The Fine Structure of the Microwave Absorption Spectrum of Oxygen*

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By means of a Zeeman modulation microwave spectrometer used with a lock-in amplifier, the 5 millimeter wave absorption lines of oxygen have been measured at low pressures, where they are completely resolved. Precise measurements of the frequencies of the lines have been made, and uniform deviations from the frequencies predicted by the theoretical formulas of Schlapp were found. The pressure variation of line-width has been measured for three of the observed lines, and found to be linear. The line-width parameter was found to vary with the rotational state. It is 0.053 cm^{-1}/atmos. for $K=3$, and 0.021 cm^{-1}/atmos. for $K=21$. Its order of magnitude is the same for low pressures ($\sim 10^{-1}$ mm Hg) as for high pressures (~ 1 atmos.).

I. INTRODUCTION

As early as 1927, Dieke and Babcock[1] measured the splitting of the rotational levels of oxygen in the optical region. Using the sun as a source, they observed the multiplet structure in the $^3\Pi - ^3\Delta$ transition of molecular oxygen in the atmosphere. Inasmuch as oxygen is in a Σ-ground state, it should have no multiplet structure of the ordinary type; i.e., one caused by the interaction of the electron spin with the quantitized component of the electronic angular momentum along the figure axis of the molecule. However, Kramers[2] showed that the spin-spin interaction of the uncompensated electrons is equivalent to an interaction between the total spin, **S**, of the molecule (=1 for oxygen), and the figure axis of the molecule, averaged over the end-over-end rotation. The result is a splitting of the rotational levels into three components, corresponding to the three ways of combining **S** and **K** vectorially to form the total angular momentum **J**. These are $J=K$, $J=K\pm 1$. The expressions for the energy of the levels obtained by Kramers were later corrected by Schlapp,[3] who made the assumption that **S** does not completely decouple from **K**. That is, he assumed that the coupling was intermediate between Hund's case (a) and (b). The expressions obtained by Schlapp are given in Eq. (2) below.

A completely different interpretation of the fine structure was given by Hebb,[4] based on the following effect. Although on the average, the electronic angular momentum in a Σ-state is zero, this angular momentum has a precessing component perpendicular to the figure axis of the molecule. This component interacts with the spin vector **S**. Curiously, Hebb's formulas were of the same form as Schlapp's although based on entirely different postulates.

With the development of microwave spectroscopy, the measurement of lines corresponding to the transitions between these fine structure terms became possible. Using the predicted energy levels and the constants determined from Dieke and Babcock's data, Van Vleck[5] calculated the form of the absorption *vs.* frequency curve for various values of the unknown parameter $\Delta\nu/c$, the so-called line breadth parameter. Comparing his curves with the measured values of the absorption reported by Beringer,[6] Van Vleck obtained a lower limit of 0.02 cm^{-1}/atmos., and an upper limit of 0.05 cm^{-1}/atmos. for this parameter. Lamont[7] has reported data that support this, using a field method of measuring attenuation as a function of distance in air. Further work at a total pressure of 80 cm Hg, both for pure oxygen, and oxygen-nitrogen mixtures in various concentrations, was carried out by Strandberg, Meng, and Ingersoll.[8] Their results indicate that $\Delta\nu/c$ is closer to 0.02 cm^{-1}/atmos. than to 0.05 cm^{-1}/atmos. Beringer and Castle[9] have measured the transitions between the Zeeman components of the rotational levels using high magnetic fields. They used a constant frequency (9360 Mc/sec.), and "pulled" the absorption lines into the frequency by varying the field. Their measurements were made at pressures ranging from 1.5 cm Hg to an atmosphere.

Because the fine structure lines are very weak, being magnetic dipole transitions, all of the previous direct measurements of them were made at pressures of the order of an atmosphere. At this pressure the lines are so broad that they overlap significantly, completely obscuring the fine structure. The present measurements were made on the individual fine structure lines at low pressures, where they were completely resolved. The line-widths are measured on the individual lines, rather than from the integrated absorption.

