THE
PHYSICAL REVIEW
A Journal of Experimental and Theoretical Physics
VOL. 47, No. 1 JANUARY 1, 1935 SECOND SERIES

Ultraviolet Absorption of Iodine Vapor

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(Received November 13, 1934)

The regularity of development of the ultraviolet absorption spectrum of iodine between λ1900 and λ3413 from shorter to longer wave-lengths with increasing temperature and pressure indicates that the bands all belong to one system. The large range of conditions under which bands studied by Pringsheim and Rosen and those found by Kimura and Miyanishi are both found leads to the same conclusion. The "long thin bridge" joining these two regions is explained as the result of the coincidence of $\Delta G' = 70$ cm^{-1} and $\Delta G'' = 210$ cm^{-1}, causing successive v' progressions to coincide. This is supported by the manner in which successive v' progressions join on to the single series. A similar explanation probably holds for the single series of spacing 90 cm^{-1} at the red end of the Pringsheim and Rosen bands, which breaks up near λ2850 into the bands found associated with the λ3413 "continuum" in fluorescence, emission and absorption. This continuum forms the absorption maximum at the long wave-length limit of the spectrum, the red end. It is therefore neither an electron affinity nor ionic recombination nor any other atomic spectrum. These results agree well with Mulliken's theory of this system.

THE existence of ultraviolet absorption in iodine vapor was indicated, according to the theory of Lenz,[1] by the ultraviolet fluorescence found by McLennan,[2] Oldenberg[3] and Wychodil.[4] This absorption was studied by three different groups of investigators in 1928–29. The region λλ2080–2760 was studied by Pringsheim and Rosen.[5] They used a sphere of 6 cm diameter, and unstated temperatures in the range 200–800°C. They found two series of bands: one at λλ2500–2760 spaced uniformly at 90 cm^{-1}, the second λλ2080–2200 spaced at 70 cm^{-1}. These they called the $v'=0$ and $v''=0$ progressions, respectively, and analyzed the intervening welter of bands according to these two frequencies, which they could readily do within the limits of their accuracy. This necessitated the identification of their lower state with an excited state of the molecule ($\omega = 90$ cm^{-1}, $\omega x = 0$) rather than the ground state ($\omega = 214$ cm^{-1}, $\omega x = 0.6$ cm^{-1}). Kimura and Miyanishi[6] extended the absorption, obtaining bands with an absorption tube 15 cm long at temperatures 35–120°C in the region λλ1950–2150. These they analyzed according to the equation

$$\nu = 52{,}800 + 78v' - v'^2 - 210v'' \text{ cm}^{-1}.$$

The value $\omega' = 78$ cm^{-1} they identified with that (70 cm^{-1}) of the upper state of the Pringsheim-Rosen bands, and the lower state they identified with the ground state of the molecule. However, their intensity distribution was incomprehensible and their method of determining v'' incorrect, hence their results are not very convincing.

* Portion of a dissertation presented for the degree of Doctor of Philosophy at Yale University.

[1] W. Lenz, Phys. Zeits. **21**, 691 (1920); Zeits. f. Physik **25**, 299 (1924).

[2] J. C. McLennan, Proc. Roy. Soc. **A88**, 289 (1913); **A91**, 23 (1914).

[3] O. Oldenberg, Zeits. f. Physik **18**, 1 (1923).

[4] P. Pringsheim, Die Naturwiss. **16**, 131 (1928); E. Hirschlaff, Zeits. f. Physik **75**, 325 (1932).

[5] P. Pringsheim and B. Rosen, Zeits. f. Physik **50**, 1 (1928).

[6] M. Kimura and M. Miyanishi, Sci. Papers Inst. Chem. and Phys. Res. Tokyo **10**, 33 (1929).

TABLE I. *Dependence of ultraviolet absorption on temperature and pressure.* Data for the observations plotted in Fig. 1 are given here.

