London, England, 1965), p. 524.
[2]J. F. Perkins, Phys. Rev. 173, 164 (1968).
[3]I. Cheshire (private communication).
[4]A. Temkin, Phys. Rev. 107, 1004 (1957).
[5]M. H. Mittleman, Phys. Rev. A 2, 1846 (1970).
[6]C. J. Joachain and M. H. Mittleman, Phys. Rev. A 4, 1492 (1971).
[7]H. Feshbach, Ann. Phys. (N.Y.) 19, 287 (1962).
[8]M. H. Mittleman and K. M. Watson, Phys. Rev. 113, 198 (1959).
[9]E. Kujawski, Phys. Rev. A 5, 2690 (1972).
[10]See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 952.
[11]E. Clementi, IBM J. Res. Develop. Suppl. 9, 2 (1965).
[12]I am indebted to Dr. H. Tai for performing this calculation.

PHYSICAL REVIEW A VOLUME 6, NUMBER 3 SEPTEMBER 1972

Hydrogenic Transitions in Multiply Charged Fe and Ni Ions*

W. N. Lennard, R. M. Sills, and W. Whaling
California Institute of Technology, Pasadena, California 91109
(Received 1 May 1972)

Ten lines in the range $3880 \leqq \lambda \leqq 5666$ Å in the beam-foil spectrum of iron have been identified with specific hydrogenic transitions in Fe IV–VIII. The same transitions were observed from Ni and Ar beams. Deviations from the hydrogenic wavelengths are shown to be consistent with that expected from core polarization. The absence of these lines in astrophysical sources is discussed. A wavelength table is presented for identification of hydrogenic transitions to be expected in beam-foil spectra.

I. INTRODUCTION

In the visible radiation from a beam of iron ions excited by passage through a thin foil, Whaling *et al.*[1] found that the strongest lines in their spectrograms had wavelengths not previously reported for any iron ion. In this paper we describe a measurement of the charge of the ions radiating the ten strongest visible lines from a 1.5-MeV Fe ion beam. We propose transitions that will account for all of these wavelengths, and suggest that these same wavelengths will be seen in other heavy-ion beams when excited by the beam-foil method.

II. EXPERIMENTAL METHODS

The charge of the ion radiating the unknown wavelength was determined by measuring the displacement of the beam in a transverse electric field. An Fe^+ beam was accelerated to 1.3-MeV energy and then further ionized and excited by passage through a thin (10-$\mu g/cm^2$) carbon foil. Collimating slits (0.25×8 mm) located both ahead of and behind the foil defined a narrow ribbon beam. This radiant beam was deflected normal to its wide dimension in a transverse electrostatic field extending 10 cm downstream from the foil.

A monochromator with a 10-Å passband was placed to accept radiation from a 1-cm length of an arbitrarily selected beam trajectory in the deflecting field. Radiation from any other trajectory was blocked by a mask. A narrow (1 cm×1 mm) slit in the mask, tangent to the selected trajectory, permitted radiation from the beam to reach the monochromator only if the beam was deflected along the selected trajectory. The deflecting voltage was varied to sweep the radiant beam across the slit. The product (deflecting voltage)×(ion charge)/(ion energy) is constant for a particular trajectory, and the value of this constant for the selected trajectory was determined by observing the voltage required to deflect a 0.65-MeV N^{2+} (λ4379) beam along this trajectory.

III. RESULTS

In Table I we present the charges measured for the ten strongest lines in the visible spectrum of the 1.5-MeV iron ion beam. The wavelengths listed in the first column were measured from the iron spectrogram in Fig. 1. In scanning these lines with the monochromator preparatory to measuring the ion charge, it was found that most of the lines are composed of two or more components with a spacing of a few Å. The wavelengths measured from the spectrogram are therefore an average over the several unresolved components. We estimate an uncertainty of ±2 Å in this average wavelength, even though the components may be spread over several Å about this average.

