

Laser Resonance Photoionization Spectroscopy of Rydberg Levels in Fr

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We investigated for the first time the high-lying Rydberg levels in the rare radioactive element francium (Fr). The investigations were conducted by the highly sensitive technique of laser resonance atomic photoionization, with Fr atoms produced at a rate of about 10^3 atoms/s in a hot cavity. We measured the wave numbers of the $7p^2P_{3/2} \rightarrow nd^2D$ ($n=22-33$) and $7p^2P_{3/2} \rightarrow ns^2S$ ($n=23, 25-27, 29-31$) transitions and found the binding energy of the $7p^2P_{3/2}$ state to be $T = -18924.8(3) \text{ cm}^{-1}$, which made it possible to establish accurately the ionization potential of Fr.

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At the present time, in the periodic system there remain very few "white spots," i.e., elements whose spectral properties have not been studied. These are rare radioactive elements which in nature are either altogether absent or extremely scarce. One such element is francium (Fr) which, unlike the other alkali metals, has no stable isotopes and only one natural radioactive isotope, ^{223}Fr (half-life $T_{1/2}=22$ min), resulting from the radioactive decay of ^{235}U , one Fr atom being found in 3×10^{18} atoms of native uranium. The low natural abundance of Fr, along with its exceedingly high chemical activity, make its spectral investigation extremely difficult. The first such study was performed only at the end of the 1970's at the ISOLDE facility,¹ with a flux of Fr atoms of around 10^8 atoms/s. To date, this group of investigators has managed to measure the energies of the four low-lying levels $7p^2P_{3/2,1/2}$ and $8p^2P_{3/2,1/2}$.²

Further progress in the studies of the spectral properties of Fr requires new and more sensitive methods. One of the most sensitive spectral methods at present is the technique of laser resonance atomic photoionization.³ In the work reported by Andreev and co-workers,⁴ a new method based on laser resonance atomic photoionization was developed and studied, which allows the spectral investigation of Fr to be carried out in samples that provide a generation rate as low as about 10^3 atoms/s.⁵ In the present work, we used this method and managed to measure for the first time the energies of high-lying levels in Fr, which enabled us to determine precisely its ionization potential.

The method, described in greater detail in Refs. 4 and 5, is essentially as follows. The atoms of the element under study are photoionized by laser radiation inside a hot cavity having two small holes in its side wall to introduce the radiation and to extract the photoions generated in the cavity for further analysis and registration. While wandering inside the cavity, the atoms have enough time, before leaving it through the hole in the wall, to cross the photoionization area many times, so that the ratio between the probabilities that an atom will be exposed to the laser radiation and that it will leave the cavity

through the hole without being exposed to the radiation is given by the formula⁴

$$P = 2fl/vK,$$

where f is the laser pulse repetition frequency, l the length of the ionization region inside the cavity, v the average atomic velocity, and K the probability of the atom passing through the cylindrical channel in the cavity wall (the diameter d of the holes in the cavity wall is assumed to be not very large and to coincide with the laser-beam diameter). With the laser pulse repetition frequency high enough, $\approx 10^4 \text{ s}^{-1}$, and with the actual values of $l=1 \text{ cm}$, $v=3 \times 10^4 \text{ cm/s}$, and $K=0.28$ ⁶ (the ratio of the cavity wall thickness to the hole diameter is $h/d=3$), we have $P \approx 2$; i.e., practically all the atoms under study will be exposed to the laser radiation at least once and thus will probably be selectively ionized.

The Fr atoms were ionized in three steps (Fig. 1). First, they were excited to the state $7p^2P_{3/2}$ by laser radiation at $\lambda_1=718 \text{ nm}$,¹ then raised to a high-lying Ryd-

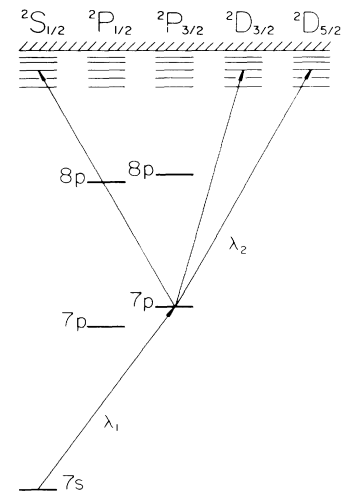


FIG. 1. Photoionization scheme for Fr atoms.

