High-lying levels in uranium atomic vapor near the ionization limit*

K. T. Lu
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 30 June 1977)

This paper comments on the recent observation of Rydberg "progressions" in atomic uranium. A multichannel quantum-defect analysis shows that the observed ion peaks are unresolved groups of levels with different total angular momenta J and approximately the same effective quantum number ν_{ln}, and configuration interactions are apparent. The possible number of channels and their assignment are outlined.

Rydberg series have been the dominant spectroscopic feature of small atoms near their first ionization limit. The special properties of highly excited Rydberg levels, e.g., large orbitals, small binding energies and, above all, regularities along a series, historically have played important roles in many areas of study. Because of their extremely complex spectra and the limitations of the traditional method of observation, Rydberg spectra have never been observed in heavy elements, like uranium, until recently.[1]

One-electron photoexcitation from the ground configuration $5f^3\,6d7s^2$ in the uranium atom leads to excited configurations of the type $5f^3\,7s^2\,np$, nf or $5f^3\,6d7snp$, with the principal quantum number $n \geq 7$. For small n ($n = 7$ or 8) the excited electron has a small orbit with large overlap of electron-charge density with other electrons, and electron-electron correlation is strong among valence electrons. The levels generated are basically "non-Rydberg." However, when the excitation energy is high enough to excite one electron far away in configuration space from the ion core which contains all the rest of the electrons, the interaction between them will then be Coulombic. This signifies the generation of Rydberg levels.

We are therefore looking for an r_0 (a.u.) such that the optical electron nl sees a Coulomb potential from the ion core, e.g., $5f^3\,7s^2$, in the region $r > r_0$. According to multichannel quantum-defect theory (MQDT),[2-4] r_0 is such a radius that the spherical surface defined by it contains the ionic core after escape of the excited electron. This can be estimated by requiring all core wave functions to vanish beyond r_0:

$$P_{\lambda k}(r) \sim 0,$$

for $r \geq r_0$ for all λk. For U I, $r_0 \sim 12$ a.u., from a Hartree-Fock estimation.[5]

The criteron for MQDT parameters to exhibit minimum energy dependence is $r_0\epsilon \ll 1$,[3]; ϵ being the energy range of interest measured relative to the ionization limit in atomic units. In the case of uranium, $r_0 \sim 12$ a.u., the spectrum range for Rydberg levels to occur is

$$\epsilon \sim 0.01 \text{ a.u.} \ll 1/r_0 \sim 0.1 \text{ a.u.}$$

That is, energy levels originating from lower ion core configurations begin to be Rydberg-like about 3000 cm^{-1} below the ionization limit in uranium.

The Livermore experiment[1] measures an energy range about 500 cm^{-1} below the ionization limit, and therefore Rydberg spectra are expected. The measured spectra were accessed from a lower level with total angular momentum $J = 6$,[6] and odd parity. Neglecting hyperfine interaction, J is a good quantum number. By dipole selection rules, the measured ion signals are a superposition of spectra with $J = 5, 6$, or 7. Since the final states are reached by three-step laser processes from the ground state, they have even parity. We begin by counting and labeling channels whose Rydberg series have total angular momentum $J = 5, 6$, or 7 and even parity, with the optical electron ϵlj converging on various ionization limits I_m[7] with the core state $C[BJ_c]^0$. Table I is a sample of possible channels. Channels consisting of an optical electron with $l > 3$ are neglected, since the experiment is performed using atomic beams,[1] and higher orbital angular momentum states populated by collisions are not likely.[8] There are at least 4, 3, and 2 channels with $J = 5$, 6, and 7, respectively, converging on the first ionization limit. There are at least 4, 4, and 3 channels with $J = 5$, 6, and 7, respectively, converging on the 2nd ionization limit. Similarly, one can count the number of channels converging on the 3rd ionization limit and so on. Since total angular momentum J is a good quantum number, configuration mixes only channels with same J. The 20 channels converging on the 1st and 2nd ionization limits form 3 independent groups: there are 8, 7, and 5 channels with $J = 5$, 6, and 7, respectively. Since the excited levels are reached by lasers from a lower level with $J = 6$,[6] the resultant spectrum is a superposition of all channels with $J = 5$, 6, or 7.

