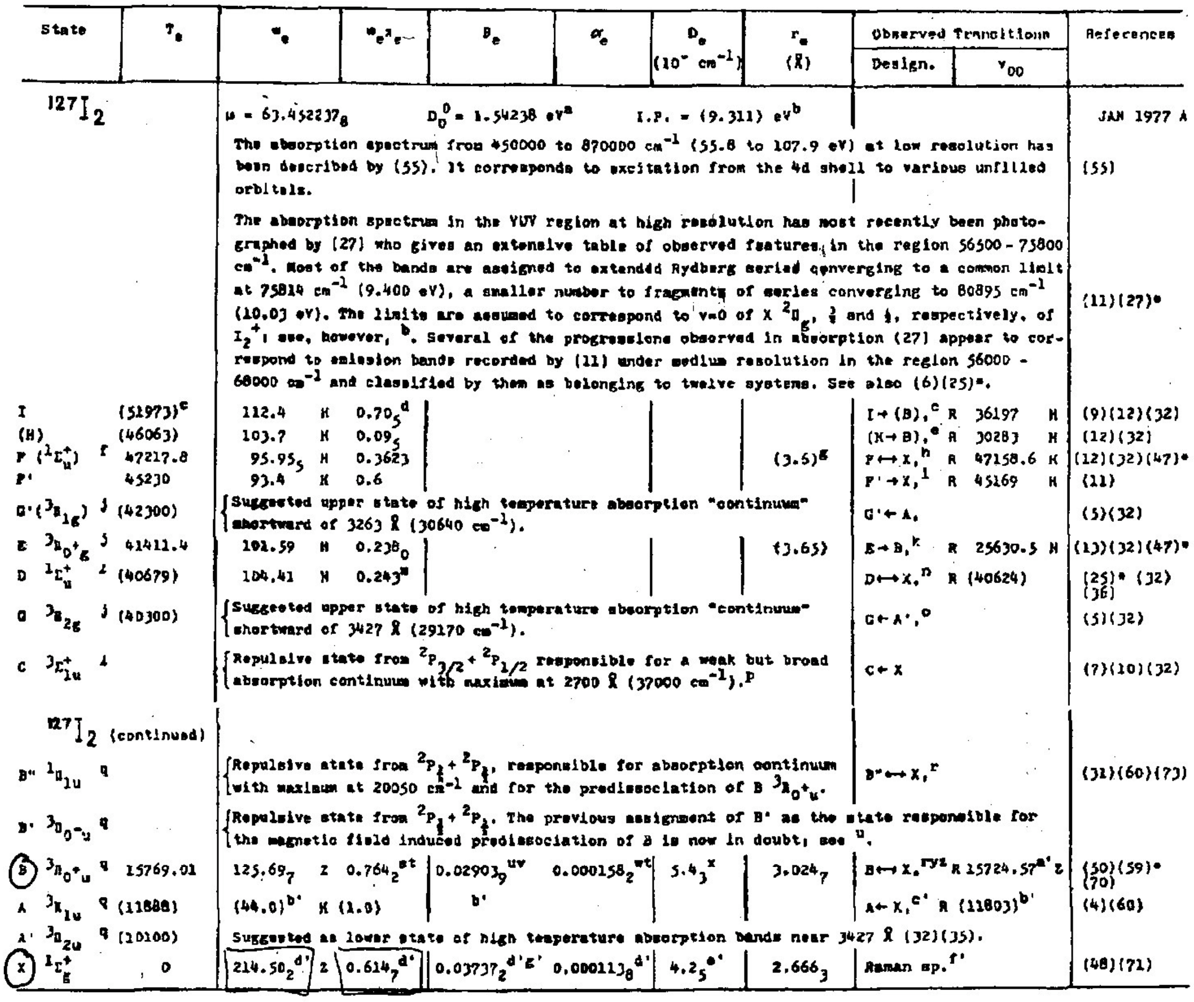
Appendix C: Molecular Constants for $^{127}I_2$

The following literature[1] data for $^{127}I_2$ is listed from highest energy electronic state to lowest energy electronic state, which means that the ground electronic state is listed last (it is designated with the symbol X ($^1\Sigma^+$)). The excited state of interest for Experiment 3 is state B ($^3\pi_0{}^+{}_u$). Many of the rotational and vibrational constants are given in the footnotes.