berg state by the radiation of a frequency-scanned laser, and finally ionized by electric-field pulses 4.3 kV/cm in amplitude and 130 ns in duration, which followed 200 ns after the laser pulses. The dye lasers used to photoionize the Fr atoms were pumped by a copper-vapor laser with an output pulse repetition frequency of 8.7 kHz (pulse energy ≈ 1 mJ, pulse duration ≈ 15 ns). The Cu-vapor laser radiation was divided by means of a selective mirror into two beams (Fig. 2) with wavelengths of 578.2 and 510.6 nm used to pump the first- and second-stage excitation dye lasers, respectively. The dye-laser beams were aligned to propagate coaxially in opposite directions inside the ionization cavity formed by two titanium plates 30 mm in diameter separated by an insulator of a quartz tube 10 mm in length and 2 mm in wall thickness. The diameter of the holes in the cavity walls was 1 mm. The Fr atoms were evaporated at a temperature of $\approx 1200^\circ\text{C}$ from a sample placed in a tantalum branch pipe and then entered the heated ionization cavity. Metallic Ba was placed inside the cavity to passivate its walls and reduce the work function of the materials that they were made of. The photoions produced in the cavity were expelled from it through the hole in its wall by the electric-field pulses used to ionize the Rydberg atoms, and were detected by a channel multiplier. To reduce the background noise signal due to thermal ions, the ions were mass and energy analyzed by means of a time-of-flight mass spectrometer and an electrostatic analyzer. The vacuum in the chamber housing the ion-

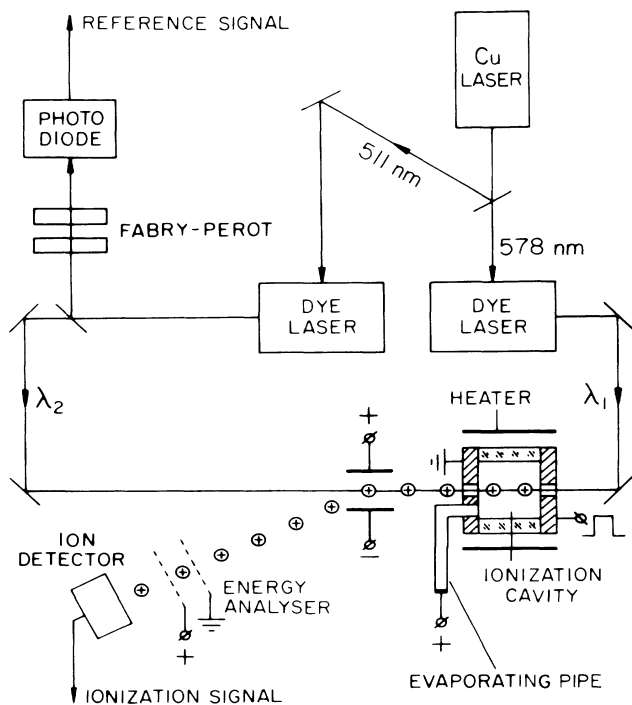
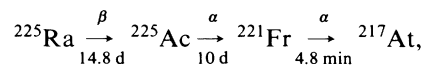


FIG. 2. Schematic diagram of experimental setup.

ization arrangement and the ion detector was kept at $\approx 10^{-7}$ Torr.

The sample used in the experiment contained $\approx 10^9$ atoms of ^{225}Ra implanted into a tantalum foil and was prepared by collection of the ^{225}Ra recoil nuclei produced as a result of a radioactive decay of ^{229}Th . The ^{225}Ra atoms decaying in the sample gave rise to the chain of elements



one of which was ^{221}Fr . Its rate of generation in the sample was measured as $\approx 10^3$ atoms/s by means of an α spectrometer.

The ion signal obtained while scanning the second-stage excitation laser with a bandwidth of $\approx 1 \text{ cm}^{-1}$ was recorded simultaneously with the signal which set frequency markers at $\approx 2.6\text{-cm}^{-1}$ intervals. This latter signal was taken from a photodiode irradiated through a Fabry-Perot interferometer with some of the radiation from the frequency-scanned laser. Using the frequency markers, we could measure the position of lines of unknown frequency in the ion signal relative to the reference line at a wavelength of 534.1 nm, corresponding to the two-photon transition of the Ba atom from its ground state to the state $6s7d^1D_2$ that occurred upon photoionization of the Ba atoms contained in the ionization cavity. To graduate the distance between the frequency markers, use was made of the two peaks in the ion signal corresponding to the transitions of the Ba atom from its ground state to the states $6s6p^1P_1^0$ and $6s8p^1P_1^0$. The energy values for these states were taken from the paper by Moore⁷ (to obtain the photoionization peak corresponding to the transition to the state $6s8p^1P_1^0$, the output frequency of the frequency-scanned laser was doubled by means of a potassium dihydrogen phosphate crystal).

Figures 3 and 4 show the ion signals obtained while scanning the output frequency of the second-stage excitation laser at the start of the experiment (Fig. 3) and ≈ 1.5 months later (Fig. 4), at the end of the spectral measurements. (The reduction of the height of the peaks

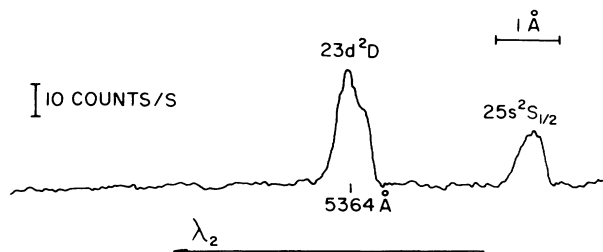


FIG. 3. Ion signal obtained when frequency scanning the second-stage excitation laser at the start of the experiment. Scanning time, 15 min; counting time at each datum point, $\Delta t = 3$ s.

