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Electronic structure of excited configurations in uranium

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Abstract

The electronic level and transition probability data obtained by calculation with the intermediate coupling scheme for the uranium atom suggest that highly excited configurations of the neutral uranium atom, such as f^3s^2nd, f^3s^2nf, f^3dsnd, f^3dsnf, are described well as systems of weak coupling between the ionic core, f^3s^2 or f^3ds, and an electron in an excited orbit, and levels are derived from the spin–orbit splitting of ionic states for each J value. This concept is applied to the ionization of f^3s^27d through f^3s^27f and that of f^3ds7d through f^3ds7f.

1. Introduction

In the laser isotope separation of atomic uranium the photoionization from a highly excited level is used as the final stage of promotion, and for achievement of efficient ionization a good deal of knowledge of the spectroscopic nature of excited levels is demanded. The neutral uranium atom is known to possess a vast number of levels. According to the literature [1] about 2000 levels for which J value, g value and isotope shift have been measured are known, and assignment of configuration and term has been made for more than 200 levels, most of which lie below 20 000 cm^{-1}. For highly excited levels, however, information is very poor. In particular, odd-parity levels above 33 000 cm^{-1} which should be the final target level for the three-step photoionization are mostly deficient in g value and isotope shift data which are indispensable to the identification of configuration. Levels higher than 38 100 cm^{-1} are not known even in energy, and no level has been assigned to the configuration f^3ds7d supposed to be most important for ionization as described below. The aim of the present work is to investigate the electronic structure of excited configurations and to find some rules available to evaluate the ionization probability on the basis of the electronic description. As a tool we used computer calculations with the intermediate coupling scheme [2] to obtain energies and eigenfunctions of levels belonging to excited configurations. The following discussion is an analysis of this computer experiment.

2. Ionization of f^37d

The configuration f^3s^27d is identified only for the ground state $^5L_6$ (27 920.942 cm^{-1}) [1]. Another level supposed to belong to that configuration is 33 119.00 cm^{-1} with $J=7$, because it is promoted from f^3s^2p and excited to the ionization limit f^3s^2 ($^4I_{9/2}$) [3]. We assume that level to be f^3s^27d. The energy level scheme calculated for $J \geqslant 5$ is shown in Fig. 1. The second excited level of $J=7$ (5184 cm^{-1} above $^5L_6$) seems to correspond

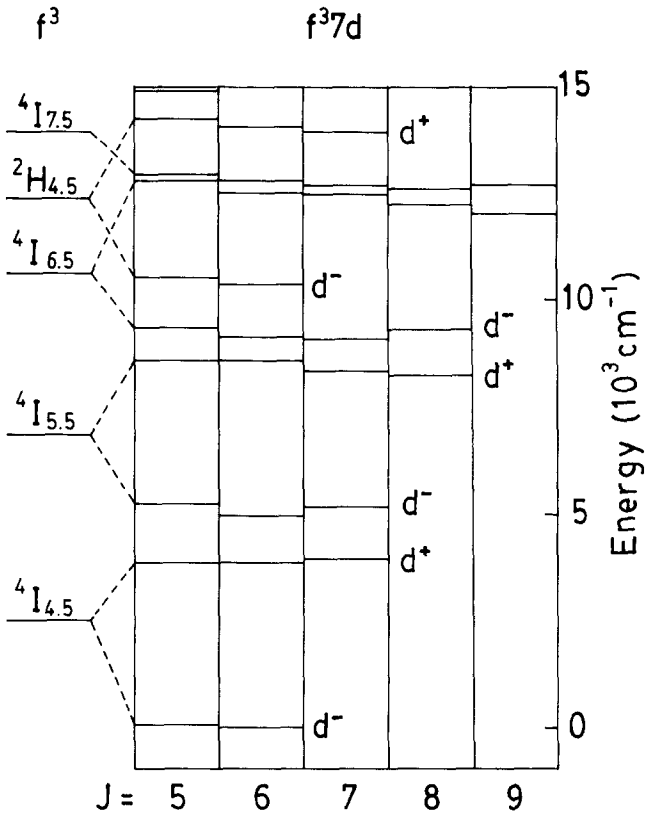

Fig. 1. Computed energy level schemes for f^37d. Broken lines indicate that the level structure of f^37d is derived from splitting of f^3 levels into spin-up states (d^+) and spin-down states (d^-).

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TABLE 1. Transition probabilities from $f^3 7d$ to $f^3 7f$[a]

$f^3 7f$ ($J=7$)	$f^3 7d$ ($J=6$)	$^4I^-_{4.5}$ 0[a]	$^4I^+_{4.5}$ 3855	$^4I^-_{5.5}$ 4976	$^4I^+_{5.5}$ 8603	$^4I^-_{6.5}$ 9135	$^2H^-_{4.5}$ 10362	$^4I^+_{6.5}$ 12492
$^4I^-_{4.5}$	191[a]	2.020	0.014					
$^4I^-_{5.5}$	4592		0.272	1.109	0.040		0.001	
$^4I^+_{4.5}$	6400	0.001	1.431	0.292			0.002	
$^4I^-_{6.5}$	7892				0.052	0.747		0.041
$^2H^-_{4.5}$	9878		0.003	0.005	0.123	0.003	1.732	0.002
$^4I^+_{5.5}$	10504				1.118	0.066	0.165	0.004
$^4I^+_{6.5}$	14083				0.007	0.005		0.846

[a]Energies are measured in reciprocal centimetres from the ground state of the corresponding configuration.

to the level 33 119.00 cm^{-1} (5199 cm^{-1} above $^5L_6$). We see that the levels are beautifully grouped in lines and given by splitting of the ion core (f^3) states. The interval is nearly equal to the spin–orbit splitting of 7d. Levels of $f^3 7d$ are thus described well by the combination of ion core term and spin state.

