THE APPEARANCE OF "FORBIDDEN LINES" IN SPECTRA

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ABSTRACT

A rough calculation shows that the quadrupole term in the radiation of a forbidden line is usually larger than the dipole produced by an external electric field. This is not true, however, when there is an intermediate state, with which both initial and final states combine, and which lies close to one of them.

If the J selection rule is violated, and the Laporte rule is obeyed, the radiation cannot be due to the quadrupole term and must be ascribed to the octopole. Hg 2270 is such a line. An octopole transition will have a Zeeman effect distinctively different from that of a dipole or quadrupole.

THE ordinary spectroscopic selection rules are derived from a consideration of the "dipole radiation" only. This dipole radiation is essentially the first term in the series when the vector potential is developed in powers of the atomic radius divided by the wave-length of the emitted light. For most practical purposes, the first term of this series is amply sufficient to represent the experimental results; but in some cases where the first term is zero, it is necessary to consider the higher terms which give the quadrupole, octopole, etc.

Rubinowicz[1] has recently written a series of papers in which he has developed general methods for dealing with multipole radiation, and has applied them in some detail to quadrupole radiation. We wish to call attention in this note to a few additional properties of quadrupole radiation, and to point out the existence of lines which represent octopole radiation.

INTENSITY OF QUADRUPOLE RADIATION COMPARED WITH THAT DUE TO THE PERTURBATION OF THE ATOM BY AN ELECTRIC FIELD

The presence of an external field will always disturb an atom so that the dipole selection rules will no longer be strictly valid. Thus, it is sometimes thought that the appearance of a "forbidden line" is to be ascribed to an interatomic field sufficient to break down these rules. It is possible, however, to express the intensity of the quadrupole radiation, and of the radiation of the disturbed atom, in so nearly the same form that their relative probabilities can be inferred from a knowledge of the ordinary features of the spectrum. This comparison shows that in most cases, and particularly in the case of the auroral line, the fields necessary to produce the perturbation are much larger than are to be expected under the conditions of the experiments. With respect to the auroral line, Frerichs and Campbell[2] have already shown

[1] A. Rubinowicz, Zeits. f. Physik **53**, 267 (1929); **61**, 338 (1930).

[2] Frerichs and Campbell, Phys. Rev. **36**, 151 (1930).

its quadrupole nature from its Zeeman effect; but it is also of interest to see how the relative intensities of quadrupole and perturbed dipole may be correlated with other features of the spectrum.

Since the total intensity, in the presence of a vanishingly small magnetic field, is the same in all directions, we may take 4π times the intensity per unit solid angle in the z direction as the total intensity. For quadrupole radiation, we may write this as follows:

$$\begin{aligned} I_{kj} &= (16\pi^4 e^2/c^5)\nu_{kj}^6\left\{\int \tilde{\psi}_k z(x+iy)\psi_j d\tau\right\}^2 \\ &= (16\pi^4 e^2/c^5)\nu_{kj}^6\left\{\sum_l z_{kl}(x+iy)_{lj}\right\}^2 \end{aligned} \tag{1}$$

where

$$z_{kl} = \int \tilde{\psi}_k z \psi_l d\tau \,.$$

In this equation k and j represent the states between which the quadrupole transition takes place, ν_{kj} represents the frequency of the emitted light in $\sec^{-1}$, while x, y, and z represent the coordinates of the electrons. A summation over all electrons is implied. The coordinates with the subscripts attached represent the components of the dipole moments connected with the indicated transition. Thus the quadrupole radiation may be expressed in terms of the dipole moments.[3]

The intensity of the quadrupole is thus expressed in terms of a sum of products of the dipole transitions to all the states l with which both k and j combine according to the dipole selection rules. In many cases the order of magnitude can be estimated by considering one term. However, an investigation of the convergence of the series would probably be rather difficult.

The intensity of a transition produced by a weak uniform electric field may be expressed in a similar way. Of course the interatomic fields which actually produce violations of the selection rules are not uniform fields, but the deviations from uniformity will produce an effect of higher order which we may neglect for a first approximation.

The solution of the Schroedinger equation with an electric field may be written in the first approximation

$$\psi_k' = \psi_k + F\sum_l A_{kl}\psi_l \tag{2}$$

where the ψ_l are the solutions with zero field and F is the field strength in electrostatic units per cm. The coefficients have the definition

$$A_{kl} = \frac{ez_{lk}}{h\nu_{lk}} \text{ and } \tilde{A}_{kl} = \frac{ez_{kl}}{h\nu_{kl}}\cdot$$

[3] Bartlett, Phys. Rev. **34**, 1247 (1929).

The electric moments connected with a transition k-j are then

$$\begin{aligned}(x+iy)_{kj} &= F\Big\{\sum_l A_{jl}(x+iy)_{kl} + \sum_l \bar{A}_{kl}(x+iy)_{lj}\Big\} \\ &= F\sum_l \frac{e}{h\nu_{lj}\nu_{kl}}\big\{(x+iy)_{kl}z_{lj}\nu_{kl} + z_{kl}(x+iy)_{lj}\nu_{lj}\big\}.\end{aligned} \tag{3}$$

With this expression, it is possible to write the intensity of the perturbed dipole transition.

$$I_{kj} = (2\pi^3\nu_{kj}{}^4F^2/c^3)\left[\sum_l \frac{e}{h\nu_{lj}\nu_{kl}}\big\{(x+iy)_{kl}z_{lj}\nu_{kl} + z_{kl}(x+iy)_{lj}\nu_{lj}\big\}\right]^2. \tag{4}$$