Temp. (°C)	Pressure (mm Hg)	Bands	Region (Å)	Temp. (°C)	Pressure (mm Hg)	Bands	Region (Å)
23	0.41	K–M and S–W	1930–1960	190	27	P–R	2130–2210
30	.50	K–M " S–W	1925–1960	190	157	None	
30	.50	K–M " S–W	1900–2000 (2 hrs.)	190	521	None	
31	.70	K–M " S–W	1930–1970	330	5.8	None	
39	1.05	K–M	1930–2010	326	8.2	P–R and K–M	2100–2200
47	1.1	K–M	2040–2125	330	18	P–R	2120–2210
120	0.9	None		330	105	P–R	2200–2250
120	1.3	P–R and K–M	2010–2120	335	217	P–R	2280–2340
120	1.9	P–R " K–M	2050–2140	330	570	P–R	2270–2330
120	2.5	P–R " K–M	2060–2150	505	27	None	
120	4.7	P–R " K–M	2070–2150	545	55	P–R	2220–2270
120	8.0	P–R " K–M	2110–2180	502	105	P–R	2220–2330
120	8.2	P–R " K–M	2080–2160	510	150	P–R	2300–2370
120	11	P–R " K–M	2080–2160	498	350	P–R	ca 2330
120	30	P–R	2100–2190	498	680	None	
190	.25	None		690	157	P–R	2350–2450
190	.75	None		640	170	P–R	2350–2480
190	1.4	P–R and K–M	2060–2140	644	294	P–R	2400–2630
190	6.0	P–R " K–M	2100–2160	630	350	P–R	2440–2630
				690	815	P–R	2500–2700

Note: K–M = bands in the Kimura-Miyanishi region; S–W = bands in the Sponer-Watson region; P–R = bands in the Pringsheim-Rosen region.

Sponer and Watson[7] carried the observations into the Schumann region, and found at least two absorption systems. The one lying at longer wave-lengths, λλ1770–1950, apparently formed a continuation of the Kimura-Miyanishi bands. However their temperatures, pressures and path lengths differed greatly from those of Kimura and Miyanishi.

The Sponer and Watson bands seemed to form two long v' progressions, and were certainly related to the ground state of the iodine molecule, since they were obtained at room temperature. They showed a $\Delta G'$ value varying in the range 35–55 cm^{-1}. Their relation to the Kimura-Miyanishi bands left little room to doubt that the value 78 cm^{-1} for the $\Delta G'$ of the latter was incorrect. Hence Sponer and Watson re-analyzed the Kimura and Miyanishi data, obtaining a value of $\Delta G'$ of 50–70 cm^{-1}. Their intensity distribution also seemed more probable than the solid block shown by Kimura and Miyanishi. Sponer and Watson also attempted to include the long series called by Pringsheim and Rosen their $v''=0$ progression. But here the relation was not so clear, and it was very difficult to make the connection between the two groups of bands consist of a single progression. However, it seemed quite possible that these bands all belonged to one system. These and some other relations of these bands have recently been discussed by Curtis and Evans.[8]

The chief difficulty concerning these bands is the relation between the bands observed by Pringsheim and Rosen and those found by Kimura and Miyanishi. This is due chiefly to the diversity in path length, temperatures, and pressures of the experimental conditions of the different investigations, and to the peculiar relation of the "long thin bridge," Pringsheim and Rosen's $v''=0$ progression, uniting them. Hence the first step in studying the relation of these bands was to investigate their dependence on temperature and pressure. For this purpose a 15 cm absorption tube with an electrically wound furnace and an appendix with a separate furnace were prepared. The temperatures of the main tube and the side limb were read by means of thermocouples. The absolute values are probably not in error by more than 10°C. The pressures were obtained from the temperature of the appendix tube by means of vapor pressure tables.

The results are shown in Fig. 1 and Table I. Table I gives the values of the quantities plotted

[7] H. Sponer and W. W. Watson, Zeits. f. Physik **56**, 184 (1929).

[8] W. E. Curtis and S. F. Evans, Proc. Roy. Soc. **A141**, 603 (1933).

in the figure. The region in which bands are found under the corresponding conditions of temperature and pressure is roughly indicated by the type of point entered, corresponding to the original investigators who found bands in the region of some of those found under those conditions, and by the contour lines. There are two important conclusions to be drawn from Fig. 1. First is the regularity of development of

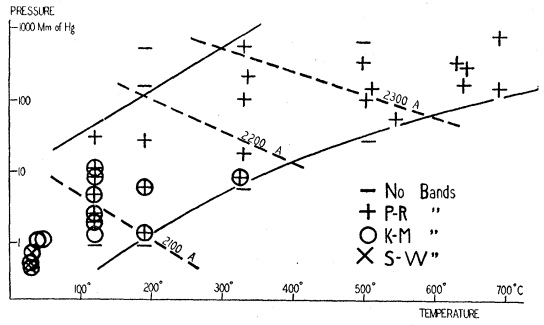


FIG. 1. Contour diagram of ultraviolet absorption bands obtained as a function of temperature and pressure. The data are for a 15 cm path length and low dispersion. The solid lines delineate the region in which bands are found, the dotted lines are wavelength contour lines. The type of point entered indicates whether the corresponding bands were observed by Pringsheim and Rosen,[5] Kimura and Miyanishi,[6] or Sponer and Watson.[7]

