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FORBIDDEN LINES IN ATOMIC SPECTRA

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INTRODUCTION

THE problem of forbidden lines in atomic spectra arose comparatively recently, 30 or 35 years ago. Prior to this time atomic spectroscopy had achieved a relatively high level of development. Atomic spectra of all the elements known at that time had been investigated in fairly great detail and both classical and quantum theories of radiation had been formulated, although the quantum theory was far from complete.

According to the classical theory, the electric dipole radiation was always produced simultaneously with the multiple radiation of all orders, although it was considerably more intense than this multipole radiation. This description was carried over completely into the quantum formulation. Hence, in both the classical and quantum theories, only the spontaneous electric dipole radiation was investigated at the beginning. It was only for this type of radiation that transition probabilities were computed and selection rules formulated. Transitions which did not obey these rules were considered impossible and were called forbidden. States from which atomic optical transitions to lower levels are impossible were called metastable. It was thought that atoms could remain in these states for rather long periods of time and usually made transitions to other states by means of collisions of the first or second kind, by absorption of radiation, or by virtue of various fields which disturb the selection rules.

A comparison of the theory of radiation with the experimental data indicated a completely satisfactory agreement. At the beginning of the 1920's almost all the lines in atomic spectra produced in the laboratory had been identified; that is to say, these lines were found to be in agreement with the Ritz combination rule, according to which lines are to be associated with differences between definite atomic energy levels. Among the lines which had not been identified were certain lines which were observed in the spectra of celestial bodies — in planetary nebulae, the solar corona and the Northern lights.

Since none of these lines could be associated with elements which were then known it was believed that they were produced by elements which had not yet been identified. Because of the circumstances under which these mysterious spectral lines were discovered, these elements were called respectively "nebulium," "coronium," and "geocoronium." In 1924, however, one of these lines was produced under laboratory conditions. In a helium discharge at a pressure of 1 mm Hg which contained a small admixture of oxygen (as an impurity) a green emission line was observed which was later identified as a line from geocoronium (λ 5577.34 A). In time it was found that there was no place for these elements in the periodic table and these mysterious lines became one of the more interesting problems in spectroscopy. An explanation was first given in 1928 by Bowen, who noted that the lines from "nebulium" were actually forbidden lines for the atoms O II, N II, and O III, while the lines in geocoronium were forbidden lines for O I. The wave numbers for the lines in nebulium and geocoronium coincided exactly with the difference in the terms corresponding to low-lying metastable states and ground states of these atoms. It was more difficult to identify the lines in coronium, but these too were found to be forbidden lines for highly ionized atoms of well-known elements.

Immediately after the identification of the forbidden lines, a new question arose — were these lines due to spontaneous or induced radiation? The second alternative was rejected because the density of the gas in the non-terrestrial bodies was obviously very small (for example in planetary nebulae this density is of the order of 1000 atoms per cubic centimeter) and the existence of a field strong enough to disturb the selection rules was excluded. An argument in support of this interpretation was the fact that the forbidden lines in O II were observed in interstellar space, where the gas density is less than 20 atoms per cubic centimeter. Thus the forbidden lines for O II, N II, and other elements were interpreted as arising from spontaneous radiation and were not bound by the selection rule for electric dipole radiation. In this connection it became necessary to reformulate the quantum theory of radiation. This was first done in 1928 by Rubinowicz, who showed that the selection rules for multipole ra-

diation are different from those for electric dipole radiation and that these rules are different for different order multipoles; thus the multipole radiation could not always be expected when electric dipole radiation was observed. It was found that the selection rule for second-order multipole radiation* (taking account of the various types of electron coupling) allowed for transitions corresponding to spectral lines which formerly had been assigned to nebulium, coronium and geocoronium.

When it was established that the majority of forbidden lines were to be associated with spontaneous multipole radiation, and that as far as "forbiddenness" was concerned these lines were equivalent to electric dipole radiation, the notion of forbiddenness was reconsidered. In 1936, Bowen had already directed attention to the provisional nature of the concept of forbidden lines and had, as a convenience, divided all lines (whether or not they obeyed the selection rules for electric dipole radiation) into two groups: (1) those characterized by high transition probabilities (10^{-3} – 10^{9} sec^{-1}), and (2) those characterized by small transition probabilities (10^{2} sec^{-1} or less).[1] A more sophisticated definition of forbiddenness was given by Mrozowski,[2] who defined as forbidden all lines which, for unexcited atoms, have a very small transition probability as compared with the usual transition probabilities for the given atoms; in this formulation the transitions being compared must refer to levels with approximately the same quantum numbers. The last provision is necessary in order to exclude remote terms in a series, since these have small transition probabilities as compared with the first lines in the series. In some cases the notion of "very small" was interpreted as 10^{-3} and in others 10^{-4}. It is apparent that the notion of forbidden lines is well taken in the Mrozowski formulation but that it leads to a classification system which involves certain difficulties. Although the old idea of forbidden lines is somewhat inconvenient, and actually reflects a particular stage in the development of atomic spectroscopy, we shall use it hereinafter (the old concept of "forbiddenness" is the generally accepted one).

Forbidden lines are observed in different regions of atomic, molecular, and nuclear spectra and encompass the frequency range from gamma rays to radio waves. A study of these lines leads to a more fundamental understanding of the properties of matter in various states. Forbidden lines are especially important in astrophysics. The intensity of these lines yields information on the density, temperature, chemical composition, and other important properties of various non-terrestrial bodies. Forbidden lines are also important in nuclear spectroscopy. This importance stems from the fact that the forbidden lines in gamma spectra are generally more intense than the allowed lines.

In the present review we shall consider the important results of theoretical and experimental research on forbidden lines in atomic spectra. Sections 1 and 2 are devoted to the general features and classification of spontaneous forbidden lines while Secs. 3 and 4 deal with the forbidden radiation of celestial bodies and lines which are induced by various fields. In conclusion we consider briefly the problem of obtaining forbidden lines in the laboratory and present a brief survey of the important unsolved problems pertaining to forbidden radiation in atoms.

1. GENERAL CHARACTERISTICS OF SPONTANEOUS FORBIDDEN LINES

As has been indicated in the introduction, the existence of intense forbidden lines in the spectra of celestial bodies made it necessary to formulate a quantum theory of multiple radiation. This theory was formulated in the 1930's. At first electric quadrupole and magnetic dipole radiation were studied, since these encompass almost all the multipole lines encountered in atomic spectra. Somewhat later an investigation was made of third-order multipoles and it was only relatively recently (in the 1940's), in connection with the rapid development of nuclear spectroscopy, that a need arose for the development of a theory for multipole radiation of any order. The simplest derivation of the formulas for the fields and for the probability of multipole radiation of any order in the nonrelativistic case is that due to Berestetskiĭ.[3] Because the present paper is concerned with atomic spectra, we deal chiefly with second-order multipole radiation. Quantum theory gives the following formulas for the radiation intensity of multipole lines of this kind[4] (for natural excitation):

$$I_q(\mathrm{A},\mathrm{B}) = N(a)\,h\nu A_q,$$

$$A_q = \frac{32\pi^6\nu^5}{5hc^5}\sum_{a,b}|(a|Q|b)|^2, \qquad (1.1)$$

$$I_m(\mathrm{A},\mathrm{B}) = N(a)\,h\nu A_m,$$

$$A_m = \frac{64\pi^4\nu^3}{3hc^3}\sum_{a,b}|(a|\mathbf{M}|b)|^2, \qquad (1.2)$$

*By second-order multipole radiation we mean electric quadrupole and magnetic dipole radiation; third-order radiation refers to electric octupole and magnetic quadrupole, etc.

where A_q and A_m are the probabilities for electric quadrupole and magnetic dipole transitions, Q is the atomic electric quadrupole moment, a tensor with components

$$Q_{\alpha\beta} = \frac{1}{3}\sum_i e_i (3x_{i\alpha}x_{i\beta} - r_i^2\delta_{\alpha\beta});$$

$\mathbf{M} = \frac{e}{2m_0c}\sum(\mathbf{L_i} + 2\mathbf{S_i})$ is the magnetic dipole moment of the atom, $\mathbf{L_i}$ and $\mathbf{S_i}$ are the orbital moment and spin of the i-th electron; N(a) is the number of atoms in the initial state a at a given instant of time; b refers to the final state; A and B are the states associated with the upper and lower energy levels between which the transition takes place; $\sum_{a,b}$ indicates that the intensity of the line (A, B) is equal to the sum of the intensities of its components, ν is the frequency.

Computing the matrix elements in Eqs. (1.1) and (1.2) we can establish the selection rules for various atomic transitions. These rules were first established by Rubinowicz, Brinkman and Blaton[5-7] who showed that these rules depend on the type of radiation and on the nature of the electron coupling in the atoms. For example, in the case of Russell-Saunders coupling, i.e., normal coupling, these rules are as follows:

Electric quadrupole radiation

A) $\Delta J = 0, \pm 1, \pm 2;\ J_1 + J_2 \geqslant 2;\ \Delta m = 0, \pm 1, \pm 2;$ { even terms — even terms, odd terms — odd terms }

B) $\Delta L = 0, \pm 1, \pm 2;\ \Delta S = 0.$

Magnetic dipole radiation

A) $\Delta J = 0, \pm 1;\ J_1 + J_2 \geqslant 1;\ \Delta n = 0;\ \Delta m = 0, \pm 1;$ { even terms — even terms, odd terms — odd terms }

B) $\Delta L = 0, \pm 1;\ \Delta S = 0,$

where ΔJ is the change in the quantum number J, the total angular momentum of the atom; Δm is the change in the magnetic quantum number (the projection of the total moment on the z axis); ΔL and ΔS are the changes in the quantum numbers for the orbital and spin moments of the atom and Δn is the change in the principle quantum number. The selection rule is easily generalized to the case of 2^k-pole radiation where k is the order of the multipole (k = 1 denotes dipole radiation, k = 2 denotes quadrupole radiation, k = 3 denotes octupole radiation and so on):

2^k-pole electric radiation

A) $\Delta J = 0, \pm 1, \pm 2, \ldots, \pm k;\ J_1 + J_2 \geqslant k;$ { even terms — even terms, odd terms — odd terms } for k even

$\Delta m = 0, \pm 1, \pm 2, \ldots, \pm k;$ { even terms — odd terms, odd terms — even terms } for k odd

B) $\Delta L = 0, \pm 1, \pm 2, \ldots, \pm k;\ \Delta S = 0;$

2^k-pole magnetic radiation

A) $\Delta J = 0, \pm 1, \pm 2, \ldots, \pm k;\ J_1 + J_2 \geqslant k;$ { even terms — even terms, odd terms — odd terms } for k odd

$\Delta m = 0, \pm 1, \pm 2, \ldots, \pm k;$ { even terms — odd terms, odd terms — even terms } for k even

B) $\Delta L = 0, \pm 1, \pm 2, \ldots \pm k;\ \Delta S = 0.$

The selection rules given under B are satisfied exactly only in the case of normal coupling. If there is a departure from normal coupling these rules are violated to a greater or lesser extent. Thus, for light atoms, which exhibit normal coupling (in particular, helium), the rule $\Delta S = 0$, i.e., the so-called intercombination rule, is strictly observed (transitions of the type $1sns\,{}^1L - 1sns\,{}^3L'$ are strictly forbidden); on the other hand, in the heavy elements (in particular, mercury) the rule $\Delta S = 0$ does not hold at all. This and the violation of the rule $\Delta L = 0, \pm 1, \pm 2, \ldots, \pm k$ are explained as follows. Departures from normal coupling occur as a result of the spin-orbit interaction in the atom; this interaction is very small for the light elements but increases with atomic number. This interaction changes the wave functions. If the change is small the modified wave function for any term is not very different from the pure Russell-Saunders wave function for the same term. A calculation shows[8] that in this case there should be a small but increasing (with atomic number) admixture of wave func-

tions of the other Russell-Saunders terms of different multiplicity and different L; however, all terms (including the given term) are characterized by the same value of J and are of the same configuration. Thus, a given state can have properties which apply to states with different values of L and multiplicity; for this reason it is possible to have weak transitions which are not compatible with rule B. For large spin-orbit interactions, i.e., j-j coupling, L and S are no longer good quantum numbers and selection rule B loses its meaning completely.

The rule $\Delta n = 0$ is satisfied strictly only in the nonrelativistic approximation. Thus, for example, a calculation of the probability for the $1s\,^2S_{1/2} - 2s\,^2S_{1/2}$, transition in H I carried out with relativistic wave functions shows that it is to be associated with magnetic dipole radiation although the transition violates the rule $\Delta n = 0$.[9]

It is apparent that the majority of the selection rules are the same for magnetic dipole and electric quadrupole radiation. Hence it is only in certain particular cases that these two effects can be distinguished by means of the selection rules. Characteristic rules are, for example, $J_1 + J_2 = 1$ for magnetic dipole radiation and $\Delta J = \pm 2$ for electric quadrupole radiation. The transitions

$$J = 0 \rightleftarrows J = 1 \quad \text{and} \quad J \rightleftarrows J + 2$$

refer respectively to pure magnetic dipole and pure electric quadrupole transitions if all the remaining rules for these multipoles are satisfied.

Having numerical values for the nonvanishing matrix elements $(a|Q|b)$ and $(a|M|b)$, it is possible to determine, as is apparent from Eqs. (1.1) and (1.2), the probabilities for various atomic transitions. A knowledge of the absolute or relative probabilities for these transitions is of considerable help in investigating multipole lines. In particular, from a knowledge of the relative probabilities of the components of the multipole lines it is possible to get some idea of the assignment to various multiplicities. A knowledge of these probabilities is especially important in work on forbidden lines in the spectra of non-terrestrial bodies. A knowledge of the absolute probability for transitions and intensities of the corresponding forbidden lines, determined from observed data, can be used to find the concentration of metastable atoms of various elements. If the electron temperature and density are known, using the quantum theory of radiation the astrophysicist can establish the density of atoms in the ground state and, in the final analysis, can determine the chemical composition of a nonterrestrial body.[10-13]

A calculation of the probabilities for multipole transitions has been carried out by a number of investigators; the most important work (aside from that cited[8]) is that of Condon, Shortley, Garstang and Pasternak.[14-17] The transitions which have been investigated in greatest detail (relative and absolute probabilities for the electric quadrupole and magnetic dipole cases) are those between levels characterized by the following electron configurations p^2, p^3, p^4, d^2, d^3, d^4, and d^5. The calculations for the p^2, p^3, and p^4 configurations have been carried out for the most general case, i.e., intermediate electronic coupling.[8] The results of the calculations are tabulated as functions of a parameter χ,* which varies from the value zero, in the case of normal coupling, to infinity, for j-j coupling. Rather good estimates of this parameter are available for various atoms.[18] The electric quadrupole transition probability (in contrast with that for magnetic dipole transitions) contains the square of the radial integral s_q:

$$s_q = \frac{2}{5} e \int_0^\infty r^2 R^2(n, p)\, dr, \tag{1.3}$$

which is of order unity (in an atomic system of units). As has been mentioned above, at small deviations from normal coupling the wave functions that correspond to definite terms in intermediate coupling can be given as a linear combination of the wave functions for Russell-Saunders terms of the same J, for the same configuration. The coefficients are functions of the parameter χ. For example, in the p^2 configuration

$$\begin{aligned} \psi(^1D_2') &= a\psi(^1D_2) + b\psi(^3P_2);\ \psi(^3P_2') \\ &= a\psi(^3P_2) - b\psi(^1D_2), \end{aligned} \tag{1.4}$$

where the primed terms denote intermediate coupling while the unprimed terms denote normal coupling. The coefficients a and b are:[8]

$$\left.\begin{aligned} a &= 1 - \frac{25}{144}\chi^2 - \frac{125}{864}\chi^3 + \ldots, \\ b &= \frac{5\sqrt{2}}{12}\chi\left(1 + \frac{5}{12}\chi - \frac{25}{72}\chi^2 + \ldots\right). \end{aligned}\right\} \tag{1.5}$$

These linear combinations mean that certain of the transitions that are forbidden in the case of pure normal coupling are allowed in intermediate coupling. Typical examples are the magnetic dipole transitions between different terms, the electric quadrupole transitions between the term systems $(^3P_2' - {}^1D_2')$, as is apparent from Eqs. (1.4) and (1.5) and so on. The probabilities for these tran-

*$\chi = \frac{\xi}{5F_2}$, where ξ and F_2 are the energies of the spin-orbit and electric interactions respectively.

sitions are proportional to χ^2 and χ^4 and are considerably smaller than the probabilities for the corresponding multipole transitions for normal coupling (for example, χ^2 for O III $2p^2$ is 10^{-4}). However, for wave lengths in the optical region (λ 4580 A), according to Shortley[8]

$$A_m = 3 \cdot 10^2 \text{ sec}^{-1}, \quad (1.6)$$
$$A_q = 8 \cdot 10^{-1} \text{ sec}^{-1}, \quad (1.7)$$

and are considerably smaller than the probability for the corresponding electric dipole transition, which is

$$A_d = 2 \cdot 10^7 \text{ sec}^{-1}. \quad (1.8)$$

The foregoing indicates how small the probabilities for these forbidden transitions are as compared with those for electric dipole transitions. The order of magnitude of these probabilities ranges from 10^{-2} sec^{-1} to 10^{-9} sec^{-1}, i.e., they are smaller than A_d by factors of $10^9 - 10^{16}$.* The same considerations apply for the probabilities for higher-order multipole transitions since the ratio of two successive multipole electric or magnetic transitions is $(2\pi a/\lambda)^2$ (a is the radius of the atom, λ is the wave length); for the optical region the numerical value of this ratio is approximately 10^{-6}.[5] This ratio increases considerably in the x-ray region and exhibits a strong dependence on atomic number:†

$$\left(\frac{2\pi a}{\lambda}\right)^2 = 10^{-5} Z^2.$$

Because of the extremely small probabilities for the forbidden transitions as compared with the allowed transitions, the forbidden lines are only weakly allowed. However there are special conditions under which both types of lines become comparable in intensity; indeed, in come cases the forbidden lines become stronger than the allowed lines. In this connection if is of interest to consider the dependence of line intensity on the conditions of excitation. In general, the intensity of any line is given by the expression[1]

$$I = \frac{N' h\nu A_i}{A_1 + A_2 + \ldots + A_i + \ldots + B + C}, \quad (1.9)$$

where N' is the number of atoms excited to the given state per unit time;* B is the probability of energy loss by the atom in collisions of the first or second kind (this depends strongly on the conditions within the radiation source); C is the probability for transition to a higher state by absorption of radiation; A_1, A_2, A_3, . . . are the probabilities for radiation of various lines and A_i is the probability for radiation of the line being considered.