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[2] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).
[3] R. Schlapp, Phys. Rev. **51**, 342 (1937).
[4] M. H. Hebb, Phys. Rev. **49**, 610 (1936).
[5] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).
[6] R. Beringer, Phys. Rev. **70**, 53 (1946).
[7] H. R. L. Lamont, Phys. Rev. **74**, 353 (1948).
[8] Strandberg, Meng, and Ingersoll, Phys. Rev. **75**, 1524 (1949).
[9] R. Beringer and J. G. Castle, Jr., Phys. Rev. **73**, 1963 (1949).

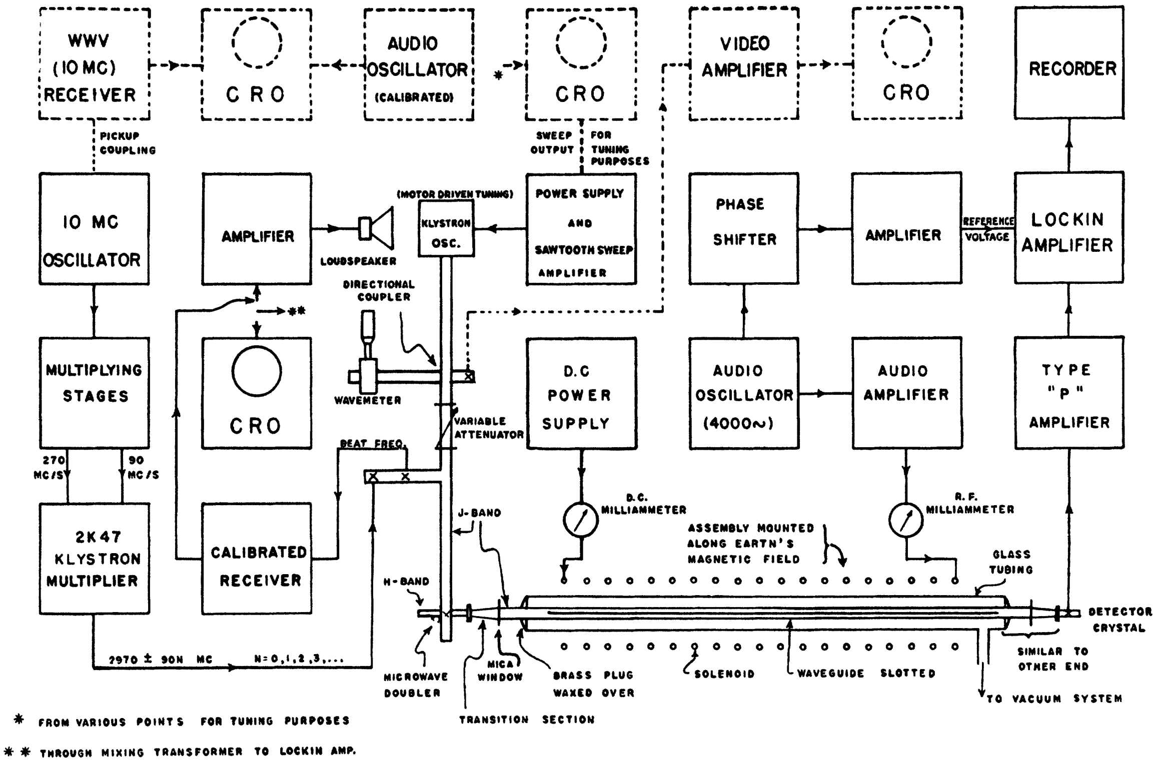

FIG. 1. Block diagram of Zeeman modulation spectroscope.

