PHYSICAL REVIEW VOLUME 99, NUMBER 6 SEPTEMBER 15, 1955

Two-Quantum Transitions in the Microwave Zeeman Spectrum of Atomic Oxygen*

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(Received May 20, 1955)

Two-quantum transitions have been observed in the microwave Zeeman spectrum of atomic oxygen in its ground $^3P_2$ state by the method of magnetic resonance absorption spectroscopy. The three lines observed originally by Rawson and Beringer are identified as arising from two-quantum transitions between Zeeman levels with the selection rule $\Delta M=\pm 2$. Each of the three lines is observed at the mean frequency of the two corresponding $\Delta M=\pm 1$ transitions to within the experimental accuracy of a few parts per million. The line width of the two-quantum transitions is approximately one-half that of the normal transitions, and the line intensity varies more rapidly with rf power, both in agreement with the theory. The principal features of these transitions are explained by second-order time-dependent perturbation theory. The two-quantum transitions reported here are essentially similar to the double-quantum transition reported by Hughes and Grabner in the electric quadrupole spectrum of $Rb^{85}F$ and to the multiple-quantum transitions seen by Kusch in the Zeeman spectra of K and O_2.

1. INTRODUCTION

A MULTIPLE quantum transition between two atomic or molecular energy levels is a transition in which the energy is supplied by two or more quanta. The transition is forbidden in first order perturbation theory and occurs through one or more intermediate states. In recent years, several examples of multiple-quantum transitions have been reported in atomic and molecular beam experiments. A double-quantum (or half-frequency) transition was first observed in the electric quadrupole spectrum of $Rb^{85}F$ by Hughes and Grabner using the molecular beam electric resonance method.[1] The transition was interpreted by second order perturbation theory, according to which two equienergetic quanta, each of one half the Bohr frequency for the transition, supply the energy for the transition.[2] Also it was pointed out that the line width for a double-quantum transition should be one-half that of a single-quantum transition in agreement with the experimental observation. Subsequently, it was shown experimentally and theoretically that the transition occurs also if two different frequencies are applied, provided that the sum of the two frequencies equals the Bohr frequency for the transition.[3] Recently Kusch observed double- and triple-quantum transitions in the Zeeman spectrum of K and O_2[4]; Braunstein and Trischka observed double-quantum transitions in the Stark spectrum of LiF molecules[5]; Hamilton *et al.* observed multiple-quantum transitions in the hyperfine spectrum of Au^{198}.[6] The theory of transitions involving the emission or absorption of two quanta (processes closely related to the Raman effect) was first discussed by M. Goeppert Mayer on the basis of the Dirac radiation theory.[7] Recently Salwen has discussed the line shapes of multiple-quantum transitions, including the effect of the velocity distribution in an atomic beam experiment.[8]

It is the purpose of this paper to point out an example of a double-quantum transition in the Zeeman spectrum of atomic oxygen observed in a microwave magnetic resonance absorption spectroscopy experiment. The double-quantum transitions being reported here were observed originally by Rawson and Beringer but remained unidentified.[9] Further, a slight variation of the second order perturbation theory originally proposed to explain double-quantum transitions in electric quadrupole spectra[2] is applied to double-quantum transitions in Zeeman spectra of the type observed by Kusch and reported here.

A preliminary report of this work has already appeared.[10]

2. EXPERIMENTAL DATA

The ground state of atomic oxygen is a $(2p)^4$ configuration with three fine-structure levels as shown in Fig. 1. In the presence of a magnetic field the $^3P_2$ level is split into five magnetic sublevels designated by the magnetic quantum number M with values from -2 to $+2$. Because of incipient Paschen-Back effect, i.e., the mixing in of $^3P_1$ state by the magnetic field, adjacent magnetic sublevels of the $^3P_2$ state are not equally spaced, and hence the magnetic resonance spectrum consists of four lines.

The method of observation was the microwave magnetic resonance absorption method developed by Beringer and his students,[11] and the apparatus was that

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* This research has been supported in part by the Office of Naval Research.

† To be submitted by J. S. Geiger in partial fulfillment of the Ph.D. thesis requirement at Yale University.

‡ Loomis-Sheffield Fellow, 1954–55.

[1] V. W. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

[2] V. W. Hughes and L. Grabner, Phys. Rev. **79**, 828 (1950).

[3] L. Grabner and V. W. Hughes, Phys. Rev. **82**, 561 (1951).

[4] P. Kusch, Phys. Rev. **93**, 1022 (1954).

[5] R. Braunstein and J. W. Trischka, Phys. Rev. **98**, 1092 (1955); private communication from J. W. Trischka on Li^6F^{19}.