The transition probability A_i between two states is usually defined as the reciprocal of the mean lifetime of the atom in the higher state if the transition being considered is the only transition available (A_i should contain terms which depend on the radiation density but these are almost always small). The probability A_i can be given in the form of a series $A_i = A_{id} + A_{iq} + A_{im} + \ldots$ the first term of which is the probability for the electric dipole transition; the other terms represent the probabilities for various multipole transitions. Even where simultaneous electric dipole and multipole radiation is possible (where both are spontaneous and obey appropriate selection rules) it is impossible to detect the multipole lines in practice. Hence, great interest attaches to forbidden lines which arise in transitions from metastable levels. As has been noted in the introduction, transitions from such levels to lower levels are usually forbidden by the selection rules for electric dipole radiation. Since most of these rules are derived on the basis of approximations some are usually discarded (usually two are retained[19]). In this case in the denominator of Eq. (1.9) we are generally left with only B and C (all the A_i are of order 10^2 sec^{-1} or smaller) and this expression becomes

$$I = \frac{N' h\nu A_{ik}}{B + C}, \quad (1.10)$$

where A_{ik} is the probability for one of the multipole transitions.

The quantity B depends on the number of collisions of the first and second kind which the metastable atom experiences with other atoms and electrons. According to the kinetic theory of gases, in air under normal conditions an atom undergoes 10^{10} collisions (elastic and inelastic) per second. At lower pressures the number of collisions is reduced in proportion to the pressure. At the lowest pressure (approximately 10^{-3} mm Hg) for which it is possible still to have radiation in discharge tubes the number of collisions per second is reduced to 10^4. In this case the probability of collisions of

*True, as the atomic number increases χ also increases and in heavy elements such as lead it becomes of order unity;[2] nonetheless, the statement concerning the small probability of electric quadrupole and magnetic dipole transitions (as compared with electric dipole transitions) still applies, as can be seen from Eqs. (1.6)–(1.8).

†It is apparent from what has been said above that there is no contradiction between the "old" and "new" concepts of forbidden lines (see introduction) for the overwhelming majority of atomic spectra. It is only in the x-ray region that contradictions arise.

* $N = \frac{N'}{B + C + A_1 + A_2 + \cdots + A_i + \cdots}$, where N is taken from Eqs. (1.1) and (1.2).

the first and second kind per unit time become much smaller than unity.

We shall consider collisions of the first and second kind in somewhat greater detail because these are frequently used to obtain atoms in metastable states.* It is of interest to note the following features which pertain to these collisions.

Collisions of the first kind between atoms and electrons occur more frequently at values of the electron kinetic energy which are greater than the excitation energy of the atom; on the other hand, collisions of the second kind occur more frequently at low electron velocities. The probability of a collision of the first or second kind between one atom and another atom or an ion is small if the excitation energy and the velocity of the second atom or ion is approximately the same as the energy and velocity of the first atom. It becomes significant, however, when the relative velocities of the colliding particles become comparable with the velocity which a free electron acquires at the excitation potential and increases as these velocities increase.[20]

The probability of a collision of the first or second kind, for which the excitation energy of one atom is transformed into energy of relative motion of the colliding particles, is usually small but may be significant in those cases in which one of the colliding atoms has a small excitation energy as compared with the other or when it can lose (or gain) only a small part of this energy in the collision (the latter situation obtains if the atom has a close-lying excited state). Examples of this type are transitions in the argon atom from the ground state $6\,^2P_{1/2}$ to the metastable state $6\,^2P_{3/2}$ in collisions of the first kind with argon atoms (in a discharge at constant temperature),[21] and in transitions of mercury atoms from the excited non-metastable state $6\,^3P_1$ to the metastable state $6\,^3P_0$ in collisions of the second kind with argon or nitrogen atoms.[19] Collisions of the second kind between two atoms are very important when one of the atoms excites the other by virtue of loss of its own energy. Such collisions are most probable in the case in which the excitation energies of both atoms are comparable. (A small difference between these energies can be compensated by the relative kinetic energy).† For example, in collisions of mercury atoms, excited to the $6\,^3P_1$ level with sodium atoms the latter are excited to states, the energy of which are approximately the same as the energy of the $6\,^3P_1$ state.[19] If there are no such levels the probability of collisions of this kind falls off rapidly. Molecules are especially effective in these collisions since they have available a large number of energy levels so that it is very likely that there will be levels with energies close to the energy of the excited atom. It should also be noted that in collisions of the second kind between two atoms the spin plays an important role. In particular, the most probable collisions of the second kind are those in which the total spin of the colliding atoms is not changed.[22]

A quantitative investigation of collisions of the first and second kind involves great experimental difficulties and work in this field has been started only in recent years. Here we should mention the work of the Soviet physicists Frish, Zapesochnyĭ, Bogdanova et al.[21,23-27]* These papers are concerned chiefly with the role of collisions of the first kind between atoms and electrons in the excitation of allowed lines in electron beams and in gas-discharge plasmas characterized by Maxwellian electron velocity distributions; in the first case an investigation has been made of the effect of cascade transitions on the population of the atomic levels. A quantitative investigation of collisions of the second kind has also been carried out for collisions between excited mercury atoms and sodium atoms; these are responsible for the sensitized fluorescence of sodium vapors. Other important problems have also been treated.

Usually the probability B [cf. Eq. (1.10)] for collisions of the first and second kind is large compared to the radiation probability; hence lines corresponding to the optical transition from a metastable state to a lower state are essentially forbidden. To obtain forbidden lines in atoms of any element the quantity B must be made as small as possible. This objective is usually achieved as follows. Atoms of the element being investigated (for example, OI) are excited to metastable states in a mixture containing an inert gas or some other gas, the atoms of which have high excitation energies compared with the energies of the metastable atoms (for example, the energy of the first metastable state in OI is 5.3 ev while the energy of the first excited state in the atom of the inert gas is of the order of 10 — 20 ev). Thus there are no collisions of the second kind between the metastable atoms of the gas being investigated and the atoms in the mixture. The gas must be kept at a low pressure (approximately 2 mm Hg) for the following

*The problem of collisions between different particles has been considered in great detail in a recently published monograph by Massey and Burhop.[79]

†These collisions are responsible for the resonance effect in so-called sensitized fluorescence.

*A comprehensive bibliography is given in the review paper by Frish.[23]

TABLE I

Electric dipole			Magnetic dipole			Electric quadrupole			Total 3rd order radiation		
Δm	$\alpha=\frac{\pi}{2}$	$\alpha=0$	Δm	$\alpha=\frac{\pi}{2}$	$\alpha=0$	Δm	$\alpha=\frac{\pi}{2}$	$\alpha=0$	Δm	$\alpha=\frac{\pi}{2}$	$\alpha=0$
+1	σ	right cir.	+1	π	right cir.	+2	σ	—	+3	σ	—
0	π	—	0	σ	—	+1	π	right cir.	+2	π	
−1	σ	left cir.	−1	π	left cir.	0	—	—	+1	σ	right cir.
						−1	π	left cir.	0	π	—
						−2	σ	—	−1	σ	left cir.
									−2	π	—
									−3	σ	—

reasons: at higher pressures there are collisions of the O I atoms with the oxygen molecules, and at lower pressures there are collisions with the walls of the container. The higher the degree of ionization of the gas being investigated the more difficult it is to use the method described above because at increased ionization there is an increase in the number of free electrons with small velocities; this situation results in an increase in the number of collisions of the second kind.

We now consider briefly the problem of removal of an atom from a metastable state via absorption of radiation. The probability of absorption of radiation will be denoted by C. As is well-known, this quantity is proportional to the radiation intensity at the wave length at which the atom in a stable or metastable state is capable of absorption.

The fact that the quantity C is large is one of the important factors which suppresses the production of intense forbidden lines in the atmospheres of many stars. For example, in the atmosphere of the sun the radiation density is so strong that the atom Ca II is removed from its ground $4s^2\ ^1S$ state by absorption of radiation 2×10^4 times per second.[1] Nevertheless, there are highly ionized atoms (belonging to the first long period in the periodic table) for which C is rather small and for which the conditions for excitation of intense forbidden lines are satisfied. This situation is explained by the fact that the transition of highly ionized atoms from a metastable or ground state to the first non-metastable state occurs at the limit of the ultraviolet, whereas the radiation density of a relatively cold star such as the sun is small in this region of the spectrum. As far as forbidden lines of weakly ionized and neutral atoms are concerned, we may note these can achieve significant intensities only when the radiation density is small in the visible region of the spectrum. This situation (and a reduction in the magnitude of B) are satisfied only in certain non-terrestrial bodies such as gaseous nebulae, young stars in recent stages of development, certain old stars with extensive atmospheres, and so on.

In investigating different orders of magnitude of the sum B + C we may note certain features which pertain to the intensities of forbidden lines. Suppose that a given metastable state of the atom gives some forbidden line. Then, the intensities of these lines [as is apparent from Eq. (1.10)] will be related as the probabilities of the corresponding transitions. The situation is completely different in the case in which the sum B + C is small so that $B + C \ll A_1 + A_2 + \ldots + A_i \ldots$; in this case Eq. (1.9) assumes the form:

$$I = \frac{N' h\nu A_{ik}}{A_1 + A_2 + \ldots + A_i + \ldots}. \qquad (1.11)$$

In the case of a single possible transition or in the case in which $A_{ik} \gg A_1 + A_2 + \ldots + A_{i-1} + (A_i - A_{ik}) + \ldots$, we have

$$I = N' h\nu. \qquad (1.12)$$

It follows from Eq. (1.12) that in the latter case the intensity of the forbidden lines is determined only by the density of metastable atoms; thus the ratio of intensities of the individual lines depends to a considerable degree on the statistical weights and the excitation potentials of the metastable levels.

Of great importance in the study of multipole

lines is the theory of the Zeeman effect, which was developed in the 1930's.[1,5,7] The results of theoretical investigations of the simple Zeeman effect are given in Table I. Here Δm denotes the change in the magnetic quantum number, α is the angle between the direction of observation and the magnetic field, π and σ denote the plane of polarization parallel and perpendicular to the magnetic field, right cir. denotes right-circular polarization, left cir. denotes left-circular polarization. It should be noted that the polarization properties of the individual Zeeman components remain the same in the complex Zeeman effect although the components for a given Δm become multiple.

It is apparent from Table I that the longitudinal effect is the same for all order of multipole radiation; this is not true for the transverse effect. The latter is different for each type of multipole radiation so that it can be used to determine the assignment of a line to one or another of the multipole orders. In this way the whole quadrupole series $p^4\,{}^1D - p^4\,{}^1S$, O I; $s\,{}^2S - d\,{}^2D$, Na I and K I was determined, as were the magnetic dipole lines of Pb I, ${}^3P_1 - {}^1S$, λ 4618 A.[28-31]

The theory of the Zeeman effect has been formulated in fairly great quantitative detail. The probability for each of the Zeeman transitions $A^{J,m}_{J',m'}$ has been computed as a function of the quantum number m. As in the case of electric dipole radiation, these probabilities obey the two sum rules:

$$\sum_m A^{J,m}_{J',m'} = \sum_{m'} A^{J,m}_{J',m'}, \qquad (1.13)$$

where $m' = m \pm 1$, $m \pm 2$, $m \pm 3$ (depending on the order of the multipole) and

$$\sum_{m'} A^{J,m}_{J',m'} = A^{J}_{J'}, \quad \sum_{m'} A^{J,m'}_{J',m} = \overline{A^{J}_{J'}}, \qquad (1.14)$$

where $A^J_{J'}$ and $A^J_{J'}$ are the transition probabilities in the absence of the field; these do not depend on m and satisfy the well-known relation

$$(2J+1)\,A^J_{J'} = (2J'+1)\,\overline{A^J_{J'}}. \qquad (1.15)$$

Different magnetic field cases have been considered: the weak field (anomalous Zeeman effect) and the intermediate and strong field cases (simple Zeeman effect). It has been found in the second case that at some definite field strength the selection rules can be violated. Thus, for example, in the case of quadrupole radiation we find the forbidden components with $\Delta J = \pm 3$.[32]

A theory has also been formulated for multipole radiation of atoms in external fields characterized by various kinds of symmetry. This theory has been of importance in the study of spectra of the rare-earth ions in crystals and solutions. Both the theory and its modifications have been considered in detail by El'yashevich in a monograph devoted to the spectra of rare-earth elements.[33] It is shown in this monograph that multipole radiation is present for any triply-charged rare-earth ion in crystals which have electron configurations of the type $4f^k$ where k varies from 1 in Ce IV to 13 in Yb IV. In transitions between individual levels pertaining to this configuration, it is possible to have both magnetic dipole and electric quadrupole lines and induced electric dipole lines. We shall direct our attention to the first two kinds.

Since the interaction of the ion with the field of the crystal lattice is small, the selection rules for electric quadrupole and magnetic dipole radiation for the quantum numbers J and L remain approximately the same as in the case of free atoms. The situation with regard to the selection rule for the quantum number m is somewhat different. These rules are satisfied rigorously only in cases in which the atomic system possesses an axis of cylindrical symmetry, i.e., an isolated axis of infinite order. In crystals characterized by a rotational axis of n-fold symmetry the selection rules for the quantum number m do not actually lose force but become a particular case of more general selection rules; more precisely, they become the selection rules for the so-called crystallographic quantum number μ, i.e.,

$$\Delta\mu = 0, \pm 1 \qquad (1.16)$$

for magnetic dipole radiation and

$$\Delta\mu = 0, \pm 1, \pm 2 \qquad (1.17)$$

for electric quadrupole radiation; the quantum number m is related to μ by the expression

$$m = \mu + kn, \qquad (1.18)$$

where k is any whole number.[33]

Furthermore, as a consequence of the existence of isolated axes in the crystal the multipole radiation of rare-earth ions must have definite polarization properties; these are characteristic of the various multipoles and of the various axes of symmetry.[33]

An estimate has also been made of the probabilities for both magnetic and quadrupole transitions for rare-earth ions in crystals; this estimate is made using Eqs. (1.1) and (1.2) and taking account of the splitting of the ionic levels and the perturbations of the ionic wave functions due to the lattice fields. According to El'yashevich[33] the maximum theoretical values for these probabilities are

$$A_m = 2 \cdot 10^2 \text{ sec}^{-1}, \quad (1.19)$$

$$A_q = 0.5 \text{ sec}^{-1}. \quad (1.20)$$

The directional properties of the radiation of these ions in crystals has been investigated theoretically by Hellwege,[34,35] whose analysis is based on the assumption that the multipole axes of the ions are oriented in definite directions with respect to the crystal lattice. On this basis theoretical predictions are made of the possible results of experimental investigations of the dependence of intensity on radiation direction for the various multipole lines (taking account of splitting in the ionic field of the crystals). Hellwege has also analyzed in detail the possibility of establishing the fixed direction for the electric and magnetic moments of ions in crystals, using the experimental data for various crystal systems. He has shown that this possibility exists if the following requirements are satisfied:

1. All the multipole moments of a given type must be parallel to one crystallographic direction.

2. This direction must coincide with one of the axes of the indicatrix.

It turns out that the first of these conditions is not satisfied in cubic crystals while the second is not satisfied in triclinal crystals. The fact that the different types of multipole radiation have different directional properties is also used as the basis for the interference method of studying multipole radiation. The interference method was proposed by S. I. Vavilov.[36,37] Vavilov showed that the nature of Fresnel interference for diverging interfering rays (distribution of intensity and polarization) depends strongly on the nature of the elementary radiator, that is to say, on whether the radiator is an electric or magnetic dipole or an electric quadrupole. For example, the dependence of the visibility of the interference bands on the angle φ between the interfering rays is different for dipole and quadrupole electric radiation:[37]

$$\left.\begin{aligned} V_d &= \frac{1+\cos\varphi}{2}; \\ V_q &= \frac{1+\cos\varphi}{2} - \sin^2\varphi, \end{aligned}\right\} \quad (1.21)$$

where $V = \frac{I+i}{I-i}$, I and i are the maximum and minimum intensities in the interference field. It is also found that in the case of magnetic dipole radiation there is a displacement of the interference pattern (by one band) as compared with electric dipole radiation.

The theoretical description given above has been verified experimentally. Experimental data obtained by Zaĭdel and Larionov, Hoogschagen, Sevchenko, and others [38-47] in observations of narrow bands in the spectra of triply charged ions of the lanthanides in crystals and in solutions* indicate that the narrow bands are actually due to forbidden transitions between levels in the f-shells. The results of an investigation of polarization and measurements of probabilities for these transitions were found to be in agreement with the theoretical predictions and indicate that some of the transitions are magnetic while the others are due to induced electric dipole radiation. It may be noted that in one of the papers by Freed and Weissman,[47] devoted to an investigation of the spectra of solutions of Eu IV salts, the Vavilov interference method was used successfully to examine the nature of the radiation.