the system from shorter to longer wavelengths with increasing temperature and pressure within the limits where discrete bands are visible. There is no irregularity or discontinuity corresponding to the transition from Kimura-Miyanishi to Pringsheim-Rosen bands. This extends the regularity of development found by the various investigators in their own regions. Second is the large number of different conditions under which both Kimura-Miyanishi and Pringsheim-Rosen bands are found. This is partly due to the fact that the two wavelength regions overlapped considerably, but in any case it shows that there must be a close connection between the two groups of bands.

Since the results so far indicated that the bands belong to a single system, it was thought possible that other progressions could be found connecting the two groups of bands. For this purpose measurements were made at medium dispersion (100 cm^{-1}/mm at λ2200) on bands in the intermediate region. A few new bands were found, but the single series with spacing 70 cm^{-1} remained. It was concluded that this series was due to the superposition of successive v' progressions, due to the coincidence of values $\Delta G' = 70$ cm^{-1}, $\Delta G'' = 210$ cm^{-1}. This could be tested by studying the manner in which different v' progressions are related to the single series. This is shown in Table II, which gives a partial

TABLE II.

TABLE II. *Kimura-Miyanishi bands and the long thin bridge.*

This gives a matrix diagram showing the relation of the single series (above the line in each column) to several progressions in the Kimura-Miyanishi region. Some new measurements are included. Other progressions in this region lie to the left of those given.

46726	*206*	46520	*207*	46313	*207*	46106
73		*71*		*70*		*67*
46799	*208*	46591	*208*	46383	*210*	46173
74		*68*		*65*		*68*
46873	*214*	46659	*211*	46448	*207*	46241
75		*67*		*72*		*72*
46948	*222*	46726	*206*	46520	*207*	46313
69		*73*		*71*		*70*
47017	*218*	46799	*208*	46591	*208*	46383
70		*74*		*68*		*65*
47087	*214*	46873	*214*	46659	*211*	46448
63		*75*		*67*		*72*
47150	*202*	46948	*222*	46726	*206*	46520
67		*69*		*73*		*71*
47217	*200*	47017	*218*	46799	*208*	46591
68		*70*		*74*		*68*
47285	*198*	47087	*214*	46873	*214*	46659
71		*63*		*75*		*67*
47356	*206*	47150	*202*	46948	*222*	46726
69		*67*		*69*		*73*
47425	*208*	47217	*200*	47017	*218*	46799
68		*68*		*70*		*63*
47493	*208*	47285	*198*	47087	*225*	46862
		71		*63*		*70*
		47356	*206*	47150	*218*	46932
		69		*62*		*68*
47636	*211*	47425	*213*	47212	*212*	47000
63		*68*		*68*		*70*
47699	*206*	47493	*213*	47280	*210*	47070
65				*60*		*67*
47764				47340	*203*	47137
66				*65*		
47830	*210*	47620	*215*	47405		
66		*61*		*65*		
47896	*215*	47681	*211*	47470	*213*	47257
60		*68*		*69*		
47956	*207*	47749	*210*	47539		
66		*67*		*66*		
48022	*206*	47816	*211*	47605		
74		*71*		*66*		
48096	*209*	47887	*216*	47671		
67		*57*		*65*		
48163	*219*	47944	*208*	47736		
		62		*61*		
		48006	*209*	47797		

matrix diagram of measured frequencies in the region where the Kimura-Miyanishi bands merge into the single series. The bands at the top (lower v' values) belong to the single series and are repeated in successive columns, as far down as the underlined band. Beyond this band, the individual progressions are clearly distinguished. It will be readily seen that the series regarded by Pringsheim and Rosen as a $v'' = 0$ progression

TABLE III. *Band measurements in the region of the Kimura-Miyanishi and Sponer-Watson overlap.* The measurements were made at low dispersion, partly by extrapolation, and are not of great accuracy. However, the general agreement indicates the close connection of the two sets of bands.