[6] Private communication from D. R. Hamilton.

[7] M. Goeppert Mayer, Ann. Physik **9**, 273 (1931). See also G. Breit, Revs. Modern Phys. **4**, 504 (1932).

[8] H. Salwen, Phys. Rev. **99**, 1274 (1955).

[9] E. B. Rawson and R. Beringer, Phys. Rev. **88**, 677 (1952).

[10] V. W. Hughes and J. S. Geiger, Bull. Am. Phys. Soc. **30**, No. 3, 66 (1955).

[11] R. Beringer and J. G. Castle, Phys. Rev. **78**, 581 (1950).

used by Beringer and Heald.[12] A spectrum of the type originally studied by Rawson and Beringer[9] is shown in Fig. 2. Essentially the derivative of the absorption is plotted as a function of the magnetic field for a fixed microwave frequency. The magnetic field was measured with the so-called regulator proton resonance probe,[12] which was placed adjacent to the microwave cavity. The inclined line indicates the zero drift of the galvanometer output and line centers are at the cross-over points on this line. The four spectral lines *a*, *b*, *c*, and *d* are the expected Zeeman transitions corresponding to the transitions indicated in Fig. 1. These lines have been shown to occur to within the experimental accuracy[9] of a few ppm (parts per million) at the fields predicted by elaborate Zeeman calculations of Abragam, Van Vleck, and Kambe[13] which take into account relativistic and quantum electrodynamic effects. The extra lines *e*, *f*, and *g* remained unidentified by Rawson and Beringer. The suggestion was made in their work that the extra lines might be due to argon impurity in the tank oxygen, since the metastable $^3P_2$ state of argon also has a *g*-value of about 1.5. However, lines of the type shown in Fig. 2 have been taken with oxygen which was 99.6% pure (Matheson Company extra dry oxygen), and any appreciable line intensity from an impurity could not be expected.

Inspection indicates first that to within the experimental accuracy of a few ppm the magnetic field at which line *e* occurs is $\frac{1}{2}$ of the sum of the fields at which lines *a* and *b* occur. Similarly, line *f* occurs at the mean field of lines *b* and *c*, and line *g* occurs at the mean field of lines *c* and *d*. Since the principal part of the Zeeman energy depends linearly on the magnetic field H, it can be concluded to sufficient accuracy that for a fixed magnetic field the frequency of line *e* would be $\frac{1}{2}$ of the sum of the frequencies of lines *a* and *b*, and similar statements apply for lines *f* and *g*. The second observation is that the widths of the unidentified lines *e*, *f*, and *g* are considerably less than—indeed approximately $\frac{1}{2}$ that of—the normal lines *a*, *b*, *c*, and *d*.

Figure 3 presents information on the relative line intensities of the extra and normal lines as a function of microwave power measured at the bolometer. It is noticed that the intensity of the extra lines decreases considerably more rapidly with decrease of microwave power than does the intensity of the normal lines for the range of powers used.

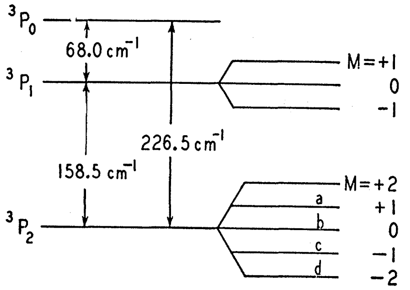

FIG. 1. Energy levels of atomic oxygen in a magnetic field.

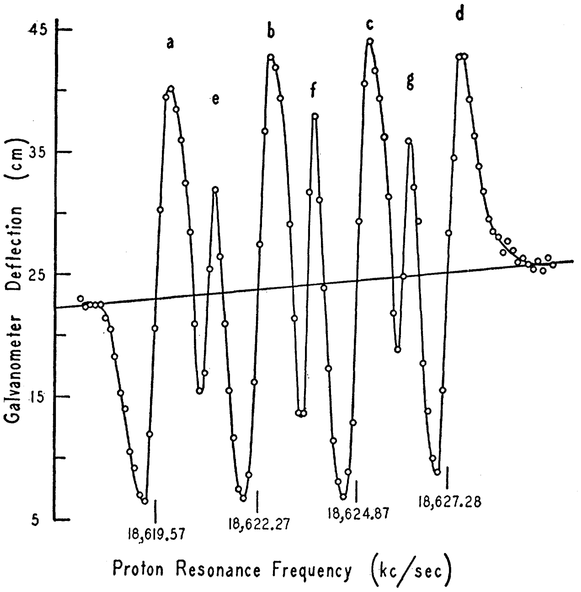

FIG. 2. Paramagnetic resonance absorption spectrum of ground state $^3P_2$ oxygen. Essentially the derivative of the absorption is plotted *vs* the magnetic field for a fixed microwave frequency of 9188.528 Mc/sec. The mean fields of single-quantum transitions and the fields of the extra lines are as follows:

