EXCITATION SPECTRUM OF I_2 INDUCED BY LASER
RADIATION NEAR THE DISSOCIATION LIMIT OF THE
B-STATE.

SIMON GERSTENKORN and PAUL LUC
Laboratoire Aimé Cotton, C.N.R.S. II,
Bâtiment 505, 91405 Orsay Cedex, France

Abstract The study of the excitation spectrum of I_2 induced by laser radiation near the dissociation limit of the B state enables us to determine the molecular constants of the vibrational levels $v' = 78, 79$ and 80 ; the latest being situated only 1.6 cm^{-1} from the dissociation limit. The molecular constants are now in good agreement with theoretical predictions. Revised values of the dissociation limits of the B and X state are proposed: they are 20043.176 ± 0.016 and $12440.200 \pm 0.020 \text{ cm}^{-1}$ respectively. The excitation spectrum from 20022 to 20039.5 cm^{-1} is entirely reproduced, together with the assignments and the wavenumbers of all observed lines, principally for calibration purposes.

INTRODUCTION

The absorption spectrum of the iodine molecule of the B-X system between 14600 and 20000 cm^{-1} published recently¹ is now widely used for the calibration of laser wavelengths. However, the quality of the published Fourier spectrum decreases rapidly when approaching the dissociation limit of the B state which is estimated to be around 20043.1 cm^{-1} ^{2,3}. This is shown in Figure 1: the extreme limit where it is still possible to extract reliable data from the Fourier absorption spectrum is around 20036 cm^{-1} . This was also the limit set with the absorption spectrum in

FIGURE 1. Fourier transform absorption spectrum near the dissociation limit.

iodine obtained by conventional methods -i.e.- using a grating spectrograph in the work of Barrow and Yee, ten years ago². The reason for this limit has a physically basis : First, the Franck-Condon factors (FCF) of the (v' ,0) bands are weak and decrease when approaching the dissociation limit⁴, second, the strong absorption of the $1\Pi_u$ dissociative state has its maximum value precisely at 20000 cm⁻¹⁵. In addition in Fourier spectroscopy the noise which is constant throughout the whole spectrum⁶, depends on the detected total light. These limitations explain the relative low $\rho = S/N$ values (signal/noise ratio) of the recorded lines. For example, if $\rho \approx 5$, the uncertainty in the line position near 20022 cm⁻¹ (Figure 1) is ± 0.003 cm⁻¹, while for weak lines near 20036 cm⁻¹ with $\rho \approx 1.5$ the uncertainties increase to ± 0.015 cm⁻¹. This prevents us from having full confidence in the assignments made in the region 20022-20036 cm⁻¹, which would allow us to extend the analysis of the vibrational levels beyond $v' = 72$ and to select isolated lines for calibration purposes in this region. However, it was expected that the excitation spectrum induced by laser radiation would yield ρ values several orders of magnitude greater than those obtained by Fourier spectroscopy. These could then be used to confirm the assignments given in Figure 1 and to extend our knowledge of the absorption spectrum beyond 20036 cm⁻¹. Indeed, in this way, we were able to determine the molecular constants of the B state up to the vibrational level $v' = 80$ which is situated only 1.6 cm⁻¹ from the dissociation limit and to show that a part of the results of the two-photon sequential absorption work of Danyluk

and King³ must be revised, as it was first suggested from theoretical studies made by R. Le Roy (see reference 19). All of the recorded excitation spectrum which is useful for calibration purposes is presented at the end of this paper. We also give the assignments and the recalculated wavenumbers of the observed lines.

INSTRUMENTATION

The experimental set-up is classical in laser induced fluorescence studies. A single-mode dye laser beam is sent into a sealed iodine cell whose length and diameter are 10 cm and 2 cm respectively : the temperature of the cell was about 20°C giving an iodine pressure of 0.25 Torr. The fluorescent light is collected in a direction at right angle to the laser beam by means of a lens and detected by a photomultiplier. The signal is sent to a four pens chart recorder together with Fabry-Perot fringes at intervals of 0.025, 0.033 and 0.250 cm^{-1} . These fringe signals obtained with the use of etalons traversed by secondary beams from the dye laser are shown at the beginning of the recorded spectrum (Figure 3). This triple fringes system permits us to detect possible accidental laser mode jumps that may occur in the cavity during the scanning. The ring dye laser (Spectral Physics, Model 380) in which we used coumarin was scanned continuously over a spectral range of about 1 cm^{-1} . Each scan was repeated four times to ensure the reproductibility of the spectrum and about one hundred, partially overlapping scans were necessary to cover the investigated 10 cm^{-1} range above 20022 cm^{-1} . In spite of the precautions taken, the reproductibility of the measure-

ments of the line positions is limited by several factors : among these first are the non-linearity of the scanning device of the laser and the lack of stability of the laser beam intensity ; second the measurement of the exact positions of the lines is in general difficult : the relative high density of the lines lead to numerous blends ; in addition the existence of a significant hyperfine structure make the determination of the line position somewhat uncertain. To summarize, the estimated uncertainty with which distances between strong and well defined lines can be estimated is about $\pm 0.005 \text{ cm}^{-1}$. To determine the absolute wavenumbers of the lines below 20036 cm^{-1} , we used for wavenumbers the data given by Fourier spectroscopic measurements, above 20036 cm^{-1} we use the Fabry-Perot fringes. The uncertainties of the measurements of the distances between the lines, much smaller than the line width (0.025 cm^{-1} , see Figure 2) in no case prevented the complete identification of the observed spectrum ; estimated uncertainties of the wavenumbers are given in the caption of Figure 3.

