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Assignments of Several Groups of Iodine (I_2) Lines in the $B-X$ System

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The spectra obtained by means of Fourier spectroscopy and the assignments of the $B-X$ lines of I_2 in the vicinity of two argon ion laser lines (5145 and 5287 Å), three krypton ion laser lines (5208, 5308, and 5683 Å), and one He–Ne laser line (6119 Å) are given. A detailed comparison, in the vicinity of the argon ion laser line (5145 Å), between the iodine wavenumbers calculated by means of the two sets of molecular constants previously published [Wei and Tellinghuisen, *J. Mol. Spectrosc.* **50**, 317–332 (1974); Barrow and Yee, *J. C. S. Faraday II*.**69**, 684–700 (1973)] with those calculated from Fourier spectroscopy data, is presented.

1. INTRODUCTION

Since the recording of the iodine absorption spectrum by means of Fourier spectroscopy, and its publication as an Atlas (*1*), there was much interest expressed in the assignments of small portions of spectra located near some Ar^+, Kr^+, and He–Ne laser lines. Indeed, these laser radiations are often used to produce excited resonance fluorescence of the visible system of iodine ($B\ ^3\Pi_{0_u^+} - X\ ^1\Sigma_g^+$), or to resolve the hyperfine structure of iodine lines and, more recently, to induce stimulated emission in the optically pumped iodine molecule itself (*2–4*). We therefore present here detailed assignments of small portions of the iodine absorption spectrum in the vicinity of two argon ion laser lines $\lambda = 5145$ Å (19 429 cm^{-1}), $\lambda = 5287$ Å (18 908 cm^{-1}), three krypton ion laser lines, $\lambda = 5208$ Å (19 192 cm^{-1}), $\lambda = 5308$ cm^{-1} (18 830 cm^{-1}), $\lambda = 5683$ Å (17 594 cm^{-1}), and one He–Ne laser line $\lambda = 6119$ Å (16 340 cm^{-1}). These identified small portions of the iodine spectrum are also given here to show the progress achieved in the assignments of the iodine lines, and to serve as an illustration of the accuracy of the molecular constants describing the entire $B-X$ system of I_2 (*5*).

2. PROCEDURE USED FOR THE LINE ASSIGNMENTS

A detailed description of the rotational analysis of a typical band (the 30, 0 band) was published in 1977 (*6*). Starting from previously available constants (*7–10*), we begin to identify lines belonging to a given band. Of course, discrepancies between our observed wavenumbers and those calculated by means of these previous constants always occur. Fortunately, these discrepancies—nearly constant at the head of the bands—increase continuously, with increasing J. The identification of the lines is also based on the intensities of the lines and the "doublet" separation as explained in Ref. (*6*). When a sufficient number of iden-

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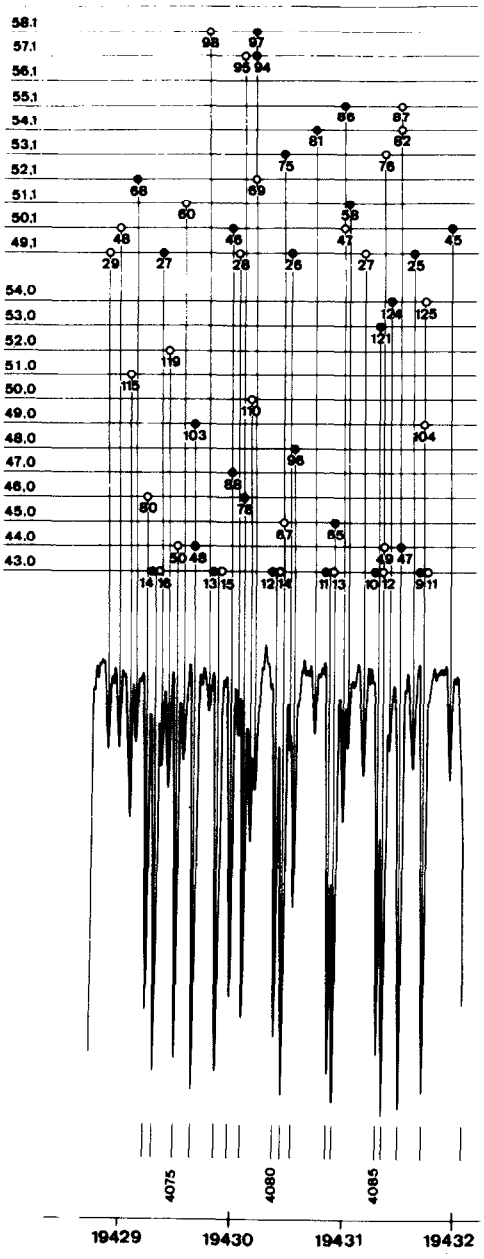

FIG. 1. Assignments of the iodine absorption lines in the vicinity of the Ar^+ laser line $\lambda = 5145$ Å ($\sigma = 19\,429$ cm^{-1}).

TABLE I

Observed and Calculated Wavenumbers around $\sigma = 19\,429$ cm^{-1} (Ar^+, $\lambda = 5145$ Å)

