THE QUANTUM ANALYSIS OF THE BAND SPECTRUM OF ALUMINUM OXIDE (λ5200–λ4650)

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Abstract

Frequencies of lines in band spectrum of AlO.—The spectrograms were taken by R. T. Birge, using a new form of aluminum arc of his design. A table of frequencies of all measured lines is given, extending over ranges of 135, 70 and 65 lines of both branches of the (0,0), (0,1) and (1,0) bands respectively. No perturbations were observed within the range of measurement. Complete numerical formulas expressing the frequencies of all individual band lines within the range of measurement are given. The doublet separations are found to agree in bands of the same *final* vibration state. Numerical formulas for the doublet separation are given, in which the coefficients are consistent with the theory applied to the mean of doublet components.

Quantum analysis of the band spectrum of AlO.—A new method of locating band origins and verifying the combination principle is given, which applies particularly to bands in which no perturbations are observed. The method is direct and considers every possible choice of origins. The combination principle is verified for these bands over a range of 50 consecutive lines. Expressing the molecular energy terms due to vibration and rotation by $E=E^n+F=E^n+B_nm^4+D_nm^4+F_nm^6+H_nm^8+\cdots$ the coefficients are evaluated for the vibration states $n=0$ and $n=1$, by a method suggested by Kemble. The coefficients are consistent with their theoretical relations, involving the vibration frequency, as deduced by Kratzer, Kemble and Birge. Further, the coefficients are used to evaluate sets of rotational energy terms by means of which the frequencies of all lines within the range of measurement are represented well within the limits of experimental error. The numerical formulas for the frequencies of band lines are therefore of theoretical significance rather than purely empirical.

Molecular constants of the AlO molecule.—The moments of inertia of the AlO molecule for infinitely small vibration are found to be $(46.02\pm0.02)\times10^{-40}$ and $(43.38\pm0.02)\times10^{-40}$ gm cm^2 for the initial and final states respectively, and the corresponding distances of nuclear separation, 1.665×10^{-8} and 1.617×10^{-8} cm. The constants of an assumed law of force of the form $F=K_1(r-r_0)+K_2(r-r_0)^2+K_3(r-r_0)^3+\cdots$ are evaluated. Expressions for K_2 and K_3 are new and are due to Birge.

Introduction

THIS paper[1] is concerned with a detailed analysis of the (0,0)(λ4842), (0,1)(λ5079), and (1,0)(λ4648) bands[2] of AlO according to the

[1] Preliminary results of this work have been reported to the American Physical Society in the following abstracts: W. C. Pomeroy and R. T. Birge, Phys. Rev. **27,** 107 (1926) (Abstract 21). William C. Pomeroy, Phys. Rev. **27,** 640 (1926) (Abstract 11).

[2] Bands are designated (n', n'') where n' and n'' are the vibration quantum numbers of the initial and final states respectively, in emission.

quantum theory[3] and the testing of recently developed theoretical relations by which the elements of the rotational energy terms are connected with vibrational energy constants. These relations permit the representation of long band series by functions which are of theoretical significance rather than purely empirical.[4]

These bands, the so-called aluminum bands of the blue and green, are degraded to the red. As will appear from the detailed discussion to follow, they have no Q branch and the P and R branches consist of doublets of the violet cyanogen type. The variation of doublet separation with the rotation quantum number, k, is nearly linear to about $k=100.5$, actually increasing somewhat more rapidly than k. The departure of the frequencies of lines from a second degree law of variation is immediately apparent from the fact that the lines of one branch shift with respect to those of the other branch, overlap, and finally cross over, this occurring twice within the measured range of the (0,0) band. This crossing, which is unique in band spectra, was first recognized by Birge and is illustrated by the numbering of the P and R lines in the accompanying spectrograms, Fig. 1. The assignment of vibration quantum numbers to these bands was made independently by Birge[5] and by Mecke.[6]

Beginning with the work of Thalen (1866), Mörikofer[7] has given a brief but complete review of the studies of the band spectra of aluminum up to the year 1924. For the most part these are concerned either with the representation of band edges only, or with the question as to whether it is the metal or the oxide which is responsible for the band emission. In a recent comparison of emitters of band spectra, Mulliken,[8] using the results of the present work together with other data, has shown conclusively that these bands are due to the oxide, AlO.

As early as 1891, Hasselberg[9] had measured the wave-lengths of about 3000 lines in the band spectrum of aluminum, photographed with the aid of a plane grating. These are tabulated by Watts in his "Index of

[3] A brief account of the quantum theory of band spectra is contained in Sommerfeld, "Atombau und Spectrallinien," 4th edition, Ch. 9. A detailed account is given in the recent report of the National Research Council on "Molecular Spectra in Gases" (in press). The manuscript of this report was rendered available to the writer through the kindness of R. T. Birge, one of its co-authors. The nomenclature of the report has been adopted throughout this paper.

[4] With reference to the empirical representation of long band series, see R. T. Birge, Astrophys. J. **46,** 85 (1917); Phys. Rev. **13,** 360 (1919).

[5] R. T. Birge, Phys. Rev. **25,** 240 (1925) (Abstract 21).

[6] R. Mecke, Phys. Zeits. **26,** 217 (1925).

[7] W. Mörikofer, Dissertation, Basel (1925).

[8] R. S. Mulliken, Phys. Rev. **26,** 561 (1925).

[9] B. Hasselberg, Svensk. Vet. Akad. Handl. N. F. 24, Nr. 15 (1891).

Spectra." Later, Lauwartz,[10] using a concave grating, photographed the bands and made an analysis of structure lines with the object of testing Deslandres' law on long band series. He measured the wave-lengths of four bands designated after Hasselberg as $A(\lambda 4471)$, $B(\lambda 4648)$, $C(\lambda 4842)$ and $D(\lambda 5079)$ and represented the frequencies of the lines of each band by four series which we now recognize as the separate components of the doublets of the R and P branches[11] respectively. In each series, for three arbitrary lines, he evaluated the constants a and b and the parameter n in the formula

$$1/\lambda = a + bn^2 \qquad (1)$$

and calculated the frequencies of all lines in the series. Having compared observed and calculated frequencies, he concluded that Deslandres' law holds within the limits of experimental error only to 50 or 60 lines from the head of the band.[12]

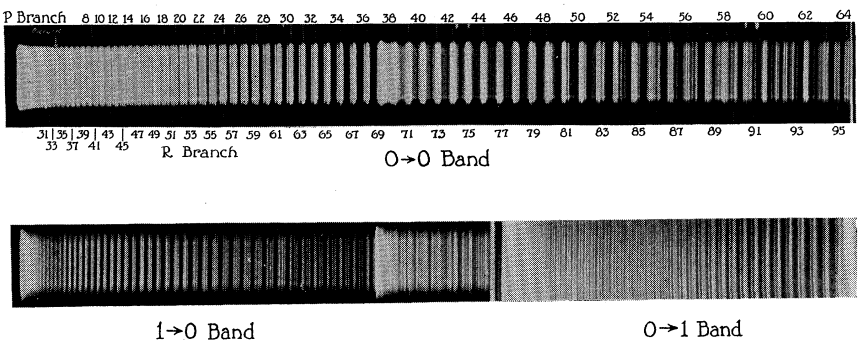

Fig. 1. Spectrograms of a portion of the band spectrum of AlO. The numerals attached to the (0,0) band indicate the quantum number of the final state corresponding to each doublet. The complete overlapping of P_{42} and R_{74} is clearly apparent.

