

double bond character as well as by the ionic character of the bond. Pauling⁸ has suggested resonance with various double bonded structures as a possible cause for the bond shortening in molecules of the above type. However, because he neglected the shortening caused

⁸L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), Ch. VII, p. 210.

by resonance with ionic structures, his treatment over-emphasizes the contributions from double bonded structures. It is of interest that $\angle \text{FGeF}$ in GeF_3Cl , 107.7° , is nearly tetrahedral like the corresponding one,¹ $\angle \text{FSiF}$, in SiF_3Cl . Pauling⁸ has pointed out that partial double bond character seems to have little influence on bond angles.

The Spectrum of Iodine Excited in the Presence of Argon

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Iodine vapor was excited by an uncondensed transformer discharge in the presence of argon. A new band system $\lambda 2785\text{--}2750\text{A}$ is recorded. In addition a large number of new bands are found in the band systems $\lambda 3455\text{--}3015\text{A}$, $\lambda 2730\text{--}2520\text{A}$, and $\lambda 4420\text{--}4000\text{A}$ reported by earlier workers. These band systems are analyzed and explained in terms of the fairly well-established term scheme of the iodine molecule. The absorption data in the region $\lambda 2000\text{--}3500\text{A}$ are discussed in the light of the present results.

I. INTRODUCTION

THE electrical and fluorescent excitations of iodine vapor are known to give a discrete band system in the visible region and a number of groups of semi-continuous (or diffuse) bands in the region $\lambda 4800$ to 2400A . The discrete band system is due to a transition from the upper electronic state $\sigma_g^2\pi_u^4\pi_g^3\sigma_u$, $0_u^+(^3\Pi_u)$ to the ground state. The groups of semicontinuous bands were explained in earlier papers by the present author¹ as due to transitions from various stable upper electronic states to various repulsive lower states dissociating into $^2\text{P}+^2\text{P}$ iodine atoms. It was known by experiments of earlier workers²⁻⁴ that the spectrum obtained by fluorescent excitation of a mixture of iodine and nitrogen is different from the fluorescent spectrum of pure iodine vapor. Elliott⁴ obtained four band systems in the regions $\lambda 4630$ to 4440A , 4321 to 4041A , 3450 to 3040A , and 2730 to 2520A . Since these band systems were obtained only in the presence of nitrogen, it was not clear which of them were actually due to the I_2 molecule. Hence, the discussion of these band systems was omitted by the present author in his earlier papers on the iodine molecule. Recently, Professor Mulliken kindly showed to the author an unpublished spectrogram which was taken a number of years ago on a medium quartz spectrograph by exciting iodine vapor by active nitrogen. It appears from the spectrum that the effect of active nitrogen on iodine

vapor is the same as that of the fluorescent excitation of iodine vapor in the presence of nitrogen.

Waser and Wieland^{5,6} excited iodine vapor in the presence of argon by a high frequency discharge and reported the last three of the above four band systems obtained by Elliott in fluorescence in the presence of nitrogen. The first system ($\lambda 4630$ to 4440A) was attributed by them to IN. They gave the vibrational formulas for the bands of the second and fourth systems but not of the third ($\lambda 3450$ to 3040A), for which, apparently, they accepted Elliott's analysis. The latter appears to be quite uncertain, since out of the 73 bands reported by Elliott in the region 3450 to 3040A , 27 bands were not classified in his vibrational scheme. Further, the constants used by Waser and Wieland for the lower state of the fourth system ($\lambda 2730$ to 2520A), which represents the ground state of the iodine molecule, are different from those obtained by Rank⁷ from the resonance spectral data of iodine. These constants used by Waser and Wieland do not fit in with the resonance spectral data; and, therefore, it has become necessary to analyze also the band system $\lambda 2730$ to 2520A .

Because of these reasons, a reinvestigation of the spectrum of iodine excited in the presence of argon was made by the present author. The band systems reported by Elliott and by Waser and Wieland, together with a new band system here obtained, were then analyzed and interpreted in accordance with the fairly well-established term scheme^{8,9} of the iodine molecule.

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TABLE I.* Band heads and vibrational analysis of the band system $\lambda 3455$ to $3015A$.

