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Forbidden Lines in the Laboratory

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INTRODUCTION

It is very hard to give a sufficiently broad definition of a forbidden line. To base the definition on the operation of selection rules and to say that lines obeying the selection rules of the electric dipole radiation are permitted and all remaining ones are forbidden is not convenient. Most of the selection rules are not rigorous after all, and the degree of their approximation depends on the coupling conditions. The best definition seems to call forbidden all lines which for undisturbed atoms have very small transition probabilities in comparison to the highest transition probabilities for the given kind of atoms and corresponding to transitions between levels of approximately the same total quantum numbers. The last restriction is made in order not to call forbidden higher members of series which have very small transition probabilities in comparison with the first few members of series. The meaning of the expression "very small" in the definition is interpreted sometimes as 1/1000, in other cases is taken around 1/10000. The choice of the name "forbidden" was to some extent unfortunate, since the lines are not forbidden after all. They are, however, "forbidden" in the first approximation; in some cases, however, only if the approximation is correspondingly chosen. For instance, intercombinations are forbidden for (L, S) coupling, but permitted for the (j, j) coupling approximation. In conclusion the accepted name has mainly a historical justification and is a result of the gradual development of the atomic theory.

Since the forbidden lines are very weak in comparison to other permitted lines, we should expect that they will constitute a minor feature of the spectrum and will not deserve the special attention of the spectroscopist. This would be true if for every excited level there would exist in addition to a forbidden transition, also a permitted one, by way of which the atom could get rid of its excitation energy in a speedy way. However, if the forbidden transitions are the only transitions downwards, the excited atom becomes metastable and possesses a considerable lifetime in this state. The concentration of metastable atoms becomes sometimes very considerable, and other processes besides the emission of the forbidden lines can be of great importance. Such processes are excitation to higher levels by absorption of light or collisions with electrons, and transfers to higher or lower energy levels by collisions with other atoms or molecules (with a change of energy into a translational, rotational, and vibrational kind or into ionization, dissociation, or excitation of the other atom or molecule). Even in cases when the emission of the forbidden lines plays a minor role relative to other processes in determining the state of equilibrium in the matter, the forbidden lines retain their importance for the investigators. Their intensity is proportional to the concentration of the metastable atoms (or molecules), and the measurements furnish us with a very good means of studying the influence of different factors on the concentration. To find the absolute concentration we need to know the lifetime of the metastable atom: that is, the probabilities of the forbidden transitions. Thus the forbidden lines become in the hands of an astrophysicist, a physicist of the upper atmosphere, a photochemist, and others, an important tool for the study of the state of matter. The task of the spectroscopist is to develop this tool to the highest degree of perfection by studying all aspects of the problem in the laboratory: that is, to study experimentally the relations of different factors and to compare the results with theoretical predictions.

I. EXPERIMENTAL METHODS OF PRODUCTION AND OBSERVATION OF FORBIDDEN LINES

Forbidden lines are observed in absorption as well as in emission. Lines belonging to the forbidden series $^2D-{}^2S$ were early discovered in the absorption of alkali vapors (Datta 1922). The line λ2270 of mercury $6^3P_2-6^1S_0$ was obtained in absorption by Lord Rayleigh (1927). These observations, especially the last one, had a great influence on the development of our understanding of the forbidden radiations (Section II). The absorption method seems to be a convenient way to study forbidden lines originating from a non-metastable upper level, since for such a level it is difficult to obtain a sufficiently high concentration of excited atoms in order to get such a line in emission. However, the absorption method is limited to lines terminating only in the ground state of neutral atoms. Only gases or substances with high vapor pressures can be investigated since the lengths of absorption tubes are limited in the laboratory, and relatively higher pressures are required to broaden the lines in order to make their detection possible with spectrographs of a not too high resolving power. Also, the determination of the intensity of such weak lines is difficult and laborious. For all these reasons, the absorption method can have a limited application only, in spite of the important feature that transition probabilities can be obtained directly from such measurements without the complicating factor of the determination of the concentration of metastable atoms (see for instance Prokofjew's measurements, Section VI).

In emission forbidden lines were observed with almost every type of discharge tube known to spectroscopists. In discharges forbidden lines were early found in the spectra of HeI, HgI, and many others. The lines found can be divided into two categories: those with an intensity increasing with the square of the electric current (or faster) and those with an intensity reaching a maximum at low current densities and decreasing steadily for higher currents. The first group of lines belongs to the class of radiation enforced by the strong electric ionic and electronic fields (Section III); since the resulting intensity is of a statistical nature and little information can be expected from such investigations, there was a tendency to avoid these ionic fields and to investigate these lines under more definite conditions (in constant external fields). The second group of lines constituting the class of spontaneously emitted radiation can be observed only at low current densities, because the metastable states are destroyed by collisions with electrons (transferring the atoms to higher excited states). In order to have an arc discharge stable at very low currents, branched arcs were often used in which a small part of the main discharge is led to a side electrode through a long tube observed in an end-on arrangement. Since the high voltage discharge is much more stable at low currents and permits a better control of different factors (for instance, there is a more uniform density of the vapor in the tube), it is preferred in the work on forbidden lines. However even recently important results could be obtained with a mercury arc (Section V; 18).*

Long discharge tubes with internal electrodes were used by McLeman and others in investigations of the famous aurora line, λ5577 (1925–31). The tubes were filled with a rare gas at a few millimeters pressure and a minute quantity of oxygen. The function of a rare gas is to increase

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* The numbers in parentheses refer to the list of references at the end of this paper.

the probability of excitation of oxygen by increasing the length of the path of diffusing electrons. The increase of the probability of excitation decreases the average energy of electrons at a collision, and in consequence, lower energy levels of oxygen atoms are preferentially excited. The rare gas atoms also prevent the metastable oxygen atoms from losing their energy by collision with other oxygen atoms and molecules or with the walls of the discharge tube. An especially great enhancement of the forbidden line was observed for an addition of argon which is probably caused by a certain kind of collisional resonance effect for the metastable argon atoms.

The presence of internal metallic electrodes in a discharge tube can be a source of impurity and presents an additional difficulty in a study of substances which are giving sufficient vapor pressures only at higher temperatures. Therefore, Niewodniczanski (1933) developed an apparatus consisting of a quartz tube with external electrodes to which an alternating high voltage taken from a high frequency oscillator was applied for his study of the PbI spectrum. This method, after introducing several minor improvements, turned out to be the most powerful way for excitation of forbidden lines in the laboratory (24). The hyperfine structure and the Zeeman effect can be easily observed with interference apparatus (24, 27), and lines can be photographed with the largest gratings (32). Unfortunately, it is a method which furnishes only very strong spectra of neutral atoms or molecules. At low pressures without admixture of a rare gas, the first ionized spectrum is obtained with good intensity. For such spectra, however, a hollow cathode discharge tube appears to be superior, since the electrons possess higher average velocities even in the presence of a rare gas (almost the total voltage drop occurs in a very short distance). With the last source, a considerable intensity of the line λ2815 in HgII was obtained (22). In order to decrease the destructive influence of higher densities of the current, it seems advantageous to build cathodes with larger cross section than was usually done in the past. At the same time greater lengths could be used in view of the more advantageous geometrical relations.

Several other methods were tried in special cases: an electrodeless high frequency discharge and controlled low voltage electrons (filament and grid) were used for excitation of the Cameron bands of CO (14), a nitrogen afterglow (10), and a discharge of a kind usually applied for production of ozone (13) were used for excitation of the Vegard-Kaplan bands of N_2. The first two methods require low pressures and long free paths for the electrons in order to give enough time to the circularly moving electrons in the electrodeless discharge to acquire sufficient speed and in the case of controlled electrons in order to have a uniform excitation over a definite volume of the tube. In vessels of finite dimensions, a low pressure leads to a very strong de-excitation of metastable molecules by collisions with the walls of the tube (no screening effect of the rare gas), and high intensities of the forbidden radiation cannot be expected. A serious drawback of the last method constitutes the relatively high pressure of the gas used and, consequently, the considerable width of the lines. However, a further development of this method seems to be worth while. A study of the influence of additions of rare gases at lower pressures should be of especial interest. The nitrogen afterglow is a very good source also for forbidden lines of nitrogen and oxygen (21); its important feature is the similarity of its spectrum with the spectrum of the aurora.

A potentially very important method seems to be the study of the emission of forbidden lines by metastable atoms which are formed by absorption transition to higher levels and a subsequent emission or collisional transfer. This method can be called the fluorescence method. Until now it was applied only to mercury. Wood, and later Wood and Gaviola (1928), obtained quite high intensities of the forbidden line λ2656 of HgI ($6^3P_0-6^1S_0$) at room temperature by adding helium or (still better) nitrogen gas into the fluorescence tube. As it is well known, the excited 6^3P_1 atoms of mercury formed by the absorption of the resonance line λ2537 are transferred to the metastable state 6^3P_0 by collisions. Such an excitation was used in the investigations of the structure of the line λ2656 (16). The fluorescence method gives one an opportunity to determine concentrations of metastable atoms (see Gaviola's study mentioned in Section V). It would be interesting if it were tried out in other cases, such as, for instance, the spectra of PbI and BiI. A rotating sector method could be applied for the determination of the lifetimes of metastable states.

As the reader can see from the review of experimental methods, almost all methods of excitation known to the spectroscopist were tried out and often found adequate. However, in principle no new methods have been devised, and it is certain that with the methods discussed above we shall not be able to go beyond the singly ionized spectra of elements. All the forbidden transitions in highly ionized elements, especially interesting for astrophysicists, are, for the time being at least, out of the reach of the experimental spectroscopist. It can be hoped that some solution of the experimental difficulties, maybe by the application of molecular rays, will be found in the not too distant future.

In the observation of forbidden lines, the laboratory spectroscopist encounters all the difficulties which he usually meets in dealing with very weak spectra. Spectrographs with high apertures, very sensitive photographic plates, Fabry-Perot etalons with high transmissivity, and other devices have to be used in order to cut down the time of exposure. An additional difficulty arises sometimes by the presence of strong permitted lines in the immediate neighborhood of the lines studied (18, 24). However on the basis of the experience of the author, it seems much more worth while to spend extra time on study of the excitation conditions than on improvement of the optical apparatus since the intensities of the forbidden lines are in most cases extremely sensitive to different factors, and unexpectedly high intensities can be obtained by seemingly minor changes in the excitation conditions. As a specific case for an example, the spectrum of lead should be mentioned; there an increase of intensity by more than 500 times in comparison with the older experiments of Niewodniczanski was recently obtained (27).

