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Structure of the Schumann-Runge bands from the 0-0 to the 13-0 band

by M. ACKERMAN and F. BIAUME

FOREWORD

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AVANT-PROPOS

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VOORWOORD

Deze tekst zal gepubliceerd worden in het "Journal of Molecular Spectroscopy".

VORWORT

Dieser Text wird in "Journal of Molecular Spectroscopy" herausgegeben werden.

STRUCTURE OF THE SCHUMANN-RUNGE BANDS FROM THE 0-0 TO THE 13-0 BAND.

by

M. ACKERMAN and F. BIAUME

Abstract

Spectra of the Schumann-Runge bands have been photographed at high resolution. The 0-0 band has been measured for the first time.

Precise values of the vibrational and rotational constants for the 7-0 to 11-0 bands have been determined. Previous results for other bands are confirmed.

Résumé

Des spectres des bandes de Schumann-Runge ont été photographiés à haute résolution. La bande 0-0 a été mesurée pour le première fois.

Des valeurs précises des constantes de vibration et de rotation ont été déterminées pour les bandes 7-0 à 11-0. Des résultats antérieurs concernant d'autres bandes sont confirmés.

Samenvatting

De spectra van het bandensysteem van Schumann-Runge werden gefotografeerd met een grote resolutie. De band 0-0 werd voor de eerste maal gemeten.

Nauwkeurige waarden van de vibratie- en rotatieconstanten werden bepaald voor de banden 7-0 tot 11-0. De vroegere resultaten betreffende de andere banden worden bevestigd.

Zusammenfassung

Schumann-Runge Bandenspektren wurden mit hohen Auflösungsvermögen photographiert. Die 0-0 Bande wurde zum ersten Mal gemessen.

Genaue Werte der Schwingungs- und Rotationskonstanten wurden für den 7-0 zu 11-0 Banden festgestellt. Frühere Ergebnisse für anderen Banden werden bestätigt.

A.- INTRODUCTION

Absorption spectra of oxygen at room temperature have been photographed in the Schumann-Runge Bands by Curry and Herzberg [1], Knauss and Ballard [2] and Brix and Herzberg [3]. More recent studies [4,5,6] have shown the need for more accurate measurements than those available for some of the bands. The measurements reported here meet this requirement and offer the advantage of having been obtained from the instrument used by Brix and Herzberg.

In addition to a list of wave numbers of the observed lines, the deduced molecular constants will be presented and discussed. Informations on line widths derived from the spectra will also be included.

B.- EXPERIMENTAL

The 3 meters vacuum spectrograph [3] of the National Research Council of Canada (Ottawa) has been used. The concave grating blazed at an angle of $21°6'$ and having a radius of 3 meters was ruled at 1200 grooves per mm over an area of 150 x 65 mm.

The absorption tube had a length of 125 cm. Oxygen pressures of 0.4, 1, 3, 10, 25, 100 and 760 mm Hg were used. The measurements of the 0-0 and 1-0 bands were obtained by filling the absorption cell and the spectrograph with oxygen at a pressure of one atmosphere.

The light source was a Lyman discharge tube and all exposures were taken on Ilford Q_2 plates.

The oxygen spectra were obtained in the fourth order of the grating and the measurements were made against Silicon lines [4,7] in the same order

and against second order iron lines. The relative wave numbers of sharp and unblended lines are reproducible to about $\pm\ 0.05$ cm^{-1}, whereas the absolute wave numbers may be in error by $\pm\ 0.1$ cm^{-1} since this is the maximum dispersion observed in the determination of standard silicon lines against iron lines. In the case of broad oxygen lines, as in the 4-0 band for instance, the accuracy is most probably not better than $\pm\ 0.4$ cm^{-1}. The accuracy for the other bands can be judged from the evaluated apparent line widths given below.

C.- RESULTS

Wave numbers and identifications of the rotational lines measured in the v'' = o sequence are presented in table I. The appearance of the same wave number for two or more lines means that these have not been separated on the spectra.