ASSIGNMENTS OF THE RECORDED LINES

The procedure used to identify the lines belonging to the bands $(v',0)$ with $v'=73$ to $v'=77$ was based on previously published constants². Then, a new determination of the vibrational G_v , and rotational B_v , constants was made using calculated values of high order Centrifugal Distortion Constants (CDC) from D_v , up to M_v . This was done by the method and program developed by J. Hutson⁷ and used with success in the iodine case up to $v'=72$ ⁸. For

these calculations a smooth RKR potential of the B state up to the dissociation limit was constructed and CDC constants were obtained up to $v'=82$. Beyond $v'=77$, the identification of the lines was first attempted with the molecular constants for $78 \leq v' \leq 82$ determined by Danyluk and King by means of a two photon sequential technique³. It turns out that only the (78,0) band was identifiable using the data of Danyluk and King. To go further, for $v' \geq 79$, we use the molecular constants calculated from our RKR potential, i.e. "a priori" G_v , B_v , and CDC values.

In this way, the (79,0) and (80,0) bands were identified without ambiguity. The bands (81,0) and (82,0) were not found, principally, because under our experimental conditions, these bands have very low intensities and most of the corresponding lines are drowned in noise or blended with other transitions.

RESULTS

Molecular constants of the analysed bands

Table I gives the number of assigned lines for each band as well as the minimum and maximum J values detected in each R and P branch. The total number of assigned lines for the seven bands (from (73,0) to (79,0)) is 265; in the last column of Table I are the standard deviations between the measured wavenumbers (σ_{mes}) and the calculated ones (σ_{cal}).

The band (80,0) which is the highest detected band in the present work is treated separately below for illustrative

TABLE I Number of assigned lines in the R and P branches in each analysed band ; last column : Standard deviation (in 10^{-3} cm^{-1} unit) between observed and calculated wavenumbers.

(v', v'')	R Branch			P Branch				S.D. 10^{-3} cm^{-1}
	J _m	J _{MAX}	N _R	J _m	J _{MAX}	N _P	N _R + N _P	
73,0	3	41	31	1	56	25	56	2.8
74,0	2	47	33	7	50	26	59	3.0
75,0	4	44	29	2	44	29	58	3.0
76,0	2	32	17	5	42	19	36	3.5
77,0	7	35	14	5	35	10	24	4.7
78,0	2	21	8	2	22	9	17	7.0
79,0	6	21	7	6	21	8	15	4.0

TABLE II Molecular constants for v'=73 to v'=79 (I₂ B state).

v'	$\sigma_{0,v'}$	$10^2 \cdot B_{v'}$	$10^6 \cdot D_{v'}$	$-10^{10} \cdot H_{v'}$	$-10^{14} \cdot L_{v'}$	$-10^{17} \cdot M_{v'}^*$
73	20028.303	.60672	.16609	.07692	.07267	.02065
74	20031.489	.56018	.18274	.09888	.10987	.03671
75	20034.161	.51340	.20215	.12927	.17082	.06819
76	20036.373	.46689	.22491	.17225	.27434	.13343
77	20038.167	.42117	.25205	.23451	.45738	.27765
78	20039.609	.37379	.28472	.32712	.79646	.62128
79	20040.729	.32912	.32455	.46889	1.45920	1.51442

purposes.

Table II contains the calculated (CDC) $D_{v'}$, $H_{v'}$, $L_{v'}$ and $M_{v'}$. The vibrational and rotational constants result from least square fits to the data, the CDC being fixed in these fits to their calculated values. As explained in a recent paper⁸, the values of $M_{v'}^*$, given in Table II are equal to 2.6 times the calculated $M_{v'}$ values, in order to take account of the neglected higher order constants $N_{v'}$, $O_{v'}$, ...

For $v' \geq 78$ the maximum observed J value is 21; it follows that the values of $L_{v'}$ and $M_{v'}$ are no longer necessary to recalculate the observed wavenumbers, but for sake of completeness we give them, both to show that they are indeed not necessary⁹ and also to illustrate the actual power of Hutson's method⁷.

The (80,0) band

Table III gives the list of unblended lines that we have assigned to the (80,0) band. The measured wavenumbers of these lines, given in column 3, are in agreement with the calculated ones (column 2). The wavenumbers of the two branches R and P equal to :

$$\begin{aligned} \sigma_R(J) = & \sigma_{Ov'} + B_{v'}\alpha - D_{v'}\alpha^2 + H_{v'}\alpha^3 + L_{v'}\alpha^4 + M_{v'}\alpha^5 \\ & - B_{v''}\gamma + D_{v''}\gamma^2 - H_{v''}\gamma^3 \end{aligned} \quad (1)$$

and

$$\begin{aligned} \sigma_P(J) = & \sigma_{Ov'} + B_{v'}\beta - D_{v'}\beta^2 + H_{v'}\beta^3 + L_{v'}\beta^4 + M_{v'}\beta^5 \\ & - B_{v''}\gamma + D_{v''}\gamma^2 - H_{v''}\gamma^3 \end{aligned} \quad (2)$$

where $\alpha = (J+1)(J+2)$; $\gamma = J(J+1)$ and $\beta = J(J-1)$

were calculated by means of the molecular constants extra-

TABLE III Transitions and molecular constants belonging to the (80,0) band.

J	R Branch			P Branch		
	Calculated	Obs.	10^{-3}cm^{-1} (Diff.)	Calculated	Obs.	10^{-3}cm^{-1} (Diff.)
1	20041.521			20041.504		
2	.389			.360		
3	.188			.148		
4	40.817			40.866		
5	.577			.516		
6	.169			.096		
7	39.692	.695	-3	39.608	.608	0
8	.144	.139	-5	.050	.045	+5
9	38.528	.513	+15	38.423	.412	+11
10	37.843			37.727		
11	37.087	.070	+13	36.961	.943	+18
12	36.262			36.126	.110	+16
13	35.367			35.221		
14	34.403			34.247		
15	33.368			33.203	.190	+13

Origin	$\sigma_{0,80}$	B'_{80}	D'_{80}
Extrapolated values	20041.579	.002840	.3723-006

Fitted values (10 lines)	20041.569 ± 0.005	.002837(50)	(.3723-006)

polated from the RKR potential and given at the bottom of Table III.