II. CLASSIFICATION OF FORBIDDEN LINES

In the introduction the writer suggested a definition of forbidden lines which would avoid a discussion of selection rules and would permit us to include under this name a broad variety of lines, all of which customarily are called "forbidden." However a classification into different types must be based on selection rules, and this will be taken up in a general way below. A more detailed discussion will be found later in the corresponding sections.

It has been earlier recognized in the analysis of spectra that certain transitions which are quite strong in spectra of heavier elements become gradually weaker for lighter elements. It was found that these transitions constitute the class of intercombination transitions which are forbidden for the case of a so-called pure (L, S) coupling between electrons in the atom. For heavier atoms, the coupling gradually changes toward the so-called (j, j) type, for which the quantum number corresponding to the total spin S is no longer defined, and the intercombination prohibition loses its validity. For light atoms and diatomic molecules composed of both light atoms, the (L, S) coupling scheme represents a good approximation, and therefore, certain excited states become metastable. The class of spontaneous transitions disobeying selection rules which have only an approximate validity in view of interelectronic interactions will be treated in Section IV.

There are two very general selection rules for atomic systems, the validity of which is independent of the coupling conditions inside of the atom. They are: (1) the total rotational momentum J of a system can change during a radiative transition not more than by one quantum, that is $\Delta J=0, \pm 1$, with the additional prohibition of transitions $J=0 \rightarrow J'=0$, and (2) the Laporte's symmetry rule which allows transitions only between levels of different symmetry even⇄odd ($\Sigma_i l_i$ for all electrons even or odd). Symmetry rules similar to the last one are operating for molecules. In the early stages of investigations, it was commonly believed that all forbidden lines disobeying these two rules were transitions occurring in atoms perturbed by some outer fields (electric or magnetic) of an ionic or intermolecular origin. Gradually, however, as the theory of such forced transitions was developed (the lines of such a type will be discussed in Section III), it was realized that only a part of all observations can be explained by such an assumption. The observed absorption of forbidden lines in Na at low pressures and still more of the line λ2270 by a pure mercury vapor (Section I) showed that lines are absorbed in absence of any stronger intermolecular fields. Mercury atoms are spherically symmetric and have a zero spin momentum in the normal state.

The identification of the aurora line λ5577 as a forbidden transition in OI by McLennan through the exact determination of its wave-length (1927) and the identification of the famous nebular lines as forbidden transitions in ionized nitrogen and oxygen by Bowen (1928) finally gave a convincing proof of the spontaneous character of some forbidden radiations (in view of the extremely low densities existing in the upper atmosphere and in the nebulae). It was Rubinowicz (1928–30) who gave an explanation in terms of the radiation theory. In the previous theoretical discussions, only the first term of a series development for the electric and magnetic vectors of the wave emitted by a vibrating electric charge was taken into consideration. The first term has the form of a wave created by an electric dipole, and for such a simplified model, all selection rules were previously derived. Rubinowicz studied the second term of the series development and showed that for this second-order radiation, all of which he called at first electric quadrupole radiation, different rules apply. Brinkman (1932) showed that the second-order term treated by Rubinowicz contains beside the electric quadrupole a part similar in behavior to the first order term and corresponding to a radiation of a magnetic dipole. Some forbidden lines are of the pure electric quadrupole type and will be discussed in Section VI; other lines which are of a pure magnetic dipole type will be treated in Section VII; finally lines of a mixed character—mixed electric quadrupole and magnetic dipole radiation—will be discussed in Section VIII.

The spontaneous emission of the forbidden lines of mercury and other elements from the second column of the periodic table could not be explained within the limits of the theory of the second order radiation. It was predicted by several investigators, but only much later definitely proven by Opechowski and the author (16, 17), that such lines are of an electric dipole type, and their emission is caused by a coupling existing between the outer electrons and the magnetic moment of the atomic nucleus. This interaction invalidates partly the $\Delta J=0, \pm 1$ selection rule in a manner quite similar to that in which the spin-orbit interaction for the electrons invalidates the intercombination prohibition. The forbidden lines of such a nuclear perturbational type will be treated in Section V.

III. ELECTRIC DIPOLE RADIATION FORCED BY EXTERNAL FIELDS

It was already mentioned in Section I that a number of forbidden lines were found emitted with an intensity which increases rapidly with the electric current in the discharge tube. A great number of such lines were observed for instance in mercury by Fukuda (1923). Since the intensity of the lines is proportional to the concentration of excited states times the transition probability and the concentration does not increase faster than proportional to the current, we see that the transition probability is increasing at least as fast as the current density or faster. The emission of these lines is forced by the electric fields of ionic origin existing in the discharge. For an atom the field created by the neighboring ions is changing in value and direction (molecular motion); however, since the coulombian field is relatively slowly decreasing with the distance, the changes are not rapid and we can consider in the first approximation the electric fields as static and constant over the whole volume of the atom.

A well known dispersion formula developed by Kramers and Heisenberg gives the electric dipole moment induced in an atomic system by an external electric field of a certain frequency. Such an induced dipole moment has beside the main component vibrating with the frequency of the external field extra components vibrating with frequencies differing from the main one by amounts equal to frequency differences of energy levels in the system (Raman effect). If the formula is applied to a case of a static field (frequency zero), extra components of the induced moment vibrating with frequencies corresponding to certain forbidden transitions are obtained (Pauli, 1925). As in the Raman effect only transitions will occur between levels which have a common third level with which both of these levels are permitted to combine in absence of the field by spontaneous electric dipole radiation. The selection rules for the electrically enforced radiation are, therefore, easily derivable from the selection rules for the permitted transitions. We find for J a rule—$\Delta J=0, \pm 1, \pm 2$ and for $\Sigma_i l_i$ a rule: even→even or odd→odd transitions are permitted. The induced moment is proportional to the strength of the electric field; the transition probability therefore is proportional to the square of the field. Since the energy differences between each of the two and of the third level appear in the denominators, strong emission will occur only if the third level is close enough to the initial or to the final level. Energy levels are more crowded for higher excitations, and forced transitions will usually occur for higher members of series with relatively greater probabilities. The intensity in a forbidden series of this type will first increase with the quantum number and after reaching a maximum will decrease at a relatively slower rate than for permitted series (Bartels, 1932; Sambursky, 1932).

Making certain simplifying assumptions, Sambursky (1931) calculated the relative intensities of lines in forbidden multiplets and compared the results with measurements performed on doublet spectra of AgI and CuI. A tolerable agreement was found. Sum rules are in general invalid for enforced multiplets, but for small multiplet separations and increasing orbital quantum number L, a gradual approach towards the sum rules should be observed. Milianczuk (5) performed more exact calculations for the relative intensities and discussed the limits of applicability of the sum rules. He showed that the results of Ornstein and Burger (1927) for the CdI spectrum and of Sambursky for AgI are in good agreement with the theoretical predictions, but that the deviations from the sum rules in case of CuI are considerably higher than expected.

The unambiguous identification of a forbidden line as an electrically enforced one is not possible on the basis of selection rules since similar selection rules are obeyed by the electric quadrupole radiation (Section VI) and an overlapping of both effects can take place. Such a case of overlapping was, for instance, observed in the absorption of the $^2D-{}^2S$ forbidden lines in potassium by Kuhn (1930). The intensity distribution in a series or the relative intensities in a multiplet can be used as indications of the character of the emission. However, only investigations with apparatus of high resolving power can give a clear distinction between different types of radiation. Enforced lines are broadened by Stark effect of the ionic fields and show a considerably greater width than other lines. Segrè and Bakker (1931) observed such a diffuseness for the line λ3680 of mercury ($7^3P_2-6^3P_2$). The Zeeman effect of enforced lines is very different from the effect of electric quadrupole lines. For the line mentioned above, Majorana previously calculated the intensities of components in the Zeeman effect assuming a random distribution of electric fields. Segrè and Bakker checked the Zeeman effect in λ3680 and found a satisfactory agreement. It appears that the line is mainly of an enforced electric dipole character. The transition probability for the electric quadrupole radiation is much smaller, and the line does not appear at low current densities.

It is definitely more advantageous to study the enforced lines in homogeneous electric fields. Intensity formulas for the Zeeman effect of electrically enforced radiation were obtained by Milianczuk (5) on basis of Dirac's equations. Experiments were performed for the helium spectrum with crossed electric and magnetic fields by Steubing and Redepenning (6) and in parallel fields by Janssons (7). In these two papers many interesting observations are reported. In absorption forbidden series were observed in a constant electric field for sodium and potassium by several investigators, and the dependence of their intensity on different factors was qualitatively explained by Segrè and Wick (1933) (see references in 8). Quite recently the Zeeman effect was studied in the potassium series by Jenkins and Segrè (8). A cyclotron with large pole pieces was used as a magnet. In all these Zeeman effect investigations, it was found that for the enforced lines the sum of the intensities of the σ-components differs from that of the π-components. However for random ionic fields, this peculiarity disappears by cancellation in the process of averaging over all relative directions of the electric and magnetic fields.

Strong magnetic fields invalidate the $\Delta J=0, \pm 1$ selection rule with the J quantum number losing its meaning (decoupling of orbital L and spin S vectors). Already at moderate fields, components belonging to forbidden transitions in a multiplet are appearing (completion of a multiplet in the beginning Paschen-Back effect). It could be expected that in a gas which consists of molecules or atoms possessing magnetic moments forbidden lines of such a type should occur. However since the Zeeman splittings are proportional to the magnetic field, such lines would be extremely diffuse (in case of electrically enforced lines their relative sharpness is caused by their quadratic Stark effect!). Furthermore, the magnetic fields decrease faster with distance than the coulombian forces and only at small distances would the fields be sufficiently strong to break the coupling between the vectors L and S. At such small distances other intermolecular interactions are also present, the atom (or molecule) even in the first approximation is no longer independent, and both colliding particles have to be considered as a single system (a quasimolecule). Since the perturbing field is of an internal rather than external origin, the discussion of such cases will be deferred to the next section.