State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	D_e $(10^{-}\ \mathrm{cm}^{-1})$	r_e (Å)	Observed Transitions		References
								Design.	ν_{00}	
$^{127}I_2$		μ = 63.452237$_8$ D_0^0 = 1.54238 eV[a] I.P. = (9.311) eV[b]								JAN 1977 A
		The absorption spectrum from 450000 to 870000 cm^{-1} (55.8 to 107.9 eV) at low resolution has been described by (55). It corresponds to excitation from the 4d shell to various unfilled orbitals.								(55)
		The absorption spectrum in the VUV region at high resolution has most recently been photographed by (27) who gives an extensive table of observed features in the region 56500 - 73800 cm^{-1}. Most of the bands are assigned to extended Rydberg series converging to a common limit at 75814 cm^{-1} (9.400 eV), a smaller number to fragments of series converging to 80895 cm^{-1} (10.03 eV). The limits are assumed to correspond to v=0 of X $^2\Pi_g$, $\frac{3}{2}$ and $\frac{1}{2}$, respectively, of I_2^+; see, however, [b]. Several of the progressions observed in absorption (27) appear to correspond to emission bands recorded by (11) under medium resolution in the region 56000 - 68000 cm^{-1} and classified by them as belonging to twelve systems. See also (6)(25)*.								(11)(27)*
I	(51973)[c]	112.4 H	0.70$_5$[d]					I→(B),[c] R	36197 H	(9)(12)(32)
(H)	(46063)	103.7 H	0.09$_5$					(H→B),[e] R	30283 H	(12)(32)
F ($^1\Sigma_u^+$) [f]	47217.8	95.95$_5$ H	0.3623				(3.5)[g]	F↔X,[h] R	47158.6 K	(12)(32)(47)*
F'	45230	93.4 K	0.6					F'→X,[i] R	45169 H	(11)
G'($^3\Pi_{1g}$) [j]	(42300)	Suggested upper state of high temperature absorption "continuum" shortward of 3263 Å (30640 cm^{-1}).						G'←A,		(5)(32)
E $^3\Pi_{0^+g}$ [j]	41411.4	101.59 H	0.238$_0$				(3.65)	E→B,[k] R	25630.5 H	(13)(32)(47)*
D $^1\Sigma_u^+$ [l]	(40679)	104.41 H	0.243[m]					D↔X,[n] R	(40624)	(25)* (32) (36)
G $^3\Pi_{2g}$ [j]	(40300)	Suggested upper state of high temperature absorption "continuum" shortward of 3427 Å (29170 cm^{-1}).						G←A',[o]		(5)(32)
C $^3\Sigma_{1u}^+$ [l]		Repulsive state from $^2P_{3/2}+{}^2P_{1/2}$ responsible for a weak but broad absorption continuum with maximum at 2700 Å (37000 cm^{-1}).[p]						C←X		(7)(10)(32)
$^{127}I_2$ (continued)										
B'' $^1\Pi_{1u}$ [q]		Repulsive state from $^2P_{\frac{3}{2}}+{}^2P_{\frac{3}{2}}$, responsible for absorption continuum with maximum at 20050 cm^{-1} and for the predissociation of B $^3\Pi_{0^+u}$.						B''↔X,[r]		(31)(60)(73)
B' $^3\Pi_{0^-u}$ [q]		Repulsive state from $^2P_{\frac{3}{2}}+{}^2P_{\frac{3}{2}}$. The previous assignment of B' as the state responsible for the magnetic field induced predissociation of B is now in doubt; see [u].								
Ⓑ $^3\Pi_{0^+u}$ [q]	15769.01	125.69$_7$ Z	0.764$_2$[st]	0.02903$_9$[uv]	0.000158$_2$[wt]	5.4$_3$[x]	3.024$_7$	B↔X,[ryz] R	15724.57[a'] Z	(50)(59)* (70)
A $^3\Pi_{1u}$ [q]	(11888)	(44.0)[b'] K	(1.0)	[b']				A←X,[c'] R	(11803)[b']	(4)(60)
A' $^3\Pi_{2u}$ [q]	(10100)	Suggested as lower state of high temperature absorption bands near 3427 Å (32)(35).								
Ⓧ $^1\Sigma_g^+$	0	$\boxed{214.50_2}$[d'] Z	$\boxed{0.614_7}$[d']	0.03737$_2$[d'g']	0.000113$_8$[d']	4.2$_5$[e']	2.666$_3$	Raman sp.[f']		(48)(71)