The measured charge is listed in the third column. The low efficiency of our photon detector (EMI 6256S) for wavelengths beyond 6000 Å made it impossible to measure the charges of the last four lines in the table, and the assignments of an ionic charge to these transitions are based on the analysis described below.

Once the charges were known, it was observed

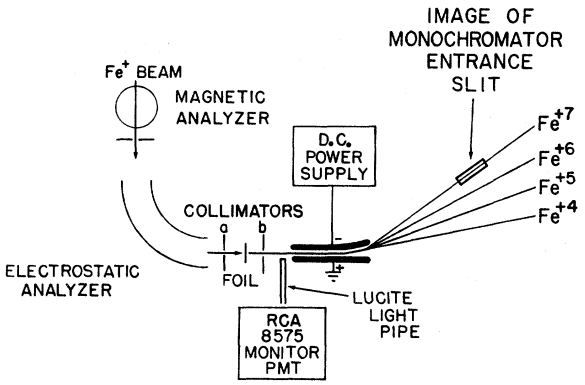

FIG. 1. Schematic diagram of the charge-deflection apparatus. The monochromator is positioned to receive light emitted out of the plane of the paper. Only light emitted from the 1-cm segment of the trajectory labeled "image of monochromator entrance slit" can reach the entrance slits of the monochromator. The deflection of the various charge states is greatly exaggerated in this figure: An actual off-axis deflection was 2 mm.

that the measured wavelengths were very close to those for $\Delta n = 1$ and $\Delta n = 2$ transitions between states of a single electron moving in a hydrogenlike orbit around a central charge $(Q+1)e^+$, where Qe^+ is the ion charge. In column 4 we list the wavelengths computed from the hydrogenic terms $T = -R(Q+1)^2/n^2$ for transitions between states with the principal quantum numbers listed in column 6. The last four wavelengths in column 1 and λ4658 were then classified by their near coincidence with transitions expected for ions with charge 3+ to 7+, the major components of our beam. The wavelengths listed in column 4 include *all* of the $\Delta n = 1$ and 2 transitions in our wavelength range $3500 \leq \lambda \leq 6500$ Å and charges $3+ \leq Q \leq 7+$.

To confirm our identification, we substituted a Ni beam for the Fe beam and repeated our measurements. The Ni spectrum is shown in the upper-half of Fig. 1. The striking similarity between the spectra of two different elements is convincing proof of the origin of these lines in common hydrogenic levels. We have seen the same lines from an argon beam, and we should expect to see the same lines in any ion beam containing ions of the same charge. Wavelengths measured from the Ni spectrogram appear in the second column of Table I.

The one-electron states excited in our experiment are expected to be more tightly bound than the Rydberg formula predicts for a one-electron ion because of (a) polarization of the ion core by the outer electron, (b) penetration of the core by the outer electron, and (c) the spin-orbit interaction. All of these interactions increase the electron binding and depend on n and l in a way that will shift transitions in which n and l decrease to the blue of the hydrogenic value, as observed in our spectra. According to Edlén,[2] the polarization effect is much the largest of these three corrections to the binding energy for states with large n

TABLE I. Identification of transitions in the Fe and Ni beam-foil spectra. The wavelengths are measured from spectrograms of Fig. 1 by comparison with an Fe reference spectrum.

λ_{obs} Fe (Å)	λ_{obs} Ni (Å)	Measured Ion Charge	λ_{calc} (Å)	Ion Charge	Δn
3879	3883	6+	3888	6+	8→7
4336	4338	7+	4342	7+	9→8
4497	4497	5+	4500	5+	10→8
4516	4515	4+	4521	4+	9→7
4553	4553	6+	4557	6+	11→9
4625	4630	3+	4660	3+	6→5
4658	4658	...	4660	7+	12→10
4680	4682	3+or 4+	4687	3+	8→6
4903	4904	...	4946	4+	7*h*→6*g*
4934	4935	4+	4946	4+	7*i*→6*h*
5283	5286	5+	5292	5+	8→7
5665	5666	6+	5671	6+	9→8
6063	6065	...	6070	7+	10→9
6079	6079	...	6086	6+	12→10
6197	6197	...	6202	5+	11→9
6475	6474	...	6480	4+	10→8

