Mean life of the 27 887-cm^{-1} level in U I†

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Measurements of the mean life of the 27 887-cm^{-1} level in U I have been made at a single vapor density using electronic excitation and a method of delayed coincidence. The lifetime values were obtained by optically detecting the decay of the 3584.9-Å resonance transition. Using branching ratios obtained from known relative f values, the average of the measured lifetimes was corrected for imprisonment of the resonance radiation, and absolute f values were derived from the corrected lifetime giving the following results: $\tau_0 = 7.3 \pm 1.1$ nsec, $f_{3585} = 0.18 \pm 0.03$, and $f_{4620} = 0.20 \pm 0.03$. The error given with each quantity is the standard deviation as determined from the dispersion of the individual measurements. A systematic error of 1% due to possible nonlinearities in the time scale of the system is also assigned to the results. Unaccounted for systematic errors affect only the correction in the measured lifetime, which is small compared to the statistical error. The lifetime and f values are presented in comparison with the experimental results of another group of workers.

INTRODUCTION

The mean life of the upper level of the 3584.878-Å resonance transition in U I (27 886.992 cm^{-1}) has been determined using electronic excitation, a newly developed beam source of heavy atoms,[1] and a previously described method of delayed coincidence.[2-5] This lifetime determination is relevant to recent developments in uranium isotope separation which emphasize the almost complete lack of data on transition probabilities in the uranium atom.[6] It will be used to place relative transition probabilities, such as those of Voigt,[7] on an absolute scale.

EXPERIMENTAL METHOD

In the lifetime measurements carried out here, the atoms in the vapor state are excited by a pulsed beam of low-energy electrons. The decay times of individual events are measured by a time-to-pulse-height converter and are stored in a pulse-height analyzer. A system time calibration of 3.01 ± 0.04 nsec per analyzer channel and an electron energy of 100 eV were used in the present measurements. In obtaining these measurements, the technique of crossed beams was utilized. In this technique the exciting beam is incident perpendicularly upon the source beam, and light from the decay of an excited state is viewed normally to the plane of the beams.

The uranium atoms in the vapor state were obtained in a diffuse beam from a Knudsen effusion device especially designed to vaporize heavy elements. The beam source, which has as its central element a tantalum or tungsten effusion cell, has been described in a previous work on Ag I.[1] In that experiment the vaporization of the silver metal and effusion of the atoms from the cell were achieved in a straightforward manner. With uranium, however, extraordinary measures must be taken in handling the molten metal. As has been noted by Ackermann and Rauh,[8] at temperatures above ≈1900 K liquid uranium rapidly passes via creep into the grain-boundary network of polycrystalline tantalum and tungsten. The same authors describe single-crystal tantalum and tungsten as excellent materials for containing molten uranium at temperatures up to at least 2400 K. In the present experiment a single-crystal tungsten liner inside a polycrystalline tungsten cell was used successfully to confine the liquid uranium and vaporize it into a beam of atoms.

The sample of uranium used was National Bureau of Standards Standard Reference Material 960. This material is of normal isotopic composition and has been determined to be 99.975% pure. The chief impurities, present in amounts of 50 ppm or less, are iron, silicon, aluminum, and nickel.

IMPRISONMENT THEORY

Since the 3584.88-Å transition has the ground state as its lower level, it is necessary to determine to what extent the measured lifetimes have been lengthened by possible imprisonment of the emitted radiation. At low optical densities and neglecting polarization effects, the theories of resonant photon imprisonment reduce to[9,10]

$$\tau_m = \tau_0(1 + ak_0LB_r), \tag{1}$$

where τ_m is the measured lifetime, τ_0 is the natural (zero vapor density) lifetime, a is a constant determined by the geometry of the source and exciting beams and by the functional form of the velocity distribution of the atoms in the source

beam, k_0 is the absorption coefficient at the center of the Doppler-broadened resonance line, L is a characteristic dimension of the source, and B_r is the branching ratio of the resonance transition. The branching ratio is defined by the relationship

$$B_r = A_r \tau_0 , \tag{2}$$

where A_r is the probability per unit time for emission of a quantum of resonance radiation by an isolated atom. The absorption coefficient is given by the expression

$$k_0 = \frac{\lambda_0^3 n}{8\pi} \frac{g_2}{g_1} \frac{A_r}{\nu_0 \pi^{1/2}} . \tag{3}$$

Here, λ_0 is the wavelength at the line center, ν_0 is the most probable thermal speed of a uranium atom, n is the particle density of unexcited uranium atoms, and g_2 and g_1 are the statistical weights of the resonance and ground levels, respectively.

Operating at densities low enough that Eq. (1) is applicable allows the correction for imprisonment to be made in a straightforward manner. At such densities, as will be seen below, the correction is small. Because high temperatures are needed to produce an appreciable vapor of uranium, a condition of low density for which Eq. (1) is valid was readily obtained. Operating in such a low density region also rules out the other important possible density effect, competing collisionally induced decay.