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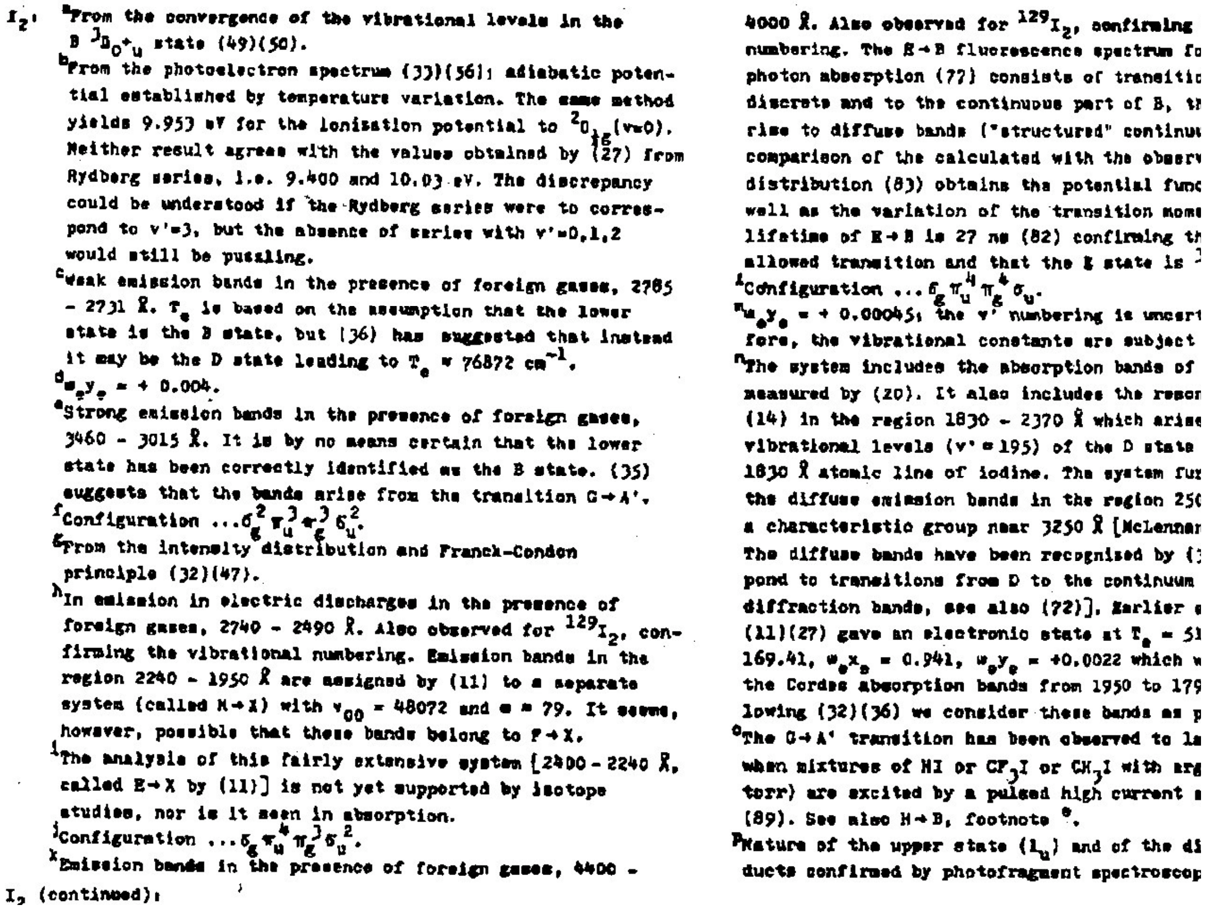
[1] Huber, K. P. and Herzberg, G., *Molecular Spectra & Molecular Structure IV: Constants of Diatomic Molecules"*, Van Nostrand, New York (1979), p.330-333.