From relation (1) and (2), it follows that in the case of the (80,0) band where only low values of J are observed, the contribution of the CDC higher than D_v , can be neglected, and that we have to a good approximation :

$$[\sigma_R(J) - \sigma_P(J)] = B_v(\alpha - \beta) - D_v(\alpha^2 - \beta^2) \quad (3)$$

Thus direct B'_{80} values can be determined from measured $(\sigma_R(J) - \sigma_P(J))$ values, as is the case for $J=7, 8, 9$ and 11 (see Table III) provided that the D_v value is known. Taking $D_v = 0.372 \cdot 10^{-6} \text{ cm}^{-1}$, the calculated value, one finds $B'_{80} = 0.002837(50)$, a value incompatible with the value $0.002591(68)$ deduced from the two photon sequential absorption work³. The result of a least square fit of the ten transitions belonging to the (80,0) band is finally given, together with the extrapolated constants which served as starting values for the identification of the (80,0) band.

Dissociation limit and related quantities

From the well-known LeRoy and Bernstein relations^{10,11}

$$G_v = -k[\bar{\Delta G}_v]^{2n/(n+2)} + D \quad (4)$$

$$\text{and } v = -h[D - G_v]^{(n-2)/2n} + v_D \quad (5)$$

it is possible to extract, by linear extrapolation, a value for the dissociation limit D and a value for v_D , the vibrational index at the dissociation limit. Truncating v_D to an integer gives the highest bound vibrational level. Near the dissociation limit, the expressions (4) and (5) are applicable in the case of the B state of iodine, as

it was shown in the past^{2,3} (Birge-Sponer plot with positive curvature, and high density vibrational levels near the dissociation limit, $\overline{\Delta G}_v$ being equal to $1/2(G_{v+1} - G_{v-1})$). The quantities h or k are related to C_n , the dominant long-range potential energy constant ($V(r) = D - C_n/r^n$); for example $h = 1/H_n$ and $H_n = \overline{H}_n/(\mu^{1/2}(C_n)^{1/n})$ where $\overline{H}_n$ is a numerical factor tabulated in ref. 12, μ is the reduced mass and theory tells us that for the B state $n=5$ ¹⁰. Table IV summarizes and compares the extrapolated values of D , v_D and C_5 deduced from the different experimental studies made near the dissociation limit.

TABLE IV Values of D , v_D and C_5

Authors	v' Range	D (cm ⁻¹)	v_D	$10^{-5} C_5$ (cm ⁻¹ /Å ⁵)
Barrow and Yee, 1972	64 - 77	20043.208 ± 0.033	87.345 ± 0.007	2.8861
Danyluk and King, 1977	72 - 82	20043.063 ± 0.020	87.183 ± 0.012	2.776 ± 0.018
Present work, 1982	73 - 80	20043.176 ± 0.008	87.364 ± 0.006	2.850 ± 0.010

The errors given in our work represent one "standard deviation" resulting from least square fits to equation (1) and (2) by means of data given in Table II and III, recalling that in our notation $\sigma_{Ov} = T_e + G_v$.

Inspection of Table IV shows that our results are in good agreement with those determined in 1972 by Barrow

and Yee², but disagree with those obtained more recently by Danyluk and King³ (D. and K.). The principal difference between our results and those of D. and K. is in the analysis of the (79,0) band, where disagreements for the vibrational and rotational constants are the most important (Table V and VI). We also give in these tables the calculated values of the vibrational and rotational constants

TABLE V Comparison between vibrational energies
of the $v' = 78-82$ levels.

v'	Danyluk and King (cm^{-1})	Present work (cm^{-1})	Differences (cm^{-1})
78	20039.6086(73)	20039.6095(20)	0.001
79	40.6972(30)	40.7292(30)	0.032
80	41.5595(26)	41.5690(50)	0.009
81	42.1618(37)	(42.180)	
82	42.5333(73)	(42.598)	

TABLE VI Comparison between rotational B'_v
constants values.

v'	Danyluk and King (cm^{-1})	Present work (cm^{-1})	Differences %
78	0.003577(49)	0.003738(10)	-4.5%
79	0.002964(59)	0.003291(10)	-11%
80	0.002591(68)	0.002837(50)	-9.5%
81	0.001784(39)	(0.002373)	
82	0.001064(189)	(0.001915)	

of the $v'=81$ and $v'=82$ levels. Only the D. and K. experimental value of the energy of the $v'=81$ level agrees with the calculated one. Our extrapolated D value being about 0.1 cm^{-1} higher than the adopted value by D. and K., we have extended the use of Eq.(4) to a larger v' range, in order to test our results. Doubling the v' range from⁸ $v'=66$ to $v'=80$ (instead from 73 to 80 in this work), then the extrapolated values of D obtained with the same procedure used by D. and K.³ (which consists of omitting successively the lowest level from the fit), vary from a minimum value of $20043.159 \text{ cm}^{-1}$ to a maximum value of $20043.181 \text{ cm}^{-1}$. All these D values are within two standard deviations, in agreement with the D value obtained from the v' range 73-80 studied here (Table IV).

