PHYSICAL REVIEW A VOLUME 42, NUMBER 5 1 SEPTEMBER 1990

Measurement and analysis of isotope shifts in ^{151,153}Eu$^+$ from hyperfine spectra

A. Sen and W. J. Childs
Argonne National Laboratory, Argonne, Illinois 60439-4843

J. Bauche and J.-F. Wyart
Laboratoire Aimé Cotton, Centre National de la Recherche Scientifique II, 91407 Orsay, France

(Received 14 May 1990)

Isotope shifts in ^{151,153}Eu$^+$ have been measured for four optical transitions between the metastable levels $4f^7(^8S^\circ)5d\,^9D^\circ_J$ and the excited levels $4f^7(^8S^\circ_{7/2})6p_{3/2};J'$ in a collinear laser and slow-ion-beam apparatus. A phenomenological interpretation and an *ab initio* calculation have been made and compared with experiment.

INTRODUCTION

The gross characteristics of atomic isotope shifts have been known for a long time.[1] Methods of measuring the hyperfine structure (hfs) and the isotope shift (IS) in Eu isotopes have improved tremendously from interferometric methods[2–4] to laser-excited fluorescence.[5–9] We have in the past few years extended the precision of hfs measurement in Eu II by another 2–3 orders of magnitude using the laser-rf double resonance technique.[10,11] By combining the kinematic compression[12] of a few keV ion beam with the high selectivity of excitation of a narrow-band laser in a collinear laser-rf double-resonance technique, very high spectral resolution has been achieved. Linewidths of 58–70 kHz have been obtained and the magnetic dipole and electric quadrupole hyperfine constants have been determined to an accuracy of a few kHz.[11] This has enabled us to investigate the isotope shift in the two stable isotopes of Eu$^+$ (masses 151 and 153) in a few excited states by optical means. A partial energy-level diagram of Eu II relevant to this work is shown in Fig. 1.

Optical transition frequencies observed for the two isotopes (^{151,153}Eu$^+$) in collinear laser–ion-beam spectroscopy are separated by the isotope shift and the differential Doppler shift. The situation in ^{151,153}Eu$^+$ is complicated by the hyperfine structure of each isotope. The differential Doppler shift is determined experimentally by a method similar to that of Borghs *et al.*,[13] from the laser-induced fluorescence spectra taken with the laser and the ion beams parallel and antiparallel to each other. This is subtracted from the observed separation of the centers of gravity of the two isotopic hfs's to obtain the isotope shift.

EXPERIMENT

The collinear laser and slow-ion-beam apparatus used for the measurement of isotope shifts has been described in detail elsewhere.[14] Only the main features of the apparatus will be given here briefly.

The Eu$^+$ ions were produced in an arc-discharge ion source, accelerated to 1.35 keV, focused by an einzel lens and a quadrupole lens, and mass analyzed by a 90° magnet before entering the interaction region. Laser light from a tunable single-mode ring dye laser (Coherent 699-21) pumped by an argon-ion laser entered the chamber through a window and was superposed collinearly with the ion beam in the interaction region. The interaction region was a biased Faraday cage (with cylindrical symmetry) about 2 in long through which the laser and the ion beam passed coaxially. The ions can be Doppler tuned into resonance with a particular hyperfine transition inside the cage by either tuning the laser frequency or the bias voltage. In our experiment, the bias voltage

