# Coriolis perturbations in the methane spectrum
# IV. Four general types of Coriolis perturbation

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## Introduction

In previous papers (Jahn 1938, Childs and Jahn 1939) a new Coriolis perturbation in the methane spectrum was investigated. This perturbation arose from a coupling of the rotational levels of an infra-red active threefold degenerate vibration with those of an inactive twofold degenerate vibration. In the present paper, which is a continuation of this work, it is our purpose to show that in a regular tetrahedral molecule there are in all four possible distinct types of Coriolis perturbation. Two of these do not produce a splitting of the rotational levels but merely a displacement of the rotational level as a whole, whilst the other two produce a splitting as well as a displacement, one of these latter perturbations being identical with the type of perturbation previously investigated.

General formulae are derived for the matrix elements of these new types of perturbation, and in the case of the new perturbation which produces a splitting of the levels, we factorize the perturbation matrices up to the tenth rotational quantum number, using the group-theoretical method previously developed. These results will be useful in elucidating the rotational structure of the overtones and combination tones of methane.

## 1. Classification of Coriolis perturbations

In Part III of this series (Childs and Jahn 1939) we gave a group-theoretical classification of the Coriolis terms in the vibrational-rotational Hamiltonian of the methane molecule. These terms all have the form

$$H = -\frac{L_X S_X + L_Y S_Y + L_Z S_Z}{I},$$

where $I$ is the moment of inertia, $L_X$, $L_Y$, $L_Z$ are the components of the total angular momentum of the molecule and $S_X$, $S_Y$, $S_Z$ are components of vibrational angular momentum. In the reference just quoted, we showed that these latter quantities transform according to the irreducible representation $F_1$ of the full tetrahedral symmetry group $T_d$ of the molecule. This fact enables us to classify the matrix elements of these Coriolis terms. All infra-red active fundamental, combination or overtone subvibrational levels of the molecule transform according to the representation $F_2$ (no matter how large the anharmonicity may be). From the reduction of the product representation of $F_1$ and $F_2$;

$$F_1 \times F_2 = A_2 + E + F_1 + F_2,$$

we see that the Coriolis terms can have non-vanishing matrix elements connecting the active vibrational level $F_2$ with four different types of vibrational levels, viz. of types $A_2$, $E$, $F_1$ and $F_2$. We shall see that these give rise to four distinct types of Coriolis perturbation of the active vibrational level $F_2$. We designate these four types of Coriolis perturbation as follows:

Type I, $A_2$–$F_2$; Type II, $E$–$F_2$; Type III, $F_1$–$F_2$; Type IV, $F_2$–$F_2$.

To obtain general formulae for the matrix elements of these perturbations we make use of the explicit reduction of the above product representation. Denoting quantities which transform according to the representations $A_2$, $E$, $F_1$, $F_2$ by $\alpha$; $e, f$; $X$, $Y$, $Z$; $x$, $y$, $z$ respectively, we find easily the explicit reduction of $F_1 \times F_2$ given in Table I below (cp. Table II, Part II).

Since the components of vibrational angular momentum $S_X$, $S_Y$, $S_Z$ transform according to $F_1$, the above explicit reduction of $F_1 \times F_2$ gives us at once the way in which the vibrational angular momenta act on the wave functions $v_x$, $v_y$, $v_z$ of the active vibrational level $F_2$ in the four types of perturbation, viz.

Type I ($A_2$–$F_2$): $$\frac{1}{\sqrt{3}}(S_X v_x + S_Y v_y + S_Z v_z) = k_1 g_\alpha,$$

Type II ($E$–$F_2$): $$\frac{1}{\sqrt{6}}(S_X v_x + S_Y v_y - 2S_Z v_z) = k_2 g_e,$$

$$-\frac{1}{\sqrt{2}}(S_X v_x - S_Y v_y) = k_2 g_f,$$

Type III ($F_1$–$F_2$): $$\frac{1}{\sqrt{2}}(S_Y v_z + S_Z v_y) = k_3 g_X,$$

$$\frac{1}{\sqrt{2}}(S_Z v_x + S_X v_z) = k_3 g_Y,$$

$$\frac{1}{\sqrt{2}}(S_X v_y + S_Y v_x) = k_3 g_Z,$$

Type IV ($F_2$–$F_2$):

$$\frac{1}{\sqrt{2}}(S_Y v_z - S_Z v_y) = k_4 g_x,$$

$$\frac{1}{\sqrt{2}}(S_Z v_x - S_X v_z) = k_4 g_y,$$

$$\frac{1}{\sqrt{2}}(S_X v_y - S_Y v_x) = k_4 g_z,$$

TABLE I. REDUCTION OF PRODUCT REPRESENTATION

| Product | Component | Linear combination | Type |
|---|---|---|---|
| $F_1 \times F_2$ | $A_2$ | $\frac{1}{\sqrt{3}}(Xx+Yy+Zz)$ | $(\alpha)$ |
| | $E$ | $\frac{1}{\sqrt{6}}(Xx+Yy-2Zz)$ | $(e)$ |
| | | $-\frac{1}{\sqrt{2}}(Xx-Yy)$ | $(f)$ |
| | $F_1$ | $\frac{1}{\sqrt{2}}(Yz+Zy)$ | $(X)$ |
| | | $\frac{1}{\sqrt{2}}(Zx+Xz)$ | $(Y)$ |
| | | $\frac{1}{\sqrt{2}}(Xy+Yx)$ | $(Z)$ |
| | $F_2$ | $\frac{1}{\sqrt{2}}(Yz-Zy)$ | $(x)$ |
| | | $\frac{1}{\sqrt{2}}(Zx-Xz)$ | $(y)$ |
| | | $\frac{1}{\sqrt{2}}(Xy-Yx)$ | $(z)$ |

where $g_\alpha$; $g_e, g_f$; $g_X, g_Y, g_Z$; $g_x, g_y, g_z$ are the wave functions of the perturbing vibrational levels (of symmetry type $A_2$, $E$, $F_1$, $F_2$ respectively), and $k_1$, $k_2$, $k_3$ and $k_4$ are numerical constants which depend upon the exact form of the angular momenta $S_X$, $S_Y$, $S_Z$ and of the vibrational wave functions. These formulae are quite general, holding for any vibrational angular momentum (i.e. for any Coriolis term in the Hamiltonian) and for any active vibrational level. When we consider any given level we may find that some of the constants $k_1$, $k_2$, $k_3$, $k_4$ vanish for all the Coriolis terms in the Hamiltonian and we may find, on the other hand, that this level is subject to two or more perturbations of the same type (for which we will need additional constants, e.g. $k_3^{\mathrm{I}}$, $k_3^{\mathrm{II}}$ etc.). All possible cases are, however, covered by these four sets of formulae.

## 2. General formulae for the matrix elements

We now proceed, as in Part II, to deduce general formulae for the matrix elements of the Coriolis operator

$$A = l_x s_x + l_y s_y + l_z s_z,$$

in the four different types of perturbation.

As before, we introduce the quantities

$$l_1 = l_x + il_y, \qquad s_1 = s_x + is_y,$$
$$l_{-1} = l_x - il_y, \qquad s_{-1} = s_x - is_y,$$
$$l_0 = l_z \qquad s_0 = s_z,$$

so that
$$A = \tfrac{1}{2}(l_1 s_{-1} + l_{-1} s_1) + l_0 s_0.$$

Further we put

$$v_1 = -\frac{v_x - iv_y}{\sqrt{2}}, \qquad g_1 = -\frac{g_x - ig_y}{\sqrt{2}}, \qquad G_1 = -\frac{g_X - ig_Y}{\sqrt{2}}$$
$$v_{-1} = \frac{v_x + iv_y}{\sqrt{2}}, \qquad g_{-1} = \frac{g_x + ig_y}{\sqrt{2}}, \qquad G_{-1} = \frac{g_X + ig_Y}{\sqrt{2}}$$
$$v_0 = v_z, \qquad g_0 = g_z, \qquad G_0 = g_Z.$$

From the expressions given in § 1 above, we find the following relations for the four types of perturbation:

Type I:
$$s_1 v_1 = -s_{-1} v_{-1} = -\sqrt{2}\, s_0 v_0 = -\sqrt{\tfrac{2}{3}}\, k_1 g_\alpha,$$

Type II:
$$s_1 v_1 = -s_{-1} v_{-1} = \frac{1}{\sqrt{2}} s_0 v_0 = -\frac{1}{\sqrt{3}} k_2 g_e,$$
$$s_1 v_{-1} = -s_{-1} v_1 = -k_2 g_f,$$

Type III:
$$s_1 v_{-1} = s_{-1} v_1 = ik_3 G_0,$$
$$s_1 v_0 = \sqrt{2}\, s_0 v_{-1} = -ik_3 G_1,$$
$$s_{-1} v_0 = -\sqrt{2}\, s_0 v_1 = -ik_3 G_{-1},$$

Type IV:
$$s_1 v_1 = s_{-1} v_{-1} = ik_4 g_0,$$
$$s_1 v_0 = -\sqrt{2}\, s_0 v_{-1} = ik_4 g_{-1},$$
$$s_{-1} v_0 = \sqrt{2}\, s_0 v_1 = ik_4 g_1,$$

those products not listed being zero.