Measured	K–M	Measured	K–M	Measured	S–W	Measured	S–W
50008	50015 (5)	50943	50942 (6)	51224	51224	51937	51939
041	045 (6)		961 (6)	291	281	990	982
075	075 (5)		983 (u)	349	334	52042	52032
109	105 (5)	50994	51007 (7)		387	094	082
	126 (u)		026 (7)	(masked)	430	148	136
139	140 (6)		033 (5)	51459		200	182
164	168 (5)	51050	044 (5)		476	250	235
	173 (u)		059 (6)	509		288 ?	289
200	198 (7)		086 (7)	522 ?	526	356	339
238	234 (6)	106	117 (8)	564	569	403	389
(masked)	259 (5)		130 (u)	589 ?		459	439
50281	287 (7)	167		616	623	517	492
(These bands	50314 (7)		185 (8)	663	673	562	542
visible but	—						
too weak to	—		206 (u)	693 ?		616	591
measure.)	50741 (7)						
		224		720	724		640
CH_3I Absorption							
	50847 (8)		237 (8)	777	777	686	691
50898	896 (6)		258 (u)	835	828	710	740
	911 (6)	291	298 (8)	889	885	761	787
						811	840

actually belongs to three or four progressions with different v'' values. The conditions are similar at the other end of the long thin bridge where the Pringsheim and Rosen bands merge into the single series.

It seemed desirable also to investigate the relation of the Sponer-Watson and Kimura-Miyanishi bands by means of overlapping measurements. The results are given in Table III, and show the continuity of the two groups of bands.

The analysis of the Pringsheim and Rosen bands is not very satisfactory in any case. An attempt was made to improve it by the use of high dispersion (40 cm^{-1}/mm at λ2300), but it was found that the rotational structure, though incompletely resolved, made the bands too diffuse for accurate measurement. Hence the relation of the bands to the other single series (Pringsheim and Rosen's $v'=0$ series, with a spacing of 90 cm^{-1}) is not clear. However, if the series is due to the coincidence of $\Delta G'=90$ cm^{-1} and $\Delta G''=180$ cm^{-1}, the series should break up at the long wavelength end. For this purpose high pressures and temperatures were used to extend the system as far as possible. It was found that the series breaks up in the neighborhood of λ2850. This is interpreted as being due to the simultaneous increase of $\Delta G'$ and decrease of $\Delta G''$ till the progressions no longer coincide.

Still further increase of temperature and pressure gave, as found by Skorko,[9] two "continua" with intensity maxima at λ3413 and λ3270. At the highest temperatures obtained, 1115°C, the bands visible in the absorption edge have progressed until they reach the region of strong absorption at λ3413, but go no farther.

[9] E. Skorko, Nature **131**, 366 (1933).

