Further Analyses of Infrared $^1\Pi \rightarrow {}^1\Sigma$ Bands of $^{89}Y^{127}I$: New Spectroscopic Data on States up to $v'' = 7$ and $v' = 4$

A. Bernard and R. Gravina

Observatoire de Lyon, Université Claude Bernard (Lyon I), Saint-Genis Laval, France, and
Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard (Lyon I),
Villeurbanne, France *

Z. Naturforsch. **39 a,** 27–31 (1984); received November 2, 1983

This paper deals with the extension of a recent study of the infrared $^1\Pi \rightarrow {}^1\Sigma$ emission system of the YI molecule (1). Thanks to the extreme regularity of the structure, rotational analyses can be completed for the previous 3-1, 2-0, 1-0, 0-0 and 0-1 bands and extended to 11 more bands detected step by step from their synthetic spectra (owing to the extremely dense structure). A unique and consistent set of accurate rotational constants is derived for both states, up to the levels $v'' = 7$ and $v' = 4$, from the reduction of 5772 line wavenumbers in the bands 3-1, 2-0, 1-0, 0-0, 0-1, 0-2, 1-3, 2-4, 2-5, 3-6 and 4-7, the v-connected bands being fitted simultaneously. The 57 estimated constants allow to reproduce the observed spectra with typical weighted rms errors between 4 and 5 mK. When using these constants to generate the bands 2-1, 1-2, 3-3, 1-4 and 3-5, ~ 1300 lines can be picked out whose experimental positions relatively to the predicted ones correspond to quite equivalent rms errors with nearly normal distributions of the residuals, therefore ensuring the reliability of the analysis. Molecular constants at equilibrium are derived; improvments are significant, particularly for vibration. Franck-Condon factors and r-centroïds appropriate to RKR potential curves are given. The observed bands correspond to those which are predicted to be the strongest ones in each v'-progression.

1. Introduction

Electronic spectra are known for yttrium halides, YCl with a unique $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ system and YF with seven systems involving 7 singlet states $\Sigma^+(3)$, $\Pi(4)$ and 2 triplet states, Δ, Φ. Of the low-lying $^1\Sigma^+$ and $^3\Delta$ states, the $^1\Sigma^+$ state is believed to be more probably the ground state on the basis of intensity comparisons in absorption. In a recent paper by Bernard, Roux and Vergès (1) (hereafter paper I), it was dealt with the observation and study of an infrared $^1\Pi \rightarrow {}^1\Sigma^{(+)}$ system of $^{89}Y^{127}I$, the first one to have been reported so far for this molecule. The 1-0, 0-0 and 0-1 bands and partially the 2-0 and 3-1 bands were analyzed up to high rotational levels (J values up to ~ 340) thus yielding very precise rotational constants. On the other hand, the extreme density of the line structure – 28 000 lines along the ~ 2000 cm^{-1} extension of the observed spectrum – the wide spread of the branches and strong overlappings, the fact that the intensity maxima in the branches occur near $J = 200$ whereas J-head values (R-branches) are very low ($\nu_H - \nu_0 < 1$ cm^{-1}) did not permit to recognize with certainty more than seven band heads. So, vibrational constants were derived with a relatively low precision. Let us remind also of the difficulty for the very first rotational analysis; in order to establish the relative rotational numbering for the 1-0, 0-0 and 0-1 bands, a computer program was written allowing to explore the many possible combinations between branches and lines and retain the unique one which agreed between 1-0 and 0-0 bands, or between 0-0 and 0-1 bands (R $(J-1)$ – P $(J+1)$ or R (J) – P (J) combinations, respectively).

Fortunately, the structure of the five bands investigated was revealed to be extremely regular, and no perturbations could be inferred in the $v' = 0$, 1, 2 (f), 3 (f) levels within three times the total standard deviation (~ 0.012 cm^{-1}). So, an extension of the analysis of the spectrum could be envisaged, anticipating the same regularity for $v' = 2$ (e), 3 (e) and higher-v' levels. Furthermore, the calculus of Franck-Condon (FC) factors had shown that several other bands could be detected in the range of a proper signal-to-noise ratio of our recordings.