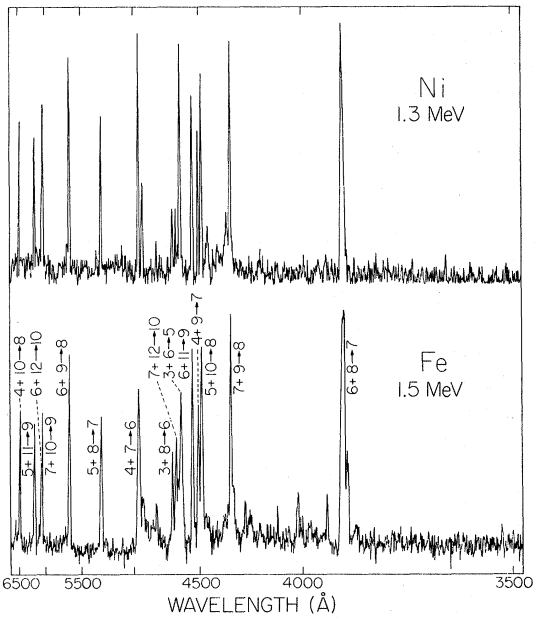

FIG. 2. Densitometer tracings of spectrograms of Ni and Fe beams excited by passage through 10-$\mu g/cm^2$ carbon foils. The angle of observation is 90°. The Fe spectrum is reproduced from Ref. 1, in which details of the exposure may be found.

and l. Edlén gives formulas for computing the wavelength shift due to polarization, but these depend on the polarizability of the core which is in general not known. For large n and l, the polarization correction approaches zero and the term values approach those given by the Rydberg formula.

The polarization of the core removes the degeneracy between states of the same n but different l and splits the hydrogenic lines into several components, and one expects the lines to exhibit a multiplet structure as well as a shift to the blue. For most of the transitions that we observed, this structure is too close to be evident in the spectrograms of Fig. 1. As mentioned above, many of the lines that appear single in the spectrograms have been found to have two or more components, separated by a few Å, but our measurements are not sufficiently precise to permit a detailed comparison of the observed structure and theoretical predictions. The only evidence for this splitting apparent in Fig. 1 is the weak line at 4903 Å which may correspond to the $7h - 6g$ satellite of the $7i - 6h$ line at 4935 Å. This weak line appears in both the Fe and Ni spectra, and there are no other likely hydrogenic transitions close to the observed wavelength. If one uses the observed shift of the 4935-Å line to compute a dipole polarizability for the Fe^{5+} core, one can then compute the expected position of the $7h - 6g$ component. In this way, we find $\alpha_d(Fe^{5+}) = 1.0a_0^3$ and compute $\lambda(7h - 6g) = 4906$ Å, close to the observed value of 4903 Å. Supporting this interpretation is the fact that one expects the reddest component of the multiplet to be strongest, since states with maximum $l = n - 1$ are favored as the electron cascades down from states with high-n values. One feature that is not accounted for in this analysis is the fact that λ4935 is actually a doublet, with two nearly equal components separated by 6 Å. This spacing is too large to be accounted for by spin-orbit splitting and must reflect some coupling of the outer electron with the Fe^{5+} core.

IV. DISCUSSION

Hydrogenic transitions between states of large n in multiply charged ions have been reported in many beam-foil (BF) spectra, but they are rarely observed in other laboratory sources and not at all in astrophysical sources. Gabriel[3] has observed such transitions in a high-density plasma pinch, and in particular has observed λ5280 in O^{5+}, the same line we have seen with Fe, Ni, and Ar beams. This same transition and several others between high-n levels have been reported from C^{5+} in the plasma generated when a high-intensity laser beam strikes a solid surface.[4] However, there is no other light source in which hydrogenic transitions are so prominent as they are in Fig. 1, and only in BF spectra have they been observed with ions as heavy as Fe or Ni.