IV. ELECTRIC DIPOLE RADIATION FORCED BY ELECTRONIC INTERACTIONS

In an atomic or molecular system, electronic interactions which are comparatively weak and are therefore disregarded in the first approximation (in setting the quantum number designations of levels), have a perturbing effect on the motions of electrons and like the external fields can force the radiation of a forbidden line. If for any reason such an interaction becomes stronger, the coupling scheme accepted as the first approximation has to be changed accordingly, and new quantum number designations introduced. Some lines called before "forbidden" become "permitted" in this new coupling scheme. A well known case of such a gradual transition from forbidden to permitted are the intercombination lines. For light atoms there is a strong interaction between orbital momenta l_i of electrons on one hand (formation of the resultant vector L) and a strong interaction between electronic spins s_i on the other (formation of the total spin S). The interaction of the vectors L and S, caused by interactions of l_i with s_i for single electrons, is very weak, and both vectors precess uniformly around their resultant J. In setting up corresponding quantum number designations in the first approximation, the interaction of L and S is assumed to be negligible (the so-called Russell-Saunders or (L, S) coupling scheme). For a negligible interaction, L and S are practically independent and an electronic orbital jump does not involve a change of spin $\Delta S=0$. However for heavier atoms, electrons move in a stronger electric field of the nucleus, and the magnetic interaction of electronic orbital momenta l_i with their own spins s_i increases. This introduces perturbations in the uniform precession of l_i around L and of s_i around S. The vectors L and S are no longer constant in value; the quantum numbers L and S become approximate; and the selection rule $\Delta S=0$ gradually becomes invalid.

Quantum mechanically, the relations can be stated in the following way: for extreme (L, S) coupling (no interactions between L and S) certain definite wave functions correspond to definite energy levels. However, these wave functions change as soon as a spin-orbital interaction is introduced. If the interaction is not too strong, the new wave functions are little different from the old ones, and we find only a slight admixture of wave functions of other levels belonging to the same electronic configuration with the same value of the quantum number J. The given energy level acquires certain properties of other levels with a different multiplicity $(2S+1)$, and transitions begin to show in the spectrum which seemingly contradict the selection rule $\Delta S=0$. In a quite similar manner, a mixing of wave functions of states with L differing by one unit occurs in external electric fields giving rise to forbidden transitions discussed in the previous section. In a strong electric field the quantum number L loses its meaning.

For the special case of atoms with two electrons in the outside shell, the wave functions of the states $^1P_1$ and $^3P_1$ belonging to the same configuration mix, and a transition from $^3P_1$ to the ground state $^1S_0$ occurs in the spectrum. The ratio R of the probabilities of the intercombination transition $^3P_1-{}^1S_0$ to the singlet transition $^1P_1-{}^1S_0$ is a function of the admixture of the $^1P_1$ wave function in $^3P_1$ state; or in other words, a function of the departure from the pure (L, S) coupling. The value of the separation $\Delta\nu$ of the levels $^3P_1$ and $^3P_0$ gives the strength of the interaction of the vectors L and S and can be therefore considered as a parameter measuring this departure for rough orientation. Transition probabilities of both resonance lines $^{1,3}P_1-{}^1S_0$ were determined experimentally for elements in the second column of the periodic table of elements on many occasions by measurements of the absorption, dispersion, depolarization of the resonance radiation, decay of emission in molecular rays and so forth. The ratios R are smaller for lighter elements, changing from about 2×10^{-2} for mercury to about 6×10^{-7} for magnesium. According to Prokofjew (1928) R is roughly proportional to $(\Delta\nu)^{2.5}$.

The probability for the permitted transitions is of the order of 10^8–10^9 sec.$^{-1}$; the probabilities for the intercombination transitions decrease from 10^7 sec.$^{-1}$ for Hg to 2×10^2 sec.$^{-1}$ for Mg. The lifetimes of the resonance level $^3P_1$ accordingly increase from 10^{-7} sec. to 5×10^{-3} sec. The point at which we shall call the level $^3P_1$ metastable is a matter of definition. For the lightest elements a very strong metastability (long lifetime) is expected which even surpasses other cases of metastability and makes it impossible to observe intercombination lines in the laboratory sources (He, Be). Zeeman effects were investigated for many intercombination lines, but they do not furnish any additional information which cannot be obtained from the study of other lines. Consequently, no efforts were made to study Zeeman effects in intercombination lines of light elements.

Transition probabilities for intercombinations in diatomic molecules should be found approximately the same as in atoms if both atoms are about of the same atomic number. Forbidden intercombination bands for light molecules are known in nitrogen N_2, in CO and some other spectra. The nitrogen bands were discovered by Vegard (1932) in luminescence at low temperature, and their excitation was studied in an afterglow by Kaplan (10). Their classification as a transition $A^3\Sigma_u^+\rightarrow X^1\Sigma_g^+$ was definitely established by an analysis of its rotational structure by Wulf and Melvin (13). Bands of CO, discovered by Cameron (1926), were later identified as a transition $^3\Pi\rightarrow{}^1\Sigma$ (definitely by a rotational analysis made by Gero in 1938). Hansche (14) studied recently the excitation conditions of these bands for electrons of various energies and found two maxima in the excitation function. In the first paper, Hansche estimated from the pressure dependence the lifetime of the molecule in the $^3\Pi$ state to 2.5×10^{-5} sec. or less. In the second paper, however, he rejected this value as unreliable. It is easy to evaluate roughly the lifetime of the triplet state of a molecule CO by extrapolating the atomic data of Prokofjew. A much longer lifetime of about 1/20 sec. is obtained. For the $^3\Sigma_u^+$ state of N_2 the lifetime may be considerably longer since the interaction of L with S is decreased by averaging out to zero the component of L along the molecular axis.

The strength of the spin-orbit coupling in diatomic molecules in cases which correspond to the so-called "coupling" scheme a of Hund probably does not depend strongly on the distance of the nuclei (as long as the distance is not very great). Therefore, approximately the same transition probabilities for different separations of the nuclei and an intensity distribution among bands of the intercombination system corresponding to the Frank-Condon parabola are expected. Investigations of the intensity distribution for intercombination bands like N_2 and CO would seem, however, not without interest.

There are known cases for which the strength of the (L, S) coupling changes considerably over short distances. Such is the case of the molecule of mercury Hg_2 for which the coupling is of the type c of Hund (the vectors L and S are coupled into a vector J, which precesses around the molecular axis with a component Ω) but changes into the type a at small internuclear distances (the interaction of the two atoms breaks the coupling of the vectors L and S and forces L and S to precess independently around the molecular axis). The transition from the state $A^3O_u^-$ (Fig. 1) to the ground state $X^1\Sigma_g^+$ is for the pure c coupling forbidden ($a\Sigma^-\rightarrow\Sigma^+$ transition), but at small distances the two states $A^3O_u^-$ and A^31_u combine into a $^3\Sigma_u^+$ state from which the probability of transition to the ground state can be as high as 10^7 sec.$^{-1}$ (of the order of the intercombinations $6^3P_1-6^1S_0$ in the mercury atom). Vibrating metastable molecules trapped in the $A^3O_u^-$ state are able to radiate only at the time of closest approach of atoms, and the band λ4850 is therefore emitted mostly by molecules with high vibrational energies (12). The observed lifetime of 10^{-2} sec. is an average dependent of

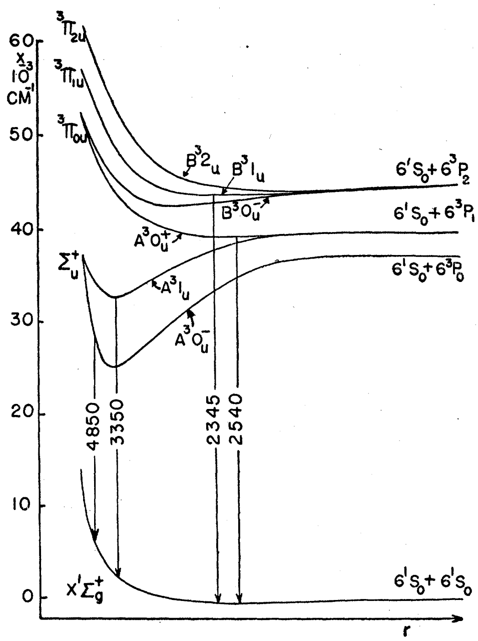

FIG. 1. Potential curves for a molecule of Hg_2 and their quantum designations. The forbidden band λ4850 is emitted only at a close approach of the nuclei.

the average vibrational energy, that is, of the temperature of the gas.

For the two curves A^31_u and $A^3O_u{}^+$ a constant transition probability over the whole range of internuclear distances is expected (Frank-Condon intensity distribution). However, for the remaining potential curves (the B^32_u or $^3\Pi_{2u}$ state does not combine with the ground state) again a variable transition probability is expected. For the curve $B^3O_u{}^-$ as for $A^3O_u{}^-$ absorption and emission should occur only at very close distances of the nuclei which correspond to very high kinetic energies of colliding atoms and, therefore, are of no interest for the explanation of the spectrum. For the B^31_u curve, the situation is very different—already for the pure *c* coupling type, a transition to the ground state should be equally probable as the atomic $6^3P_1-6^1S_0$ transition. But for great distances in which atoms can be considered as independent, the corresponding transition $6^3P_2-6^1S_0$ (λ2270) is forbidden. Two colliding atoms, one of them excited to the 6^3P_2 level, emit light only at close approach, this time, however, already at considerably greater nuclear distances than in the case of the band λ4850, giving rise to an emission band adjoining the forbidden line λ2270 on the side of short wavelengths (if the minimum of the potential curve B^31_u is shallow). Actually the corresponding band has not been found in pure mercury vapor on the long wave-length side of the line (a deeper minimum in the potential curve B^31_u). A band on the short wave-length side (collisional type) was detected, however, by Preston (11) in mercury-argon and mercury-helium mixtures. It is quite clear that the general character of the curves $6^3P_2(B)$ remains the same as long as an atom with a closed shell ($^1S_0$) is colliding with a metastable 6^3P_2 atom of mercury.

In the discussion above it was tacitly assumed that atomic transitions $6^3P_{2,0}-6^1S_0$ are exactly forbidden; that is, they do not occur at all. This assumption was justified since the transition probabilities of these forbidden atomic transitions λ2270 and λ2656 are of the order of 10^{-1} sec.$^{-1}$ (see Section V) which is negligible in comparison to transition probabilities observed in bands of mercury (10^2 sec.$^{-1}$ or more).

A system of very weak absorption bands of oxygen has been interpreted as a $^3\Sigma_u{}^+ \rightarrow {}^3\Sigma_g{}^-$ forbidden transition violating the approximate selection rule $\Delta K=0$. The character of violation is of a little different nature (there are two alternate explanations), and the lack of space prevents the writer discussing this case. The reader interested in this problem is referred to the original paper by Present (9).