In the early 1940's a theory was developed for hyperfine structure and for the Zeeman effect in second-order, hyperfine multiple radiation. It was established[48] that the intensity ratios for hyperfine components in magnetic dipole radiation obeyed the rules derived in the usual theory for hyperfine structure in electric dipole lines.[49] However the relative intensities of the components of the hyperfine structure of electric quadrupole lines were first obtained by Rubinowicz[50] for the intensities of the components of the fine structure multiplets by substituting the quantum number F, J and I ($\mathbf{F} = \mathbf{J} + \mathbf{I}$, where I is the nuclear spin) for J, L and S. The selection rule for F remains the same as for J, i.e.,

$$\Delta F = 0, \pm 1, \pm 2, \ldots, \pm k; \quad F_1 + F_2 \geqslant k; \quad (1.22)$$

$$\Delta M = 0, \pm 1, \pm 2, \ldots, \pm k (M = -F, -F+1, \ldots, F-1, F) \quad (1.23)$$

for 2^k-pole radiation.

These theoretical analyses played an important part in determining the multipole assignments of various forbidden lines. For example: the electric quadrupole assignment of the 5313-A line, the magnetic dipole assignment of the 4618-A line and the mixed nature of the 7330-A line in the spectrum of lead, and the quadrupole assignment of the 2815-A line ($^2D_{5/2} - {}^2S_{1/2}$) in Hg II.[51-54] The theory of hyperfine structure was also used for multipole lines in Bi I, Sb and As I.[55,56]

2. ATOMIC MULTIPOLE RADIATION

We now make a more detailed analysis of different kinds of multipole radiation. We consider first electric quadrupole radiation. We shall not dwell here on the laws of this radiation, developed in the preceding section, which was devoted to the general

*A comprehensive bibliography is given by El'yashevich.[33]

properties of multipoles, but shall deal chiefly with the multiplet structure of quadrupole lines. As is well known, the intensity ratio for the components of a quadrupole multiplet is equal to the ratio of the corresponding transition probabilities. The relative probabilities $A^{L,J}_{L',J'}$ have been computed for the case of Russell-Saunders coupling and terms of the same multiplicity. These probabilities are functions of the quantum numbers J, L, and S. As an example we present two of the formulas from Condon and Shortley:[4]

$$A^{L,J}_{L-1,J-2} = \frac{Q(J-1)P(J-2)P(J-1)P(J)}{(J-1)J(2J-1)}H^2, \quad (2.1)$$

$$A^{L,J}_{L,J+2} = \frac{P(J+1)P(J+2)Q(J)Q(J+1)}{(J+1)(J+2)(2J+3)}G^2, \quad (2.2)$$

where

$$H = -e\sum_i \frac{1}{4}\sum_{\alpha''}[(\alpha SL\,|\,x_i\,|\,\alpha''SL)(\alpha''SL\,|\,y_i\,|\,\alpha'SL-1) + (\alpha SL\,|\,x_i\,|\,\alpha''SL-1)(\alpha''SL-1\,|\,y_i\,|\,\alpha'SL-1)], \quad (2.3)$$

$$P(J) = (J+L)(J+L+1) - S(S+1),$$
$$Q(J) = S(S+1) - (J-L)(J-L+1), \quad (2.4)$$

the expression for G is similar to that for H (cf. reference 4).

All the formulas for the probabilities have twenty-five possible transitions $L \to L' = L$, $L \pm 1$, $L \pm 2$ and $J \to J' = J$, $J \pm 1$, $J \pm 2$. It is easy to see that the formulas satisfy the selection rule $J_1 + J_2 \geq 2$. The probabilities for the $A^{L,J}_{L',J'}$ transitions obey the following sum rules:

$$\sum_{J'} A^{L,J}_{L',J'} = A^{L}_{L'}; \quad (2.5)$$

$$\sum_{J'} g_{J'} A^{L,J}_{L',J'} = g_J \overline{A^{L}_{L'}}, \quad (2.6)$$

where $A^{L}_{L'}$ and $\overline{A^{L}_{L'}}$ are independent of J; $J' = J$, $J \pm 1$, ± 2; $g_J = 2J+1$ is the statistical weight for a sublevel with a given J. The rules given in (2.5) and (2.6) are similar to those in (1.13) and (1.15) and the well known rules given by Ornshteĭn, Burger, and Dorgelo for electric dipole radiation. In general, Eqs. (2.1) — (2.5) do not apply for intercombination transitions and for multiplets induced by external fields. Calculations show[57] that in the latter cases the departures from the relations in (2.1) — (2.5) become less important as the multiplet splitting is reduced and as the quantum number L increases. Equations (2.1) — (2.5) have been verified experimentally for the quadrupole multiplets $^2S - {}^2D$ in alkaline metals[58] and

$$3d^64s\,{}^6D - 3d^54s^2\,{}^6S, \quad 3d^7\,{}^4F - 3d^64s\,{}^4S, \quad \text{FeII}$$

in the spectrum of the star η-Carinae,[59] although the last multiplet has not been resolved completely.

We consider the first multiplet in somewhat greater detail. This multiplet, more precisely the quadrupole doublet $1\,{}^2S_{1/2} - 3\,{}^2D_{3/2,5/2}$* ($\lambda$4642.17 A, K I; λ5165.35 A, Rb I; λ6894.7 A, Cs I),† was investigated by means of anomalous dispersion in 1929 by Prokof'ev.[58] The Rozhdestvenskiĭ "hook" method was used in this work. Prokof'ev showed that the intensity ratio for the components of the doublet was $\frac{2J+1}{2J'+1} = \frac{2}{3}$ and also for the first time verified experimentally the fact that the ratio of the probabilities for the quadrupole and corresponding (i.e., occupying approximately the same places in the spectral series) electric dipole transitions was of the order of 10^{-6} as predicted by theory. For example, in Rb I the calculated ratio for $A^{3D}_{1S} : A^{2P}_{1S}$ where A^{2P}_{1S} is the probability for electric dipole transition for the first line of the resolved series $1\,{}^2S_{1/2} - 2\,{}^2P_{1/2,3/2}$ is 2.9×10^{-6} while the experimental value is 2.7×10^{-6}.[58,5]

Somewhat later Blaton[60-62] developed a theory of anomalous dispersion for electric quadrupole radiation. One result of this theory showed that the quantity $N-1$ (N is the refractive index) in the vicinity of a quadrupole absorption line is 4 times larger than in the vicinity of the dipole line with the same transition probability and frequency.

Electric quadrupole lines are also found in x-ray spectra. For example, the line $K - M_{IV}$ in the spectra of elements with atomic number $Z = 20 - 50$, $56 - 58$, $73 - 79$, 82, 90 the line $K - N_{IV,V}$ in the spectra of elements with $Z = 39 - 50$, 56, 57, $73 - 74$, $77 - 79$, and the line $L_{III} - N_{VI,VII}$ in the spectra of elements with $Z = 72 - 82$, 90, 92 and so on.[63]

Theoretical and experimental investigations[5,58] have also been made of the dependence of the intensity of electric quadrupole lines formed in a given spectral series as a function of the quantum number n. The behavior of these lines is completely different from the behavior of lines associated with induced radiation, frequently even those which obey the same selection rules. Whereas the intensity of the quadrupole lines falls off rapidly with increasing n, the intensity of the induced lines increases up to a certain value of n and then falls off. These features of the behavior of quadrupole and induced lines are frequently used experimentally as a means of distinguishing between the two effects.

Of the remaining features of electric quadrupole radiation, we note the small width of quad-

*Numbers 1, 3, and 2 are introduced purely arbitrarily (for listing the terms).

†Here we give the first lines of the doublets being considered.

rupole lines as compared with dipole lines (a consequence of the long life time of metastable atoms Δt and the relation $\Delta E \cdot \Delta t \geq h/2\pi$, where where ΔE is the width of the level) and the directional dependence of the radiation intensity. For example a maximum radiation intensity is found at an angle $\alpha = 45°$ rather than $\alpha = 90°$ (α is the angle between the radiation direction and the multipole axis) as is the case in dipole radiation.

We now consider magnetic dipole radiation. The analyses of magnetic and electric dipole radiation are very similar both in the classical and quantum mechanical formulations. For example, the formulas for the intensities of the electric and magnetic fields of a magnetic dipole are obtained from the corresponding formulas for electric dipole radiation by making the substitutions $\mathbf{E} \rightarrow \mathbf{H}$, $\mathbf{H} \rightarrow -\mathbf{E}$, and $\mathbf{D} \rightarrow \mathbf{M}$, where $\mathbf{D}$ and $\mathbf{M}$ are the electric and magnetic dipole moments respectively. The formulas for the relative intensities of the components of ordinary multiplets and hyperfine structure multiplets are the same for both types of radiation. There is also a similarity between the Zeeman effects. As is apparent from Table I, the data on polarization properties of magnetic dipole lines are obtained from the corresponding data for electric dipole lines by interchanging π and σ.

An important distinguishing feature of magnetic dipole radiation is the fact that its production is intimately related with the existence of spin in the electron and the fact that the electron has different gyromagnetic ratios for the orbital and inherent magnetic moments. If there were no spin, or if the gyromagnetic ratios were the same, the magnetic moment of the atom would be proportional to the total angular momentum and would become an integral of the equations of motion. Its components would be expressed by diagonal matrices in the quantum theory formulation and would vanish for transitions.

All magnetic dipole lines can be divided into three groups:

(1) "Pure lines," i.e., lines that obey the selection rule for Russell-Saunders coupling (with the necessary exclusion of the rule $J_1 + J_2 = 1$) since it is only in this case that they cannot also be in an electric quadrupole radiation state,

(2) intercombination lines, and

(3) "practical" magnetic dipole lines, i.e., lines due to magnetic dipole and electric quadrupole radiation, with the former predominating (these lines will be discussed below).

Of the first two groups, the second has been investigated in greater detail. This group includes magnetic dipole lines, some of which have been mentioned above, and also a series of other lines which are found chiefly in the spectra of celestial bodies. As a consequence of the fact that they arise chiefly by virtue of perturbation, these lines are characterized by small transition probabilities, even as compared with the probabilities of "pure" electric quadrupole transitions. For example,[2] the probability for the intercombination magnetic dipole transition $^1S_0 \rightarrow {}^3P_1$ in O I is 9×10^{-2} sec^{-1} while the probability for the electric quadrupole transition $^1S_0 \rightarrow {}^1D_2$ in O I is 2 sec^{-1}. As the atomic number increases the probability for intercombination transitions also increases (in particular, in the case of lead the transition $^1S_0 \rightarrow {}^3P_1$ has a probability of 50 sec^{-1}).

According to Mrozowski[2] the lines in the first group cannot be resolved by ordinary spectroscopic methods.* They arise predominantly in transitions between components of both fine structure and hyperfine structure of the same term. A more careful investigation has been made of the transitions between levels of the hyperfine structure of the ground states of the alkali atoms. These levels are due to the magnetic interaction between nuclei having nonvanishing spin and the outer electrons. Since the ground state is characterized by $J = \frac{1}{2}$, the levels are determined by the quantum numbers $F = I - \frac{1}{2}$ and $F = I + \frac{1}{2}$, where I is the nuclear spin. These transitions are defined by the selection rule $\Delta F = \pm 1$. These transitions are investigated most effectively by the magnetic resonance methods. The effectiveness of this method results from the following.[64-66]

As is well known, hyperfine levels are very close to each other and for this reason the Bohr frequency corresponding to the level difference is extremely low — say 1.5×10^8 to 1.2×10^{10} sec^{-1}, that is to say, these frequencies fall in the radio-frequency region. Because of the low frequencies, the lifetime of the excited level of the hyperfine structure is very long and the intensity of the corresponding spontaneous magnetic dipole lines is so weak that direct observation is essentially impossible. To strengthen these lines, it is necessary to reduce the lifetime, say to 10^{-4} sec.[66] This possibility is realized inside a magnetic resonance apparatus which is traversed by a beam of excited atoms. As is well known (cf. Fig. 1), four magnetic fields are used in a magnetic resonance system: two deflection fields H_A and H_B, a fixed field H_C, and an oscillating field H_ω. In general the roles played by these fields are as follows.

*With the exclusion of lines corresponding to the transition $^3P_1 - {}^3P_0$, which are observed in the spectrum of the solar corona.

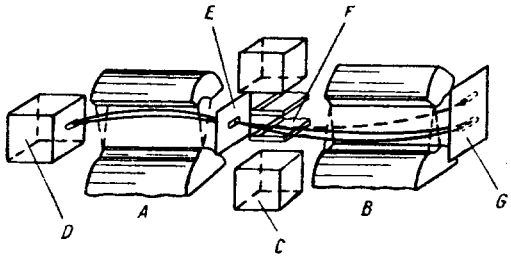

FIG. 1. Motion of an atomic beam in a magnetic resonance apparatus: D) heater, E) slit, G) detector, A, B, C) magnets. (H_A and H_B are the deflection fields, H_C is the fixed field.) F) region of high-frequency field, H_ω.

The oscillating magnetic field H_ω acting on the excited atoms at the appropriate frequency, produces rather intense induced magnetic dipole lines which can be observed either in absorption or emission. The presence of the fixed field results in a Zeeman effect for these lines. The emission or absorption of any of the Zeeman components corresponds to a change in the effective magnetic moment of the atom and this change is detected by means of the deflection fields H_A and H_B. It should be noted that the magnitude of this change depends to a considerable degree on the field H_C. It has been shown[66] that at small values of H_C the above mentioned change is much larger than is the case in strong fields,* although the Zeeman splitting goes in the opposite way. Hence in resolving these lines one usually uses a weak magnetic field for H_C (several hundred gausses). The Zeeman splitting is then used to find the frequency $\Delta\nu$ corresponding to magnetic dipole transition between hyperfine structure levels in the ground state of the atom.

As an example we may present the data obtained in an experiment carried out with this method in lithium. The field H_C ranged from 0.25 to 1.5 gauss for Li^6 and 0.15 to 3500 gausses for Li^7. In the latter case only those Zeeman components were investigated which corresponded to the selection rules $\Delta F = 0$, $\Delta M = \pm 1$, where M is the magnetic quantum number. The values of $\Delta\nu$ are found to be $(228.28 \pm 0.01) \times 10^6$ sec^{-1} and $(803.54 \pm 0.04) \times 10^6$ sec^{-1} for Li^6 and Li^7 respectively. Using the measured values of $\Delta\nu$ it is possible to determine the ratio of the magnetic moments of the two isotopes; this ratio agrees with the results obtained by nuclear resonance experiments.[65-68]

The results of measurements of $\Delta\nu$ for the other alkali metals (and indium) are shown in Table II. The third column contains $\Delta\nu$ in wave numbers. As is apparent from Table II, the uncertainty in the measurements is rather small, approximately 0.01%.[66]

The quantity $\Delta\nu$ has been measured with extremely high precision in hydrogen and deuterium, as is indicated by the following data:[69]

$$\Delta\nu(HI) = (1420.40573 \pm 0.00005)\, 10^6 \text{ sec}^{-1}, \quad (2.7)$$

$$\Delta\nu(DI) = (327.384302 \pm 0.000030)\, 10^6 \text{ sec}^{-1}. \quad (2.8)$$

Lines at frequencies given by (2.7) and (2.8) have been observed in the radio spectra of interstellar gas.

Recently the magnetic resonance method has been used to study hyperfine structure in excited atomic states of hydrogen and the alkali metals. The results were used to determine the nuclear electric quadrupole moments.[70-74]

A large number of forbidden lines (in particular the above mentioned "practical" magnetic dipole lines) are due to electric quadrupole and magnetic dipole radiation simultaneously, that is to say, so-called mixed radiation. As an example we have lines corresponding to the transitions $^1D \rightarrow {}^3P$, $^3P_2 \rightarrow {}^3P_1$ in the p^2 configuration; $^2P \rightarrow {}^2D$, $^2P \rightarrow {}^4S$ and $^2D \rightarrow {}^4S$ in the p^3 configuration, and so on. The mixed nature and the relative contribution due to each type of second-order radiation in the intensity of any forbidden line assigned to the p^2, p^3, and p^4 configurations are given in reference 8. The probabilities for these second-order multipole transitions are expressed as functions of a known (tabulated for various elements) parameter χ (cf. above) and the unknown radial integral (1.3). For example, the corresponding strengths for the lines in the $^1D_2 \rightarrow {}^3P_1$ transition for small deviations from Russell-Saunders coupling are:

$$S_m(^1D_2', {}^3P_1) = \frac{125}{144}\chi^2\left(1 + \frac{5}{6}\chi - \frac{25}{48}\chi^2 + \dots\right), \quad (2.9)$$

$$S_q(^1D_2', {}^3P_1) = \frac{125}{16}s_q^2\chi^2\left(1 + \frac{5}{6}\chi + \dots\right), \quad (2.10)$$

where s_q is the radial integral. It is apparent from Eqs. (2.9) — (2.10) that to find the relative

TABLE II

Atom	$\Delta\nu \cdot 10^{-6}$ sec^{-1}	$\Delta\nu$ (in cm^{-1})
Na^{23}	1771.75±0.01	0.059102
K^{39}	461.75±0.02	0.015403
K^{40}	1285.7 ±0.01	0.042887
K^{41}	254.02±0.02	0.008474
Rb^{85}	3035.7 ±0.2	0.10127
Rb^{87}	6834.1 ±1.0	0.22797
Jn^{113}	11387.0 ±4	0.3799
Jn^{115}	114139.0 ±3	0.3807
Cs^{113}	9192.6 ±0.5	0.30665

*So long as the effective magnetic moment does not change sign in the transition.

probabilities for the multipole transitions it is necessary to know the integral s_q. It is extremely difficult to compute this integral because the electron density distribution in the outer part of the atom is not known with the required accuracy. Pasternack[16] has estimated one of these integrals for light atoms, using an approximation method (the Hartree-Fock fields and hydrogen-like wave functions with a constant shielding term). More exact values of this integral, especially for the heavy atoms, have been obtained by semi-empirical methods. From the intensity ratios of two lines which derive from the same excited level it is possible to determine the ratio of the probabilities for the magnetic dipole and electric quadrupole transitions at the outset; then, comparing this ratio with the theoretical ratios obtained by expressions such as (2.9) and (2.10) (for different lines) one can determine s_q. The calculation (and the considerations given above) can be verified by applying the same method to other lines which derive from the same level.