The constants v_o, B_v and D_v were derived from these data by graphicals methods [5]. In order to calculate band origins, the following formula was used

$$R(N) + P(N) - 2\overline{(B_{v'} - B_{v''})} \, N(N + 1)$$

$$= 2(v_o + B_{v'}) + 2\Delta\overline{(B_{v'} - B_{v''})} \, N(N + 1) \tag{1}$$

where $\overline{(B_{v'} - B_{v''})}$ is an approximate difference between the rotational constants of the upper and of the lower states and $\Delta\overline{(B_{v'} - B_{v''})}$ is the residual between the approximate and the real difference. The residual can be more accurately determined from the plot

$$[P(N) + R(N) - 2\overline{(B_{v'} - B_{v''})} \, N(N + 1) - 2(v_o + B_{v'})]/N(N + 1)$$

$$= 2\Delta\overline{(B_{v'} - B_{v''})} + 2(D_{v'} - D_{v''}) \, N(N + 1) \tag{2}$$

where the D term is taken into account and from which $(D_{v'} - D_{v''})$ can be

obtained. The values of $B_{v''}$ and $D_{v''}$ determined by Badcock and Herzberg [8]

are then introduced in Eq. (1) and in Eq. (2) in order to obtain v_o, B_v,

and $D_{v'}$. In the bands where the triplet components are resolved the wave

numbers of the transitions between the F_2 levels for which $N = J$ have been

used in the calculations. The band origins and the rotational constants are

collected in Table II where, for the sake of completeness and comparison the

data given in previous investigations are included.

Half widths of lines have been evaluated on microphotometric tracings

of the photographed spectra. For this purpose, weak neighbouring lines were

chosen from which the photographic contrast was also determined by means of

the theoretical rotational intensity distribution.

The results are presented in Fig. (1).

DISCUSSION

The wave numbers of the 0-0 band measured for the first time and

listed in table I lead to a value of the band origin in agreement with the

early work of Curry and Herzberg[1]. This concludes the controversy on

the subject [2,9].

The band origins obtained in the present work are in excellent

agreement with the other values derived from high resolution spectra [1,3].