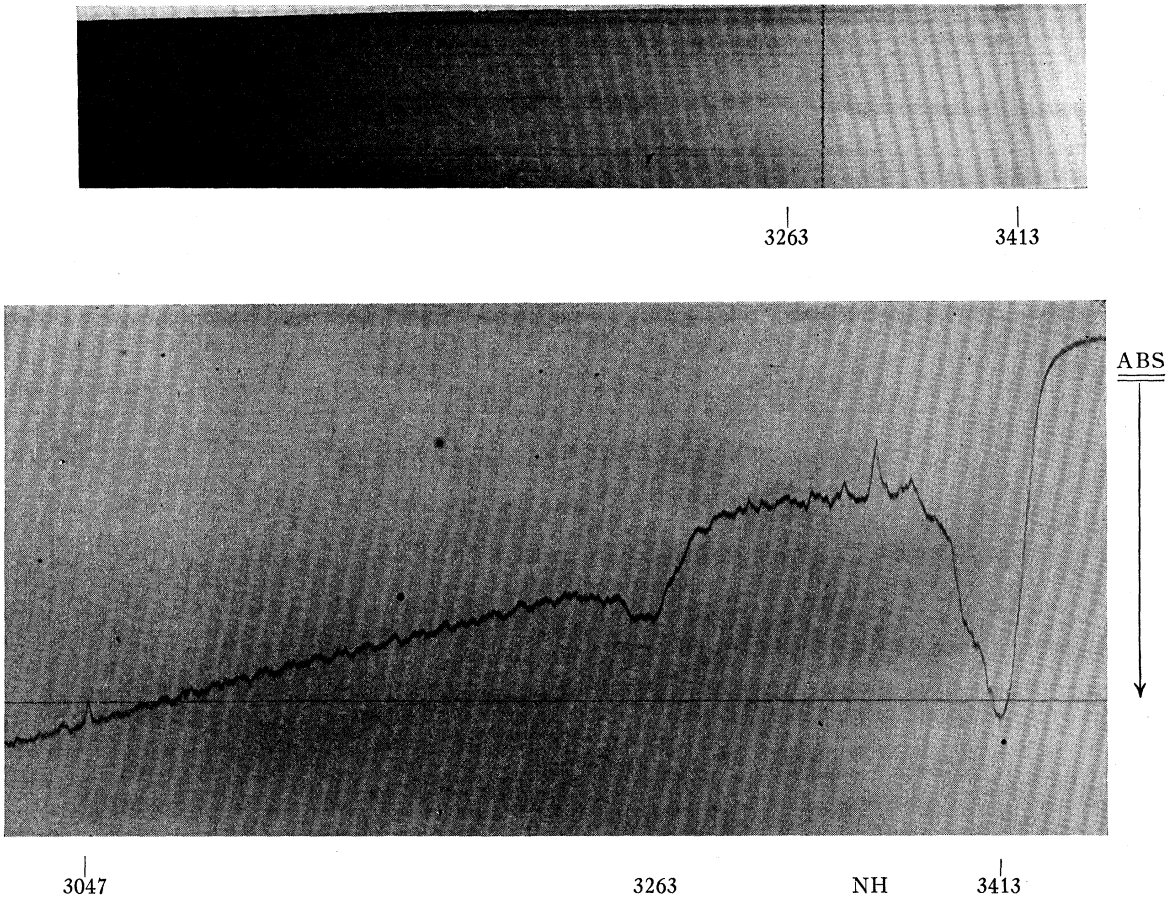


FIG. 2. Enlargement (4×) and microphotometer trace (6×) of two plates showing the absorption bands of iodine at the red end of the ultraviolet absorption system.

This condition is illustrated in Fig. 2. It will be noticed that there is no visible absorption at wavelengths greater than λ3413. Hence this "continuum," which has been the subject of much discussion,[8] appears to be the red end[10] of this strong absorption system. Naturally, when it is observed in emission the bands with lowest values of v' are most strongly developed, and these correspond to the red end. That the "continuum" and the discrete bands belong to the same system is indicated by their being found associated under such diverse circumstances (fluorescence at high temperatures[4] and pressures,[11] electrical discharge,[12] and absorption). Hence the upper state involved is that of the ultraviolet absorption, not electron+atom[13] or ions.[11] Its presence in fluorescence with conditions of high collision probability must be because collisions favor the emission of these bands over the McLennan bands. This may also be the reason why these bands appear so strongly in heated vapor in the discharge.[13, 14]

The bands measured in absorption have been compared with previous measurements, but it has not been possible to obtain a satisfactory quantum analysis. Further work in fluorescence is under way, and it is hoped to obtain an analysis of these bands by relating them to the fluorescence series.

[10] F. W. Loomis and S. W. Nile, Jr., Phys. Rev. **32**, 873 (1928).
[11] O. Oldenberg, Zeits. f. Physik **25**, 136 (1924).
[12] G. Cario and O. Oldenberg, Zeits. f. Physik **31**, 914 (1925).
[13] W. Gerlach and F. Gromann, Zeits. f. Physik **18**, 239 (1923).
[14] H. F. Fruth, Phys. Rev. **31**, 614 (1928).

The second absorption maximum at λ3263 has been observed by Skorko with a similar arrangement. It may possibly correspond to a band given by Konen[15] as "continuous maximum at 3300," though this latter seems more probably the λ3413 continuum, which is almost always present in emission. Again Fruth[14] reports three bands across the tail of λ3460, of which the first is λ3265, in good agreement with this edge, though the appearance of the band seems to be different. Hirschlaff[4] has obtained it in fluorescence at high temperatures, apparently associated with six narrow bands, which may, however, belong to the absorption system. In any case, it may similarly form the red end of an absorption system. If so, the upper state would lie about 1400 cm^{-1} higher than the upper state of the discrete bands. It was at first thought that these two states might form the components of a multiplet, presumably $^3\Pi_{0,1u}$. But the conclusions reached by Mulliken[16] make it seem unlikely that the upper state can be other than $^1\Sigma_u^+(0_u^+)$, with no multiplicity. In any case, it indicates a second excited state of the iodine molecule lying close to the one concerned in the discrete absorption. If there is any discrete absorption connected with the maximum λ3263, it presumably lies higher than that belonging to the Pringsheim and Rosen bands, in the region of total absorption (to which it would contribute) under given conditions of temperature and pressure.

[15] H. Konen, Ann. d. Physik **65**, 257 (1898).