Recently Eriksson and Hulthèn[13] have published some results of their analysis of these bands which are not in agreement with those of the

[10] J. Lauwartz, Zeit. f. wiss. Phot. **1**, 160 (1903).

[11] According to Deslandres' formulation, there are two series starting at the head of a band. The first of these—Lauwartz' C_3C_4 (in the case of the λ4842 band)—includes not only all of the P branch, but also that portion of the R branch between the head and the origin. The other series—Lauwartz' C_1C_2—includes the remaining portion of the R branch. However, at a point about 50 lines from the head, where the C_1C_2 series actually crosses the C_3C_4, Lauwartz failed to recognize the crossing, hence from this point to the red, his C_1C_2, instead of being the R branch, is actually the P branch, with a similar error for the series C_3C_4.

[12] It is of interest to note here that, according to the results of this paper, the assumption of a second degree law of variation leads to an error of about 24 cm^{-1} in the frequencies of lines which are about 160 lines distant from the head of the (0,0) band.

[13] Eriksson and Hulthèn, Zeits. f. Physik **34**, 775 (1925).

writer. Their location of origins is based upon data which allow a verification of the combination principle only for the final states, and leads to an assignment of rotational quantum numbers which causes the doublet separation to exhibit a marked discontinuity at the origin, while the writer finds no evidence of such a discontinuity. The present assignment of rotation quantum numbers is based upon a complete verification of the combination principle and the exclusion of all other possibilities of assignment, which facts should establish its correctness. The satellite system observed on their spectrograms does not appear on those measured by the writer, possibly because of differences in conditions of excitation.

The Spectrograms and Their Measurement

The following analysis is based upon the writer's measurements of spectrograms taken by R. T. Birge in 1915 in the second order of the 21 foot concave grating of the University of Wisconsin with a dispersion of about 1.33A per mm. As a source of emission, Birge devised a new form of aluminum arc, the lower electrode (anode) consisting of a 1/2 in. carbon rod into which short lengths of 1/8 in. aluminum rod were inserted so as to project about 1/2 in. above the end of the carbon. A solid 1/2 in. carbon rod served as the cathode. The arc was operated at 160 volts and with as high a value of current as was possible without causing the aluminum to collapse (about 9 amps.). The discharge from the cathode was confined to the aluminum tip of the anode rendering it in the spheroidal state as in the Pfund iron arc. The spectrograms, which contained considerably more data than had previously been obtained, were measured with the 200 mm comparator purchased by Professor Birge through the generosity of the Rumford Fund Committee. The standards of wave-length used were those of Meggers, Kiess and Burns.[14] Both components of each doublet line were measured at least twice, in most cases on different spectrograms. For each doublet, the wave-lengths of the separate components, their difference and mean value were calculated. Each difference and mean was converted to wave numbers (cm^{-1}) and corrected to vacuum. Results for the most part should be accurate within 0.005A (0.02 cm^{-1}) or better for distinct lines. All series relations are based upon the mean of frequencies of the doublet components, the values of which are tabulated in Tables I, II and III. While it was expected that small irregularities in successive differences of frequencies would occur, none were observed which could be classed as perturbations, a fact which is quite significant.

[14] Meggers, Kiess and Burns, "Redetermination of Secondary Standards of Wave-Length from the New International Arc," Bull. Bur. Stan. **19**, 263 (1924).

Verification of the Combination Principle

In addition to the fact that no perturbations were observed within the range of measurement, the band lines faded out toward the origin to such an extent that the establishment of the origins by the usual criterion of missing lines was impossible. Their approximate locations were determined, however, by a visual examination of enlargements of spectrograms, bearing in mind that the intensities of lines of the R and P branches should be roughly symmetrical with respect to the origin. The method adopted for considering every possible choice of origins may be readily understood with reference to the following representation of the combination principle which is taken from the report of the National Research Council.[3]

$$R_j = F'_{j+1} - F''_j \tag{2}$$

$$P_j = F'_{j-1} - F''_j \tag{3}$$

$$R_j - P_j = F'_{j+1} - F'_{j-1} = 2\Delta F'_j \tag{4}$$

$$R_j - P_{j+2} = F''_{j+2} - F''_j = 2\Delta F''_{j+1} \tag{5}$$

R and P represent the frequencies of lines, the subscript referring to the final state in emission. F' and F'' are the initial and final rotational energy "term" values respectively, the functional form of which will be discussed later. j is an integer, the meaning of which is explained by the following considerations of nomenclature: according to experimental results which will be discussed later, the nuclear angular momentum, m, has been shown to have very nearly half integral values. If the *resultant* angular momentum is parallel with the nuclear, i.e., the electrons have no angular momentum about the figure axis, we write $m = j - \epsilon = k - \alpha$. Now, it is uncertain whether the resultant angular momentum is an integer (j) or a half integer (k). If the former, the electronic momentum $\epsilon (= j - m)$ is for these bands essentially 0.5, and if the latter, the electronic momentum $\alpha (= k - m)$ is essentially zero. The adoption of the integer $j (= k + \frac{1}{2})$ leads to the condition that missing lines correspond to $j' = 0$, or $j'' = 0$.

Eqs. (2) and (3) may be regarded as defining the lines of the R and P branches of the band. $2\Delta F'$ and $2\Delta F''$ represent changes in the rotational term values for a change of two units in j, and may be termed "combination differences." According to the combination principle, all bands having the same initial vibration state should yield sets of values of $2\Delta F'$ which are numerically identical and similarly, all bands having the same final vibration state should give like sets of values of $2\Delta F''$. The problem then consists in assigning values of j to the lines of the three

bands such that the combination differences defined by Eqs. (4) and (5) will give the required agreement.

The following is a direct method by which every possible assignment of origins (or values of j) may be considered. Having arbitrarily designated each line by its numbering from the head, for each band an array of differences was constructed of the following form:

$$\begin{array}{llll} R_s - P_t & R_s - P_{t+1} & R_s - P_{t+2} & \cdots \\ R_{s+1} - P_t & R_{s+1} - P_{t+1} & R_{s+1} - P_{t+2} & \cdots \\ R_{s+2} - P_t & R_{s+2} - P_{t+1} & R_{s+2} - P_{t+2} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{array}$$

and each diagonal of each array was arbitrarily numbered. The form of

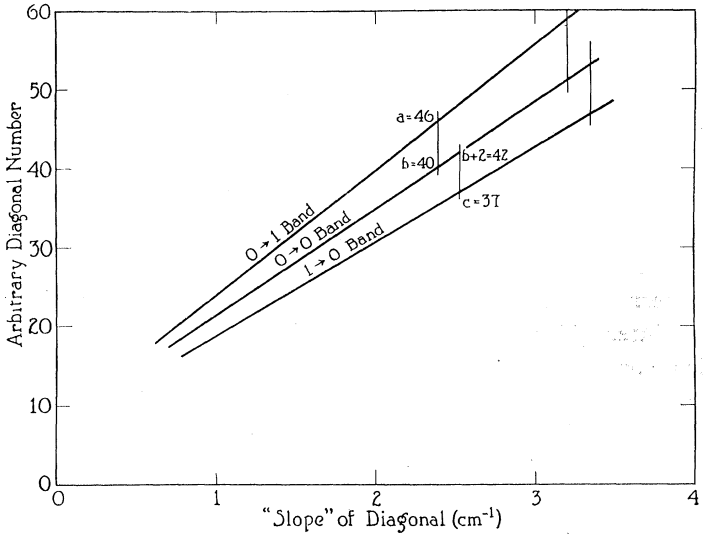

Fig. 2. Graphical construction employed in a direct verification of the combination principle.