N° Atlas	σ (cm^{-1}) (observed)	I	Assignments	σ (cm^{-1}) (calculated)
	19428.8372	18	29R (49,1)	19428.8333
	.9350	18	48R (50,1)	.9361
	19429.0317	30	115R (51,0)	19429.0268
	.0830	17	68P (52,1)	.0798
4073	.1831	63	80R (46,0)	.1837
4074	.2612	74	14P (43,0)	.2582
			16R (43,0)	.2679
	.3184	21	27P (49,1)	.3160
	.3770	25	119R (52,0)	.3965
4075	.4501	72	50R (44,0)	.4491
	.5085	20	60R (51,1)	.5088
4076	.6064	77	48P (44,0)	.6040
			103P (49,0)	.6156
	.7382	12	98R (58,1)	.7359
4077	.8204	74	13P (43,0)	.8157
			15R (43,0)	.8250
4078	.9343	61	46P (50,1)	.9267
			88P (47,0)	.9362
	.9997	16	28R (49,1)	19430.0020
4079	19430.0505	64	78P (46,0)	.0505
			95R (57,1)	.0617
	.1107	34	110R (50,0)	.1069
	.1491	25	69R (52,1)	.1457
			94P (57,1)	.1506
			97P (58,1)	.1634
4080	.3385	68	12P (43,0)	.3361
			14R (43,0)	.3449
			75P (53,1)	.3821
4081	.4123	78	67R (45,0)	.4095
	.4652	18	26P (49,1)	.4669
4082	.5036	45	96P (48,0)	.5042
	.5418	10	104R (61,1)	.5316
	.6885	16	81P (54,1)	.6844
4083	.8226	74	11P (43,0)	.8193
			13R (43,0)	.8276
4084	.8726	79	65P (45,0)	.8713
	.9426	31	47R (50,1)	.9400
			86P (55,1)	.9457
	.9866	18	58P (51,1)	.9865
	19431.1313	22	27R (49,1)	19431.1290
4085	.2653	71	10P (43,0)	.2654
			121P (53,0)	.2680
			12R (43,0)	.2731
4086	.3197	81	49R (44,0)	.3169
			76R (53,1)	.3202
			87R (55,1)	.4577
4087	.4689	80	47P (44,0)	.4668
			82R (54,1)	.4347
	.5757	21	25P (49,1)	.5763
4088	.6779	77	9P (43,0)	.6743
			104R (49,0)	.6747
			11R (43,0)	.6814
	.9099	23	45P (50,1)	.9071

tified lines is obtained, we then recalculate the molecular constants describing the band under investigation by a least-squares procedure (nonlinear SIMPLEX). Using these new molecular constants we extend the identification process to higher J transitions; in general, three iterations were enough to identify lines not buried in

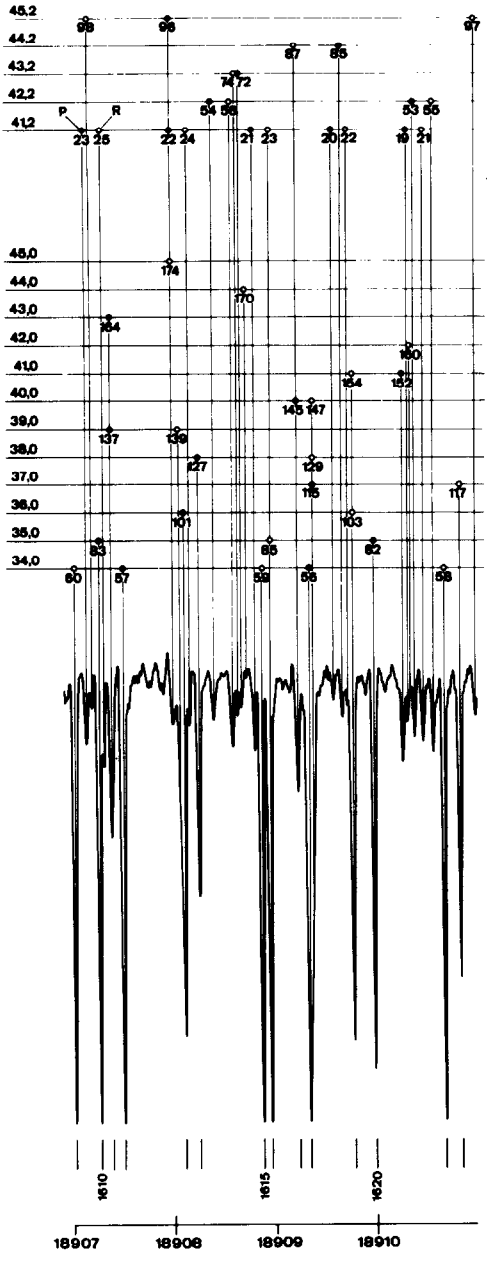

FIG. 2. Assignments of the iodine absorption lines in the vicinity of the Ar^+ laser line $\lambda = 5287$ Å ($\sigma = 18\,908$ cm^{-1}).

TABLE II

Observed and Calculated Wavenumbers around $\sigma = 18\,908$ cm^{-1} (Ar^+, $\lambda = 5287$ Å)

N° Atlas	σ (cm^{-1}) (observed)	I	Assignments	σ (cm^{-1}) (calculated)
1609	18907.0140	81	60R (34,0)	18907.0113
	.1327	17	23P (41,2)	.1284
	.1888	10	98R (45,2)	.1889
1610	.2582	84	83P (35,0)	.2555
	.2988	21	25R (41,2)	.2996
1611	.3739	35	164P (43,0)	.3609
			137P (39,0)	.3714
1612	.4929	85	57P (34,0)	.4857
	.5503	10		
	.7415	6		
	.7788	6		
	.8622	7		
	.8916	7		
	.9800	13	22P (41,2)	.9795
			174R (45,0)	.9927
			96P (45,2)	18908.0108
			139R (39,0)	.0510
1613	18908.0900	72	101P (36,0)	.0889
	.1449	13	24R (41,2)	.1442
1614	.2378	46	127P (38,0)	.2360
	.3866	12	54P (42,2)	.3875
	.5722	17	56R (42,2)	.5707
	.6240	11	74R (43,2)	.6260
	.6611	12	72P (43,2)	.6635
	.7946	18	21P (41,2)	.7954
1615	.8623	87	59R (34,0)	.8550
1616	.9427	83	85R (35,0)	.9399
			23R (41,2)	.9533
	18909.1426	7		
1617	.2195	26	145P (40,0)	18909.2188
			87R (44,2)	.2776
1618	.3250	80	56P (34,0)	.3193
			115P (37,0)	.3477
			147R (40,0)	.3490
			129R (38,0)	.3739
	.5731	8	20P (41,2)	.5757
	.6618	12	85P (44,2)	.6566
1619	.7674	74	22R (41,2)	.7270
			103R (36,0)	.7666
			154R (41,0)	.7927
	.8980	8		
1620	.9731	79	82P (35,0)	.9732
	18910.0941	7		
	.2655	20	152P (41,0)	18910.2890
	.3136	13	19P (41,2)	.3207
			160R (42,0)	.3445
	.3801	16	53P (42,2)	.3781
	.4665	16	21R (41,2)	.4653
	.5660	18	55R (42,2)	.5601
1621	.6702	85	58R (34,0)	.6669
	.7300	7		
1622	.8281	62	117R (37,0)	.8264
	.9849	11	97R (45,2)	.9896