II. THE ZEEMAN MODULATION SPECTROSCOPE

The block diagram of the apparatus used appears in Fig. 1. Its operation is as follows. A J to H crystal multiplier[10] is used for obtaining energy in the 4 to 5 mm wave region and a K to I doubler in the 5 to 6 mm wave region. The same absorption cell is used for all measurements. It is a 12 foot section of J-band waveguide slotted along the broad side for most of its length to reduce eddy currents, and oriented along the earth's magnetic field so that the latter can be conveniently neutralized. It is surrounded by a glass tube that is part of the vacuum system, and is sealed to the glass tube near the ends. The assembly is surrounded by a solenoid which carries a current modulated at 4000 c.p.s. The modulated current produces a varying magnetic field which modulates the absorption lines of the gas at the same frequency. By using a phase-sensitive lock-in amplifier whose reference voltage is fed from the same audio source, this audio modulation can be detected and amplified with a one c.p.s. band pass. Thus, the noise level is reduced, so that sufficient amplification to detect the lines can be used. Since the Zeeman splitting of the energy levels is independent of the direction of the field, it is necessary that the alternating field be biased to zero at one point in the cycle. Otherwise, the absorption at a given frequency would occur at twice the frequency of the reference voltage. The fields used were of the order of a gauss, so that the effect of the earth's field is not negligible. Thus, the cell is oriented along the earth's field, and a d.c. field superimposed on the a.c. field. This is adjusted to the value that both neutralizes the earth's field and biases the a.c. field.

All frequency measurements are made at the undoubled frequency. A Bethe-hole directional coupler directs a portion of the energy to a wave meter, and a Tee section couples a somewhat larger portion to a mixer crystal, used with a frequency standard. The frequency standard is described elsewhere.[11] It multiples the output of a 10 Mc oscillator, monitored by Station WWV, to the desired region. The mixer crystal detects the beat frequency of these harmonics with the microwave source. Its output is amplified by a calibrated radio receiver.

The J-band klystron is tuned mechanically by a very slow drive motor. As the frequency is driven through an absorption line, the detector crystal detects the audio modulation of the Zeeman components of the line. This signal is amplified by a lock-in amplifier, and fed as a d.c. signal to an Esterline-Angus recorder. A wavemeter reading is made at the time the line appears, to determine the approximate frequency of the line. When the difference between the microwave frequency and

[10] For a definition of the region covered by the designated bands, see W. Gordy, Rev. Mod. Phys. 20, 668 (1948).

[11] R. R. Unterberger and W. V. Smith, Rev. Sci. Inst. 19, 580 (1948).

one of the harmonics of the frequency standard is equal to the receiver setting, the receiver detects their beat frequency. This is marked on the recorder tape. The identity of the markers is determined from the wave meter reading. By bracketing the line with several frequency markers, the frequency of the line can be accurately determined. These same markers establish the frequency scale on the recorder tape, from which line widths are determined.

The shape of the recorder trace is that of a center positive maximum (corresponding to the line frequency) with two negative minima, vanishing for frequencies far from resonance (see Fig. 2). If ν_0 is the center maximum, and $\nu_{\text{min.}}$ is either of the symmetrically located minima, it can be shown (see Appendix A) that in the limit of small modulations,

$$\Delta\nu = (\nu_{\text{min.}} - \nu_0), \qquad (1)$$

where $\Delta\nu$ is the line-breadth parameter, or half the width at half power. Thus, in making measurements on line widths, runs are made at constant pressure and successively decreasing modulations, with two or more frequency markers on each run. The values of $(\nu_{\text{min.}} - \nu_0)$ are extrapolated to zero modulation. This process is repeated at different pressures, and the value of $\Delta\nu/c$ per atmosphere is inferred.

III. THE FINE STRUCTURE

The theoretical formulas for the energy of the fine structure levels, as given by Schlapp,[3] are

$$\begin{aligned} W_{K+1} &= W_0 + (2K+3)B - \lambda + \mu(K+1) \\ &\quad - [(2K+3)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \\ W_K &= W_0 \qquad (2) \\ W_{K-1} &= W_0 - (2K-1)B - \lambda - \mu K \\ &\quad + [(2K-1)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \end{aligned}$$

where, $B = h^2/8\pi^2 Ic$, $W_0 = BK(K+1)$, and λ and μ are coupling constants which must be determined empirically; λ is a measure of the energy of coupling proportional to the factor $[3\cos^2(\mathbf{S}, \mathbf{K}) - 1]$, and μ is a measure of the coupling energy proportional to $\cos(\mathbf{S}, \mathbf{K})$. The values used by Van Vleck[5] were

$$B = 1.43777\ \text{cm}^{-1}, \quad \lambda = 1.985\ \text{cm}^{-1}, \quad \mu = -0.00837\ \text{cm}^{-1}.$$