Actually, we could fairly extend in rotation the 1-0, 0-0 and 0-1 bands and complete the 2-0 and 3-1 bands (R and P branches), while analyses for 11 more bands (namely, 0-2, 1-3, 2-4, 2-5, 3-6, 4-7, 1-2, 2-1, 1-4, 3-3 and 3-5) were carried out. Thus, more

---

Reprint requests to Dr. A. Bernard, Observatoire de Lyon, 69230 St.-Genis Laval, France.

* 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France.

accurate or new spectroscopic data up to the levels $v' = 4$ and $v'' = 7$ can now be made available both in rotation and vibration, which correspond to the observation of ~ 7000 line wavenumbers between 10250 and 8850 cm^{-1}. The present paper reports upon the results of these investigations.

Experimental details can be found in Paper I. Let us mention here that the spectrum was excited in a high frequency electrodeless discharge in YI_3 and recorded with the Fourier transform interferometer of Laboratoire Aimé-Cotton (Orsay, France) by Dr. J. Vergès.

2. Analysis and Data Processing

It appeared impossible to dectect with certainty series of R and P lines in bands (other than the 1-0, 0-0 and 0-1 bands), long enough for the J-numbering to be established with the help of the computer program described in Paper I. Thanks to the extreme regularity of the structure of bands and linearity in the vibrational dependence of the parameters it was possible to proceed by calculating the synthetic spectra for new bands on the basis of the constants given in Paper I or extrapolated constants (changing v' or v'' by one unit only) and picking out the lines throughout the observed spectrum. The new bands were then added to the global fitting and improved constants were obtained, thus allowing to proceed further in the same manner. So, step by step, 10 bands (namely, 3-1, 2-0, 1-0, 0-0, 0-1, 0-2, 1-3, 2-4, 2-5 and 3-6) could be fitted simultaneously, yielding a consistent and homogeneous set of parameters. No other bands could be added owing to the capacity limits of the computer. Extrapolation of the constants in both states permitted the analysis of the 4-7 band.

In order to check the reliability of the procedure we calculated the synthetic spectra for 5 more bands (2-1, 1-2, 3-3, 1-4 and 3-5) with large enough FC factors, all involving already known levels. About 1300 lines belonging to these bands were detected, thus confirming the validity of the analysis (see Section IIIa). On the other hand, a similar search for lines in the 4-4 and 5-8 bands was not convincing in the sense that coincidences were too sparse to secure the identifications.

The program used for the reduction of the line wavenumbers to molecular constants has been described in Paper I. Let us recall that the observed line positions in all interconnected bands are fitted simultaneously to calculated term-value differences using an iterative, non linear least-squares procedure thus generating a unique set of parameters. The final adjustments are operated after checking the significance of the parameters within ±2 standard deviation limits ($2\sigma_p$), removing line wavenumbers deviating from their calculated positions by more than three times the total standard deviation (3σ), and weighting each branch with σ_b^{-2} (σ_b^2 being the variance for this branch obtained after a direct fitting with equal weights).

3. Results

a) Rotational Constants

In Tables 1 and 2 are gathered the rotational constants for the states $^1\Sigma$ ($v = 0$ to 7) and $^1\Pi$ ($v = 0$ to 4) respectively, which were obtained after simultaneous fitting of (i) 5356 line wavenumbers in the 3-1, 2-0, 1-0, 0-0, 0-1, 0-2, 1-3, 2-4, 2-5 and 3-6 bands (ii) 416 line wavenumbers in the 4-7 band. Several trials were made in order to check the significance of the small parameters. Thus, a term of the fourth degree in $J(J+1)$ was found to be not significant, as were the differences $T_{v\,(e)} - T_{v\,(f)}$ and $H_{v\,(e)} - H_{v\,(f)}$ in the upper state, in spite of the observation of very high rotational levels (J's up to ~ 410). On the other hand, the difference $D_{0\,(e)} - D_{0\,(f)}$ is found highly significant though the absolute values $D_{0\,(e)}$ and $D_{0\,(f)}$ do not differ within the uncertainty (the 95% confidence limits overlap each other). In the same way, the differences $B_{v\,(e)} - B_{v\,(f)}$ are estimated with

Table 1. Rotational constants (in cm^{-1}) in the $^1\Sigma$ state of YI*.