the noise present in our spectrogram (lines with a signal to noise greater than 4). In this way we identified nearly the entire iodine absorption spectrum observed under our experimental conditions (*1*). Figures 1 and 2 show the iodine spectrum in the vicinity of the two argon ion laser lines and Tables I and II give the observed

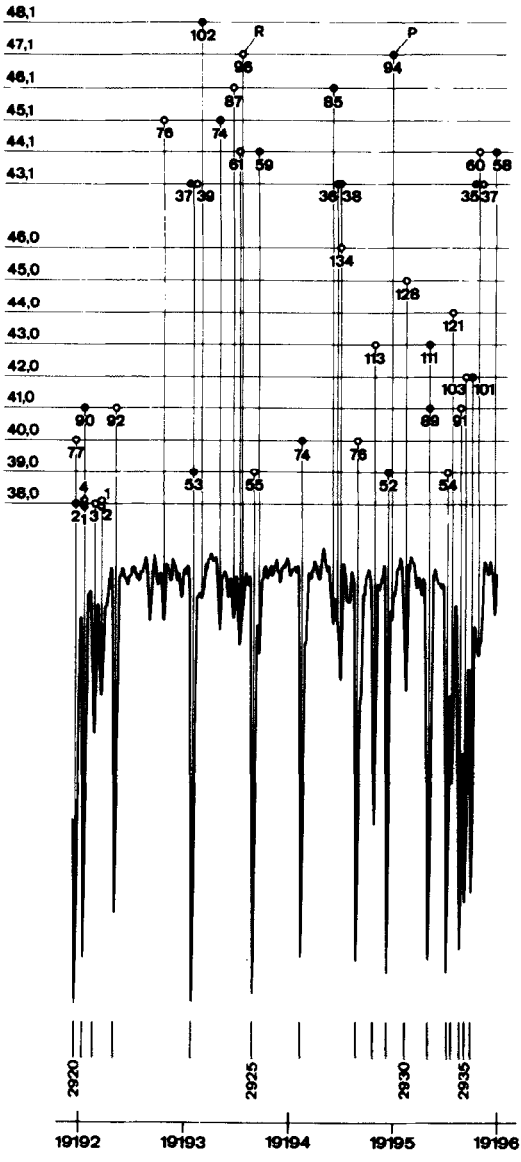

FIG. 3. Assignments of the iodine absorption lines in the vicinity of the Kr^+ laser line $\lambda = 5208$ Å ($\sigma = 19\ 192\ cm^{-1}$).

TABLE III

Observed and Calculated Wavenumbers around $\sigma = 19\ 192\ cm^{-1}$ (Kr^+, $\lambda = 5208$ Å)

N° Atlas	σ (cm⁻¹) (observed)	I	Assignments		σ (cm⁻¹) (calculated)
2920	19191.9229	84	77R	(40,0)	19191.9197
			2P	(38,0)	.9564
2921	19192.0036	76	90P	(41,0)	19192.0038
			4R	(38,0)	.0064
			1P	(38,0)	.0648
2922	.1024	36	5R	(38,0)	.1005
	.1693	28	2R	(38,0)	.1608
			1R	(38,0)	.1874
2923	.2978	68	92R	(41,0)	.2984
	.6235	15			
	.6965	8			
	.7577	15	76R	(45,1)	.7573
	.8250	8			
	.9267	11			
2924	19193.0456	84	37P	(43,1)	19193.0206
			39R	(43,1)	.0340
			53P	(39,0)	.0404
	.1225	11	102P	(48,1)	.1344
	.2922	16	74P	(45,1)	.2912
	.3760	11			
	.4275	14	87R	(46,1)	.4299
	.4854	19	61R	(44,1)	.4806
			96R	(47,1)	.5141
2925	.6285	83	55R	(39,0)	.6242
	19193.6740	21	59P	(44,1)	.6729
2926	19194.0855	76	74P	(40,0)	19194.0842
	.2565	7			
	.3844	15	85P	(46,1)	.3837
			36P	(43,1)	.4277
			38R	(43,1)	.4506
	.4593	25	134R	(46,0)	.4750
	.5329	11			
2927	.6176	77	76R	(40,0)	.6166
2928	.7653	52	113R	(43,0)	.7848
	.8304	9	147R	(49,0)	.8355
2929	.9152	79	52P	(39,0)	.9134
	.9555	15	94P	(47,1)	.9545
2930	19195.0895	27	128R	(45,0)	19195.0884
	.1983	9			
2931	.3130	76	111P	(43,0)	.3011
			89P	(41,0)	.3167
			103R	(48,1)	.4691
2932	.4886	79	54R	(39,0)	.4884
2933	.5354	44	121R	(44,0)	.5324
2934	.6147	75	91R	(41,0)	.6145
2935	.6618	66	103R	(42,0)	.6607
			75R	(45,1)	.6813
2936	.7214	64	101P	(42,0)	.7209
	.7684	20	60R	(44,1)	.7609
	.7906	21	35P	(43,1)	.7975
			37R	(43,1)	.8209
	.9463	13	58P	(44,1)	.9470

and calculated wavenumbers. Figures 3, 4, 5, and Tables III, IV, and V present the same data for the three krypton lines, and Fig. 6 and Table IV for the He–Ne laser line. The calculated wavenumbers given in these tables are those obtained from the molecular constants determinated by the band-by-band studies. The next step, obtaining the most adequate spectroscopic constants capable of reproducing the iodine spectrum within experimental errors, was then undertaken: the first results