Now that such data are available for comparison, a systematic and relatively

large difference appears with all the values obtained by Knauss and

Ballard [2]. The discrepancy increases from $v' = 4$ to higher v' values and

then decreases slightly. Since this variation is slow the ΔG values are

much more consistent. This fact gives confidence in the accuracy of the

differences.
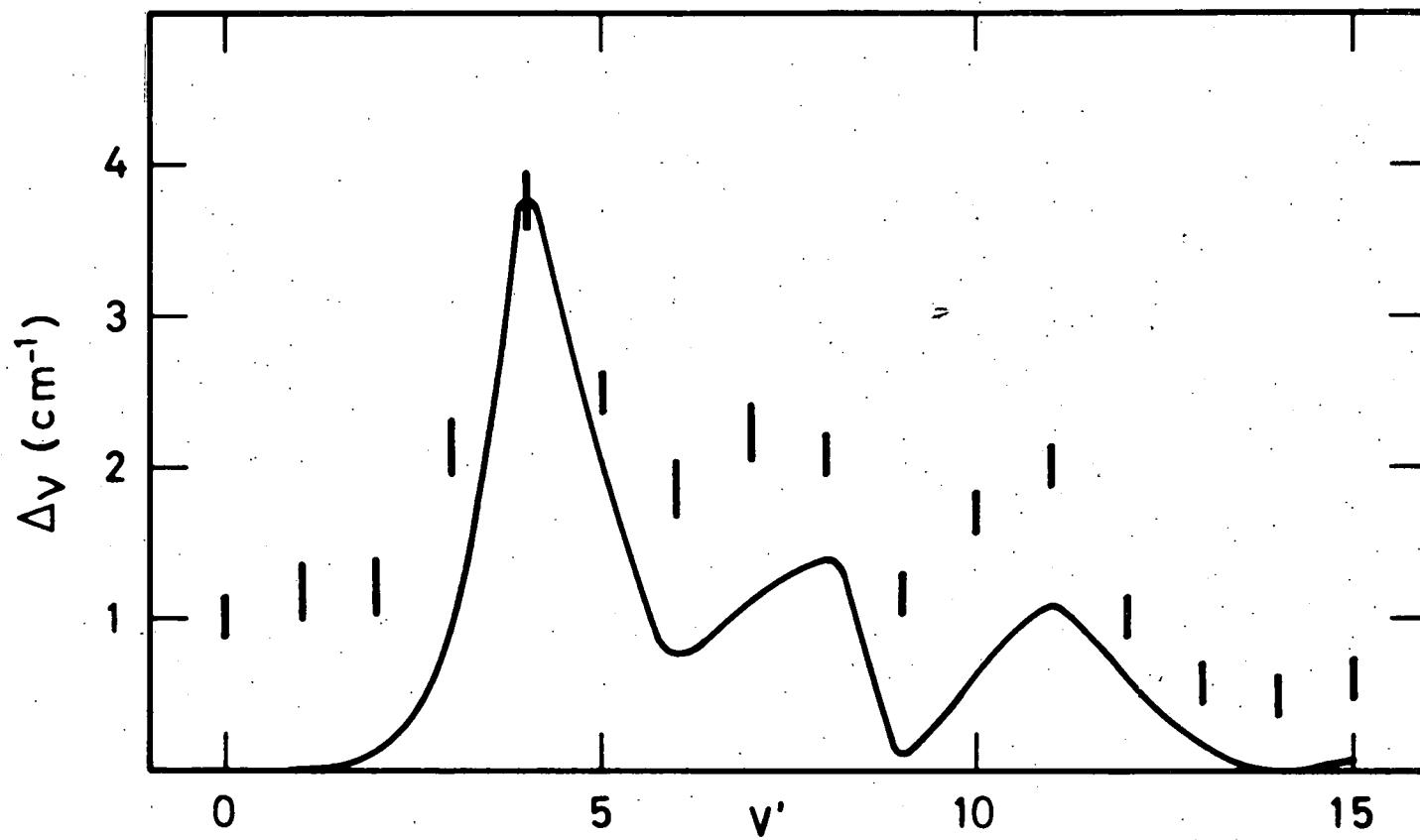
Fig. 1.- Apparent line half width $\Delta\nu$ in cm^{-1} versus vibrational quantum number (v') of the upper state. The solid curve represents the theoretical values given by Murrel and Taylor [12], normalized at v' = 4.

From our data ($0 \le v' \le 12$) associated with the values obtained by Brix and Herzberg [3] ($13 \le v' \le 20$) the following least squares formula

$$\Delta G'_c = 676.798 - 9.2935 \, v' - 2.9221 \, v'^2 + 0.088033 \, v'^3$$

has been deduced for the vibrational quanta. The differences between all the measured values $\Delta G'_m$ and the calculated $\Delta G'_c$ have been plotted versus v' in Fig. (2). The purpose of this procedure is only to show the scattering of the measurements. However it also reveals a systematic discontinuity at $v' = 5$.

To visualize the scattering of the B' measurements, the least squares formula

$$B'_c = 0.80944 - 6.0191 \times 10^{-3} \, (v' + \tfrac{1}{2}) - 1.1189 \times 10^{-3} \, (v' + \tfrac{1}{2})^2$$

$$- 1.217 \times 10^{-6} \, (v' + \tfrac{1}{2})^3$$

has been calculated from our values ($0 \le v' \le 13$) associated with those ($14 \le v' \le 21$) obtained by Brix and Herzberg [3]. The differences between all the measurements B'_m and the calculated B'_c are plotted in Fig. (3).