v	T_v	B_v	$D_v \times 10^8$	$H_v \times 10^{15}$
0	0	0.04216122(98)	0.64929(74)	−0.2655
1	214.7887 (9)	0.04204859(97)	0.64943(74)	−0.2711
2	428.7546(17)	0.04193622(98)	0.64964(75)	−0.2771
3	641.9050(11)	0.04182386(98)	0.64985(74)	−0.2821
4	854.2372(20)	0.04171173(98)	0.65009(74)	−0.2880
5	1065.7621(20)	0.04159957(98)	0.65021(74)	−0.2964
6	1276.4746(25)	0.04148754(99)	0.65038(78)	−0.2985
7	1486.3681	0.0413751 (53)	0.6505 (59)	−0.3069

* Numbers in parentheses represent the uncertainty $2\sigma_p$ (twice the standard deviation on the estimated value of the parameter) in units of the last quoted digit. In the final fitting some parameters were kept fixed to the values given without indication of $2\sigma_p$ (see text, § IIIa). The value $T_{v=7}$ has been extrapolated.

Table 2. Rotational constants (in cm^{-1}) in the $^1\Pi$ state of YI*.

v	T_v	B_v	$D_v \times 10^8$	$H_v \times 10^{15}$
0	9 905.5210 (7)	(e) 0.03985576 (97) (f) 0.03985826 (98)	0.69072 (73) 0.69092 (74)	− 0.3883(31)
1	10 096.8497 (7)	(e) 0.03974059 (98) (f) 0.03974291 (98)	0.69109 (74)	− 0.3981(36)
2	10 287.3781(17)	(e) 0.03962561 (98) (f) 0.03962794 (98)	0.69166 (74)	− 0.395 (13)
3	10 477.1202(21)	(e) 0.03951017(100) (f) 0.03951255(100)	0.69143(107)	− 0.410 (83)
4	10 666.0493(17)	(e) 0.0393949 (53) (f) 0.0393973 (53)	0.6920 (59)	− 0.410 (29)

* Numbers in parentheses represent the uncertainty $2\sigma_p$ (twice the standard deviation on the estimated value of the parameter) in units ot the last quoted digit. The T_v-values originate from the $^1\Sigma$ ($v = 0$) state.

much more accuracy than the individual constants. This is to be attributed to the very strong correlations which exist between these related parameters (in all cases the correlation coefficients are greater than 0.99995), so that the precisions on these differences can be determined by keeping one of the constants fixed to its final value, the other one being free to vary. So, the Λ-type splittings in the upper $^1\Pi$ ($v = 0$ to 4) levels (i.e., $B(\Pi^+) - B(\Pi^-) = B(\mathrm{R,P}) - B(\mathrm{Q})$ if Σ^+ lower state is assumed) can be expressed accurately as

$$F_{0(e)}(J) - F_{0(f)}(J) = -0.24982(70) \times 10^{-5} J(J+1) - 0.206(27) \times 10^{-11} J^2 (J+1)^2,$$

$$F_{1(e)}(J) - F_{1(f)}(J) = -0.23191(77) \times 10^{-5} J(J+1),$$

$$F_{2(e)}(J) - F_{2(f)}(J) = -0.23386(91) \times 10^{-5} J(J+1),$$

$$F_{3(e)}(J) - F_{3(f)}(J) = -0.23861(193) \times 10^{-5} J(J+1),$$

$$F_{4(e)}(J) - F_{4(f)}(J) = -0.2340(27) \times 10^{-5} J(J+1).$$

Strong correlations also exist between H constants in the lower states and H constants in the upper states with individual values which are determined only very roughly. It appeared better in view of obtaining constants of more realistic physical meaning in the final adjustment, to keep all the H'' ($v = 0$ to 7) parameters fixed to theoretical values, the quality of the adjustment remaining quite equivalent. To this end, we used a computational method elaborated by Hutson (2) for calculating centrifugal distortion constants for diatomic molecules from a numerically specified potential curve (Rydberg-Klein-Rees potentials, in the circumstances). The values H_v'' ($v = 0$ to 7) so obtained are in Table 1. The adjusted H_v' constants are found very close to the theoretical ones as are the D_v' and D_v'' constants (see § III b).