The method described above for determining s_q and the use of this determination for finding the percentage composition of the radiation has been applied to Pb I. On the basis of the measurements the ratio of the line intensities for λ 4618 A, $^1S_0 - {}^3P_1$ and λ 5313 A, $^1S_0 - {}^3P_2$ in lead and the formulas in (2.7) and (2.8), a value $s_q^2 = 240$ is obtained.[2] Then, from the known value of s_q and (2.9) and (2.10) a theoretical determination is made of the electric quadrupole percentage in the mixed line λ 7330 A, $^1D_2 - {}^3P_1$, in Pb I (about 6%). However a direct measurement of the intensities of the electric quadrupole and magnetic dipole Zeeman components of the λ 7330 A line gives the electric quadrupole percentage as 2.2%. According to Mrozowski the second result is more reliable. In reference 2 examples are given of forbidden multiplets in Te I, O I and Bi I which are especially convenient for carrying out experiments to determine s_q.

The Zeeman effect offers a powerful method for investigating mixed multipole radiation. The theory of the Zeeman effect for mixed multipole lines has been given in references 8 and 48. The most important results of this work is the conclusion that there is an interference effect between the electric quadrupole and magnetic dipole radiation. The calculated theoretical intensities of the Zeeman components corresponding to the selection rule $\Delta m = \pm 1$ consists of three parts: two of these correspond to the probabilities for pure magnetic dipole and pure electric quadrupole transitions, while the latter results form the interference of the two radiations. It has been shown by calculation that the presence of these interference terms does not affect the total probability for a transition between two levels; the only effect is a change in the angular distribution of the radiation. The dependence of the interference terms on the percentage composition of the mixed radiation has also been established. For example, if the ratio of intensities of the Zeeman π components for "pure" dipole magnetic triplet are (in accordance with the intensity rule) 6 : 3 : 1, in the presence of electric quadrupole radiation the indicated ratio is (transverse) $(6-2x):(3+x):(1-x)$, while the longitudinal factor is $(6+2x):(3-x):(1-x)$, where x is the interference correction, which is proportional to the square root of the percentage of electric quadrupole radiation. In particular,[2] for the 7330-A line x is 0.6.

So far the interference effect has been observed only in the observation of the transverse Zeeman effect of the mixed line λ 7330 A, $^1D_2 - {}^3P_1$ in Pb I.[53] The intensities of the individual π components have been measured and the results of the measurements have been compared with the values of these intensities computed on the basis of the work in reference 48. The interference corrections and the hyperfine structure lines produced as a result of the presence of the odd isotope Pb^{207} are found to be very important for obtaining good agreement between the experimental and theoretical results.

Of the other work on mixed multipole radiation we may mention the pure electric quadrupole nature of the $^2D \rightarrow {}^4S$ transition in N I,[75-76] and the almost pure magnetic dipole nature of the $^2P \rightarrow {}^4S$ transition in N I;[2] estimates have also been made of the component percentages in the radiation of the well-known nebular lines λ 4959 A, $^1D_2 \rightarrow {}^3P_1$ and λ 5007 A, $^1D_2 \rightarrow {}^3P_2$ in O III.[77] Because of the small percentage of electric quadrupole radiation (0.1%) the latter may be assumed essentially magnetic dipole lines. However the radiation composition has not been determined for very many of these lines and further work will be required for solution of this problem.

In concluding the present section, we consider the problem of observing third-order multipole radiation in atomic spectra. Lines of this type have not been observed in the optical region and their observation in the x-ray region is open to doubt.[78] The difficulty in observing magnetic quadrupole and electric octupole lines is a result of the following. As has already been mentioned, the probability of third-order multipole transitions is very small, even as compared with second-order

multipole transitions. For λ4580 A these are respectively:[78]

$$A'_m = 10^{-4}\ \text{sec}^{-1}, \quad (2.11)$$
$$A'_q = 4\cdot 10^{-7}\ \text{sec}^{-1}. \quad (2.12)$$

Consequently the time interval between two successive excitations of the atom (for example between two collisions with other atoms) must be several hours (A'_m) or even more than a month (A'_q) in order for the atom to lose its excitation energy by emission of a photon. Furthermore it should be noted that these lines obey the Laporte selection rule, as do electric dipole lines, and are produced in transitions between states with different electron configurations. When $|J - J'| \leq 1$ it is completely possible for both types of lines to be excited simultaneously; the magnetic quadrupole and electric octupole are very much weaker and are rather completely masked by the electric dipole lines. It is true that there can be those lines which satisfy the selection rule $2 \leq |L - L'| \leq 3$, which are not subject to the masking effect indicated above; however, these are extremely weak.[78] From what has been indicated above it follows that these lines can be observed only under conditions which obtain in gaseous nebulae and only in cases in which the atom has metastable levels and other levels between which only third-order multipole transitions can take place. As has been shown in reference 78, cases of this kind are extremely rare.

Obviously everything that has been said with respect to the observation of third-order multipole lines applies for higher order multipoles.

3. FORBIDDEN LINES IN THE SPECTRA OF CELESTIAL BODIES

Forbidden lines have been observed in the spectra of planetary nebulae, the solar corona, new stars, and other celestial bodies. The wave length region available to astronomical observation lies between 3,000 and 10,000 A.* Although forbidden lines were discovered a long time ago (as far back as the 1880's), because of the extreme difficulty of producing them in the laboratory (cf. reference 2) the identification of these lines has been very slow. Even at the present time there are unidentified lines in the spectra of the solar corona and other celestial bodies.

The method of identification is simple in concept but complicated in execution. The wave number of the investigated line is compared with the difference of any two terms of the tentatively proposed atom; these terms are taken from a preliminary careful analysis of the spectrum of this element. If it is found that these differences coincide the investigated line is assigned to a definite element and transition. If there is no complete spectral analysis of the atoms or ions of the element in question the terms are determined by extrapolation or interpolation from atomic spectra of other elements which have the same spectral structure. The validity of the identification, as can be seen from the foregoing, depends to a considerable degree on the accurate determination of the wave lengths of the lines being investigated and the terms in the various atoms or ions. It has been found that almost all forbidden lines in the spectra of celestial bodies are due to second-order spontaneous multipole radiation (i.e., magnetic dipole or electric quadrupole radiation) for neutral or ionized atoms of the various elements.

The most intense forbidden lines are found in the spectra of planetary nebulae. This situation arises because of the physical conditions which prevail. The density of matter in these nebulae is extremely small (of the order of 10^{-18} g/cm^3) and the temperature is relatively low (approximately 10,000° K); thus there is a long mean time between collisions (the order of a minute) and the resulting radiation density is small ($10^{-6} - 10^{-8}$ of the radiation density at the surface of the sun). Consequently neither collisions nor the radiation field are able to keep metastable atoms from decaying spontaneously to lower levels and, as is apparent from Eqs. (1.11) — (1.12), the intensity of the forbidden lines is determined chiefly by the number of such atoms. Since this number is large in these nebulae the intensity of the forbidden lines is appreciable. However, the accumulation of metastable atoms depends on the excitation mechanism.

Astrophysicists have considered three excitation mechanisms for these spectral lines: (1) photoionization with subsequent recombination, (2) fluorescence, and (3) excitation by electron impact. In all three cases the emission of the nebulae derives from the radiant energy of the central star.

It is difficult to believe that the forbidden lines are excited by the first of these mechanisms. In the case of ionized atoms such as O III, N II, etc., this mechanism cannot be reconciled with the observed data. This can be shown by using the example of the well-known nebular lines λ5007 A and λ4959 A from O III. Let us assume that these lines are excited by a recombination mechanism, i.e., the O III atoms are first ionized and then capture free electrons; this capture is followed by cascade allowed transitions to the metastable state,

*If we neglect the radio-frequency region, which has become important in recent years (cf. below).

whence the system decays to a lower level via the emission of forbidden lines. However, because the ionization potentials in O III and He II (54.5 ev and 54.2 ev) are almost the same,[80] both of these atoms should absorb energy from the star in the same region of the spectrum and the O III and He II lines should be of approximately of the same intensity. However, in actual fact, the O III line is much stronger than the He II line.

The accumulation of metastable atoms (resulting in the excitation of forbidden lines) by means of the other two mechanisms was first considered theoretically by Ambartsumyan.[81] He showed that if the excitation of atoms to metastable levels is due exclusively to radiation, in order for metastable atoms to accumulate the following condition must be satisfied:

$$w \ll \frac{A_{21}}{A_{23}}, \tag{3.1}$$

where w is the ratio of the spectral radiation densities of the particular nebula and the central star. A_{21} is the probability for emission of a forbidden line, A_{23} is the probability for a transition to a higher level, the subscript 2 denotes the metastable level and the subscripts 1 and 3 denote levels below and above the metastable level. Because w is so small ($w = 10^{-13}$) the condition in (3.1) is usually satisfied in planetary nebulae (with the exception of those cases in which the lifetime of the metastable state is extremely long; for example, the $2\,^3S$ state in helium). If, however, excitation of the atoms obtains by virtue of collisions with free electrons (the electrons usually arise in photo ionization of atomic hydrogen) the accumulation of metastable states requires that the following inequality be satisfied:

$$a_{21} \ll A_{21}, \tag{3.2}$$

where a_{21} is the probability of a collision of the second kind between the metastable atom and an electron while A_{21} is the probability for a spontaneous transition. This situation also obtains in these nebulae, as is apparent from a consideration of the physical conditions which exist.

The latest calculations[82] for O III show that the efficiency of collision excitation of forbidden lines requires that still another requirement must be satisfied:

$$N_e > 4 \cdot 10^2, \tag{3.3}$$

where N_e is the density of free electrons. This inequality is also satisfied in these nebulae; according to an estimate of the electron density carried out by various methods,[11] N_e is approximately $10^3 - 10^4$.

It should be noted that the inequalities in (3.1) and (3.3) also are satisfied in other celestial bodies whose spectra exhibit forbidden lines in spite of the fact that the physical conditions are somewhat different from those in planetary nebulae.

The prevailing opinion is that collision excitation of forbidden lines is more effective than fluorescence excitation. This situation is indicated by the lower excitation energies (order of 1 — 10 ev) of the majority of metastable levels as compared with the kinetic energies of the free electrons. The electron temperatures in various planetary nebulae generally lie within the limits 6,000 — 10,000°K,[10] corresponding to a mean kinetic energy of 1 — 1.5 ev for the electrons.

According to collision theory the number of electron collisions F_{12} which transfer atoms from the ground state 1 to the excited state 2 is given by the following expression when the electron velocity distribution is Maxwellian:[82]

$$F_{12} = 8.54 \cdot 10^{-6} \frac{N_1 N_e}{T_e^{\frac{1}{2}}} \frac{\Omega(1,2)}{2J_1+1} e^{\frac{-h\omega_{21}}{kT_e}}, \tag{3.4}$$

where N_1 is the number of atoms in state 1, T_e and N_e are respectively the temperature and density of the free electrons, $2J_1 + 1$ is the statistical weight for state 1, $h\omega_{21}$ is the excitation energy, $\Omega(1, 2)$ is the so-called collision strength (analogous to the line strength), which is related to the effective cross section $\sigma(1, 2)$ for collisions between an atom and electron with mass m and velocity v by the expression

$$\sigma(1,2) = \frac{1}{2J_1+1} \frac{h^2}{4\pi m^2 v^2} \Omega(1,2). \tag{3.5}$$

The number of collisions of the second kind F_{21}, which transfer excited atoms back to the ground state, is computed from the expression

$$F_{21} = 8.54 \cdot 10^{-6} \frac{N_2 N_e}{T_e^{\frac{1}{2}}} \frac{\Omega(1,2)}{2J_2+1} \tag{3.6}$$

and represents only several percent of the number of optical transitions, under the conditions which obtain in these nebulae.[10]

If the atom has several metastable levels, through the use of statistical equilibrium it is possible to determine the relative populations from statistical equilibrium considerations; from this knowledge it is then possible to determine the intensity ratios for the corresponding forbidden lines. For example, if there are two metastable levels, 2 and 3, where $E_3 > E_2$ from statistical equilibrium considerations we have:[10]

$$F_{13} + F_{23} = N_3(A_{31} + A_{32}) + F_{31} + F_{32}, \tag{3.7}$$

$$F_{12} + F_{32} + N_3 A_{32} = N_2 A_{21} + F_{21} + F_{23}, \tag{3.8}$$

TABLE III

q=2	Ω (1,2)	Ω (1,3)	q=3	Ω (1,2)	Ω (1,3)	q=4	Ω (1,2)	Ω (1,3)
NII	2.39	0.223	OII	1.44	0.218	FII	0.95	0.057
OIII	1.73	0.195	FIII	1.00	0.221	NeIII	0.76	0.077
FIV	1.21	0.172	NeIV	0.68	0.234	NaIV	0.61	0.092
NeV	0.84	0.157	NaV	0.43	0.255	MgV	0.54	0.112

where A_{21}, A_{31}, and A_{32} are the probabilities for the corresponding optical transitions. The left sides of Eqs. (3.7) and (3.8) represent the transitions which increase the populations of levels 3 and 2 respectively while the right sides indicate the transitions which reduce these populations. By substituting the values of F and A in Eqs. (3.7) and (3.8) and eliminating N_1 it is possible to find the ratio N_3/N_2, the relative populations in levels 3 and 2, and the quantity $N_2A_{21}h\omega_{21}/N_3A_{32}h\omega_{32}$, the relative intensity of the 1 — 2 and 2 — 3 lines.

So far the theory indicated above for collision excitation has been verified only for forbidden lines in O III, which are the most intense lines in these nebular spectra. According to Ambartsumyan[80] the ratio of the total intensity of well-known nebular lines N_1 (λ 4958.93 A, $^3P_1 - {}^1D_2$, O III) and N_2 (λ 5006.86 A, $^3P_2 - {}^1D_2$, O III) to the ratio of the aurora line λ 4363.19 A, $^1D_2 - {}^1S_0$, O III is:

$$\frac{I_{N_1}+I_{N_2}}{I_{\lambda\,4363}} = 4.5e^{\frac{33000}{T_e}}, \qquad (3.9)$$

where T_e is the electron temperature.

Equation (3.9) is found to be in satisfactory agreement with the observed data. The theory developed for forbidden lines in O III should make it possible in the future to use the absolute intensities to determine the temperature of the central star and the abundance of O III in these nebulae.[12]

Equations (3.4) — (3.9) indicate the important role played in this theory by the accuracy of the determination of the numerical values of the parameters Ω and the transition probability A. Because it is extremely difficult to determine these quantities experimentally, for the most part they have been found purely theoretically, using quantum-mechanical methods. The calculation of the parameter Ω (the effective cross section for electron excitation of forbidden lines in various atoms and ions) has been undertaken by Hebb and Menzel (O III), Aller (O II) and others.[82,83-85] The calculations are based on the quantum theory of collisions.[79,86] The partial wave method is used and an analytic approximation of the wave function is obtained by the Slater method,[82] the Hartree-Fock method, and so on. The most accurate values of σ and Ω for forbidden transitions in various ions (N II, O II, O III, and Ne III) have been obtained by Seaton, who used the Hartree-Fock method.[85] However even in the most accurate calculation errors of ±40% are possible (in the absolute values of σ and Ω). Seaton also has made estimates of the corresponding parameters Ω for the ions F IV, Ne V, F III, Ne IV, Na V, F II, Na IV, and Mg V (with accuracy up to a factor of 2). Table III lists the values of Ω from Seaton for transitions in various ions from the normal level ^3P (level 1) to the metastable ^1D and ^1S levels (levels 2 and 3) in the np^q configuration (q = 2 and q = 4) and also from the normal ^4S (level 1) to metastable ^2D and ^2P levels (levels 2 and 3) of the np^q (q = 3) configuration. The numerical values of Ω obtained by these estimates are shown in heavy type.

If Ω is known, the effective cross sections σ are computed from Eq. (3.5). In those cases in which the kinetic energy of the colliding electron is comparable with the excitation energy of the atom or ion these cross sections turn out to be sizeable — approximately 10 — 100 times greater than the gas-kinetic cross sections.

We have already indicated the great value of a knowledge of both the relative and absolute probabilities for forbidden transitions for lines which are of interest in astrophysics. Probability calculations have been given chiefly by Shortley, Aller, Baker, and Menzel.[8] The accuracy of the results of these calculations depends to a large extent on the accuracy with which the wave functions for complex atoms are known, i.e., to the extent to which it is possible to compute various types of atomic interactions (spin-spin, spin-orbit, configuration). As an example, Table IV lists the results of the most accurate (at the present time) calculation of the transitions for $1s^2\,2s^2\,2p^2$ configurations for the iso-electronic sequence C I, N II, O III, and F IV.[87] The calculation has been carried out with refined wave functions which take into account the correlation between electrons; these functions have been found by a variational method which is a development of the method described in reference 88. As is apparent from

TABLE IV

	CI	NII	OIII	FIV
$A_m\,(^1D_2,^3P_2)$	0.0^318	0.0027	0.0195	0.0937
$A_q\,(^1D_2,^3P_2)$	0.0^515	0.0^4114	0.0^451	0.0^3161
$A_m\,(^1D_2,^3P_1)$	0.0^460	0.0^292	0.0066	0.034
$A_q\,(^1D_2,^3P_1)$	0.0^621	0.0^5176	0.0^578	0.0^426
$A_q\,(^1D_2,^3P_0)$	0.0^732	0.0^630	0.0^514	0.0^547
$A_q\,(^1S_0,^1D_2)$	0.62	1.350	2.00	2.60
$A_m\,(^1S_0,^3P_1)$	0.002	0.030	0.214	0.94
$A_q\,(^1S_0,^3P_2)$	0.0^423	0.0^316	0.0^389	0.0028

Table IV, in the probabilities for mixed multiple transitions $^1D_2 \rightarrow {}^3P_1$ and $^1D_2 \rightarrow {}^3P_2$ the magnetic dipole part is considerably greater than the electric-quadrupole part.