The half width measurements presented in Fig. (1) correspond to the line half width appearing on the spectra and limiting the accuracy of wave number measurements. The variation of this width in function of the vibrational quantum number may be partly interpreted in terms of predissociation. This is the case for the 4-0 band where the conclusion of Carroll [11] is supported here. However, the maximum in the 7-0 band is partly due to the fact that the P and R components appear superposed in the 6-0 band and move away from each other for v' values larger or smaller than 6. A similar argument applies to the maximum observed at $v' = 11$ since there one component of the triplet begins to be more and more separated from the two other ones. In both cases, the separation of adjacent lines is far from complete and the real width is difficult to measure.
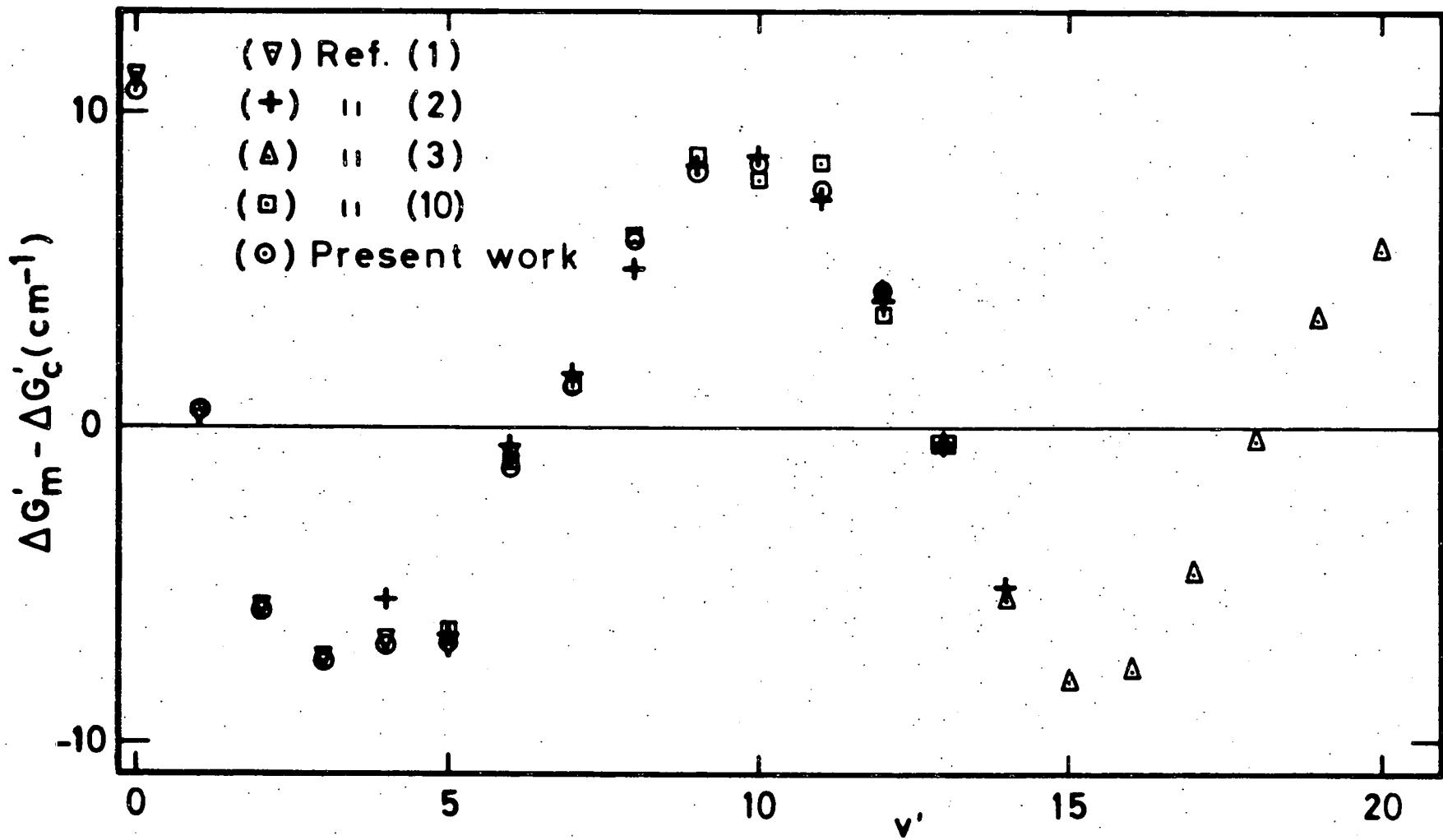
Fig. 2.- Differences between the measured $(\Delta G'_m)$ and calculated $(\Delta G'_c)$ values of the vibrational quanta in cm^{-1} versus v'.
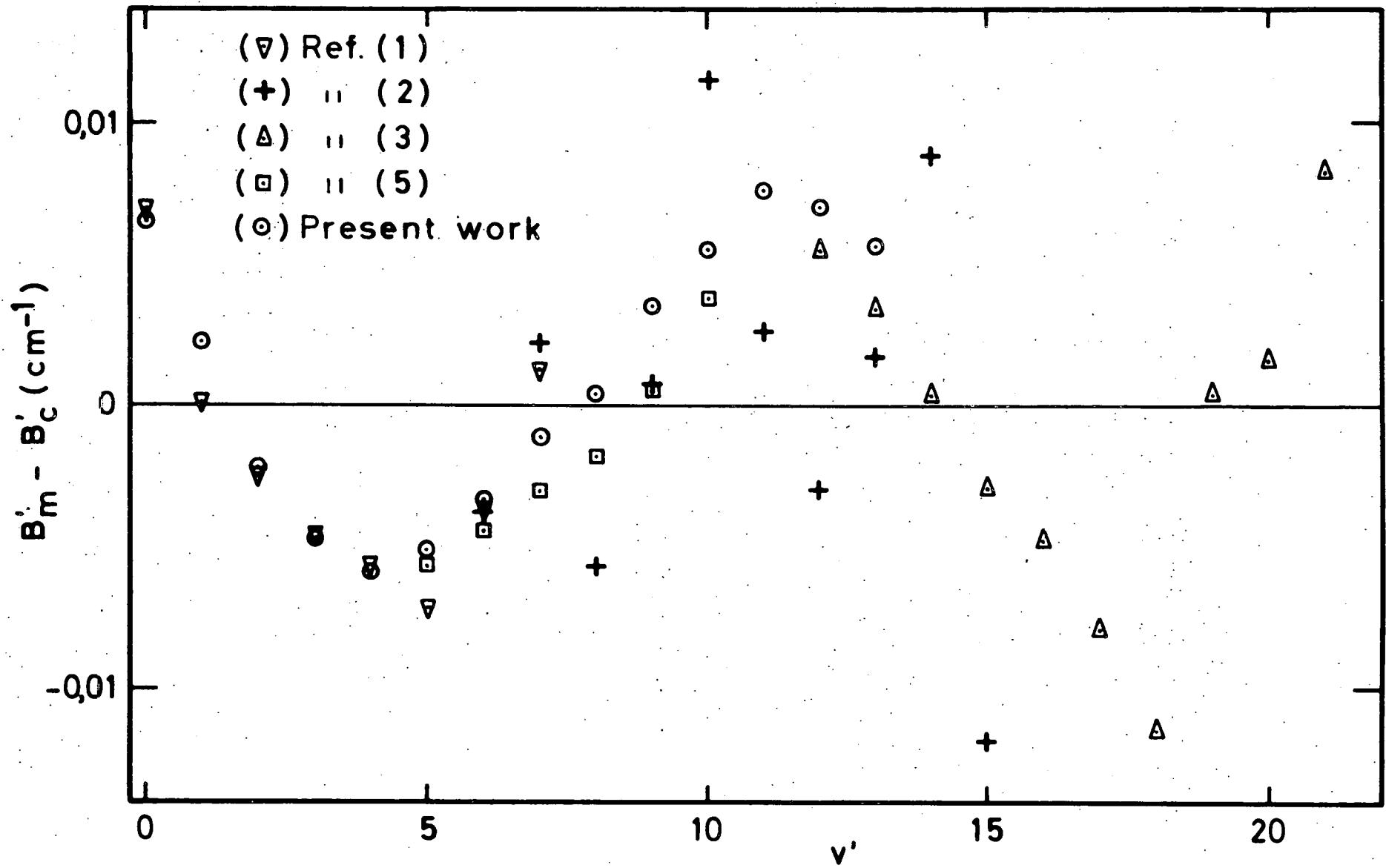
Fig. 3.- Differences between the measured (B'_m) and calculated (B'_c) values of the rotational constant B' in cm^{-1} versus v'.