The relations for Type II perturbation are the same as those given in Part II, p. 501, with $k_2 = \sqrt{6}$, so that we need not consider this perturbation any further.

We introduce now, as in Part I, p. 477, the wave functions for the three Coriolis vibrational-rotational levels of $F_2$ defined by

$$W_K^{(F_2)}(J_{J-1}) = \sqrt{\frac{(J+K)(J+K+1)}{2J(2J+1)}}\, u_{K+1}^J v_{-1} - \sqrt{\frac{(J+K)(J-K)}{J(2J+1)}}\, u_K^J v_0 + \sqrt{\frac{(J-K)(J-K+1)}{2J(2J+1)}}\, u_{K-1}^J v_1,$$

$$W_K^{(F_2)}(J_J) = \sqrt{\frac{(J-K)(J+K+1)}{2J(J+1)}}\, u_{K+1}^J v_{-1} + \frac{K}{\sqrt{\{J(J+1)\}}}\, u_K^J v_0 - \sqrt{\frac{(J-K+1)(J+K)}{2J(J+1)}}\, u_{K-1}^J v_1,$$

$$W_K^{(F_2)}(J_{J+1}) = \sqrt{\frac{(J-K)(J-K+1)}{2(J+1)(2J+1)}}\, u_{K+1}^J v_{-1} + \sqrt{\frac{(J-K+1)(J+K+1)}{(J+1)(2J+1)}}\, u_K^J v_0 + \sqrt{\frac{(J+K)(J+K+1)}{2(J+1)(2J+1)}}\, u_{K-1}^J v_1,$$

where the $u_K^J$ are the rotational wave functions. Using the relations given above and the relations

$$l_1 u_K^J = i\sqrt{\{(J+K)(J-K+1)\}}\, u_{K-1}^J,$$
$$l_{-1} u_K^J = i\sqrt{\{(J-K)(J+K+1)\}}\, u_{K+1}^J,$$
$$l_0 u_K^J = iK u_K^J,$$

one finds easily for Type I perturbation

$$A W_K^{(F_2)}(J_{J-1}) = A W_K^{(F_2)}(J_{J+1}) = 0,$$

$$A W_K^{(F_2)}(J_J) = i\sqrt{\{J(J+1)\}}\, \frac{k_1}{\sqrt{3}}\, W_K^{(A_2)}(J),$$

where $$W_K^{(A_2)}(J) = u_K^J g_\alpha.$$

Thus in a Type I perturbation (i.e. in a Coriolis coupling of the rotational levels of an $F_2$ vibrational level with the rotational levels of an $A_2$ vibrational level) the $R$ branch $(J_{J-1})$ and $P$ branch $(J_{J+1})$ levels of $F_2$ are not perturbed at all, whilst the $Q$ branch $(J_J)$ levels undergo a perturbation which is proportional to $J(J+1)$ if the perturbation is small (i.e. if the $F_2$ and $A_2$ levels do not lie very close together).

For Type IV perturbation one finds in the same way

$$A W_K^{(F_2^{(1)})}(J_{J-1}) = (J+1)\frac{k_4}{\sqrt{2}} W_K^{(F_2^{(2)})}(J_{J-1}),$$

$$A W_K^{(F_2^{(1)})}(J_J) = \frac{k_4}{\sqrt{2}} W_K^{(F_2^{(2)})}(J_J),$$

$$A W_K^{(F_2^{(1)})}(J_{J+1}) = -J\frac{k_4}{\sqrt{2}} W_K^{(F_2^{(2)})}(J_{J+1}),$$

so that here (perturbation of an $F_2$ vibrational level by another $F_2$ level) we have the reverse case to Type I: the $P$ and $R$ branch levels are perturbed, whilst the $Q$ branch levels are not. It is clear that neither of these two perturbations produces a splitting of the individual rotational levels.

The corresponding formulae for Type III perturbation (Coriolis coupling of the rotational levels of an $F_1$ and an $F_2$ vibrational level) are more complicated. The Coriolis vibrational-rotational wave functions $W_K^{(F_1)}(J_L)$ (with $L = J+1, J$ or $J-1$) of the vibrational level $F_1$ are given by the same formulae defining the functions $W_K^{(F_2)}(J_L)$, except of course with $v_1$, $v_0$, $v_{-1}$ replaced by $G_1$, $G_0$, $G_{-1}$. We introduce real vibrational-rotational wave functions for $F_1$ and $F_2$ defined in both cases by

$$U_K(J_L) = \frac{1}{\sqrt{2}}\{W_{-K}(J_L) + (-1)^K W_K(J_L)\},$$

$$V_K(J_L) = \frac{1}{i\sqrt{2}}\{W_{-K}(J_L) - (-1)^K W_K(J_L)\},$$

$$W(J_L) = W_0(J_L)$$

(see Part I, p. 481). In terms of these functions the matrix elements of the Coriolis operator $A$ in Type III perturbation are then found to be as follows. (The common factor $k_3$ has been omitted.)

*General formulae for the matrix elements of Type III perturbation*

***R** branch* $(J_{J-1})$ *levels.*

$$A W^{(F_2)}(J_{J-1}) = -\frac{J-1}{2J+1}\sqrt{\{(J+2)(J+3)\}}\, U_2^{(F_1)}(J_{J+1})$$
$$+\frac{J-3}{2}\sqrt{\left\{\frac{(J-1)(J+2)}{J(2J+1)}\right\}}\, V_2^{(F_1)}(J_J)$$
$$+\frac{3}{2(2J+1)}\sqrt{\left\{\frac{(J-2)(J-1)(J+1)}{J}\right\}}\, U_2^{(F_1)}(J_{J-1}),$$

$$AU_K^{(F_2)}(J_{J-1}) = -\frac{1}{2\sqrt{2}}\frac{2J-3K-2}{2J+1} \times \sqrt{\left\{\frac{(J+K)(J+K+1)(J+K+2)(J+K+3)}{J(J+1)}\right\}}\, U_{K+2}^{(F_1)}(J_{J+1})$$

$$-\frac{1}{2\sqrt{2}}\frac{2J+3K-2}{2J+1}\sqrt{\left\{\frac{(J-K)(J-K+1)(J-K+2)(J-K+3)}{J(J+1)}\right\}}\, U_{K-2}^{(F_1)}(J_{J+1})$$

$$+\frac{1}{2\sqrt{2}}\frac{J-3K-3}{J}\sqrt{\left\{\frac{(J-K-1)(J+K)(J+K+1)(J+K+2)}{(J+1)(2J+1)}\right\}}\, V_{K+2}^{(F_1)}(J_J)$$

$$-\frac{1}{2\sqrt{2}}\frac{J+3K-3}{J}\sqrt{\left\{\frac{(J-K)(J-K+1)(J-K+2)(J+K-1)}{(J+1)(2J+1)}\right\}}\, V_{K-2}^{(F_1)}(J_J)$$

$$+\frac{3}{2\sqrt{2}}\frac{K+1}{J(2J+1)}\sqrt{\{(J-K-2)(J-K-1)(J+K)(J+K+1)\}}\, U_{K+2}^{(F_1)}(J_{J-1})$$

$$-\frac{3}{2\sqrt{2}}\frac{K-1}{J(2J+1)}\sqrt{\{(J-K)(J-K+1)(J+K-1)(J+K-2)\}}\, U_{K-2}^{(F_1)}(J_{J-1}),$$

$AV_K^{(F_2)}(J_{J-1})$: this can be obtained from the expression for $AU_K^{(F_2)}(J_{J-1})$ above by replacing $U$ by $V$ and $V$ by $U$ on the right-hand side, at the same time changing the signs before the two $J_J$ functions.

*Q branch* $(J_J)$ *levels.*

$$AW^{(F_2)}(J_J) = \frac{J-2}{2}\sqrt{\left\{\frac{(J+2)(J+3)}{(J+1)(2J+1)}\right\}}\, V_2^{(F_1)}(J_{J+1})$$

$$-\frac{3}{2}\sqrt{\left\{\frac{(J-1)(J+2)}{J(J+1)}\right\}}\, U_2^{(F_1)}(J_J)$$

$$-\frac{J+3}{2}\sqrt{\left\{\frac{(J-2)(J-1)}{J(2J+1)}\right\}}\, V_2^{(F_1)}(J_{J-1}),$$

$$AU_K^{(F_2)}(J_J) = \frac{1}{2\sqrt{2}}\frac{J-3K-2}{J+1} \times \sqrt{\left\{\frac{(J-K)(J+K+1)(J+K+2)(J+K+3)}{J(2J+1)}\right\}}\, V_{K+2}^{(F_1)}(J_{J+1})$$

$$-\frac{1}{2\sqrt{2}}\frac{J+3K-2}{J+1}\sqrt{\left\{\frac{(J+K)(J-K+1)(J-K+2)(J-K+3)}{J(2J+1)}\right\}}\, V_{K-2}^{(F_1)}(J_{J+1})$$

$$-\frac{3}{2\sqrt{2}}\frac{K+1}{J(J+1)}\sqrt{\{(J-K-1)(J-K)(J+K+1)(J+K+2)\}}\, U_{K+2}^{(F_1)}(J_J)$$

$$+\frac{3}{2\sqrt{2}}\frac{K-1}{J(J+1)}\sqrt{\{(J-K+1)(J-K+2)(J+K-1)(J+K)\}}\, U_{K-2}^{(F_1)}(J_J)$$

$$-\frac{1}{2\sqrt{2}}\frac{J+3K+3}{J}\sqrt{\left\{\frac{(J-K-2)(J-K-1)(J-K)(J+K+1)}{(J+1)(2J+1)}\right\}}\, V_{K+2}^{(F_1)}(J_{J-1})$$

$$-\frac{1}{2\sqrt{2}}\frac{J-3K+3}{J}\sqrt{\left\{\frac{(J-K+1)(J+K-2)(J+K-1)(J+K)}{(J+1)(2J+1)}\right\}}\, V_{K-2}^{(F_1)}(J_{J-1}),$$

$AV_K^{(F_2)}(J_J)$: obtained from $AU_K^{(F_2)}(J_J)$ by interchanging $U$ and $V$ on the right-hand side and changing the signs before the $J_{J+1}$ and $J_{J-1}$ functions.