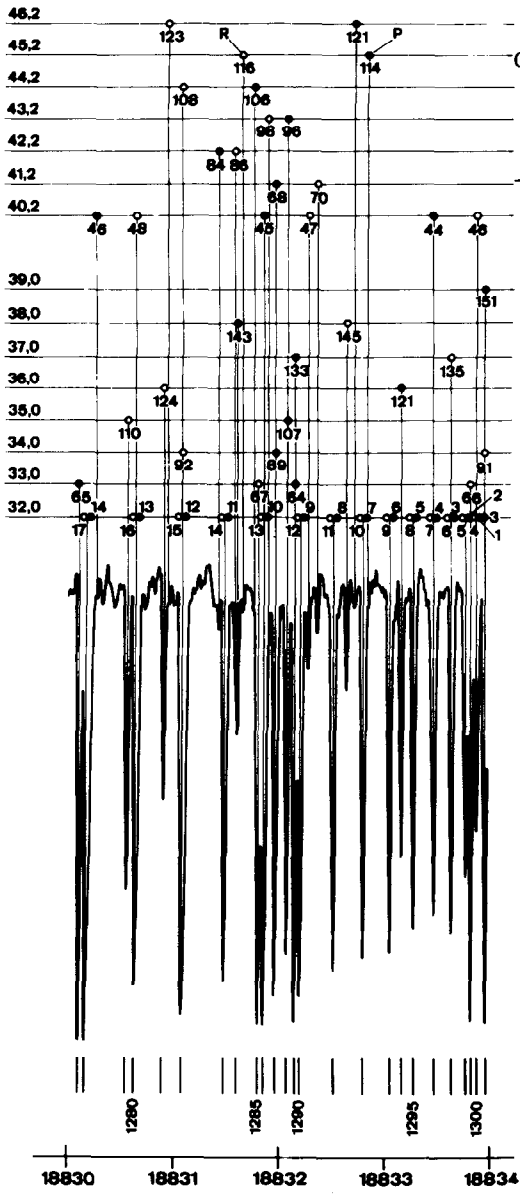

FIG. 4. Assignments of the iodine absorption lines in the vicinity of the Kr^+ laser line $\lambda = 5308$ Å ($\sigma = 18\,830$ cm^{-1}).

TABLE IV

Observed and Calculated Wavenumbers around $\sigma = 18\,830$ cm^{-1} (Kr^+, $\lambda = 5308$ Å)

N° Atlas	σ (cm^{-1}) (observed)	I	Assignments		σ (cm^{-1}) (calculated)
1277	18830.0722	88	65P	(33,0)	18830.0662
1278	.1329	85	17R	(32,0)	.1281
			14P	(32,0)	.1472
			46P	(40,2)	.1745
1279	.5159	61	110R	(35,0)	.5162
1280	.6000	79	16R	(32,0)	.5951
			48R	(40,2)	.6094
			13P	(32,0)	.6128
1281	.8629	44	124R	(36,0)	.8629
			123R	(46,2)	.8881
1282	18831.0546	84	15R	(32,0)	18831.0320
			12P	(32,0)	.0484
			92R	(34,0)	.0579
			108R	(44,2)	.0614
	.3884	12	84P	(42,2)	.3933
1283	.4500	78	14R	(32,0)	.4387
			11P	(32,0)	.4539
			86R	(42,2)	.5344
1284	.5648	32	143P	(38,0)	.5635
	.6141	9	116R	(45,2)	.6133
			106P	(44,2)	.7365
1285	.7711	86	67R	(33,0)	.7672
1286	.8231	87	45P	(40,2)	.812
			13R	(32,0)	.8154
			10P	(32,0)	.8293
			98R	(43,2)	.8803
1287	.9297	81	89P	(34,0)	.9269
			68P	(41,2)	.9472
1288	18832.0405	73	107P	(35,0)	18832.0381
			96P	(43,2)	.0996
1289	.1188	86	64P	(33,0)	.1156
			133P	(37,0)	.1157
1290	.1661	81	12R	(32,0)	.1619
			9P	(32,0)	.1746
	.2423	20	47R	(40,2)	.2397
	.3292	13	70R	(41,2)	.3279
1291	.4846	76	11R	(32,0)	.4784
			8P	(32,0)	.4899
	.6123	24	145R	(38,0)	.6105
	.6888	8	121P	(46,2)	.6774
1292	.7697	74	10R	(32,0)	.7647
			7P	(32,0)	.7750
			114P	(45,2)	.8117
1293	18833.0252	73	9R	(32,0)	18833.0210
			6P	(32,0)	.0301
1294	.1395	55	121P	(36,0)	.1386
1295	.2504	68	8R	(32,0)	.2471
			5P	(32,0)	.2551
			44P	(40,2)	.4154
1296	.4465	66	7R	(32,0)	.4432
			4P	(32,0)	.4500
1297	.6136	69	6R	(32,0)	.6092
			3P	(32,0)	.6149
			135R	(37,0)	.6180
1298	.7481	59	5R	(32,0)	.7451
			2P	(32,0)	.7496
1299	.7951	85	66R	(33,0)	.7932
1300	.8487	50	46R	(40,2)	.8350
			4R	(32,0)	.8510
			1P	(32,0)	.8543
1301	.9368	85	3R	(32,0)	.9267
			91R	(34,0)	.9337
			151P	(39,0)	.9375

of this global fit and Dunham expansions of the molecular constants have been given at a recent conference (*5*).