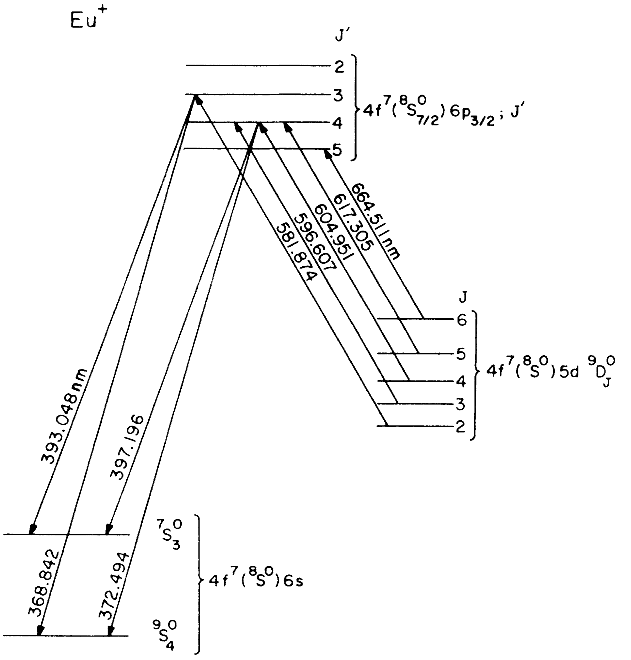

FIG. 1. Partial energy-level diagram of Eu$^+$ showing optical excitation and fluorescence. The electron configurations of the states are also indicated. The resonant laser excitation of the metastable $^9D^\circ_J$ states are shown by upward arrows and the fluorescence from the excited states are indicated by downward arrows. The transition wavelengths are given in nanometers.

was kept fixed at −100 V and the laser frequency was scanned. The resulting fluorescence from the optical excitation inside the cage was collected by a spherical mirror and aspheric lens onto a cooled photomultiplier tube (EMI 9658R) with appropriate filter. The signal from the photomultiplier tube was processed with standard electronics and sent to a computer and dual-pen chart recorder. Frequency markers on the same chart recorder were provided from a portion of the laser light going through a Fabry-Pérot interferometer of free spectral range 150 MHz. Typical ion-beam currents of 80 nA and laser powers of 100 mW were used.

From the measurements of hfs of $^{151,153}\mathrm{Eu}^+$ by the laser-rf double-resonance technique,[11] the magnetic dipole hfs constant A and the electric quadrupole hfs constant B have been determined with a high precision. With these values, the center of gravity of each hfs spectrum was determined accurately.

For the measurement of the isotope shift, an ion beam with both the species in it was created. This was achieved by deliberately degrading the mass resolution of the magnet and with the help of the quadrupole lens after the magnet. The mixed ion beam interacted with the laser and the hfs spectra of both the isotopes were recorded together with the laser and the ion beam parallel to each other. Several spectra were recorded for each optical transition. The same procedure was repeated with the laser and the ion beam going antiparallel to each other in the interaction region. The differential Doppler shift was determined from the frequency separation of any two lines (one belonging to each isotope) in the combined hfs spectra in the parallel and antiparallel configuration. The separation of the centers of gravity of the hfs of the two isotopes was measured and the isotope shift determined.

MEASUREMENTS

In Figs. 2 and 3 we show the laser-induced fluorescence spectra for the optical transitions between $4f^7(^8S^0)5d\ ^9D_4^\circ$ and $4f^7(^8S^0_{7/2})6p_{3/2};\ J'=4$ at a transition wavelength of 604.951 nm for both the isotopes present together in the parallel and antiparallel configurations of the laser and the ion beam. The centers of gravity of the hfs are indicated in the figures. The measured isotope shifts for four optical transitions between the metastable levels $4f^7(^8S^0)5d\ ^9D_J^0$ and the levels $4f^7(^8S^\circ_{7/2})6p_{3/2};\ J'$ are given in Table I.