ANALYSIS

The decay-time distribution of the lifetime runs showed no obvious evidence of multiexponential decay. Nevertheless, the runs were analyzed using a least-squares computer program to fit two exponentials and a background to the raw data. The results of the computer analysis, which gave pairs of exponentials with lifetimes of approximately 7 and 10 000 nsec, support the initial finding of single-exponential decay.

In obtaining the runs, the optical monochromator was adjusted so that only radiation from the transition of interest was transmitted. The setting of the monochromator was determined from the results of auxiliary moderate-resolution ($\lesssim$1.5 Å) spectrographic exposures made with the lifetime apparatus under typical conditions of a lifetime run. The exposures, which covered the wavelength range 3500–3900 Å, showed only the strong lines from U I at 3514.61, 3566.60, 3584.88, 3659.16, 3812.00, 3854.22, and 3871.04 Å. No lines from U II were present. Thus, with the 3585-Å line separated from its nearest neighbor by $\approx$18 Å, a broad slit setting of 1.0 mm, representing a bandpass of 16 Å, was adequate to isolate the subject spectral line.

The 100-eV electron energy used is considerably greater than the 3.5-eV threshold excitation energy of the 27 887-cm^{-1} level, and thus one could expect cascading from simultaneously excited higher levels feeding the one under investigation. However, the absence of evidence of such an effect can be attributed to cascading transitions which are very much weaker than the transition of interest. Very little information can be obtained from U I line and level lists concerning downward transitions which terminate in the 27 887-cm^{-1} level. From the level lists of Guyon,[11] only one allowed transition could be derived as a possible source of population of the subject level by cascading. This transition, which has an upper level of 34 160.567 cm^{-1} and a calculated wavelength in air of 15 935.521 Å, has not been observed. Thus, the absence of detectable cascading is consistent with the present state of knowledge of the U I spectrum.

Four measurements were used to obtain the final result for the mean life of the 27 887-cm^{-1} level. The runs were made consecutively at the same vapor density and yielded an average value for the lifetime of 7.4 nsec with a standard deviation of 1.1 nsec. This average value must now be corrected for the imprisonment of the 3585-Å radiation.

CORRECTION FOR IMPRISONMENT

In applying Eqs. (1)–(3) to the correction of the measured mean life, a procedure of self-consistent parameter adjustment was utilized. In this procedure a value of τ_0 is initially assumed. With B_r known, A_r is determined from Eq. (2), and k_0 is evaluated using Eq. (3). With a and L known, Eq. (1) is then used to determine τ_0. If the value of τ_0 obtained from Eq. (1) is different from its assumed value, the assumed value is adjusted, and the procedure is repeated until the assumed and corrected values agree.

In making use of Eq. (1) here, the quantities L, a, and B_r are taken as known and therefore must be evaluated by independent means. The quantity L in the present work corresponds to $\frac{1}{2}L_{\text{eff}}$ in a previous work on lifetime measurement in Ag I.[1] In that work, carried out with apparatus almost identical to that used in the present experiment, L_{eff} is the effective thickness of the layer of atoms. An effective thickness had to be used in the previous work because of experimental deviations from an assumed infinite slab used in a derivation. The value of L_{eff} for the previous experiment was found to be 1.3 cm. In accord with the slightly different configuration of the atomic beam source used in the present experiment, the value of L_{eff} was

scaled up to give $L = 0.85$ cm.

The quantity a has not been evaluated for the case of the present experiment, a Doppler-broadened line initially emitted near the center of a layer of atoms. However, the quantity a has been evaluated for the cases of a sphere with excitation at its center and an infinite cylinder with excitation along its axis, both for Doppler broadening, giving values of $1/\sqrt{2} = 0.7$ and $\pi/2\sqrt{2} = 1.1$, respectively.[10] Since the geometry of the present experiment is similar to the above example of the cylinder, a value of $a = 1.0$ was chosen for use in Eq. (1). In the calculation carried out below to correct the measured mean life, a may be varied as much as 50% without producing a change greater than 1% in the corrected value of τ_m.

The quantity B_r, the branching ratio for the 3585-Å transition, is determined from the relative gf value measurements in UI of Voigt.[7] As many as 54 allowed downward transitions from the 27 887 cm^{-1} level can be derived from the level lists of Guyon.[11] However, observation of only 11 of these transitions has been reported.[11,12] Of the ten observed spectral lines in the wavelength range 3500–8400 Å, two are much stronger than the others; and only these two, at 3585 and 4620 Å, were of sufficient intensity to be included in the measurements of Voigt. Thus, the branching ratio had to be determined on the basis of these two transitions and was found to be 0.6. The work of Voigt indicated an uncertainty in the branching ratio of $\lesssim 10\%$ due to statistical and systematic errors in the relative gf values. A further systematic error might be attributed to the omission of transitions above 8400 Å. This seems unlikely in the region 8400–14 000 Å since the single transition observed by Guyon in this region was quite weak. No information is presently available on the existence of transitions with wavelengths longer than 14 000 Å.