Skorko absorption	Present experiments (electrical excitation of I_2^+ argon)				Skorko absorption	Present experiments (electrical excitation of I_2^+ argon)				
	λ_{air}	ν_{vac}	ν', ν''	ν_{calc}		λ_{air}	ν_{vac}	ν', ν''	ν_{calc}	
3419	3454.4f	28940	2,62	28940	3353	3358.6	29766	9,61	29762	
	3452.3	28958	0,60	28957		3357.8f	29773	19,71	29770	
	3450.2	28976	11,71	28975		3356.3f	29786	8,60	29774	
	3448.3f	28992	12,72	28991				1,54	29785	
	3446.7	29005	13,73	29009				7,59	29788	
	3444.1	29027	14,74	29031		3354.2f	29805	6,58	29804	
	3442.0	29045	3,62	29042		3353.0	29815	0,53	29811	
	3440.6	29056	15,75	29054		3352.3	29822	5,57	29821	
	3439.7	29064	11,70	29062		3351.0	29833	15,66	29837	
			1,60	29060		3349.8	29844	4,56	29841	
	3438.1f	29078	12,71	29075		3348.2f	29858	19,70	29856	
	3437.3	29084	16,76	29080		3346.2f	29876	9,60	29875	
	3436.3f	29093	13,72	29091		3343.4	29901	22,73	29897	
	3432.0f	29129	15,74	29130		3342.0	29914	1,53	29914	
	3430.0	29146	4,62	29144		3339	3338.4	29946	13,63	29947
	3427.6f	29167	2,60	29163				0,52	29941	
	3425.0	29189	0,58	29190	3336.7f	29961	11,61	29964		
	3424.0f	29197	14,72	29191	3335.3f	29974	10,60	29976		
	3422.9	29207	15,73	29208	3333.3	29992	3,54	29990		
	3419.1f	29239	10,67	29239			9,59	29990		
			6,63	29241	3331.9	30004	8,58	30007		
	3417.5	29253	4,61	29254	3330.1	30021	2,53	30016		
			12,69	29252	3329.2	30029	7,57	30025		
	3416.4	29262	13,70	29262	3327.9	30040	15,64	30040		
	3415.4	29271	14,71	29275	3325.6	30061	12,61	30064		
	3413.5f	29287	15,72	29290	3324.8	30068	5,55	30068		
	3412.8	29293	1,58	29293	3324.2	30074	0,51	30074		
	3411.7	29303	19,77	29306			11,60	30077		
	3409.4f	29322	17,74	29328	3317.6	30134	17,65	30135		
	3406.3f	29349	6,62	29348	3316.3	30145	15,63	30146		
			12,68	29345	3315.6	30152	14,62	30154		
	3405.7	29354	13,69	29352	3313.9	30167	13,61	30164		
			5,61	29356	3312.2	30183	1,51	30177		
	3404.5	29364	4,60	29367	3311.1	30193	5,54	30194		
		14,70	29362			11,59	30192			
3403	3403.1f	29377	19,76	29376	3309	3309.0	30212	0,50	30212	
	3402.4	29383	3,59	29380		3307.1	30229	9,57	30227	
	3401.9	29387	16,72	29389		3305.8	30241	16,63	30245	
	3400.3f	29401	20,77	29404		3304.3	30255	15,62	30253	
	3399.5	29408	17,73	29406		3303.0	30267	14,61	30264	
			1,57	29412		3302.1	30275	7,55	30272	
	3397.5f	29425	18,74	29427		3300.2	30293	12,59	30292	
	3395.9	29439	9,64	29439		3299.0	30304	11,58	30310	
			11,66	29438	3295	3296.2	30329	10,57	30328	
			12,67	29440		3294.1	30349	0,49	30346	
	3394.7f	29449	7,62	29450				9,56	30349	
			13,68	29445		3292.6	30362	15,61	30363	
	3393.2	29462	15,70	29461		3291.1	30376	14,60	30377	
	3391.5f	29477	20,76	29474				8,55	30373	
	3389.0f	29499	3,58	29498		3290.0	30386	3,51	30382	
3386	3385.6	29528	19,74	29528		3288.5	30400	7,54	30398	
	3384.1	29541	13,67	29540		3287.0	30414	2,50	30415	
			10,64	29540		3286.1	30422	6,53	30425	
	3382.2f	29558	0,55	29556		3285.0	30433	19,64	30435	
			7,61	29560	3283	3284.0	30442	18,63	30443	
	3381.5f	29564	16,70	29560		3282.2	30459	16,61	30462	
	3379.6f	29581	5,59	29584		3279.9	30480	4,51	30484	
	3377.3f	29601	4,58	29600		3278.6	30492	14,59	30492	
	3374.5f	29626	20,74	29623		3278.0	30498	8,54	30499	
	3371.8f	29649	10,63	29646		3276.6	30511	13,58	30510	
			9,62	29652		3274.7	30528	7,53	30527	
3369	3369.2f	29672	7,60	29673				12,57	30529	
	3367.9f	29684	19,72	29685	3273	3271.7	30556	6,52	30555	
			6,59	29686				2,49	30552	
			0,54	29682		3271.2	30561	17,61	30561	
	3366.4	29697	23,77	29698		3269.5	30577	10,55	30575	
			20,73	29701		3267.6	30611	14,58	30610	
	3365.2	29707	5,58	29702		3264.5	30624	0,47	30627	
	3363.8	29720	4,57	29719	3263	3263.4	30634	21,64	30630	
	3362.4f	29732	13,65	29738		3262.2	30645	19,62	30648	
	3360.7	29747	11,63	29747		3261.8	30649	12,56	30651	
	3359.1f	29761	2,55	29762		3260.9	30658	7,52	30657	

* The bands marked *f* have been observed also in the fluorescence of I_2+N_2 by Elliott.

TABLE I.*—(Continued).

Skorko absorption	Present experiments (electrical excitation of I ₂ ⁺ argon)				Skorko absorption	Present experiments (electrical excitation of I ₂ ⁺ argon)			
	λ_{air}	ν_{vac}	ν', ν''	ν_{calc}		λ_{air}	ν_{vac}	ν', ν''	ν_{calc}
			3,49	30654		3166.0f	31576	5,44	31574
	3259.6	30670	17,60	30674		3164.4	31592	15,51	31593
	3258.9	30676	11,55	30676		3163.4	31602	11,48	31606
	3257.9	30686	6,51	30688		3162.3	31613	1,41	31617
	3256.2	30702	10,54	30701				23,57	31613
3253	3253.6	30726	9,53	30729	3161	3161.2	31624	4,43	31621
	3251.4	30747	20,62	30746		3160.0	31636	7,45	31631
	3249.4	30766	0,46	30770		3159.5f	31641	10,47	31646
	3248.4	30776	12,55	30776		3154.8	31689	9,46	31688
3245	3245.7	30801	11,54	30802		3151.7	31720	2,41	31720
	3243.6	30821	6,50	30823	3151	3150.4f	31733	8,45	31732
	3241.9	30837	2,47	30833		3146.7f	31770	4,42	31772
	3240.9f	30847	21,62	30844		3142.3	31815	30,61	31817
	3239.7	30858	5,49	30858	3141	3140.6f	31832	9,45	31833
			9,52	30859		3137.1f	31867	15,49	31865
3238	3237.7f	30877	13,55	30876		3134.0	31899	26,57	31902
	3236.2	30892	8,51	30891		3133.2f	31907	14,48	31906
	3234.8f	30905	12,54	30902	3132	3130.9f	31930	1,39	31929
	3233.7	30915	0,45	30915				7,43	31927
	3232.1	30931	11,53	30931		3128.6f	31954	20,52	31953
	3230.2f	30949	15,56	30950		3127.9	31961	24,55	31957
	3228.8	30962	10,52	30960				16,49	31964
			6,49	30960	3123	3124.9f	31992	12,46	31990
3228	3227.7	30973	2,46	30976		3121.4f	32028	5,41	32026
	3224.3f	31006	18,58	31006				8,43	32028
	3222.7f	31021	1,45	31018		3119.4	32048	14,47	32047
3219	3220.4f	31043	23,62	31038		3118.5	32057	25,55	32053
	3218.1	31065	0,44	31062		3117.5	32068	29,58	32069
	3217.1	31075	15,55	31075		3116.3	32080	4,40	32079
			3,46	31078				10,44	32081
	3214.5f	31100	6,48	31100	3112	3113.1f	32113	23,53	32115
	3213.5	31110	26,64	31114		3105.3	32194	2,38	32191
	3212.2f	31122	2,45	31121	3105	3104.1	32206	17,48	32203
3211	3210.8	31136	5,47	31139		3099.9	32250	1,37	32246
	3209.6f	31148	17,56	31148	3095	3096.4f	32286	6,40	32283
	3208.6	31157	12,52	31161		3092.7	32325	21,50	32319
	3203.1	31211	0,43	31211		3088.1f	32373	27,54	32370
3199	3200.1f	31240	6,47	31241	3084	3083.8f	32418	22,50	32416
	3197.7f	31263	9,49	31264		3082.2	32435	15,45	32434
	3195.2	31288	12,51	31294		3081.1	32447	18,47	32443
	3193.0	31309	1,43	31314				3,37	32451
	3191.7	31322	20,57	31321	3076	3075.9f	32501	27,53	32499
			4,45	31325	3067	3067.3f	32593	28,53	32595
3188	3189.7f	31342	7,47	31343				6,38	32597
	3186.2	31376	23,59	31376	3059	3058.9f	32682	13,42	32682
	3184.7f	31391	13,51	31394	3052	3053.7f	32738	21,47	32737
	3184.0	31398	17,54	31399		3048.7f	32791	23,48	32790
	3182.7	31411	2,43	31417		3045.3	32828	19,45	32829
	3181.7	31421	27,62	31422	3042	3043.0	32853	28,51	32858
3180	3180.3	31435	26,61	31437		3040.5f	32880	15,42	32881
	3179.1f	31446	8,47	31444				21,46	32880
	3177.6	31461	15,52	31460		3037.8	32909	9,38	32903
	3173.1f	31506	10,48	31505	3035	3032.8	32963	8,37	32960
3171	3169.9f	31538	21,56	31541	3029	3027.3	33023	21,45	33025
	3167.6	31561	16,52	31559		3019.7	33106	11,38	33105
	3166.8	31569	2,42	31568		3014.6	33162	10,37	33162