At each energy level postion E_n, a set of effective quantum numbers $(\nu_1, \nu_2, \ldots \nu_m)$ relative to the ion-

TABLE I. Possible channels in U I.

I_m (cm^{-1}) [a]	C $[BJ_c]^\circ$	$\epsilon_m lj$	J
$I_1 = (49\,958.1)$ [b]	$5f^3 7s^2[^4I^9_2]^\circ$	$\epsilon_1 p\frac{1}{2}$	5
$I_1 = (49\,958.1)$ [b]	$5f^3 7s^2[^4I^9_2]^\circ$	$\epsilon_1 p\frac{3}{2}$	5,6
$I_1 = (49\,958.1)$ [b]	$5f^3 7s^2[^4I^9_2]^\circ$	$\epsilon_1 f\frac{5}{2}$	5,6,7
$I_1 = (49\,958.1)$ [b]	$5f^3 7s^2[^4I^9_2]^\circ$	$\epsilon_1 f\frac{7}{2}$	5,6,7
$I_2 = I_1 + 289.04$	$5f^3 6d7s[^6L^{11}_2]^\circ$	$\epsilon_2 p\frac{1}{2}$	5,6
$I_2 = I_1 + 289.04$	$5f^3 6d7s[^6L^{11}_2]^\circ$	$\epsilon_2 p\frac{3}{2}$	5,6,7
$I_2 = I_1 + 289.04$	$5f^3 6d7s[^6L^{11}_2]^\circ$	$\epsilon_2 f\frac{5}{2}$	5,6,7
$I_2 = I_1 + 289.04$	$5f^3 6d7s[^6L^{11}_2]^\circ$	$\epsilon_2 f\frac{7}{2}$	5,6,7
$I_3 = I_1 + 914.765$	$5f^3 6d7s[^6K^9_2]^\circ$	$\epsilon_3 p\frac{1}{2}$	5
$I_3 = I_1 + 914.765$	$5f^3 6d7s[^6K^9_2]^\circ$	$\epsilon_3 p\frac{3}{2}$	5,6
$I_3 = I_1 + 914.765$	$5f^3 6d7s[^6K^9_2]^\circ$	$\epsilon_3 f\frac{5}{2}$	5,6,7
$I_3 = I_1 + 914.765$	$5f^3 6d7s[^6K^9_2]^\circ$	$\epsilon_3 f\frac{7}{2}$	5,6,7

[a] Reference 7.
[b] Reference 1.

ization limit $(I_1, I_2, \ldots I_m)$, respectively, is evaluated according to Eq. (1a).[9]

$$E = I_i + \epsilon_i = I_i - 1/2\nu_i^2, \quad i = 1, 2, \ldots M \tag{1a}$$

or

$$I_i - 1/2\nu_i^2 = I_j - 1/2\nu_j^2, \quad i \neq j. \tag{1b}$$

This set of ν_i spans an M-dimensional space for the M-limit problem. An M-limit problem may be viewed as a set of $1/2\,M(M\text{-}1)$ two-limit problems by plotting various pairs of values (ν_i, ν_j) for each energy level E_n on a two-dimensional plot ν_i vs ν_j. The procedure is equivalent to projecting the M-dimensional plot onto two-dimensional (ν_i, ν_j) planes.[10] Since each term is a trigonometrical function in the equation