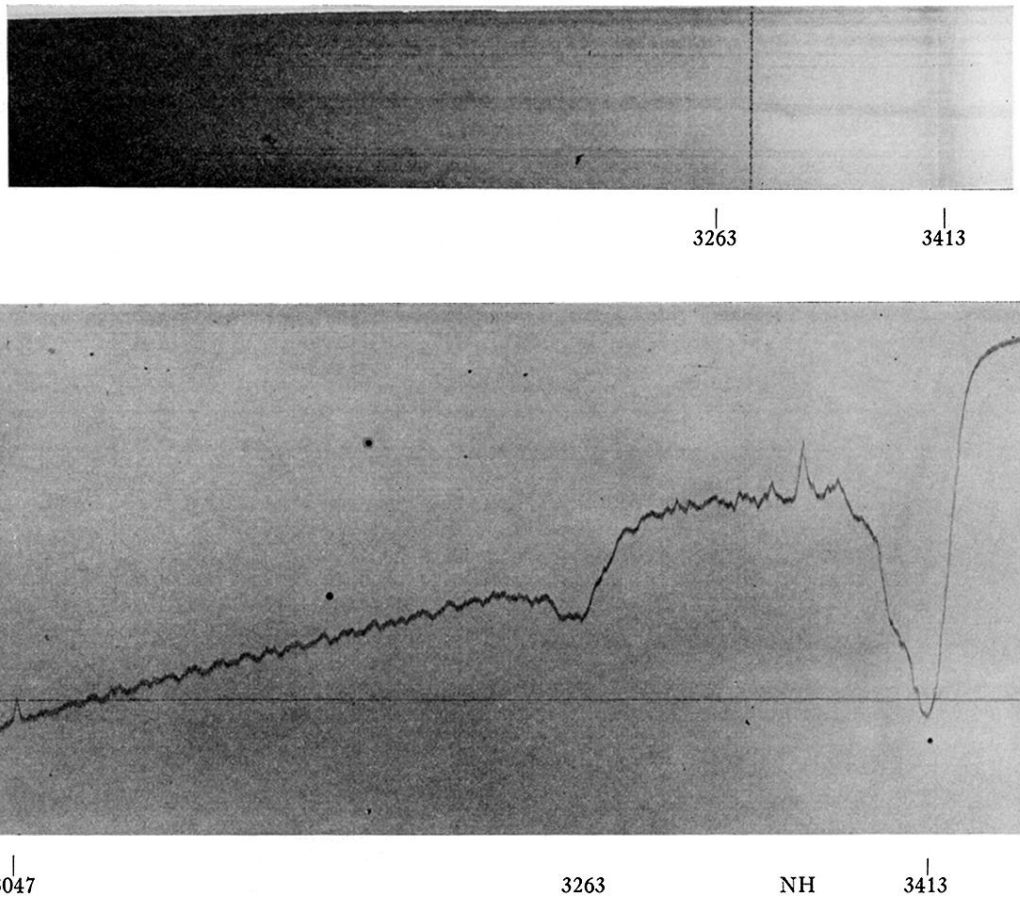
[16] R. S. Mulliken, Phys. Rev. **46**, 549 (1934) and private communication.

Concerning the excited state involved in this absorption (called by Jevons[17] *C* and *C'*, by Mulliken[16] and Curtis and Evans[8] *D*) a few conclusions may be drawn. The ω value must be at least as great as 90 cm^{-1} as found in the single progression, and may be estimated as close to 100 cm^{-1} from the series found connected with λ3413 in emission[11, 12] and fluorescence.[4] The highest possible value of $\nu(0,0)$ is given by adding 29,229 cm^{-1} (λ3413) to the heat of dissociation of the ground state, $D''=12{,}439$ cm^{-1}, giving $\nu(0,0)\leq 41{,}670$. This is because the r_e value of the excited state is so large that the transitions corresponding to the intensity maximum of the red end belong to very low v' values. Extrapolation of Oldenberg's intervals[11] gives the value 41,210 cm^{-1} for $\nu(0,0)$. The corresponding heat of dissociation (based on a long and doubtful extrapolation in the vacuum region) is 19,000 cm^{-1}.

These unusual characteristics lead to an absorption system covering a very long spectral region (3.3 volts), which is unusual for such a heavy molecule. This difficulty has been explained by Mulliken,[16] who shows that these characteristics are due to the relation of this state to ionic dissociation with Coulomb forces acting at large internuclear distances.

The author's sincere thanks are due to Professor W. W. Watson who suggested the problem and gave constant assistance in the investigation and in interpretation of results.

[17] W. Jevons, *Report on Band-Spectra of Diatomic Molecules*, London, The Physical Society (1932).



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