With the selection rules $\Delta J = \pm 1$, $\Delta K = 0$, Eqs. (2) give the wave numbers of the lines:

$$\begin{aligned} \nu_+(K) &= -(2K+3)B + \lambda - \mu(K+1) \\ &\quad + [(2K+3)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \\ \nu_-(K) &= +(2K-1)B + \lambda + \mu K \\ &\quad - [(2K-1)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \qquad (3) \end{aligned}$$

where $\nu_+(K)$ represents the transition $J = K+1 \rightarrow K$, and $\nu_-(K)$ represents the transition $J = K-1 \rightarrow K$. From (3), the relation

$$\nu_+(K-2) + \nu_-(K) = 2\lambda + \mu = \text{constant}, \qquad (4)$$

follows immediately. The most populated state at room temperature is the one for $K = 13$, although states with K ranging from $K = 1$ to $K = 25$ have significant populations. Because of symmetry considerations, only states with odd values of K are populated, so that (3) predicts 26 lines, 25 of which are in the region of 2 cm^{-1}. The exception is the $\nu_-(1)$ line, which falls at 4 cm^{-1}. This line was not included in the observations.

The experimental frequencies and wave numbers of the lines are listed in Table I. Table II lists the values of the function $\nu_+(K-2) + \nu_-(K)$. It is seen that this function is not a constant, as predicted by (4). This means that regardless of the values chosen for λ and μ, an empirical fit of the data to (3) cannot be obtained. It was found, however, that the $\nu_+(K)$ series in (3) could be fitted by appropriate choices of λ and μ, but no choice of λ and μ would satisfy the $\nu_-(K)$ series, and that added terms were necessary. Attempts to apply symmetric connections to the $\nu_+(K)$ and $\nu_-(K)$ series have been unsuccessful. The empirical version of the formulas (3) are

$$\begin{aligned} \nu_+(K) &= -(2K+3)B + \lambda - \mu(K+1) \\ &\quad + [(2K+3)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \\ \nu_-(K) &= +(2K-1)B + \lambda + \mu K \\ &\quad - [(2K-1)^2B^2 + \lambda^2 - 2\lambda B]^{\frac{1}{2}} \\ &\quad + \delta K + \alpha/[K(K+1)]^{\frac{1}{2}}, \qquad (5) \end{aligned}$$

where $\lambda = 1.983971\ \text{cm}^{-1}$, $\mu = -0.0085114\ \text{cm}^{-1}$, $B = 1.437770\ \text{cm}^{-1}$, $\delta = +0.0015617\ \text{cm}^{-1}$, $\alpha = +0.0049345\ \text{cm}^{-1}$. Table III gives the deviations of (5) from experiment. The theoretical significance of the parameters λ and μ is not understood at present. It appears that the δ-term can be explained by assigning the constant $(\mu + \delta)$ the same significance in the $\nu_-(K)$ series that the constant μ has in the $\nu_+(K)$ series. That is, for the states corresponding to $J = K-1$, the $\cos(\mathbf{S}, \mathbf{K})$ coupling energy is different from that in the $J = K+1$ states. The α-term, on the other hand, has no immediately apparent significance. It probably represents a higher order effect not taken into account in Schlapp's theory. In view of the fact

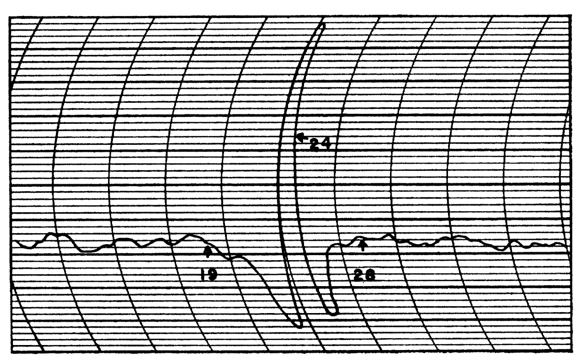

FIG. 2. The $J = 14 \rightarrow 13$ transition at 0.865 mm Hg, and 5 ma a.c. solenoid modulation. The numbers are receiver settings in Mc/sec.

TABLE I. Experimentally determined frequencies.