$$F(\nu_1, \nu_2, \ldots \nu_m; \mu_\alpha, U_{i\alpha}) = 0 \tag{2}$$

which determines all the discrete spectra[4] where μ_α and $U_{i\alpha}$ are quantum-defect parameters,[4] it is sufficient to plot the modulus of ν_i.[9] Figure 1 is a ν_1 (mod 1) vs ν_2 plot with (ν_1, ν_2) evaluated relative to the 1st and 2nd ionization limits according to Eq. (1a) for all the experimental data as shown in Fig. 2. The solid oblique line in Fig. 1 represents the parabolic line $\nu_1(\nu_2)$ defined by Eq. (1b) and modulus 1 plotted on ν_1. The number marked on each branch of the line indicates the integer number of the effective quantum number ν_1, $n = \nu_1 - \nu_1(\text{mod}\,1)$. The hand-drawn dashed curves passing through the data points in order of increasing ν_2 (or increasing in energy) represents the projection of Eq. (12) onto (ν_1, ν_2) plane. The prescription of MQDT[4] requires that all the data points lie on the intersections of these curves connecting the data points with the oblique lines. The number of intersections of the curves represented by Eq. (2) with the oblique line within one unit, from n to $n+1$, determines the minimum number of channels associated with the plane (ν_i, ν_j). It is expected that there ought to be around 20 such intersections according to Table I corresponding to 20 channels converging to the 1st and 2nd ionization limits.

Note that in Fig. 1, the maximum number of data points lying on one branch of the oblique line is only 5 (e.g., $n = 32$ and 35). Although some of the transitions into channels listed in Table I may be very weak, the absence of a large number of channels is bothering. Figure 2 shows the experimentally measured spectrum.[1] Note that the spacing between two neighboring peaks is comparable with

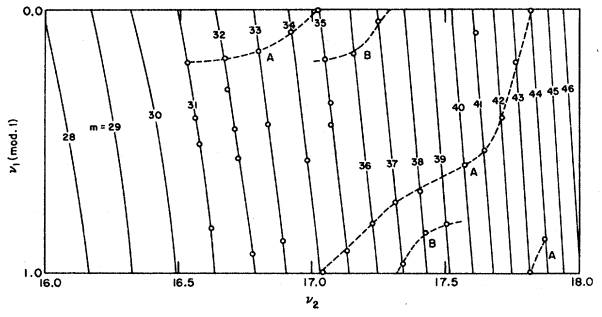

FIG. 1. Quantum defect ν_1 (mod 1) vs ν_2 plot. Open circles are experimental data from Fig. 2. Hand-drawn dashed curves (marked A or B) represent the projection of Eq. (2) onto the (ν_1, ν_2) plane. Solid oblique lines represent the parabolic line $\nu_1(\nu_2)$ defined by Eq. (1b) and modulus 1 plotted on ν_1. The numbers marked on each branch of the line indicate the integer number of the effective quantum number ν_1, $n = \nu_1 - \nu_1(\text{mod}\,1)$.

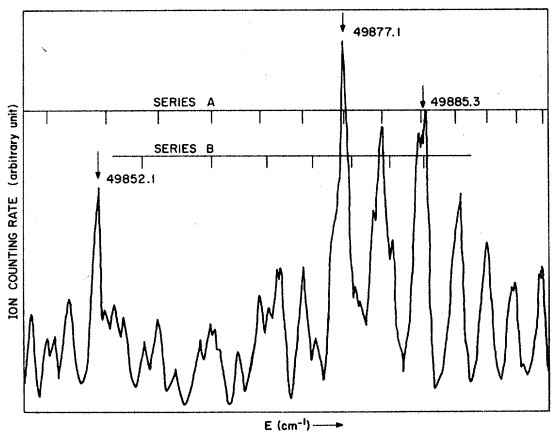

FIG. 2. Experimental data from Refs. 1 and 6.

full width at half maximum (FWHM) of each peak which is about $1 \sim 2\,\mathrm{cm}^{-1}$. However, the estimated spacing between levels belonging to the same configuration with different J values but the same large n value ($n \gtrsim 30$), $n = \nu_1 - \nu_1 (\mathrm{mod}\,1)$, is less than $1\ \mathrm{cm}^{-1}$.[11] Namely, for a given configuration, the effective quantum number ν_{ln} depends only weakly on J, while the spacing between two consecutive Rydberg levels for a given channel for n around 40 is a few cm^{-1}.[11] It is therefore plausible to assert that the observed ion peaks are unresolved groups of levels with different total angular momenta J and approximately the same effective quantum number ν_{ln}.