V. ELECTRIC DIPOLE RADIATION FORCED BY THE INTERACTION WITH THE NUCLEUS

Investigations of the line λ2270 in absorption by Rayleigh and of the line λ2656 in fluorescence by Wood seemed to establish the spontaneous character of the emission of these lines of mercury (Section I, II). However, no explanation for the cause of violation of selection rule $\Delta J=0, \pm 1$ in terms of electronic interactions or multipole radiation could be found. (A transition $J=0 \rightarrow J'=0$ is forbidden for all multipole radiations). It was suggested (by Bowen and others) that the emission is due to a coupling with the nuclear magnetic moment. Since mercury is a mixture of 6 stable isotopes, two of which have odd nuclei with magnetic moments differing from zero, it was expected that both lines actually are emitted only by the two odd isotopes 199 and 201. In

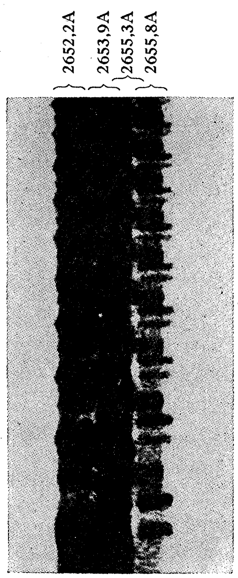

FIG. 2. Structure of the forbidden line λ2655.8 ($6^3P_0-6^1S_0$) of mercury. A Fabry-Perot etalon was crossed with a large spectrograph. Exposure time 6 hours.

view of the considerable isotope shift in the ground level of mercury, the lines belonging to different isotopes do not overlap and can be separated by instruments of high resolving power. Photographs of the structure of the line λ2656 were obtained only recently (17) after overcoming considerable experimental difficulties. One of them, obtained by crossing a Fabry-Perot etalon with a medium spectrograph, is reproduced in Fig. 2. Two components are observed, their intensity ratio being somewhat different from the ratio of the concentration of isotopes 199 and 201.

In terms of the vector model, the violation of the prohibition $J=0\rightarrow J'=0$ is explained by the fact that in case of a coupling between the electrons and the nucleus, the prohibition refers really not to J but to the total rotational momentum F of the system, a resultant of J and the spin of the nucleus I, the last being different from zero ($F=I$) for the two isotopes 199 ($I=\frac{1}{2}$) and 201 ($I=\frac{3}{2}$). For a strong coupling, the vector J would lose its meaning but for a weak coupling the interaction of the nucleus with the electrons introduces only a slight perturbation, which in turn causes the violation of the prohibition $J=0\rightarrow J'=0$. Quantum mechanically this is expressed as a mixing of wave functions of the state 6^3P_0 with the wave function of a hyperfine structure level of the state 6^3P_1 which has the same quantum number F ($F=I$). The slight admixture of the 6^3P_1 wave function in the 6^3P_0 energy state makes the emission of the forbidden line possible. Its amount is proportional to the ratio of the hyperfine separation in the 6^3P_1 state[1] and the energy difference of the states 6^3P_1 and 6^3P_0; it is also a function of the magnetic moment of the nucleus. Calculations performed by Opechowski gave for the ratio of intensities of the two components a value which is in a reasonably good agreement with the experimental results. For the ratio of transition probabilities of the lines λ2656 ($6^3P_0-6^1S_0$) and λ2537 ($6^3P_1-6^1S_0$), Opechowski finds 5×10^{-9} and a value of about 20 second for the lifetime of the metastable level 6^3P_0 for the odd isotopes of mercury. In most of the experiments with metastable atoms of mercury, a lifetime of around 10^{-2} sec. was obtained. It is certain, however, that in all these cases the life of metastable atoms was considerably shortened by collisions. The only dependable estimation of the ratio of transition probabilities was made by Gaviola (1929) on the basis of measurements of concentration of excited atoms 6^3P_1 and 6^3P_0 and of the intensities of lines, and led to a value agreeing closely with the value found much later by Opechowski (17).

Before discussing the other line of mercury λ2270, let us consider first the line λ2967.5 of mercury. The line is analogous to the line λ2270 since it is a forbidden line corresponding to a transition $J=2\rightarrow J=0$ ($6^1D_2-6^3P_0$). Not far above the 6^1D_2 level there is present a level 6^3D_1 for which the transition to 6^3P_0 is a permitted one. For the even isotopes the wave functions of 6^1D_2 and 6^3D_1 do not mix, but for odd isotopes the wave functions of hyperfine structure components with the same quantum number F are mixed, and strong perturbations in the positions of levels (repulsion) are observed. In Fig. 3 level schemes for both isotopes 199 and 201 are presented according to Goudsmit and Bacher (1933). The perturbations, and the emitted components of the forbidden line are indicated. The emission of the components occurs only from perturbed levels and is caused by the admixture of the wave

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[1] The separation gives the strength of the coupling of the electrons with the nucleus.

functions of the hyperfine levels of the state 6^3D_1. The predicted structure of the line is given in the lower part of Fig. 3. A recently obtained photograph of this line (Fig. 4) made with a big grating spectrograph (19) shows all components in distances and with intensities which are in complete agreement with the predicted pattern. In spite of the nearness of the allowed line λ2967.3, it was comparatively easy to obtain a good picture since, on one hand, the allowed line was weakened by re-absorption in the arc discharge, and, on the other, the forbidden line is relatively strong. The nearness of the two levels 6^3D_1 and 6^1D_2 causes a very strong mutual perturbation (repulsion) of hyperfine structure levels (which is easily detectable with an instrument of high resolution), and a strong mixing of wave functions follows. For the forbidden lines λ2656 and λ2270, however, the perturbing level 6^3P_1 is at such a big distance that a perturbation of position is far too small to be detectable, and the induced transition probabilities are very small, of the order of 10^{-1} sec.$^{-1}$

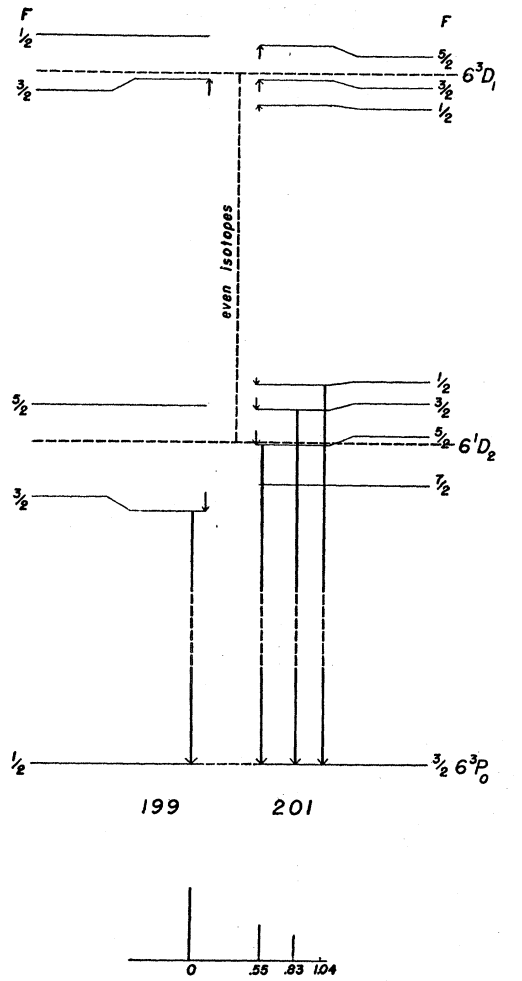

FIG. 3. The level scheme for the isotopes 199 and 201 of mercury. Unperturbed levels outside, levels after introduction of the mutual perturbational repulsion in the center. Below the predicted structure of the forbidden line λ2967.5 according to Goudsmit and Bacher (corrected for isotope shift).

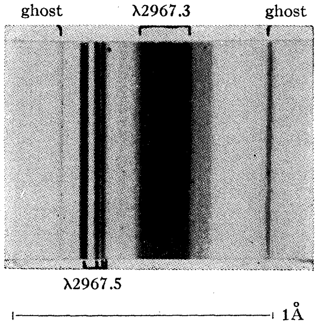

FIG. 4. Photograph of the forbidden line λ2967.5 obtained in the third order of a 30-foot grating (dispersion 0.2 A per mm).

The origin of the line λ2270 is analogous to the line λ2967.5, with the only difference that the perturbing level 6^3P_1 is below the perturbed level 6^3P_2 and, as mentioned above, at a far greater distance. The expected structure is similar to the one shown in Fig. 3. Exact distances of components can be predicted from the analysis of the structure of other mercury lines. The expected intensities were calculated some time ago by Einaudi (16). As Takamine (1923) and others have shown, the line can be obtained in an arc discharge in pure mercury vapor. Photographs of the line were made recently by the author (19) with an aluminized Fabry-Perot etalon and an arc of special design as a source. The pictures show three components, the fourth one being unobservable since its intensity is less than 3 percent of the strongest component. The distances of components and their relative intensities agree with Einaudi's predictions.

From our discussion we see that there is a class of forbidden lines observed in spectra of Hg, Cd, and Zn which are emitted only by odd isotopes of these elements. The even isotopes have infinitely long lifetimes in metastable states.

In an isotopic mixture in which a continuous exchange of excitation energy is occurring between different isotopes (collisions), the even isotopes supply the odd ones continuously with energy of excitation which the odd isotopes transform into radiation. For a pure even isotope, for instance Hg_{198} (obtained by Wiens and Alvarez from gold by nuclear reaction, 1941), no emission of forbidden lines is expected.

Zeeman effects for nuclear perturbational lines were not yet studied. Interesting Back-Goudsmit transformations are expected. The investigations, however, will probably be connected with considerable experimental difficulties.

VI. ELECTRIC QUADRUPOLE RADIATION

In the preceding three sections, forbidden radiations were discussed which are caused by an admixture of properties of other levels to one of the levels involved in the forbidden transition. Although weak, the radiation is of the regular electric dipole type, that is, of the same type as for the strongest atomic transitions. The weakness is explained by the smallness of the perturbation. In this and the two following sections, a different type of radiation will be discussed for which a low transition probability represents an inherent property, since the radiation is a process of the second order. The meaning of this last statement will now be explained.

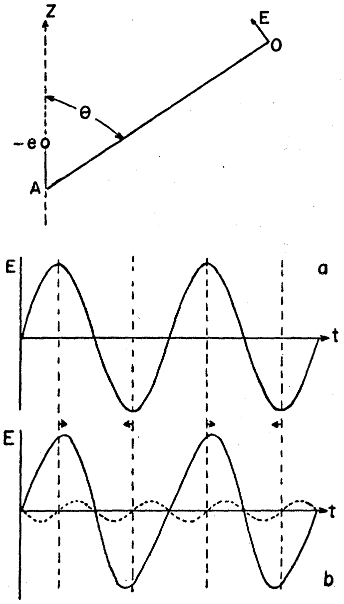

FIG. 5. Electric charge $-e$ vibrating around A along the direction Z. The electric vector E of the wave emitted is observed in O. If the amplitude of vibrations of the electric charge is negligibly small the vibration of E are represented by the sine curve (a), but for an amplitude which is not very small in comparison to the wave-length λ a distortion occurs and the vibration of E can be decomposed into two vibrations with frequencies ν and 2ν (curve b), corresponding to electric dipole and electric quadrupole radiations.

