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THE APPLICATION OF SPREADSHEET PROGRAMS FOR ANALYSIS OF VIBRATION-ROTATIONAL BANDS

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ABSTRACT

The use of commercially produced spreadsheets is demonstrated to be an efficient and rapid method for the determination of the spectral parameters of a vibration-rotational band with resolved fine structure.

INTRODUCTION

Even if the rotational analysis of vibrational bands of polyatomic molecules in gaseous samples is not the primary objective of measurements of absorption spectra, occasionally one finds that even under only moderate resolution some rotational structure is discernible although not necessarily completely resolved. In such cases some analysis of the band may lead not only to a more definite assignment of the type of vibrational mode but also to some information about the molecular structure or conformation. For these cases, a rapid and accurate method of analysis of the observable fine structure is desirable.

Although spreadsheet programs operating on common microcomputers may have been intended originally for applications in business and economics, their applicability to scientific and technical problems was soon recognised[1]. A *spreadsheet* is a computer program which provides for use of a matrix or array of cells to store objects between which the interrelations are to be defined. The *cells* can contain numbers, labels, comments, formulae or definitions of functions. By means of such cells, the programs can be instructed to evaluate sequences, formulae and instructions once only, or repetitively, so as to resolve recursive features of relations defined by the user. Further useful features of spreadsheet programs are the provision of regression and convenient graphical display of results. We here demonstrate how these capabilities can be applied to the vibration-rotational analysis of molecular spectra.

PROCEDURE

For the purpose of demonstration, we describe the application of the spreadsheet to the case of a gaseous sample of diatomic molecules in $^1\Sigma$ electronic states. Additional complications arise for polyatomic molecules and for other electronic states, but obvious modifications of this procedure may be applied. We therefore suppose that we have measured the frequencies (or wavenumbers) of the lines in the P and R branches of a particular vibration-rotational band, to each line of which we assign the value of the rotational quantum number J for the vibrational state of lesser energy. The two primary columns, B and C for instance, of the spreadsheet contain the numerical values of these frequencies, the values of R(J) and P(J) for a given value of J being in the same row. The column A contains the consecutive non-negative integers that are the corresponding values of J in each row. The combination difference R(J)-P(J) in column D is formed simply by direct subtraction of adjacent values in columns B and C, for instance by using the formula "+B5-C5" followed by the command "/copy" to duplicate this formula to all cells of this column. The other combination difference R(J-1)-P(J+1) and the sum R(J-1) +P(J) in columns E and F respectively are analogously formed by the formulae "+B4-C6" and "+B4+C5" followed by the copy commands. The heading placed above each column denotes its content.

The determination of the band parameters is best done by means of standard regression techniques[2]. For this purpose, for the two combination differences as dependent variables the independent variables are $(J+\frac{1}{2})$ to various odd powers. To the values of J in column A are added 0.5 in column G; then the latter values are raised to the powers 3, 5 etc., in separate columns, as many as required. For the combination sum as dependent variable, the independent variables are J^2, J^4 etc. appropriately formed in further separate columns. At this point the spreadsheet is sufficiently constructed. Invocation of the regression command, followed by the specification of the Y range (the column of the dependent variable) and the X range (one column or more, as required, starting from one degree and then increasing) initiates the quantitative determination of the spectral parameters. The constant term is constrained to be zero for the combination difference relations[3], such as

$$R(J)-P(J) = (4B'-6D')(J+\tfrac{1}{2}) - 8D'(J+\tfrac{1}{2})^3 + \ldots$$

but not zero for the combination sum,

$$R(J-1)+P(J) = 2\nu_0 + 2(B'-B''-D'+D'')J^2 + \ldots$$

in which case the constant term is proportional to the value of the band centre ν_0. The best indicator of the goodness of fit is the F value, but this statistical parameter[4] is not directly provided by most existing spreadsheets. In its absence, the basis of selection of the appropriate model for regression may be the sample correlation coefficient r (or its square r^2), the standard deviation of the fit, or the standard error of the derived parameters in relation to the magnitudes of the corresponding parameters and the known or estimated errors of frequency measurement. To derive the values of the spectral parameters, such as B' and D' in the combination difference relation above, from the regression coefficients, such as (4B'-6D') and -8D', we can use matrix inversion and then multiply the coefficients to solve the simultaneous equations.

Finally, plots of the combination differences or sum, or the deviations between these quantities and the calculated values on the basis of the values of the spectral parameters B', D', ν_0 etc. derived from the regression coefficients, can be automatically generated with a few further simple commands.

CONCLUSIONS

A commercial spreadsheet program, such as LOTUS 1-2-3, EXCEL or QUATTRO that is commonly available for microcomputers, may be usefully applied to rotational analysis of vibrational bands of gaseous samples in absorption, emission or scattering spectra, each step operating as described above. Furthermore we have confirmed that the accuracy of the spectral parameters (provided by LOTUS 1-2-3 version 2.2 for instance) is equivalent to that obtained through the use of more conventional regression programs[5] that supply adequate statistical precision, but the latter procedures involve much more work in transferring data as input and output. Beginning with the typing of lists of frequencies of the spectral lines and ending with the plots (on the monitor) of the combination differences, sum and the deviations between calculated and observed values, a spreadsheet thus enables the entire analysis of one band in only half an hour. The method is useful not only in research applications but also in the teaching of molecular spectroscopy.

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