II. EXPERIMENTAL RESULTS AND VIBRATIONAL ANALYSIS

The iodine vapor was excited in the presence of argon (5 to 60 mm) by an uncondensed transformer discharge and the spectrum obtained was photographed on large and medium Hilger quartz spectrographs. The spectrum of iodine without the introduction of argon was also taken on the same plates for comparison. The discrete band system 6700 to 5000A, which one obtains in all kinds of excitation of pure iodine vapor is absent in the experiments with the mixture of iodine and argon.

The several groups of semicontinuous bands obtainable in fluorescence or by electrical excitation of pure iodine vapor, discussed previously,¹ are all absent except for the three bands at 4747, 4662, and 4575A. However, some diffuse bands which were not obtainable in the excitation of pure iodine vapor appear in the present experiments with the mixture of iodine and argon. They are at 5100, 3524, 3481, 2880, 2868, 2857, 2847, 2836, and 2825A. Some of these bands were obtained by Elliott and by Waser and Wieland. These bands are presumably due to transitions from upper stable elec-

TABLE II. Band heads and vibrational analysis of the band system $\lambda 2785$ to 2750\AA .

Intensity	λ_{air}	ν_{vac}	ν', ν''	ν_{calc}
1	2784.5	35903	5,62	35904
2	2779.8	35963	0,57	35959
5	2776.0	36012	5,61	36014
2	2775.3	36022	4,60	36023
5	2774.6	36031	3,59	36035
?	2773.2	36049	2,58	36049
6	2772.1	36063	1,57	36063
2	2771.4	36072		
$\frac{1}{2}$	2770.3	36086	0,56	36081
3	2769.4	36098	9,64	36103
			10,65	36103
?	2768.7	36107	8,63	36106
6	2768.2	36114	6,61	36117
			7,62	36111
1	2767.3	36126	5,60	36127
3	2765.4	36150	3,58	36153
3	2764.1	36167	2,57	36168
2	2762.8	36184	1,56	36185
2	2762.4	36190		
?	2761.5	36202	11,65	26205
			10,64	26206
2	2760.1	36220	7,61	36221
1	2759.3	36230	6,60	36230
1	2758.6	36240	5,59	36242
?	2757.5	36254	4,58	36254
4	2756.1	36272	3,57	36272
?	2755.0	36287	2,56	36290
1	2750.7	36344	6,59	36345
?	2748.3	36375	4,57	36375

tronic levels to repulsive states dissociating into $^2\text{P}+^2\text{P}$ iodine atoms. We hope to discuss these bands in a later paper.

Beside the above bands, there are four band systems in the regions: (1) 4420 to 4000 \AA , (2) 3455 to 3015 \AA , (3) 2785 to 2750 \AA , and (4) 2730 to 2520 \AA . Of these, the system $\lambda 2785$ to 2750\AA is new, and the other three are the same as those obtained by earlier workers,^{4,5} except that a large number of additional bands belong-

ing to these systems are found in the present work. The band heads of all these systems are degraded to longer wavelengths.

The band system $\lambda 3455$ to 3015\AA is very extensive, and its band heads are very close to one another. The wavelengths and wave numbers of the band heads in this system are given in Table I. All the bands were found to fit into a single vibrational scheme and could be expressed by the formula,

$$\nu = 39131 + (103.0\nu' - 0.1\nu'^2 - 0.001\nu'^3) - (213.798\nu'' - 0.614\nu''^2 - 0.000932\nu''^3 - 0.0000187\nu''^4),$$

with $\nu' = 0-30$ and $\nu'' = 37-77$. The constants of the lower state of the system which represents the ground state of the iodine molecule are those obtained by Rank⁷ from the resonance spectral data. The (ν', ν'') values and the corresponding wave numbers calculated from the above formula are given in Table I.

The band system $\lambda 2785$ to 2750\AA is not extensive, and it is weaker than the 3455-3015 \AA system. The band heads of this system are also quite close to one another. The wavelengths and the wave numbers of the bands, together with their estimated intensities, are given in Table II. The bands could be fairly well represented by the formula,

$$\nu = 45781 + (104.5\nu' - 0.1\nu'^2) - (213.798\nu'' - 0.614\nu''^2 - 0.000932\nu''^3 - 0.0000187\nu''^4),$$

with $\nu' = 0-11$ and $\nu'' = 56-65$. The lower state is again the ground state of the iodine molecule. The (ν', ν'') values and the corresponding wave numbers calculated according to the above equation are also given in Table II.

The vibrational scheme of the band system $\lambda 2730$ to 2520\AA is shown in Table III. The bands could be well

TABLE III. The vibrational scheme of the band system $\lambda 2730-2520\text{\AA}$.