In classical theory a vibrating electric charge $-e$ is surrounded by an electromagnetic field for which, in the immediate neighborhood of the charge, the electrostatic part is predominant. At larger distances, only the field of the electromagnetic wave remains of importance, since all other parts decrease faster than inversely proportional to the distance. For simplicity, we shall consider a single charge $-e$ performing a harmonic vibration around a point A with an amplitude a and frequency ν along a direction z (see Fig. 5). The electromagnetic wave sent in the direction of the observer O will be in the first approximation a pure sine wave, which is represented in the central part of Fig. 5. However, this will be only true if the amplitude a of the vibration is small in comparison with the wavelength of the light emitted, $a \ll \lambda$. The shape of the real wave process observed in O (distance OA large in comparison with a) will deviate from a pure sine wave, since the distance of the charge $-e$ from the observer varies and the time separation of the maxima for the electric vector E will be smaller for the part of the cycle when the charge is moving toward the observer and longer for the other half of the vibration. The resulting vibration of the electric vector E in O is represented in the lower part of the Fig. 5 and as can be seen the vibration can be decomposed approximately into two pure sine vibrations with frequencies ν and 2ν. The ratio of the amplitudes of the vibration 2ν and the main vibration ν is proportional to the distortion (shift of maxima), which in turn is proportional to the ratio a/λ. A vibrating electric charge, therefore, beside the main wave of frequency ν is emitting a wave of frequency 2ν with an intensity smaller by a factor $(a/\lambda)^2$. This last radiation is the so-called second-order radiation. A more detailed discussion of the wave process observed in O shows the presence of still weaker component radiations with higher frequencies (harmonics), and the decomposition into pure sine waves gives for E a series with amplitude coefficients decreasing in the ratio a/λ (higher order or multipole radiations).

In order to have a model radiating a pure sine electromagnetic wave, which as a first approximation would resemble the wave emitted by the vibrating charge Fig. 5 in frequency ν and intensity distribution in different directions, the model of an electric dipole is introduced. This is a harmonic oscillator of an infinitely small amplitude a', ($a'/\lambda=0$, no distortion of the sine wave), but infinitely great charge $-e'$, so that $\mu_0=-e'\cdot a'=-e\cdot a$ is finite and represents the amplitude μ_0 of the electric moment of the dipole. A variable electric moment $\mu_z=\mu_0\cdot\cos 2\pi\nu t$ at the point A is consequently producing a pure sine wave in all directions. In order to get rid of an electrostatic field around A, a non-vibrating charge $+e$ is usually added in point A.

An appropriate model for the second-order radiation is obtained for the simple case presented in Fig. 5 by two electric dipoles (zero dimensions) vibrating with a frequency ν but with opposite phases and placed at the point A. Such a system of two electric dipoles in A is called a quadrupole. The intensity of the quadrupole radiation emitted in the direction of the axis Z and in any direction perpendicular to it is zero. There is no distortion of the sine wave for $\theta=90°$ (see Fig. 5); the distortion increases to a limiting value for $\theta=0°$, but the total intensity for this direction drops to zero. The intensity of the quadrupole radiation has therefore a maximum for intermediate θ. It is interesting to note that this property of the quadrupole radiation was utilized in a recent work by Freed and Weissman (30) in order to find the type of radiation for a fluorescence of europium in solution. The electric vector E is obtained by a triple differentiation relative to the time of the expression μ_z^2 (for the electric dipole by a double differentiation of μ_z). In the general case of a charge $-e$ performing a periodic motion, vector E is found by differentiation of a linear combination of components of a symmetrical tensor $Q_{xx}=\mu_x^2-\frac{1}{3}\mu^2$, $Q_{xy}=\mu_x\cdot\mu_y$, $\cdots$, $Q_{zz}=\mu_z^2-\frac{1}{3}\mu^2$.

In classical theory a single vibrating electric charge is emitting at the same time all kinds of multipole radiations. If two real dipoles like the one in Fig. 5 would be put close together near A and vibrate with opposite phases the wave form observed in E would closely resemble the radiation of a quadrupole, since in the first approximation the electric dipole part disappears by mutual cancellation. The cancellation would be almost exact for the dipole and all higher multipole radiations of an odd order, if the position of both charges $-e$ on the Z-axis would be at all times symmetrical relative to the point A. Similarly a pair of charges $-e$ and $+e$ vibrating perfectly symmetrically around point A would emit only odd multipole radiations, since the quadrupole and higher multipole radiations of even order almost exactly disappear by cancellation of waves emitted by the two opposite charges. The expression "almost exactly" in both of the last sentences means the cancellation occurs as long as the amplitude a is relatively small, $a\ll\lambda$.

Although the radiation of most spectral lines is caused by a jump of a single electron, according to the quantum mechanics the charge distributions for different energy states and also the distribution of oscillations created during a transition are highly symmetrical in respect to the nucleus. The oscillations of charges at a certain point for a transition $m\rightarrow n$ are given by the expression $e\psi_m{}^*\psi_n$ and the corresponding components of the dipole moment vector (matrix elements) are $\int\psi_m{}^*\mu_x\psi_n d\tau$, of the quadrupole tensor are $\int\psi_m{}^*Q_{xx}\psi_n d\tau$, and so on. If one of the energy levels is even and the other odd, all expressions for even multipole radiations vanish and such transitions are permitted only for electric dipole, octopole, . . . radiations. On the other hand, if both levels are even or both odd only quadrupole and higher even multipole radiations are permitted. The exact vanishing of odd or even integrals is not surprising since in writing the integrals the smallness of the atomic dimentions has been assumed (the phase differences between different parts of the atom were neglected). From the quantum mechanical expressions an additional rule can be derived for multipole radiations, namely that for a 2^n-pole radiation $J+J'\geqslant n$, where J and J' are quantum numbers for the lower and the upper states. The last rule is a generalization of the prohibition $J=0\rightarrow J'=0$ for the electric dipole radiation.

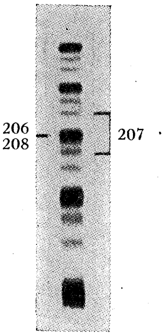

FIG. 6. Hyperfine structure of the electric quadrupole line λ5313 of PbI.

For the visible spectrum and the ground configurations $(a/\lambda)^2$ is of the order 10^{-7} or less. This means that the transition probability for the quadrupole radiation is at least 10^7 times smaller than for electric dipole lines. It is evident therefore that higher multipole radiations are of no practical importance. Electric quadrupole transitions can occur between levels of the same symmetry type with additional prohibitions $J=0 \rightarrow J'=0$, $J=\frac{1}{2}\rightarrow J'=\frac{1}{2}$ and $J=1\rightarrow J'=0$ (see above). From the expressions of the components of the quadrupole tensor Q the intensity and selection rules for multiplets and Zeeman effect were derived by Rubinowicz (1930). The J selection rule is $\Delta J=0, \pm 1, \pm 2$, and for the Zeeman effect $\Delta M=0, \pm 1, \pm 2$. The intensity rules of Rubinowicz for quadrupole multiplets (extreme (L, S) coupling) are in agreement with measurements of intensities in forbidden doublets of caesium $(^2D-{}^2S)$, for which Prokofjew (1929) found in absorption and in absence of an electric field approximately the theoretical ratio 3:2. Since for doublet spectra the intensity rules are predictable from the sum rules, therefore a check of the theoretical formulas for higher multiplicities would be desirable. Unfortunately no such forbidden multiplets have been observed yet in the laboratory. The transition probabilities in a forbidden series like $^2D-{}^2S$ decrease rapidly with the number of the line, quite a different behavior from the case of radiation enforced by an electric field (Section III). The ratio of transition probabilities of the forbidden lines $^2D-{}^2S$ to corresponding strongest electric dipole lines was found by Prokofjew (1929) to be of the order 5×10^{-6} (Na, K, Rb, Cs). The higher probability of quadrupole transitions than given above (10^{-7}) expresses the fact that the size of the excited alkali atoms is quite considerable. Prokofjew's data are in good agreement with theoretical calculations of Stevenson (1930).

The famous aurora line λ5577, which has been identified by McLennan as a forbidden transition $^1S_0-{}^1D_2$ of oxygen OI is of a quadrupole type (both levels belong to the same electronic configuration and therefore are of the same symmetry). The final proof of its character was given by Frerichs and Campbell (1930) who investigated the Zeeman effect of this line and found for the σ- and π-components at transverse observation a perfect agreement with theoretical predictions. The best confirmation of the theory was obtained by Segrè and Bakker (1931) who investigated the Zeeman effect in the forbidden lines $^2D-{}^2S$ of sodium and potassium. Since the doublet separations are small a Paschen-Back effect was observed. Extra components which disappear for longitudinal or transversal observation were found for intermediate directions. Rubinowicz's calculations were extended by Milianczuk (1932) over the whole range from weak to strong magnetic fields and a perfect agreement with Segrè's and Bakker's results was obtained.

More recently the investigations of quadrupole lines were directed towards investigation of their hyperfine structure. Opechowski (22) pointed out that intensity formulas and selection rules for hyperfine structure can be obtained simply from formulas of Rubinowicz by replacing the quantum numbers L, S and J by J, I and F, a procedure formerly applied in obtaining hyperfine structure intensity rules for permitted lines

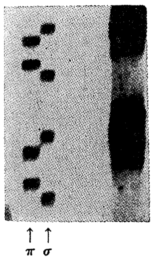

FIG. 7. Zeeman effect of the main component of the line λ5313 of PbI (isotopes 206 and 208).

from Hönl-Kronig formulas. On basis of the new formulas the hyperfine structure of the line λ2815 of Hg II ($^2D_{5/2}-{}^2S_{1/2}$) was satisfactorily explained by the author (22). The structure of another quadrupole line namely λ5313 of PbI was investigated (Fig. 6) and exact intensity measurements performed (24). For the isotope Pb_{207} the intensity ratio of h.f.s. components was found to be 1.55 ± 0.06, as expected (3:2). Unfortunately again only a doublet system has been investigated. The Zeeman effect of the same line was studied by Jenkins and the author (26) and for the main component (isotopes 206 and 208, no hyperfine structure) separations and intensities following from formulas of Rubinowicz were confirmed (Fig. 7). The more important part of this study was the investigation of the Zeeman effect in the h.f.s. components belonging to the isotope 207. The applicability of formulas of Rubinowicz after substituting in quantum numbers F for J was established.