Our data do not fully support the theoretical results obtained by Murrel and Taylor [12]. Even if their values represented by the solid curve in Fig. (1) show the same general behavior as the measurements do, a confirmation from an other type of experimental measurement seems to be needed.

CONCLUSION

A complete set of accurate experimental values for vibrational and rotational constants obtained from measurements of the Schumann-Runge bands are now available. It appears that information on line width deduced from photographic spectra mainly obtained for purely spectroscopic purposes have to be very carefully examined before they are used as absorption cross section data.

AKNOWLEDGMENT

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TABLE I
Wave numbers of the observed lines

N"	0-0 Band $\nu_0 = 49358.15$ cm^{-1}		1-0 Band $\nu_0 = 50045.68$ cm^{-1}		2-0 Band $\nu_0 = 50710.83$ cm^{-1}	
	P	R	P	R	P	R
1	49355.27	49360.12	50042.90	50047.49	50708.06	50712.57
3	345.83	357.10	033.19	044.48	698.27	709.25
5	331.33	349.18	018.59	036.15	683.36	700.69
7	311.75	336.16	49998.82	022.73	663.36	686.85
9	287.31	318.11	973.93	004.25	638.02	667.77
11	257.72	295.11	943.95	49980.61	607.44	643.50
13	223.24	267.22	908.85	951.92	571.68	614.00
15	183.75	234.13	868.65	918.01	530.73	579.24
17	139.32	195.97	823.28	879.12	484.54	539.28
19		154.03	772.83	835.02	433.14	494.20
21			717.39	785.67	376.49	443.66
23				731.51	314.73	388.00
25						327.57

TABLE I (continued)

	3–0 Band $\nu_0 = 51352.26$ cm^{-1}		4–0 Band $\nu_0 = 51969.81$ cm^{-1}		5–0 Band $\nu_0 = 52561.39$ cm^{-1}	
N"	P	R	P	R	P	R
1	51349.72	51353.99	51967.55	51970.85	52558.85	52563.01
3	339.93	350.20	957.03	967.55	548.57	558.85
5	324.56	341.35	941.81	958.26	532.89	549.28
7	303.96	326.92	921.70	942.80	511.79	533.82
9	278.47	307.40	894.84	923.14	484.98	513.16
11	247.21	282.49	863.03	897.59	452.92	486.42
13	210.73	252.12	825.94	865.93	414.89	454.49
15	168.87	216.63	783.02	829.75	371.44	416.41
17	121.74	175.51	735.19	787.24	322.12	373.17
19	069.41	129.49	681.43	740.35	267.39	324.25
21	011.73	077.50	622.62	687.20	206.99	269.76
23	50948.52	020.16		628.43	140.96	209.34
25	880.12	50957.81			068.75	143.55
27	806.51	890.40				072.98
29		818.00				

TABLE I (continued)

	6–0 Band $\nu_0 = 53122.79$ cm^{-1}		7–0 Band $\nu_0 = 53656.27$ cm^{-1}		8–0 Band $\nu_0 = 54156.28$ cm^{-1}	
N"	P	R	P	R	P	R
1	53119.75	53124.07	53653.10	53657.41	54152.63	54157.56
3	109.86	119.75	642.81	653.10	143.03	152.63
5	094.05	109.86	626.71	642.81	126.62	141.73
7	072.54	094.05	604.94	626.71	104.03	124.58
9	045.22	072.54	577.24	604.30	075.53	101.45
11	012.12	045.22	543.28	575.80	041.07	072.13
13	52973.36	012.12	503.63	541.57	000.15	036.76
15	928.81	52973.36	458.10	501.63	53953.38	53995.18
17	878.31	928.81	406.61	455.40	900.43	947.66
19	822.55	878.31	349.05	403.52	841.55	893.95
21	760.13	822.55	285.54	345.48	776.12	834.31
23	693.11	760.13	216.38	281.36	704.87	768.09
25	619.77	693.11	140.96	211.44	627.25	695.85
27		619.77		134.93		617.78