*P branch* $(J_{J+1})$ *levels.*

$$AW^{(F_2)}(J_{J+1}) = \frac{3}{2(2J+1)}\sqrt{\left\{\frac{J(J+2)(J+3)}{J+1}\right\}}\,U_2^{(F_1)}(J_{J+1})$$

$$-\frac{J+4}{2}\sqrt{\left\{\frac{(J-1)(J+2)}{(J+1)(2J+1)}\right\}}\,V_2^{(F_1)}(J_J)$$

$$+\frac{J+2}{2J+1}\sqrt{\{(J-2)(J-1)\}}\,U_2^{(F_1)}(J_{J-1}),$$

$$AU_K^{(F_2)}(J_{J+1}) = \frac{3}{2\sqrt{2}}\frac{K+1}{(J+1)(2J+1)}$$

$$\times\sqrt{\{(J-K)(J-K+1)(J+K+2)(J+K+3)\}}\,U_{K+2}^{(F_1)}(J_{J+1})$$

$$-\frac{3}{2\sqrt{2}}\frac{K-1}{(J+1)(2J+1)}\sqrt{\{(J-K+2)(J-K+3)(J+K)(J+K+1)\}}\,U_{K-2}^{(F_1)}(J_{J+1})$$

$$-\frac{1}{2\sqrt{2}}\frac{J+3K+4}{J+1}\sqrt{\left\{\frac{(J-K-1)(J-K)(J-K+1)(J+K+2)}{J(2J+1)}\right\}}\,V_{K+2}^{(F_1)}(J_J)$$

$$+\frac{1}{2\sqrt{2}}\frac{J-3K+4}{J+1}\sqrt{\left\{\frac{(J-K+2)(J+K-1)(J+K)(J+K+1)}{J(2J+1)}\right\}}\,V_{K-2}^{(F_1)}(J_J)$$

$$+\frac{1}{2\sqrt{2}}\frac{2J+3K+4}{2J+1}\sqrt{\left\{\frac{(J-K-2)(J-K-1)(J-K)(J-K+1)}{J(J+1)}\right\}}\,U_{K+2}^{(F_1)}(J_{J-1})$$

$$+\frac{1}{2\sqrt{2}}\frac{2J-3K+4}{2J+1}\sqrt{\left\{\frac{(J+K-2)(J+K-1)(J+K)(J+K+1)}{J(J+1)}\right\}}\,U_{K-2}^{(F_1)}(J_{J-1}),$$

$AV_K^{(F_2)}(J_{J+1})$: obtained from $AU_K^{(F_2)}(J_{J+1})$ in the same way as $AV_K^{(F_2)}(J_{J-1})$ is obtained from $AU_K^{(F_2)}(J_{J-1})$.

We see from these formulae that Type III perturbation will produce a splitting of the rotational levels just as Type II perturbation produced a splitting. The energies of the resulting sublevels can be found in the same way as we calculated them for Type II perturbation in Part II. We make use of the proper linear combinations for the tetrahedrally symmetrical vibrational-rotational wave functions of $F_2$ given in Part I, Table IV. The same table can be used to derive the tetrahedral vibrational-rotational wave functions for the perturbing vibrational level $F_1$: we have merely to note that those linear combinations which gave us the $(a)$, $(\alpha)$, $(e)$, $(z)$, $(\zeta)$ wave functions

TABLE II. WAVE FUNCTIONS OF TYPE (*e*) FOR THE CORIOLIS SUBLEVELS OF $F_1$

| Wave function | Linear combination |
|---|---|
| $(1_2)_e$ | $-W(1_2)$ |
| $(2_2)_e$ | $U_2(2_2)$ |
| $(3_2)_e$ | $-W(3_2)$ |
| $(3_4)_e$ | $\frac{\sqrt{7}}{2\sqrt{3}}U_4(3_4)-\frac{\sqrt{5}}{2\sqrt{3}}W(3_4)$ |
| $(4_4)_e$ | $-U_2(4_4)$ |
| $(4_5)_e$ | $-V_2(4_5)$ |
| $(5_4)_e$ | $\frac{\sqrt{7}}{2\sqrt{3}}U_4(5_4)-\frac{\sqrt{5}}{2\sqrt{3}}W(5_4)$ |
| $(5_5)_e$ | $V_4(5_5)$ |
| $(5_6)_e$ | $-\frac{1}{2\sqrt{2}}U_4(5_6)-\frac{\sqrt{7}}{2\sqrt{2}}W(5_6)$ |
| $(6_5)_e$ | $-V_2(6_5)$ |
| $(6_6)_e$ | $\frac{\sqrt{5}}{4}U_2(6_6)+\frac{\sqrt{11}}{4}U_6(6_6)$ |
| $(6_7)_e$ | $-\frac{\sqrt{11}}{2\sqrt{6}}V_2(6_7)+\frac{\sqrt{13}}{2\sqrt{6}}V_6(6_7)$ |
| $(7_6)_e$ | $-\frac{1}{2\sqrt{2}}U_4(7_6)-\frac{\sqrt{7}}{2\sqrt{2}}W(7_6)$ |
| $(7_7)_e$ | $-V_4(7_7)$ |
| $(7_8)_e^{(1)}$ | $\frac{\sqrt{77}}{4\sqrt{31}}U_4(7_8)+\frac{\sqrt{(13.55)}}{8\sqrt{31}}U_8(7_8)-\frac{\sqrt{31}}{8}W(7_8)$ |
| $(7_8)_e^{(2)}$ | $-\sqrt{\frac{5.13}{3.31}}U_4(7_8)+\frac{2\sqrt{7}}{\sqrt{(3.31)}}U_8(7_8)$ |
| $(8_7)_e$ | $-\frac{\sqrt{11}}{2\sqrt{6}}V_2(8_7)+\frac{\sqrt{13}}{2\sqrt{6}}V_6(8_7)$ |
| $(8_8)_e^{(1)}$ | $-\frac{\sqrt{(5.21)}}{2\sqrt{62}}U_2(8_8)-\frac{\sqrt{(11.13)}}{2\sqrt{62}}U_6(8_8)$ |
| $(8_8)_e^{(2)}$ | $-\frac{\sqrt{(11.13)}}{2\sqrt{62}}U_2(8_8)+\frac{\sqrt{(5.21)}}{2\sqrt{62}}U_6(8_8)$ |
| $(8_9)_e$ | $-\frac{\sqrt{13}}{4}V_2(8_9)-\frac{\sqrt{3}}{4}V_6(8_9)$ |
| $(9_8)_e^{(1)}$ | $\frac{\sqrt{77}}{4\sqrt{31}}U_4(9_8)+\frac{\sqrt{(13.55)}}{8\sqrt{31}}U_8(9_8)-\frac{\sqrt{31}}{8}W(9_8)$ |
| $(9_8)_e^{(2)}$ | $-\sqrt{\frac{5.13}{3.31}}U_4(9_8)+\frac{2\sqrt{7}}{\sqrt{(3.31)}}U_8(9_8)$ |
| $(9_9)_e$ | $\frac{\sqrt{7}}{2\sqrt{6}}V_4(9_9)+\frac{\sqrt{17}}{2\sqrt{6}}V_8(9_9)$ |
| $(9_{10})_e^{(1)}$ | $-\frac{\sqrt{(5.13)}}{4\sqrt{(2.29)}}U_4(9_{10})-\frac{\sqrt{(5.13.17)}}{8\sqrt{(6.29)}}U_8(9_{10})-\frac{\sqrt{(11.29)}}{8\sqrt{6}}W(9_{10})$ |
| $(9_{10})_e^{(2)}$ | $-\sqrt{\frac{17}{29}}U_4(9_{10})+\frac{2\sqrt{3}}{\sqrt{29}}U_8(9_{10})$ |
| $(10_9)_e$ | $-\frac{\sqrt{13}}{4}V_2(10_9)-\frac{\sqrt{3}}{4}V_6(10_9)$ |
| $(10_{10})_e^{(1)}$ | $\frac{7\sqrt{15}}{8\sqrt{(2.29)}}U_2(10_{10})+\frac{3\sqrt{(13.15)}}{16\sqrt{29}}U_6(10_{10})+\frac{\sqrt{(13.17.19)}}{16\sqrt{29}}U_{10}(10_{10})$ |
| $(10_{10})_e^{(2)}$ | $\frac{\sqrt{(13.17)}}{4\sqrt{(3.29)}}U_2(10_{10})-\frac{11\sqrt{17}}{4\sqrt{(6.29)}}U_6(10_{10})+\frac{\sqrt{(5.19)}}{4\sqrt{(2.29)}}U_{10}(10_{10})$ |

for $F_2$ give us the $(\alpha)$, $(a)$, $(f)$, $(\zeta)$, $(z)$ functions for $F_1$. Since we listed the $(e)$ but not the $(f)$ functions of $F_2$ in Table IV, Part I, we give below in Table II the $(e)$ functions for $F_1$ (or the $(f)$ functions for $F_2$).