As yet no bands of an electric quadrupole type were found in molecular spectra.

VII. MAGNETIC DIPOLE RADIATION

Brinkman (1932) showed that for the general case of a vibrating electron the second-order radiation beside the part representing the quadrupole radiation contains an additional part, corresponding to a wave created by the changes of the magnetic field at the point A (Fig. 5). The source of this wave is the vibrating magnetic dipole moment $M=-(e/2mc)r\times v$, where r is the distance of the electron from A and v its velocity. For the simple case discussed in Section VI of a linearly vibrating charge the vectorial product vanishes and no magnetic dipole radiation is emitted. Higher order radiations similarly contain parts corresponding to a radiation of a magnetic quadrupole (third order), octopole, and so on. In quantum mechanics it is calculated from the corresponding matrix elements of the magnetic dipole moment

$$M=-(eh/4\pi mc)(L+2S),$$

that the ratio of the transition probabilities of the magnetic dipole and electric dipole radiations for the magnetic moments occurring in the atomic systems is of the order of 10^{-5}. The magnetic dipole radiation is therefore in the visible and ultraviolet considerably more probable than electric quadrupole. However, the selection rules derived from the matrix elements cut down considerably the number of possible transitions, so that not many "permitted" magnetic dipole lines are observed. The symmetry of M (axial vector) relative to a reflection at the origin A is the same as for the quadrupole tensor, therefore only even→even and odd→odd transitions are permitted. For the pure (L, S) coupling no changes in quantum numbers L, S, or the electronic configuration are permitted; the only change occurs in J, for which $\Delta J=\pm1$ (Brinkman, 1932; Blaton, 1934). In other words transitions between levels of a multiplet differing in J by one unit are permitted. The magnetic dipole radiation corresponds to a change of relative directions of the vectors of the spin S and the orbital momentum L. Only one line satisfying all these selection rules was found in the past; Sambursky (1932) drew attention to the line λ6647 of HgII ($^2D^1_{3/2}-{}^2D^1_{5/2}$), which was recorded in the tables by Naudé (1929). The transition would correspond to a pure reversal of the spin. Unfortunately no closer study of its intensity, excitation conditions, or Zeeman effect was attempted. Quite recently Edlén (29) identified three lines in XeII, XeIII, and RnII as of a "permitted" magnetic dipole type. However all these lines are "permitted" for an electric quadrupole radiation (since $J+J'\geqslant 2$), and they all may have therefore a slight admixture of the quadrupole character (a few percent or less). As far as the author is aware, no pure "permitted" magnetic dipole line was ever observed. It would have to be a line $J'=1\rightleftarrows J=0$, since only such a transition is forbidden for electric quadrupole radiation.

Intercombination magnetic dipole lines were more frequently observed. Both selection rules $\Delta L=0$ and $\Delta S=0$ are at the same time violated. In Fig. 8 a level scheme for the ground configuration $6p^2$ of the atom of lead PbI is given. The arrangement of levels is typical for any p^2 or p^4 configuration, except for the order of the three ^3P levels in the p^4 case. For a pure (L, S) coupling only one transition of the second order is permitted; namely, a pure quadrupole line $^1S_0-{}^1D_2$ (not inserted in Fig. 8). For the oxygen

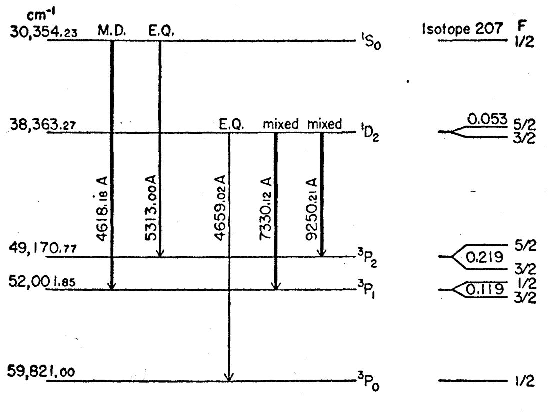

FIG. 8. The lowest levels of PbI, all belonging to the configuration $6p^2$. Arrows show transitions giving the forbidden lines investigated. On the right, the hyperfine separation of levels of the isotope 207 is shown, but not to scale. *M.D.* = magnetic dipole, *E.Q.* = electric quadrupole.

OI spectrum this is the famous aurora line λ5577, and this transition has the greatest probability in the whole group of forbidden lines of OI. Therefore the lifetime of the state $^1S_0$ is relatively short and of the order of $\frac{1}{2}$ sec. (assuming for el. dipole a trans. prob. 2×10^8 sec.$^{-1}$ and for $(a/\lambda)^2=10^{-8}$ in view of the small size of the oxygen atom). The probabilities of intercombinations for such a light element as oxygen are smaller by at least a factor of 10^6 (Section IV). The probability[2] of magnetic dipole intercombination transitions is therefore about 2×10^{-3} sec.$^{-1}$. The line $^1S_0-{}^3P_1$ is much weaker than λ5577, and its emission is of no importance for the lifetime of the $^1S_0$ state. In fact exact calculations, referred to in Section VIII, give a higher probability 9×10^{-2} sec.$^{-1}$, which however is still small in comparison to 2 sec.$^{-1}$, the exact value for the $^1S_0-{}^1D_2$ transition. This applies still more to the electric quadrupole transition $^1S_0-{}^3P_2$, since all intercombination electric quadrupole have transition probabilities of the order of 2×10^{-6} sec.$^{-1}$ (2×10^8 sec.$^{-1}\times10^{-8}\times10^{-6}$). From the state $^1D_2$ there are only intercombination transitions downwards, and therefore, the lifetime of the $^1D_2$ state is much longer, of the order of 500 seconds (the correct value is 100 sec.). Again the electric quadrupole intercombination transitions are negligibly weak. For this reason the observation reported several times about the detection of the line λ6391 ($^1D_2-{}^3P_0$, pure electric quadrupole intercombination) seems to the writer very doubtful. The other two lines λ6364 and λ6300 ($^1D_2-{}^3P_{1,2}$) are practically magnetic dipole, and their intensity ratio is calculated by methods given in Section VIII to 1:3. The intensity ratio has not been checked in the laboratory. In the spectra of nebulae Wright finds 1:3 for OI and 1:2 for NII.

The relations are different in the spectrum of lead PbI, since the coupling is considerably deviating from the pure (L, S) coupling. Here the highest transition probabilities of around 50 sec.$^{-1}$ correspond to the three magnetic dipole intercombination lines (assuming a factor 40 for intercombinations like in Hg). The lifetimes of both states $^1S_0$ and $^1D_2$ are approximately equal. The relatively high transition probabilities explain the high intensity of forbidden lines which can be obtained in a discharge tube. The probability of the permitted electric quadrupole transitions is also somewhat increased since the lead atom has a bigger size than oxygen—instead of 2 sec.$^{-1}$; here it is of the order of 40 sec.$^{-1}$ (for intercombinations around 1 sec.$^{-1}$). The percentage admixture of the electric quadrupole radiation for this element is considerably higher and can become of importance (see Section VIII).

As Blaton and Niewodniczanski (1934) recognized, there is among the lines of lead one line namely λ4618 ($^1S_0-{}^3P_1$) of a pure magnetic dipole type. By investigation of the Zeeman effect in this line, Niewodniczanski (1934) obtained the first proof of the existence of magnetic dipole radiation. In transverse observation the effect should be similar to an effect for an electric dipole line (the same selection and intensity rules), only the polarization of the π- and σ-components should be interchanged, since the source of the wave is not an electric but a magnetic dipole. This is exactly what is observed. In Fig. 9 a photograph of the Zeeman effect obtained with a Fabry-Perot etalon for the main component of λ4618 (isotopes 206 and 208) is

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[2] The factor 10^{-5} for magnetic dipole and 10^{-6} for intercombination, together give a factor 10^{-11} times the transition probability for electric dipole 2×10^8 sec.$^{-1}$. Why no additional factor for the violation of the rule $\Delta L=0$ is added, is explained in Section VIII.

reproduced (26). This photograph was obtained by consecutive illumination of the two halves of the slit of the spectrograph with light of different polarizations. (Like the Fig. 7.) The line λ4618 shows a reversed pattern in comparison to several weaker electric dipole lines visible on the same photograph.

The hyperfine structure of the isotope Pb_{207} in λ4618 gives two components with intensities proportional to the statistical weights of the h.f.s. levels (24). Only components for $\Delta F=0, \pm 1$ are observed. The same rules are also approximately holding true for the h.f.s. components of the line λ7330, which has a predominantly magnetic dipole character. The applicability in hyperfine structure of electric dipole intensity formulas to the magnetic dipole radiation has been shown by Gerjuoy (28) to be based on the similarity of commutation rules for the vectors $M(L+2S)$ and μ in respect to J. He pointed out further that these rules are still almost exactly true for intercombination lines in spite of their perturbational nature. The perturbational nature is shown for instance by the failure of the sum rules to give the relative intensities in the fine structure multiplets. The same holds true in respect to the quadrupole radiation and explains why in the intercombination line λ5313 the Rubinowicz-Opechowski formulas have been confirmed. The Zeeman effect in h.f.s. (isotope Pb_{207}) was observed in the lines λ4618 and λ7330 for fields high enough to produce a partial Back-Goudsmit effect and results similar to electric dipole lines only with reversed polarizations were obtained (26, 27).

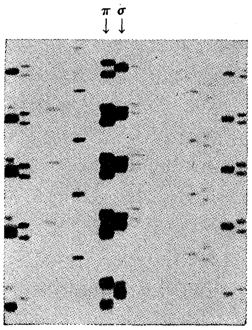

FIG. 9. Zeeman effect in the magnetic dipole line λ4618 and adjacent electric dipole lines of PbI (main components, isotopes 206 and 208).

In band spectra the only band system until now identified as a magnetic dipole transition is the atmospheric absorption bands of oxygen ${}^1\Sigma_g{}^+ - {}^3\Sigma_g{}^-$. The transition was identified as such on basis of its rotational structure by Van Vleck (1934). The radiation may have a slight admixture of electric quadrupole character; however, no branches for $\Delta J = \pm 2$ were detected. The absorption coefficient is too high for an electric quadrupole but agrees well with a magnetic dipole radiation. Another band of oxygen in infra-red is possibly of the same type (${}^1\Delta_g - {}^3\Sigma_g{}^-$).