To summarize, it is tempting to propose for the dissociation limit the value $D = 20043.176 \pm 0.016 \text{ cm}^{-1}$, in so far as this extrapolated value represents the true D value. Indeed, above $v'=80$ we don't yet know, if there are perturbations from other states. Perturbations between the hyperfine levels of the B state certainly occur¹³ and we have to consider that in the 1 cm^{-1} region before the extrapolated dissociation limit, the distances between the rotational and vibrational levels become of the order of magnitude of the hyperfine splitting. Nevertheless, if the value of $20043.176 \text{ cm}^{-1}$ is adopted and assumed to correspond to the center of gravity of the $^2P_{1/2}$ state it follows that the value of the dissociation limit of the X state has to be revised. From the well-known¹⁴ separation of $^2P_{1/2}$ and $^2P_{3/2}$ states equal to $7602.977 \pm 0.005 \text{ cm}^{-1}$

the dissociation limit of the X state becomes :
 $12440.200 \pm 0.020 \text{ cm}^{-1}$.

Intensities of the analysed bands

From the Franck-Condon density values calculated by J. Tellinghuisen near the dissociation limit⁴, one should observe between a $(v',0)$ and a $((v'+1),0)$ band, in the range where $v' = 73$ to $v' = 80$, a decrease of the intensities of the bands of about a factor ~ 1.25 (in fact, proportional to the ratio of the $\bar{\Delta G}_v$ quantities). Despite the lack of stability of the laser beam it was possible to estimate the decrease of the intensities. This decrease turns out to be a factor of 1.5 rather than a factor 1.25. Between adjacent bands differing by one unit, the difference between 1.25 and 1.50 is not significant, but if we consider the intensity ratio of the $(73,0)$ band and the $(80,0)$ band, the ratio is 5 instead ~ 25 . In fact, the $(80,0)$ band is about two orders of magnitude weaker than the $(73,0)$ band. Attempts to calculate directly the Franck-Condon factors near the dissociation limit will be undertaken together with the global treatment of the spectroscopic data of the B state from $v' = 0$ to the dissociation limit ; this task is out of the scope of this paper, and will be undertaken in the near future¹⁵.

DISCUSSION

Assignments based only on wavenumber measurements need to be confirmed, for example, by an agreement between measured and calculated intensities of the lines¹⁶. This procedure failed in our case : neither precise FCF are known, nor

FIGURE 2 Observed band origins in the iodine excitation spectrum induced by laser radiation.

are the estimated intensities reliable enough. Fortunately, it was sometimes possible to observe in the excitation spectrum band origins, the R_0 transitions as shown in Figure 2. The widths of the R_0 components ($\sim 0.016 \text{ cm}^{-1}$), which are formed by only a few hyperfine components are much smaller than "ordinary" transitions ($\sim 0.026 \text{ cm}^{-1}$, Figure 2) which contain 15 or 21 hyperfine components, according the parity of the line¹⁷. Weak components in the vicinity of the band origins R_0 designated by R'_1 were not assignable to any analysed band ; it turns out that these components are groups of hyperfine transitions belonging to the R_1 lines as observed by Pique et al.¹³. These fine details and the fact that the measured wavenumbers of the band origins R_0 agree within $\pm 0.005 \text{ cm}^{-1}$ with the calculated ones are valuable confirmations of the assignments made previously. Thus, the study of the excitation spectrum in a relative short range of wavenumbers ($20022 - 20039.5 \text{ cm}^{-1}$) confirms directly the assignments made in the larger region $19900 - 20036 \text{ cm}^{-1}$, which was recorded by Fourier spectroscopy and which contains the data corresponding to the $(73,0) \dots (77,0)$ bands. The analysis of the $(78,0)$, $(79,0)$ and $(80,0)$ bands based exclusively on data furnished by the excitation spectrum represents, actually, the most important progress in our knowledge of the properties of the vibrational levels near the dissociation limit. This, not only permits us to determine a new value of the dissociation limit, in good agreement with those obtained previously by Barrow and Yee², but also shows that, effectively, a smooth RKR potential can be built from $v' = 0$ to the dissociation limit¹⁵. The $v' = 80$ vibrational level is situated about 1.6 cm^{-1} from

the dissociation limit and the last bound vibrational level is $v' = 87$. To go further in the analysis of the B state will be difficult. There is no doubt that soon after the $v' = 80$ level, problems of hyperfine structure will occur, principally at the heads of the bands¹³. For higher J transitions, however, the study of the excitation spectrum should still be a valuable method for detecting at least the (81,0) and (82,0) bands. Improved recordings of the excitation spectrum in the range 20038.0 - 20041.0 cm^{-1} will be in our opinion, not too difficult to achieve by means of some technical ameliorations. Later, the analysis of the excitation spectrum by means of a Fourier spectrometer will be undertaken if necessary ; this latest method being, of course, more difficult than the recording of the simple excitation spectrum. The determination of the molecular constants of vibrational levels higher than $v' = 77$ is important for theoretical considerations : Born-Oppenheimer approximation, mechanical model of the molecule, LeRoy's near dissociation expansion expressions^{18,19}, and the limit of applicability of Hutson's method⁷ for the calculation of CDC ; in particular, in a case of an unperturbed state as the B state. Indeed, the fact that we were able to classify all (except one) observed lines of the excitation spectrum in the 20022 - 20039 cm^{-1} region (four of the five weak unblended lines not classified in Figure 3 are now assigned as belonging to the (80,0) bands, see Table III) is a good indication of the absence of perturbations from other states - in other words no extra lines were found. It is the purity of the B state, which we have now established to be valid to 99.95% of the well depth, which will assure the

B state remaining for a long time a textbook example in studies of diatomic molecules²⁰.

CONCLUSION

It is essentially the increase in the S/N ratio observed in the excitation spectrum of I_2 induced by laser radiation - about two orders of magnitude, compared to the value of the S/N ratio in the Fourier-spectrum, which allowed us to progress in the analysis of the B state near the dissociation limit. Compared to the results obtained by the two photon sequential method³ our results are more reliable owing the unambiguously structure of the excitation spectrum which is easy to interpret and to the fact that the agreement between theory and experiment is now satisfactory²¹. Accordingly, revised values for the dissociation limits of the B and X states are proposed and finally, the limit of the usefulness of the iodine spectrum for calibration purposes is now extended from 12600 cm^{-1} to 20039 cm^{-1} (see Figure 3 : "the excitation spectrum of iodine").