each diagonal indicates that it represents a possible set of combination differences. The problem thus reduces to finding four diagonals which agree in pairs, two for the initial state and two for the final state. Now, suppose that a particular diagonal numbered b represents a set of values of $R_j - P_j$. Then a set of values of $R_j - P_{j+2}$ is given by the diagonal $b+2$. Thus, according to Eqs. (4) and (5), we must find a diagonal a of the (0,1) array which agrees with diagonal b of the (0,0) array (same initial vibration state), and a diagonal c of the (1,0) array which agrees with diagonal $b+2$ of the (0,0) array (same final vibration state). The process of finding the particular set of diagonals which gave agreement was greatly facilitated by plotting for each array the "slope" of diagonals (average of

approximately constant first differences) as a function of the arbitrary numbering. These slope curves were practically straight lines as shown in Fig. 2. Now, it is quite obvious that a pair of diagonals whose elements agree throughout must have the same slope, hence we examine the slope curves systematically and note every set of four diagonals for which the slopes agree in pairs, the two diagonals of the (0,0) array differing by two in numbering. Two such sets are indicated in the figure. We now refer back to the diagonals of the arrays by number and find that but one of these sets of four (in this case a, b, and $c=46$, 40, and 37 respectively) gives agreement of absolute values of the elements of the diagonals. The combination principle is thus verified and the values of j determined to the exclusion of all other possibilities of assignment.

Having verified the combination principle and determined the combination differences, it is required to assign values of j to these differences and to the lines which were combined to give them. The approximate expression for any combination difference is[15]

$$2\Delta F=4Bm \tag{6}$$

and its rate of change with m is $4B$, the diagonal slope mentioned above. The experimentally determined values of $m(=2\Delta F/4B)$ are found to form a set of approximate half integers and each m is increased by approximately $\frac{1}{2}$ to give the integral j which designates the corresponding $2\Delta F$. Eq. (4) indicates that the value of j which designates each $2\Delta F'$ also applies to the corresponding R and P lines while Eq. (5) indicates that the value of j which designates each $2\Delta F''$ is to be diminished by 1 and increased by 1 to give the values of j which apply to the corresponding R and P lines respectively.

Tables I, II and III, arranged with j as argument, give the values of the frequencies of all measured lines (mean of doublet components corrected to vacuum) and the combination differences. The agreement between the values of R_j-P_j for the (0,0) and the (0,1) bands and between the values of R_j-P_{j+2} for the (0,0) and the (1,0) bands, indicates the accuracy with which the combination principle is verified.

[15] See Eq. (20) below.

TABLE I

Frequencies and combination differences of all measured lines of the (0, 0) band

j	Rj	P_j	R_j-P_j	R_j-P_{j+2}	j	Rj	P_j	R_j-P_j	R_j-P_{j+2}
6									
7		20626.53			13		20615.14		
8		24.82			14		12.98		
9		23.04			15		10.74		
10		21.18			16		08.46		
11		19.24			17		06.11		
12		17.24			18		03.67		

TABLE I—Continued

Frequencies and combination differences of all measured lines of the (0, 0) band

j	Rj	P_j	R_j-P_j	R_j-P_{j+2}	j	Rj	P_j	R_j-P_j	R_j-P_{j+2}
19		01.14			81	20590.80	20301.86	188.94	203.28
20		598.54			82	85.92	294.74	191.18	205.71
21		95.88			83	80.92	87.52	193.40	208.08
22		93.16			84	75.84	80.21	195.63	210.43
23	20644.46	90.33	54.13	59.96	85	70.68	72.84	197.84	212.80
24	43.94	87.45	56.49	62.48	86	65.44	65.41	200.03	215.16
25	43.37	84.50	58.87	65.02	87	60.12	57.88	202.24	217.50
26	42.73	81.46	61.27	67.56	88	54.71	50.28	204.43	219.81
27	42.00	78.35	63.65	70.08	89	49.25	42.62	206.63	222.18
28	41.20	75.17	66.03	72.60	90	43.68	34.90	208.78	224.51
29	40.33	71.92	68.41	75.11	91	38.09	27.07	211.02	226.89
30	39.40	68.60	70.80	77.65	92	32.36	19.17	213.19	229.19
31	38.38	65.22	73.16	80.16	93	26.58	11.20	215.38	231.50
32	37.30	61.75	75.55	82.68	94	20.71	03.17	217.54	233.83
33	36.13	58.22	77.91	85.22	95	14.74	195.08	219.66	236.12
34	34.88	54.62	80.26	87.75	96	08.73	86.88	221.85	238.45
35	33.56	50.91	82.65	90.26	97	02.59	78.62	223.97	240.72
36	32.18	47.13	85.05	92.78	98	396.42	70.27	226.15	243.04
37	30.71	43.30*	87.41	95.28	99	90.15	61.87	228.28	245.35
38	29.17	39.40	89.77	97.80	100	83.79	53.38	230.41	247.59
39	27.57	35.43	92.14	100.34	101	77.40	44.80	232.60	249.90
40	25.86	31.37	94.49	102.84	102	70.90	36.20	234.70	252.17
41	24.12	27.23	96.89	105.36	103	64.30	27.50	236.80	254.43
42	22.28	23.02	99.26	107.86	104	57.65	18.73	238.92	256.70
43	20.34	18.76	101.58	110.34	105	50.90	09.87	241.03	258.98
44	18.36	14.42	103.94	112.86	106	44.10	00.95	243.15	261.23
45	16.29	10.00	106.29	115.37	107	37.21	091.92	245.29	263.49
46	14.17	05.50	108.67	117.88	108	30.20	82.87	247.33	265.69
47	11.95	00.92	111.03	120.37	109	23.13	73.72	249.41	267.91
48	09.63	496.29	113.34	122.83	110	15.98	64.51	251.47	270.16
49	07.28	91.58	115.70	125.34	111	08.79	55.22	253.57	272.40
50	04.84	86.80	118.04	127.85	112	01.50	45.82	255.68	274.64
51	02.31	81.94	120.37	130.33	113	294.14	36.39	257.75	276.83
52	599.70	76.99	122.71	132.80	114	86.66	26.86	259.80	279.01
53	97.03	71.98	125.05	135.29	115	79.12	17.31	261.81	281.20
54	94.27	66.90	127.37	137.75	116	71.52	07.65	263.87	283.38
55	91.44	61.74	129.70	140.24	117	63.81	19997.92	265.89	285.59
56	88.52	56.52	132.00	142.68	118	56.01	88.13	267.88	287.73
57	85.55	51.20	134.35	145.15	119	48.16	78.22	269.94	289.90
58	82.51	45.84	136.67	147.66	120	40.24	68.28	271.96	292.09
59	79.37	40.40	138.97	150.10	121	32.22	58.26	273.96	294.22
60	76.17	34.85	141.32	152.55	122	24.13	48.15	275.98	296.38
61	72.88	29.27	143.61	155.00	123	15.96	38.00	277.96	298.53
62	69.50	23.62	145.88	157.43	124	07.71	27.75	279.96	300.67
63	66.03	17.88	148.15	159.85	125	199.40	17.43	281.97	302.81
64	62.51	12.07	150.44	162.29	126	91.00	07.04	283.96	304.94
65	58.94	06.18	152.76	164.76	127	82.54	896.59	285.95	307.08
66	55.27	00.22	155.05	167.20	128	73.98	86.06	287.92	309.18
67	51.55	394.18	157.37	169.66	129	65.30	75.46	289.84	311.23
68	47.69	88.07	159.62	172.08	130	56.61	64.80	291.81	313.35
69	43.80	81.89	161.91	174.51	131	47.82	54.07	293.75	315.43
70	39.80	75.61	164.19	176.93	132	38.93	43.26	295.67	317.52
71	35.75	69.29	166.46	179.35	133	29.97	32.39	297.58	319.57
72	31.59	62.87	168.72	181.75	134	20.93	21.41	299.52	321.62
73	27.38	56.40	170.98	184.20	135	11.85	10.40	301.45	323.70
74	23.10	49.84	173.34	186.59	136	02.65	799.31	303.34	325.73
75	18.72	43.18	175.54	188.97	137	093.40	88.15	305.25	327.78
76	14.30	36.51	177.79	191.41	138	84.60	76.92	307.14	329.82
77	09.75	29.75	180.00	193.80	139	74.64	65.62	309.02	331.84
78	05.14	22.89	182.25	196.17	140	65.15	54.24	310.93	333.85
79	00.45	15.95	184.50	198.59	141		42.80		
80	495.65	08.97	186.68	200.91	142		31.30		