THEORETICAL ANALYSIS

Methods for interpreting high-resolution measurements of isotope shifts have already been devised.[15,16] The experimental values in Table I all relate to impure Russell-Saunders (RS) and Jj terms of two configurations of the Eu^+ spectrum. Therefore, they are typical J-dependent field isotope shifts. Because these terms are the lowest in the first and second configurations of the

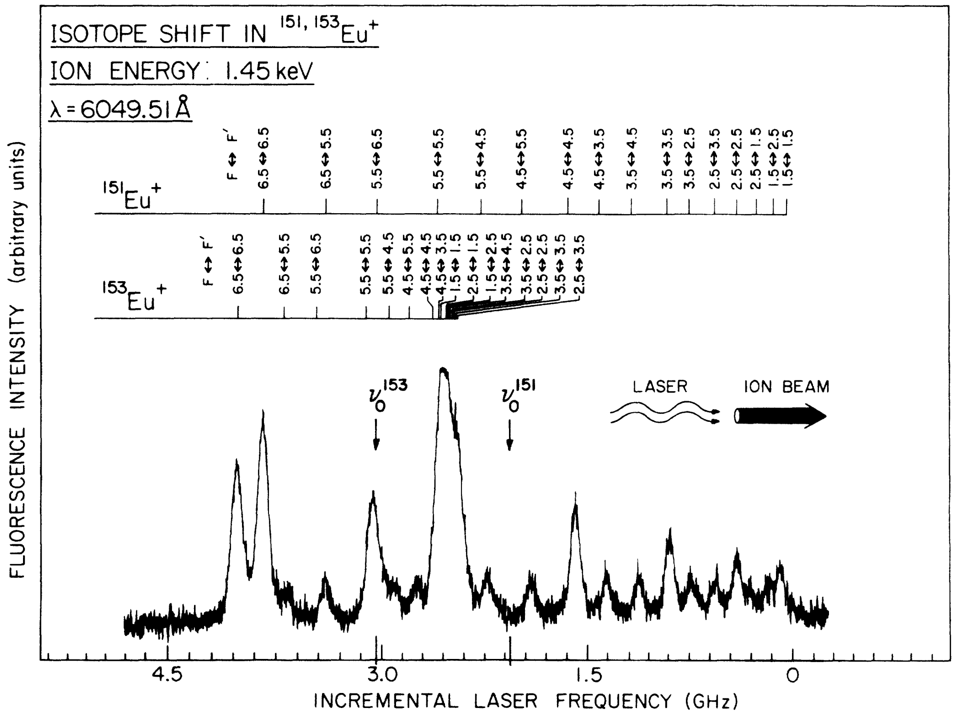

FIG. 2. Hyperfine spectra of $^{151,153}\mathrm{Eu}^+$ for the optical transition $^9D_4^\circ \leftrightarrow 6p_{3/2};\ J'=4$ at a wavelength of 604.951 nm with the laser propagating parallel to the ion beam. The hyperfine transitions and the centers of gravity of the spectra for each isotope are also indicated.

