

DETERMINATION OF THE ROTATIONAL TEMPERATURE USING PHOTODIODE ARRAY SPECTROMETER¹⁾

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A method for the rotational temperature calculation from the partially resolved multichannel emission spectra of diatomics has been developed. The experimental spectra are taken using a selfscanning photodiode array spectrometer and the procedure is based on computer simulated rotational structure of the vibronic band. The program searches for a suitable parameter T by which the simulated bandprofile would correspond to the experimental one as much as possible. The proposed method was verified using the partially resolved structure of the $(0,0)$ sequence of the first negative system of the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$.

I. INTRODUCTION

Linear photodiode array detectors (PDA) have been used as effective analytical tools in experimental spectroscopy for twenty years. The PDA mounted horizontally in the exit focal plane of the monochromator enables simultaneous detection of the whole spectral region of interest with a large dynamic range, linear response, low noise and temporal as well as thermal stability. The principle, operational characteristics and scientific applications have been reviewed recently by many authors [1-3].

For diagnostics purpose (e.g. plasma temperature measurements) an understanding of the detected lineprofiles (or bandprofiles) is necessary. In case of the PDA spectrometer an instrumental lineshape is defined both by the instrumental function of the grating monochromator and the response function of the PDA. This response function may generate some errors in the detected spectra which can be reduced both by the right selection of the slit width and correct analysis [4,5].

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II. DETECTION SYSTEM

An integrated spectrometric system used for experiments (Instruments SA / Jobin-Yvon) consists of a monochromator, a PDA detectorhead and the control centre SPECTRALINK which is interfaced to an IBM/AT compatible computer [6]. The monochromator used is the J. Y. model HR-320, with the Czerny-Turner mount ($f=0.320$ m). The gratings used are 58×58 mm holographic grating 2400 lines/mm and ruled grating 1200 lines/mm (blaze 500 nm). The PDA detector used is a thermoelectrically cooled Reticon model RY/1024 (array of 1204 photodiodes $13 \mu\text{m}$ wide mounted on $25 \mu\text{m}$ centres, each with a height of 2.5 mm [1]). The data acquisition, data management and monochromator control are performed using the I.S.A./J.Y. Enhanced Prism Software package (version 2.2.).

III. SLIT WIDTH AND "SHIFT" EFFECTS

Correct analysis requires understanding the way of generating the band profile by the whole spectrophotometric system. If we assume that for the medium resolution monochromator the line profile in the exit focal plane is given by instrumental broadening, the band profile picture on the PDA can be written:

$$i(\lambda, T, W) = \sum_N I_N(T) g(\lambda - \lambda_N, W), \quad (1)$$

where T is a rotational temperature, λ_N the rotational line wavelength for the rotational quantum number N , W is the entrance slit width, g is the instrumental function of the monochromator, I_N is the intensity of the rotational line.

The whole surface of the PDA is photosensitive but only the p -type regions (diodes) can accumulate the charge produced by the incident light. The charge produced in the n -type regions is divided between the adjacent diodes [1]. The response function of the PDA is shown in Fig. 1. Thus each element of the PDA integrates the radiant energy in a small spectral interval of the band and the signal registered by the i th diode can be expressed:

$$I_i(T, W, \delta) = \int_{\lambda_i - \epsilon}^{\lambda_i + \epsilon} i(\lambda + \delta, T, W) R_i(\lambda - \lambda_i) d\lambda, \quad (2)$$

where R_i is an aperture function and λ_i is the centre wavelength of the i th diode, 2ϵ is a spectral width of a single photodiode, δ is a "shift" constant representing an intensity misregistration error [4]. This intensity misregistration error resulting from the redistribution of the charge produced in the n -type region can noticeably affect the observed bandshape.

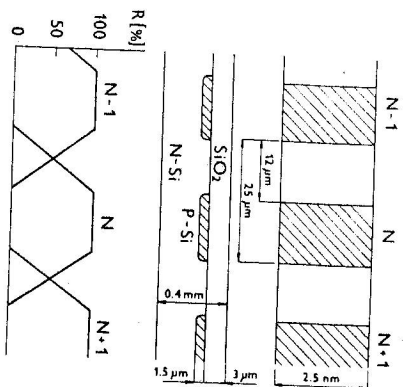


Fig. 1. Geometry and the response function of the PDA.