In applying the imprisonment theory, the particle density of unexcited uranium atoms in the beam, n, must be determined to correct τ_m. Referring to Ramsey[13] and Klose,[1]

$$n = \frac{2}{3\pi}\frac{1}{l_0^2}\frac{p'}{kT}r_s^2 \quad (4)$$

for an effusion cell with a very thin lid. In Eq. (4), l_0 is the distance from the effusion cell to the center of the observation window, p' is the pressure inside the cell, T is the absolute temperature, and r_s is the radius of the aperture in the lid of the cell. For the configuration of the beam source used in the present work, $l_0 = 5.35$ cm and $r_s = 0.1$ cm.

To determine n, the pressure of the uranium vapor inside the effusion cell must be obtained at the true temperature of the cell. The temperature was measured by sighting an optical pyrometer on the aperture in the lid of the cell. Column one in Table I gives the brightness temperature T_B as measured through a 7056 glass window. Column two gives the brightness temperature corrected for reflections at the window surfaces, T_{BC}. The true temperature, obtained by correcting for the nonblackbody character of the glowing cell, is given in column three. The corrections to arrive at the true temperature were made using information given in a compendium of radiometry by Kaspar.[14]

Two sources of vapor pressure data were utilized to obtain values for the pressure of uranium inside the cell given in column four of Table I. The determinations of Storms[15] and Ackermann and Rauh[8] were judged to be more reliable than the evaluation of Hultgren *et al.*,[16] which was completed in 1967 and did not include the results of these two works. Finally, the particle densities in the beam were calculated from Eq. (4) and are given in column five of the same table. The difference in the particle densities as determined from the two values of vapor pressure is an indication of the magnitude of a possible systematic error in n.

In Eq. (3) the quantity ν_0 represents the component of velocity in the observing direction of an atom in the beam with the most probable speed. The half-angle divergence of the beam, θ, determined from the configuration of the source was 9.96°. Since the divergence angle was small and the angular distribution of atoms in the beam was continuous, all atoms in the beam were assigned a half-angle divergence of $\theta/2 = 4.98°$. Referring to Ramsey,[13] the value of ν_0 is given by the expression

$$\nu_0 = \left(\frac{3}{2}\right)^{1/2}\left(\frac{2RT}{M}\right)^{1/2}\sin(\theta/2) \quad (5)$$

and is listed in column six of Table I.

TABLE I. Experimental parameters used in correcting the measured mean life for radiative imprisonment.

T_B (K)	T_{BC} (K)	T (K)	p' (10^{-6} atm)	n (10^9 cm^{-3})	ν_0 (10^3 cm sec^{-1})	τ_m (10^{-9} sec)	τ_0 (10^{-9} sec)	A_{3585} (10^8 sec^{-1})	A_{4620} (10^8 sec^{-1})
2113	2130	2323	7.08 [a]	1.66	4.28	7.4	7.3	0.82	0.55
			6.92 [b]	1.62			7.3	0.82	0.55

[a] Reference 8.

[b] Reference 15.

TABLE II. The natural mean life and absolute f values for the 27 887-cm^{-1} level in U I.

Authors	Method	Mean life (nsec)	f_{3585}	f_{4620}
Present work	Delayed Coin.	7.3 ± 1.1 [a]	0.18 ± 0.03 [a]	0.20 ± 0.03 [a]
Corliss and Bozman [b]	Arc	11	0.16	0.058

[a] Determined using branching ratios of Voigt (Ref. 7).
[b] Reference 17.

Finally, using the values given above for L, a, and B_r and evaluating k_0 by means of Eq. (3), we solve Eq. (1) for the natural mean life τ_0 given in column eight of Table I. Columns nine and ten display the values of the probabilities determined here for the 3585- and 4620-Å transitions. It is seen from Table I that the results for the mean life and transition probabilities are the same for either of the values of p', the vapor pressure inside the cell.

RESULTS

Table II gives the natural mean life and absolute f values as determined in the present experiment, with the results of one other group of workers for comparison. Throughout the runs of the present work, the temperature of the effusion cell was maintained constant with a reproducibility in measurement of ±2 absolute degrees. Thus, the particle density of the atomic beam was assumed to be constant with a maximum variation of $\pm 0.034 \times 10^9$ cm^{-3} as determined from the maximum temperature variation. The electron beam was also highly stable over the duration of the runs which ranged in length from 12 to 40 min.

The error given with the present results in Table II is the standard deviation as determined from the dispersion of the individual measurements. In addition, a systematic error of ≈1% due to possible nonlinearities in the time scale of the system is assigned to the present results. Other possible systematic errors in L, a, B_r, and n are presently difficult to evaluate. In this connection it should be emphasized that errors in these four quantities affect only the correction to the measured lifetime (1%) which is small compared to the statistical error (15%). Finally, errors arising from the maximum variation in the particle density of the atomic beam due to temperature fluctuations were found to be negligible.

The mean life and f values of Corliss and Bozman[17] given in Table II are the only such quantities available for comparison with the results of the present work. These workers determined gf values for the 3585- and 4620-Å transitions, from which their value of the lifetime is derived. From Table II we see that their value of the lifetime is ≈60% larger than that of the present work. However, they indicate that their lifetime value for the 27 887 cm^{-1} level is uncertain by a factor of ≈1.8, and thus their error limits are seen to overlap the present lifetime result.

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