It is known that the spectrum recorded on ionization exhibits a set of lines corresponding to discrete valence states rather than a continuum [3]. Therefore, ionization from an excited state would be looked on as consisting of two processes although these are experimentally not separable. One is photoexcitation to a level above the ionization limit and the other is autoionization of that state. Accordingly, the ionization cross-section is given by the product of the transition probability of photoexcitation and the autoionization cross-section. The former is the product of the angular part and the radial part which is called the transition integral. Since the transition integral has a particularly large value for a couple with the same principal quantum number, we choose $f^3 7f$ as a photoexcitation target from a level belonging to $f^3 7d$.

The phototransition probability from $f^3 7d$ to $f^3 7f$ caused by the absorption of electric dipole radiation has been computed for level pairs with $J \geqslant 5$ in the intermediate coupling scheme. In Table 1 is shown the result of the calculation for transitions from some low-lying $f^3 7d$ levels with $J=6$ to $f^3 7f$ levels with $J=7$. Since each level is well characterized by the ion core term and the spin state, a level is designated by the term with the superscript $\pm$ according to the spin component of the excited electron. In Table 1 we see that a transition between levels of the same term and the same spin component has a large value.

Calculation of photoemission intensity with the fractional parentage method has been made for 4f and 5f states to explain the photoemission spectra of f^n elements [4]. This mathematical process is equivalent to the calculation of the overlap integral between a state before ionization and a state after. The overlap integral is the contribution of an ion core state to the level under consideration. Thus as far as the angular part of the wavefunction is concerned, the autoionization

TABLE 2. Contribution (per cent) of ion core states to $f^3 7f$ levels with $J=7$

Energy (cm^{-1})	$^4I_{4.5}$	$^4I_{5.5}$	$^4I_{6.5}$	$^2H_{4.5}$	$^4I_{7.5}$
191	100				
4592	1	99			
6400	98	2			
7892			98		
9878		5	1	90	3
10504		93		5	
11245				3	94
14083			93	2	

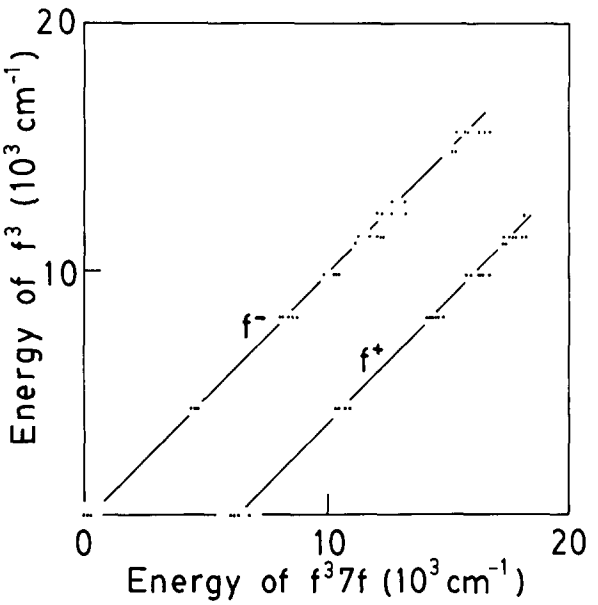

Fig. 2. Relation between energies of $f^3 7f$ and those of free ion (f^3) generated by autoionization of $f^3 7f$ with a probability greater than 0.1. Energy is measured from the ground state of the corresponding configuration.

TABLE 3. Selected transition couples for ionization of f^3ds7d to $^4L_{5.5}$ of f^3ds

f^3ds7d		f^3ds7f		Probability			GS[a] (cm^{-1})
Energy (cm^{-1})	J	Energy (cm^{-1})	J	Transition	Autoionization	Ionization	
6671	6	6060	7	0.635	0.166	0.105	44190
4315	6	6162	6	0.369	0.510	0.203	44090
6035	6	6166	7	1.480	0.143	0.212	44080
4315	6	6320	7	0.393	0.294	0.116	43930
4410	7	6558	8	1.097	0.468	0.513	43690
4468	8	7159	9	1.201	0.193	0.232	43090
7332	7	7695	8	0.712	0.113	0.080	42550
7334	6	8172	7	0.635	0.123	0.078	42070
7583	8	9092	9	0.261	0.125	0.033	41160
7583	8	9190	9	0.853	0.269	0.229	41060
7583	8	10368	9	0.713	0.211	0.150	39880

[a]Energy required to the ground state of f^3ds7f for the autoionization.