ACKNOWLEDGMENTS

We are deeply indebted to Drs. R. Pelletier and N. Pelletier for the recording of the excitation spectrum. We wish to express our gratitude to H. Calvignac and B. Demarets for having prepared the graphs and figures. Dr. K. Rajnak has kindly read this manuscript and has given us valuable advice .

REFERENCES

1. S. Gerstenkorn and P. Luc, Atlas du spectre d'absorption de la molécule de l'iode
  - a) 14800 - 20000 cm⁻¹, Editions du CNRS (1978)
15 quai Anatole France, 75700 Paris
  - b) 14000 - 15600 cm⁻¹ available at Laboratoire Aimé Cotton, CNRS II, 91405 Orsay, France
  - c) Complement 15780 - 15815 cm⁻¹, Rev. Phys. Appl. **16**, 529 (1981).
2. R. F. Barrow and K. K. Yee, J. Chem. Soc. Faraday II **69**, 684 (1973).
3. M. D. Danyluk and G. W. King, Chem. Phys. **25**, 343 (1977).
4. J. Tellinghuisen, J. Quant. Spectrosc. Radiat. Transfer. **19**, 149 (1978).
5. J. Tellinghuisen, J. Chem. Phys. **58**, 2821 (1973).
6. S. Gerstenkorn and P. Luc, Nouv. Rev. Optique **7**, 149 (1976).
7. J. M. Hutson, J. Phys. B : At. Mol. Phys. **14**, 851 (1981).
8. J. M. Hutson, S. Gerstenkorn, P. Luc and J. Sinzelle (to appear in J. M. S.).
9. D. L. Albritton, A. L. Schmeltekopf and R. N. Zare, Molecular Spectroscopy, Modern Research, edited by K. Narahari Rao (Academic Press, New York, 1976) II, p. 1-67.
10. R. J. Le Roy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970).
11. R. J. Le Roy and R. B. Bernstein, J. Mol. Spectrosc. **37**, 109 (1971).
12. R. J. Le Roy, in : Report on electronic spectroscopy, ed. R. F. Barrow (Chemical Society, London, 1973) ch.3.
13. J. P. Pique, R. Bacis, S. Churassy, F. Hartmann and J. B. Koffend (to appear, private communication).
14. E. Luc-Koenig, C. Morillon et J. Vergès, Physica **70**, 175 (1973).
15. S. Gerstenkorn and P. Luc (to be published).
16. R. N. Zare, J. Chem. Phys. **40**, 1934 (1964).
17. M. Krol and K. K. Innes, J. Mol. Spectrosc. **36**, 295 (1970).
18. R. J. Le Roy, in Semiclassical Methods in Molecular Scattering and Spectroscopy, edited by M. S. Child, (D. Reidel, Dordrecht, 1980) p. 109.
19. R. J. Le Roy, J. Chem. Phys. **73**, 6003 (1980).
20. G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, Princeton, 1950).

21. J. W. Tromp, R. J. Le Roy, S. Gerstenkorn and P. Luc, (to appear).
22. J. D. Simmons and J. T. Hougen, J. Res. Nat. Bur. Stand. (U.S.A.), 81A, 25 (1977).

THE IODINE EXCITATION SPECTRUM

Figure 3 represents the iodine excitation spectrum recorded from 20022 to 20039 cm^{-1} . Since some of the recorded lines (43 on the whole) are selected to serve for calibration purposes¹, it is necessary to know the reliability of the wavenumbers associated to these selected lines listed in Table VII, column 5 (σ_{cal}). Accordingly, we give in column 2 the values of the wavenumbers deduced from the Fourier measurements (σ_{Fourier}) with their corresponding uncertainties; in column 3 are the wavenumbers measured by means of the Fabry-Perot fringes ($\sigma_{\text{F.P.}}$).

In every scan of the excitation spectrum we can choose, at least, one reference line; the wavenumber of which being taken equal to the value obtained from the Fourier data; these values are given in parentheses (column 3); with these 12 references values, the differences ($\sigma_{\text{F.P.}} - \sigma_{\text{Fourier}}$), in column 4, show that within a range of about 0.8 cm^{-1} from a given reference line, the $\sigma_{\text{F.P.}}$ wavenumbers agree

TABLE VII Wavenumbers of selected lines,
useful for calibration purposes.

N	σ_{Fourier} (cm ⁻¹)	$\sigma_{\text{F.P.}}$	$\sigma_{\text{F.P.}} - \sigma_{\text{Four.}}$ (10 ⁻³ cm ⁻¹)	$\sigma_{\text{cal.}}$
2	20022.2297(20)	(.2297)	0	.2300
4	.4509(10)	.453	+2.1	.4517
11	23.0361(16)	.041	+4.9	.0371
12	.1777(25)	.187	+9.3	.1794
17	.7041(10)	(.7041)	0	.7056
19	.8838(23)	.884	+0.2	.8828
21	24.0469(10)	.047	+0.1	.0442
34	.7444(25)	.751	+6.6	.7439
39	25.2322(26)	(.2322)	0	.2334
43	.5679(14)	.570	+2.1	.5674
46	.8674(21)	.867	-0.4	.8665
47	.9565(20)	.955	-1.0	.9563
50	26.2749(20)	(.2749)	0	.2759
51	.4048(18)	.402	-2.8	.4043
54	.5881(31)	.592	+3.9	.5881
57	.9170(41)	(.9170)	0	.9182
61	27.1785(19)	.182	+3.5	.1775
62	.2537(28)	.259	+5.3	.2537
67	.6316(17)	.640	+8.4	.6321
70	.9773(42)	(.9773)	0	.9771
79	28.4419(27)	.444	+2.1	.4399
81	.6719(22)	.679	+7.1	.6719
82	.7439(23)	.752	+8.1	.7446
84	29.0134(15)	(.0134)	0	.0149

TABLE VII Wavenumbers of selected lines, useful for calibration purposes (continued).