## 3. Matrix elements for the sublevels in Type III perturbation

When we introduce the wave functions for the tetrahedral sublevels of $F_2$ and $F_1$, the perturbation matrix factorizes in the manner described in Part II. The corresponding matrix elements are listed in Table III below (up to $J = 10$). Since each individual $(J_L)$ level of $F_2$ can be perturbed by the three levels $(J_{J+1})$, $(J_J)$, $(J_{J-1})$ of $F_1$, we have introduced a notation in which $a$, $b$, $c$ are used to denote the matrix elements of these three perturbations in this order. Thus we find, for instance, from Table IV, Part I,

$$(F_2 3_3)_\zeta = W^{(F_1)}(3_3),$$

and (interchanging $z$ and $\zeta$ in the table)

$$(F_1 3_4)_\zeta = V_2^{(F_1)}(3_4),$$
$$(F_1 3_3)_\zeta = U_2^{(F_1)}(3_3),$$
$$(F_1 3_2)_\zeta = V_2^{(F_1)}(3_2).$$

Now from the general formulae given in § 2 above for the matrix elements of Type III perturbation we find

$$A W^{(F_1)}(3_3) = \frac{\sqrt{15}}{2\sqrt{14}} V_2^{(F_1)}(3_4) - \frac{\sqrt{15}}{2\sqrt{2}} U_2^{(F_1)}(3_3) - \sqrt{\frac{6}{7}} V_2^{(F_1)}(3_2).$$

Thus we have

$$A(F_2 3_3)_\zeta = \frac{\sqrt{15}}{2\sqrt{14}} (F_1 3_4)_\zeta - \frac{\sqrt{15}}{2\sqrt{2}} (F_1 3_3)_\zeta - \sqrt{\frac{6}{7}} (F_1 3_2)_\zeta.$$

This is expressed in the table by putting for the level $3_3 F_1$

$$a = \frac{\sqrt{15}}{2\sqrt{14}}, \quad b = -\frac{\sqrt{15}}{2\sqrt{2}}, \quad c = -\sqrt{\frac{6}{7}}.$$

Just as in Part II, when two or more sublevels of the same symmetry type occur, we use subscripts to distinguish the matrix elements. Thus the equations for the levels $5_6 F_2$, viz.

$$A(F_2 5_6)_z^{(1)} = \frac{9\sqrt{15}}{22} (F_1 5_6)_z - \sqrt{\frac{21}{11}} (F_1 5_5)_z^{(1)} + \frac{3\sqrt{15}}{2\sqrt{11}} (F_1 5_5)_z^{(2)} + \frac{2\sqrt{10}}{11} (F_1 5_4)_z,$$

$$A(F_2 5_6)_z^{(2)} = -\frac{5\sqrt{3}}{2\sqrt{11}} (F_1 5_6)_z + \frac{3\sqrt{3}}{2} (F_1 5_5)_z^{(2)} - \frac{6\sqrt{2}}{\sqrt{11}} (F_1 5_4)_z,$$

TABLE III. MATRIX ELEMENTS OF TYPE III PERTURBATION

| $R$ branch ($J_{J-1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $1_0$ | $A_1$ | — | $0$ |
| $2_1$ | $F_2$ | $a$ | $-\frac{2}{\sqrt{5}}$ |
| | | $b$ | $-\frac{1}{\sqrt{10}}$ |
| $3_2$ | $E$ | $a$ | $\frac{2\sqrt{30}}{7}$ |
| | | $c$ | $\frac{\sqrt{6}}{7}$ |
| | $F_2$ | $a$ | $\sqrt{\frac{10}{7}}$ |
| | | $b$ | $\sqrt{\frac{6}{7}}$ |
| $4_3$ | $A_1$ | $b$ | $\sqrt{\frac{7}{2}}$ |
| | $F_1$ | $a_1$ | $-\frac{2\sqrt{2}}{\sqrt{3}}$ |
| | | $b$ | $-\frac{\sqrt{35}}{2\sqrt{6}}$ |
| | | $c$ | $-\frac{\sqrt{5}}{2\sqrt{6}}$ |
| | $F_2$ | $a$ | $-\sqrt{\frac{14}{3}}$ |
| | | $b$ | $\frac{1}{2\sqrt{2}}$ |
| | | $c$ | $\frac{\sqrt{5}}{2\sqrt{6}}$ |
| $5_4$ | $A_1$ | $a$ | $-\frac{4\sqrt{6}}{\sqrt{11}}$ |
| | $E$ | $a$ | $-\frac{4\sqrt{42}}{11}$ |
| | | $b$ | $\frac{4\sqrt{21}}{5\sqrt{11}}$ |
| | | $c$ | $-\frac{18\sqrt{6}}{55}$ |

| $Q$ branch ($J_J$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $1_1$ | $F_1$ | $b$ | $-\frac{1}{\sqrt{2}}$ |
| $2_2$ | $E$ | $b$ | $\sqrt{\frac{3}{2}}$ |
| | $F_1$ | $a$ | $\frac{2\sqrt{3}}{\sqrt{5}}$ |
| | | $c$ | $\frac{1}{\sqrt{10}}$ |
| $3_3$ | $A_2$ | $a$ | $\sqrt{\frac{15}{2}}$ |
| | $F_1$ | $a$ | $\frac{\sqrt{15}}{2\sqrt{14}}$ |
| | | $b$ | $-\frac{\sqrt{15}}{2\sqrt{2}}$ |
| | | $c$ | $-\sqrt{\frac{6}{7}}$ |
| | $F_2$ | $a$ | $-\frac{5}{2\sqrt{2}}$ |
| | | $b$ | $\frac{\sqrt{15}}{2\sqrt{2}}$ |
| $4_4$ | $A_2$ | $c$ | $-\sqrt{\frac{7}{2}}$ |
| | $E$ | $a$ | $\frac{2\sqrt{14}}{5}$ |
| | | $b$ | $-\frac{9\sqrt{3}}{5\sqrt{2}}$ |
| | $F_1$ | $a_1$ | $\frac{4\sqrt{2}}{\sqrt{5}}$ |
| | | $a_2$ | $\frac{2\sqrt{14}}{5}$ |
| | | $b$ | $-\frac{9\sqrt{7}}{10\sqrt{2}}$ |
| | | $c$ | $-\frac{1}{2\sqrt{2}}$ |
| | $F_2$ | $a$ | $\frac{7\sqrt{2}}{5\sqrt{3}}$ |
| | | $b$ | $\frac{9\sqrt{7}}{10\sqrt{2}}$ |
| | | $c$ | $\frac{\sqrt{35}}{2\sqrt{6}}$ |

| $P$ branch ($J_{J+1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $0_1$ | $F_2$ | — | $0$ |
| $1_2$ | $E$ | $a$ | $\sqrt{\frac{3}{2}}$ |
| | $F_2$ | $b$ | $\frac{1}{\sqrt{2}}$ |
| $2_3$ | $A_1$ | — | $0$ |
| | $F_1$ | $a$ | $-\sqrt{\frac{6}{5}}$ |
| | | $c$ | $\frac{2}{\sqrt{5}}$ |
| | $F_2$ | $a$ | $\sqrt{\frac{6}{5}}$ |
| | | $b$ | $-\frac{2\sqrt{3}}{\sqrt{5}}$ |
| $3_4$ | $A_1$ | $b$ | $-\sqrt{\frac{15}{2}}$ |
| | $E$ | $a$ | $-\frac{9\sqrt{3}}{7\sqrt{2}}$ |
| | | $c$ | $\frac{2\sqrt{30}}{7}$ |
| | $F_1$ | $a$ | $\frac{9}{2\sqrt{14}}$ |
| | | $b$ | $\frac{5}{2\sqrt{2}}$ |
| | | $c$ | $-\sqrt{\frac{10}{7}}$ |
| | $F_2$ | $a$ | $\frac{9}{2\sqrt{14}}$ |
| | | $b$ | $-\frac{\sqrt{15}}{2\sqrt{14}}$ |
| $4_5$ | $E$ | $a$ | $\frac{3\sqrt{6}}{5}$ |
| | | $b$ | $-\frac{2\sqrt{14}}{5}$ |