The resulting optimum set of 57 rotational constants allows to reproduce the measured line wavenumbers to within a weighted standard deviation of $0.0039\ \mathrm{cm}^{-1}$ ($0.0049\ \mathrm{cm}^{-1}$ for the 4-7 band) with a nearly normal distribution of the residuals (Figure 1). Moreover, these constants when used to generate the five bands (2-1, 1-2, 3-3, 3-5 and 1-4) chosen to serve as a check of the analysis reproduce

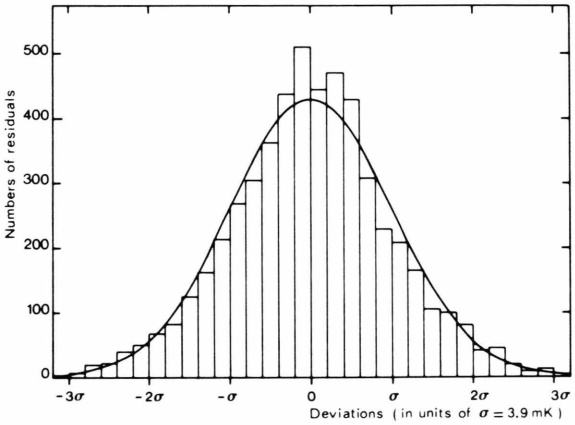

Fig. 1. Histogram of the distribution of the residuals between observed and calculated line wavenumbers for the final multiband fitting. The solid curve is a normal distribution: $\Phi(x) = \dfrac{n\,l}{\sigma\sqrt{2\pi}} \exp\left[-\dfrac{1}{2}\left(\dfrac{x}{\sigma}\right)^2\right]$, with $n = 5356$, $l = \sigma/5$, $\sigma = 0.0039\ \mathrm{cm}^{-1}$.

~ 1300 experimental line wavenumbers in these bands with accuracies comparable to the statistical errors. For example, the differences between the 265 observed line positions in the 3-5 band and the generated ones correspond to a standard deviation of 0.0054 cm^{-1} with a moderate departure from normality of their distribution (Figure 2); only a small systematic shift ($\sim \sigma/4$) can be observed. Thereby, on the basis of these results the reliability of the entire analysis can be ensured.

Table 3. Equilibrium constants (in cm^{-1}) for the $^1\Sigma$ and $^1\Pi$ electronic states of YI*.

Parameter	$^1\Sigma$	$^1\Pi$
T_e	0	9917.254
ω_e	215.598	192.128
$\omega_e x_e$	0.408	0.399
B_e	0.0422171	0.0399147
$\alpha_e \times 10^3$	0.11227	0.11522
$D_e \times 10^8$	0.6492 (0.6474)	0.6907 (0.6891)
$\beta_e \times 10^{11}$	0.19 (0.25)	0.29 (0.36)
$H_e \times 10^{15}$	... (− 0.262)	− 0.385 (− 0.376)
$\alpha_H \times 10^{17}$	... (0.58)	0.64 (0.75)
r_e (Å)	2.7637	2.8423

* Centrifugal distortion constants calculated from Hutson's method are given in parentheses. The constants α_e and β_e have the usual definitions (3); α_H results from $H_v = H_e - \alpha_H (v + 1/2)$.

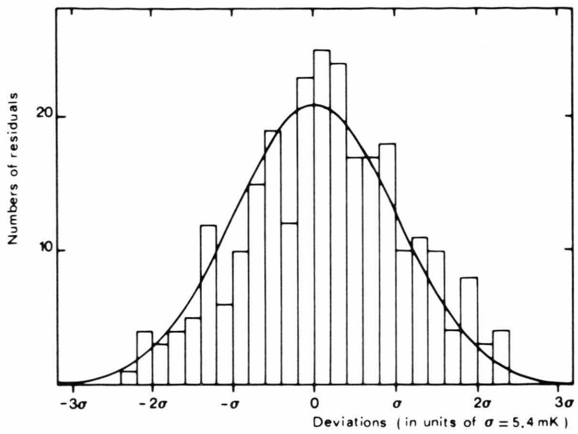

Fig. 2. Histogram of the distribution of the residuals between the observed line wavenumbers in the 3-5 band and the recalculated ones when using constants quoted in Tables 1 and 2. Here: $n = 265$, $l = \sigma/5$, $\sigma = 0.0054\ \mathrm{cm}^{-1}$.