TABLE I (continued)

9–0 Band
$\nu_o = 54622.17$ cm^{-1}

N"	P$_1$	P$_2$	P$_3$	R$_1$	R$_2$	R$_3$
1	54619.31	——	——	54623.24	54623.24	54623.24
3	608.78	54608.78	54608.78	618.03	618.03	618.03
5	592.14	592.14	592.14	606.53	606.53	606.53
7	569.17	569.17	569.17	588.74	588.74	588.74
9	539.89	539.89	539.89	564.56	564.56	564.56
11	504.31	504.31	504.31	534.19	534.19	534.19
13	462.35	462.62	462.62	497.42	497.68	497.68
15	414.24	414.39	414.39	454.46	454.76	454.76
17	359.60	360.22	360.22	405.06	405.63	405.63
19	298.82	299.41	299.41	349.11	349.82	349.82
21	231.54	232.31	232.31	287.14	287.90	287.90
23	157.91	158.95	158.95	218.63	219.46	219.46

TABLE I (continued)

16 . -

10–0 Band
$\nu_o = 55050.90$ cm^{-1}

N"	P_1	P_2	P_3	R_1	R_2	R_3
1	55048.01	——	——	55051.62	55051.62	55051.62
3	037.46	55037.46	55037.46	046.27	046.27	046.27
5	020.43	020.43	020.43	034.23	034.23	034.23
7	54996.89	54996.89	54996.89	015.60	015.60	015.60
9	966.77	966.77	966.77	54990.41	54990.41	54990.41
11	930.10	930.10	930.10	958.82	958.82	958.82
13	886.92	886.92	886.92	920.45	920.82	920.82
15	837.20	837.57	837.57	875.58	876.09	876.09
17	780.87	781.53	781.53	824.29	824.92	824.92
19	718.27	718.92	718.92	766.67	767.43	767.43
21	648.94	649.70	649.70	701.82	702.71	702.71
23	572.91	574.10	574.10	630.84	631.92	631.92
25	490.39	491.09	491.09	552.83	553.98	553.98
27	401.03	402.27	402.27	468.11	469.34	469.34
29	304.99	306.24	306.24	376.81	378.05	378.05
31				277.73	278.85	278.85

TABLE I (continued)

11–0 Band
$\nu_0 = 55438.90$ cm^{-1}

N"	P$_1$	P$_2$	P$_3$	R$_1$	R$_2$	R$_3$
1	55435.76	—	—	55439.44	55439.44	55439.44
3	425.20	55425.20	55425.20	433.74	433.74	433.74
5	407.86	407.86	407.86	421.00	421.00	421.00
7	383.61	383.61	383.61	401.40	401.40	401.40
9	352.61	352.61	352.61	375.22	375.22	375.22
11	314.84	314.84	314.84	342.15	342.15	342.15
13	270.31	270.31	270.31	302.35	302.35	302.35
15	218.83	219.58	219.58	255.43	256.18	256.18
17	160.43	161.60	161.60	201.71	202.98	202.98
19	095.69	096.74	096.74	141.44	142.60	142.60
21				072.41	074.86	074.86

TABLE I (continued)