$$\tfrac{1}{2}(a+b)=18\,620.92\text{ kc/sec};\quad e=18\,620.93\text{ kc/sec},$$
$$\tfrac{1}{2}(b+c)=18\,623.57\text{ kc/sec};\quad f=18\,623.58\text{ kc/sec},$$
$$\tfrac{1}{2}(c+d)=18\,626.08\text{ kc/sec};\quad g=18\,626.08\text{ kc/sec}.$$

The magnetic field was measured with the regulator proton resonance probe, which is placed adjacent to the microwave cavity. An additive correction would have to be applied to obtain the magnetic field in the cavity. This correction would not affect significantly the foregoing result that the extra lines occur at the mean field of corresponding single-quantum transitions. This curve was taken with ordinary tank oxygen.

Finally, a search indicated no additional unexpected lines in the oxygen spectrum. The two lines associated with the $^3P_1$ Zeeman splittings were seen, of course, as has been reported in the work of Rawson and Beringer.[9]

3. THEORY OF TWO-QUANTUM TRANSITIONS

Consider an atomic state with three equally spaced Zeeman energy levels as, for example, the $^3S_1$ state of helium. The Zeeman energies are given by $W=\mu_0 g_J HM$, in which the symbols have their usual significance and $M=+1$, 0, or -1. It should be emphasized that the energy spacings between adjacent Zeeman energy levels are equal. It is well known that if such an atom is initially in the state $M=-1$ and a radio-frequency magnetic field with a component perpendicular to the static field and a frequency equal to $\mu_0 g_J H/h$ is applied, then after a time t the atom will have a certain probability of being in the states $M=0$ or $M=+1$.[14] The

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[12] R. Beringer and M. A. Heald, Phys. Rev. **95**, 1474 (1954).

[13] A. Abragam and J. H. Van Vleck, Phys. Rev. **92**, 1448 (1953); K. Kambe and J. H. Van Vleck, Phys. Rev. **96**, 66 (1954).

[14] V. W. Hughes *et al.*, Phys. Rev. **91**, 828 (1953).

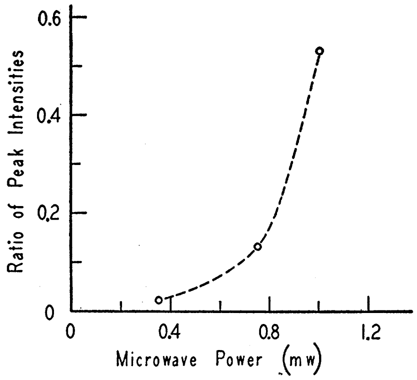

FIG. 3. Ratio of line intensities of extra to normal lines as a function of microwave power. The power is measured at the bolometer, and these data were taken with the Matheson Company extra dry oxygen.

transition to the $M=0$ state is the usual one predicted by first order time-dependent perturbation theory because the selection rule allows $\Delta M=\pm 1$. The transition to the $M=+1$ state occurs by virtue of the intermediate state $M=0$, and, since the energy levels are equally space, the usual interpretation would be that a resonance transition occurs from the $M=-1$ to $M=0$ state with the absorption of one quantum, and then a second resonance transition occurs from the $M=0$ to the $M=+1$ state with the absorption of a second quantum. The transition probability is given by the well known Majorana formula.[15]

The Zeeman spectrum of atomic oxygen presents a different situation because adjacent energy levels are not equally spaced, as was pointed out in the previous section. Thus, for example, if we consider an atom in the $M=-2$ magnetic substate of the $^3P_2$ level and apply a radio-frequency magnetic field whose frequency is the Bohr frequency for the transition from $M=-2$ to $M=-1$ the atom will, of course, have a substantial probability of making the transition to the $M=-1$ state, but the frequency will be far off resonance for a transition from the $M=-1$ to the $M=0$ state, so there will be negligible probability for the atom to reach the $M=0$ state.

