

DIRECT DETERMINATION OF MOLECULAR CONSTANTS FROM ROVIBRONIC SPECTRA WITH GENETIC ALGORITHMS

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Recently, attempts to automate the interpretation of rovibronic spectra have been undertaken. Automation becomes increasingly important when spectra become more difficult to interpret and/or pre-knowledge about the molecule is little or lacking. The group of Neusser^a used a procedure which directly fits the experimental data, without any preceding assignment of lines, with the help of the so called correlation automated rotational fitting algorithm. This algorithm still relies on accurate initial estimates of the rotational constants obtained from other experiments. Unfortunately, the method still has limited applicability.

The approach of fine-tuning the parameters of the Hamiltonian model so that the theoretical spectrum is in close agreement with the experimental one, can be seen as an optimisation problem. The process of determining molecular constants can be automated with global optimisation methods like Simulated Annealing (SA), Tabu Search (TS) or Genetic Algorithms (GA's). In this paper it is shown that a GA with a specially developed fitness function is very successful in directly determining the molecular constants from LIF spectra. This is done without using any initial estimates of these constants, except their global limits. This new approach is demonstrated for 4 rotationally resolved (LIF) spectra from indole, indazole, imidazole and 4-aminobenzonitril (4-ABN). The spectra were measured by Berden *et al.*^b

In addition, the robustness of this GA-based method has been assessed by artificially deteriorating the quality of the data. It will be shown that the method is quite robust and, therefore, widely applicable.

^aR.M. Helm, H.-P. Vogel and H.J. Neusser, *Chem. Phys. Lett.* 270, 185 (1997).

^bG. Berden, W.L. Meerts and E.J. Jalviste, *J. Chem. Phys.* 103, 9596 (1995).