The summation is seen to contain the same quantities as are in Eq. (1) but with a slightly different dependence upon the frequencies. If we consider only one intermediate state, we can divide out the frequencies and determine the ratio of the radiation caused by an electric field to that normally due to the quadrupole term. For the auroral line if we consider only the ^1P state next above the ^1S and the ^1D states, we get this ratio equal to $3.10^{-16}V^2$ where V is the electric field in volts per cm. This indicates that, under ordinary conditions of excitation, the quadrupole term is much larger than the dipole. If, however, the intermediate state were closer to the two states involved in the transition or to one of them, so that the frequencies in Eq. (4) were smaller, the dipole would be relatively somewhat stronger. This is the case in the Stark effect in He where the intermediate level l is very close to the initial level k.[4]

Eq. (1) shows that a quadrupole transition between terms of different multiplicities will be weaker than the corresponding transition between terms of the same multiplicity in the same ratio as in dipole radiation, since one of the dipole moments must be that of an inter-combination. This explains why the auroral line is so much easier to produce in the laboratory than the corresponding intercombinations which appear in the nebulae.

Selection Rules for Multipole Radiation

Rubinowicz has worked out the selection and intensity rules which are to be derived from Eq. (1). It is important, however, to notice the place which Laporte's rule holds. As this rule is now formulated, there are two kinds of terms which may be designated as odd and even terms. The rule states that for dipole radiation, odd terms combine only with even terms, and vice versa. In the quadrupole, however, odd terms may combine with odd terms, and even with even, since there are terms of the other kind with which each combine. But an odd term cannot combine with an even, since there can be no common state with which both can combine with a dipole moment. This can also be shown by the group theory of Neuman and Wigner.[5] It is essential, then, for the existence of a quadrupole moment, that the Laporte rule be violated.

[4] Jane Dewey, Phys. Rev. **28**, 1108 (1926).
[5] Neumann and Wigner, Zeits. f. Physik **49**, 73 (1928).

The two selection rules which are rigorously valid for dipole radiation in any atom are Laporte's rule and the inner quantum number or the J rule. If the Laporte rule is obeyed, and the J rule is violated, neither the dipole nor the quadrupole moments can be different from zero. If such lines do appear, and ${}^1S_0-{}^3P_2$, $\lambda 2270$ in Hg is one of them, the radiation must be ascribed to an octopole moment.

We may make the following tabulation of the selection rules where the first column gives the first term in the series expansion which can be different from zero.

Radiation	*Laporte's Rule*	*J Rule*
Dipole	Obeyed	Obeyed
Quadrupole	Violated	Obeyed or Violated
Octopole	Obeyed	Violated

The 0-0 transition for J is always forbidden in the absence of an external field.

The intensity for an octopole transition can be represented in the same form as the quadrupole in Eq. (1), except that it is a function of a sum of products of three dipole moments involving two intermediate states. The intensity is correspondingly less than for a quadrupole.

The Zeeman Effect of Octopole Radiation

The fact that the line Hg 2270 is much harder to produce than the auroral line lends some experimental support to the idea it is an octopole transition. If would be of some interest, however, to confirm the fact by an observation of the Zeeman effect. In an octopole line the magnetic quantum number can change by 0, ± 1, ± 2, ± 3, but in the line Hg 2270 the change of ± 3 cannot appear since one state has an inner quantum number 2 and the other 0. Hence the pattern will be equivalent to a quadrupole except for the polarization. By the method of Rubinowicz it is possible to determine this polarization. It is not necessary to indicate the calculations since they follow Rubinowicz exactly; but the results are given in the table. This is distinctly different from the quadrupole polarization when viewed at right angles to the lines of force.

Polarization of the octopole Zeeman effect.

					Polarization	
Octopole Moment	m jumps to	$\alpha=0$	$\alpha=35°$	$\alpha=45°$	$\alpha=55°$	$\alpha=90°$
z^3	m	0	π	π	π	0
$z(x+iy)(x-iy)$	m	π	π	π	π	0
$z^2(x+iy)$	$m-1$	0	Elliptical	Elliptical	σ	Left Circular
$z^2(x-iy)$	$m+1$	0	"	"	σ	Right Circular
$(x+iy)^2(x-iy)$	$m-1$	σ	"	"	Elliptical	0
$(x+iy)(x-iy)^2$	$m+1$	σ	"	"	"	0
$z(x+iy)^2$	$m-2$	π	σ	"	"	0
$z(x-iy)^2$	$m+2$	π	σ	"	"	0
$(x+iy)^3$	$m-3$	σ	Elliptical	"	"	0
$(x-iy)^3$	$m+3$	σ	"	"	"	0

It is interesting to notice that the longitudinal effect has the same pattern in the octopole term as in the dipole and the quadrupole. Although in general an undisplaced component is permitted in the transverse effect, for the line Hg 2270 this will have zero intensity, so that the pattern will be the same as the quadrupole except for the reversed polarizations.

Note Added August 15: Dr. Bowen has called our attention to the fact that the line $\lambda 2270$ in Hg is probably due to the coupling of the nuclear spin with the electronic angular momentum. An estimate based on the relative separation of the multiplets and the hyperfine structure gives the right order of magnitude for the intensity. The statements made above with respect to J really refer strictly to the total angular momentum.