3. COMPARISON WITH PREVIOUSLY PUBLISHED ASSIGNMENTS

Previously published adequately reliable assignments which can be compared with the ones obtained from our studies are available only for three of the six small

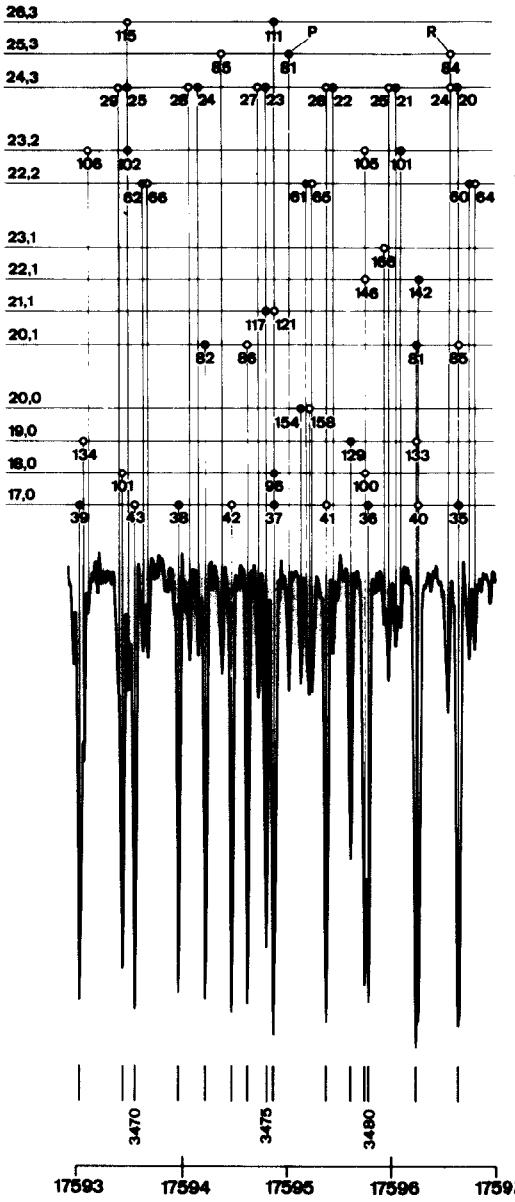

FIG. 5. Assignments of the iodine absorption lines in the vicinity of the Kr^+ laser line $\lambda = 5683$ Å ($\sigma = 17\ 594\ cm^{-1}$).

TABLE V

Observed and Calculated Wavenumbers around $\sigma = 17\ 594\ cm^{-1}$ (Kr^+, $\lambda = 5683$ Å)

N° Atlas	σ (cm⁻¹) (observed)	I	Assignments	σ (cm⁻¹) (calculated)
3468	17593.0277	85	39P (17,0)	17593.0283
	.0697	39	134R (19,0)	.0656
			106R (23,2)	.1073
			29R (24,3)	.3928
3469	.4331	78	101R (18,0)	.4318
			102P (23,2)	.4710
	.4896	26	25P (24,3)	.4859
			115R (26,3)	.5046
3470	.5498	86	43R (17,0)	.5484
	.6318	18	62P (22,2)	.6292
	.6794	20	66R (22,2)	.6785
3471	.9687	83	38P (17,0)	.9680
	17594.0743	20	28R (24,3)	17594.0748
	.1575	19	24P (24,3)	.1622
3472	.2243	85	82P (20,1)	.2242
	.3848	23	85R (25,3)	.3820
3473	.4766	86	42R (17,0)	.4761
3474	.6276	85	86R (20,1)	.6284
	.7330	27	27R (24,3)	.7315
3475	.8076	74	117P (21,1)	.8042
3476	.8772	91	23P (24,3)	.8154
			96P (18,0)	.8829
			111P (26,3)	.8863
			121R (21,1)	.8848
			37P (17,0)	.8850
	17595.0227	26	81P (25,3)	17595.0200
	.1355	24	154P (20,0)	.1358
	.2166	27	61P (22,2)	.2011
			158R (20,0)	.2274
	.2460	26	65R (22,2)	.2511
3477	.3808	89	26R (24,3)	.3630
			41R (17,0)	.3810
	.4457	19	22P (24,3)	.4433
3478	.6092	58	129P (19,0)	.6084
3479	.7418	82	105R (23,2)	.7354
			146R (22,1)	.7394
			100R (18,0)	.7421
3480	.7812	85	36P (17,0)	.7791
	.9304	13	166R (23,1)	.9344
	.9730	24	25R (24,3)	.9693
	17596.0448	17	21P (24,3)	17596.0460
	.0896	14	101P (23,2)	.0910
3481	.2318	93	133R (19,0)	.2321
			81P (20,1)	.2376
			142P (22,1)	.2585
			40R (17,0)	.2631
	.5446	30	84R (25,3)	.5348
			24R (24,3)	.5503
			20P (24,3)	.6236
3482	.6352	89	85R (20,1)	.6396
			35P (17,0)	.6505
	.7481		60P (22,2)	.7483
	.7850		64R (22,2)	.7991

portions given here: the region around 19 429.8 cm^{-1} (5145 Å, Ar^+ laser), investigated by a great number of authors [(*11*, *12*), for example] was carefully reassigned by Tellinghuisen (*13*); the other two regions around 18 908 cm^{-1} (5287 Å, Ar^+ laser), and 18 830 cm^{-1} (5308 Å, Kr^+ laser) are identified in the atlas (18000–19000 cm^{-1}) recently published by Simons and Hougen at the National Bureau of Standards (*14*).