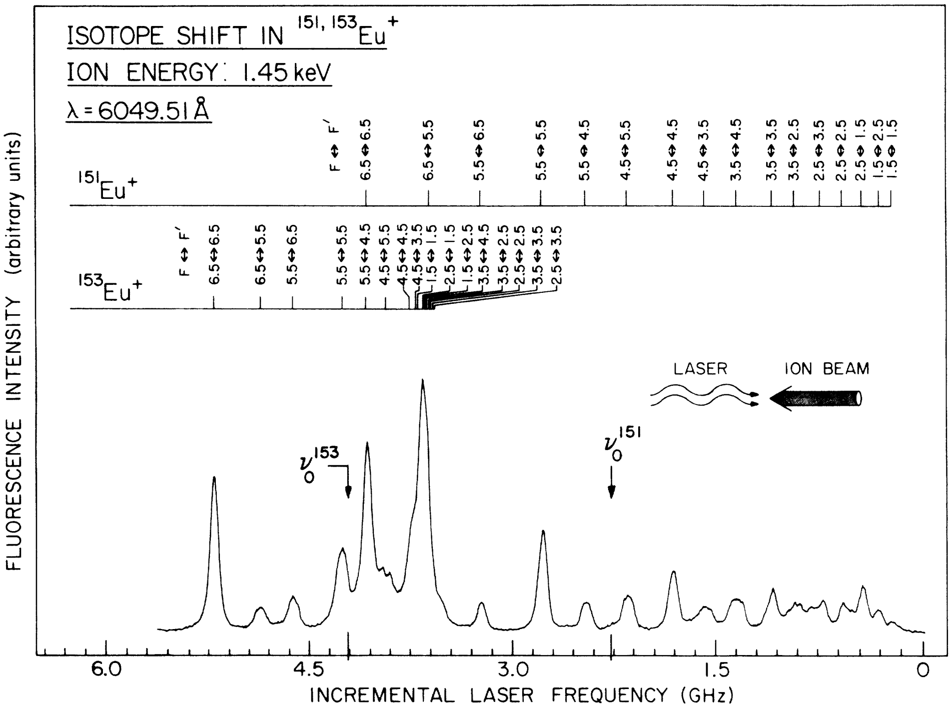

FIG. 3. Same as in Fig. 2 except for the laser propagating antiparallel to the ion beam.

spectrum, the effects of configuration interaction are expected to be moderate. Thus the predominant isotope shift contributions include the following.

(i) All the line shifts contain the same additive constant, which is the difference between the average shifts of the two terms.

(ii) In the $4f^76p$ configuration, only the $6p_{1/2}$ electron possesses a first-order field isotope shift. The intermediate coupling results in the various levels containing different admixtures of $6p_{1/2}$ and $6p_{3/2}$. Phenomenologically, this effect can be described by means of an isotope-shift parameter, denoted by Z_{6p}, whose angular coefficients are equal to those of the spin-orbit parameter ζ_{6p}, the radial integral in the electronic energy. The crossed second-order effects of the spin-orbit and field-shift interactions, which ought to be much smaller, are accounted for by the same parameter.

(iii) In the $4f^75d$ configuration, the largest effects are due to the similar crossed third order, with corresponding Z_{4f} and Z_{5d} parameters. There could also appear a first-order specific-mass isotope shift, described by a g^1 parameter having the same angular coefficients as the $G^1(4f,5d)$ Slater integral, but this can be neglected in such a heavy element as europium.

TABLE I. Isotope shift in ^{151,153}Eu$^+$. The values within parentheses denote the uncertainty in MHz.

Optical transition	Transition wavelength (nm)	Isotope shift (MHz)
$^9D^\circ_2\leftrightarrow 6p_{3/2};J'=2$	581.874	1538.5(4.9)
$^9D^\circ_3\leftrightarrow 6p_{3/2};J'=4$	596.607	1476.2(4.8)
$^9D^\circ_4\leftrightarrow 6p_{3/2};J'=4$	604.951	1463.3(4.9)
$^9D^\circ_5\leftrightarrow 6p_{3/2};J'=4$	617.305	1441.6(4.6)

PHENOMENOLOGICAL INTERPRETATION

An intermediate-coupling calculation has been carried out for the levels of $4f^75d$ that are built on the lowest LS terms of $4f^7$, namely, ^8S, ^6P, ^6D, and ^6I. The coefficients $C(\zeta_{4f})$ and $C(\zeta_{5d})$ obtained for the (impure) ^9D levels are listed in Table II. It appears that the ζ_{4f} coefficient is nearly J independent. (It would be equal to zero if those levels were pure ^9D levels.) Consequently, the phenomenological interpretation in $4f^75d$ is restricted to the determination of Z_{5d}, from the shifts measured from the three levels $^9D_{3,4,5}$ (see Table I). These shifts are total shifts, from which the (small) normal-mass shifts can first be subtracted. Then the parameter value obtained is $(Z_{5d})_{\text{expt}}=33.7(6.6)$ MHz.

TABLE II. Coefficients of the spin-orbit parameters ζ_{4f} and ζ_{5d} in the electronic energies of the $(4f_7{}^8S,5d)^9D_J$ levels, in intermediate coupling.