*Band lines obscured by heads of other bands. Frequencies obtained by interpolation.

Representation of the structure lines of the bands. Let it now be required to formulate expressions for the frequencies of band lines on a definite theoretical basis. The theory which has been applied in this analysis has been outlined by Birge[16] and further details are contained in the report of the National Research Council.[3] The following account is intended as an explanation of the method of analysis used by the writer, rather than as a development of the theory.

TABLE II

Frequencies and combination differences of all measured lines of the (0,1) band

j	R_j	P_j	R_j-P_j	R_j-P_{j+2}	j	R_j	P_j	R_j-P_j	R_j-P_{j+2}
6					41	19668.20	19571.33	96.87	104.37
7					42	66.85	67.60	99.25	106.85
8		19659.68			43	65.43	63.83	101.60	109.33
9		58.00			44	63.94	60.00	103.94	111.83
10		56.21			45	62.36	56.10	106.26	114.30
11		54.40			46	60.76	52.11	108.65	116.80
12		52.52			47	59.08	48.06	111.02	119.27
13		50.60			48	57.33	43.96	113.37	121.74
14		48.60			49	55.51	39.81	115.70	124.21
15		46.54			50	53.64	35.59	118.05	126.65
16		44.40			51	51.70	31.30	120.40	129.11
17		42.21			52	49.69	26.99	122.70	131.58
18		39.96			53	47.63	22.59	125.04	134.03
19		37.66			54	45.50	18.11	127.39	136.46
20		35.29			55	43.29	13.60	129.69	138.90
21		32.86			56	41.04	09.04	132.00	141.37
22		30.38			57	38.73	04.39	134.34	143.83
23		27.84			58	36.32	499.67	136.65	146.20
24		25.22			59	33.87	94.90	138.97	148.76
25		22.53			60	31.37	90.06	141.31	151.15
26	19681.01	19.78	61.23	66.89	61	28.78	85.17	143.61	153.55
27	80.61	16.96	63.65	69.40	62	26.12	80.22	145.90	155.98
28	80.14	14.12	66.02	71.92	63	23.40	75.23	148.17	158.42
29	79.61	11.21	68.40	74.44	64	20.60	70.14	150.46	160.81
30	79.02	08.22	70.80	76.94	65	17.76	64.98	152.78	163.25
31	78.37	05.17	73.20	79.46	66	14.85	59.79	155.06	165.67
32	77.63	02.08	75.55	81.95	67	11.89	54.51	157.38	168.10
33	76.82	598.91	77.91	84.44	68	08.84	49.18	159.66	170.50
34	75.96	95.67	80.29	86.94	69	05.74	43.79	161.95	172.92
35	75.05	92.38	82.67	89.44	70	02.56	38.34	164.22	175.32
36	74.06	89.02	85.04	91.91	71	599.30	32.82	166.48	177.67
37	73.04	85.61	87.43	94.44	72	96.00	27.24	168.76	180.09
38	71.91	82.15	89.76	96.91	73	92.62	21.63	170.99	182.47
39	70.74	78.60	92.14	99.41	74	89.21	15.91	173.30	
40	69.50	75.00	94.50	101.90	75	85.66	10.15	175.51	

We assume the molecular energy "terms" due to vibration and rotation to be given by[17]

$$E=E^n+F=E^n+B_nm^2+D_nm^4+F_nm^6+H_nm^8+\cdots \qquad (7)$$

where $m=j-\epsilon=k-\alpha$.

[16] R. T. Birge, Nature **116**, 783 (1925); Phys. Rev. **27**, 245 (1926).

[17] For convenience we use the value of the energy "term" which is defined as energy in ergs divided by ch and is therefore measured in cm^{-1}.

Kemble,[18] using only the first three terms of the right member of Eq. (7) has considered in some detail the dependence of E^n, B_n and D_n upon the value of the vibration quantum number, n, and the resulting relations between rotational and vibrational energy. The relations are much simplified by considering the special case of the non-vibrating molecule, i.e., $n=0$, for which the molecular energy, neglecting electronic, is entirely rotational and is given by

$$F=B_0m^2+D_0m^4+F_0m^6+H_0m^8+\cdots \tag{8}$$

TABLE III

Frequencies and combination differences of all measured lines of the (1,0) band

j	R_j	P_j	R_j-P_j	R_j-P_{j+2}	j	R_j	P_j	R_j-P_j	R_j-P_{j+2}
6					46	21467.56	21359.71	107.85	117.89
7					47	64.93	54.73	110.20	120.38
8					48	62.19	49.67	112.52	122.85
9					49	59.37	44.55	114.82	125.34
10					50	56.49	39.34	117.15	127.84
11					51	53.49	34.03	119.46	130.28
12					52	50.44	28.65	121.79	132.79
13					53	47.30	23.21	124.09	135.29
14					54	44.05	17.65	126.40	137.76
15					55	40.72	12.01	128.71	140.22
16					56	37.32	06.29	131.03	142.72
17					57	33.83	00.50	133.33	145.15
18					58	30.26	294.60*	135.66	147.64
19		21462.88			59	26.58	88.67	137.91	150.08
20		60.13			60	22.85	82.62	140.23	152.54
21		57.29			61	19.00	76.50	142.50	154.98
22		54.36			62	15.08	70.31	144.77	157.42
23	21505.00	51.35	53.65	59.92	63	11.09	64.02	147.07	159.87
24	04.31	48.25	56.06	62.47	64	07.02	57.66	149.36	162.32
25	03.49	45.08	58.41	64.97	65	02.83	51.22	151.61	164.76
26	02.62	41.84	60.78	67.51	66	398.56	44.70	153.86	167.20
27	01.69	38.52	63.17	70.06	67	94.22	38.07	156.15	169.66
28	00.65	35.11	65.54	72.59	68	89.80	31.36	158.44	172.11
29	499.53	31.63	67.90	75.12	69	85.28	24.56	160.72	174.52
30	98.32	28.06	70.26	77.65	70	80.67	17.69	162.98	176.97
31	97.02	24.41	72.61	80.18	71	75.96	10.76	165.20	179.37
32	95.65	20.67	74.98	82.70	72	71.22	03.70	167.52	181.81
33	94.19	16.84	77.35	85.21	73	66.34	196.59	169.75	184.19
34	92.64	12.95	79.69	87.73	74	61.40	89.41	171.99	186.61
35	91.02	08.98	82.04	90.27	75	56.34	82.15	174.19	188.99
36	89.32	04.91	84.41	92.80	76	51.21	74.79	176.42	191.40
37	87.53	00.75	86.78	95.32	77	46.00	67.35	178.65	193.81
38	85.63	396.52*	89.11	97.80	78	40.70	59.81	180.89	196.19
39	83.71	92.21	91.50	100.34	79	35.31	52.19	183.12	198.57
40	81.65	87.83	93.82	102.85	80	29.83	44.51	185.32	200.93
41	79.50	83.37	96.13	105.34	81	24.26	36.74	187.52	203.33
42	77.29	78.80	98.49	107.84	82	18.60	28.90	189.70	205.69
43	74.97	74.16	100.81	110.35	83	12.87	20.93	191.94	208.07
44	72.59	69.45	103.14	112.88	84	07.06	12.91	194.15	
45	70.12	64.62	105.50	115.39	85		04.80		

*Band lines obscured by heads of other bands. Frequencies obtained by interpolation.