$\nu'' \backslash \nu'$	45	50	55	60	65	
0	38932, 38787, 38643, 38502, 38366, 38230, 38097, 37961, 37834, 37706, 37580, 37457	38643, 38502, 38366, 38230, 38097, 37961, 37834, 37706, 37580, 37457	38502, 38366, 38230, 38097, 37961, 37834, 37706, 37580, 37457	38366, 38230, 38097, 37961, 37834, 37706, 37580, 37457	38230, 38097, 37961, 37834, 37706, 37580, 37457	38097, 37961, 37834, 37706, 37580, 37457
2	39275, 39121, 38834, 38697, 38555, 38421, 38285, 38020, 37890, 37647, 37525	38834, 38697, 38555, 38421, 38285, 38020, 37890, 37647, 37525	38697, 38555, 38421, 38285, 38020, 37890, 37647, 37525	38555, 38421, 38285, 38020, 37890, 37647, 37525	38421, 38285, 38020, 37890, 37647, 37525	38285, 38020, 37890, 37647, 37525
4	39366, 39215, 39069, 38932, 39605, 39456, 39310, 39167, 39019	39215, 39069, 38932, 39069, 39019	39069, 38932, 39019	38932, 39019	38932, 39019	38932, 39019
6	39258, 38973, 38391, 37772, 37647, 3746	38973, 38391, 37772, 37647, 3746	38391, 37772, 37647, 3746	37772, 37647, 3746	37772, 37647, 3746	37772, 37647, 3746
8	39767, 37580, 37367, 37197, 37176	37580, 37367, 37197, 37176	37367, 37197, 37176	37367, 37197, 37176	37367, 37197, 37176	37367, 37197, 37176
10						

* The bands marked * are from Elliott's data in fluorescence.

TABLE IV.* The vibrational scheme of the band system $\lambda 4420-4000\text{\AA}$.

V''	10	15	20	25	30	35														
0	24566 104	24462 104	24140 101	24040 101	23939 99	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22955	22731				
2	24784	24566	24140 99	24040 101	23939 101	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22955	22766				
4	24985	24658	24239 103	24134 105	23939 101	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22955	22638				
6	24641 98	24540 101	24342 98	24340 102	24134 105	23939 101	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22840				
8	24947 107	24840 95	24739 101	24641 98	24540 101	24342 98	24340 102	24134 105	23939 101	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22955	22766
10	24919	24724	24628 96	24540 101	24342 98	24340 102	24134 105	23939 101	23840 99	23745 99	23646 94	23552 93	23459 89	23370 89	23282 87	23201 87	23032 77	22955	22766	

* The bands marked * are from Elliott's data in fluorescence.

represented by the expression,

$$\nu = 47150 + (96.21v' - 0.49v'^2) - (213.798v'' - 0.614v''^2 - 0.000932v''^3 - 0.0000187v''^4),$$

with $v' = 0-10$ and $v'' = 43-66$. The lower state of the band system is again the ground state of the molecule. We see from the equation that the present analysis of this system does not change the vibrational constants⁹ of the upper level, but changes its position^{9a} to 47150 cm^{-1} from the previous value 46441 cm^{-1} obtained by Waser and Wieland.⁵

Waser and Wieland, as mentioned above, gave the vibrational formula for the bands of the system $\lambda 2730$ to 2520\AA , but have not yet published their experimental data and their vibrational analysis. The vibrational scheme of this band system as obtained from the present work is therefore shown in Table IV. The following formula of Waser and Wieland represents fairly well the bands of this system:

$$\nu = 25757.2 + (101.88v' - 0.3v'^2) - (126.57v'' - 0.75v''^2 - 0.0033v''^3).$$

Bands with $v' = 0-11$ and $v'' = 9-38$ are recorded in the present work. The lower state of this system is the $\sigma_g^2\pi_u^4\pi_g^3\sigma_u, 0_u^+(^3\Pi)$ state at 15598 cm^{-1} .

III. ELECTRONIC TRANSITIONS INVOLVED

According to the vibrational analyses discussed above, three of the band systems have their upper electronic levels at 39131 cm^{-1} , 45781 cm^{-1} , and 47150 cm^{-1} , respectively, and have the ground state of the iodine molecule as their lower state. The fourth system in the region $\lambda 4420$ to 4000\AA has its upper level at

^{9a} Dr. Wieland, in a recent private communication to Dr. Herzberg, mentioned that the position of the upper level of the above band system has probably to be changed from 46441 cm^{-1} to 47151 cm^{-1} , which is in perfect agreement with the above result. The author wishes to express his thanks to Dr. Herzberg for this information.

$15598 + 25757 = 41355 \text{ cm}^{-1}$ and its lower level at 15598 cm^{-1} . The lower level in this case, as mentioned above, is well known to be $\sigma_g^2\pi_u^4\pi_g^3\sigma_u, 0_u^+(^3\Pi_u)$, which dissociates into $^2P_{3/2} + ^2P_{3/2}$ iodine atoms. Therefore, the upper state according to the selection rules should be 0_g^+ or 1_g . A consideration of the electronic term scheme of the iodine molecule, discussed in earlier papers and shown to some extent in Table VII, shows that the upper state of the band system is very probably a 0_g^+ state corresponding to $\sigma_g^2\pi_u^4\pi_g^3\sigma_u^2, ^1\Sigma_g^+$. This state is predicted^{1,8} to be stable because it dissociates probably into ions $I^+(^4p, ^1D) + I^-(^6s, ^1S)$, while its very low ω_e (102 cm^{-1}) is understandable in view of the presence of two strongly antibonding electrons (σ_u^2).

We now consider the probable electronic terms for the three levels at 39131 cm^{-1} , 45781 cm^{-1} , and 47150 cm^{-1} . The electron configuration $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$ gives rise among others to the terms $^1\Sigma_u^+(0_u^+)$, $^3\Sigma_u^-(0_u^+, 1_u)$, and $^1\Delta_u(2_u)$, the symbols in the parentheses being those for case *c* type coupling. These terms are predicted to dissociate into ions $I^+ + I^-$, and so are expected to be stable. The remaining terms of the configuration are predicted to dissociate into $^2P + ^2P$ atoms, and so (in view of their height) should be unstable. For case *a* coupling the only possible transition from the above terms to the ground state $^1\Sigma_g^+(0_g^+)$ is that from $^1\Sigma_u^+(0_u^+)$. However, in the iodine molecule, where we expect a strong tendency towards case *c* coupling, the transitions $^3\Sigma_u^-(0_u^+, 1_u) \rightarrow ^1\Sigma_g^+(0_g^+)$ are also allowed.