VIII. MIXED SECOND-ORDER RADIATION

In the preceding section it was shown how to evaluate roughly the transition probabilities of electric quadrupole and magnetic dipole transitions. The exact values for these quantities are of special importance for the astrophysicists. The early calculations of Stevenson (1932) and of Condon (1934) were superseded a few years ago by new ones performed by Pasternack (25) for configurations p^2, p^3, p^4, d^2, and d^3 and for a series of light elements and their ions. For the whole range of couplings (from (L, S) all through to a pure (j, j)-coupling) and for the configurations p^2, p^3, and p^4, extensive calculations were performed by Shortley, Aller, Baker, and Menzel (26), and the results published in tabular form.

In such calculations the extent of the mixing of the wave functions of levels with the same quantum number J is first determined. If the assumption is made that only levels belonging to the given configuration mix (which in actual cases is not always true; see below), then the coefficients of the wave functions can be represented as a function of a single parameter χ which measures the deviation from the limiting case of coupling. For a given deviation χ, the coefficients of the wave functions are easily calculated and consecutively the matrix elements of the magnetic dipole and of electric quadrupole determined. The transition probabilities for magnetic dipole transitions are then directly obtained from the squares of the matrix elements by multiplication with a certain factor containing the cube of the frequency of the line. However for electric quadrupole transitions, they have to be multiplied by a factor containing the fifth power of the frequency and also by the square of the radial integral

$$s=\int_0^\infty r^2\cdot R^2(r)dr,$$

where $R(r)$ is the radial part of the orbital (wave function). The last factor expresses the dependence of the intensity of the electric quadrupole radiation from the size of the emitting source (Section VI).

Shortley, Aller, Baker, and Menzel (26) tabulated quantities proportional to the squares of the matrix elements; from their tables the absolute transition probabilities of all magnetic dipole lines for the given configuration and also the relative probabilities of all electric quadrupole lines can be found. In order to find the absolute transition probabilities for the electric quadrupole lines and to calculate the lifetimes of metastable levels by combining the transitions of both types, the knowledge of the radial integral is necessary. This integral, which is also of importance for the diamagnetic susceptibility of the gas, is very hard to determine exactly because the distribution of the electronic density in the outer parts of the atom is not known with high enough accuracy. Only estimates can be made in taking Hartree fields or using hydrogenic wave functions with screening constants. Pasternack (25) performed such calculations for a number of light atoms and tabulated the theoretical transition probabilities. However in view of the uncertainty of calculations, especially in case of heavier elements, a different approach seems to be more promising. A measurement of a ratio of intensities of two lines originating from the same upper level is sufficient for experimental determination of the ratio of the magnetic dipole to electric quadrupole transition probabilities and consequently of the radial integral s. Intensity ratios for other pairs of lines would serve as an additional determination of s and as a check for the theoretical relations.

Such measurements of intensities have at present been performed only in one case, namely for the spectrum of lead PbI (24). In order to find the matrix elements, the deviation from the (L, S) coupling had to be determined by fitting the actual energy levels as closely as possible by a parametric formula (small deviations which cannot be removed by variation of the parameters are explained as caused by admixtures of wave functions of levels of other configurations). From the experimental ratio of intensities of the lines λ4618 (magnetic dipole) and λ5313 (electric quadrupole, see Fig. 8), a value of

$$s^2=\left(\int_0^\infty r^2R^2(6p)dr\right)^2=171$$

was obtained in this way by Gerjuoy (29). The value should, however, be increased to around 240, since in the evaluation of the measurements the author forgot to introduce a correction for the change of the dispersion of a spectrograph (24), and Gerjuoy on the other hand took the intensity ratio as the ratio of transition probabilities without correcting it for the difference in frequencies of the lines.

The ratios of intensities in the other group of lines of PbI, λ9250, λ7330, and λ4659, found equal to 0.9 : 1 : 0.01 (after making all corrections) are in a reasonable agreement with the theory (29). They do not furnish however an additional check for the relations, since the percentage admixture of the electric quadrupole radiation is relatively low (which can be seen from the intensity of the line λ4659), and the ratio of the first two lines is consequently insensitive to a change in s^2. In view of the discrepancy with the results found in the interference effect (see end of this section), all intensity measurements for this spectrum should be repeated, and it is believed the accuracy could be considerably increased without meeting special difficulties.

From other known forbidden spectra which deserve special attention in connection with this problem, the spectrum of tellurium TeI should be mentioned first, since the intensity ratios of three lines originating from the level $^1S_0$ could be determined: namely, of λ7909, $^1S_0-{}^1D_2$ permitted electric quadrupole, λ5420, $^1S_0-{}^3P_1$ intercombination magnetic dipole, and λ4309, $^1S_0-{}^3P_2$ intercombination electric quadrupole. According to Niewodniczanski and Lipinski (20), the lines can be obtained with considerable intensity. The case is also interesting in connection with the mixed arrangement of levels in the multiplet ^3P.

A determination of the ratio of intensities of lines λ5577, ${}^1S_0-{}^1D_2$ and λ2972, ${}^1S_0-{}^3P_1$ in oxygen OI (21) would also present a good opportunity for determination of s^2. Equally interesting would be an investigation of the forbidden lines of BiII (not yet observed), in view of the high spin moment of the nucleus ($I=9/2$).

More recently a group of forbidden lines in the spectrum of bismuth BiI was studied with a spectrograph of high resolving power (32). In Fig. 10 the level scheme for the normal configuration of bismuth $6p^3$ is given, and all lines found on the spectrograms indicated. Two lines marked by broken lines were not observed, but it seems certain they would be found if the investigation were carried out with a medium spectrograph. The spectrum of bismuth presents an excellent opportunity for an experimental study of the intensity relations since four lines originate from the same upper level ${}^2P_{3/2}$. As the study of the hyperfine structure of the lines reveals, most of the lines seem to have a predominantly magnetic dipole character. However, quite considerable admixtures of an electric quadrupole character are highly probable. Since the coupling is deviating strongly from the (L, S) coupling, the intercombination factor is about equal or smaller than for mercury (40). Therefore the lifetimes of the metastable levels are probably all about equal and of the order of 10^{-2} sec.

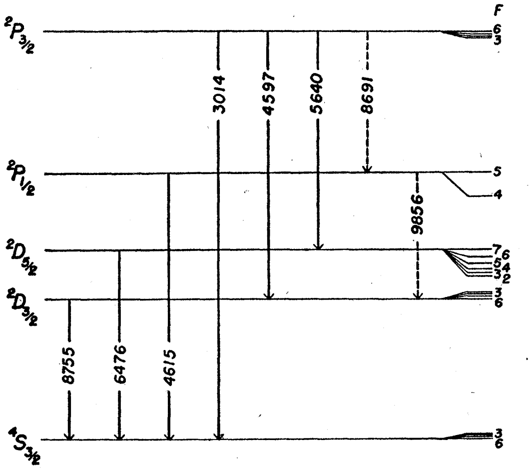

FIG. 10. The lowest levels of BiI, all belonging to the configuration $6p^3$. Full arrows show transitions giving the forbidden lines investigated. On the right, the hyperfine separation of levels in a 1000 times larger scale.

(the intercombination factor has to be applied to the lines λ4597 and λ5640; for reasons see the discussion of NI). Only for the lowest metastable level ${}^2D_{3/2}$ may the lifetime be a little longer, because the transition ${}^2D_{3/2}-{}^4S_{3/2}$ is forbidden for the magnetic dipole radiation and pure (j, j) coupling.

Different relations are found in the spectrum of nitrogen (NI), where the lifetimes of the two doublet states ${}^2P$ and ${}^2D$ differ very strongly. The situation is somewhat similar to the case of OI discussed in Section VII. The lifetime in the ${}^2P$ level is of the order of 2 seconds, since the ${}^2P-{}^2D$ transitions are the only ones permitted for electric quadrupole radiation. All other transitions are forbidden for the second-order radiation and the pure (L, S) coupling. The magnetic dipole part is also forbidden for the transition ${}^2P-{}^2D$, since it violates the selection rule $\Delta L=0$. The violation of both selection rules $\Delta L=0$ and $\Delta S=0$ has the same origin—mixing of wave functions, therefore transition probabilities for lines violating one of the rules or both of them are approximately equal. No extra factor for violation of both rules at the same time is necessary; therefore the intercombination factor will take care of both or any of the two violations (see the evaluations for OI in Section VII, where the violation of $\Delta L=0$ was not taken in consideration). The magnetic dipole transition probability for ${}^2P-{}^2D$ is therefore small, of the order of 5×10^{-3} sec.$^{-1}$ and approximately equal to the probability of the transition ${}^2P-{}^4S$.

The lifetime of the state ${}^2D$ of nitrogen is unusually long, around 3×10^4 sec. or 8 hours. A simple evaluation of the transition probability for the intercombination line ${}^2D-{}^4S$ gives for magnetic dipole 5×10^{-3} sec.$^{-1}$ (see above ${}^2P-{}^2D$ and ${}^2P-{}^4S$) and for electric quadrupole 10^{-5} sec.$^{-1}$. The exact calculations (25) show, however, a presence of an additional prohibition for the magnetic dipole radiation, the meaning of which in terms of the vector model is not clear to the author, but which cuts down the magnetic dipole transition probability by a factor of 10^{-4}, that is far below the electric quadrupole probability (a similar additional prohibition acts for the ${}^2P-{}^4S$ transition but this time in relation to the electric quadrupole only). The line λ5200, ${}^2D-{}^4S$ is therefore of an almost pure electric quadrupole type. It is really remarkable that a line with such a terribly low transition probability of 3×10^{-5} sec.$^{-1}$ can be observed at all in the laboratory (21). It is regrettable that until now no fuller report of the work, and no photographs of the spectra were published by Kaplan and his associates.

In the discussion of the intensities of mixed lines, the additivity of the intensities of radiations of both types was assumed. In the classical theory the waves emitted in a certain direction will in general interfere with each other if the system of vibrating charges is emitting at the same time two waves of the same frequency and polarization. The phase difference between the two waves will change with the direction, and for a great number of systems with a random distribution of direction of axes, the effect should average out to zero. When, however, an external field is applied and single components are observed into which a spectral line separates, it is the light emitted by transitions corresponding to atoms with a certain definite directional distribution of axes which is studied. It should therefore be expected that the relative intensities of components in the Zeeman effect will not be represented by a simple overlapping of two patterns corresponding to a magnetic dipole and an electric quadrupole radiations taken in proportion to their emission probabilities. Components which are emitted by both kinds of radiation should show departures from the simple additivity of intensities caused by interference; the sum of departures for all components of a definite polarization should, however, be equal to zero. Also for a single component and all directions of observation relative to the field, the interference effect should average out to zero.