[18] E. C. Kemble, J.O.S.A. **12**, 1 (1926).

For this condition, D_0, F_0 and H_0 have been evaluated in terms of other constants as follows:

$$D_0 = -4B_0^3/\omega^{0^2} \tag{9}$$

$$F_0 = (2-\bar{\alpha}\omega^0/6B_0^2)D_0^2/B_0 \tag{10}$$

$$H_0 = 3F_0D_0/B_0 - 5D_0^3/B_0^2 + F_0^2/D_0 - 8D_0^2x/3\omega^0 \tag{11}$$

Eq. (9) was obtained by Kratzer,[19] Kemble[18] and others while Eqs. (10) and (11) were first obtained by Birge.[16] ω^0 and x have the same meaning as in Kratzer's equations[19]

$$\omega^n = \omega^0(1-2xn+\cdots) \tag{12}$$

$$E^n = n\omega^0(1-xn+\cdots) \tag{13}$$

i.e., ω^0 is the vibration frequency for infinitely small amplitude expressed in cm^{-1} and $2\omega^0x$ is its initial rate of change with the vibration quantum number, n. From Eq. (13) it follows that

$$E^{n+1} - E^n = \omega^0 - (n+\tfrac{1}{2})2\omega^0x \tag{14}$$

Eq. (14) states that the difference of two adjacent vibration terms yields a frequency equal to the mean of the corresponding vibration frequencies.[20] We are thus enabled by extrapolation to determine the vibration frequency for the zero state, i.e., ω^0. Values of ω^0 and ω^0x for these bands have been calculated by Birge (unpublished), using frequencies of band heads as vibration terms. The final analysis indicates, however, that the separation of band heads is in only approximate agreement with the separation of origins, hence these values are not exact.

As just noted, Eqs. (9), (10) and (11) apply only to the zero vibration state. For higher states, Kemble's formulas may be written

$$B_n = B_0 - \bar{\alpha}n \tag{15}$$

$$D_n = D_0 + \beta''n \tag{16}$$

thus defining

$$\bar{\alpha} = B_0 - B_1 \tag{17}$$

$$\bar{\beta}'' = D_1 - D_0 \tag{18}$$

$\bar{\alpha}$ is required[21] for the evaluation of F_0 in Eq. (10). β'' has been evaluated by the writer from Kemble's formulas as

$$\bar{\beta}'' = (2-4H_0B_0^2/D_0^3 + 9B_0^2F_0^2/2D_0^4)12B_0^4/\omega^{0^3} \tag{19}$$

[19] A. Kratzer, Zeit. f. Physik **3**, 289 (1920).

[20] This is of course only a particular instance of the so-called correspondence theorem.

[21] Kratzer's α will be designated $\bar{\alpha}$ as defined by Eq. (17) and is not to be confused with the electronic momentum, α, previously defined.

Expressions for F_n and H_n for the higher vibration states have not yet been derived. For the present purpose, however, it is sufficient to assume that $F_1=F_0$ and that $H_1=H_0$.

Now, Eqs. (4) and (5) indicate the well known fact that the experimental data lead to the direct evaluation, not of F, but of $2\Delta F$, i.e., of the variation of F for a variation of two units in j. If ϵ (or α) is a constant, as will be assumed for the present, dF/dm and dF/dj are identical and it may easily be shown[22] that the values of $2\Delta F/2$ differ from dF/dm by negligible amounts. Hence we obtain from Eq. (7)

$$2dF/dm=2\Delta F=4B_nm+8D_nm^3+12F_nm^5+16H_nm^7+\cdots \quad (20)$$

and

$$\Delta F/m=2B_n+4D_nm^2+6F_nm^4+8H_nm^6+\cdots \quad (21)$$

The immediate problem to be solved may now be more definitely stated in terms of the above formulas. In Tables I, II and III are tabulated four sets of values of $2\Delta F$, two for the zero vibration state (initial and final molecular configuration respectively), and two for the vibration state, $n=1$. It is required to determine the four corresponding sets of coefficients in Eq. (7) yielding four sets of rotational energy terms, combinations of which will accurately represent the observed lines of the (0,0), (0,1) and (1,0) bands respectively. Further, it is required to compare the relations among calculated coefficients with the theoretical relations given by Eqs. (9), (10) and (11). The problem is largely a matter of the best method of handling the data, taking into account the amount of labor required and the accuracy of the final results. The method used herein is a combination of the methods of successive approximation and least squares and will be described in some detail.

With reference to Eq. (21) it may be noted that the left member may not be evaluated accurately until ϵ (or α) is known. Preliminary analysis shows, however, that in the case of bands such as the violet cyanogen bands or those discussed in this paper, the value of α is either zero or is very small. Hence, to a close approximation, m may be replaced by k.[23]

Using the four sets of values of $2\Delta F$ tabulated in Tables I, II and III, values of $\Delta F/k$ were calculated and each $\Delta F/k$ was plotted as a function of k. Omitting the last two terms of Eq. (21) as a first approximation, values of B and D for each of the four cases were calculated from two suitable points on the $\Delta F/k : k$ curve. For the zero state, values of B_0 and D_0 thus determined and combined with the previously calculated values of ω^0 satisfied Eq. (9) within a fraction of a percent. Having determined

[22] Report of National Research Council, Ch. IV, Eq. (78).

[23] More accurately, $\Delta F/k=2B_n-2B_n\alpha/k+4D_nk^2+6F_nk^4+\cdots$

fairly accurate values of B_0 and D_0, we calculate approximate values of F_0 and H_0 from Eqs. (10) and (11). $\bar{\alpha}$ may be taken as the difference between B_0 and B_1 as obtained from the $\Delta F/k : k$ curves, or may be found analytically from the approximate relation deduced from Eq. (21), with m replaced by k:

$$\Delta F_0/k - \Delta F_1/k = 2\bar{\alpha} - 16B_0^3k^2(1/\omega^{0^2} - 1/\omega^{1^2}) \tag{22}$$

Following Kemble's suggestion,[18] we now transform Eq. (20) as

$$2\Delta F^* = 2\Delta F - 8D_nm^3 - 12F_nm^5 - 16H_nm^7 - \cdots \tag{23}$$

$$= 4B_nm \tag{24}$$

$$= 4B_n(k-\alpha) \tag{25}$$

Now, as just noted, $m=k$ approximately, and D_n, F_n and H_n are small quantities compared to B_n. Therefore it is entirely legitimate to replace the unknown m by the known k in the third and higher degree terms of Eq. (23). By this substitution, a set of numerical values of $2\Delta F^*$ is obtained which should be linear in k provided that D_n, F_n and H_n are known with sufficient accuracy and α is constant. The outstanding feature of this method of solution is the transformation of the higher degree $2\Delta F : k$ curve into the linear $2\Delta F^* : k$ curve. This permits the use of all of the experimental data in the evaluation of $4B$ as the constant slope of the linear $2\Delta F^* : k$ curve as compared with the extrapolation of the lower end of the non-linear $2\Delta F : k$ curve to determine $4B$ as its limiting slope for $k=0$.