TABLE III (*continued*)

| *R* branch ($J_{J-1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $5_4$ | $F_1$ | $a_1$ | $-\frac{2\sqrt{10}}{11}$ |
| | | $a_2$ | $\frac{6\sqrt{2}}{\sqrt{11}}$ |
| | | $b$ | $\frac{14}{5\sqrt{11}}$ |
| | | $c$ | $-\frac{9\sqrt{14}}{55}$ |
| | $F_2$ | $a$ | $-\frac{\sqrt{84}}{11}$ |
| | | $b_1$ | $\frac{8\sqrt{3}}{\sqrt{55}}$ |
| | | $b_2$ | $\frac{4\sqrt{21}}{5\sqrt{11}}$ |
| | | $c$ | $\frac{9\sqrt{14}}{55}$ |
| $6_5$ | $E$ | $a$ | $\frac{4\sqrt{165}}{13\sqrt{7}}$ |
| | | $b$ | $\frac{6\sqrt{15}}{\sqrt{91}}$ |
| | | $c$ | $\frac{9\sqrt{3}}{13\sqrt{2}}$ |
| | $F_1$ | $a_1$ | $-\frac{16\sqrt{5}}{13}$ |
| | | $a_2$ | $-\frac{4\sqrt{165}}{13\sqrt{7}}$ |
| | | $b$ | $-\frac{3\sqrt{15}}{\sqrt{182}}$ |
| | | $c_1$ | $-\frac{\sqrt{105}}{13\sqrt{2}}$ |
| | | $c_2$ | $\frac{9\sqrt{3}}{13\sqrt{2}}$ |

| *Q* branch ($J_J$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $5_5$ | $E$ | $a$ | $\frac{6\sqrt{3}}{\sqrt{11}}$ |
| | | $b$ | $\frac{9\sqrt{3}}{5\sqrt{2}}$ |
| | | $c$ | $-\frac{4\sqrt{21}}{5\sqrt{11}}$ |
| | $2F_1$ | $a_{11}$ | $\sqrt{\frac{21}{11}}$ |
| | | $a_{21}$ | $-\frac{3\sqrt{15}}{2\sqrt{11}}$ |
| | | $a_{22}$ | $-\frac{3\sqrt{3}}{2}$ |
| | | $b_{11}$ | $-\sqrt{\frac{21}{10}}$ |
| | | $b_{21}$ | $\frac{9\sqrt{3}}{5\sqrt{2}}$ |
| | | $c_{11}$ | $-\frac{8\sqrt{3}}{\sqrt{55}}$ |
| | | $c_{21}$ | $-\frac{4\sqrt{21}}{5\sqrt{11}}$ |
| | $F_2$ | $a$ | $-\frac{3\sqrt{3}}{\sqrt{22}}$ |
| | | $b_1$ | $\sqrt{\frac{21}{10}}$ |
| | | $b_2$ | $-\frac{9\sqrt{3}}{5\sqrt{2}}$ |
| | | $c$ | $-\frac{14}{5\sqrt{11}}$ |
| $6_6$ | $A_1$ | $b$ | $\sqrt{\frac{165}{14}}$ |
| | $A_2$ | $a$ | $\frac{4\sqrt{6}}{\sqrt{7}}$ |
| | | $b$ | $-\sqrt{\frac{165}{14}}$ |
| | $E$ | $a$ | $\frac{4\sqrt{66}}{7\sqrt{13}}$ |
| | | $b$ | $\frac{5\sqrt{3}}{7\sqrt{2}}$ |
| | | $c$ | $-\frac{6\sqrt{15}}{\sqrt{91}}$ |

| *P* branch ($J_{J+1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $4_5$ | $F_1$ | $a_1$ | $-\sqrt{\frac{14}{15}}$ |
| | | $a_2$ | $\frac{3\sqrt{6}}{5}$ |
| | | $b$ | $-\frac{7\sqrt{2}}{5\sqrt{3}}$ |
| | | $c$ | $\sqrt{\frac{14}{3}}$ |
| | $2F_2$ | $a_{11}$ | $\sqrt{\frac{14}{15}}$ |
| | | $a_{21}$ | $-\frac{3\sqrt{6}}{5}$ |
| | | $b_{11}$ | $-\frac{4\sqrt{2}}{\sqrt{5}}$ |
| | | $b_{21}$ | $-\frac{2\sqrt{14}}{5}$ |
| | | $c_{11}$ | $\frac{2\sqrt{2}}{\sqrt{3}}$ |
| $5_6$ | $A_1$ | $a$ | $\sqrt{\frac{105}{22}}$ |
| | $A_2$ | $a$ | $-\sqrt{\frac{105}{22}}$ |
| | | $c$ | $\frac{4\sqrt{6}}{\sqrt{11}}$ |
| | $E$ | $a$ | $\frac{5\sqrt{3}}{11\sqrt{2}}$ |
| | | $b$ | $-\frac{6\sqrt{3}}{\sqrt{11}}$ |
| | | $c$ | $-\frac{4\sqrt{42}}{11}$ |
| | $F_1$ | $a_1$ | $-\frac{9\sqrt{15}}{22}$ |
| | | $a_2$ | $\frac{5\sqrt{3}}{2\sqrt{11}}$ |
| | | $b$ | $\frac{3\sqrt{3}}{\sqrt{22}}$ |
| | | $c$ | $\frac{2\sqrt{21}}{11}$ |

TABLE III (*continued*)

**$R$ branch ($J_{J-1}$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $6_5$ | $2F_2$ | $a_{11}$ | $-\frac{30\sqrt{2}}{13}$ |
| | | $a_{21}$ | $-\frac{11\sqrt{10}}{13\sqrt{7}}$ |
| | | $a_{22}$ | $\sqrt{\frac{110}{91}}$ |
| | | $b_{11}$ | $\sqrt{\frac{15}{13}}$ |
| | | $b_{21}$ | $-\frac{15\sqrt{3}}{2\sqrt{91}}$ |
| | | $b_{22}$ | $-\frac{3\sqrt{165}}{2\sqrt{91}}$ |
| | | $c_{11}$ | $\frac{\sqrt{105}}{13\sqrt{2}}$ |
| | | $c_{21}$ | $-\frac{9\sqrt{3}}{13\sqrt{2}}$ |
| $7_6$ | $A_1$ | $b$ | $\frac{2\sqrt{78}}{\sqrt{35}}$ |
| | | $c$ | $\sqrt{\frac{66}{35}}$ |
| | $A_2$ | $a$ | $-\frac{6\sqrt{2}}{\sqrt{5}}$ |
| | | $c$ | $-\sqrt{\frac{66}{35}}$ |
| | $E$ | $a_1$ | $\frac{6\sqrt{6}}{\sqrt{31}}$ |
| | | $a_2$ | $\frac{6\sqrt{286}}{\sqrt{1085}}$ |
| | | $b$ | $\frac{2\sqrt{66}}{7\sqrt{5}}$ |
| | | $c$ | $\frac{\sqrt{6}}{7}$ |

**$Q$ branch ($J_J$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $6_6$ | $2F_1$ | $a_{11}$ | $\frac{10\sqrt{10}}{\sqrt{91}}$ |
| | | $a_{12}$ | $\frac{\sqrt{330}}{7\sqrt{13}}$ |
| | | $a_{22}$ | $\frac{11\sqrt{6}}{7\sqrt{13}}$ |
| | | $b_{11}$ | $-\frac{9\sqrt{15}}{14}$ |
| | | $b_{21}$ | $\frac{5\sqrt{33}}{14}$ |
| | | $c_{11}$ | $-\sqrt{\frac{15}{13}}$ |
| | | $c_{12}$ | $\frac{15\sqrt{3}}{2\sqrt{91}}$ |
| | | $c_{22}$ | $\frac{3\sqrt{165}}{2\sqrt{91}}$ |
| | $F_2$ | $a_1$ | $\frac{40\sqrt{2}}{7\sqrt{13}}$ |
| | | $a_2$ | $\frac{4\sqrt{22}}{7}$ |
| | | $b_1$ | $\frac{9\sqrt{15}}{14}$ |
| | | $b_2$ | $-\frac{5\sqrt{33}}{14}$ |
| | | $c$ | $\frac{3\sqrt{15}}{\sqrt{182}}$ |
| $7_7$ | $A_2$ | $a$ | $\sqrt{\frac{143}{10}}$ |
| | | $c$ | $-\frac{2\sqrt{78}}{\sqrt{35}}$ |
| | $E$ | $a_1$ | $\frac{11\sqrt{33}}{\sqrt{310}}$ |
| | | $a_2$ | $\frac{5\sqrt{13}}{2\sqrt{434}}$ |
| | | $b$ | $-\frac{45\sqrt{3}}{14\sqrt{2}}$ |
| | | $c$ | $-\frac{2\sqrt{66}}{7\sqrt{5}}$ |