	K	Series	Frequency (Mc/sec.)	Wave number (cm^{-1})
1	25	−	53,592.2	1.78774
2	23	−	54,130.0	1.805682
3	21	−	54,672.5	1.823779
4	19	−	55,220.8	1.842067
5	17	−	55,784.1	1.860859
6	1	+	56,265.1	1.876905
7	15	−	56,362.8	1.880165
8	13	−	56,968.7	1.900377
9	11	−	57,612.0	1.921836
10	9	−	58,324.0	1.945587
11	3	+	58,446.2	1.949663
12	7	−	59,163.4	1.973586
13	5	+	59,610*	1.9885
14	5	−	60,306.4	2.011715
15	7	+	60,436*	2.0160
16	9	+	61,120*	2.0389
17	11	+	61,800.2	2.061546
18	13	+	62,411.7	2.081944
19	3	−	62,486.1	2.084428
20	15	+	62,970*	2.1006
21	17	+	63,568.3	2.120525
22	19	+	64,127.6	2.139185
23	21	+	64,678.9	2.157575
24	23	+	65,220*	2.1756
25	25	+	65,770*	2.1940

* Measured by wave meter only.

that the added terms appear only in the $\nu_-(K)$ series, it is reasonable to assume that they arise only in the energy levels corresponding to $J=K-1$, and not in those corresponding to $J=K$, or $J=K+1$.

Note added in proof:—It is interesting to compare these microwave frequencies with the most recent infra-red valves (H. Babcock and L. Herzberg, Astrophys. J. **108**, 167 (1948)). The comparison indicates that the infra-red data are accurate to one less significant figure than estimated by the authors. The microwave measurements are at least two significant figures more precise than the infra-red measurements—hence the present observed departures from Schlapp's theory.

IV. LINE WIDTHS

Formula (1) expresses the line-width parameter as a function of frequencies on the recorder tape only in the limit of small modulation fields. However, as the fields are decreased, a decrease in signal to noise ratio occurs, which lowers the sensitivity of the spectroscope. Thus, line-width measurements with the apparatus described require a very good signal to noise ratio. As a result of tube and crystal limitations, only three line widths have been measured to date. These are given in Table IV. The observed line widths may be related to the collision diameters b_K for the interruptions of state K by collisions according to the kinetic theory relation

$$2\Delta\nu=\sqrt{2}n\bar{v}b_K^2 \qquad (6)$$

where $\bar{v}$ is the mean velocity of the molecules. The kinetic theory value of b_K (all K) is 3.61A. Thus, Table IV shows that the microwave collision diameters for low K exceed the kinetic theory value, whereas for high K, they are much less. This implies that, while the larger diameters can be explained by electrostatic interactions, as has been done in the pressure broadening of ammonia[12–14] the smaller diameters may involve other forces, of shorter range. (The magnetic dipole-dipole interactions are too small by orders of magnitude).

Since oxygen has no electric dipole, the only possible electrostatic interactions are quadrupole-quadrupole and polarizability ones. Anderson[15] has shown that polarizability interactions account for slightly more than half of the observed line width, ranging from 0.025 cm^{-1}/atmos. for $K=3$ to 0.014 cm^{-1}/atmos. for $K=21$. Mizushima[16] has derived a line breadth contribution from quadrupole-quadrupole broadening which for high K is of the form

TABLE II. Experimental sum relations.

K	$\nu_+(K-2)+\nu_-(K)$ (Mc/sec.)	(cm^{-1})
3	118,751.2	3.961333
5	118,752.6	3.961378
13	118,768.7	3.961923
15	118,774.5	3.962109
19	118,789.1	3.962592
21	118,800.1	3.962964
23	118,808.9	3.963257

$$\Delta\nu=2.24\times10^{15}Q\left(\frac{1}{K}-\frac{3}{8K^2}\right)^{\frac{1}{2}}$$

$$cm^{-1}/\text{atmosphere for } K+1\rightarrow K \qquad (7)$$

$$\Delta\nu=2.24\times10^{15}Q\left(\frac{1}{K}+\frac{3}{8K^2}\right)^{\frac{1}{2}}$$

$$cm^{-1}/\text{atmosphere for } K-1\rightarrow K,$$

where Q is the quadrupole moment. The physical assumptions of the theories differ. Nevertheless, the combined polarizability-quadrupole effects calculated from one theory should not differ greatly from those calculated from the other theory,[17] as judged by their similarity when applied to the ammonia self-broadening problem.[12–14]