The following procedure is carried out for both the initial and final states respectively. Considering first the zero vibration state, values of $2\Delta F^*$ were calculated by Eq. (23) using the observed values of $2\Delta F$ and the values of D_0, F_0 and H_0 given by Eqs. (9), (10) and (11). In these equations the value of B_0 determined from the $\Delta F/k : k$ curve was used. The resulting set of Eqs. (25) considered as linear in k was solved by least squares, giving a better value of B_0 and also a value of α. Should the new value of B_0 differ sufficiently from its first approximation to affect D_0, F_0, and H_0 materially, a second solution is necessary. It may be mentioned here that the greatest obstacle to accuracy is the lack of trustworthy values of vibration frequency since we must resort to Eq. (9) in order to improve upon the values of D_0 obtained from the $\Delta F/k : k$ curves. Unfortunately an accurate set of vibration frequencies may be obtained only from an extended fine structure analysis which will determine a relatively large number of band origins rather closely. A set of values of $2\Delta F^*$ is now calculated by Eq. (25), using the results of the least squares solution, and the linearity of "observed" values is tested

by plotting differences of observed and calculated values of $2\Delta F^*$. Any appreciable trend in the residuals is to be corrected by an adjustment of coefficients.

Turning now to the vibration state $n=1$, we note that β'' may be calculated from Eq. (19), knowing the values of the coefficients B_0, D_0, F_0 and H_0. The resulting value of D_1 may be compared with that obtained from the $\Delta F/k : k$ curve for the state $n=1$. It was assumed that $F_1=F_0$ and $H_1=H_0$, the error introduced being negligible since the contribution of these terms to the rotational energy is small within the range of measurement of the (1,0) and (0,1) bands. Values of $2\Delta F^*$ for $n=1$ are then calculated and the equations solved as described above.

Having evaluated the four sets of coefficients B, D, F and H, we calculate the four corresponding sets of rotational energy terms and the six sets of differences to be used in the representation of the six sets of lines, i.e., the P and R lines of the three measured bands. For each band, we write

$$\underset{n'\to n''}{R_j} = \underset{n'\to n''}{\nu_0} + \underset{n'}{F_j'}_{+1} - \underset{n''}{F_j''} \tag{26}$$

$$\underset{n'\to n''}{P_j} = \underset{n'\to n''}{\nu_0} + \underset{n'}{F_j'}_{-1} - \underset{n''}{F_j''} \tag{27}$$

where ν_0 is the frequency of the origin of the band. The calculated value of ν_0 for each of the three bands, using in Eqs. (26) and (27) the observed frequencies of lines and the calculated values of the rotational energy terms, should be constant throughout the range of measurement. As a matter of fact, although the variations were not large, they exceeded the limits of experimental error as might be expected from the fact that we are virtually building up a function from the values of successive differences.

This difficulty, however, may be overcome as follows: for each band, the differences between calculated values of ν_0 and an arbitrary constant (conveniently, a round number approximating the average) were plotted as a function of k, giving a curve of residuals with ordinates, $\Delta\nu$, ranging within a few tenths of a cm^{-1}. Each residual curve was expressed analytically by passing a curve through six arbitrary points to satisfy an equation of the form

$$\Delta\nu = A + ak + bk^2 + dk^4 + fk^6 + hk^8 \tag{28}$$

The coefficients in the above equation give the corrections to be applied to the differences of corresponding coefficients of the rotational energy terms which are concerned. For example, b of the (0,0) residual curve is the correction to be applied to the difference $(B_0'-B_0'')$. From the (0,1) and (1,0) curves we obtain the corrections to $(B_0'-B_1'')$ and

$(B_1'-B_0'')$ respectively. Having three correction equations containing the four unknowns, B_0', B_0'', B_1', and B_1'', there remains an element of arbitrariness in fixing the correction to each value of B. Similarly, for each of the sets of coefficients, D, F and H, we write three correction equations. In every case the corrections were small and were adjusted in such a manner that the final results satisfied Eqs. (9), (10) and (11) as nearly as possible.

It may be emphasized here that since the frequencies of long band series may be satisfactorily represented by a number of arbitrarily chosen forms of polynomial, the problem is not to find the form of function which best represents the band lines but rather to determine whether or not the lines of the bands can be represented accurately by means of rotational energy terms of the form of Eq. (8) in which the coefficients satisfy Eqs. (9), (10) and (11).

The final values of calculated coefficients follow:

$$B_0' = 0.60190 \text{ cm}^{-1} \qquad D_0' = -1.1630\times10^{-6} \text{ cm}^{-1}$$
$$B_0'' = 0.63860 \qquad D_0'' = -1.1094\times10^{-6}$$
$$B_1' = 0.59737 \qquad D_1' = -1.1571\times10^{-6}$$
$$B_1'' = 0.63285 \qquad D_1'' = -1.1181\times10^{-6}$$

$$\alpha_0' = +0.0074 \qquad F_0' = F_1' = +0.440\times10^{-12} \text{ cm}^{-1}$$
$$\alpha_0'' = +0.0100 \qquad F_0'' = F_1'' = -0.530\times10^{-12}$$
$$\alpha_1' = +0.0050 \qquad H_0' = H_1' = 0.0$$
$$\alpha_1'' = +0.0132 \qquad H_0'' = H_1'' = -5.2\times10^{-18}$$

$$\bar{\alpha}' = B_0' - B_1' = +0.00453 \text{ cm}^{-1}$$
$$\bar{\alpha}'' = B_0'' - B_1'' = +0.00575$$

As a final test of the accuracy with which the frequencies of the lines of each band were represented with the use of the above coefficients, the four sets of rotational energy terms and the six sets of differences to be used in Eqs. (26) and (27) were recalculated. For each band, the appropriate differences were combined with the observational data of Tables I, II and III and in every case yielded a set of values of ν_0 which was constant within the limits of experimental error throughout the range of measurement. This fact was indicated by constructing for each band a table of differences between calculated and most probable values of ν_0 (not reproduced in this paper). These residuals showed no systematic trend and in every case the average of the absolute values was less than 0.02 cm^{-1} (0.005A) and very few exceeded 0.04 cm^{-1} (0.01A). The most

probable value of ν_0 was arbitrarily taken as its average from $j=30$ to $j=70$ thus avoiding the less reliable observational data for the smaller values of j and the less accurate values of the rotational energy terms for the larger values of j.

It is interesting to note the rather unusual occurrence of the coincidence of a band line with the origin. It was found that for the (1,0) band, the frequency of the line R_{30} is the same as that of the origin. In the case of the (0,1) band, one component of the line R_{40} very nearly coincides in position with the origin.[24] In such instances as these, the recognition of missing lines is difficult if not impossible.

Agreement of coefficients with theoretical relations. From Eq. (9), we find

$$\omega^0=\sqrt{-4B_0^3/D_0} \tag{29}$$

The determination of ω^0 from the final calculated coefficients gives

$$\omega^{0\prime}=866\ \text{cm}^{-1} \qquad \omega^{0\prime\prime}=969\ \text{cm}^{-1}$$

whereas Birge, using frequencies of band heads as vibration terms has calculated

$$\omega^{0\prime}=866\ \text{cm}^{-1} \qquad \omega^{0\prime\prime}=970\ \text{cm}^{-1}$$

While this agreement is very close, it appears from the meager data available that these frequencies would be slightly higher if calculated from the frequencies of origins (see Eq. (36) ahead).