By taking account of the various interactions between electrons it is possible to get better values for the probabilities for forbidden transitions and for atomic energy levels;[89-90] these more refined values provide improved means of identification for lines. In particular, it has been shown in references 91 and 92 that taking account of configuration interactions makes it possible to avoid certain uncertainties in the identification of the Ca XV lines in the corona. In 1954 Layzer[91] established the fact that in highly ionized atoms the strongest interaction takes place between configurations which have the same sequence of principle quantum numbers and the same parity. In work carried out by Garstang[92] a more general expression for the strength of lines which correspond to all possible forbidden transitions between levels assigned to the $1s^2\,2s^2\,2p^2$ configuration was found taking account of the perturbing effect of the $1s^2\,2p^4$ configuration. On the basis of an analysis of these expressions and the appropriate expressions from reference 8, Garstang has shown that if in these formulas one takes the line strengths derived by neglecting the configuration interaction, using the experimental values rather than the theoretical values for the terms, the largest part of the configuration interaction is still taken into account. This result is illustrated by a detailed calculation for Ca XV. In reference 92 formulas have also been obtained for the transition probability between terms of the $1s^2\,2s^2\,2p^4$ configuration which take account of the interaction with $1s^2\,2p^6$ configuration. This interaction makes possible the following two-electron configuration transitions:

$$2p^6\,{}^1S_0 - 2s^2 2p^4\,{}^3P_1,\quad 2p^6\,{}^1S_0 - 2s^2 2p^4\,{}^3P_2$$
$$\text{and}\quad 2p^6\,{}^1S_0 - 2s^2 2p^4\,{}^1D_2{}^*\,.$$

We now present a brief analysis of individual forbidden lines, starting from the nature of the metastable states of atoms with different electronic systems. Knowing the exact values of the differences between metastable states and the ground levels for different atoms it is possible to predict all possible forbidden lines.

One-electron systems (H I, He II, Li III, etc.). These systems are characterized by one metastable state — $2s\,{}^2S_{1/2}$.* For a long time, in accordance with the Dirac theory, it was assumed that the $2s\,{}^2S_{1/2}$ level coincides with the $2p\,{}^2P_{1/2}$ level. In 1947, it was shown by means of the magnetic-resonance method that these levels are shifted with respect to each other by 1062 ± 5 Mcs.[94] This shift was interpreted in terms of quantum electrodynamics.[95] Calculations showed[96] that the $2s\,{}^2S_{1/2} \rightarrow 1s\,{}^2S_{1/2}$ transition could be accompanied by the emission of one or two photons, with the two-photon transition being almost 10^8 times more probable than the single-photon transition. The lifetime of the atom in the metastable $2s\,{}^2S_{1/2}$ state is 0.14 seconds. Neither one-photon nor two-photon transitions have been observed in the spectra of celestial bodies.

Two-electron systems (He I, Li II, Be III, etc.). The metastable states are the $1s\,2s\,{}^1S$ and $1s\,2s\,{}^3S$ states. The forbidden transitions are: $1s\,2s\,{}^1S \rightarrow 1s^2\,{}^1S$ and $1s\,2s\,{}^3S \rightarrow 1s^2\,{}^1S$. Because strictly normal coupling obtains in the helium atom the spontaneous transition $1s\,2s\,{}^3S \rightarrow 1s^2\,{}^1S$ is not very likely in either the one-photon or two-photon case. For this reason transitions from the ^3S level to the ^1S level take place chiefly by means of collisions. However the $1s\,2s\,{}^1S \rightarrow 1s^2\,{}^1S$ transitions are more probable if accompanied by the emission of two photons. It is believed that a two-photon transition of this kind takes place in nebulae.[13]

Three-electron systems (Li I, Be II, B III, etc.) do not have metastable levels.

Four-electron systems (Be I, B II, C III, N IV, etc.). The basic metastable states are $2s\,2p\,{}^3P_0$

*Two-electron transitions are discussed in reference 93.

*Metastable states which arise as a consequence of level splitting into hyperfine sub-levels are not taken into account. Transitions between the hyperfine sub-levels are considered above.

TABLE V

		$^3P_1-{}^1D_2$	$^3P_2-{}^1D_2$	$^1D_2-{}^1S_0$	$^3P_1-{}^1S_0$	$^1D_2$	$^1S_0$	First non-metastable
CI	Calculated	9822.9	9849.5±0.3	8727.4±0.1	4621.4±0.1	1.3	2.7	9
	Calculated	6548.4	6583.9±0.1	5755.0±0.1	3063.0±0.1	1.9	4.0	20
NII	Observed	6548.06	6583.37	5754.57				
	Calculated	4959.5	5007.6±0.2	4363.2±0.1				
OIII	Observed	4958.93±0.03	5006.86±0.02	4363.19±0.01		2.5	5.3	36
	Calculated	3996.3	4059.3±0.3	3532.2±0.3		3.1	6.6	58
FIV	Observed	3997.40±0.04	4060.23±0.03					
	Calculated	3344	3424	2972		3.8		86
NeV	Observed	3345.84±0.01	3425.87±0.03					

and 2s 2p $^3P_2$. As an approximation it may also be assumed that the 2s 2p $^3P_1$ level is metastable, especially in the light elements, since the probability for the 2s 2p $^3P_1 \rightarrow 2s^2\ ^1S$ transition is very small in these elements because of the almost pure normal coupling; the order of magnitude of this transition is the same as that for ordinary forbidden transitions. In Be I the $^1S \rightarrow {}^3P$ line lies in a region available to observation and corresponds to wavelengths lying in the limits λ 4548 ± 5 A.[1]

Five-electron systems (B I, C II, N III, O IV, etc.). There are two metastable states: 2s^2 2p $^2P_{1/2}$ and 2s 2p^2 ^{4}P. The metastability of the latter is explained by the small probability for intercombination transitions. The 2s 2p^2 $^4P \rightarrow 2s^2$ 2p $^2P_{1/2}$ transitions have been observed astronomically only for B I, at wavelengths of 3300 ± 300 A). For the atoms indicated above the 2s^2 2p $^2P_{3/2} \rightarrow 2s^2$ 2p $^2P_{1/2}$ transition lies in the far infrared; however as the atomic number of the element is increased it slowly shifts towards wavelengths which are amenable to astronomical observation. It has been observed in the spectrum of the solar corona only for argon XIV (λ 4412 A).[97]*

Six-electron systems (C I, N II, O III, F IV, Ne V, etc.). The ground state is the $^3P_0$ state; the metastable states are the $^3P_1$, $^3P_2$, $^1D_2$ and $^1S_0$ states. All these belong to the 2s^2 2p^2 configuration. To a considerable degree it may also be assumed that the 2s 2p^3 ^{5}S level is metastable since the intercombination transitions $^3P - {}^5S$, $^1D - {}^5S$ and $^1S - {}^5S$ are characterized by low probabilities. The $^3P - {}^5S$ lines may be significant under atmospheric conditions and are found in the observed region of the spectrum only for C I. With regard to the transitions between the $^3P_0$, $^3P_1$ and $^3P_2$ terms we may note that two of these have been observed in the highly ionized atom Ca XV. These are the corona lines λ 5694.42 A, $^3P_1 \rightarrow {}^3P_0$ and λ 5446 A, $^3P_2 \rightarrow {}^3P_1$.*

The calculations indicate that the probability of the forbidden transition $^1S \rightarrow {}^3P_0$ is zero while the probabilities for the transitions $^1D_2 \rightarrow {}^3P_0$ and $^1S \rightarrow {}^3P_2$ are small (1000 times smaller than the probability for the $^1S \rightarrow {}^3P_1$ transition).[1] Consequently the main forbidden lines are: $^3P_1 - {}^1D_2$, $^3P_2 - {}^1D_2$, $^1D_2 - {}^1S_0$ and $^3P_1 - {}^1S_0$. There is some historical background with regard to the terminology of these forbidden lines. The first two lines are called nebular lines since lines of this type were most intense in nebulae, while the third line is called an aurora line since the most intense line in the spectra of the polar aurora and night sky arises from the $^1S_0 \rightarrow {}^1D_2$ transition. Lines arising from $S^1 \rightarrow {}^3P$ transitions are called trans-aurora lines.

In Table V are given the results of the identification of these lines for various elements according to the data of Bowen.[1,99] Columns 4 – 6 list data on the excitation potentials of the metastable levels ^{1}D and ^{1}S as compared with the lowest potentials for the non-metastable levels. All of the former are considerably below the latter.

Only one of the forbidden lines in C I has been observed: λ 4621.5 A, $^3P_1 - {}^1S$.[99] Lines of the other elements have been found in spectra of various celestial bodies and the data of the observations are in excellent agreement with the calculated results. It may be noted that the lines in Ne V were predicted by extrapolation.

The lines investigated in greatest detail are those of O III (cf. Fig. 2). Only three of these (given in Table V) are available to astronomical observation. Bowen first proposed that these were due to electron impact (these lines were used to verify the theory of collision excitation).

The relative intensities of the $^3P - {}^1D_2$ and

*It had been assumed earlier that the 4359-A corona line was due to the $^2P_{3/2} \rightarrow {}^2P_{1/2}$ transition. The correction was made by Edlen in 1954.[97]

*This identification now seems to be open to question[97-98] (cf. below).

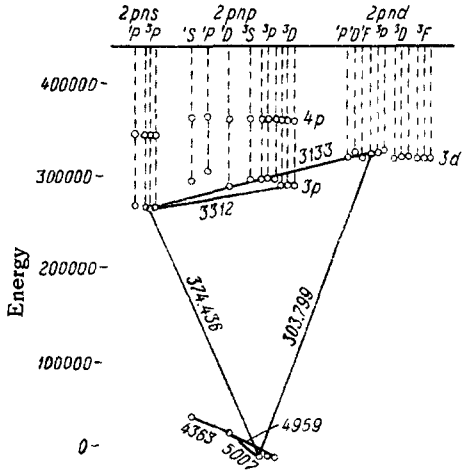

FIG. 2. Diagram for the terms in the O III ion. The forbidden transitions are indicated in the lower part of the diagram.

$^1D_2 - {}^1S_0$ lines are different in the spectra of different celestial bodies. Whereas in nebulae the nebular lines are more intense than the aurora lines, in the polar aurora (and also in early stages of new stars) the opposite hold true. This is explained by the difference in the prevailing physical conditions. In the nebulae the intensity of the lines is determined chiefly by the number of metastable states and not by the transition probabilities, because almost all of the metastable atoms make spontaneous transitions to lower states. Since the $^1D_2$ state has a lower excitation potential and a higher statistical weight than the $^1S_0$ state, the number of atoms in the $^1D_2$ state is greater than in the $^1S_0$; consequently the $3P - {}^1D_2$ line is more intense than the $^1D_2 - {}^1S_0$ line.

In the polar aurora, where the density of matter and radiation is not as small as in nebulae, the intensity of the lines depends to a considerable degree on transition probabilities. Since the probability for the $^1S_0 \rightarrow {}^1D_2$ transition is much greater than that of the $^1D_2 \rightarrow 3P$ transition (cf. Table IV),* the aurora line is more intense than the nebular line. These conclusions may be generalized to all forbidden lines of the P — D and D — S type for the p^2 and p^4 configurations and lines of the S — D and D — P type for the p^3 configuration since the metastable D states are characterized by much lower excitation potentials and longer lifetimes than the S and P states.

Seven-electron systems (N I, O II, F III, Ne IV, Na V, Mg VI, etc.). The metastable states, which are chiefly $s^2 p^3$ configuration are the $^2D_{5/2}$, $^2D_{3/2}$, $^2P_{1/2}$, and $^2P_{3/2}$. The stable level is the ^4S level. The observed forbidden multiplets $^4S - {}^2D$ and $^2D - {}^2P$ are given in Table VI, taken from Bowen.[1,99]

The first of the multiplets in O II (λ 3726.16 A, λ 3728.91 A) are the brightest lines in the spectra of the nebulae and interstellar space. The lifetime of the ^2D state is approximately 5 hours and is almost 15,000 times greater than that of the ^2P state, while the excitation potential is $1\frac{1}{2}$ times smaller. Thus, the features indicated above with respect to the ^2D and ^2P levels are verified in O II. The N I lines $^4S - {}^2D$ (λ 5199 A) and $^4S - {}^2P$ (λ 3466 A) have been observed in the spectra of polar aurora; however the observation of the N I lines $^2D - {}^2P$ (λ 10400 A) in the infrared region

TABLE VI

		$^4S-{}^2D_{3/2}$	$^4S-D_{5/2}$	$^2D_{5/2}-{}^2P_{3/2}$	$^2D_{5/2}-{}^2P_{1/2}$	$^2D_{3/2}-{}^2P_{3/2}$	$^2D_{3/2}-{}^2P_{1/2}$
N I	Calculated	5198.5	5200.7	10397.8		10407.3	
	Observed	5197.94	5200.41			7318.6	7319.4
O II	Calculated	3726.2	3729.1±1				
	Observed	3726.04 ±0.02	3728.80 ±0.03	7319.92±0.08		7330.19±0.06	
Ne IV	Observed			4714.25 ±0.03	4715.61 ±0.06	4724.15 ±0.02	4725.62 ±0.02

of the radiation of the night sky are open to question[100] (cf. below).

Eight-electron systems (O I, F II, Ne III, Na IV, Mg V, Al VI, etc.). A feature of these systems is the fact that all the metastable states of the $2p^4$ and $2p^2$ configurations are ^3P, ^1D, and ^1S. The first configuration differs from the second only in the inversion of the 3P term (the stable state is the $^3P_2$ state). The main transitions are $^1D_2 \rightarrow {}^3P_1$, $^1D_2 \rightarrow {}^3P_2$, $^1S_0 \rightarrow {}^1D_2$ and $^1S_0 \rightarrow {}^3P_1$ (the transitions $^1D_2 \rightarrow {}^3P_0$, $^1S_0 \rightarrow {}^3P_0$ and $^1S_0 \rightarrow {}^3P_2$ are characterized by much smaller probabilities.

The following lines of O I are observed in the nebulae: λ 6363.82 ± 0.02 A, $^3P_1 - {}^1D_2$; λ 6300.31 ± 0.004 A, $^3P_2 - {}^1D_2$; and the following lines from Ne III: λ 3967.47 ± 0.002 A, $^3P_1 - {}^1D_2$ and λ 3868.76 ± 0.02 A, $^3P_2 - {}^1D_2$.[99] The solar corona exhibits the following line from Ca XIII: λ 4086.3 A, $^3P_2 - {}^3P_1$.[98] Some of the forbidden lines from A XI have been observed in the spectra of new stars.[101]

Forbidden lines of O I corresponding to the

*This is true both for O III and O I.

TABLE VII

		$^3P_2-{}^1D_2$	$^3P_2-{}^1D_2$	$^1D_2-{}^1S_0$	$^3P_1-{}^1S_0$
SIII	Observed			6312.06±0.05	3721.8
CIIV	"	7530.54±0.01	8045.63±0.05	5323.29±0.10	
AV	"	6435.10±0.05	7005.67±0.09	4625.54±0.04	

TABLE VIII

		$^4S-{}^2D_{5/2}$	$^4S-{}^2D_{3/2}$	$^4S-{}^2P_{3/2}$	$^4S-{}^2P_{1/2}$	$^2D_{5/2}-{}^2P_{3/2}$	$^2D_{3/2}-{}^2P_{3/2}$	$^2D_{3/2}-{}^2P_{1/2}$
SII	Observed	6716.42	6730.78	4068.6 ±0.03	4076.35 ±0.03			
ClIII	"	5577.66 ±0.08	5537.60 ±0.24					
AIV	"	4711.33 ±0.02	4740.2 ±0.02			7237.26 ±0.22	7170.62 ±0.08	7262.76 ±0.24
KV	"	4122.63 ±0.05	4163.3 ±0.05					

TABLE IX

		$^3P_2-{}^1D_2$	$^3P_1-{}^1D_2$	$^1D_2-{}^1S_0$	$^3P_1-{}^1S_0$
SI	Observed			7726.5	6526.9
AIII	"	7135.80±0.05	7751.06±0.15	5191.82±0.03	
KIV	"	6101.83±0.08		4510.9±0.08	
CaV	"	5309.18±0.04	6086.92±0.11		

transitions $^1S_0 \rightarrow {}^1D_2$ and $^1D_2 \rightarrow {}^3P$ have been observed in the spectra of the polar aurora and the radiation of the night sky (these are considered in greater detail below).

Nine-electron systems (F I, Ne II, Na III, Mg IV, etc.). Only two forbidden lines have been observed (in the solar corona): λ 3328 A, Ca XII and λ 5536 A, Ar X;[98] both of these correspond to the transition $^2P_{1/2} \rightarrow {}^2P_{3/2}$. The other transitions between metastable states do not lie in the region in which astronomical observations are possible.

Ten-electron systems (Ne I, Na II, Mg III, Al IV, etc.). All the forbidden transitions lie in the far ultraviolet and have not been observed.

Eleven-electron systems (Na I, Mg II, Al III, etc.) have no metastable states.

Twelve-electron systems (Mg I, Al II, Si III, etc.). The metastable states are: 3s 3p $^3P_0$ and 3s 3p $^3P_2$; the stable state is $3s^2\ {}^1S_0$. Forbidden transitions have not been observed for these systems.