I_2: [a] From the convergence of the vibrational levels in the $B\ {}^3\Pi_{0^+u}$ state (49)(50).

[b] From the photoelectron spectrum (33)(56); adiabatic potential established by temperature variation. The same method yields 9.953 eV for the ionisation potential to ${}^2\Pi_{\frac{1}{2}g}(v=0)$. Neither result agrees with the values obtained by (27) from Rydberg series, i.e. 9.400 and 10.03 eV. The discrepancy could be understood if the Rydberg series were to correspond to $v'=3$, but the absence of series with $v'=0,1,2$ would still be puzzling.

[c] Weak emission bands in the presence of foreign gases, 2785 - 2731 Å. T_e is based on the assumption that the lower state is the B state, but (36) has suggested that instead it may be the D state leading to $T_e = 76872\ \mathrm{cm}^{-1}$.

[d] $\omega_e y_e = +\ 0.004$.

[e] Strong emission bands in the presence of foreign gases, 3460 - 3015 Å. It is by no means certain that the lower state has been correctly identified as the B state. (35) suggests that the bands arise from the transition G → A'.

[f] Configuration $\ldots\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$.

[g] From the intensity distribution and Franck-Condon principle (32)(47).

[h] In emission in electric discharges in the presence of foreign gases, 2740 - 2490 Å. Also observed for $^{129}I_2$, confirming the vibrational numbering. Emission bands in the region 2240 - 1950 Å are assigned by (11) to a separate system (called H → X) with $\nu_{00} = 48072$ and $\omega = 79$. It seems, however, possible that these bands belong to F → X.

[i] The analysis of this fairly extensive system [2400 - 2240 Å, called E → X by (11)] is not yet supported by isotope studies, nor is it seen in absorption.

[j] Configuration $\ldots\sigma_g\pi_u^4\pi_g^3\sigma_u^2$.

[k] Emission bands in the presence of foreign gases, 4400 -

I_2 (continued):

4000 Å. Also observed for $^{129}I_2$, confirming
numbering. The E → B fluorescence spectrum fo
photon absorption (77) consists of transitio
discrete and to the continuous part of B, th
rise to diffuse bands ("structured" continuu
comparison of the calculated with the observ
distribution (83) obtains the potential func
well as the variation of the transition mome
lifetime of E → B is 27 ns (82) confirming th
allowed transition and that the E state is ³

[l] Configuration $\ldots\sigma_g\pi_u^4\pi_g^4\sigma_u$.

[m] $\omega_e y_e = +\ 0.00045$; the v' numbering is uncert
fore, the vibrational constants are subject

[n] The system includes the absorption bands of
measured by (20). It also includes the reson
(14) in the region 1830 - 2370 Å which arise
vibrational levels (v' = 195) of the D state
1830 Å atomic line of iodine. The system fur
the diffuse emission bands in the region 250
a characteristic group near 3250 Å [McLennan
The diffuse bands have been recognised by (3
pond to transitions from D to the continuum
diffraction bands, see also (72)]. Earlier e
(11)(27) gave an electronic state at $T_e = 51$
169.41, $\omega_e x_e = 0.941$, $\omega_e y_e = +0.0022$ which w
the Cordes absorption bands from 1950 to 179
lowing (32)(36) we consider these bands as p

[o] The G → A' transition has been observed to la
when mixtures of HI or CF_3I or CH_3I with arg
torr) are excited by a pulsed high current e
(89). See also H → B, footnote [e].