Substitution of the final calculated coefficients in Eq. (10) yields for the left members, initial and final states respectively, $+0.440\times10^{-12}$, and -0.530×10^{-12} and for corresponding right members $+0.439\times10^{-12}$ and -0.534×10^{-12}, a very satisfactory agreement.

The evaluation of the right member of Eq. (11), using Birge's values of $\omega^{0\prime}x^{\prime}=3.75$ and $\omega^{0\prime\prime}x^{\prime\prime}=7.00$ gives $H_0{}^{\prime}=+0.9\times10^{-18}$ and $H_0{}^{\prime\prime}=-5.2\times10^{-18}$ as compared with the finally adopted values of $H_0{}^{\prime}=0.0\times10^{-18}$ and $H_0{}^{\prime\prime}=-5.2\times10^{-18}$. In view of the fact that the contribution of the term in x is relatively large and that the values of x are rather uncertain, we may assume that Eq. (11) is satisfied within the limits of experimental error.

Substitution of the final calculated coefficients in the right member of Eq. (18) gives for $\beta^{\prime\prime}$, initial and final states respectively, $+0.0059\times10^{-6}$ and -0.0087×10^{-6}, while the right member of Eq. (19) gives for corresponding values, $+0.0055\times10^{-6}$ and -0.0085×10^{-6}. Considering the uncertainty of the values of H_0, this agreement is quite satisfactory.

Lastly, Eq. (17) is satisfied exactly by the final calculated coefficients.

[24] This statement anticipates the discussion of doublet separation which is to follow.

The relatively good agreement indicated in the preceding discussion is rather conclusive evidence of the validity of the relations between rotational and vibrational constants given by Eqs. (9), (10) and (11), at least in the case of the bands discussed in this paper.

Accuracy of calculated coefficients. From a physical point of view, the constants in which we are most interested are α and B since these determine the electronic momentum, the moment of inertia and the nuclear separation. In the table of final calculated coefficients, a sufficient number of significant figures has been indicated to give a mathematically consistent evaluation of rotational energy terms to the nearest 0.001 cm^{-1} in order that differences may be given to the nearest 0.01 cm^{-1}. It is not to be inferred, however, that the coefficients have been determined with this degree of accuracy. The probable errors may be estimated on the basis of experience in the progressive steps of the calculation.

The values of B_0 are probably correct within two units in the fourth place, an accuracy of 0.03 percent, permitting the evaluation of the moment of inertia and nuclear separation with an accuracy exceeding that of any previous determination. The accuracy of the former is comparable with that with which Planck's constant is known, while that of the latter is limited primarily by the accuracy with which the relative atomic weights of Al and O are known. With regard to α, it is clear that a small change in the coefficients of the higher degree terms in $2\Delta F^*$ will quite appreciably affect the percent change in the intercept of the $2\Delta F^* : k$ curve, even though the absolute value of the change may be small. Thus, α may be in error by as much as 50 percent. For the remaining coefficients, the writer estimates the following accuracy: B_1, 0.05 percent; D_0, 0.25 percent; D_1, 0.50 percent; F_0 and F_1, 5 percent: H_0 and H_1, 20 percent.

Calculation of molecular constants. The moments of inertia of the AlO molecule, for the zero vibration state, calculated from the relation[25]

$$I_0 = h/8\pi^2 B_0 c = 27.70 \times 10^{-40}/B_0 \qquad (30)$$

are, for the initial and final states respectively

$$I_0' = (46.02 \pm .02) \times 10^{-40} \text{ gm cm}^2$$
$$I_0'' = (43.38 \pm .02) \times 10^{-40} \text{ gm cm}^2$$

The corresponding distances of nuclear separation calculated from the relation[25]

$$r_0^2 = I_0/\mu \qquad (31)$$

[25] Formulas for moment of inertia and nuclear separation appear in the report of the National Research Council, Ch. IV, as Eqs. (134) and (187) respectively. The "reduced molecular weight" of the AlO molecule is 10.06 giving a "reduced mass."

$$\mu = 10.06 \times 1.650 \times 10^{-24} = 16.6 \times 10^{-24} \text{ gm}$$

where μ is the "reduced mass" of the molecule, are

$$r_0' = 1.665 \times 10^{-8} \text{ cm}$$
$$r_0'' = 1.617 \times 10^{-8} \text{ cm}$$

Calculation of the constants of the law of force. The derivation of Eqs. (9), (10) and (11) is based upon an assumed law of nuclear force of attraction of the form[26]

$$F = K_1(r-r_0) + K_2(r-r_0)^2 + K_3(r-r_0)^3 + \cdots \tag{32}$$

where $(r-r_0)$ represents the increase in the distance of nuclear separation. Eq. (10) and (11) were derived by Birge[27] by obtaining new expressions for K_2 and K_3 in terms of rotational energy constants. Together with the previously known expression for K_1, these are

$$K_1 = -2hcB_0^2/D_0r_0^2 \tag{33}$$
$$K_2 = -(3D_0^2 - B_0F_0)3K_1/2r_0D_0^2 \tag{34}$$
$$K_3 = +(18F_0B_0D_0^2 - 25D_0^4 - 9F_0^2B_0^2 + 4H_0D_0B_0^2)hcB_0^2/r_0^4D_0^5 \tag{35}$$

in which all quantities have been defined previously.

The evaluation of these constants, using the numerical results of this analysis, gives for the initial and final states respectively

$K_1' = +4.42 \times 10^5$ dyne cm^{-1} $\quad K_1'' = +5.55 \times 10^5$ dyne cm^{-1}
$K_2' = -1.12 \times 10^{14}$ dyne cm^{-2} $\quad K_2'' = -1.69 \times 10^{14}$ dyne cm^{-2}
$K_3' = +1.81 \times 10^{22}$ dyne cm^{-3} $\quad K_3'' = +2.60 \times 10^{22}$ dyne cm^{-3}

The doublet separation. Contrary to conditions found in other band systems, the doublet separations for the (0,0) and (1,0) bands were found to agree, indicating a possible double rotational energy level in the *final* state. This may indicate a relatively stable initial state and hence explain the absence of perturbations which are usually associated with the initial state. The fact that $\omega^0{}'x'$ is small compared to $\omega^0{}''x''$ is possible further evidence of this conclusion.

Doublet separations were plotted as a function of k of the final state and the agreement for the (0,0) and (1,0) bands is indicated in Fig. 3. For the comparatively short range of measurement of the (0,1) band, the doublet separation was assumed to be linear, given by the equation

$$\Delta\nu = 0.014k \tag{36}$$

[26] The expressions for K_1, K_2 and K_3 in terms of vibrational energy constants are given in the report of the National Research Council, Ch. IV, as Eqs. (189), (190), and (191) respectively, while the corresponding expressions in terms of rotational energy constants (here quoted) appear as Eqs. (194), (195), and (196) respectively.

[27] R. T. Birge, Nature **116**, 783 (1925).