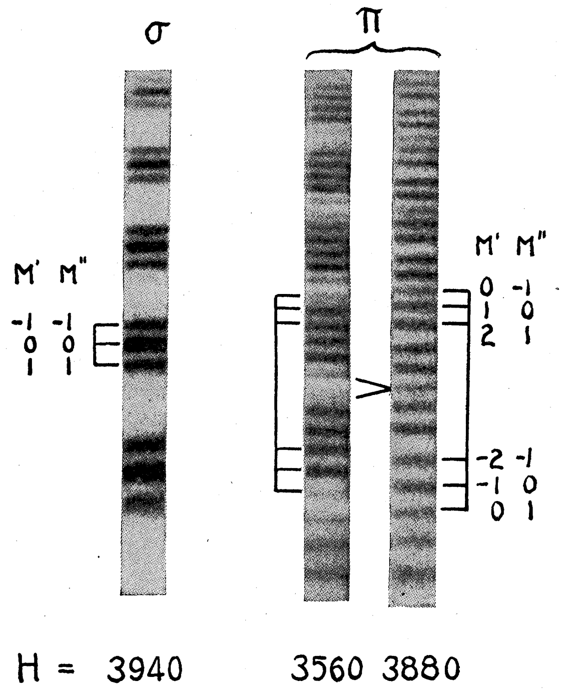

FIG. 11. Fabry-Perot pattern of the Zeeman effect for the line λ7330 of PbI and with magnetic fields indicated. The components belonging to one order are marked in each case.

The probable existence of such an effect was pointed out by Dr. L. I. Schiff in discussions in the spring of 1940. Quantum mechanical calculations of Gerjuoy (29) confirmed Schiff's expectation. Quite independently a similar prediction was made by Shortley, Aller, Baker, and Menzel (26). The existence of the interference effect has been experimentally established by Jenkins and the author (28) in a study of the Zeeman effect of the central component of the line λ7330 of lead PbI (isotopes 205 and 208). All six π components polarized parallel to the field in transverse observation are of a mixed nature. None of the σ-components in the perpendicular polarization is of a mixed type. By measuring the ratio of intensities of the electric quadrupole σ-components to the magnetic dipole the admixture of the electric quadrupole radiation was determined to be approximately 2 percent. For the two triplets of π-components the ratio of intensities for pure magnetic dipole radiation should be 6:3:1 (usual dipole formulas), for a pure electric quadrupole 4:2:6 (Rubinowicz formulas). If one assumes additivity of intensities and a 2 percent electric quadrupole admixture, the expected ratio would be 6:3:1.09—ratios almost not differing from the pure magnetic dipole case. The observed intensities are very different from that, as can be seen from photographs of Fabry-Perot patterns reproduced in Fig. 11. The measured ratio, after making some corrections for hyperfine structure overlappings (isotope 207), is rather close to 4.5:3.9:1.7. This shows that the first π-component is too weak by 1.5, the two other too strong by 0.9 and 0.6. This presents a definite proof of the existence of the interference, especially since the theory predicts a weakening of the first component by $2X$ and an increase of the two others by X, where X is a number proportional to the square root of the quadrupole percentage.[3] For 2 percent quadrupole X is equal to about 0.6, and the predicted pattern would be 4.8:3.6:1.7, not very far off from the observed ratio.

The great importance of the interference effect lies in furnishing a method of determination of very small admixtures of the electric quadrupole radiation with high accuracy.[3] The establishment of an interference between two kinds of radiations emitted simultaneously by the atom is very interesting. There are however several difficulties which in the writer's opinion have to be cleared before the agreement with the theory can be considered as satisfactory. First of all, as already mentioned, corrections had to be introduced because of the overlapping by Zeeman components of the isotope Pb_{207}. It is very doubtful if the positions and intensities of these components can be predicted with sufficient accuracy. Further an unsymmetry in intensities is observed in the main pattern which could not be explained by overlapping of components belonging to Pb_{207}. Finally, the result of 2 percent quadrupole is in disagreement with the percentage calculated by using the value 240 for the square of the radial integral s determined from the ratio of intensities of lines λ4618 and λ5313 (more than 6 percent is obtained). New precise intensity measurements of the interference effect in the line λ7330 should therefore be performed for transverse and for longitudinal observation. The interesting feature of the interference effect predicted is that the effect is reversed in longitudinal observation, the ratios of intensity being for triplets $\Delta M = \pm 1$ for transverse effect $(6-2X):(3+X):(1+X)$ and for the longitudinal effect $(6+2X):(3-X):(1-X)$. In order to avoid all difficulties introduced by overlappings of components of Pb_{207}, this time a pure isotope of lead (uranium lead) should be used. In such a way a highly accurate value of the quadrupole percentage could be obtained. The interference effect should be further looked for in mixed lines of other elements and also in the Zeeman effect of hyperfine structure components, and the results should be compared with results of measurements of relative intensities of lines originating from the same upper level (see the first half of this section). In general our present knowledge of mixed radiation is still quite fragmentary and of a rather qualitative character.

CONCLUSION

Two general methods were developed for identification of the type of a forbidden line in atomic spectra. One is the study of the Zeeman effect; the other is the investigation of the structure of the line (width, isotope effect and hyperfine structure). In both methods an investigation of the line with an apparatus of high resolving power is necessary. For molecular spectra the identification can be best performed by a study of the rotational structure of the band.

This report attempted to give a simple presentation of newer developments in the field of forbidden radiations. The content has been limited to a discussion of results obtained by the spectroscopists in the laboratory and their theoretical interpretation. Only atoms and diatomic molecules were treated in this report, and discussion of forbidden transitions in polyatomic molecules was not included. A discussion of many other topics has been also omitted for lack of space and time. A great number of very interesting and important results were obtained recently by the astrophysicists. We mention only the identification of the corona lines (Edlén). The forbidden transitions are of great importance in liquids and solids, for instance in the case of absorption, fluorescence, and phosphorescence of dye molecules (Jablonski), and of the rare earths (Freed and Weissman). Finally forbidden transitions occur in x-rays and also in γ-rays. In this last case an interesting method for determination of the multipole order of γ-radiation from the ratio of the conversion coefficients has been worked out recently (Berkeley group). In view of the definition adopted in the introduction, it

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[3] If A is the amplitude of the magnetic dipole and a of the electric quadrupole wave the intensities of magnetic dipole and electric quadrupole radiations will be proportional to A^2 and a^2, the interference effect however is proportional to $A \cdot a$, and is therefore many times stronger than the electric quadrupole admixture (this is true only for $a \ll A$).

appears doubtful, however, if second order γ-radiation should be called forbidden, since the factor $(a/\lambda)^2$ makes the intensities of the first- and second-order radiations differ much less than for the optical and even less than for the x-ray case.

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Three excellent reviews on the subject of forbidden lines were published in the past (No. 1–3). These reviews contain quite complete lists of references. References to papers mentioned there or in some other papers listed below will be omitted here. Recently the author published a very condensed review of the newer results in this field (No. 4). The list of references is probably quite incomplete, especially for Section III and IV.

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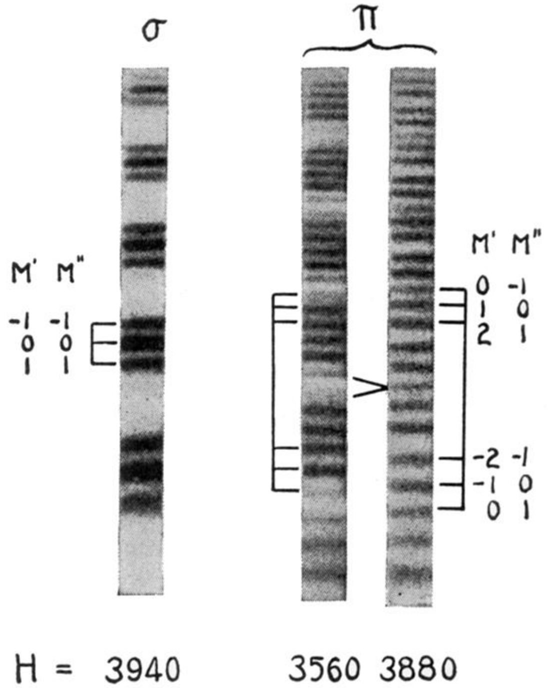

FIG. 11. Fabry-Perot pattern of the Zeeman effect for the line λ7330 of PbI and with magnetic fields indicated. The components belonging to one order are marked in each case.

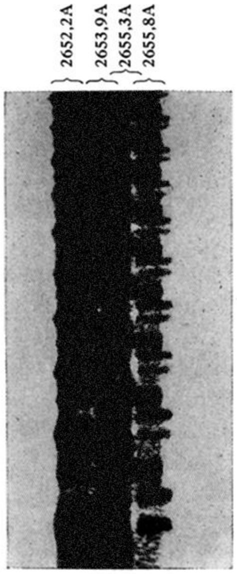

Fig. 2. Structure of the forbidden line λ2655.8 ($6^3P_0-6^1S_0$) of mercury. A Fabry-Perot etalon was crossed with a large spectrograph. Exposure time 6 hours.

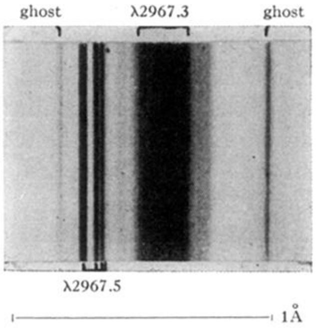

FIG. 4. Photograph of the forbidden line λ2967.5 obtained in the third order of a 30-foot grating (dispersion 0.2 A per mm).

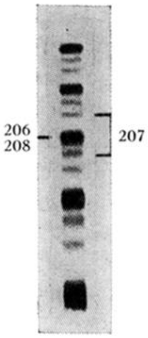

FIG. 6. Hyperfine structure of the electric quadrupole line λ5313 of PbI.

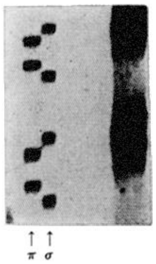

Fig. 7. Zeeman effect of the main component of the line λ5313 of PbI (isotopes 206 and 208).

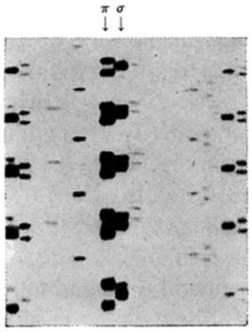

FIG. 9. Zeeman effect in the magnetic dipole line λ4618 and adjacent electric dipole lines of PbI (main components, isotopes 206 and 208).