It is possible to draw two smooth curves (marked A and B) passing through the data points in Fig. 1. Since each data point represents approximately a term energy with unresolved levels, and since, furthermore, the evaluated effective quantum numbers depend on the ionization potential used ($I_1 = 49\,958.1\ \mathrm{cm}^{-1}$), the detailed shape of the curves cannot be taken seriously. Nonetheless, all the data points that lie on one curve represent one series of Rydberg terms. The quantum defect $\mu = [-\nu_1 (\mathrm{mod}\,1)]$ varies substantially along a series (increasing order of energy) rather than being a constant, indicating that strong configuration interactions exist. Configuration interactions on a given Rydberg series could arise either from mutual interaction among different Rydberg channels or from perturbation by interloping valence levels. The latter interaction would result in a redistribution of oscillator strength from interlopers into Rydberg levels and therefore enhance the intensities of the higher Rydberg levels which are otherwise inversely proportional to ν_{in}^3. The experimental setups of Livermore did not permit a sensible judgement on the cross sections of ion peaks. However, the absence of Rydberg levels in the energy region above $45\,000\ \mathrm{cm}^{-1}$ in the recent photoabsorption measurement in uranium[12] suggests that these high-lying Rydberg levels are not disturbed by the interloping valence levels and that their oscillator strengths follow a ν_{in}^{-3} scaling rule are thus too weak to be detected.

In conclusion, MQDT has been applied to analysis of the spectrum in uranium vapor near its ionization limit. Rydberg series are expected to occur $3000\ \mathrm{cm}^{-1}$ below the first ionization limit and around 20 channels are anticipated and their assignments are outlined. The theory asserts that the observed ion signals are series of Rydberg terms rather than Rydberg levels. These Rydberg terms consist of an unresolved group of levels with different total angular momenta J ($J = 5, 6,$ or 7) and approximately similar effective quantum number ν_{ln}. The graphic method regiments most of the ion peaks into two series of Rydberg terms and configuration interaction is apparent. Detailed identification and assignment awaits improved data in resolved energy levels. The latest results from Livermore show that the formerly unresolved ion peaks split now into 8 or more peaks after the laser band width has been narrowed.[6] Significantly, there are no detectable ion signals between two formerly unresolved peaks.

The extreme complexity of the spectrum near the ionization limit in the uranium atom indeed provides a formidable challenge to the spectroscopist. A multichannel, multilimit MQDT analysis may prove to be a plausible method to disentangle the problem. On the other hand, a new type of experiment which selects energy levels according to their set of good quantum numbers, in this case parity and total angular momentum, is needed.

---

*Work performed under the auspices of the Division of Physical Research of the U. S. Energy Research and Development Administration.

[1]R. W. Solarz, C. A. May, L. R. Carlson, E. F. Worden, S. A. Johnson, J. A. Paisner, and L. J. Radziemski, Jr., Phys. Rev. A 14, 1129 (1976).
[2]M. J. Seaton, Proc. Phys. Soc. Lond. 88, 801 (1966).
[3]U. Fano, Phys. Rev. A 2, 353 (1970); J. Opt. Soc. Am. 65, 979 (1975).
[4]K. T. Lu, Phys. Rev. A 4, 579 (1971).
[5]C. Froese-Fischer, Comput. Phys. Commun. 1, 151 (1969).
[6]R. W. Solarz (private communication).
[7]D. W. Steinhaus, J. Radziemski, Jr., R. D. Cowan, J. Blaise, G. Guelachvili, Z. B. Osman, and J. Verges, Los Alamos Report No. LA-4501 (1971) (unpublished).
[8]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 35, 644 (1975).
[9]K. T. Lu and U. Fano, Phys. Rev. A 2, 91 (1970).
[10]J. A. Armstrong, P. Esherick, and J. J. Wynne, Phys. Rev. A 15, 180 (1977).
[11]K. T. Lu (unpublished).
[12]F. S. Tomkins, H. Crosswhite, and H. M. Crosswhite, Jr., J. Opt. Soc. Am. 66, 1068 (1976) (Tucson Annual Meeting Abstracts).