**$P$ branch ($J_{J+1}$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $5_6$ | $2F_2$ | $a_{11}$ | $\frac{9\sqrt{15}}{22}$ |
| | | $a_{21}$ | $-\frac{5\sqrt{3}}{2\sqrt{11}}$ |
| | | $b_{11}$ | $-\sqrt{\frac{21}{11}}$ |
| | | $b_{12}$ | $\frac{3\sqrt{15}}{2\sqrt{11}}$ |
| | | $b_{22}$ | $\frac{3\sqrt{3}}{2}$ |
| | | $c_{11}$ | $\frac{2\sqrt{10}}{11}$ |
| | | $c_{21}$ | $-\frac{6\sqrt{2}}{\sqrt{11}}$ |
| $6_7$ | $A_1$ | $b$ | $-\frac{4\sqrt{6}}{\sqrt{7}}$ |
| | $E$ | $a$ | $-\frac{90\sqrt{6}}{91}$ |
| | | $b$ | $-\frac{4\sqrt{66}}{7\sqrt{13}}$ |
| | | $c$ | $\frac{4\sqrt{165}}{13\sqrt{7}}$ |
| | $2F_1$ | $a_{11}$ | $-\frac{18\sqrt{3}}{13\sqrt{7}}$ |
| | | $a_{12}$ | $\frac{45\sqrt{11}}{91}$ |
| | | $a_{22}$ | $-\frac{45}{7\sqrt{13}}$ |
| | | $b_{11}$ | $-\frac{40\sqrt{2}}{7\sqrt{13}}$ |
| | | $b_{21}$ | $-\frac{4\sqrt{22}}{7}$ |
| | | $c_{11}$ | $\frac{30\sqrt{2}}{13}$ |
| | | $c_{12}$ | $\frac{11\sqrt{10}}{13\sqrt{7}}$ |
| | | $c_{22}$ | $-\sqrt{\frac{110}{91}}$ |

TABLE III (*continued*)

**R branch ($J_{J-1}$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $7_6$ | $F_1$ | $a_1$ | $-\frac{6\sqrt{2}}{\sqrt{35}}$ |
| | | $b_1$ | $\frac{4\sqrt{10}}{7}$ |
| | | $b_2$ | $\frac{2\sqrt{286}}{7\sqrt{5}}$ |
| | | $c_1$ | $-\frac{9\sqrt{3}}{7\sqrt{5}}$ |
| | | $c_2$ | $\frac{\sqrt{33}}{7}$ |
| | $2F_2$ | $a_{11}$ | $-\frac{3\sqrt{33}}{\sqrt{70}}$ |
| | | $a_{21}$ | $-\sqrt{\frac{3}{14}}$ |
| | | $a_{22}$ | $\sqrt{\frac{78}{5}}$ |
| | | $b_{11}$ | $\frac{5\sqrt{2}}{\sqrt{7}}$ |
| | | $b_{12}$ | $\frac{\sqrt{33}}{7\sqrt{2}}$ |
| | | $b_{22}$ | $\frac{11\sqrt{3}}{7\sqrt{10}}$ |
| | | $c_{11}$ | $\frac{9\sqrt{3}}{7\sqrt{5}}$ |
| | | $c_{21}$ | $-\frac{\sqrt{33}}{7}$ |
| $8_7$ | $A_1$ | $a$ | $-\frac{2\sqrt{110}}{\sqrt{51}}$ |
| | | $b$ | $\sqrt{\frac{1001}{102}}$ |
| | $E$ | $a$ | $-\frac{2\sqrt{910}}{17\sqrt{3}}$ |
| | | $b_1$ | $\frac{11\sqrt{77}}{\sqrt{1054}}$ |
| | | $b_2$ | $\frac{5\sqrt{65}}{2\sqrt{3162}}$ |
| | | $c$ | $-\frac{45\sqrt{3}}{34\sqrt{2}}$ |

**Q branch ($J_J$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $7_7$ | $2F_1$ | $a_{11}$ | $\frac{5\sqrt{3}}{4}$ |
| | | $a_{21}$ | $-\frac{17\sqrt{11}}{8\sqrt{7}}$ |
| | | $a_{22}$ | $-\frac{7\sqrt{39}}{8\sqrt{5}}$ |
| | | $b_{11}$ | $-\frac{9\sqrt{3}}{4\sqrt{7}}$ |
| | | $b_{21}$ | $\frac{45\sqrt{11}}{56}$ |
| | | $b_{22}$ | $-\frac{45\sqrt{13}}{56}$ |
| | | $c_{11}$ | $-\frac{5\sqrt{2}}{\sqrt{7}}$ |
| | | $c_{21}$ | $-\frac{\sqrt{33}}{7\sqrt{2}}$ |
| | | $c_{22}$ | $-\frac{11\sqrt{3}}{7\sqrt{10}}$ |
| | $2F_2$ | $a_{11}$ | $-\frac{\sqrt{55}}{8\sqrt{7}}$ |
| | | $a_{21}$ | $-\frac{23\sqrt{13}}{8\sqrt{35}}$ |
| | | $a_{22}$ | $-\frac{13}{4}$ |
| | | $b_{11}$ | $\frac{9\sqrt{3}}{4\sqrt{7}}$ |
| | | $b_{12}$ | $-\frac{45\sqrt{11}}{56}$ |
| | | $b_{22}$ | $\frac{45\sqrt{13}}{56}$ |
| | | $c_{11}$ | $-\frac{4\sqrt{10}}{7}$ |
| | | $c_{21}$ | $-\frac{2\sqrt{286}}{7\sqrt{5}}$ |
| $8_8$ | $A_2$ | $a$ | $\frac{2\sqrt{10}}{\sqrt{17}}$ |
| | | $c$ | $-\sqrt{\frac{1001}{102}}$ |

**P branch ($J_{J+1}$) levels**

| Level | | Matrix element | |
|---|---|---|---|
| $6_7$ | $2F_2$ | $a_{11}$ | $\frac{18\sqrt{3}}{13\sqrt{7}}$ |
| | | $a_{21}$ | $-\frac{45\sqrt{11}}{91}$ |
| | | $a_{22}$ | $\frac{45}{7\sqrt{13}}$ |
| | | $b_{11}$ | $-\frac{10\sqrt{10}}{\sqrt{91}}$ |
| | | $b_{21}$ | $-\frac{\sqrt{330}}{7\sqrt{13}}$ |
| | | $b_{22}$ | $-\frac{11\sqrt{6}}{7\sqrt{13}}$ |
| | | $c_{11}$ | $\frac{16\sqrt{5}}{13}$ |
| | | $c_{21}$ | $\frac{4\sqrt{165}}{13\sqrt{7}}$ |
| $7_8$ | $A_1$ | $b$ | $-\sqrt{\frac{143}{10}}$ |
| | | $c$ | $\frac{6\sqrt{2}}{\sqrt{5}}$ |
| | $2E$ | $a_{11}$ | $-\frac{21\sqrt{3}}{31\sqrt{2}}$ |
| | | $a_{12}$ | $-\frac{3\sqrt{1001}}{31\sqrt{10}}$ |
| | | $a_{21}$ | $-\frac{3\sqrt{1001}}{31\sqrt{10}}$ |
| | | $a_{22}$ | $\frac{135\sqrt{3}}{62\sqrt{2}}$ |
| | | $b_{11}$ | $-\frac{11\sqrt{33}}{\sqrt{310}}$ |
| | | $b_{21}$ | $-\frac{5\sqrt{13}}{2\sqrt{434}}$ |
| | | $c_{11}$ | $\frac{6\sqrt{6}}{\sqrt{31}}$ |
| | | $c_{21}$ | $\frac{6\sqrt{286}}{\sqrt{1085}}$ |

TABLE III (*continued*)