Thirteen-electron systems (Al I, Si II, P III, S IV, etc.). Only two forbidden lines have been observed: λ 5302.9 A from Fe XIV and λ 3001 A from Ni XVI, corresponding to the transition $^2P_{3/2} \rightarrow {}^2P_{1/2}$. The first of these is the brightest line in the solar corona. It has also been observed in the spectra of new stars.[101]

Fourteen-electron systems (Si I, P II, S III, Cl IV, A V, K VI, etc.). The metastable states which are of astrophysical interest are ^1S, ^1D, and ^3P. All of these are in the $3s^2\ 3p^2$ configuration. The forbidden lines observed in the spectra of nebulae are given in Table VII.[99] In addition, identification has been made of three corona lines which are assigned to transitions between components of the ^3P term: namely, λ 6701.8 A, Ni XV ($^3P_2 \rightarrow {}^3P_1$), λ 10746.8 A F XIII ($^3P_1 \rightarrow {}^3P_0$) and λ 10798 A Fe XIII ($^3P_2 \rightarrow {}^3P_1$), and one line from Fe XIII λ 3388 A assigned to the transition $^1D_2 \rightarrow {}^3P_2$.[98]

Fifteen-electron systems (P I, S II, Cl III, A IV, K V, Ca VI, etc.). The basic configuration is $3s^2\ 3p^3$. The stable level is ^4S; the metastable levels are ^2D and ^2P. In Table VIII are given the results of observations in nebulae of the forbidden lines $^4S-{}^2P$, $^4S-{}^2D$ and $^2D-{}^2P$.[99] The $^4S-{}^2P$ lines in Cl III are masked by one of the lines from Ne III. Transitions between components of the metastable levels have not been observed.

Sixteen-electron systems (S I, Cl II, A III, K IV, Ca V, etc.). The metastable states are assigned to the ground configurations $3s^2\ 3p^4$ are ^3P, ^1D, and ^1S. The results of observations of forbidden lines assigned to this system are given in Table IX.[99] These lines are observed chiefly in the spectra of

nebulae. Forbidden lines have not been observed in Cl II. Both components of $^3P_0 - {}^1D$ in Ca V have also been observed in the spectra of new stars, where λ 6087 A of Ca V is one of the brightest lines in the spectra. The following corona lines are assigned to sixteen-electron systems: λ 7891.9 A Fe XI, $^3P_1 \rightarrow {}^3P_2$ and λ 5116 A Ni XIII, $^3P_1 \rightarrow {}^3P_2$.[98]

17, 18 and 19-electron systems, with a few exceptions, have no metastable states characterized by transitions which lie in regions available to astronomical observations. The spectrum of the solar corona exhibits two forbidden lines: λ 6374.5 A Fe X, $^2P_{1/2} \rightarrow {}^2P_{3/2}$ and λ 4232.4 A Ni XII, $^2P_{3/2} \rightarrow {}^2P_{1/2}$; the first of these lines is assigned to the seventeen-electron system while the second is assigned to a nineteen-electron system. The line from Fe X has also been observed in the spectra of new stars.[102]

The terms of other electron systems have not been classified with sufficient completeness and the identification of the forbidden lines for these configurations in the spectra of celestial bodies is far from complete. The most reliable investigations have been of lines of various iron ions — Fe II, Fe III, Fe V, Fe VI, Fe VII, and Fe VIII[103] (the Fe lines in the corona have been already mentioned above). Twenty-six lines of this kind are observed in nebulae. Also observed are eight forbidden lines from Mn V and Mn VI and ions of titanium, chromium and other elements in the first long period of the periodic table (K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn). The absence of lines for heavier elements is apparently a result of the fact that these elements do not occur in large amounts in the nebulae.

Usually the atoms that are more highly ionized emit more intense forbidden lines; this can be explained as follows. As is well known, the difference between the low excitation potential of metastable levels and the relatively high excitation potential of the first non-metastable level increases with the degree of ionization. For example, whereas the excitation potential of the first non-metastable level for Mn II and Fe II is 5 volts, in Mn VI and Fe VI these potentials are 65 — 70 volts; at the same time the excitation potential of the metastable levels remains approximately the same in both cases: 1.9 — 2.5 volts.[1] Consequently transitions of a highly ionized atom from a metastable level to the first non-metastable level and back occur in the far ultraviolet and the forbidden lines of highly ionized atoms may arise even when the total intensity of the radiation is large if the spectral density of the radiation in the far ultraviolet is small. An example of this kind is the presence or absence of forbidden lines of highly ionized atoms in slightly ionized atoms in the solar corona and in the spectra of other celestial bodies, under suitable physical conditions.

The majority of the forbidden lines are due to mixed radiation, i.e., electric quadrupole and magnetic dipole radiation. Only a relatively few of these lines are pure electric quadrupole, intercombination or pure magnetic dipole lines. For example in the p^2 and p^4 configurations the pure electric quadrupole transitions are $^1S - {}^1D$, $^3P_2 - {}^3P_0$ and $^1D - {}^3P_0$ while the pure magnetic dipole transitions are $^1S - {}^3P_1$ and $^3P_1 - {}^3P_0$. In the case of the p^3 configuration there is only one pure electric quadrupole transition $^2D_{5/2} - {}^2P_{1/2}$.

The two radio lines at 21 cm and 91.5 cm discovered recently (in 1951 and 1955 respectively) in spectra from interstellar gas are pure magnetic dipole lines. These lines arise in transitions between sublevels of the hyperfine structure of the ground states of atomic hydrogen (21 cm) and deuterium (91.5 cm). The lifetime of the metastable sublevel of the hyperfine structure of atomic hydrogen is extremely long — on the order of 10^7 years. In deuterium this lifetime is a hundred times larger. The possibility of a spontaneous radiated transition to the normal level is due to the extremely rarified nature of interstellar gas.

Investigations of radio waves from hydrogen are of extreme importance in astronomy. At the present time, on the basis of observations of this radiation it has been possible to draw some very important conclusions as to the density and temperature of interstellar gas, the structure and motion of the galaxy, the hydrogen mass which surrounds the Magellanic clouds and so on.[104]

We shall consider in somewhat greater detail the forbidden lines observed in the spectra of the polar aurora, the radiation of the night sky, and the solar corona, since an investigation of these lines is of great importance in the study of the physical processes which are involved.

The green line from O I ($^1D_2 - {}^1S_0$), the wavelength of which is 5577.3445 ± 0.0027 A according to the data of Wegard and Harang (1937) along with the so-called "red triplet" $^3P - {}^1D$ (Fig. 3)

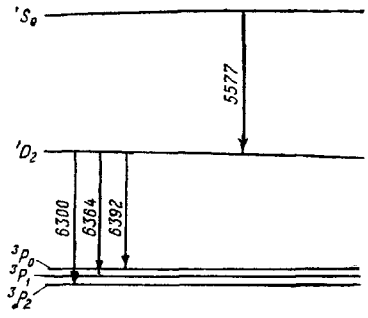

FIG. 3. Forbidden transitions in atomic oxygen.

TABLE X

	Transition	$^1S_0 \rightarrow {}^1D_2$	$^1S_0 \rightarrow {}^3P$	$^1D_2 \rightarrow {}^3P_0$	$^1D_2 \rightarrow {}^3P_1$	$^1D_2 \rightarrow {}^3P_2$
OI	Probability	2.2	0.0908	0.0000022	0.0026	0.0078

are the brightest lines in the spectra of the polar aurora and the radiation of the night sky. The identification of the forbidden lines from OI has been carried out by laboratory methods,[106] as mentioned in the introduction. The most precise values for the transition probabilities for these lines have been obtained by Pasternak[16] (cf. Table X).

Starting from the data in Table X it is easy to find that the mean lifetime for the $^1S_0$ level is 0.43 sec; the mean lifetime for the $^1D_2$ level is 95 sec. This great difference in lifetimes for the $^1D_2$ and $^1S_0$ levels is responsible for the change in color of the polar aurora as a function of height. In the upper part of the polar aurora the pressure is lower than in the bottom part. Hence the number of collisions which metastable atoms experience there [OI ($^1D_2$)] is much smaller and almost all of these atoms can radiate; as a consequence the red triplet is found to be brightest. With a reduction in height the number of collisions increases and the total number of metastable atoms [OI ($^1D_2$)] does not radiate, and some make transitions to the metastable $^1S_0$ state. However, as a consequence of the shorter lifetime atoms in the $^1S_0$ state these radiate to a greater degree than the OI ($^1D_2$) atoms. As a result, the intensity of the red lines falls off with height while that of the green line increases. Obviously, to obtain a complete quantitative picture of the behavior of these lines the excitation mechanism must be known.

Three different mechanisms have been proposed for the excitation of forbidden lines in the spectra of the polar aurora and the radiation of the night sky: collision effects, photo-chemical effects, and fluorescence.

The first of these is somewhat similar to the mechanism for excitation of forbidden transitions in nebulae. The basic role is played by electrons with low energies (approximately 7 — 10 ev). In collisions between such electrons and hydrogen molecules the latter dissociate into two atoms (dissociation energy 5.09 ev); one of these remains in the ground state while the second is excited to the metastable $^1D_2$ state (excitation potential 2 volts) or to the $^1S_0$ state (excitation potential 4.2 volts). This is followed by spontaneous transitions $^1S_0 \rightarrow {}^1D_2$ and $^1D_2 \rightarrow {}^3P$ of the OI atoms with the emission of the green and red lines. These optical transitions are possible because of the low density of the upper layers of the atmosphere.

The next question concerns the origin of these low-energy electrons. According to Dauvillier[107-108] these electrons are a result of ionization of atoms by fast particles emitted by the sun. In the composition of the corpuscular radiation of the sun* there are light ions and a large number of electrons, some with energies ranging up to 10^6 ev; ionization of the atoms and molecules of the atmosphere takes place chiefly as a result of collisions with these electrons.

Even if the collision excitation mechanism is able to explain the production of forbidden radiation in the polar aurora it is certainly not capable of explaining the radiation of the night sky. In contrast with the polar aurora, the radiation of the night sky exhibits a very weak latitude effect, if any.[113,100] Dauvillier, in order to establish the validity of electron excitation for forbidden lines assumes in this case that the sun, in addition to emitting powerful periodic fluxes, also emits a constant low intensity flux of charged particles.[108] However the marked differences in the spectra of the polar aurora and the radiation of the night sky, and other effects, in particular the fact that the green line in the spectrum of the night sky exhibits an intensity maximum soon after midnight, indicates some other mechanism for the excitation of the forbidden radiation, probably a photo-chemical mechanism.

According to Chapman the photo-chemical excitation mechanism may be described as follows.[100] During the day oxygen molecules dissociate into atoms as a result of the absorption of ultraviolet radiation from the sun. During the night these oxy-

*At the present time the corpuscular theory for the production of the polar aurora is generally accepted since no other theory can explain the relation between the polar aurora and the periodic processes that take place on the sun (for example the relation to sun spots), the dependence of these effects on the magnetic field of the earth (the so-called latitude effect), or other characteristic features (the shape and time variation). Although this theory, in the form in which it has been formulated by Birkelaud, Störmer, and Boguslavskiĭ[109-111, 105] has a number of shortcomings, it would seem to be the only available means of explaining these effects. Obviously some modifications of the theory will be required. An important attempt along these lines is that suggested by Chapman and Ferraro.[112]

gen atoms recombine when triple collisions take place; the result is the excitation of one of the atoms to the metastable $^1S_0$ level in accordance with the relation

$$O + O + O \rightarrow O_2 + O(^1S_0). \qquad (3.10)$$

This is followed by the transitions

$$OI - {}^1S_0 \rightarrow {}^1D_2 \text{ and } {}^1D_2 \rightarrow {}^3P \qquad (3.11)$$

which are accompanied by the emission of the green line and the red triplet.

According to a calculation carried out by Elvey,[115] the recombination process described by (3.10) takes place with greatest intensity at a height of 160 km; on the other hand the total height of the atmospheric layer in which radiation of the forbidden lines from O I is observed is approximately 50 km (from 120 km to 170 km).

The intensity of the green line does not reach a maximum immediately at twilight but considerably later, around midnight. Khvostikov explains this effect by the fact that the height at which maximum photo-ionization of O_2 molescules takes place does not coincide with the height at which maximum recombination, described in Eq. (3.10), occurs. The first height level is associated with the height at which the highest concentration of oxygen atoms is found and is much higher than the second; the delay is due to the time required for the O I atoms to descend by diffusion to the height at which the recombination is a maximum.

However, there are some difficulties in the photo-chemical excitation hypothesis. The dissociation energy of the oxygen molecule, which is liberated in recombination, is 5.1 ev while the excitation energy of the $^1S_0$ level is 4.2 ev. Hence part of the energy goes into relative kinetic energy of the particles which are produced and should lead to Doppler broadening of the emitted forbidden lines. This broadening has not yet been observed. The chief shortcoming of the photo-chemical theory is the fact that it cannot explain the polarization of the forbidden lines from O I; this polarization effect has been established by Khvostikov.[116]

It is possible that both excitation mechanisms (collision and photo-chemical) operate simultaneously, with the first predominating in the polar aurora and the second in the radiation of the night sky.

A third mechanism—fluorescence—can also explain certain of the features of the radiation of the twilight sky.

The increase in intensity of the red line from O I ($^3P_2 - {}^1D_2$, λ 6300A) at twilight with the absence of a twilight effect in the green line from

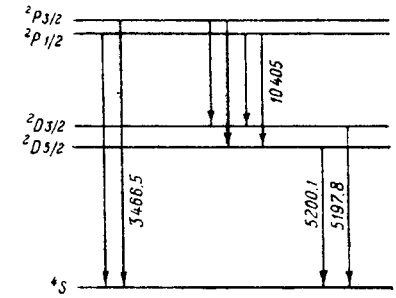

FIG. 4. Forbidden transitions in atomic nitrogen.

O I ($^1D_2 - {}^1S_0$, λ 5577A) indicates that the excitation mechanisms are different for the red and green lines. On the basis of a careful analysis of the excitation conditions of these lines, taking account of the dependence of the density of oxygen atoms on height on the diffusion of O I atoms and the fact that the brightness of the red line increases strongly with the appearance of the first slash even at the uppermost layers of the atmosphere, Khvostikov[100] has proposed a resonance fluorescence mechanism for the production of the λ 6300A line at twilight. The O I atoms ($^3P_2$) absorb radiation from that part of the continuous spectrum of the sun which corresponds to wavelengths near λ 6300A and make transition to the $^1D_2$ level; then, in returning, they radiate the red line.* The high intensity of the O I line at λ 6300A when the sun has set below the horizon is due to the abnormally high selective reflection of the sun's rays at 6300A in the upper layers of the atmosphere, which contain atomic oxygen.[100]

Great interest attaches to the presence of forbidden lines of atomic nitrogen in the radiation from the high levels of the atmosphere. We have already noted that only two of the forbidden lines of N I (cf. Fig. 4), namely $^4S - {}^2P$ λ 3466A and $^4S - {}^2D$ λ 5199A have been observed in the spectrum of the polar aurora; these are found to be much weaker than the forbidden lines of O I. Searches for forbidden lines of N I in the radiation spectrum of the night sky have not as yet been successful. In order to facilitate identification a good deal of preliminary work has been carried out on these lines. The transition probabilities,[16] precise wavelengths,[118] and excitation potentials of the metastable level have been determined; also, a self-consistent field analysis has been used to compute the relative intensity of the components of the doublet $^4S - {}^2D: I(^4S_{3/2} - {}^2D_{5/2}) / I(^4S_{3/2} - {}^2D_{3/2}) = 0.87$.[119]

*The absorption of solar radiation also occurs in the polar aurora, which is illuminated by the sun, but leads to a different effect—a considerable weakening of the green line. It is probable that this effect is due to absorption of ultraviolet photons by metastable atoms [O I ($^1S_0$)].[117]

The analysis of the excitation of forbidden lines in N I is as yet not complete. It is assumed that these lines arise chiefly as a result of inelastic collisions between nitrogen molecules and atoms and metastable oxygen atoms. However, an estimate of the intensity ratio for $^4S - ^2D$ and $^4S - ^2P$ lines made on this basis does not agree with the observed data.[100]

As we have seen, the forbidden lines observed in the spectrum of the solar corona may be assigned to a few elements, the atoms of which are highly ionized (Fe X — XI, XIII — XIV; Ca XII — XIII, XV; Ni XIII, XV — XVI; A X, XIV). The absence of forbidden lines from other elements may be explained either by the small quantities of these elements in the solar corona, the small concentration of metastable ions, or the fact that the lines from the metastable ions lies in a region of the spectrum which cannot be observed.

Almost all of the corona lines have been identified by Edlen (the first two lines were identified in 1939). Four lines remain unidentified: λ 3454, λ 4567, λ 3801 and λ 4359 A. The identification was attended by great difficulties. Only four lines were identified on the basis of the location of the corresponding term differences as obtained from resolved lines in the spectra of Fe X — XI, Ca XII — XIII.[120-121] The remaining lines were identified by a complicated extrapolation procedure in which intermediate electron coupling and various features of atomic spectra were taken into account. For example, in finding the ^2P terms assigned to the $3s^2\,3p$ and $3s^2\,3p^5$ configurations, the so-called "proper" doublet rule was used: $\nu(^2P_{3/2} - {}^2P_{1\,2}) \sim (Z-\sigma)^4$, where Z is the atomic number and σ is a constant which is essentially independent of Z.[98]

When lines are associated with a given ion the identification of the corona lines is verified by a comparison of the relative intensities obtained from the observed data with those obtained theoretically. The theoretical calculation is based on the assumption that the corona lines are excited by electron impact* and is carried out by the method described below. The comparison of the theoretical and observed values of the relative intensities of these lines has been found satisfactory.[98] The only discrepancy occurs for lines from Ca XV. Edlen has identified the λ 5694 A line with the $^3P_1 \rightarrow {}^3P_0$ transition in Ca XV while Waldmeyer assigns the line λ′5446 A to the $^3P_2 \rightarrow {}^3P_1$ transition. The observed intensity ratio for these lines (the ratio of the first to second) is approximately 6. The theoretical calculations carried out by Shklovskiĭ[98] give a value lying in the range 1.05 — 1.58 (for all possible values of the concentration of free electrons and electron temperature in the corona). If we assume that the λ 5694 A line corresponds to the $^3P_2 \rightarrow {}^3P_1$ transition and the λ 5446 A line corresponds to the $^3P_1 \rightarrow {}^3P_0$ transition, according to Shklovskiĭ the results of the theory (0.38 — 0.97)[98] show a still greater contradiction with the observations. In this connection Shklovskiĭ has maintained that the identification of the λ 5694 A and λ 5446 A lines is incorrect. Later, however, it was found according to the data of reference 122 that the λ 5445 A line was considerably weakened by certain Fraunhoffer lines. If account is taken of this weakening, the intensity ratio for the λ 5694 A and λ 5446 A lines becomes 1.6, in good agreement with the first of the Shklovskiĭ results indicated above.