IV. PROGRAM DESIGN

The technique is based on the computer simulated bandprofile for a given experimental configuration. The bandprofile is calculated according to Eqs. (1) and (2):

$$I_i(T, W, \delta) = \sum_{\lambda_j = \lambda_i + \epsilon}^{\lambda_j = \lambda_i - \epsilon} \left\{ \sum_N I_N(T) g(\lambda_j + \delta - \lambda_N, W) R_i(\lambda_j - \lambda_i) \right\}, \quad (3)$$

where $\Delta\lambda_j \ll \Delta\lambda_i$. The program searches for parameter $T \equiv T_{rot}$ with which the simulated profile corresponds as much as possible to the experimental one. Figs. 2a-2c demonstrate the band simulation procedure (for illustration a part of the R-branch of the (0,0) sequence of 1. neg. syst. of the N_2^+ was used).

Step 1: Stick spectrum (set of intensities of individual rotational lines I_N) is evaluated (Fig. 2a).

Step 2: The diffraction band profile using the instrumental function of the monochromator is calculated (Fig. 2b).

Step 3: The PDA profile is calculated taking into account the response function of the PDA (Fig. 2c).

Mean relative deviation was used as the criterion of the best fitting:

$$S(T, W, \delta) = \frac{1}{n} \sum_{i=1}^n |(f_i - y_i)/y_i|, \quad (4)$$

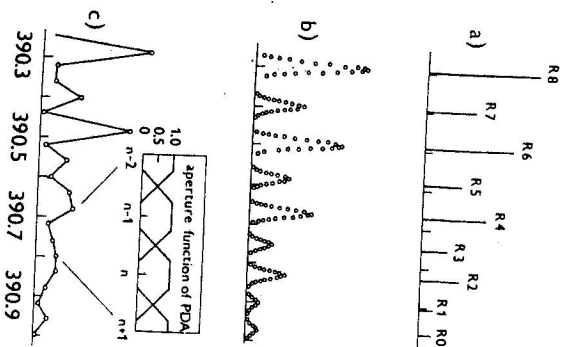


Fig. 2. Band profile generation.

where y_i is the set of experimentally observed spectrum intensities, $f_i = f_i(T, W, \delta)$ represent the simulated spectrum.

Spectra are normalized according to:

$$\sum y_i = \sum f_i. \quad (5)$$

The temperature calculation is an iterative process of searching for T, W and δ to minimize $S(T, W, \delta)$. The rate of convergence strongly depends on the initial estimates of T, W, δ .

V. RESULTS AND DISCUSSION

The emission from an rf low pressure discharge (13.56 MHz, ~ 40 W, ~ 0.1 torr) in pure nitrogen (99.998%) was taken as the reference spectrum (Fig. 3). The spectrum was acquired under the same conditions using twelve different entrance slit widths (30, 50, 70, 90, 110, 130, 150, 200, 250, 300, 400, 500 μm). The prominent 1_1 negative system of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and especially the (0, 0) sequence seems to be the most suitable spectrum both for numerical simulation [7] and verification of

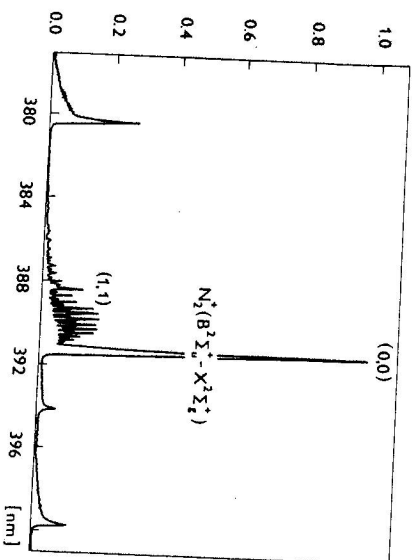


Fig. 3. Spectrum of the rf low pressure nitrogen discharge.

the equation (3). Fig. 4 shows a partially resolved bandshape of the (0, 0) sequence for three different entrance slit widths (holographic grating 2400 lines/mm).