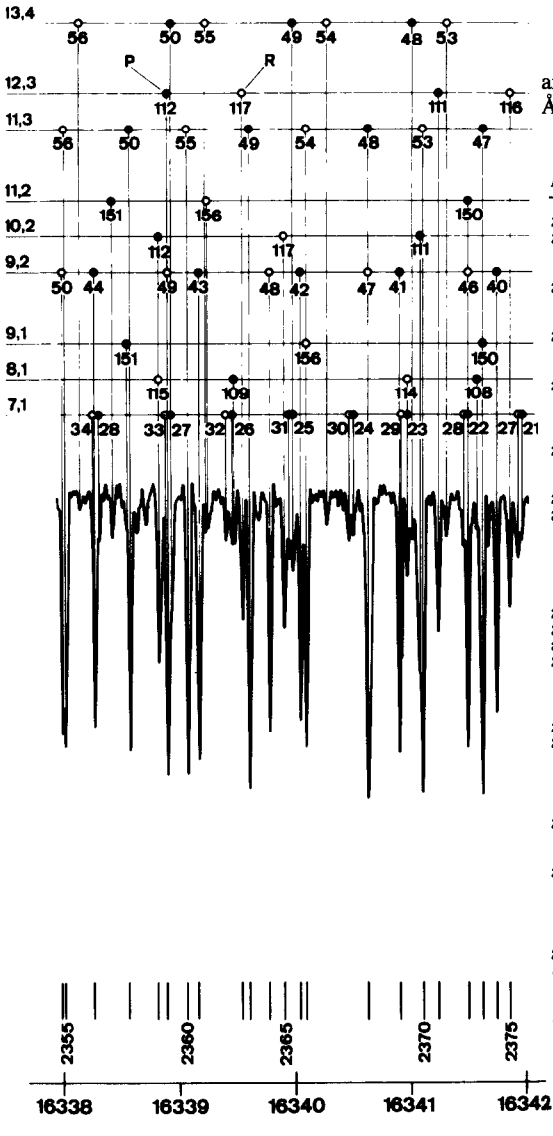

FIG. 6. Assignments of the iodine absorption lines in the vicinity of the He–Ne laser line $\lambda = 6119$ Å ($\sigma = 16\,340$ cm^{-1}).

TABLE VI

Observed and Calculated Wavenumbers around $\sigma = 16\,340$ cm^{-1} (He–Ne, $\lambda = 6119$ Å)

N° Atlas	σ (cm^{-1}) (observed)	I	Assignments	σ (cm^{-1}) (calculated)
2354	16337.9936	41	50R (9,2)	16337.9924
2355	16338.0198	43	56R (11,3)	16338.0202
			56R (13,4)	.1429
			34R (7,1)	.2529
2356	.2701	40	44P (9,2)	.2703
	.3052	9	28P (7,1)	.3018
	.4165	8	151P (11,2)	.4188
2357	.5740	44	50P (11,3)	.5727
			151P (9,1)	.6280
	.7098	6		
2558	.8223	29	112P (10,2)	.8180
			115R (8,1)	.8258
			33R (7,1)	.8362
			27P (7,1)	.8853
2359	.9008	48	49R (9,2)	.9010
			112P (12,3)	.9298
			50P (13,4)	.9411
2360	16339.0755	48	55R (11,3)	16339.0731
2361	.1739	45	43P (9,2)	.1725
			55R (13,4)	.2254
	.2462	6	156R (11,2)	.2591
	.4031	8	32R (7,1)	.4007
			26P (7,1)	.4460
	.4801	9	109P (8,1)	.4764
2362	.5528	22	117R (12,3)	.5507
2363	.6171	50	49P (11,3)	.6144
2364	.7897	40	46R (9,2)	.7905
2365	.9142	23	117R (10,2)	.9115
			31R (7,1)	.9464
	.9908	13	25P (7,1)	.9900
			49P (13,4)	16340.0080
2366	16340.0566	38	42P (9,2)	.0554
2367	.1064	43	156R (9,1)	.1051
			54R (11,3)	.1061
	.2834	6	54R (13,4)	.2876
	.4790	8	30R (7,1)	.4732
	.5150	7	24P (7,1)	.5152
2368	.6439	52	48P (11,3)	.6363
			47R (9,2)	.6602
			29R (7,1)	.9813
2369	.9197	44	41P (9,2)	.9190
	.9851	14	114R (8,1)	.9877
			23P (7,1)	16341.0216
			48P (13,4)	.0543
			111P (10,2)	.0836
2370	16341.1219	51	53R (11,3)	.1192
2371	.2539	24	111P (12,3)	.2528
	.3255	8	53R (13,4)	.3294
	.4738	9	28R (7,1)	.4705
2372	.5117	43	22P (7,1)	.5091
			46R (9,2)	.5109
			150P (11,2)	.5317
2373	.6399	51	108P (8,1)	.6295
			47P (11,3)	.6384
			150P (9,1)	.6530
	.6876	9		
2374	.7636	37	40P (9,2)	.7633
	.8737	20	116R (12,3)	.8720
	.9461	11	27R (7,1)	.9410
	.9791	8	21P (7,1)	.9780

3.1. The Spectral Region around 19 429.8 cm^{-1} (5145 Å, Ar$^+$ Laser)

(a) Comparison between the assignments based on the molecular constants determinated by Wei and Tellinghuisen (10), and those deduced from Fourier spectroscopy. Inspection of Table VII shows the improvements reached by the Fourier spectroscopy measurements in the region around 19 429.8 cm^{-1}. The agreement between observed and calculated wavenumbers is, in general, good especially for unperturbed single lines as, for example, the intense rotational line (44,0) $R(50)$ [Fig. 7, Table VII (where $\sigma_{cal} - \sigma_{obs} \simeq 0.001$ cm^{-1})]. The assignments differ

TABLE VII

Comparison between Wavenumbers Calculated with Different Sets of Constants in the Vicinity of the Ar^+ Laser Line λ = 5145 Å (σ = 19 429.8 cm^{-1})