The rather sizeable discrepancy between the differences of the extrapolated terms $^3P_1 - {}^3P_0$ and $^3P_2 - {}^3P_1$ and the wave numbers of the corona lines λ 5694 A and λ 5446 A which was first found was later removed by taking account of the configuration interaction in the extrapolation procedure, as we have already indicated.[91,92,97]

The corona lines are characterized by sizeable widths (approximately 1 A); this value far exceeds the natural width for spontaneous forbidden lines and indicates the existence of high velocities for the radiating ions. It is impossible to explain this Doppler broadening by the motion of matter in the corona since the velocity associated with this motion is small (5 — 10 km/sec). It is assumed at the present time that the Doppler broadening of the corona lines is a consequence of the high temperature of the matter in the corona; this temperature reaches millions of degrees. Other indications of this high temperature are the high degree of ionization of F, Ca, Ni and A, the absence of recombination lines for hydrogen in the spectrum of the corona, and a number of other effects.[80] The mechanism by which the solar corona is heated has been analyzed in detail by Shklovskiĭ.[98] According to this author the heating of the corona results from the existence of electric fields inside the corona;* although these fields are weak they continuously transfer kinetic energy to charged particles, chiefly electrons. Shklovskiĭ has shown that even very weak fields (of the order of 10^{-8} v/cm) are sufficient for achieving a high electron temperature in the corona.

Artificial earth satellites have been of great

*We are not neglecting photo-excitation, but this mechanism is important only in certain cases.[98]

*The variable magnetic fields on the sun are postulated as the source of the electric fields in the corona.

importance in investigations of radiation in the solar corona and in the upper levels of the earth's atmosphere. On the basis of results obtained with rocket experiments Krasovskiĭ[123] concludes that the mechanism described in Eq. (3.11) cannot be used to explain the emission of the line λ 5577 A and the red triplet. A careful analysis has been made of the possibility of other reactions for the excitation of metastable levels in oxygen and Krasovskiĭ has shown that the reactions responsible for the excitation of the $^1S_0$ and $^1D_0$ levels must be different; he has proposed the following as more probable reactions:

(1) for the $^1S_0$ level

$$\begin{aligned} O_2^* + CO &\rightarrow CO_2 + O\,(^1S_0), \\ OH^* + OH &\rightarrow H_2O + O\,(^1S_0), \end{aligned} \qquad (3.12)$$

(2) for the $^1D_2$ level

$$\begin{aligned} O_2^* + O &\rightarrow O_2^* + O(^1D_2), \\ O_2^* + H &\rightarrow OH^* + O\,(^1D_2), \end{aligned} \qquad (3.13)$$

$$\begin{aligned} OH^* + O &\rightarrow OH^* + O\,(^1D_2), \\ OH^* + H &\rightarrow H_2^* + O\,(^1D_2), \end{aligned} \qquad (3.14)$$

where O_2^* and OH_2^* are used to indicate vibration excitation of the oxygen and hydroxyl molecules.

Rocket experiments have also served to furnish an interesting correlation between the ultraviolet radiation from the sun (in the region 0 — 20 A) and the intensity of certain corona lines (λ 5303 A Fe XIV, λ 6702 A Ni XV).[124]

4. FORBIDDEN LINES INDUCED BY VARIOUS FIELDS

It is possible to obtain forbidden radiation of two kinds in discharge tubes. The first kind is characterized by lines whose intensity reaches a maximum at low current densities and falls off as the current is increased. The lines of the second kind are characterized by different behavior: the intensity of these lines is proportional to the square of the current density. The first group of lines is due to spontaneous radiation, such as has been considered in the earlier sections; the second kind is radiation which is induced by ionic fields. Although the field due to neighboring ions which acts on an atom varies in magnitude and direction, because of the relatively slow variation of the Coulomb field with distance it may be assumed as a first approximation that the ionic field is constant over the entire atom.[2] Hence it is of importance to study forbidden lines which are induced by external constant electric or magnetic fields.

The analysis of electric dipole radiation induced by a fixed electric field is relatively easy. The effect of the fixed electric field on the atom may be considered as a limiting case; i.e., the effect of a variable periodic electric field of zero frequency.* The quantum theory of Raman scattering of light gives the following expression for the dipole moment induced by a field $\mathbf{E}$ of frequency ω:[125]

$$\mathbf{d}_{mk}^{(i)} = -e^{i(\omega_{mk}+\omega)t}\frac{1}{2h}\sum_i\left\{\frac{(\mathbf{E}_0\cdot\mathbf{d}_{ik})\,\mathbf{d}_{mi}}{\omega_{ki}-\omega}+\frac{(\mathbf{E}_0\cdot\mathbf{d}_{im}^*)\,\mathbf{d}_{ik}}{\omega_{mi}+\omega}\right\}$$

$$-e^{i(\omega_{mk}-\omega)t}\frac{1}{2h}\sum_i\left\{\frac{(\mathbf{E}_0\cdot\mathbf{d}_{ik})\,\mathbf{d}_{mi}}{\omega_{ki}+\omega}+\frac{(\mathbf{E}_0\cdot\mathbf{d}_{im}^*)\,\mathbf{d}_{ik}}{\omega_{mi}-\omega}\right\}, \qquad (4.1)$$

where $\mathbf{d}_{ik}$ and $\mathbf{d}_{mi}$ are the dipole moments of the system in the absence of the field, ω_{mk} and ω_{mi} are the Bohr frequencies, $\mathbf{E}_0$ is the field amplitude. If we set $\omega = 0$ in Eq. (4.1) we obtain the dipole moment induced by the fixed electric field:

$$\mathbf{d}_{mk}^{(i)} = -e^{i\omega_{mk}t}\frac{1}{h}\sum_i\left\{\frac{(\mathbf{E}_0\cdot\mathbf{d}_{ik})\,\mathbf{d}_{mi}}{\omega_{ki}}+\frac{(\mathbf{E}_0\cdot\mathbf{d}_{im}^*)\,\mathbf{d}_{ik}}{\omega_{mi}}\right\}. \qquad (4.2)$$

It is apparent from Eq. (4.2) that the induced dipole moment $\mathbf{d}_{mk}^{(i)}$ differs from zero only in the case in which there is a level i and levels m and k such that electric dipole transitions are possible in the absence of a field. Assuming this, we obtain for the induced electric dipole lines the selection rules $\Delta J = 0, \pm 1, \pm 2$, even states $\rightleftarrows$ even states, odd states $\rightleftarrows$ odd states and, in the case of Russell-Saunders coupling, $\Delta L = 0, \pm 1, \pm 2$, $\Delta S = 0$, i.e., the same selection rules (with the exception of $J_1 + J_2 \geq 2$) as for electric quadrupole radiation. It also follows from Eq. (4.2) that the probability for induced electric dipole transitions is proportional to the square of the electric field intensity of current density, in complete agreement with experimental results. Furthermore, this probability depends to a considerable extent on the location of level i with respect to the k and m levels. If level i is close to either k or m, one of the denominators in Eq. (4.2) is markedly reduced and the probability for an induced transition is increased considerably. Since the energy levels tend to approach each other as the principle quantum number n is increased the intensity of the induced electric dipole lines must first increase (with the number of the line index) to some maximum and then fall off (as a consequence of the fact that $\mathbf{d}_{mi}$ is reduced with increasing n). The existence of this maximum serves to explain the experimental fact that with a gradual increase in the field first one observes only those lines of the forbidden series which correspond to these maxima; there-

*The radiation of atoms induced by periodic fields exhibits, as is well known, resonance effects.

after the other lines are gradually observed. The unique dependence of the intensity of induced lines on the quantum number n sharply distinguishes these lines from spontaneous electric quadrupole lines. The induced dipole lines are also distinguished from the spontaneous quadrupole lines by the considerable width, a result of the Stark effect. In the general case the sum rules do not apply for induced forbidden lines (as contrasted with the quadrupole lines); it is only in the case of large L and small multiplet splitting that they have any meaning.[126,57]

All these features of electric dipole radiation induced by a fixed electric field were first reported experimentally in the lines of the forbidden series in He I and K I, observed in absorption.[127-129]

It should be noted that forbidden lines induced by a rather strong (not molecular) electric field are polarized.[157] The degree of polarization of the different components has been studied by Miliyanchuk, who has established, for example, that the π-component in the $n^2 S_{1/2} - m^2 S_{1/2}$ lines of single-electron atoms observed in a direction perpendicular to the direction of the electric field is weaker than that of the σ component.[158]

If the density of charged particles in the discharge is high enough or if the atoms are in high excited states, the molecular field over the entire atom cannot be assumed to be uniform. The electric dipole radiation induced by a weak inhomogeneous electric field has been investigated theoretically in great detail by Miliyanchuk.[158-162] The selection rules for this radiation are found to be the same as those for octupole electric radiation, with the exception of the requirement $J_1 + J_2 \geq 3$ which here takes the form $J_1 + J_2 \geq 1$. The intensity variation of the lines is almost the same in series induced by non-uniform and uniform electric fields, but in the first case the intensity of the lines increases much more rapidly with the quantum number n (as n^8) than in the second case (as n^4).[160]

If uniform and non-uniform electric fields act simultaneously (as is usually the case in a discharge), in the first approximation the non-uniform field has no effect on the intensity of the forbidden lines induced by the uniform field.[161] This theoretical conclusion has been verified in the work carried out by Prilezhaeva and her colleagues,[163] who measured the intensity of the forbidden lines in the P — P series of lithium in the spectrum of a carbon arc.

Forbidden transitions induced by uniform and non-uniform electric fields are easily distinguished from each other since they obey different Laporte rules. However, it is more difficult to distinguish the electric dipole transitions induced by non-uniform electric fields from the spontaneous dipole transitions (electric) since most of the selection rules are the same in both cases. However, one can make use of the Zeeman effect to distinguish between these lines.[159]

In a non-uniform electric field (or in a magnetic field) one sometimes encounters a so-called "complementary multiplet." The essence of this effect is that additional components with $\Delta J = \pm 2, \pm 3$ appear in an ordinary electric dipole multiplet. The complementary multiplet $4\,^3P - 4\,^3D$ Zn I observed in the arc is apparently an effect of this kind.[164]

Examples of forbidden lines induced by a non-uniform electric field are the lines of the $2\,^2S - m^2\,F$ in Tl I, observed in the positive column of a glow discharge[165] and the weak lines $1\,^1S_0 - 5\,^1F_3$, $1\,^1S_0 - 6\,^1F_3$, in Ba I and $1\,^2S - 6\,^2F$ in K I observed in a spark discharge.[166]

A rather detailed investigation of electric dipole radiation of rare-earth ions, induced by electric fields in crystals and solutions, has been carried out in reference 33. The production of induced electric dipole transitions between the levels of the f^k-shell of the ion and the crystal, i.e., transitions between levels of the same parity, is due to the absence of a center of symmetry in the field, as is the case in many point symmetry groups in crystals. The central symmetry of the field can also be disturbed by ionic vibrations. The absence of a center of symmetry in the field leads to the appearance of an odd part U'_{odd} in the lattice potential where U'_{odd} consists of two terms — a static term and a dynamic term:[33]

$$U'_{odd} = U_{odd} + U_{vib}. \qquad (4.3)$$

Here U_{odd} represents the interaction of the lattice field with the ion in an equilibrium position while U_{vib} represents the same interaction when the ion is not at the equilibrium position.

The order of magnitude of U_{vib} is determined from the expression

$$U_{vib} \sim U_{odd} \cdot \frac{R}{r_0}, \qquad (4.4)$$

where U_{even} is the even part of the lattice potential, R is the amplitude of the ionic vibrations, and r_0 is of the order of the dimensions of the electron shell. The existence of an odd part in the lattice potential leads to a violation of the selection rules. For the quantities J and L we obtain the selection rules $|\Delta J| \leq 4$ and $|\Delta L| \leq 4$ in the case of a field without a center of symmetry and $|\Delta J| \leq 2$ and $|\Delta L| \leq 2$ in the case of a field with a center of symmetry, but with account being taken

of the odd dynamic part of the lattice potential U_{vib}. It is also possible to have transitions which obey the selection rules $|\Delta J| \leq 6$, $|\Delta L| \leq 6$ and $|\Delta J| \leq 4$, and $|\Delta L| \leq 4$ respectively, but these are characterized by extremely small probabilities.[33] The selection rules for the quantum number m are the same as those in the case of magnetic and quadrupole radiation which become in the corresponding rules for the crystallographic number μ: $\mu = 0, \pm 1$ if we do not take account of the dynamic part of the lattice potential and $|\Delta\mu| \leq 2$ or $|\Delta\mu| \leq 4$ if we consider the linear or cubic terms of this part respectively. In a particular case, when the crystal is characterized by inversion axes of order n, these selection rules assume the form

$$\Delta\mu = \pm\frac{n}{2},\ \pm\left(1 \pm \frac{n}{2}\right). \qquad (4.5)$$

The maximum probability for induced electric dipole transitions has been computed by El'yashevich[33] and found to be 10^4 sec^{-1}; as is apparent from Eqs. (1.19) – (1.20) this is much larger than the maximum probabilities for quadrupole and magnetic transitions.

The induced electric dipole radiation of rare-earth ions in crystals and solutions has been observed experimentally by a number of the investigators who have already been mentioned.

The Zeeman effect is very characteristic of induced electric dipole lines, and is frequently used as a means of identification. Both the longitudinal and transverse effects are different for the dipole and spontaneous quadrupole lines. Thus, for longitudinal observation in the case of quadrupole radiation, components with $\Delta m = \pm 2$ are absent; in the case of dipole radiation induced by a constant electric field, these components appear. The same applies to the component with $\Delta m = 0$ under transverse observation. In addition it has been found that for this induced dipole radiation the sum of the Zeeman σ and π components are not equal.[2]

The Zeeman effect has also been studied in detail for electric dipole lines induced by isotropic electric fields.[130–132] These fields are usually produced by a random distribution of ions; under these conditions the mean values of the field components are the same in any direction. In this case the Zeeman pattern is again different for spontaneous quadrupole and induced electric dipole lines. In Fig. 5, as an example, we show the Zeeman components for these two types of lines produced in P – S transitions in He I as obtained under transverse observation.[133] The schemes refer to the quadrupole (1) and dipole (2) lines where the upper and lower vertical lines denote the σ and π components respectively; the numbers on the horizontal lines denote the values of the respective Δm components while the lengths of these lines denote the relative intensities for the σ and π components are equal (in contrast with the behavior of lines induced by a fixed electric field).

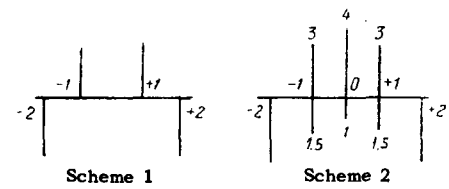

FIG. 5. Zeeman effect for electric dipole lines induced by isotropic electric fields (detailed explanation given in text).

An investigation has also been made of the Zeeman effect in lines induced by molecular electric fields in which there are no components parallel to the magnetic field. In this case it is found that for transverse observation the Zeeman splitting of the induced dipole lines arising from P – F and P – P transitions is almost identical with the Zeeman splitting of spontaneous electric quadrupole and magnetic dipole lines respectively. These splittings are different, however, for longitudinal observation. By means of this effect it has been possible to establish the induced nature of the lines $2\,^1P - 4\,^3F$ (λ 4921 A), $2\,^3P_{1,2} - 4\,^3F$ (λ 4471 A) and $2\,^1P - 5\,^1P$ (λ 4383 A) in the spectrum of helium. One of these lines, $2\,^3P_{1,2} - 4\,^3F$, has been observed in the spectra of certain class B stars, indicating the existence of ionic fields. The P – G lines in the spectrum of helium have been assigned to induced radiation (rather than spontaneous octupole radiation as had been believed earlier).[133–136]

Miliyanchuk[159] has investigated the Zeeman effect in lines induced by a weakly inhomogeneous electric field for the general case. The selection rules for the magnetic quantum numbers are found to be $\Delta m = 0, \pm 1, \pm 2, \pm 3$. The polarization of the component characterized by $\Delta m = \pm 3$ is the same as that of the component with $\Delta m = \pm 1$ in the resolved line. The remaining components are elliptically polarized for all directions of observation. The shifts and intensities of the components $m \rightarrow m + \delta$ and $-m \rightarrow -m - \delta$ ($\delta = 0, 1, 2, 3$) are different.

Forbidden atomic transitions can be induced in a strong magnetic field alone (without an electric field). For this effect to take place it is necessary that the field strength be sufficient to break the coupling between the L and S moments of the atom; under these conditions, the perturbed wave functions cannot be found in the first approxima-

tion alone. Thus the moment $J = L + S$ is no longer constant in direction and the selection rule $\Delta J = 0, \pm 1$ no longer applies. A calculation of the corrections which arise in the higher approximations leads to the additional selection rule $\Delta J = \pm 2$; in very strong fields we find the selection rule $\Delta J = \pm 3$. It should be noted that forbidden lines can appear in relatively weak fields if these fields are strong enough to produce a "partial" Paschen-Back effect. Forbidden lines induced by a magnetic field have been observed in the (P — D) triplets of Ca I, Zn I, Cd I and in the (P — D) doublets of Al I and Ca II.[37]

All the above considerations relating to the production of forbidden fine-structure lines under the effect of a magnetic field also apply to hyperfine structure. Because the hyperfine splitting of terms is small, even relatively small fields break the coupling between **J** and **I**, leading to the appearance of the forbidden transitions $\Delta F = \pm 2, \pm 3$.

The production of forbidden lines of the type described above is also possible in the spectra of atoms or molecules which have magnetic moments if these atoms or molecules approach each other very closely; under these conditions the magnetic fields which are set up become rather large. Since the Zeeman splitting is proportional to the first power of the magnetic field these forbidden lines should be considerably more diffuse than the forbidden lines induced by an electric field (in the latter case the relative sharpness of the forbidden lines arises by virtue of the quadratic Stark effect[2]).