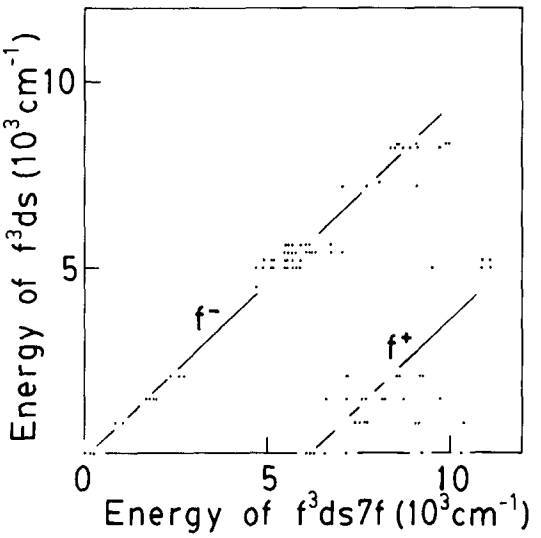

Fig. 3. Relation between energies of f^3ds7f and those of free ion (f^3ds) generated by autoionization of f^3ds7f with a probability greater than 0.2. Energy is measured from the ground state of the corresponding configuration.

probability to an ionic state is equal to the contribution of the ion core term. The contribution of the ion core term to each state of f^37f has been calculated for 60 levels of f^37f and the result for $J=7$ is given in Table 2, where we see that f^37f is also a system in which a level is essentially deduced from the splitting of an ionic state. The energy interval between two components is about 6000 cm^{-1} corresponding to the spin–orbit splitting of the 7f electron. In Fig. 2 is shown the relation between the energy of f^37f and that of the ion for which the overlap integral is larger than 0.1. We see that plotted points are arrayed on two straight lines; one line crossing the origin indicates that the energy of f^37f measured from the ground state is nearly equal to that of f^3 measured from the ionization limit. This means that these f^37f states could only be ionized under an unrealistic condition that the ground state of f^37f lies very near the ionization limit. On the contrary, the second straight line parallel to the first shows that the energy of f^37f is about 6000 cm^{-1} lower than that of the ion, and it seems to suggest the possibility of ionization. However, this requires the ground state of f^37f to lie at an energy higher than about 44 000 cm^{-1}, and taking into consideration the fact that the ground state of f^37d lies at 27 921 cm^{-1}, we cannot expect this requirement to be satisfied. It would easily be recognized that the first group is composed of spin-down states and the second of spin-up states.

3. Ionization of f^3ds7d

The ionization process of f^3ds7d through f^3ds7f is treated in a quite similar way to that from f^37d to f^37f discussed above. We have calculated the energies and eigenvectors for each of 45 levels of f^3ds7d and 70 levels of f^3ds7f both with $J \geqslant 6$. The level structure of f^3ds7d–$7f$ is much more complicated than that of f^37d–$7f$. This may be due to the structure of f^3ds with much more densely located states than f^3 and a strong interaction between 7d–7f and 7s. In spite of the complicated level structure, the same scheme as seen in the f^3–core system still works well. The relation between the energy of f^3ds7f and that of the ion with an autoionization probability larger than 0.2 is given in Fig. 3. As in the case of f^37f (Fig. 2), the plotted points are grouped into two; one in a diagonal line and the other parallel to that but about 7000 cm^{-1} separated and scattered. From the discussion above it is clear that ionization is energetically impossible for the former group. For the second group, we note that levels with large autoionization probability are found in a much higher energy region compared with Fig. 2. If we focus

on the autoionization to the lowest level of the ion, $^6L_{5.5}$, a level with probability 0.21 is found at an energy about 10 000 cm^{-1} above the ground state of f^3ds7f and a level with the value of 0.27 at about 9000 cm^{-1}. This allows those levels to autoionize if the ground state of f^3ds7f lies at an energy higher than about 40 000 cm^{-1}. Here we take the f^3ds7f levels of the second group with the autoionization probability to $^6L_{5.5}$ larger than 0.10 and make a couple for each of them with an f^3ds7d level that has the largest transition probability to the corresponding f^3ds7f state. Table 3 gives the result. The highest value for the ionization probability is about 0.5 for the couple at 4410 cm^{-1} of f^3ds7d and 6558 cm^{-1} of f^3ds7f. This is indeed a high value, because the sum of the probabilities for transitions from a level of f^3ds7d ($J=7$) to all possible f^3ds7f states is theoretically given to be 3.0 and the autoionization probability is at most unity.

4. Conclusion

(1) The levels of a highly excited configuration of a uranium atom are essentially deduced from the splitting of an ion core state into the spin-up and spin-down states.

(2) The largest transition probability between two configurations is found when the levels have the same ion core term and the same spin component of the excited electron.

(3) The autoionization is possible only when the level is characterized by the spin-up state.

(4) Ionization of f^3s^27d with a large cross-section is not expected. Ionization of f^3ds7d with a high value of the ionization probability is possible if the ground state of f^3ds7f is higher than 40 000 cm^{-1}.

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