	$^9D_2$	$^9D_3$	$^9D_4$	$^9D_5$	$^9D_6$
$C(\zeta_{4f})$	-1.5087	-1.5271	-1.5448	-1.5462	-1.5050
$C(\zeta_{5d})$	-1.3505	-1.1048	-0.7213	-0.1028	$+1.0000$

TABLE III. Dirac-Fock contributions to the field isotope shifts of four levels (in atomic units). Each entry is the contribution of an orbital to the field shift, except the numbers at the bottom, which are the total shifts T, including the occupation numbers equal to 2 for each complete subshell and to $\frac{1}{3}$ for $6p_{1/2}$ in ${}^9P_{\text{av}}$.

	$(4f^7\,{}^8S,5d){}^9D_6$	$(4f^7\,{}^8S,6p){}^9P_5$	$(4f^7\,{}^8S,5d){}^9D_{\text{av}}$	$(4f^7\,{}^8S,6p){}^9P_{\text{av}}$
$1s$	3 108 172.8	3 108 170.0	3 108 173.0	3 108 170.0
$2s$	404 863.3	404 863.7	404 863.3	404 863.7
$2p_{1/2}$	16 537.9	16 537.8	16 537.8	16 537.8
$3s$	86 707.1	86 709.4	86 707.1	86 709.4
$3p_{1/2}$	3917.5	3917.6	3917.5	3917.6
$4s$	19 821.2	19 821.7	19 821.1	19 821.7
$4p_{1/2}$	864.8	864.8	864.8	864.8
$5s$	2945.3	2975.1	2944.2	2975.2
$5p_{1/2}$	106.6	108.3	106.0	108.3
$6p_{1/2}$				7.3
T	7 287 872.8	7 287 937.1	7 287 869.6	7 287 939.7

AB INITIO INTERPRETATION

For calculating *ab initio* field isotope shifts, the Hartree-Fock and Dirac-Fock methods have been found to be excellent tools.[17,18] Their high quality has been traced to Brillouin's theorem.[19] We have applied the Dirac-Fock (DF) code of Desclaux[20] to four levels of Eu$^+$, denoted $A=(4f^7\,{}^8S,5d){}^9D_6$, $B=(4f^7\,{}^8S,6p){}^9P_5$, $C=(4f^7\,{}^8S,5d){}^9D_{\text{av}}$, and $D=(4f^7\,{}^8S,6p){}^9P_{\text{av}}$. Only the former two are genuine levels. The latter two are fictitious levels: each of them is defined through its formal energy expansion being the $(2J+1)$-weighted average over the J levels of the relevant RS term, i.e., five and three J levels, respectively. The results are listed in Table III, in terms of the square of the coefficient to the leading term in the expansion near $r=0$ of each s and $p_{1/2}$ wave function. If the relevant combination of squares for level x is denoted as T_x, then $T_A-T_C=(Z_{5d})_{\text{DF}}=3.2$, and $2(T_B-T_D)=(Z_{6p})_{\text{DF}}=-5.2$ can be called the Dirac-Fock values of the parameters, in atomic units.

COMPARISON BETWEEN THEORY AND EXPERIMENT

Extensive comparison between theory and experiment is not possible within the scope of these limited measurements, but the following comparisons can be attempted.

(i) The value of $(Z_{5d})_{\text{expt}}$ above is computed from the shifts of ${}^9D_3$ and ${}^9D_5$ levels. The pair ${}^9D_3$-${}^9D_4$ alone yields the equation $(-1.1048+0.7213)Z_{5d}=-12.6\pm6.9$ MHz (using the numbers in Tables I and II and including the small normal-mass-shift correction), whence $(Z_{5d})_{\text{expt}}=32.9\pm18.0$ MHz. In the same way, for the pair ${}^9D_4$-${}^9D_5$, one writes $(-0.7213+0.1028)Z_{5d}=-21.2\pm6.7$ MHz, whence $(Z_{5d})_{\text{expt}}=34.3\pm10.8$ MHz. There appears an excellent agreement between the two values of $(Z_{5d})_{\text{expt}}$.