It will now be pointed out that by a consideration of second-order time-dependent perturbation theory a substantial probability for the transition from the $M=-2$ to the $M=0$ state of $^3P_2$ oxygen is expected at a frequency one half the Bohr frequency for the $M=-2$ to $M=0$ transition. The Hamiltonian is:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}',$$

$$\mathcal{H}'=\mu_0 g_J \mathbf{J}\cdot\mathbf{H}_{\mathrm{rf}}=\mathcal{H}'(0)e^{-i\omega t};\quad \mathbf{H}_{\mathrm{rf}}=\mathbf{H}_1 e^{-i\omega t},$$

in which $\mathcal{H}_0$ is the time-independent part of the Hamiltonian which leads to Zeeman levels as shown in Fig. 1. $\mathcal{H}'$ is the interaction with the rf magnetic field, and in this expression μ_0 is the Bohr magneton, g_J is the atomic g-value, $\mathbf{J}$ is the total atomic angular momentum operator, and $\mathbf{H}_{\mathrm{rf}}$ is the applied radio-frequency magnetic field.[16]

First-order time-dependent perturbation theory gives the probability amplitude that an atom initially in the state n shall be in the state m after it has been subjected to the radio-frequency field for a time t [see Eq. (1)].

$$a_m^{(1)}(t)=(-i/\hbar)(m|\mathcal{H}'(0)|n)\times\frac{\{\exp[-i\omega t+i(E_m-E_n)t/\hbar]-1\}}{[-i\omega+i(E_m-E_n)/\hbar]}\simeq-(it/\hbar)(m|\mathcal{H}'(0)|n),\quad (1)$$

The usual resonance denominator appears for ω near the Bohr frequency. Provided t is sufficiently small so that the initial state amplitude can still be considered approximately 1, the expression is approximately that given on the right. Similarly, second-order time-dependent perturbation theory gives the probability amplitude:

$$a_m^{(2)}(t)=-\frac{1}{\hbar^2}\frac{(m|\mathcal{H}'(0)|l)(l|\mathcal{H}'(0)|n)}{[-i\omega+i(E_l-E_n)/\hbar]}\times\left\{\frac{\exp[-i2\omega t+i(E_m-E_n)t/\hbar]-1}{[-i2\omega+i(E_m-E_n)/\hbar]}-\frac{\exp[-i\omega t+i(E_m-E_l)t/\hbar]-1}{[-i\omega+i(E_m-E_l)/\hbar]}\right\}$$
$$\simeq\frac{it}{\hbar^2}\frac{(m|\mathcal{H}'(0)|l)(l|\mathcal{H}'(0)|n)}{[-\omega+(E_l-E_n)/\hbar]},\quad (2)$$

where l designates an intermediate state.

Consider the case realized for the $^3P_2$ magnetic substates of oxygen because of the unequal spacing of adjacent Zeeman levels, in which the applied frequency ω can be far off resonance from the Bohr frequencies for either the $M=-2$ to $M=-1$ or the $M=-1$ to $M=0$ transitions but approximately equal to one-half the Bohr frequency for the transition $M=-2$ to $M=0$. If the atom is initially in the $M=-2$ state, there is negligible transition probability to the $M=-1$ state which is the only allowed transition in first-order perturbation theory. In second-order perturbation theory the transition from the $M=-2$ to $M=0$ state is allowed, because of the occurrence of the intermediate state l corresponding to $M=-1$. Furthermore, it will be observed in the expression for the probability amplitude in second-order perturbation theory that one of the terms in the bracket involves a resonance denominator for $2\omega=(E_m-E_n)/\hbar$. This term will be dominant, and provided t is sufficiently small so that the amplitude of the initial state n can still be regarded as approximately 1, the expression is that given on the second line of Eq. (2). The occurrence of 2ω instead of ω in the

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[15] E. Majorana, Nuovo cimento **9**, 43 (1932); F. Bloch and I. I. Rabi, Revs. Modern Phys. **17**, 237 (1945).

[16] As usual it is only necessary to consider a single rotating component of the radiofrequency field. F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

resonance denominator implies that two equienergetic quanta are involved in the transition. It also implies that the line width for these two-quantum transitions will be $\frac{1}{2}$ that of the normal transitions. It was pointed out above that this was one of the characteristics of the unidentified lines.

The principal surprise about these two-quantum transitions is their substantial intensity relative to the normal transitions. This fact can be understood by reference to Eqs. (1) and (2). It will be noticed that the probability amplitude for a two quantum transition at its resonance frequency differs from the probability amplitude for a single-quantum transition at its different resonance frequency by a factor which is the ratio of a matrix element of the interaction with the rf field to the energy difference between the half-frequency for the transition from $M=-2$ to $M=0$ and the Bohr frequency for the transition from $M=-1$ to $M=0$. In the experimental situation the rf magnetic field was of the order of 0.1 gauss and the energy difference between the half-frequency and the $M=-1$ to $M=0$ frequency corresponds to about 0.28 gauss. Thus the ratio is of the order of 1 and hence the intensity of a two-quantum transition is comparable to that of a single-quantum transition. It will be noticed, however, that the intensity of a two-quantum transition should decrease more rapidly with decrease of rf field than the intensity of a single-quantum transition. This prediction is in agreement with the experimental results shown in Fig. 3. It should be emphasized that these remarks on line intensities are only intended in a qualitative sense.[17] The actual experimental conditions are such that the transition probabilities are high so that perturbation theory is not a very good approximation. A better knowledge of the experimental factors influencing line intensity such as relaxation phenomena and saturation effects, and a careful comparison with Salwen's theory[8] would be required for a more quantitative understanding of the line intensities.