It is interesting to inquire why these states are so readily excited in the BF interactions, and why they are seldom seen in other sources. Turning to the latter question first, their high excitation energy, hundreds of eV, is responsible for their weakness in a low-density plasma such as the solar corona, where Huang[5] has shown that excitation by electron capture is negligible compared to excitation by collision. The upper levels of identified coronal lines are typically at only a few eV of excitation energy. Dalgarno[6] has pointed out that the relatively long radiative lifetime of the hydrogenic states, increasing roughly as $n^{4.5}$, combined with their large cross section for collisional destruction, account for their weakness in a local thermodynamic equilibrium (LTE) plasma.

The same argument explains their absence in beams excited by passage through a gas. Brown *et al.*[7] have compared the radiation from a 900-keV sodium beam excited by passage through a carbon foil with the radiation from the same beam passing through helium at a pressure of 0.1 torr. The strongest line observed in the BF spectrum, λ4649, was not seen at all in the gas-excited spectrum. The charge of the ion radiating this strong line was measured by Brown, and later by Dufay *et al.*,[8] to be 3+. The $n = 6 - 5$ transition in the 3+ ion is at 4660 Å. From our estimate of the dipole polarizability of the seven-electron core, $\alpha_d = 0.51a_0$,[3] we would expect a wavelength shift of −12 Å, in good agreement with the observed shift of −11 Å.

The absence of this line in Brown's gas-excited spectrum can be understood by comparing the mean time between collisions, 1.5×10^{-10} sec, on the assumption of $\sigma_{coll} = \pi(n^2 a_0/Z)^2$, with the radiative lifetime of the hydrogenic state, 24×10^{-10} sec.[9] The large collision cross section favors nonradiative deexcitation of the state. It would be of interest to repeat Brown's experiment with the gas pressure reduced by a factor of 100 to see if the hydrogenic line appears.

The prominence of hydrogenic transitions in BF spectra suggests that electron capture makes an important contribution to the excitation of the beam. In the usual picture of the passage of a charged particle through matter, the moving ion continually loses and recaptures its more loosely bound electrons in repeated encounters with the atoms of the absorber. The charge on the ion emerging from the surface is the net result of this sequence of many capture and loss events. The excitation of the emerging ion is brought about either by the last capture into an excited state, or by the last collision before the ion emerges into

TABLE II. Hydrogenic wavelengths: $\lambda^{-1}=R(Q+1)^2\,[1/n^2-1/(n+\Delta n)^2]$. Values in the table are for mass $A=46$, $R=109\,736\ \mathrm{cm}^{-1}$. For other masses, $\lambda_A=\lambda_{46}\,[1+1.2\times10^{-5}(46-A)/A]$. Table includes all transitions with $\Delta n=1$, 2, or 3, in the wavelength range 1000–8000 Å.