The fact that the three observed levels under consideration have vibrational frequencies of the same magnitude suggests that the electronic terms responsible for these levels arise from the same configuration, presumably $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$. Then the low ω_e values observed for these three levels will be in harmony with the presence of the two strongly antibonding σ_u electrons. Assuming that $^1\Sigma_u^+$ is above $^3\Sigma_u^-$, one could

TABLE V. Identification of electronic terms.

Position of the levels	Three different possible electronic terms		
	First	Second	Third
39131 cm ⁻¹	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^-(0_u^+)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^1\Sigma^+(0_u^+)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^-(0_u^+)$
45781 cm ⁻¹	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^-(1_u)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^-(1_u)$	$\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^3\Sigma^+(1_u)$
47150 cm ⁻¹	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^1\Sigma^+(0_u^+)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^-(0_u^+)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^1\Sigma^+(0_u^+)$

attribute $^1\Sigma_u^+(0_u^+)$ to the level at 47150 cm⁻¹ and the components of $^3\Sigma_u^-$ to those at 39131 cm⁻¹ and 45781 cm⁻¹. As the band system that arises in 39131 cm⁻¹ is more intense than the one that arises in 45781 cm⁻¹, we might attribute $^3\Sigma^-(0_u^+)$ to 39131 cm⁻¹ and $^3\Sigma^-(1_u)$ to 45781 cm⁻¹; but it is very difficult to understand how the separation of the two components 0_u^+ and 1_u of $^3\Sigma_u^-$ could be as much as 45781 - 39131 = 6650 cm⁻¹. To avoid this difficulty one might attribute $^3\Sigma_u^-(0_u^+)$, $^3\Sigma^-(1_u)$, and $^1\Sigma_u^+(0_u^+)$ to the levels at 47150 cm⁻¹, 45781 cm⁻¹, and 39131 cm⁻¹, respectively. This assignment is in good agreement with the observed relative intensities of the respective band systems; i.e., the 39131 system is most intense and the 45781 system is weakest of the three. Further, the component separation of $^3\Sigma_u^-$ will be 47150 - 45781 = 1369 cm⁻¹, which appears to be reasonable for the case *c* coupling. The only questionable point about this assignment is that the relative positions of $^3\Sigma_u^-$ and $^1\Sigma_u^+$ are reversed; i.e., $^3\Sigma_u^-$ is above $^1\Sigma_u^+$. Recknagel¹⁰ has worked out the relative positions of $^1\Sigma^+$ and $^3\Sigma^-$ for the configurations $\pi^3\pi'$ and $\pi\pi'$. For the configuration $\pi\pi'$, $^3\Sigma^-$ is lower than $^1\Sigma^+$; and for the configuration $\pi^3\pi'$, $^3\Sigma^-$ is higher than $^1\Sigma^+$. However, the relative positions of $^3\Sigma$ and $^1\Sigma$ of the configuration $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$ have not been calculated so far. But one will presumably expect in simple molecules that the $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$ case will be similar to $\pi\pi'$; i.e., $^3\Sigma^-$ will be lower than $^1\Sigma^+$. However, in the case of iodine molecules, it is conceivable that the calculations for $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$ may show that $^3\Sigma^-$ is higher than $^1\Sigma^+$. Therefore, the assignment of $^3\Sigma^-(0_u^+)$, $^3\Sigma^-(1_u)$, and $^1\Sigma_u^+(0_u^+)$ to the levels at 47150 cm⁻¹, 45781 cm⁻¹, and 39131 cm⁻¹, respectively, appears to be reasonable.

TABLE VI. Alternative configurations in I₂ for dissociation into atoms in ²P states.

Dissociation products	Odd electron terms derived according to case <i>c</i> type coupling	Case A	Case B
		The electron configurations of odd unstable states if $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^3\Sigma_u^+(1_u)$ does not dissociate into $^2P_{1/2} + ^2P_{1/2}$ atoms and so is stable	The electron configurations of odd unstable states if $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^3\Sigma_u^+(1_u)$ dissociates into $^2P_{1/2} + ^2P_{1/2}$ atoms and so is unstable
$^2P_{1/2} + ^2P_{1/2}$	0 ⁻ , 1	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^+(1_u)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^+(0_u^-)$	$\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^3\Sigma^+(1_u)$ $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^3\Sigma^+(0_u^-)$
$^2P_{3/2} + ^2P_{1/2}$	0 ⁻ , 1, 1, 2 0 ⁺ (stable)	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^1\Sigma^-(0_u^-)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Delta(1_u)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Delta(2_u)$ $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\ ^1\Pi(1_u)$	$\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Delta^+(0_u^-)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma^+(1_u)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Delta(1_u)$ $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Delta(2_u)$

¹⁰ A. Recknagel, Z. Physik **87**, 396 (1934).