N	σ_{Fourier} (cm^{-1})	$\sigma_{\text{F.P.}}$	$\sigma_{\text{F.P.}} - \sigma_{\text{Four.}}$ (10^{-3} cm^{-1})	$\sigma_{\text{cal.}}$
89	20029.3806(22)	.387	+6.4	.3804
92	.7991(17)	.799	-0.1	.7986
104	30.7297(19)	(.7297)	0	.7312
109	31.1643(18)	.166	+1.7	.1653
120	.7617(25)	(.7617)	0	.7617
124	32.1721(21)	.176	+3.9	.1711
127	.4414(19)	(.4414)	0	.4404
130	.7493(34)	.751	+1.7	.7480
136	33.2576(39)	.262	+4.4	.2571
137	.3506(39)	.354	+3.4	.3503
140	.5264(28)	(.5264)	0	.5261
153	34.2805(33)	.287	+6.5	.2770
157	.6143(22)	(.6143)	0	.6143
158	.9480(30)	.946	+2.0	.9460
162	35.2686(40)	.275	+6.4	.2690
164	.4492(45)	.459	+9.8	.4497
176	36.2041(33)	(.2041)	0	.2053
181	.3794(38)	.384	+4.6	.3794
185	.8406(51)	.847	+6.4	.8350
193	37.5522(43)	.550	-2.2	.5469

with the σ_{Fourier} ones, within 0.010 cm^{-1} , a quantity always inferior of the width of the iodine lines (0.025 cm^{-1}). In fact we have used 43 σ_{Fourier} values as "standards" in order to obtain reliable $\sigma_{\text{F.P.}}$ values of the recorded

lines of the excitation spectrum. Briefly, despite the Fabry-Perot etalons used were not temperature stabilized (but protected), the comb of σ_{Fourier} values was narrow enough (3 values per cm^{-1} in average) to ensure a reproducibility of about $\pm 0.005 \text{ cm}^{-1}$ for repeated scans.

Beyond the last selected line $20037.547 \text{ cm}^{-1}$ (number 193 in the excitation spectrum, Column 1, Table VII) until the last observed line 20039.43 cm^{-1} , the line positions were determined solely by means of the Fabry-Perot fringes. From the trend of the differences ($\sigma_{\text{F.P.}} - \sigma_{\text{Fourier}}$) given in Column 4, one can expect that the uncertainties of the wavenumbers measurements in this $\sim 2 \text{ cm}^{-1}$ region do not exceed 0.025 cm^{-1} . However, the adopted values of the wavenumbers are not the observed values but the calculated ones. They are deduced from the molecular constants given in Table II. These calculated values (σ_{cal} , Column 5) reproduce within $\pm 0.001 \text{ cm}^{-1}$, in average, the Fourier data given in Column 2. Since the molecular constants are based on set of lines (P and R branches) spread out on relative large spectral region, the recalculated values σ_{cal} should be smoother and therefore are a better representation of the wavenumbers of the recorded lines ; they are given below each part of the spectrum. Estimation of the accuracy of the wavenumbers can be obtained either from the uncertainties of the Fourier data (Column 2, Table VII), which are the "basically" data, or either from the standard deviation ($\sigma_{\text{cal}} - \sigma_{\text{mes}}$) given in Table II for each analysed band.

The recorded excitation spectrum from 20022 to 20039.5 cm^{-1} is divided in twelve parts ; every part contains a portion of about 1.5 cm^{-1} , the wavenumber scale

being 0.120 cm^{-1} per cm. All the recorded lines are marked by vertical lines and numbered in a way similar to those adopted by Simmons and Hougen in their atlas²².

Blended lines have same line number and the same intensity. Intensities given in column four are only estimated. Lines marked with an asterisk are lines selected for calibration purposes.

FIGURE 3.

1	20022.1033	R19(75-0)	120	7	20022.7795	R13(73-0)	310
*2	20022.2300	P 8(72-0)	180	8	20022.8105	R20(76-0)	65
3	20022.394	P22(78-0)	7	9	20022.9314	R 7(72-0)	315
4	20022.4441	P20(76-0)	440	9	20022.9531	P18(75-0)	315
*4	20022.4517	R 8(72-0)	440	10	20022.9932	R21(77-0)	25
4	20022.4553	P13(73-0)	440	*11	20023.0371	R16(74-0)	180
5	20022.6526	P21(77-0)	200	*12	20023.1794	P 6(72-0)	175
5	20022.6741	P16(74-0)	200	13	20023.2810	P12(73-0)	220
6	20022.702	R22(78-0)	240	14	20023.3225	R18(75-0)	125
6	20022.7356	P 7(72-0)	240	15	20023.3494	R 6(72-0)	180

16	20023.5620	P 5(72-0)	290	27	20024.3208	R11(73-0)	245
16	20023.5818	R12(73-0)	290	27	20024.3396	P 2(72-0)	245
17	20023.7024	P15(74-0)	390	28	20024.3865	R20(77-0)	55
*17	20023.7056	R 5(72-0)	390	28	20024.4050	R 2(72-0)	55
18	20023.7654	P19(76-0)	50	29	20024.4758	P 1(72-0)	140
*19	20023.8828	P 4(72-0)	115	29	20024.4761	R17(75-0)	140
19	20023.890	P21(78-0)	115	30	20024.5151	R 1(72-0)	60
20	20024.0005	R 4(72-0)	120	31	20024.53	R'1(72-0)	25
21	20024.0437	P11(73-0)	430	32	20024.5640	R 0(72-0)	25
*21	20024.0442	R15(74-0)	430	33	20024.6670	P14(74-0)	140
21	20024.0596	P20(77-0)	430	*34	20024.7439	P10(73-0)	150
22	20024.1155	R19(76-0)	90	35	20024.813	P21(79-0)	5
23	20024.1257	P17(75-0)	230	36	20024.9873	R14(74-0)	190
24	20024.1421	P 3(72-0)	90	36	20024.9973	R10(73-0)	190
25	20024.186	R21(78-0)	10	37	20025.0205	P18(76-0)	55
26	20024.2334	R 3(72-0)	110				