Ion	n	$(n+1)$	$(n+2)$	$(n+3)$	Ion	n	$(n+1)$	$(n+2)$	$(n+3)$	Ion	n	$(n+1)$	$(n+2)$	$(n+3)$
X^{+}	2	1640	1215	1085	X^{8+}	6	1527	926	729	X^{12+}	7	1127	669	518
	3	4687	3204	2734		7	2352	1395	1081		8	1644	959	733
	4	10125	6561	5412		8	3431	2000	1528		9	2299	1321	998
X^{2+}	3	2083	1424	1215		9	4796	2757	2083		10	3107	1765	1321
	4	4500	2916	2406		10	6482	3682	2756		11	4085	2297	1705
	5	8284	5168	4154		11	8523	4793	3558		12	5249	2927	2157
	6	13739	8332	6561		12	10952	6106	4500		13	6615	3661	2681
X^{3+}	3	1172	801	683		13	13802	7639	5595		14	8200	4509	3284
	4	2531	1640	1353		14	17108	9408	6852		15	10019	5479	3971
	5	4660	2907	2337	X^{9+}	6	1237	750	591		16	12089	6577	4746
	6	7728	4687	3691		7	1905	1130	876		17	14426	7813	5616
	7	11907	7064	5472		8	2779	1620	1238		18	17046	9195	6585
	8	17368	10125	7738		9	3885	2233	1687		19	19965	10731	7660
X^{4+}	4	1620	1050	866		10	5251	2982	2232	X^{13+}	8	1418	827	632
	5	2982	1861	1495		11	6904	3882	2882		9	1982	1139	861
	6	4946	2999	2362		12	8871	4946	3645		10	2679	1522	1139
	7	7621	4521	3502		13	11180	6188	4532		11	3522	1981	1470
	8	11115	6480	4952		14	13858	7621	5550		12	4526	2524	1860
	9	15540	8931	6749		15	16932	9259	6710		13	5704	3157	2312
X^{5+}	4	1125	729	601	X^{10+}	6	1022	620	488		14	7070	3888	2832
	5	2071	1292	1038		7	1575	934	724		15	8639	4724	3424
	6	3435	2083	1640		8	2297	1339	1023		16	10424	5671	4092
	7	5292	3140	2432		9	3211	1845	1394		17	12439	6737	4842
	8	7719	4500	3439		10	4339	2465	1845		18	14698	7928	5678
	9	10791	6202	4687		11	5705	3208	2381		19	17215	9252	6605
	10	14585	8284	6200		12	7331	4088	3012		20	20004	10716	7626
X^{6+}	5	1522	949	763		13	9239	5114	3745	X^{14+}	8	1235	720	550
	6	2524	1530	1205		14	11453	6298	4587		9	1727	992	750
	7	3888	2307	1787		15	13993	7652	5546		10	2334	1325	992
	8	5671	3306	2527		16	16885	9186	6629		11	3068	1725	1281
	9	7928	4557	3443		17	20148	10913	7843		12	3943	2198	1620
	10	10716	6086	4555	X^{11+}	7	1323	785	608		13	4969	2750	2014
	11	14089	7923	5881		8	1930	1125	860		14	6159	3387	2467
	12	18104	10094	7439		9	2698	1551	1172		15	7525	4115	2982
X^{7+}	5	1165	727	584		10	3646	2071	1550		16	9080	4940	3565
	6	1932	1172	923		11	4794	2696	2001		17	10835	5869	4218
	7	2977	1766	1368		12	6160	3435	2531		18	12803	6907	4946
	8	4342	2531	1934		13	7764	4297	3147		19	14996	8060	5753
	9	6070	3489	2636		14	9623	5292	3854		20	17425	9335	6643
	10	8204	4660	3487		15	11758	6430	4660		21	20104	10737	7621
	11	10787	6066	4502		16	14188	7719	5570					
	12	13861	7728	5695		17	16930	9170	6591					
	13	17468	9668	7081		18	20005	10791	7728					

the vacuum.

The excited levels observed in this experiment have very large mean radii, 10–20 Å, whereas the mean spacing between atoms of the foil is ~2 Å. They have excitation energies of several hundred eV, whereas the electron energy at the ion velocity is only 14 eV. It seems clear that these levels are populated by the last capture event at the surface, not by collisional excitation. There is a high electron density at the surface, and the surface can absorb energy to permit nonradiative capture.

Different models of electron capture at a surface lead to different distributions of population of the excited levels. (a) If one assumes, following Bohr,[10] that the states favored in the capture process are those for which the electron velocity $[2\times(\text{binding energy})/m_0]^{1/2}$ is close to the velocity of the moving ion, one expects an ion of charge Q to show large initial population in states with

$n \approx (Q+1)[24.8A_{ion}/E_{ion}(\text{keV})]^{1/2}$. (b) If one adopts Oliphant and Moon's[11] assumption that capture is favored into states bound to the ion by an amount close to the work function of the surface, one would expect the primary population to be concentrated in states with $n \sim 1.7(Q+1)$, assuming a work function of 4.6 eV for the C surface. (c) Free-electron recombination that takes place after the ion has escaped from the influence of the surface would lead to an initial population that decreases with increasing excitation energy as $1/n^3$. We have examined our own results and the published observations of others and conclude that the third assumption is favored by the meager information presently available. The pertinent observations are these:

(i) The levels that are observed are limited only by the wavelength range of the experiment. For the ions which compose the major components of the beam, every $\Delta n = 1$ and 2 transition lying within the wavelength range of the detector is observed. There seems to be no upper bound on the excitation energy of the initial states populated.