As Eq. (7) contains the quadrupole moment as an adjustable constant, and gives approximately the correct K dependence, it can be adjusted to fit the data fairly well. Alternatively, the combination of polarizability and quadrupole interactions can be so adjusted. Either procedure, however, requires an assumed oxygen quadrupole moment several times too large. This quantity has not yet been measured, but Smith

[12] H. Margenau, Phys. Rev. **76**, 121 (1949).
[13] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[14] W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1949).
[15] P. W. Anderson, Harvard Ph.D. Thesis, (1949).
[16] M. Mizushima, private communication.
[17] For other than dipole-dipole interactions, these two theories give a different dependence of line width on temperature. The difference is not great, however.

and Howard[14] have obtained an upper bound for it of about 0.1×10^{-16} cm^2. Their observations were made on the pressure broadening of NH_3 lines in NH_3-O_2 mixtures. Thus, it seems probable that still other interactions, important at small collision diameters, contribute to the observed line breadths.[18]

TABLE III. Deviations from experiment.

K	$\nu_-(K)$	$\nu_+(K)$
1		+0.000009
3	+0.000000	+0.000176
5	+0.000089	
7	+0.000063	
9	+0.000081	
11	+0.000036	−0.000036
13	+0.000131	+0.000030
15	−0.000014	
17	−0.000001	−0.000023
19	−0.000037	−0.000009
21	+0.000032	+0.000024
23	−0.000001	
25	−0.00010	

APPENDIX A

If $\delta\nu_i$ is the maximum frequency separation of the ith pair of Zeeman components from the undisplaced line ν_0, $\nu 1_i$, $\nu 2_i$ are the frequencies of these components, and ω is the frequency with which the magnetic field alternates, we have

$$\begin{aligned}\nu 1_i&=\nu_0+(1-\cos\omega t)\delta\nu_i\\ \nu 2_i&=\nu_0-(1-\cos\omega t)\delta\nu_i.\end{aligned}\tag{a}$$

The intensity of absorption is proportional to the shape factor,[5]

$$I=\sum_i\left\{\frac{1}{(\nu-\nu 1_i)^2+\Delta\nu^2}+\frac{1}{(\nu-\nu 2_i)^2+\Delta\nu^2}\right\},\tag{b}$$

where $\Delta\nu$ is the line breadth parameter. Now, the lock-in amplifier detects only the coefficient of $\cos\omega t$. Substituting (a) into (b), expanding into a Fourier series with arbitrary phase angle γ, this coefficient is found to be

$$a_1=\sum_i 2\delta\nu_i\cos\gamma\left\{\frac{(\nu-\nu_0+\delta\nu_i)}{[(\nu-\nu_0+\delta\nu_i)^2+\Delta\nu^2]^2}-\frac{(\nu-\nu_0-\delta\nu_i)}{[(\nu-\nu_0-\delta\nu_i)^2+\Delta\nu^2]^2}\right\},\tag{c}$$

provided $(\delta\nu)^4\ll(\Delta\nu)^4$. Note that γ appears only as an amplitude factor. Differentiating (c) with respect to ν, and equating to zero, one obtains formula (1), provided $\delta\nu_i$ is small. Note that (1) is now independent of $\delta\nu_i$.

TABLE IV. Line breadth parameters.

K	Series	$\Delta\nu/c$ (cm^{-1}/atmos.)	b_K (A)
3	−	0.053	4.4
13	+	0.022	2.8
21	−	0.021	2.8

[18] The purely electrostatic interactions actually contribute more to low K transitions, according to Anderson's general theory, than the values he calculates for O_2. The reason for this is that he calculates specifically for the case $\Delta K=0$, whereas for $K=1$ and $K=3$, there will be an appreciable contribution for $\Delta K\neq 0$ collisions. For higher values of K, these contributions vanish much more rapidly than the $\Delta K=0$ contributions.