b) Equilibrium Molecular Constants

The molecular constants relative to the equilibrium positions in the $^1\Sigma$ and $^1\Pi$ states are given in

Table 4. Franck-Condon factors and r-centroïds for the infrared band system of YI. [a]

v'	v''								
	0	1	2	3	4	5	6	7	8
0	0.376 0.337^b 2.804	0.380 0.380^b 2.847	0.179 0.200^b 2.890	0.053 0.065 2.935	0.011 0.015 2.981	0.002 0.003 3.028	0.000 0.000 3.076	0.000 0.000 3.126	0.000 0.000 3.178
1	0.354 0.352^b 2.766	0.000 0.003 2.858	0.210 0.170^b 2.852	0.261 0.263^b 2.896	0.129 0.150^b 2.940	0.037 0.050 2.986	0.007 0.011 3.033	0.011 0.018 3.081	0.000 0.000 3.130
2	0.180 0.197^b 2.729	0.171 0.133^b 2.772	0.087 0.116 2.812	0.045 0.019 2.859	0.227 0.199^b 2.901	0.190 0.205^b 2.945	0.077 0.097 2.990	0.019 0.028 3.037	0.003 0.006 3.086
3	0.065 0.079 2.693	0.227 0.221^b 2.735	0.024 0.007 2.780	0.162 0.166^b 2.818	0.000 0.010 2.814	0.139 0.097^b 2.906	0.214 0.210^b 2.950	0.121 0.143 2.995	0.038 0.053 3.042
4	0.019 0.025 2.658	0.139 0.155 2.699	0.163 0.131 2.740	0.005 0.021 2.771	0.145 0.117 2.823	0.037 0.066 2.862	0.055 0.023 2.913	0.198 0.172^b 2.955	0.158 0.176 3.000
5	0.005 0.007 2.624	0.058 0.072 2.663	0.173 0.174 2.704	0.072 0.039 2.746	0.053 0.081 2.783	0.081 0.045 2.829	0.091 0.115 2.869	0.008 0.000 2.925	0.154 0.113 2.960

[a] First entry: rotationless FC factor; second entry: FC factor, $J = 300$ (Q-branch); third entry: rotationless r-centroïd (Å).
[b] Analyzed band.

Table 3. They result from linear adjustments of the rotational constants as functions of $v + 1/2$. A quite excellent agreement appears when one compares the observed centrifugal distortion constants D_v'', D_v' and H_v' to the theoretical ones derived from the method of Hutson and expressed with the linearly fitted coefficients in parentheses.

Relatively to the values published in Paper I those of the vibrational parameters are improved the most significantly, in particular ω_e and $\omega_e x_e$, while $\omega_e y_e$ does not appear necessary.

c) *Franck-Condon (FC) Factors and r-Centroïds*

In order to get a further check of the consistency of the analysis on the intensity distribution in the system, RKR potentials were evaluated for both states and FC factors $q(v', v'')$ were calculated. Rotationless *FC* factors and r-centroïds are reported in Table 4 together with *FC* factors for larger rotation ($J = 300$) in the range $0 \leqq v' \leqq 5$, $0 \leqq v'' \leqq 8$. The rotational dependence of the *FC* factors in the analyzed bands is rather small or moderate. So, in the 0-0 band the *FC* factor for the Q-branch decreases by ~10% from $J = 0$ to $J = 300$ (~5% from $J = 0$ to $J = 200$). Similarly, $q(1, 2)$ and $q(2, 1)$ decrease by ~19 and 22% from $J = 0$ to $J = 300$ (8 and 10% from $j = 0$ to $J = 200$). On the other hand, increases of $q(2, 0)$, $q(0, 2)$ and $q(1, 4)$ by ~10, 12 and 16% are observed from $J = 0$ to $J = 300$ (~4, 6 and 8% from $J = 0$ to $J = 200$).

Finally, it appears very satisfactory that the bands which could be detected and analyzed are indeed those which are predicted to be the strongest ones in each v'-progression.

[1] A. Bernard, S. Roux, and J. Vergès, J. Molec. Spectrosc. **80,** 374 (1980).
[2] J. M. Hutson, J. Phys. B **14,** 851 (1981).
[3] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 1, Spectra of Diatomic Molecules, Van Nostrand, New York 1950.