Band v',v"	Line	Int. Obser. [1]	Wavenumber σ (cm^{-1}) Observed: Fourier Spectroscopy [1]	Calculated: Fourier Spectrosc. [5]	Wei [10] Tel. [13]	Barrow Yee [9]	(J_{max}) [9]
46,0	R (80)	63	19429.1831	.1837		.17	94
43,0	P (14)	74	.2612	.2582	.27	.24	60
43,0	R (16)			.2672	.28	.25	
49,1	P (27)	21	.3184	.3160	.30	.33	82
52,0	R(119)	25	.3770	.3900	.87	(30.150)	64
44,0	R (50)	72	.4501	.4491	.46	.44	68
60,2	R (49)			.4810	.44	.56	67
51,1	R (60)	20	.5085	.5088	.48	.50	62
44,0	P (48)	77	.6064	.6040	.62	.60	68
49,0	P(103)			.6156	.70	.71	82
60,2	P (48)			.6680	.63	.75	67
58,1	R (98)	12	.7382	.7359	.94	.61	62
61,2	R (54)			.8050	.76	.84	62
43,0	P (13)	74	.8204	.8157	.83	.80	60
43,0	R (15)			.8250	.84	.81	
50,1	P (46)	61	.9343	.9267	.91	.93	50
47,0	P (88)			.9362	.95	.91	99
49,1	R (28)	16	.9997	.0020	.98	.01	82
46,0	P (78)	64	19430.0505	.0505	.06	.03	94
57,1	R (95)			.0617	.17	.14	59
50,0	R(110)	34	.1107	.1069	.31	(29.650)	50
62,2	R (58)	25	.1491	.138	.10	.17	66
52,1	R (69)			.146	.12	.13	64
57,1	P (94)			.151	.22	.19	59
58,1	P (97)			.176	.32	.03	62
61,2	P (53)			.184	.15	.22	62

slightly from those deduced from the molecular constants published by Wei and Tellinghuisen (*10*). For example, the line (58,1) R(98) is now correctly assigned. In this region five pairs of lines, namely, the pairs [(43,0) P(14), R(16)], [(43,0) P(13), R(15)], [(50,1) P(46), (47,0) P(88)], [(44,0) P(48), (49,0) P(103)], and [(46,0) P(78), (57,1) R(95)], coincide within 0.010 cm^{-1} (see column 5, Table VII). Now if we consider the calculated wavenumber based on the molecular constants given by Wei and Tellinghuisen (*10*), one notes that the calculated distances be-

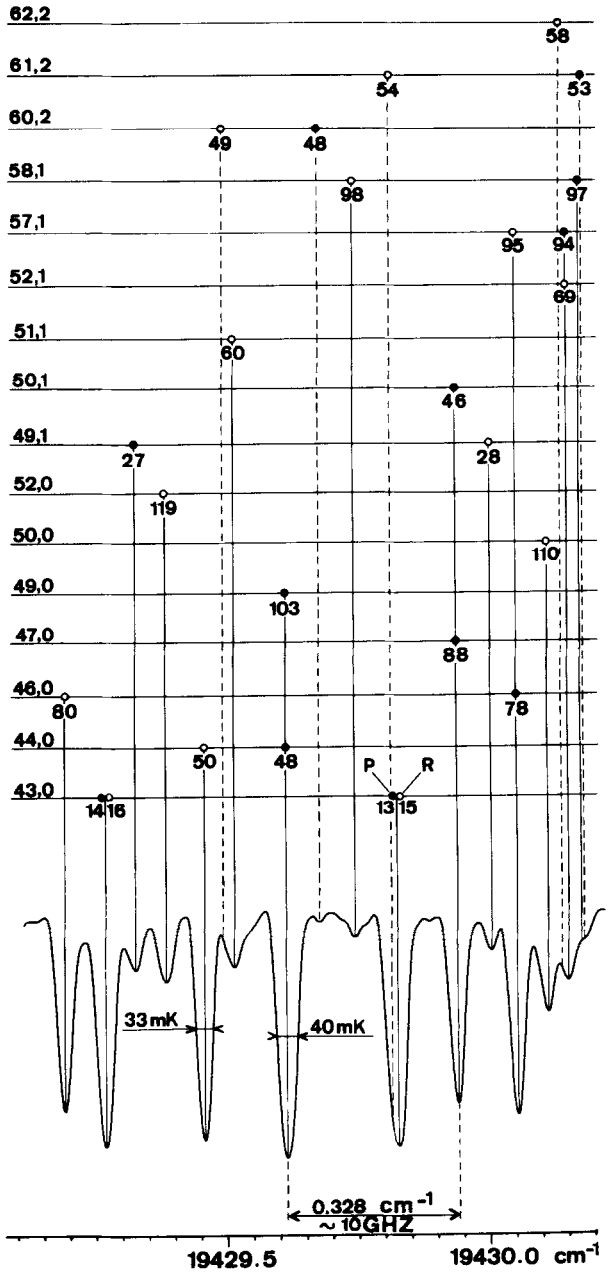

FIG. 7. Assignments and widths of the iodine absorption lines in the vicinity of the Ar^+ laser line $\lambda = 5145$ Å (19 429.8 cm^{-1}). The distance between the two complex lines [$P(48)$, $P(103)$] and [$P(88)$, $P(46)$] is found to be 0.328 cm^{-1} or ~10 GHz [see Ref. (*17*)].

tween the lines of each pair increase with the J values of the rotational lines involved in these pairs: for the [$P(14)$, $R(16)$] and the [$P(13)$, $R(15)$] pairs of lines the calculated separations are 0.010 cm^{-1} in agreement with our estimate, but the

TABLE VIII

Doublets Splittings Measurements: Comparison between Fabry–Perot Measurements (*17*) and Fourier Measurements