We may also consider one other type of forbidden line which appears in an external magnetic field. As is well known, the Zeeman components of lines for which there is no fine structure obey the following selection rules: $\Delta m_J = 0$, $\Delta m_I = 0$ (π components) and $\Delta m_J = \pm 1$, $\Delta m_I = 0$, (σ components), where m_J and m_I are quantum numbers which determine the projection of the moments **J** and **I** respectively. If the lines exhibit hyperfine structure the first of the indicated selection rules refers to the number m_F, i.e., the π components obey the rule $\Delta m_F = 0$ while the σ components obey the rule $\Delta m_F = \pm 1$ where m_F is the magnetic quantum number, corresponding to the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$. Since $m_F = m_J + m_I$, the selection rule for m_F will be satisfied for various changes of the quantum numbers m_J and m_I which lead to the appearance of "extra" Zeeman components. For example, in addition to the resolved π-components which satisfy the selection rules $\Delta m_I = 0$, $\Delta m_F = 0$, and $\Delta m_J = 0$, there must be π components that obey the selection rules $\Delta m_F = 0$, $\Delta m_J = \pm 1$ and $\Delta m_I = \pm 1$. The intensity of these components is proportional to $(Ahc/2g(J)\mu_0 H)^2$ (A is the hyperfine structure constant, g is the Landé g factor, H is the magnetic field) and consequently decreases with increasing field and with diminishing A.[138-139] Forbidden π and σ components have been observed experimentally by Gerasimov and Frish,[140] who observed the Zeeman effect for the absorption lines in cesium (λ 4593.2 A, λ 4555.3 A, and λ 8521.1 A), rubidium (λ 7800.3 A), and sodium (λ 5889.56 A). It should be noted that the hyperfine structure of the lines listed above was not resolved; the existence of the effect was indicated indirectly — in the appearance of the forbidden components.

TABLE XI

Polarization	Component shift		Fractional parts of normal splitting
	Δλ (Å)	Δν (cm⁻¹)	
π	*0.232	*−1.090	$-\frac{4}{3}\Delta\nu_0 = -1.109$
	0.117	−0.552	$-\frac{2}{3}\Delta\nu_0 = -0.554$
	−0.117	0.552	$\frac{2}{3}\Delta\nu_0 = 0.554$
	*−0.232	*1.090	$\frac{4}{3}\Delta\nu_0 = 1.109$
σ	0.237	−1.114	$-\frac{4}{3}\Delta\nu_0 = -1.109$
	*0.107	*−0.503	$-\frac{2}{3}\Delta\nu_0 = -0.554$
	−0.107	0.597	$\frac{2}{3}\Delta\nu_0 = 0.554$
	−0.237	1.114	$\frac{4}{3}\Delta\nu_0 = 1.109$

Table XI shows the results of these observations on one of the cesium lines (λ 4593.2 A; $6\,^2S_{1/2} - 7\,^2P_{1/2}$) through the use of a magnetic field of 17,800 gausses; also shown are the corresponding displacements of the components of the fractional parts of the normal Lorentz splitting (the forbidden components are denoted by the asterisks). As we have seen the forbidden π components are found close to $\pm\frac{4}{3}\Delta\nu_0$, while the σ components are close to $\pm\frac{2}{3}\Delta\nu_0$ where the location of the latter exhibits some asymmetry. This asymmetry is explained by the non-uniform intensity of the forbidden components; this effect means that their common center of gravity is somewhat displaced.[140*]

Forbidden lines arise in the magnetic field of

*The existence of an asymmetry in the displacements and intensities of the forbidden components is explained by Miliyanchuk[158] by the fact that under the experimental conditions of Frish and Gerasimov these components arise under the effect of the intermolecular inhomogeneous field.

the nucleus (without external fields). The existence of nonvanishing spin and magnetic moment in a nucleus leads not only to hyperfine structure but also to the appearance of forbidden transitions. As is well known, the hyperfine terms are found by means of perturbation theory.[141] The perturbation operator used is the energy of the magnetic interaction between the electron shell and the nuclear spin

$$V = -\mu_I \cdot \mathbf{H}_J, \tag{4.6}$$

where μ_I is the magnetic moment of a nucleus with spin I, while $\mathbf{H}_J$ is the magnetic field produced by the electron shell with a total angular momentum J (neglecting the spin of the nucleus). The corrections for the energy in the first approximation are computed from the unperturbed functions in the representation γ, $\mathbf{J}^2$, $\mathbf{I}^2$, $\mathbf{F}^2$, F_Z where $\mathbf{F} = \mathbf{J} + \mathbf{I}$ is the total angular momentum (including the spin of the nucleus), γ represents all the remaining mechanical variables, which are not written explicitly. In this case the selection rules for the various multipole transitions remain the same as in the case in which there is no interaction between the magnetic moment of the nucleus and the atomic shell (if we do not take account of the additional analogous rules for the quantum numbers F and m_F). The result of a calculation will be more precise, the larger the spin-orbital interaction as compared with the interaction V. If this second quantity is not small compared with the first, in order to obtain the energy correction and the selection rules it is necessary to use the first-approximation wave functions. These are of the form

$$\psi(\gamma, J, F) = \psi^{(0)}(\gamma, J, F) + \sum_{\gamma', J' \neq J} \frac{(\gamma', J', F' | V | \gamma, J, F)}{E(\gamma', J') - E(\gamma, J)} \psi^{(0)}(\gamma', J', F'), \tag{4.7}$$

where $(\gamma', J', F' | V | \gamma, J, F)$ is the nondiagonal perturbation matrix element and $E(\gamma', J') - E(\gamma, J)$ is the difference between the fine-structure levels. The nondiagonal elements are comparable in magnitude with the difference between the hyperfine structure sublevels and vanish when $\Delta F \neq 0$; $\Delta J \neq 0, \pm 1$.[142]

It is apparent from Eq. (4.7) that the hyperfine structure terms for given J and F are, in the first approximation, linear combinations of the other terms of the zeroth approximation with the same F but with the other quantum numbers different; all terms will be larger for a value of J' for which the difference in levels of the fine structure $E(\gamma', J') - E(\gamma, J)$ is smaller. The existence of these linear combinations or, to put it another way, this mixing of fine structure states, leads to violations of the selection rule and thus explains the production of forbidden lines.

Forbidden lines induced by the magnetic field of the nucleus have already been observed in atomic spectra of bivalent elements — mercury and cadmium. These lines are Hg I: λ 2269.80 A, $6s^2\ {}^1S_0 - 6sp\ {}^3P_2$ (first investigated in 1927 by Rayleigh),[143] λ 2655.58 A, $6s^2\ {}^1S_0 - 6sp\ {}^3P_0$ (first obtained in fluorescence by Wood) and λ 2967.5 A, $6sp\ {}^3P_0 - 6sd\ {}^1D_2$,[144] and also the lines in Cd I:

λ 3141 Å, $5s^2\ {}^1S_0 - 5sp\ {}^3P_2$ and λ 3320 Å, $5s^2\ {}^1S_0 - 5sp\ {}^3P_0$,

first observed in 1931.[145] The nature of these lines was not established immediately. For some time they were something of a puzzle. On the one hand they could not be assigned to one of the spontaneous multipole radiation lines since they did not obey any of the appropriate selection rules; on the other hand, from an analysis of the excitation conditions it was impossible to draw any conclusion as to the possible production of these lines by virtue of external fields.* Bowen was the first to propose that these lines were induced by the magnetic field of the nucleus. This theoretical proposal of Bowen was first investigated by Goudsmit and Bacher in 1932 who used the line λ 2967.5 A.[146] Taking account of the interaction of the nuclear spin with only one of the outer s electrons in the mercury atom (the interaction with d electrons is a hundred times weaker) and considering only the first term in the summation in (4.7), (using the $^3D_1$ term (because of the fact that it was closest to the $^1D_2$ term), these authors were able to obtain corrections for the hyperfine structure sublevels of the $^1D_2$ and $^3D_2$ terms for both odd isotopes of mercury: Hg^{199} ($I = 1/2$) and Hg^{201} ($I = 3/2$). It was found that the difference between the hyperfine structure levels with the same F for the terms $^1D_2$ and $^3D_1$ increases as compared with the ideal scheme (i.e., as compared with the results of calculations in the zeroth approximation). Goudsmit and Bacher also verified the appearance of the forbidden line $^3P_0 - {}^1D_2$, also in the case in which the interacting terms have only one sublevel with the same F; the ratio of intensities for the forbidden and corresponding displaced line is given by the simple expression

$$\frac{I}{I_0} = \frac{\delta}{\Delta + \delta}, \tag{4.8}$$

*Later Miliyanchuk[160] showed theoretically that at high pressures the probability for forbidden transitions of the type $^1S_0 - {}^3P_2$ to a considerable degree was affected by the inhomogeneity of the molecular field.

where Δ is the distance between the indicated sublevels when the term interaction is neglected, and δ is the change in this distance due to the interaction of the terms.

Three papers have been devoted to the theory of other forbidden lines. In all this work the same hypothesis has been used concerning the production of these lines under the effect of the magnetic moment of the nucleus. In the first of these papers[147] calculations have been made of the relative intensities of the hyperfine structure components of the Hg I line $^1S_0 - {}^3P_2$. In the second[142] investigation has been made of the forbidden line Hg I $^1S_0 - {}^3P_0$. The intensity ratio was obtained for the two odd isotopes Hg^{199} and Hg^{201} which have spins $I_1 = 1/2$ and $I_2 = 3/2$ respectively (the spin of the other isotopes is zero); in particular,

$$\frac{I}{I_0} = \frac{g^2(I_1)\, I_1 (I_1+1)\, p_1}{g^2(I_2)\, I_2 (I_2+1)\, p_2}, \qquad (4.9)$$

where $g(I_1)$ and $g(I_2)$ are the gyromagnetic ratios and p_1 and p_2 are the percentage composition of these isotopes. It has been established that the term causing the strongest perturbation of the $^3P_0$ terms is $^3P_1$; on the assumption that the nondiagonal and diagonal elements of the perturbation matrix are the same $(\gamma', J', F'|V|\gamma, J, F)$ an estimate has been made of the intensity ratio for the transitions A $(^3P_0 \rightarrow {}^1S_0)$ and A $(^3P_1 \rightarrow {}^1S_0)$. In the last paper[148] an investigation has been made of the forbidden transitions $^3P_0 \rightarrow {}^1S_0$ and $^3P_2 \rightarrow {}^1S_0$ for mercury, cadmium and zinc. The $^3P_2$ term is also most highly perturbed by the $^3P_1$ term. It has been found that the ratio in (4.9) also applies for the transition $^3P_2 \rightarrow {}^1S_0$.

In addition, a semi-empirical method (using the experimental data on hyperfine structure and the calculated results of the nondiagonal elements of the perturbation matrix) has been used to obtain numerical values for the ratios of the probabilities for the $^3P_0 \rightarrow {}^1S_0$ and $^3P_2 \rightarrow {}^1S_0$ transitions as compared with the resonance transition $^3P_1 \rightarrow {}^1S_0$ for mercury, cadmium, and zinc. These numerical values are found to be of the same order of magnitude. However, lines corresponding to these transitions have been found only in mercury and cadmium. The absence of such lines in zinc may be explained by the fact that the multiplet levels $^3P_0$, $^3P_1$, and $^3P_2$ for the zinc atom are very close to each other so that transitions of the atom from the metastable levels $^3P_0$ and $^3P_2$ to the non-metastable level $^3P_1$ are enhanced, thereby implying that it is difficult to achieve the concentration of metastable atoms required to obtain an observable intensity for the $^1S_0 - {}^3P_0$ and $^1S_0 - {}^3P_2$ lines.

To supplement the cited results of the theoretical work, we should also note that the Bowen hypothesis concerning the origin of the lines $^1S_0 - {}^3P_0$, $^1S_0 - {}^3P_2$ and $^3P_0 - {}^1D_2$, leads in itself to the following features of the lines: First, only the odd isotopes Hg I, Cd I, and Zn I should radiate (the magnetic moments of nuclei of the even isotopes of these elements are zero); second, the hyperfine structure of these elements should be different for different values of the spin; third, when several odd isotopes are present an isotopic shift should be observed.

All these features and the results of the theoretical work cited above have been verified in the experimental work of Gaviola, Mrozowski and other authors.[149-153] Gaviola[149] has found the ratio of the probabilities for Hg I A $(^3P_0 \rightarrow {}^1S_0)$ and Hg I A $(^3P_1 \rightarrow {}^1S_0)$. Mrozowski[150-151] has investigated all three forbidden lines of mercury. These lines were obtained by optical excitation in mercury vapor containing an admixture of nitrogen. Mrozowski was able to establish the presence of an isotopic shift in all of these lines and has measured the relative intensities of the hyperfine structure components for the $^1S_0 - {}^3P_2$ and $^3P_0 - {}^1D_2$ lines; he has also observed other features which are found to be in good agreement with theory. In references 152 and 153 it has been shown that the intensity of these lines for both mercury and cadmium are proportional to the number of odd isotopes (the lines were excited in mercury vapor and cadmium vapor containing different isotopic composition).

On the basis of all that has been said concerning the effect of the magnetic moment of the nucleus on forbidden transitions, it can be concluded that the interaction between the electric quadrupole moments of the nucleus with the electron shells should also lead to the production of forbidden lines. As yet only the effect of the electric quadrupole moment of the nucleus on the hyperfine structure levels of various atoms has been investigated (in particular, europium, potassium, cesium, and so on[154-155]). The electric quadrupole moments of nuclei are determined mainly from the experimental data on the hyperfine structure.

CONCLUSION

Of all the possible forbidden lines, only a relatively few have been obtained under laboratory conditions.* These lines have been observed in both absorption and emission spectra. In absorption† it is especially convenient to investigate the lines

*This is discussed in greater detail in Mrozowski.[2]

†In absorption spectra both spontaneous and induced forbidden lines have been observed; for example, the $^2S - m\,{}^2D$ series in the alkali metals,[93] the $^1S_0 - {}^3P_2$ line mercury[143], etc.

that arise in transitions between high metastable states and ground states, because it is very difficult to obtain a high density of atoms in high metastable states. The absorption method of studying forbidden lines has advantages and disadvantages. On the one hand this method allows a considerable simplification in the measurements of the transition probabilities since there is no concern with the populations of metastable levels; on the other hand it is extremely difficult to measure the intensities of weak absorption lines and this makes it necessary to study very thick layers of gases or vapors. It should also be noted that the absorption method can be used only for studying transitions in which one level must correspond to the ground state.

Emission forbidden lines are obtained most frequently in discharge tubes. These tubes can have internal or external electrodes; the external electrodes are especially convenient in cases in which the required vapor pressure can be achieved only at high temperatures. As has already been indicated, to obtain sufficiently intense spontaneous forbidden lines, the investigated gas must be mixed with small amounts of intert gases or other gases whose atoms or molecules have high excitation potentials. The presence of an inert gas leads to an increase in the probability of excitation of the investigated atoms, since elastic collisions of atoms of this gas with free electrons reduce the mean kinetic energy of the latter to values comparable with the energy of the metastable levels. The actual role played by the inert gas in the production of forbidden lines has as yet not been clarified.

Another important method of obtaining forbidden lines is the fluorescence method. In this case the atoms of the material investigated first absorb radiation and make a transition to high excited states; then, by radiation or collision with other atoms, they make transitions to metastable levels. So far this method has been applied only in mercury (Wood and Gaviola[149]). Mercury vapors have been investigated at room temperature; in this work helium or nitrogen was present in the fluorescence tube. The mercury atoms are excited to the $^3P_1$ level by irradiation with resonance radiation at λ 2537 A and then, via collisions, make transitions to the metastable $^3P_0$ state. It would appear to be desirable to apply this method in other cases.

A third important method for the production and investigation of forbidden lines is the radio-spectroscopy method. We have considered the method and its application above.

All optical methods involve great difficulties in the measurements of intensities of weak forbidden lines, all the more so since the latter are frequently close to smeared-out lines. In order to overcome these difficulties, generally speaking, one prefers to take steps which result in an improvement in the excitation conditions for the forbidden lines rather than improvement of the detection apparatus, since small changes in the excitation conditions can result in intensity increases of several hundred times.[2]

Under laboratory conditions one usually investigates forbidden lines in neutral atoms. Forbidden lines of singly ionized atoms can be obtained with reasonable intensity only at very low pressures and only in the absence of an inert gas.[2] Research in the laboratory production of forbidden lines in highly ionized gases is just beginning.* This problem is one of great importance.

Up to this time the overwhelming majority of forbidden lines observed in the spectra of celestial bodies have not been obtained in the laboratory and a second very important problem is a complete and accurate calculation of the transition probabilities associated with these lines. A calculation of this kind for the basic configurations of atoms in the first two short periods of the periodic table has been carried out rather carefully, as we have already indicated. However, the calculation of the probabilities for forbidden transitions pertaining to the configurations d^n, $d^{n-1}s$, etc., which are characteristic of atoms in the first long period, has only just begun (with the exception of the work by Pasternack and Garstang[16-156]). It should be noted that in order to obtain accurate numerical values for these probabilities one must have highly accurate values for the radial integral s_q.

Although the general theory of forbidden lines is of interest in astrophysics and has been considered in a rather large number of papers, cases in which this theory has been applied to actual lines are rare. At the present time only the theory of "nebular" lines may be considered well-developed.

A number of problems relating to the theoretical and experimental aspects of forbidden atomic radiation are still not solved. These include the following: (1) further development of the theory of inter-configuration and other interactions, (2) the identification of the remaining unidentified four corona lines and other lines in the spectra of celestial bodies, (3) the discovery of spontaneous multipole lines higher than the second order, (4) further investigations of the interference effect in mixed radiation, (5) the observation of pure magnetic dipole lines in the optical region, and so on.

*If we neglect ions in crystals and solutions.

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