Note

A FORTRAN Program for Rotational Analysis of the Spectra of Diatomic Molecules

The analysis of electronic spectra of diatomic molecules is a complex and time-consuming work. For this reason the application of an electronic computer to different steps of the analysis of experimentally obtained spectra can be divided into four steps: (1) reduction to wavelengths and wavenumbers of the measured rotational lines on the plate; (2) identification of branches in a band; (3) assignment of rotational quantum numbers; and (4) calculation of different molecular constants.

Since the first paper by Phillips [1], who developed a program for the first and second steps, several papers have treated this problem [2, 3, 5], including the elaborate program of Kataev and Mal'tsev [4] for the Soviet M–50 computer.

The program described here was developed for a CDC–3600 computer and enables us to carry out the last three steps mentioned above. It has been applied to the rotational analysis of the $^2\Pi$–$^2\Sigma$ transition of the CO^+ molecule.

The method developed here is based on the following assumptions: (1) the centrifugal distortion and the difference between rotational constants, which is due to the Λ-type doubling in terms where $\Lambda \neq 0$, can be neglected in singlet and multiplet terms; and (2) in multiplet terms each subsystem can be expressed as a singlet term with different B constants.

The first assumption can be applied to heavier molecules up to relatively high rotational quantum number J, without resulting in a significant departure, whereas in the case of light molecules it is applicable only to low J values.

By this assumption the difference $\delta\nu$ (cm^{-1}), between two successive lines in a branch is given by the relation

$$\nu_{J+1} - \nu_J = mB' + 2(B' - B'')(J + n), \tag{1}$$

where m and n are constants and depend on ΔJ, $\Delta\Lambda$, and $\Delta\Sigma$. The variables B' and B'' are rotational constants of corresponding terms, and ΔJ, $\Delta\Lambda$, and $\Delta\Sigma$ have the usual meanings in molecular spectroscopy [6].

At the beginning of the operation, the computer reads the following input data: wavenumbers of measured lines, initial values for the coefficients a ($a = mB'$) and b ($b = 2(B' - B'')$), ordered steps δa and δb for a and b, respectively, and numbers iterations for a and b. In this way the intervals $[a, a + \Delta a]$ and $[b, b + \Delta b]$, which include the true values for a and b, are determined. Some previous knowledge of

432

the order of magnitude of the rotational constants is necessary. The ranges Δa and Δb are chosen in advance, and are based on the known variations of their magnitudes. The given values of the constants a and b are varied until five successive lines satisfy Eq. (1) with required accuracy. At the same time, the rotational quantum numbers for these lines are determined. The error, $\Delta \nu$, depends on the accuracy of the line measurements as well as on the undetermined constants a and b. It can be shown that $\delta a/2$ and $\delta b/2$ are the uncertainties of a and b, respectively.

Using experimental values of the wavenumbers of previously sorted lines, the computer calculates, by the least-squares method, the coefficients a and b, their errors, the wavenumber of the next line, and the error $\Delta \nu$. If for some reason there are no measured lines in the interval $\Delta \nu$, the computer employs the calculated line value and uses it in a further procedure. If there are several lines in the ordered interval the computer accepts as the true line the one nearest to that calculated, namely the line from the $[\nu \pm \Delta \nu]$ interval with the minimum rms value. If there are not five successive lines in the spectrum, the computer begins to sort out the lines for $J \leqslant J_{\text{head}}$, namely, to search through the vertex of the branch. In this part of the program the computer uses the last calculated values of a, δa, b, and δb. This operation terminates the program and depending on the instruction, the cycle can be applied to another branch or the program is ended.

The analysis of the red-degraded (0,2) band of the $A^2\Pi - X^2\Sigma$ system of the CO^+ molecule was used to test the performance of the program. The spectrum of this band system was obtained at a dispersion of 0.4 $\mathring{A}$/mm. The band of this transition consists of 12 overlapped branches, and more than 400 lines in the investigated region. The running time for one band is about three minutes. For example the following values of the parameters were used in the analysis: For the R_{21} branch, $a = 5.7$, $\delta a = 0.1$, $b = -0.6$, $\delta b = -0.1$, $\Delta a = 0.4$, $\Delta b = -0.4$; and for the R_2 branch, $a = 1.9$, $\delta a = 0.05$, $b = -0.6$, $\delta b = -0.1$, $\Delta a = 0.4$, $\Delta b = -0.4$. We assume that $J_{\text{head}} \leqslant 10.5$ for both the R_{21} and R_2 branches.

The present program has been tested in a number of cases representing unperturbed rotational levels of the $^2\Pi-^2\Sigma$ transition with various initial values and step size values for the constants a and b. The step has been varied from 0.01 to 0.2 cm^{-1}. The constant a has been varied from 0.5 to 1.0 of its true value, and the initial value of the constant b has been varied from 0.0 to 0.6 cm^{-1}. In all of these cases the correct branch has been selected and the rotational quantum numbers have been correctly assigned.

The program can be obtained from the authors.

References

1. J. G. PHILLIPS, *Astrophys. J.* **130** (1959), 308.
2. S. P. DAVIS AND J. G. PHILLIPS, "The Red System of the CN Molecule," University of California Press, Berkeley, 1963.
3. N. ASLUND, *Arkiv Fysik*, **30** (1965), 377.
4. D. I. KATAEV AND A. A. MAL'TSEV, *Zhurn. Prikl. Spektroskopii*, **6** (1967), 777; **8** (1968), 113, 401.
5. C. B. SUAREZ AND M. GALLARDO, *J. Comp. Phys.* **4** (1969), 424.
6. G. HERZBERG, "Molecular Spectra and Molecular Structure," Vol. 1, Van Nostrand, Princeton, N.J., 1950.

B. R. VUJISIĆ
D. S. PEŠIĆ

Institute of Nuclear Sciences "Boris Kidrič"
Vinča, Belgrade, Yugoslavia