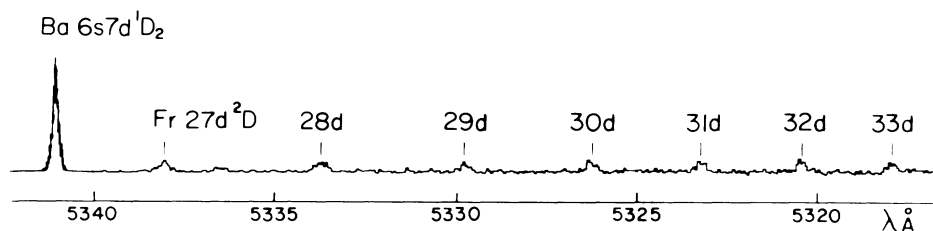


FIG. 4. Ion signal at the end of the spectral measurements. Scanning time, 20 min; counting time at each datum point, $\Delta t = 2.5$ s.

is due to the decay of ^{225}Ra and, probably, its partial evaporation together with Fr from the sample upon heating.) The Fr-atom generation rate in the sample at the initial moment was $\approx 5 \times 10^3 \text{ s}^{-1}$, and therefore, considering that the maximum Fr ion signal was $\approx 35 \text{ s}^{-1}$, the efficiency of detecting Fr in the sample amounted to $\approx 0.7\%$. The width of the spectrum containing the ion signal peaks related to transitions of the Fr atom to Rydberg states was $\approx 62 \text{ \AA}$ and was limited on the short-wavelength side by the lasing region of the dye laser pumped by the green line of the Cu-vapor laser, and on the long-wavelength side, by the amplitude of the electric-field pulse used to ionize the Fr atoms from the high-lying Rydberg states. The lines in the spectrum are grouped in pairs, which correspond to the transitions from the state $7p \ ^2P_{3/2}$ to the Rydberg states $^2S_{1/2}$ and 2D (with the laser bandwidth being $\approx 1 \text{ cm}^{-1}$, the states $nd \ ^2D_{5/2}$ and $nd \ ^2D_{3/2}$ are not resolved) (Fig. 1). In the experiment, we measured the wave numbers of the transitions to the $nd \ ^2D$ ($n=22-33$) and $ns \ ^2S_{1/2}$ ($n=23, 25-27, 29-31$) states (the peaks corresponding to the $24s \ ^2S_{1/2}$ and $28s \ ^2S_{1/2}$ states of Fr were obscured by two much stronger peaks corresponding to the Ba ion signal). To reduce random errors in measuring the transition frequencies, spectral scans were repeated several times and the frequency values obtained were then averaged.

Table I lists the energies of the Rydberg levels in Fr

TABLE I. Energies of Rydberg levels in Fr relative to $7p \ ^2P_{3/2}$ state.

n	$E_n \text{ (cm}^{-1}\text{)}$	
	$^2S_{1/2}$	2D
22	...	18 607.13(18)
23	18 583.36(23)	18 638.87(19)
24	...	18 665.95(12)
25	18 648.27(30)	18 689.28(8)
26	18 674.26(25)	18 709.72(9)
27	18 696.47(13)	18 727.66(9)
28	...	18 743.36(10)
29	18 733.07(10)	18 757.32(13)
30	18 748.05(13)	18 769.63(16)
31	18 761.74(18)	18 780.62(15)
32	...	18 790.56(26)
33	...	18 799.50(18)

measured in the present experiment. The $^2S_{1/2}$ and 2D series limits were calculated by the Rydberg formula $E_I - E_n = R/n^{*2}$ ($R=109737.04 \text{ cm}^{-1}$) which yielded $E_S=18924.80(25) \text{ cm}^{-1}$ and $E_D=18924.91(16) \text{ cm}^{-1}$. The effective quantum numbers $n^* = n - \delta$ corresponding to each level were then calculated and the principal quantum numbers n and quantum defects δ_n were deduced by comparison of the data obtained with the theoretical data taken from the work by Dzuba, Flambaum, and Sushkov.⁸ The quantum defects turned out to be $\delta_S=5.074(8)$ and $\delta_D=3.417(3)$ for the $^2S_{1/2}$ and 2D series, respectively. The series limits E_S and E_D yield the binding energy of the $7p \ ^2P_{3/2}$ state in Fr to be $T = -18924.8(3) \text{ cm}^{-1}$. Since the energy of the transition from the ground state $7s \ ^2S_{1/2}$ to the $7p \ ^2P_{3/2}$ state for ^{221}Fr is known² to be $E_0=13923.2 \text{ cm}^{-1}$, we established the ionization potential of ^{221}Fr , $I=E_0 - T = 32848.0(3) \text{ cm}^{-1}$. It should be noted that this value of the ionization potential is close to the theoretically predicted value $I'=32841 \text{ cm}^{-1}$ reported by Dzuba, Flambaum, and Sushkov.⁸

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