Absorbed lines [17]	Assignments of the fluorescence doublets [13][16][17]	Doublet splittings (cm^{-1})		
		Fabry-Perot Data	Fourier Data	
		Measured [17]	Measured [1]	Calculated [5]
44,0 P (48)	44,0 P (48) R (46)	7.1 ± 0.3	7.085	7.085
49,0 P (103)	49,0 P (103) R (101)	15.3 ± 0.3	15.270	15.258
58,1 R (98)	58,1 R (98) P (100)	14.8 ± 0.3	14.767	14.782
43,0 P (13)	43,0 P (13) R (11)	1.87 ± 0.3	1.858	1.866
43,0 R (15)	43,0 R (15) P (17)	2.46 ± 0.3	2.454	2.462
47,0 P (88)	47,0 P (88) R (86)	13.1 ± 0.3	13.036	13.035

separations for the pairs [$P(46)$, $P(88)$], [$P(48)$, $P(103)$], and [$P(78)$, $R(95)$], would be 0.040, 0.080, and 0.110 cm^{-1}, respectively. [In fact, the recorded half-widths of the spectral lines in this region (Fig. 7) have a maximum value of 0.040 cm^{-1}, of which the hyperfine structure contributes about 0.025–0.030 cm^{-1} (*11, 15*)]. This is a good illustration of the observation made in Section 2, viz., that at the head of the bands (low J) the discrepancy is low and nearly constant, following which it increases continuously with J. Finally it can be noted that using a monomode Ar^+ laser the rotational line (49,1) $R(28)$ cannot be easily excited simultaneously with the composite line [(50,1) $P(46)$, (47,0) $P(88)$], which is located 0.065 cm^{-1}, toward the lower wavenumbers.

(b) Comparison between the assignments based on the molecular constants determinated by Barrow and Yee (9), and the assignments deduced from Fourier spectroscopy. Other molecular constants describing the $B-X$ system of I_2 were published by Barrow and Yee (*9*). The wavenumbers calculated by means of these constants, which are listed in Table 2 of Ref. (*9*), are given in Table VII, column 7. When the J values of the transitions are below the maximum J values identified in each band by these authors [J_{max} of Table I of Ref. (*9*), and reproduced in column 8, Table VII of the present work], then the differences between the observed Fourier wavenumbers (column 4) and those calculated using the absorption data of Barrow and Yee (column 7) do not exceed ±0.020 cm^{-1}. However, for J values higher than those J_{max} values, the discrepancies increase rapidly; for example, for the lines (57,1) $P(94)$, (57,1) $R(95)$, (58,1) $P(97)$, (58,1) $R(98)$, (49,0) $P(103)$, (50,0) $R(110)$,

and (52,0) $R(119)$ the discrepancies are -0.040, -0.090, $+0.140$, $+0.130$, -0.090, $+0.460$, and $-0.770\ cm^{-1}$, respectively. Therefore, the use of the constants of Barrow and Yee has to be limited to the maximum J values of each band observed by these authors. Since the molecular constant H_v' has been neglected in their study, the extrapolation to high J values remains questionable and, in any case, has to be made with extreme caution. For instance, in the recent laser fluorescence studies [Clark and McCaffery (*16*)] the assignments of the fluorescence series, although correct, are given for two of them with wrong wavenumbers: the wavenumbers of the observed transitions (49,0) $P(103)$ and (58,1) $R(98)$ must be inverted, as can be seen by inspection of Table VII. These misassignments have, obviously, their origin in the use and the extrapolation to relatively high J values, of the data of Barrow and Yee. [Another fluorescence series (61,2) $P(54)$ is given in Ref. (*16*); it should be (61,2) $R(54)$, which is in agreement both with our assignments (Table VII), and with their own observations; see Fig. 2 of Ref. (*16*).]

(c) Comparison between fluorescence doublet splittings measurements by means of a Fabry–Perot interferometer and doublet measurements obtained by Fourier spectroscopy. In view of the precise nature of the data obtained by Fourier spectroscopy it is also now possible to give a comprehensive interpretation of the fluorescence doublet measurements, in this region, made by Patterson *et al.* using a Fabry–Perot interferometer (*17*). Table VIII contains the splittings of the six doublets observed by these authors (*17*) and their corresponding assignments. The agreement between the measured splittings (column 3, Table VIII) with those calculated by means of our molecular constants (*5*), or with those obtained from the observed wavenumbers (*1*) of the doublet components, is excellent.

Again, in the experiment of Patterson *et al.* (*17*) the separation between the lines (44,0) $P(48)$ and (49,0) $P(103)$ is found to be of the order of 571 MHz ($0.019\ cm^{-1}$) in agreement with our observation; Clark and McCaffery found them to be about $0.110\ cm^{-1}$ apart, a value not compatible with the half-width ($0.040\ cm^{-1}$) of the complex line $P(48)$ $P(103)$ recorded in our spectrum (see Fig. 7).

Finally, for completeness and to conclude the discussion of the assignments of the iodine lines in this spectral region, Table VII and Fig. 7 also contain transitions (dashed lines) connected to the "hot" band $v'' = 2$. These bands, very weak in our experimental conditions (*1*, *18*), were not analyzed; only the calculated wavenumbers are given here; transitions belonging to the (v',2) bands with $v' > 62$ were not searched, our assignments being limited to $v' = 62$.

3.2. The Spectral Regions around 18 908 cm^{-1} (5287 Å, Ar^+ Laser) and 18 830 cm^{-1} (5308 Å, Kr^+ Laser)

In these two regions the number of recorded lines by Fourier spectroscopy is about 30% higher than those recorded in the spectrum published by Simons and Hougen (*14*). Of course, the 30% additional lines are weak and are in general close to intense lines: the lines could be detected because of the high instrumental resolving power used, which was of the order of 10^6.

For the (v',0) transitions, the assignments of Simons and Hougen agree completely with ours. Moreover, recently we were made aware of the Franck–Condon

factors calculated by Tellinghuisen (*18*). Consequently, we have systematically searched in these two regions for the lines belonging to the bands (v',v'') with $28 \leqslant v \leqslant 46$ and $v'' = 2$. For these bands the Franck–Condon factors should be high enough so that transitions belonging to the bands $(v',2)$ would be detectable in our spectrograms. Indeed, we find these bands and the identification of the corresponding lines is given in Fig. 2, Table II and Fig. 4, Table IV.

In conclusion, we wish to point out that assignments in other regions of the iodine absorption spectrum can be made equally well with the use of the molecular constants deduced (*5*) from our Fourier spectroscopy measurements.

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