[p] Nature of the upper state (1_u) and of the di
ducts confirmed by photofragment spectroscop

I_2 (continued):

from magnetic quenching data (43)(53). The recent observation, however, of a quantum interference effect between *magnetic and spontaneous predissociations* (64)(68)(85) has established that the magnetic predissociation, too, is produced by the B" $^1\Pi_{1u}$ state.

[v] g_J varies from -0.059 at low v to $-5.4_5\ \mu_N$ near the dissociation limit; from Hanle effect observations (38)(79)(87)(88). See also (69).

[w] $-3.3_6\times10^{-7}(v+\frac{1}{2})^2-4.7_8\times10^{-8}(v+\frac{1}{2})^3+3.2_6\times10^{-10}(v+\frac{1}{2})^4$, from levels with $46\le v\le 77$ (50).

[x] $\beta_e = +0.3_0\times10^{-9}$ for $v\le 10$ (50). D_v increases rapidly above v=20; for more details see (51)(70).

[y] The continuum joining onto the discrete bands is overlapped by the B"← X continuum. A resolution of these two continua and the A← X continuum was given by (60). See also (61).

[z] The hyperfine structure of several lines has been observed by various high resolution laser techiques; electric quadrupole, magnetic octupole, and other magnetic hfs constants have been evaluated (23)(24)(28)(30)(34)(40)(45)(63)((65)(74)(81); similar analyses for $^{129}I_2$ and $^{127,129}I_2$ (84).

[a'] Extrapolated from data with v' ≥ 4. The vibrational numbering, changed (19) by 1 from the previous table in MOLSPEC 1, has been confirmed by isotope studies (18).

[b'] (60) suggests that the v' numbering of (4) may have to be raised substantially. Preliminary results of a rotational analysis (92) of nine bands in the A← X, v"=5 progression and of three bands in the v"=4 progression indicate that $\omega' \approx 57.5$, $\omega'x' \approx 1.85$, B'(for the lowest analyzed level) $= 0.02375$, $\alpha' \approx 0.0005$.

[c'] The continuum joining onto the discrete bands has been studied by many investigators, most recently by (60) who derives an f value of 0.00062; see also (78).

[d'] These constants (50) represent the levels v=0-5; (70), for v=0-6, give $\omega_e \approx 214.502$, $\omega_e x_e = 0.6243$, $B_e = 0.037363$, $\alpha_e = 0.0001145$ using calculated D_v values. On the basis of the resonance series of (8)(16) and (14), (26) has given polynomial formulae for G(v), B_v, and D_v valid up to v=82: $\omega_e = 214.548$, $\omega_e x_e = 0.6163$, ..., $B_e = 0.037395$, $\alpha_e = 0.0001244$, ..., $D_e = 4.54\times10^{-9}$, $\beta_e = 0.017\times10^{-9}$, ... The most accurate constants for v=0 were derived (91) from the analysis by means of Fourier transform spectroscopy of the B← X, 30-0 band: $B_0 = 0.037311_5$, $D_0 = 4.5_5\times10^{-9}$, $H_0 = -0.76\times10^{-15}$.

The vibrational levels of the ground state have been observed up to v=84 [D → X resonance series (14)], i.e. to within 400 cm^{-1} of the dissociation limit. The levels v" = 98...115 originally reported by (14) were found to be due to an NO impurity (67). As a consequence the RKR potential function of (14) must be corrected at high v. The RKR curves of (17) and (26) extend only to v=82 and are unaffected by this correction.

[e'] $\beta_e = +0.32\times10^{-9}$, see d'.

[f'] High resolution resonance Raman spectra of I_2 vapour up to the eleventh overtone (12-0). Raman spectra in rare gas matrices (75).

[g'] g_J(v=0, J=12,14) $= 9.13\times10^{-4}\ \mu_N$ from non-linear level crossing (44).

References on p.335 and 337.