(ii) For a given ion, transitions from levels of lower n appear to be stronger. Cascading contributes to this behavior and obscures the initial population.

(iii) Light decay curves for the level with quantum number n_u typically indicate cascading into the upper level from still higher levels with $n \geqq n_u + 1$, consistent with our conclusion from observation (i). However, there are no observations of *increasing* decay curves that would indicate a population in the n_u+1 level much greater than that in the n_u level. Observations (ii) and (iii) suggest an initial population that is either independent of n or decreases with increasing n.

One is led to the conclusion that only assumption (c) is consistent with the observations. However, it is surprising that levels with $n \sim 10$ are seen at all if the population falls off as rapidly as n^{-3}. Jordan *et al.*[12] observed a population in He^+ that falls off more rapidly than n^{-3}, but it has been suggested that the behavior of helium and of heavy ions are qualitatively different. Dmitriev *et al.*[13] report that "electron capture by ions with $Z \geqq 4$ (unlike protons) occurs mainly in excited states." Further study of the initial populations should provide a valuable insight into the excitation process.

In conclusion, it should be noted that observation (i) above should aid experimenters in identifying unknown lines in their spectra. Hydrogenic lines appear in many published spectra without identification. As an aid to identification we list in Table II the wavelengths computed from the Rydberg formula for ions of charge 1^+–14^+. We list transitions for $\Delta n = 1$, 2, and 3, although $\Delta n = 3$ transitions in heavy ions are rare.[14]

ACKNOWLEDGMENTS

The authors are indebted to Alan Gabriel, L. C. Cocke, and S. Bashkin for helpful disucssions and access to unpublished results.

*Supported in part by NSF Grant No. GP-28027 and the Office of Naval Research Grant No. N00014-67-A-0094-0022.

[1]W. Whaling, R. B. King, and P. L. Smith, in *Beam-Foil Spectroscopy*, edited by S. Bashkin (Gordon and Breach, London, 1968), Vol. I. p. 81.

[2]B. Edlén, in *Handbüch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1964), Vol. 27, p. 80.

[3]A. H. Gabriel, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases*, edited by N. R. Nilsson (North-Holland, Amsterdam, 1960), p. 829.

[4]B. C. Boland, F. E. Irons, and R. W. P. McWhirter, J. Phys. B 1, 1180 (1968).

[5]K. Huang, Astrophys. J. 101, 187 (1945).

[6]A. Dalgarno, in *Proceedings of the First International Conference on Atomic Physics*, edited by B. Bederson (Plenum, New York, 1969), p. 169.

[7]L. Brown, W. K. Ford, V. Rubin, W. Trachslin, and W. Brandt, in Ref. 1, p. 45.

[8]M. Dufay, M. Gaillard, and S. M. Carré, Phys. Rev. A 3, 1367 (1971).

[9]H. A. Bethe and E. E. Salpeter, in Ref. 2, Vol. 35, p. 88.

[10]N. Bohr, Phys. Rev. 59, 270 (1941).

[11]M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. (London) A127, 388 (1930).

[12]J. A. Jordan, Jr., G. S. Bakken, and R. E. Yager, J. Opt. Soc. Am. 57, 530 (1967).

[13]I. S. Dmitriev, Y. A. Teplova, and V. S. Nikolaev, Zh. Eksperim. i Teor. Fiz. 61, 1359 (1971) [Sov. Phys. JETP 34, 723 (1972)].

[14]R. Hallin, J. Lindskog, A. Marelius, J. Pihl, and R. Sjodin, in Proceedings of the Second European Conference on Beam-Foil Spectroscopy, Lyon, 1971 (unpublished).