Phys. Rev.* **153**, 81 (1967), and private communication.

⁵P. Feldman, M. Levitt, and R. Novick, *Phys. Rev. Lett.* **21**, 331 (1968); L. M. Blau, R. Novick, and D. Weinflash, *Phys. Rev. Lett.* **24**, 1268 (1970).

⁶J. D. Garcia and J. L. Mack, *Phys. Rev.* **138**, 987 (1965); J. D. Garcia, private communication.