One may also consider another point of view. The electron configuration $\sigma_g\pi_u^4\pi_g^4\sigma_u$ gives the terms $^1\Sigma_u^+(0_u^+)$ and $^3\Sigma_u^+(1_u, 0_u^-)$. The transitions $^1\Sigma_u^+(0_u^+) \leftrightarrow ^1\Sigma_g^+(0_g^+)$ and $^3\Sigma_u^+(1_u) \leftrightarrow ^1\Sigma_g^+(0_g^+)$ are both allowed. The level $^1\Sigma_u^+(0_u^+)$ is expected¹¹ to dissociate into I⁺+I⁻ and it is stable. Its position¹¹ is at 51683 cm⁻¹ with ω value 165 cm⁻¹, and it forms the upper level of iodine absorption bands in the region 1770 to 1950 Å. According to case *a* coupling, the level $\sigma_g\pi_u^4\pi_g^4\sigma_u\ ^3\Sigma_u^+(1_u)$ is expected to dissociate into $^2P_{3/2} + ^2P_{3/2}$ iodine atoms, and hence to be unstable. In the case of the iodine molecule, one might expect that $\sigma_g\pi_u^4\pi_g^4\sigma_u\ ^3\Sigma_u^+(1_u)$ will go to higher dissociation products to avoid crossing the $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma_u^-(1_u)$. In this case the latter will dissociate into $^2P_{3/2} + ^2P_{3/2}$ atoms, and so be an unstable state, and $\sigma_g\pi_u^4\pi_g^4\sigma_u\ ^3\Sigma_u^+(1_u)$ will be a stable state. Then we will have $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^3\Sigma_u^-(0_u^+)$, $\sigma_g\pi_u^4\pi_g^4\sigma_u\ ^3\Sigma_u^+(1_u)$, and $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2\ ^1\Sigma_u^+(0_u^+)$ for the three levels at 39131, 45781, and 47150 cm⁻¹, respectively. The validity of this assignment is somewhat doubtful, since, according to it, $\sigma_g\pi_u^4\pi_g^4\sigma_u\ ^3\Sigma_u^+(1_u)$ is at 45781 cm⁻¹ and its ω value is 104.5 cm⁻¹, whereas the ω value of $^1\Sigma_u^+(0_u^+)$ at 51683 cm⁻¹ from the same configuration is 165 cm⁻¹. Moreover, the value 104.5 cm⁻¹ is much nearer to the ω values 103.0 and 96.2 cm⁻¹ of the other two states arising from the configuration $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$. This difference in ω value of the two states, 0_u^+ at 51683 cm⁻¹ and 1_u at 45781 cm⁻¹, can be understood if they dissociate into different components of I⁺+I⁻. For example, we know that the vibrational frequencies of $^3\Pi(0_u^+)$ and $^3\Pi(1_u)$ of the configuration $\sigma_g^2\pi_u^4\pi_g^4\sigma_u$ are 128 cm⁻¹ and 44 cm⁻¹, respectively. This is because $^3\Pi(0_u^+)$ dissociates into $^2P_{3/2} + ^2P_{3/2}$ iodine atoms and $^3\Pi(1_u)$ dissociates into $^2P_{3/2} + ^2P_{3/2}$ iodine atoms. Thus, there are three different possible ways of identifying the electronic terms at 39131, 45781, and 47150 cm⁻¹, which are summarized in Table V.

The rotational analysis of the band systems, which requires quite large resolution instruments, will show which one of the three possible configurations in Table V is correct. However, from the considerations of relative intensities of the band systems, the vibrational frequencies of the three levels, and their relative mutual separation, we prefer the second assignment, which is included in Table VII.

If one accepts the second assignment, a change in the assignment of electronic terms for the odd unstable states, dissociating into $^2P + ^2P$ iodine atoms, is neces-

¹¹ P. Venkateswarlu, Proc. Indian Acad. Sci. **24A**, 473 (1946).

sary, as those assignments in the earlier papers¹ were made with the assumption that $\sigma_g\pi_u^4\pi_g^4\sigma_u^3\Sigma_u^+(1_u)$ would be a stable state.¹¹ The two alternative configurations for the odd unstable states dissociating into ${}^2P+{}^2P$ iodine atoms are given in Table VI for the cases (A) if $\sigma_g\pi_u^4\pi_g^4\sigma_u^3\Sigma_u^+(1_u)$ dissociates into higher dissociation products, say $I^+ + I^-$, and hence is a stable state, and (B) if $\sigma_g\tau_u^4\pi_g^4\sigma_u^3\Sigma_u^+(1_u)$ dissociates into ${}^2P_{3/2}+{}^2P_{3/2}$ atoms and is therefore unstable. The assignment (A) was adopted in the earlier papers¹ by the writer, but the assignment (B) is to be preferred to (A) if one accepts the second possible configuration given in Table VI for the levels at 39131, 45781, and 47150 cm^{-1} .

IV. REMARKS ON THE KIMURA-MIYAMISHI, PRINGSHEIM-ROSEN, AND SKORKO BANDS IN ABSORPTION IN THE REGION 2000 TO 3500A

In an earlier paper¹² the present author arranged the Pringsheim-Rosen, Kimura-Miyamishi (P-R, K-M) bands in one vibrational scheme; but the wave number separations were so irregular that no equation was developed for the bands. However, with the assumption that the P-R, K-M bands are all due to a single electronic transition from the ground state, the upper electronic level was extrapolated to be 44900 cm^{-1} . According to the present experiments, we have a level at 45781 cm^{-1} which forms the upper level of the band system $\lambda 2785$ to 2750A discussed above. Though one might argue that, in view of the large extrapolation involved, the position of the level extrapolated from the analysis of the P-R, K-M bands coincides roughly with the position of the level at 45781 cm^{-1} , it is uncertain whether all the P-R, K-M bands have this upper level. For (1) the ω -value for the single vibrational scheme of the P-R, K-M bands was about 90 cm^{-1} , and the present level has $\omega=104.5$ cm^{-1} ; (2) as stated above, the wave number separations in the analysis of the P-R, K-M bands were irregular and no equation had been developed. Further, we see that all the transitions from the ground state to the states at 47150 cm^{-1} , 45781 cm^{-1} , and 39131 cm^{-1} are possible in absorption, since the reverse transitions do occur in emission. These transitions in absorption can be expected to give rise to the bands in the region 2000A to 3500A. It is probably for this reason that the attempts so far made to develop a single vibrational scheme for all the P-R, K-M, and Skorko^{13,14} bands did not succeed. Future reinvestigation of the absorption spectra of iodine in the region 2000 to 3500A at varying temperatures from room temperature to 1300°C and the reanalysis of all the absorption bands in that region may show definitely the existence of the above three transitions in absorption. With the present knowledge about

the iodine molecule we can say that the P-R, K-M bands are due to the overlapping of transitions from the ground state to the two levels at 45781 cm^{-1} and 47150 cm^{-1} ; and the Skorko bands to a transition from the ground state to the one at 39131 cm^{-1} . The wavelengths of the Skorko bands in absorption are included in Table I, where the emission bands from the level at 39131 cm^{-1} to the ground state are given. The agreement of the wavelengths confirms the above statement with regard to the transition of the Skorko bands. Therefore, the tentative explanation suggested for these Skorko bands in an earlier paper¹² must be abandoned.^{14a}

For convenience, the positions of all the stable electronic levels of the I_2 molecule observed either in absorption or emission, their term designations and probable electron configurations are given in Table VII together with their vibrational frequencies.