36	20024.9973	R10(73-0)	190	44	20025.6108	R 9(73-0)	200
37	20025.0205	P18(76-0)	55	45	20025.7119	R19(77-0)	40
38	20025.067	R21(79-0)	7	*46	20025.8665	R13(74-0)	180
*39	20025.2334	P16(75-0)	100	*47	20025.9563	P 8(73-0)	140
40	22025.3240	P20(78-0)	6	48	20026.1616	R 8(73-0)	160
41	20025.3540	R18(76-0)	35	49	20026.2095	P17(76-0)	80
42	20025.3813	P 9(73-0)	195	50	20026.260	P20(79-0)	135
42	20025.3992	P19(77-0)	195	*50	20026.2759	P15(75-0)	135
43	20025.5647	R16(75-0)	260	*51	20026.4043	P12(74-0)	145
*43	20025.5674	P13(74-0)	260	52	20026.4685	P 7(73-0)	160
44	20025.602	R20(78-0)	200				

52	20026.4685	P 7(73-0)	160	63	20027.3054	P 5(73-0)	140
53	20036.505	R20(79-0)	50	64	20027.3323	P16(76-0)	50
53	20026.5261	R17(76-0)	50	65	20027.4331	R11(74-0)	310
*54	20026.5881	R15(75-0)	138	65	20027.4387	R 5(73-0)	310
55	20026.6499	R 7(73-0)	200	66	20027.5464	R14(75-0)	105
55	20026.6714	P18(77-0)	200	67	20027.6299	P 4(73-0)	130
55	20026.675	P19(78-0)	200	*67	20027.6321	R16(76-0)	130
56	20026.6816	R12(74-0)	200	67	20027.637	P19(79-0)	130
*57	20026.9182	P 6(73-0)	120	68	20027.7390	R 4(73-0)	90
58	20026.949	R19(78-0)	25	69	20027.872	R19(79-0)	220
59	20026.9695	R18(77-0)	30	69	20027.8765	P17(77-0)	220
60	20027.0757	R 6(73-0)	125	69	20027.8872	P10(74-0)	220
*61	20027.1775	P11(74-0)	170	69	20027.8921	P 3(73-0)	220
*62	20027.2537	P14(75-0)	100				

70	20027.966	P18(78-0)	90	*79	20028.4399	R13(75-0)	125
*70	20027.9771	R 3(73-0)	90	80	20028.5330	P 9(74-0)	130
71	20028.0918	P 2(73-0)	30	*81	20028.6719	R15(76-0)	70
71	20028.1206	R10(74-0)	130	*82	20028.7446	R 9(74-0)	137
73	20028.1523	R 2(73-0)	205	83	20028.944	P18(79-0)	2
73	20028.1599	R17(77-0)	205	84	20029.0144	P16(77-0)	115
73	20028.1667	P13(75-0)	205	*84	20029.0149	P12(75-0)	115
74	20028.228	R18(78-0)	25	85	20029.1155	P 8(74-0)	90
74	20028.2288	P 1(73-0)	25	86	20029.170	R18(79-0)	12
75	20028.2651	R 1(73-0)	45	86	20029.187	P17(78-0)	12
76	20028.28	R'1(73-0)	25	87	20029.2683	R12(75-0)	90
77	20028.3150	R 0(73-0)	20	87	20029.2830	R16(77-0)	90
78	20028.3892	P15(76-0)	75	88	20029.3049	R 8(74-0)	95

88	20029.3049	R 8(74-0)	95	97	20030.3057	P13(76-0)	55
*89	20029.3804	P14(76-0)	50	98	20030.341	P16(78-0)	45
90	20029.436	R17(78-0)	11	98	20030.3389	R15(77-0)	45
91	20029.6343	P 7(74-0)	140	99	20030.398	R17(79-0)	4
91	20029.6455	R14(76-0)	140	100	20030.4812	P 5(74-0)	60
*92	20029.7985	P11(75-0)	190	101	20030.5172	P10(75-0)	70
92	20029.8015	R 7(74-0)	190	102	20030.5532	R13(76-0)	65
93	20030.0322	R11(75-0)	95	102	20030.577	R16(78-0)	65
94	20030.0857	P15(77-0)	100	103	20030.6042	R 5(74-0)	75
94	20030.0894	P 6(74-0)	100	*104	20030.7312	R10(75-0)	70
95	20030.182	P17(79-0)	2	105	20030.8096	P 4(74-0)	40
96	20030.2346	R 6(74-0)	75				

105	20030.8096	P	4(74-0)	40	113	20031.427	P15(78-0)	55
106	20030.9104	R	4(74-0)	50	114	20031.4475	R 1(74-0)	40
107	20031.0745	P	3(74-0)	50	115	20031.47	R*1(74-0)	12
108	20031.0896	P14	(77-0)	50	116	20031.5000	R 0(74-0)	15
109	20031.1528	R	3(74-0)	150	117	20031.555	R16(79-0)	1
*109	20031.1653	P12	(76-0)	150	118	20031.6100		1
109	20031.1719	P	9(75-0)	150	119	20031.650	R15(78-0)	10
110	20031.2759	P	2(74-0)	17	*120	20031.7617	P 8(75-0)	55
111	20031.3276	R14	(77-0)	60	121	20031.9353	R 8(75-0)	75
111	20031.3318	R	2(74-0)	60	122	20031.9590	P11(76-0)	55
112	20031.351	P16	(79-0)	85	123	20032.0271	P13(77-0)	20
112	20031.3655	R	9(75-0)	85	*124	20032.1711	R11(76-0)	46
113	20031.3950	R12	(76-0)	55	125	20032.2495	R13(77-0)	35
113	20031.4140	P	1(74-0)	55	126	20032.2871	P 7(75-0)	65