(ii) For the comparison with *ab initio* results, one can resort to the calibration published by Brüggemeyer *et al.*[21] for Eu I. These authors in their Eq. (13) give the value 17.9 MHz/a.u. for the ratio of the calculated shift over the Dirac-Fock result of Desclaux's code. From the result $(Z_{5d})_{\text{DF}}=3.2$ a.u. derived above, one deduces $(Z_{5d})_{\text{calc}}=57.3$ MHz for the *ab initio* evaluation of Z_{5d}. This is about 65% larger than the experimental value $(Z_{5d})_{\text{expt}}=33.7\pm6.6$ MHz.

(iii) For the Z_{6p} parameter, the above calibration leads to the *ab initio* value $(Z_{6p})_{\text{calc}}=-93$ MHz. Only one experimental measurement is available, that relating to the $(6p_{3/2};J'=2)$ level. This level obeys pure Jj coupling $[({}^8S_{7/2},p_{3/2})J'=2]$ in the present level set, and it can be checked, by diagonalizing the 2×2 matrix built on ${}^9P_4$ and ${}^7P_4$, that the $(6p_{3/2};J'=4)$ level is very close to the same coupling. However, the experimental shift of the former level is about 54 MHz larger than that of the latter [for obtaining this number, one uses the line shifts, the ζ_{5d} coefficients of Table II, and the value of $(Z_{5d})_{\text{expt}}$]. Such a large difference cannot be understood in our simple assumptions. It is likely that the neighboring $4f^6 5d6s$ configuration, which perturbs the hfs of $4f^7 6p$ (Guthöhrlein, Himmel, and Steudel[22]), also perturbs the isotope shifts. This is consistent with the fact that close-configuration interaction effects are second-order effects for both hfs and field isotope shift.

The *ab initio* value $(Z_{6p})_{\text{calc}}$ is negative in contrast with the usual positive sign of the spin-orbit isotope-shift parameters (see Z_{5d} above and other Z_{nl} field-shift quantities[16,22,23]). It appears from Table III that the genuine field-shift contribution of the $6p$ electron is responsible for the positive sign, whereas for $5d$ (and more generally, for any d or f electron) only the screening effects on the complete s and p subshells contribute.

CONCLUSION

The present field-isotope-shift experimental results are accurate to about 5 MHz. There is a need for more refined calculations of the isotope shifts. This is difficult in very complex spectra like those of the rare earths. In the present example of Eu^+, the theoretical interpretation is reasonable for the lower configuration, but not in the excited one, in which perturbations by a close electronic configuration have already been detected. More precisely, the $5d$ (effective) field-shift contribution fits well with the behavior observed in similar spectra,[24] but the sign of the $6p$ contribution remains uncertain. Further theoretical progress depends on the experimental determination of more hfs splittings in the neighboring levels.

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

---

[1] H. Kopfermann, *Nuclear Moments* (Academic, New York, 1958).

[2] K. Krebs and R. Winkler, Z. Phys. **160**, 310 (1960).

[3] R. Winkler, Phys. Lett. **16**, 156 (1965).

[4] G. Guthöhrlein, Z. Phys. **214**, 332 (1968).

[5] A. Arnesen, A. Bengtson, R. Hallin, C. Nordling, Ö. Staaf, and L. Ward, Phys. Scr. **24**, 7474 (1981).

[6] K. Dörschell, W. Heddrich, H. Huhnermann, E. W. Peau, W. Wagner, G. D. Alkhazov, E. Ye Berlovich, V. P. Denisov, V. N. Pantoleev, and A. G. Polyakov, Z. Phys. A **312**, 296 (1983).

[7] H. Brand, V. Pfeufer, and A. Steudel, Z. Phys. A **302**, 291 (1981).

[8] G. J. Zaal, W. Hogervorst, E. R. Eliel, K. A. H. van Leeuwen, and J. Blok, Z. Phys. A **290**, 339 (1979).