The Absence of the Band System $\lambda 6700$ to 5000A

As mentioned in the beginning, the discrete band system $\lambda 6700$ to 5000A which is due to a transition from 0_u^+ to the ground state, is absent in the excitation of the mixture of argon and iodine. Normally, when there is no foreign gas, the molecules which are excited to 0_u^+ come back to the ground state giving the discrete band system. However, when foreign gas is introduced, the excited molecules in the 0_u^+ state very probably go over, by collisions, to the repulsive state 0_u^- which either touches or crosses the 0_u^+ and dissociate into ${}^2P_{3/2}+{}^2P_{3/2}$ iodine atoms as suggested by Van Vleck¹⁵ in explaining the magnetic quenching of iodine fluorescence and Turner's fluorescence experiments¹⁶ in a mixture of iodine and argon. Turner¹⁶ also reported that he compared the spectra in the visible region of the discharges in pure iodine and in iodine and argon mixtures. All bands of wavelength longer than 5440A were reported to appear to have normal intensities, while the bands of shorter wavelength were considerably weakened in spectra of the mixture, but in the present experiments the whole band system is absent. The difference between the present experimental results and those of Turner may be due to the higher pressure of argon used in the present experiments.

The other characteristic features of the spectrum of the mixture of iodine and argon, as already described, are (1) the absence of certain groups of semicontinuous emission bands which are present when iodine is excited alone and which arise in levels whose r_e values are not very different from the r_e values of the ground state, and (2) the presence of the four band systems which arise

¹² P. Venkateswarlu, Indian J. Phys. 21, 43 (1947).

¹³ Skorko, Nature 131, 366 (1933).

¹⁴ Skorko, Acta Phys. Polonica 3, 191 (1934).

^{14a} The explanation given in the earlier papers (references 9 and 12) for the continua in absorption at 3413A and 3263A still holds good. They are not due to the same transition as the narrow absorption bands (Skorko bands discussed above).

¹⁵ J. H. Van Vleck, Phys. Rev. 40, 544 (1932).

¹⁶ L. A. Turner, Phys. Rev. 38, 574 (1931).

TABLE VII. Observed stable electronic states of iodine molecule.

Electron configuration	Electron states Case <i>a</i> or <i>b</i> type coupling	Case <i>c</i> or Ω - <i>s</i> coupling	Name	Position of the levels ^a T_0 in cm ⁻¹	ω_0 in cm ⁻¹	Probable dissociation products if there is to be no effect of crossing ^a	Remarks
$\sigma_g \pi_u^3 \pi_g^4 \sigma_u^2$	$^1\Pi_u$	1_u	<i>Q</i>	64329	(93)	$5p^4 \ ^1D_2 + 5p^6 \ ^1S_0$	<i>J, K, M, N, O, P,</i> and <i>Q</i> form the upper levels of the seven groups of bands obtained by Cordes ^b in absorption in the region 1770–1500Å. The wave number separations in all these seven groups are very irregular, and so the positions and frequencies of these levels are to be taken as doubtful until they are confirmed by future experiments.
$[\sigma_g^2 \pi_u^4 \pi_g^3 \ ^2\Pi_{\frac{1}{2}}] \sigma_u \ 6p$		$\Pi_{1,0u^+}$	<i>P</i>	62802	(297)	$\text{ex} + 5p^6 \ ^2P$	
$\sigma_g \pi_u^3 \pi_g^4 \sigma_u^2$	$^3\Pi_u$	0_u^+	<i>O</i>	61824	(96)	$5p^4 \ ^2P_0 + 5p^6 \ ^1S_0$	
$[\sigma_g^2 \pi_u^3 \pi_g^4 \ ^2\Pi_{\frac{1}{2}}] \sigma_g \ 6s$		$\Pi_{1,0u^+}$	<i>N</i>	59217	(212)	$\text{ex} + 5p^6 \ ^2P$	
$\sigma_g \pi_u^3 \pi_g^4 \sigma_u^2$	$^3\Pi_u$	1_u	<i>M</i>	58937	(203)	$5p^4 \ ^2P_1 + 5p^6 \ ^1S_0$	
$\sigma_g \pi_u^4 \pi_g^3 \sigma_u^2$	$^1\Pi_g$	1_g	<i>L</i>	58578	120	$5p^4 \ ^1D_2 + 5p^6 \ ^1S_0$	Three groups of diffuse emission bands arise in this level (reference 1).
$[\sigma_g^2 \pi_u^4 \pi_g^3 \ ^2\Pi_{\frac{1}{2}}] \sigma_u \ 6p$		$\Pi_{1,2u}$	<i>K</i>	57794	(246)	$\text{ex} + 5p^6 \ ^2P$	<i>X</i> → <i>K</i> gives part of absorption bands in the vacuum region.
$[\sigma_g^2 \pi_u^3 \pi_g^4 \ ^2\Pi_{\frac{1}{2}}] \sigma_g \ 6s$		$\Pi_{1,2u}$	<i>J</i>	56933	(207)	$\text{ex} + 5p^6 \ ^2P$	<i>X</i> → <i>J</i> gives part of absorption bands in the vacuum region.
$[\sigma_g^2 \pi_u^4 \pi_g^3 \ ^2\Pi_{\frac{1}{2}}] \sigma_g \ 6s$		$\Pi_{1,2g}$	<i>I</i>	56000	(360)	$\text{ex} + 5p^6 \ ^2P$	Five groups of semicontinuous bands arise in this level (reference 1). The abnormally high value for the frequency separation (360 cm ⁻¹) for these bands may be partly only apparent and due to the shape of the repulsion curves of the lower states of these bands.
$\sigma_g \pi_u^4 \pi_g^4 \sigma_u$	$^1\Sigma_u^+$	0_u^+	<i>H</i>	51683	164.5	$5p^4 \ ^1S_0 + 5p^6 \ ^1S_0$	<i>X</i> → <i>H</i> gives Cordes absorption bands λ 1950–1770 ¹¹ . Five groups of semicontinuous bands in emission (reference 1) arise in this level <i>H</i> .
$\sigma_g \pi_u^4 \pi_g^3 \sigma_u^2$	$^3\Pi_g$	1_g	<i>G</i>	51528	215	$5p^4 \ ^3P_1 + 5p^6 \ ^1S_0$	Five groups of diffuse semicontinuous emission bands arise in <i>G</i> and have for their lower levels different repulsive states dissociating into $^2P + ^2P$ iodine atoms (references 1 and 9).
$\sigma_g^2 \pi_u^3 \pi_g^3 \sigma_u^2$	$^3\Sigma_u^-$	0_u^+	<i>F</i>	47150	96.2	$5p^4 \ ^3P_2 + 5p^6 \ ^1S_0$	<i>X</i> ↔ <i>F</i> gives emission bands 4420–4000Å in the presence of a foreign gas and also probably part of P-R, K-M absorption bands.
$\sigma_g^2 \pi_u^3 \pi_g^3 \sigma_u^2$	$^3\Sigma_u^-$	1_u	<i>E</i>	45781	104.5	$5p^4 \ ^3P_2 + 5p^6 \ ^1S_0$	<i>X</i> ↔ <i>E</i> gives emission bands 2785–2750Å in the presence of a foreign gas, and also probably part of P-R, K-M absorption bands.
$\sigma_g^2 \pi_u^2 \pi_g^4 \sigma_u^2$	$^1\Sigma_g^+$	0_g^+	<i>D</i>	41355	101.9	$5p^4 \ ^1D_2 + 5p^6 \ ^1S_0$	<i>D</i> → <i>B</i> gives emission bands 2730–2520Å in the presence of a foreign gas.
$\sigma_g^2 \pi_u^3 \pi_g^3 \sigma_u^2$	$^1\Sigma_u^+$	0_u^+	<i>C</i>	39131	103.0	$5p^4 \ ^1D_2 + 5p^6 \ ^1S_0$	<i>X</i> ↔ <i>C</i> gives emission bands 3455–3015Å in the presence of a foreign gas, and absorption bands recorded by Skorko at high temperatures.
$\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u$	$^3\Pi_u$	0_u^+	<i>B</i>	15598	126.6	$5p^6 \ ^2P_{\frac{3}{2}} + 5p^6 \ ^2P_{\frac{1}{2}}$	<i>X</i> ↔ <i>B</i> gives absorption bands 8600–4300Å and emission bands 6700–5000Å (reference 9).
		1_u	<i>A</i>	11803	44	$5p^6 \ ^2P_{\frac{3}{2}} + 5p^6 \ ^2P_{\frac{1}{2}}$	<i>X</i> → <i>A</i> gives absorption bands in the region 9300–8375Å (reference 9).
$\sigma_g^2 \pi_u^4 \pi_g^4$	$^1\Sigma_g^+$	0_g^+	<i>X</i>	0	213.8	$5p^6 \ ^2P_{\frac{3}{2}} + 5p^6 \ ^2P_{\frac{1}{2}}$	Ground state.