126	20032.2871	P	7(75-0)	65	135	20033.1900		
127	20032.445	P14	(78-0)	85	*136	20033.2571	R 5(75-0)	55
*127	20032.4404	R	7(75-0)	85	*137	20033.3503	P 9(76-0)	45
127	20032.450	P15	(79-0)	85	138	20033.3970	P13(78-0)	11
128	20032.645	R15	(79-0)	11	139	20033.4766	P 4(75-0)	35
128	20032.654	R14	(78-0)	11	139	20033.482	P14(79-0)	35
129	20032.6875	P10	(76-0)	40	*140	20033.5261	R 9(76-0)	50
*130	20032.7480	P	6(75-0)	45	141	20033.5688	R 4(75-0)	45
131	20032.8811	R	6(75-0)	105	142	20033.591	R13(78-0)	14
131	20032.8813	R10	(76-0)	105	143	20033.664	R14(79-0)	2
132	20032.8979	P12	(77-0)	11	144	20033.7021	P11(77-0)	25
133	20033.1045	R12	(77-0)	20	145	20033.7444	P 3(75-0)	27
134	20033.1445	P	5(75-0)	50				

145	20033.7444	P 3(75-0)	27	154	20034.4397	P10(77-0)	30
146	20033.8162	R 3(75-0)	35	154	20034.444	P13(79-0)	30
147	20033.8926	R11(77-0)	20	155	20034.459	R12(78-0)	30
148	20033.9475	P 8(76-0)	55	156	20034.4795	P 7(76-0)	40
148	20033.9478	P 2(75-0)	55	*157	20034.6143	R10(77-0)	60
149	20033.9990	R 2(75-0)	20	157	20034.615	R13(79-0)	60
150	20034.0867	P 1(75-0)	65	157	20034.6189	R 7(76-0)	60
150	20034.1052	R 8(76-0)	65	*158	20034.9460	P 6(76-0)	30
150	20034.1174	R 1(75-0)	65	159	20035.0669	R 6(76-0)	35
151	20034.14	R'1(75-0)	8	160	20035.092	P11(78-0)	20
152	20034.1760	R 0(75-0)	8	161	20035.1108	P 9(77-0)	25
*153	20034.277	P12(78-0)	6				

162	20035.260	R11(78-0)	30	173	20036.0188	R 3(76-0)	20
*162	20035.2690	R 9(77-0)	30	174	20036.1100		1
163	20035.337	P12(79-0)	30	175	20036.1587	P 2(76-0)	15
163	20035.3472	P 5(76-0)	30	175	20036.162	P11(79-0)	15
*164	20035.4497	R 5(76-0)	35	*176	20036.2053	R 2(76-0)	15
165	20035.497	R12(79-0)	3	177	20036.2539	P 7(77-0)	15
166	20035.6831	P 4(76-0)	20	178	20036.2986	P 1(76-0)	20
167	20035.7156	P 8(77-0)	15	178	20036.309	R11(79-0)	20
168	20035.7668	R 4(76-0)	20	179	20036.3267	R 1(76-0)	15
169	20035.839	P10(78-0)	10	180	20036.35	R'1(76-0)	5
170	20035.8574	R 8(77-0)	15	*181	20036.3794	R 7(77-0)	25
171	20035.9536	P 3(76-0)	15	181	20036.3826	R 0(76-0)	25
171	20035.994	R10(78-0)	15	182	20036.519	P 9(78-0)	10
172	20036.0100		10	183	20036.659	R 9(78-0)	10

183	20036.6489	R	9(78-0)	10	*193	20037.5469	R	4(77-0)	13
184	20036.7258	P	6(77-0)	15	194	20037.606	P	9(79-0)	5
*185	20036.8350	R	6(77-0)	10	195	20037.676	P	7(78-0)	7
186	20036.918	P	10(79-0)	4	196	20037.729	R	9(79-0)	8
187	20036.9430			4	196	20037.7444	P	3(77-0)	8
188	20037.053	R	10(79-0)	5	197	20037.787	R	7(78-0)	9
189	20037.0700			3	198	20037.8032	R	3(77-0)	12
190	20037.1316	P	5(77-0)	15	199	20037.9514	P	2(77-0)	4
190	20037.131	P	8(78-0)	15	200	20037.9934	R	2(77-0)	6
191	20037.2241	R	5(77-0)	15	201	20038.0923	P	1(77-0)	2
191	20037.257	R	8(78-0)	15	202	20038.117	R	1(77-0)	6
192	20037.4712	P	4(77-0)	10					

202	20038.117	R	1(77-0)	4	210	20038.875	R	7(79-0)	5
203	20038.154	P	6(78-0)	4	211	20038.908	P	4(78-0)	2
204	20038.18	R	0(77-0)	3	212	20038.975	R	4(78-0)	3
205	20038.226	P	8(79-0)	4	213	20039.184	P	3(78-0)	2
205	20038.250	R	6(78-0)	4	214	20039.236	R	3(78-0)	3
206	20038.336	R	8(79-0)	2	215	20039.260	P	6(79-0)	5
207	20038.565	P	5(78-0)	4	216	20039.345	R	6(79-0)	2
208	20038.646	R	5(78-0)	4	217	20039.393	P	2(78-0)	1
209	20038.777	P	7(79-0)	4	218	20039.430	R	2(78-0)	1