| *R* branch ($J_{J-1}$) levels | | | | *Q* branch ($J_J$) levels | | | | *P* branch ($J_{J+1}$) levels | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Level | | Matrix element | | Level | | Matrix element | | Level | | Matrix element | |
| $8_7$ | $2F_1$ | $a_{11}$ | $-\frac{10\sqrt{42}}{17}$ | $8_8$ | $2E$ | $a_{11}$ | $\frac{2\sqrt{1430}}{\sqrt{527}}$ | $7_8$ | $2F_1$ | $a_{11}$ | $-\frac{9\sqrt{11}}{8\sqrt{5}}$ |
| | | $a_{12}$ | $-\frac{2\sqrt{1430}}{17\sqrt{3}}$ | | | $a_{21}$ | $-\frac{10\sqrt{42}}{\sqrt{527}}$ | | | $a_{12}$ | $\frac{\sqrt{273}}{8}$ |
| | | $a_{22}$ | $-\frac{8\sqrt{10}}{17\sqrt{3}}$ | | | $b_{11}$ | $-\frac{35\sqrt{3}}{31\sqrt{2}}$ | | | $a_{22}$ | $-\frac{7\sqrt{3}}{4\sqrt{5}}$ |
| | | $a_{23}$ | $\frac{2\sqrt{70}}{\sqrt{51}}$ | | | $b_{12}$ | $-\frac{\sqrt{5005}}{31\sqrt{2}}$ | | | $b_{11}$ | $\frac{\sqrt{55}}{8\sqrt{7}}$ |
| | | $b_{11}$ | $-\frac{5\sqrt{11}}{8\sqrt{51}}$ | | | $b_{21}$ | $-\frac{\sqrt{5005}}{31\sqrt{2}}$ | | | $b_{12}$ | $\frac{23\sqrt{13}}{8\sqrt{35}}$ |
| | | $b_{21}$ | $-\frac{23\sqrt{13}}{8\sqrt{51}}$ | | | $b_{22}$ | $\frac{225\sqrt{3}}{62\sqrt{2}}$ | | | $b_{22}$ | $\frac{13}{4}$ |
| | | $b_{22}$ | $-\frac{13\sqrt{35}}{4\sqrt{51}}$ | | | $c_{11}$ | $-\frac{11\sqrt{77}}{\sqrt{1054}}$ | | | $c_{11}$ | $\frac{3\sqrt{33}}{\sqrt{70}}$ |
| | | $c_{11}$ | $-\frac{9\sqrt{21}}{68}$ | | | $c_{21}$ | $-\frac{5\sqrt{65}}{2\sqrt{3162}}$ | | | $c_{12}$ | $\sqrt{\frac{3}{14}}$ |
| | | $c_{12}$ | $\frac{90\sqrt{11}}{272}$ | | $2F_1$ | $a_{11}$ | $\frac{2\sqrt{70}}{\sqrt{17}}$ | | | $c_{22}$ | $-\sqrt{\frac{78}{5}}$ |
| | | $c_{22}$ | $-\frac{45\sqrt{13}}{136}$ | | | $a_{22}$ | $\frac{2\sqrt{70}}{\sqrt{51}}$ | | $2F_2$ | $a_{11}$ | $\frac{9\sqrt{11}}{8\sqrt{5}}$ |
| | $2F_2$ | $a_{11}$ | $-\frac{7\sqrt{110}}{17}$ | | | $a_{23}$ | $\frac{2\sqrt{10}}{\sqrt{3}}$ | | | $a_{21}$ | $-\frac{\sqrt{273}}{8}$ |
| | | $a_{21}$ | $-\frac{13\sqrt{35}}{17\sqrt{6}}$ | | | $b_{11}$ | $-\frac{3\sqrt{55}}{8}$ | | | $a_{22}$ | $\frac{7\sqrt{3}}{4\sqrt{5}}$ |
| | | $a_{22}$ | $-\frac{\sqrt{455}}{17\sqrt{2}}$ | | | $b_{21}$ | $\frac{5\sqrt{91}}{8\sqrt{3}}$ | | | $b_{11}$ | $-\frac{5\sqrt{3}}{4}$ |
| | | $b_{11}$ | $\frac{5\sqrt{35}}{4\sqrt{17}}$ | | | $b_{22}$ | $-\frac{7\sqrt{5}}{4\sqrt{3}}$ | | | $b_{12}$ | $\frac{17\sqrt{11}}{8\sqrt{7}}$ |
| | | $b_{21}$ | $-\frac{\sqrt{935}}{8\sqrt{3}}$ | | | $c_{11}$ | $-\frac{5\sqrt{35}}{4\sqrt{17}}$ | | | $b_{22}$ | $\frac{7\sqrt{39}}{8\sqrt{5}}$ |
| | | $b_{22}$ | $-\frac{7\sqrt{91}}{8\sqrt{17}}$ | | | $c_{12}$ | $\frac{\sqrt{935}}{8\sqrt{3}}$ | | | $c_{11}$ | $\frac{6\sqrt{2}}{\sqrt{35}}$ |
| | | $c_{11}$ | $\frac{9\sqrt{21}}{68}$ | | | $c_{22}$ | $\frac{7\sqrt{91}}{8\sqrt{17}}$ | $8_9$ | $A_1$ | $a$ | $\sqrt{\frac{182}{17}}$ |
| | | $c_{21}$ | $-\frac{45\sqrt{11}}{136}$ | | $2F_2$ | $a_{11}$ | $\frac{3\sqrt{35}}{\sqrt{34}}$ | | | $b$ | $-\frac{2\sqrt{10}}{\sqrt{17}}$ |
| | | $c_{22}$ | $\frac{45\sqrt{13}}{136}$ | | | $a_{12}$ | $\frac{\sqrt{455}}{\sqrt{102}}$ | | | | |
| $9_8$ | $A_1$ | $a$ | $-\frac{8\sqrt{26}}{\sqrt{57}}$ | | | $a_{22}$ | $\frac{5\sqrt{2}}{\sqrt{51}}$ | | | | |
| | | $b$ | $\frac{4\sqrt{2}}{\sqrt{19}}$ | | | $b_{11}$ | $\frac{3\sqrt{55}}{8}$ | | | | |

TABLE III (*continued*)

| R branch ($J_{J-1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $9_8$ | $2E$ | $a_{11}$ | $-\frac{168\sqrt{110}}{19\sqrt{899}}$ |
| | | $a_{12}$ | $-\frac{32\sqrt{2431}}{19\sqrt{899}}$ |
| | | $a_{21}$ | $-\frac{88\sqrt{546}}{19\sqrt{899}}$ |
| | | $a_{22}$ | $-\frac{28\sqrt{595}}{19\sqrt{2697}}$ |
| | | $b_{11}$ | $\frac{4\sqrt{286}}{\sqrt{589}}$ |
| | | $b_{21}$ | $-\frac{4\sqrt{210}}{\sqrt{589}}$ |
| | | $c_{11}$ | $-\frac{140\sqrt{6}}{589}$ |
| | | $c_{12}$ | $-\frac{4\sqrt{10010}}{589}$ |
| | | $c_{21}$ | $-\frac{4\sqrt{10010}}{589}$ |
| | | $c_{22}$ | $\frac{450\sqrt{6}}{589}$ |
| | $2F_1$ | $a_{11}$ | $-\frac{28\sqrt{7}}{19\sqrt{3}}$ |
| | | $a_{12}$ | $-\frac{4\sqrt{182}}{19\sqrt{3}}$ |
| | | $a_{22}$ | $-\frac{4\sqrt{10}}{19\sqrt{3}}$ |
| | | $a_{23}$ | $\frac{4\sqrt{3}}{\sqrt{19}}$ |
| | | $b_{11}$ | $\frac{3\sqrt{14}}{\sqrt{19}}$ |
| | | $b_{12}$ | $\sqrt{\frac{182}{57}}$ |
| | | $b_{22}$ | $\frac{2\sqrt{30}}{3\sqrt{19}}$ |
| | | $c_{11}$ | $-\frac{3\sqrt{55}}{19}$ |
| | | $c_{12}$ | $\frac{5\sqrt{91}}{19\sqrt{3}}$ |
| | | $c_{22}$ | $-\frac{14\sqrt{5}}{19\sqrt{3}}$ |

| Q branch ($J_J$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $8_8$ | $2F_2$ | $b_{12}$ | $-\frac{5\sqrt{91}}{8\sqrt{3}}$ |
| | | $b_{22}$ | $\frac{7\sqrt{5}}{4\sqrt{3}}$ |
| | | $c_{11}$ | $\frac{5\sqrt{11}}{8\sqrt{51}}$ |
| | | $c_{12}$ | $\frac{23\sqrt{13}}{8\sqrt{51}}$ |
| | | $c_{22}$ | $\frac{13\sqrt{35}}{4\sqrt{51}}$ |
| $9_9$ | $A_1$ | $a$ | $\frac{2\sqrt{238}}{5\sqrt{3}}$ |
| | | $b$ | $\frac{\sqrt{1547}}{5\sqrt{2}}$ |
| | $A_2$ | $a$ | $\frac{6\sqrt{286}}{5\sqrt{19}}$ |
| | | $b$ | $-\frac{\sqrt{1729}}{5\sqrt{2}}$ |
| | | $c$ | $-\frac{4\sqrt{2}}{\sqrt{19}}$ |
| | $E$ | $a_1$ | $\frac{26\sqrt{78}}{\sqrt{2755}}$ |
| | | $a_2$ | $-\frac{14\sqrt{17}}{5\sqrt{1653}}$ |
| | | $b$ | $\frac{7\sqrt{3}}{5\sqrt{2}}$ |
| | | $c_1$ | $-\frac{4\sqrt{286}}{\sqrt{589}}$ |
| | | $c_2$ | $\frac{4\sqrt{210}}{\sqrt{589}}$ |
| | $3F_1$ | $a_{11}$ | $\frac{7\sqrt{33}}{\sqrt{190}}$ |
| | | $a_{21}$ | $-\frac{\sqrt{1729}}{5\sqrt{6}}$ |
| | | $a_{22}$ | $-\frac{5\sqrt{7}}{\sqrt{57}}$ |
| | | $a_{32}$ | $-\frac{31\sqrt{17}}{10\sqrt{57}}$ |
| | | $a_{33}$ | $-\frac{17}{2\sqrt{5}}$ |
| | | $b_{11}$ | $-\sqrt{\frac{11}{5}}$ |

| P branch ($J_{J+1}$) levels | | | |
|---|---|---|---|
| Level | | Matrix element | |
| $8_9$ | $A_2$ | $a$ | $-\sqrt{\frac{182}{17}}$ |
| | | $c$ | $\frac{2\sqrt{110}}{\sqrt{51}}$ |
| | $E$ | $a$ | $\frac{7\sqrt{6}}{17}$ |
| | | $b_1$ | $-\frac{2\sqrt{1430}}{\sqrt{527}}$ |
| | | $b_2$ | $\frac{10\sqrt{42}}{\sqrt{527}}$ |
| | | $c$ | $-\frac{2\sqrt{910}}{17\sqrt{3}}$ |
| | $2F_1$ | $a_{11}$ | $-\frac{2\sqrt{55}}{17}$ |
| | | $a_{21}$ | $\frac{3\sqrt{91}}{17}$ |
| | | $a_{22}$ | $-\frac{25\sqrt{7}}{17\sqrt{3}}$ |
| | | $a_{23}$ | $\frac{14}{\sqrt{51}}$ |
| | | $b_{11}$ | $-\frac{3\sqrt{35}}{\sqrt{34}}$ |
| | | $b_{21}$ | $-\frac{\sqrt{455}}{\sqrt{102}}$ |
| | | $b_{22}$ | $-\frac{5\sqrt{2}}{\sqrt{51}}$ |
| | | $c_{11}$ | $\frac{7\sqrt{110}}{17}$ |
| | | $c_{12}$ | $\frac{13\sqrt{35}}{17\sqrt{6}}$ |
| | | $c_{22}$ | $\frac{\sqrt{455}}{17\sqrt{2}}$ |