^a In column 7 of this table, "ex" stands for an excited neutral atom of the configuration of the type $5p^4 \ 6p$ or $5p^4 \ 6s$. The positions of the levels in column 5 represent the heights of the zero vibrational levels of the respective states over that of the ground state.

^b H. Cordes, *Z. Physik* **97**, 603 (1935).

in levels with smaller ω_e values and hence larger r_e values than those of the ground state. This shows that collisions with the foreign gas make molecules in the higher excited states go over into lower excited electronic states in the energy range 39131 to 47150

cm^{-1} , with larger r_e values and smaller ω_e values, in the manner discussed by Wieland.⁶

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Relation between Lattice Vibration and London Theories of Superconductivity

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A gas of noninteracting electrons of small effective mass, m_{eff} , has a large diamagnetic susceptibility. It is shown that the London phenomenological equations of superconductivity follow as a limiting case when m_{eff} is so small that the Landau-Peierls theory yields a susceptibility $< -1/4\pi$. Justification is given for the use of an effective mass, $m_e \sim 10^{-4} m$, for superconducting electrons in the lattice-vibration theory of superconductivity. This value is sufficiently small to show that the theory gives the London equations and, as a consequence, the typical superconducting properties. The concentration of superconducting electrons, n_s , is smaller than the total electron concentration, n , by about the same ratio as the effective masses, so that $m_e/n_s \sim m/n$, and thus the penetration depth is of the same order as that given by the usual London expression.

I. INTRODUCTION

A THEORY of superconductivity based on interactions between electrons and lattice vibrations has been discussed in two previous communications.^{1,2} The second of these (to be denoted by the letters WF), deals with wave functions for superconducting electrons. Fröhlich³ has independently developed a theory along similar lines. These earlier papers have been concerned primarily with the energy of the lowest state of a superconductor and have not discussed in any detail how the electrodynamic characteristics of the superconducting state—perfect diamagnetism and infinite conductivity—follow from the model. We shall show here that the theory leads to the London phenomenological equations⁴ in the manner indicated in our earlier papers.

The present theory is similar in many respects to one suggested some years ago by the author.⁵ In the earlier theory it was proposed that in the superconducting state there is a small distortion of the lattice which produces Brillouin zone boundaries with small energy gaps, $\sim \kappa T_c$ (T_c = transition temperature) at the Fermi surface. There would be a resultant decrease in energy of electrons in states on the low energy side of the gap. Associated with the small energy gap is a small effective mass ratio, $\sim \kappa T_c/E_F$, for electrons with energies near

the Fermi surface, E_F . It was shown that a sufficiently large diamagnetism for superconductivity will occur if there is a sufficient number of electrons of small effective mass. The difficulty with the theory as formerly proposed is that it appears that the energy required to distort the lattice and so to produce the zone boundaries is larger than the energy gained by the electrons.

In the present theory, zero-point vibrations replace the small permanent distortion of the lattice. The effective mass of the superconducting electrons is small as in the earlier theory, and we have suggested^{1,2} that the explanation of the superconducting properties in terms of a large diamagnetic effect of the electrons is similar.

It has been recognized for some years that the Meissner effect ($\mathbf{B}=0$), is a more basic property of the superconducting state than infinite conductivity ($\mathbf{E}=0$), although, from a purely macroscopic point of view, neither one is a consequence of the other. Both follow from the London equations which can be derived most readily from a consideration of the magnetic properties.

From a formal point of view, a perfect diamagnetism can be described by a diamagnetic susceptibility equal to $-1/4\pi$. Landau⁶ has shown that, as a consequence of quantum theory, a gas of free noninteracting electrons obeying Fermi-Dirac statistics has a diamagnetic susceptibility:

$$\chi_0 = -(n/2E_F)(e\hbar/2mc)^2 = -n\mu^2/2E_F, \quad (1.1)$$

Here n is the number of electrons/cm³, E_F is the

¹ J. Bardeen, Phys. Rev. **79**, 167 (1950).

² J. Bardeen, Phys. Rev. **80**, 567 (1950) (referred in the text as WF).

³ H. Fröhlich, Phys. Rev. **79**, 845 (1950).

⁴ F. and H. London, Physica **2**, 341 (1935).

⁵ J. Bardeen, Phys. Rev. **59**, 928 (A) (1941). This work, done while the author was at the University of Minnesota, was interrupted by the war and was never published in full.

⁶ L. Landau, Z. Physik **64**, 629 (1930).