[9] S. A. Ahmad, W. Klempt, C. Ekström, R. Neugart, and K. Wendt, Z. Phys. A **321**, 35 (1985).

[10] A. Sen, L. S. Goodman, W. J. Childs, and C. Kurtz, Phys. Rev. A **35**, 3145 (1987).

[11] A. Sen and W. J. Childs, Phys. Rev. A **36**, 1983 (1987).

[12] S. L. Kaufman, Opt. Commun. **17**, 309 (1976).

[13] G. Borghs, P. de Bisschop, J.-M. van den Cruyce, M. Van Hove, and R. E. Silverans, Opt. Commun. **38**, 101 (1981).

[14] A. Sen, L. S. Goodman, and W. J. Childs, Rev. Sci. Instrum. **59**, 74 (1988).

[15] K. Heilig and A. Steudel, At. Data Nucl. Data Tables **14**, 613 (1974).

[16] J. Bauche and R.-J. Champeau, Adv. At. Mol. Phys. **12**, 39 (1976).

[17] M. Wilson, Phys. Rev. **176**, 58 (1968).

[18] M. Wilson, Phys. Rev. **3A**, 45 (1971).

[19] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[20] J.-P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).

[21] H. Brüggemeyer, H. Esrom, V. Pfeufer, A. Steudel, and J. Bauche, Z. Phys. D **1**, 55 (1986).

[22] G. Guthöhrlein, G. Himmel, and A. Steudel, J. Phys. (Paris) Colloq. **30**, C1-66 (1969).

[23] H.-D. Kronfeldt and G. Sinn, Z. Phys. D **14**, 205 (1989).

[24] H.-D. Kronfeldt (private communication).

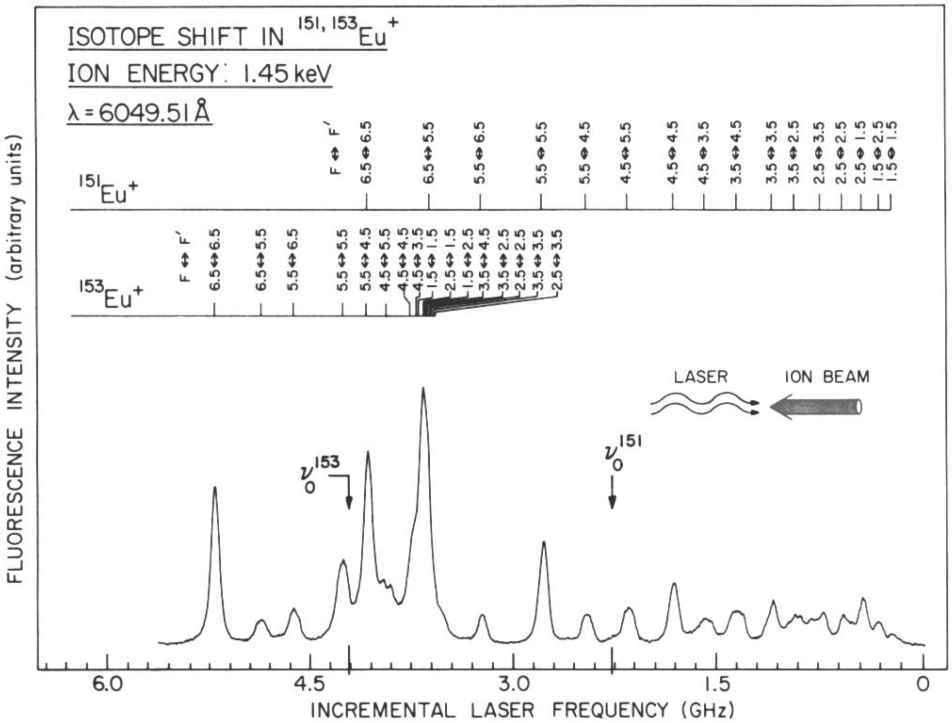

FIG. 3. Same as in Fig. 2 except for the laser propagating antiparallel to the ion beam.