As a test of the accuracy of the algorithm, the rotational temperatures from different entrance slit width data were calculated. The single rotational line intensities $I_N(T)$ in the expression for the bandprofile (3) were generated according to:

$$I_N^P(T) = A(N) \exp \left[-\text{const} \frac{F'(N+1)}{T} \right], \quad (6)$$

$$I_N^R(T) = B(N) \exp \left[-\text{const} \frac{F'(N-1)}{T} \right], \quad (7)$$

with

$$A(N) = g^l(N) \cdot \nu_R^4(N+1), \quad N = 0, 1, 2, 3, \dots, \quad (8)$$

$$B(N) = g^l(N) \cdot \nu_R^4(N), \quad N = 0, 1, 2, 3, \dots, \quad (9)$$

and

$$\text{const} = \frac{hc}{k},$$

where F' is the wavenumber of the upper rotational level, g^l is the nuclear statistical weight taking into account an alternation in the intensities of rotational lines for homonuclear molecules [8], $\lambda_{R,P}$ are the rotational line frequencies in the R or P branches (the line splitting caused by interaction between the electron spin and the nuclear rotation is not taken into account), $(N+1)$ and (N) are the Hönl-London



Fig. 4. Shape of the (0,0) sequence for different entrance slit widths.

factors for the R and P branch (given as a sum of the Hönl-London factors of their main and satellite components) [7].

As the instrumental function of the monochromator, the function

$$g(\Delta\lambda) = \begin{cases} 0 & \text{if } |\Delta\lambda| > \frac{1}{2}\omega\sqrt{a} \\ \frac{a - (2\Delta\lambda/\omega)^2}{a + (a - 2)(2\Delta\lambda/\omega)^2} & \text{if } |\Delta\lambda| \leq \frac{1}{2}\omega\sqrt{a} \end{cases} \quad (10)$$

was used [9,10]. The corresponding line shape has the width at half maximum of ω and wings extending to $\pm \frac{1}{2}\omega\sqrt{a}$.

The same initial estimates of T and δ were used for all the slit width values and the iteration was stopped after three cycles.

The iteration converged always to the same temperature $T = (860 \pm 35)K$. The minimum of $S(T, W, \delta) = 0.099$ was attained for $W = 110\mu m$. Strong dependency of $S = S(\delta)$ was verified.

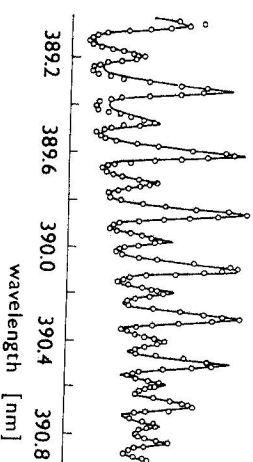


Fig. 5. Part of the observed and the simulated band profile.

IV. CONCLUSION

The technique for determining the rotational temperature from partially resolved multichannel PDA's spectra has been described. Test with a (0,0) band of the first negative system of N_2 shows that Eq. (3) is correct and could be used, with appropriate data, to calculate rotational temperature from PDA's emission spectra of many diatomic molecules.

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ОПРЕДЕЛЕНИЕ РОТАЦИОННОЙ ТЕМПЕРАТУРЫ С ПРИМЕНЕНИЕМ СПЕКТРОМЕТРА НА ФОТОДИОДНОЙ СБОРКЕ

В работе приводится метод расчета ротационной температуры на неполнотью размеренных эмиссионных диаграммных спектров. Экспериментальные спектры получены с применением спектрометра со самосканвирующей фотодиодной сборкой. Процедура обработки основана на компьютерной симуляции ротационной структуры вибрационных полос. Величину параметра T определяет программа на основании сходства симулированной и экспериментальной структуры полос.