Lines *e*, *f*, and *g* are, of course, being identified with the double-quantum transitions from $M=0\rightarrow M=+2$, $M=-1\rightarrow M=+1$, and $M=-2\rightarrow M=0$, respectively. The question arises about the double-quantum transition predicted in connection with the $^3P_1$ Zeeman spectrum. This line would be expected to be much weaker than the double-quantum transitions associated with the $^3P_2$ levels, because of the greater difference between the half-frequency for the transition $M=-1$ to $M+1$ and the Bohr frequency from $M=0$ to $M=+1$. Furthermore, this half-frequency line is predicted to occur at the field value for which a normal line in the $^3P_2$ spectrum occurs. Hence it is understandable that this double-quantum line was not observed.

The extension of the perturbation theory given for double-quantum transitions to the case of triple-quantum transitions is apparent.[18] Since the separations between adjacent lines *a*, *b*, *c*, and *d* are equal, it will be appreciated that triple-quantum transitions will coincide in field with single-quantum or double-quantum transitions [e.g., $(a+b+c)/3=b$, etc.]. This situation differs from Kusch's case in which adjacent single-quantum transitions are not equally spaced.[4]

The essential similarity of the double-quantum transitions discussed in this paper and of the double-quantum transition in the electrical quadrupole spectrum of RbF is clear. In the RbF case also second order time-dependent perturbation theory explains the basic features of the transition—the necessity of an intermediate state, resonance at one-half the Bohr frequency, and the line width one-half that of a normal transition. In the RbF example, the normal electric quadrupole transition can occur only when a static electric field is present, and the two-quantum transition can occur in the absence of the static electric field. The factor by which the probability amplitude for a two-quantum transition differs from that of a single-quantum transition is the ratio of the matrix element of the interaction with the radio-frequency electric field to the matrix element of the interaction with the static electric field. The ratio is of the order of 1 when the radio-frequency electric field is nearly equal to the static electric field.

The microwave magnetic resonance absorption method has certain advantages compared with conventional atomic beam experiments for a further study of the line intensities of multiple-quantum transitions as given in Salwen's theory: first, a more definite knowledge of the microwave field in a cavity than in an "rf-hairpin" of the type used in atomic beams, and, secondly, perhaps a better knowledge of the velocity distribution of the atoms, since no loss of low velocity atoms is involved as in the atomic beam case.

Finally, it might be pointed out that in conventional microwave spectroscopy involving transitions between different rotational states of a molecule, the conditions for the occurrence of double-quantum lines are not met because the separations of adjacent rotational levels differ by large factors. It seems possible that in the field of nuclear paramagnetic resonance where the level spacings are equal, one might find appropriate perturbations in some cases so that the conditions for a double- or multiple-quantum transition of the type discussed in this paper might be realized.

It is a pleasure to thank Professor R. Beringer for several helpful discussions about the apparatus.

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[17] E. B. Rawson reports in his thesis [Yale, 1952 (unpublished)] that the relative intensity of the unidentified lines to the normal lines depends on pressure. Indeed a decrease in pressure caused this relative intensity to change from a value of about $\frac{1}{3}$ to a value of about 3. Possibly relaxation phenomena affect the double-quantum lines and the single-quantum lines differently, but no careful study has been made of this question.

[18] The principal term characteristic of a triple-quantum transition is found by third-order time-dependent perturbation theory to be:

$$a_m^{(3)}(t)=+\left(\frac{i}{\hbar^3}\right)\frac{(m|\mathcal{H}'(0)|k)(k|\mathcal{H}'(0)|l)(l|\mathcal{H}'(0)|n)}{[-i\omega+i(E_l-E_n)/\hbar][-i2\omega+i(E_k-E_n)/\hbar]}\times\frac{\exp[-i3\omega t+i(E_m-E_n)t/\hbar]-1}{[-i3\omega+i(E_m-E_n)/\hbar]},$$

where *l* and *k* designate intermediate states.