TABLE III (*continued*)

| $R$ branch ($J_{J-1}$) levels | | | | $Q$ branch ($J_J$) levels | | | | $P$ branch ($J_{J+1}$) levels | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Level | | Matrix element | | Level | | Matrix element | | Level | | Matrix element | |
| $9_8$ | $2F_2$ | $a_{11}$ | $-\frac{\sqrt{10010}}{19\sqrt{3}}$ | $9_9$ | $3F_1$ | $b_{21}$ | $\frac{3\sqrt{91}}{10}$ | $8_9$ | $3F_2$ | $a_{11}$ | $\frac{2\sqrt{55}}{17}$ |
| | | $a_{21}$ | $-\frac{17\sqrt{2}}{19}$ | | | $b_{22}$ | $-\frac{5\sqrt{7}}{2\sqrt{3}}$ | | | $a_{21}$ | $-\frac{3\sqrt{91}}{17}$ |
| | | $a_{22}$ | $\frac{2\sqrt{102}}{19}$ | | | $b_{32}$ | $\frac{7\sqrt{17}}{5\sqrt{3}}$ | | | $a_{22}$ | $\frac{25\sqrt{7}}{17\sqrt{3}}$ |
| | | $b_{11}$ | $\frac{4\sqrt{14}}{\sqrt{19}}$ | | | $c_{11}$ | $-\frac{4\sqrt{14}}{\sqrt{19}}$ | | | $a_{32}$ | $-\frac{14}{\sqrt{51}}$ |
| | | $b_{22}$ | $\frac{4\sqrt{14}}{\sqrt{57}}$ | | | $c_{22}$ | $-\frac{4\sqrt{14}}{\sqrt{57}}$ | | | $b_{11}$ | $-\frac{2\sqrt{70}}{\sqrt{17}}$ |
| | | $b_{23}$ | $\frac{4\sqrt{34}}{\sqrt{57}}$ | | | $c_{32}$ | $-\frac{4\sqrt{34}}{\sqrt{57}}$ | | | $b_{22}$ | $-\frac{2\sqrt{70}}{\sqrt{51}}$ |
| | | $c_{11}$ | $\frac{3\sqrt{55}}{19}$ | | $2F_2$ | $a_{11}$ | $\frac{7\sqrt{13}}{10\sqrt{57}}$ | | | $b_{32}$ | $-\frac{2\sqrt{10}}{\sqrt{3}}$ |
| | | $c_{21}$ | $-\frac{5\sqrt{91}}{19\sqrt{3}}$ | | | $a_{21}$ | $-\frac{25}{2\sqrt{19}}$ | | | $c_{11}$ | $\frac{10\sqrt{42}}{17}$ |
| | | $c_{22}$ | $\frac{14\sqrt{5}}{19\sqrt{3}}$ | | | $a_{22}$ | $-\frac{11\sqrt{51}}{5\sqrt{19}}$ | | | $c_{21}$ | $\frac{2\sqrt{1430}}{17\sqrt{3}}$ |
| | | | | | | $b_{11}$ | $\sqrt{\frac{11}{5}}$ | | | $c_{22}$ | $\frac{8\sqrt{10}}{17\sqrt{3}}$ |
| | | | | | | $b_{12}$ | $-\frac{3\sqrt{91}}{10}$ | | | $c_{32}$ | $-\frac{2\sqrt{70}}{\sqrt{51}}$ |
| | | | | | | $b_{22}$ | $\frac{5\sqrt{7}}{2\sqrt{3}}$ | | | | |
| | | | | | | $b_{23}$ | $-\frac{7\sqrt{17}}{5\sqrt{3}}$ | | | | |
| | | | | | | $c_{11}$ | $-\frac{3\sqrt{14}}{\sqrt{19}}$ | | | | |
| | | | | | | $c_{21}$ | $-\frac{\sqrt{182}}{\sqrt{57}}$ | | | | |
| | | | | | | $c_{22}$ | $-\frac{2\sqrt{10}}{\sqrt{57}}$ | | | | |

are expressed in the table by putting

$$a_{11} = \frac{9\sqrt{15}}{22}, \qquad b_{11} = -\sqrt{\frac{21}{11}}, \quad b_{12} = \frac{3\sqrt{15}}{2\sqrt{11}}, \qquad c_{11} = \frac{2\sqrt{10}}{11},$$

$$a_{21} = -\frac{5\sqrt{3}}{2\sqrt{11}}, \qquad b_{22} = \frac{3\sqrt{3}}{2}, \qquad c_{21} = -\frac{6\sqrt{2}}{11}.$$

Those matrix elements which are not listed vanish.

The matrix elements listed here have been subjected to a check in the following manner. If we take $\zeta = 0$ for the perturbing $F_1$ set of levels, then the $F_1 J_{J+1}$, $F_1 J_J$, $F_1 J_{J-1}$ levels coincide. When the perturbation of the $F_2$ levels is evaluated in this special case one obtains a splitting which is identical in nature with that caused by the $E$–$F_2$ perturbation previously evaluated. The centre of gravity of the patterns follows a simple law with respect to $J$ and furthermore the pattern of the $P$ and $R$ branch sublevels referred to their centres of gravity are simple multiples (depending on $J$) of the pattern of the $Q$ branch sublevels referred to their centres of gravity. The relations are

$$g(J_J) \quad = \tfrac{1}{10}(2J-1)(2J+3),$$

$$g(J_{J+1}) = \tfrac{3}{10}J(J+2),$$

$$g(J_{J-1}) = \tfrac{3}{10}(J-1)(J+1),$$

where $g$ denotes the centre of gravity taking into account the weights of the sublevels and

$$\frac{p\{R(J)\}}{p\{Q(J)\}} = -\frac{J}{2J+3},$$

$$\frac{p\{P(J)\}}{p\{Q(J)\}} = -\frac{J+1}{2J-1},$$

for the ratio of the patterns. The perturbations for this special case have been evaluated for all the levels here listed and these relations verified. We are hence pretty confident that the matrix elements listed are free from errors.

## Conclusion

The formulae contained in this paper and in Part II form a basis wherewith a complete analysis of the vibrational-rotational spectrum of methane can be carried out. The rotational structure of any infra-red absorption band of methane will be determined by the predominant Coriolis perturbations to which the levels involved are subject. If the perturbations are small, their effects will be additive, but if they are large, the corresponding energy matrix must be diagonalized directly. The matrix elements listed above and in Part II will enable us to write down the energy matrix and carry out the calculation in all cases, up to the tenth rotational quantum number. It should be pointed out that if the anharmonicity is large, then the anharmonic intercombination will mix the harmonic wave functions and it is possible that a small intercombination may produce a large Coriolis perturbation. This is similar to the effect of intercombination on the hyperfine structure of atomic levels: a level for which the spin-orbit matrix elements are large can, by intercombination, produce a large hyperfine splitting of another level which would normally show only a small hyperfine effect.

Detailed applications to specific overtones and combination bands of methane are being undertaken and will be reported upon later.

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## Summary

In this paper a group-theoretical classification is made of the types of Coriolis perturbation which are possible in a tetrahedral molecule. It is shown that there are in all four distinct types of Coriolis perturbation of an infra-red active vibrational level. These arise from a Coriolis coupling of the rotational levels of this $F_2$ type vibrational level with the rotational levels of $A_2$, $E$, $F_1$ and $F_2$ type vibrational levels respectively. The $E$–$F_2$ type perturbation has been investigated in previous papers and here general formulae are derived for the matrix elements of the $A_2$–$F_2$, $F_1$–$F_2$ and $F_2$–$F_2$ type perturbations. It is shown that the $A_2$–$F_2$ and $F_2$–$F_2$ type perturbations do not produce a splitting of the individual rotational levels, the first causing a displacement of the $Q$ branch levels alone and the second a displacement of the $P$ and $R$ branch levels alone. The $F_1$–$F_2$ type like the $E$–$F_2$ type perturbation produces a splitting as well as a displacement of the rotational levels. The energy matrix determining this splitting is factorized up to the tenth rotational quantum number with the help of group theory. The formulae given here form the necessary basis for an analysis of any infra-red absorption band of methane.

## References

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