JOURNAL OF COMPUTATIONAL PHYSICS 4, 424–426 (1969)

A Fortran Program to Analyze the Rotational Structure of Diatomic Molecules

The great amount of data handled in the study of molecular spectra makes the application of digital computers to the different steps in the analysis of band spectra imperative. These steps can be summarized as follows: 1) the measurement and reduction of plate positions to wavelengths and wavenumbers; 2) the picking out of branches; 3) the assignment of the rotational quantum numbers; and 4) the calculation of constants. This paper will deal only with the second step.

Two previous papers [1, 2] have treated this problem, and as far as we know, their programs are available for use with large core storage machines such as the IBM 7090 or CDC 6400. Although many interesting features can be introduced into these programs, their nominal speed is reduced in practice because of their limited availability. In Berkeley, for example, the usual turnaround time is more than four hours with the CDC 6400, and breakdowns are not infrequent.

Our version makes use primarily of the ideas given in ref. [1], employing Fortran II language, and fitting perfectly the 20 k core storage of an IBM 1620 II, which is run by the users themselves.

The difference in wavenumber between two consecutive lines of a molecular spectrum can be written as (3):

$$\sigma_{m+1} - \sigma_m = 2B' + 2m(B' - B''). \tag{1}$$

The notation is the familiar one used in molecular spectroscopy. Eq. (1) is solved for the parameters B' and B'' in our program.

The main technique used is the least-squares fitting of the wavenumbers of the lines. Provision has been made to take into account perturbations. This may involve the position of the line, its intensity, or both at the same time. So the program can, if desired, instruct the machine to keep calculated wavenumbers or averaged intensities, using the figures belonging to lines already picked out. The number of these adopted "lines" can be varied. According to our experience, we feel that the retention of more than one is unwise when one has picked out only a short portion of the branch, and only two of them should be used for the whole branch.

The branch picked out may contain up to 25 lines, and, if this number is reached, the search will stop for the particular parameters used. These parameters may be changed, and, if so, the procedure repeated. When the 25 (or less, if specified) lines are found, the machine will punch the parameters used, the wavenumbers of the lines picked out, and their intensities, for the branch found. To display the branch

with first and second differences and the averaged second difference with its standard deviation, we use a separate program. If stored on disk this program can be executed at once, feeding the reader with the previous output as it comes, with just the control cards ahead.

One of us (CBS) has used this program extensively to analyze the branches of LaO^{16} and LaO^{18}. A typical result is shown in Table I for the 0–0 band at 5600 A of LaO^{18}. In the row after the title the parameters used are given. $P = 2B'$ has been varied between 0.50 and 1.20 cm^{-1}, with an adopted error $\Delta P = (B' - B'') = 0.01$ cm^{-1}, in intervals of 0.04 cm^{-1}. The error of measurement, which is taken into account in this program, is 0.02 cm^{-1}. The minimum number of lines asked for was 15, but all 25 were found. Although two adopted "lines" were instructed to be kept, none was adopted. Since 104 lines and their intensities can be fed to the com-

TABLE I

LAO BANDA 0–0 5600 (0.50–1.20) ZONA 17840–17816 AGO 9 1968 NUM. 86
$P = .62$ DEL $P = .01$ DELF = .02 DELL = .02
NU = 104 PASO = .04 COTA = 1.20 IMAG = 2 PRINT = 25

SIGMA	DIF. PRIMERA	DIF. SEG.	INT.
17837.184			333.
17836.573	.61	0.000	304.
17835.962	.61	.036	339.
17835.315	.64	.015	304.
17834.653	.66	.023	314.
17833.968	.68	.020	301.
17833.263	.70	.020	317.
17832.538	.72	.037	304.
17831.776	.76	.014	314.
17831.000	.77	0.000	298.
17830.224	.77	.067	298.
17829.381	.84	−.018	310.
17828.556	.82	.029	282.
17827.702	.85	.023	272.
17826.825	.87	.043	339.
17825.905	.92	−.005	298.
17824.990	.91	.032	272.
17824.043	.94	.042	317.
17823.054	.98	.004	314.
17822.061	.99	.038	291.
17821.030	1.03	−.015	310.
17820.014	1.01	.050	339.
17818.948	1.06	−.009	333.
17817.891	1.05	.010	314.
17816.824	1.06		358.

PROMEDIO = .01 DESV. STANDARD = .02 LINEAS TOTALES = 25

puter, different versions of the same branch (not shown here) were found beginning at different points in the list of wavenumbers. For the case shown about three minutes time was necessary for the computation.

CONCLUSION

The program we have written to analyze molecular spectra has been used extensively, proving to be reliable in picking out branches of rather complex band spectra such as those of the green-yellow systems of LaO^{16} and LaO^{18} and also of less complex systems in the red of both spectra. Since the program fits small computers, the lack of big machines is not important. Even with these, the authors feel the saving of time (and money) is considerable with the program described in this paper, since the results are obtained in a short time. Also the results can be checked much faster. The number of lines that can be picked out may seem limited. However, if the lines are too numerous, Eq. (1) does not hold, and higher degree polynomials must be used in the fitting. In such a case the program will lose its simplicity.

The program can be requested from the authors.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Dr. David Goorvitch (NASA-Ames Research Center) for reading and correcting the manuscript.

REFERENCES

1. J. G. PHILLIPS, *Astrophys. J.* **130**, 308 (1959).
2. S. P. DAVIS AND J. G. PHILLIPS, "The Red System of the CN Molecule." University of California Press, Berkeley and Los Angeles, 1963.
3. G. HERZBERG, "Molecular Spectra and Molecular Structure," Vol. I, p. 169. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1950.

RECEIVED: October 2, 1968

CARLOS B. SUÁREZ*
Department of Physics,
University of California, Berkeley 94720

MARIO GALLARDO
Departamento de Física,
Universidad Nacional de la Plata,
La Plata, Argentina

* Post-doctoral fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, during 1966-68 at the University of California, Berkeley, California. Present address: Departamento de Fisica, Universidad Nacional de La Plata, C.C. 67—La Plata, Argentina.