For the (0,0) and (1,0) bands, it was found that

$$\Delta\nu = 0.0116k + 12\times10^{-6}k^2 - 6.2\times10^{-11}k^4 \tag{37}$$

represented the doublet separation for both the P and the R branches. While $\Delta\nu$ could have been represented equally well by other polynomials, the significance of the above is the fact that the coefficients are com-

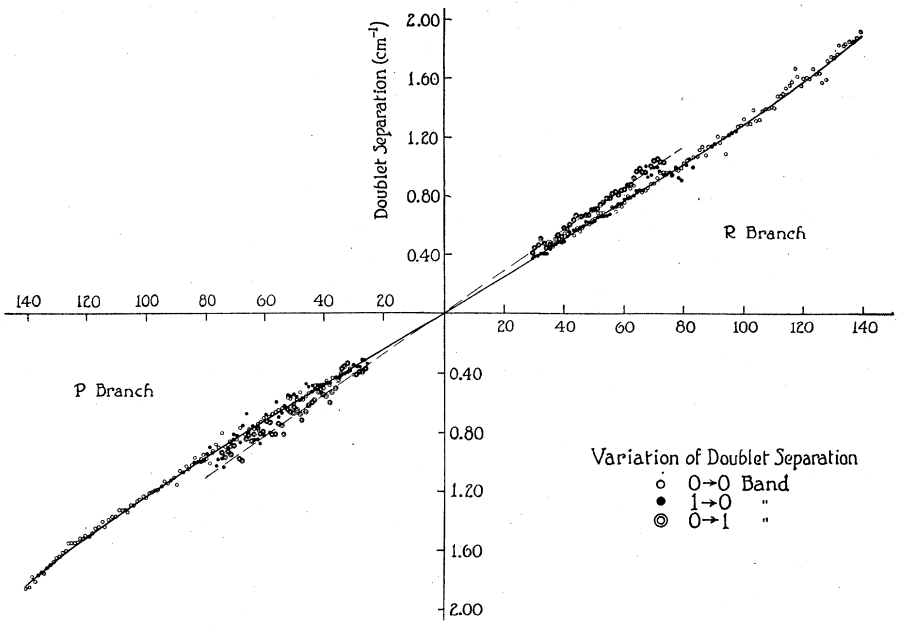

Fig. 3. Variation of doublet separation with rotation quantum number indicating that the doublet separation is a function of the final state.

patible with the theory applied to the mean of the doublet components. That is, we consider the double rotational energy term of the final state given by

$$\begin{aligned} F^{+-} &= F \pm \Delta\nu/2 \\ &= -2B(\alpha \mp \Delta\alpha/2)k + (B \pm \Delta B/2)k^2 + (D \pm \Delta D/2)k^4 \\ &= (B \pm \Delta B/2)m^2 + (D \pm \Delta D/2)m^4 \end{aligned} \tag{38}$$

where $m = k - \alpha \pm \Delta\alpha/2$.

If the theory which has been applied to the mean of the doublet components applies to the separate components as well, the relation between ΔD and ΔB must be, by Eq. (9)

$$\Delta D = -12B^2\Delta B/\omega^{0^2} \tag{39}$$

and this relation is satisfied by the coefficients of k^4 and k^2 respectively in Eq. (37). Obviously, $\Delta\alpha/2$ is found by dividing the coefficient of the linear term by $4B$.

Final representation of individual band lines. The calculated frequencies of the respective origins of the three bands are

$$\begin{aligned} &(0,0)\text{ Band},\ \nu_0 = 20635.27\ \text{cm}^{-1} \\ &(0,1)\text{ Band},\ \nu_0 = 19669.75\ \text{cm}^{-1} \\ &(1,0)\text{ Band},\ \nu_0 = 21498.30\ \text{cm}^{-1} \end{aligned} \tag{40}$$

The frequencies of individual band lines may now be written:

$$\begin{aligned} (0,0)\text{ Band}\quad R_j^{+-} &= 20635.27 + {}_{n'=0}F'_{j+1} - {}_{n''=0}F''^{+-}_{j} \\ P_j^{+-} &= 20635.27 + {}_{n'=0}F'_{j-1} - {}_{n''=0}F''^{+-}_{j} \\ (0,1)\text{ Band}\quad R_j^{+-} &= 19669.75 + {}_{n'=0}F'_{j+1} - {}_{n''=1}F''^{+-}_{j} \\ P_j^{+-} &= 19669.75 + {}_{n'=0}F'_{j-1} - {}_{n''=1}F''^{+-}_{j} \\ (1,0)\text{ Band}\quad R_j^{+-} &= 21498.30 + {}_{n'=1}F'_{j+1} - {}_{n''=0}F''^{+-}_{j} \\ P_j^{+-} &= 21498.30 + {}_{n'=1}F'_{j-1} - {}_{n''=0}F''^{+-}_{j} \end{aligned} \tag{41}$$

The subscripts in Eqs. (41) have been written to conform with Eqs. (2) and (3), although each F has been evaluated in powers of m. No confusion should arise, however, if it is understood that the F_m in the following expansions in powers of m has the same meaning as F_j in Eqs. (41), where j is greater than m by approximately one half.

Using the final calculated coefficients, the rotational energy terms of Eqs. (41) become

$$\begin{aligned} {}_{n'=0}F_m' &= 0.60190m^2 - 1.1630\times10^{-6}m^4 + 0.440\times10^{-12}m^6 \\ &\quad \text{where } m = k - 0.0074 \\ {}_{n''=0}F_m''^{+-} &= (0.63860 \pm 6.0\times10^{-6})m^2 - (1.1094\times10^{-6} \pm 3.1\times10^{-11})m^4 \\ &\quad - 0.530\times10^{12}m^{-6} - 5.2\times10^{-18}m^8 \\ &\quad \text{where } m = k - 0.01 \pm 0.00482 \\ {}_{n'=1}F_m' &= 0.59737m^2 - 1.1571\times10^{-6}m^4 + 0.440\times10^{-12}m^6 \\ &\quad \text{where } m = k - .005 \\ {}_{n''=1}F_m''^{+-} &= 0.63285m^2 - 1.1181\times10^{-6}m^4 - 0.530\times10^{-12}m^6 - 5.2\times10^{-18}m^8 \\ &\quad \text{where } m = k - 0.0132 \pm 0.00553 \end{aligned} \tag{42}$$

In conclusion, the writer wishes to express his deep appreciation of the continued interest and helpful advice, throughout the progress of this work, of Professor R. T. Birge, who suggested the problem and generously placed an excellent set of spectrograms at the writer's disposal.

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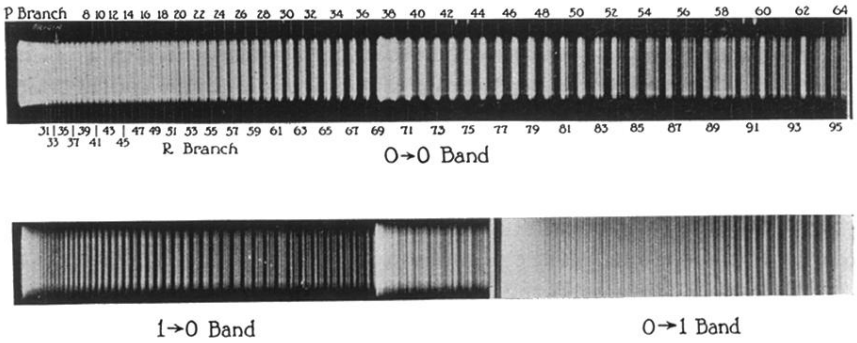

Fig. 1. Spectrograms of a portion of the band spectrum of AlO. The numerals attached to the (0,0) band indicate the quantum number of the final state corresponding to each doublet. The complete overlapping of P_{42} and R_{74} is clearly apparent.