12–0 Band
$\nu_0 = 55784.57 \ cm^{-1}$

N"	P_1	P_2	P_3	R_1	R_2	R_3
1	55780.72	—	—	55784.35	55785.26	55785.26
3	770.18	55770.78	55770.78	778.07	778.60	778.60
5	752.30	752.71	752.71	764.56	765.11	765.11
7	727.19	727.73	727.73	743.87	744.51	744.51
9	695.13	695.73	695.73	716.18	717.15	717.15
11	655.84	656.74	656.74	681.33	682.55	682.55
13	609.65	610.71	610.71	639.56	640.89	640.89
15	556.31	557.64	557.64	590.63	592.16	592.16
17	495.94	497.45	497.45	534.61	536.23	536.23
19	428.39	430.22	430.22	471.43	473.20	473.20

TABLE I (continued)

13-0 Band
$\nu_o = 56085.47$ cm^{-1}

N"	P_1	P_2	P_3	R_1	R_2	R_3
1	56080.97	—	—	56084.37	56085.70	56085.70
3	070.13	56071.38	56071.38	077.46	078.69	078.69
5	051.67	052.91	052.91	063.09	064.39	064.39
7	025.71	027.09	027.09	041.23	042.78	042.78
9	55992.41	55993.95	55993.95	012.05	013.79	013.79
11	951.72	953.51	953.51	55975.52	55977.36	55977.36
13	903.69	905.58	905.58	931.52	933.46	934.01
15	848.25	850.30	850.69	880.13	882.24	882.91
17	785.26	787.52	788.15	821.24	823.51	824.49
19				754.80	757.16	758.32

TABLE II

Band origins, vibrational quanta and rotational constants of the Schumann-Runge absorption bands

v'	ν_0 (cm⁻¹)				$\Delta G'(v'+\frac{1}{2})$ (cm⁻¹)				$B_{v'}$ (cm⁻¹)				$D_{v'}$ (10⁻⁶ cm⁻¹)		
	KB(2)	CH(1) BH(3)	OC(10)	Present work	KB(2)	CH(1) BH(3)	OC(10)	Present work	KB(2)	CH(1) BH(3)	O(5)	Present work	CH(1) BH(3)	O(5)	Present work
0		49357.6		49358.15		688.05		687.53		0.813		0.8127			5.06
1		50045.65		50045.68		665.1		665.15		0.798		0.8001			6.61
2		50710.75		50710.83		641.45		641.43		0.785		0.7852			5.10
3		51352.2		51352.26		617.64		617.55		0.770		0.7699	4.38		4.54
4	51969.6	51969.84		51969.81	593.0	591.81		591.58		0.754		0.7537			3.56
5	52562.6	52561.65	52560.8	52561.39	561.7	561.15	561.7	561.40		0.735	0.7367	0.7372		4.5	5.71
6	53124.3	53122.8	53122.5	53122.79	534.2	534.0	533.6	533.48	0.719	0.719	0.7183	0.7194		4.75	5.71
7	53658.5	53656.8	53656.1	53656.27	500.4		500.0	500.01	0.703	0.702	0.6978	0.6997		5.3	6.96
8	54158.9		54156.1	54156.28	465.5		466.4	465.89	0.671		0.6749	0.6771		5.9	6.71
9	54624.4		54622.5	54622.17	428.9		429.2	428.73	0.651		0.6508	0.6538		4.9	7.21
10	55053.3		55051.7	55050.90	388.2		387.5	388.00	0.633		0.6243	0.6270		9.5	9.75
11	55441.5		55439.2	55438.90	345.4		346.5	345.67	0.593			0.5980			9.31
12	55786.9	55784.59	55785.7	55784.57	300.7	300.92	300.1	300.90	0.554	0.5625		0.5640	13		14.16
13	56087.6	56085.51	56085.8	56085.47	255.0	254.96	255.0		0.523	0.5247		0.5269	16.8		23.91
14	56342.6	56340.47	56340.8		208.4	210.07			0.492	0.4836			21.2		
15	56551.0	56550.54				168.96			0.431	0.4399			25.7		
16		56719.50				132.91				0.3953			34.3		
17		56852.41				102.13				0.347			45		
18		56954.54				75.64				0.296			152		
19		57030.18				52.65				0.258			49		
20		57082.83				31.94				0.207			76		
21		57114.77								0.159			105		