

Simulated annealing procedure as a tool for molecular constants retrieval: The electronic transition $A^2\Sigma^+-X^2\Pi$ of N_2O^+ radical 000-000 band case.

L. L. Lessa^{†1}, A. S. Martins^{†2}, C. E. Fellows^{†3}

[†] Instituto de Ciências Exatas, Universidade Federal Fluminense, Volta Redonda Rio de Janeiro, Brazil

Synopsis In this work, the electronic transition $A^2\Sigma^+-X^2\Pi$ of N_2O^+ radical 000-000 band molecular constants are calculated by using the simulated annealing method.

One of the hardest problems found in high resolution molecular spectroscopy is the fitting of spectral lines to theoretical models through non-linear fitting methods. The non-linear routines are iteratives and thus often very sensitive to the starting conditions, i. e., the guess initial values of the constants.

In this work the simulated annealing procedure is used in order to reduce the wavenumbers from the lowest vibrational band of the electronic transition $A^2\Sigma^+-X^2\Pi$ of the N_2O^+ radical, 000-000, into molecular constants. The N_2O^+ radical was produced by Penning ionization of N_2O by colliding with metastable atoms of $He(2^3S)$ in a vacuum chamber and recorded by high resolution Fourier transform spectroscopy. The spectra were recorded in a spectral range of 24500-30000 cm^{-1} and obtained from 200 coadded interferograms recorded at an unapodized resolution of 0.08 cm^{-1} . Few words about the proposal of Vanderbilt and Louie for performing a simulated annealing minimization of a objective function where the parameters are continuous variables whose values vary in a specific range.

Simulated Annealing (SA) is a general designation for a class of methods for non-linear optimization which employ an stochastic approach to find the global minimum of a given function in a large search space. The method was independently described by Kirkpatrick, Gelatt and Vecchi in 1983 [1] and by Cerný in 1985 [2], being an adaptation of the Monte Carlo (MC) method.

The ion N_2O^+ , like all of the 15 valence electrons linear triatomic molecules, is characterized by a strong $^2\Sigma^+-^2\Pi$ electronic transition situated in the near U.V.. The first extensive analysis of the electronic emission spectrum of the $A^2\Sigma^+-X^2\Pi$ electronic transition of N_2O^+ has been performed by Callomon and Creutzberg [3], followed

by many others experimental studies, using different techniques [4], [5], [6], [7], [8].

More recently, an analysis of 000-000 band of the $A^2\Sigma^+-X^2\Pi$ electronic transition has been presented by Fellows [9]. In this study the ions were produced in the excited state by Penning ionization and the emission was analyzed by Fourier transform spectroscopy and the wavenumbers fitted to molecular constants through a deterministic non-linear model.

The simulated annealing method proved to be an extremely powerful technique to fit spectroscopic data to hamiltonian models, and the molecular constants values found using this technique are completely satisfactory. The molecular constants obtained by this method will be presented, as well as the steps used to implement it.

References

- [1] S. Kirkpatrick, C. D Gelatt Jr and M. P. Vecchi, *Science* **220**, 671 (1978)
- [2] V. Cerný, *Journal of Optimization Theory and Applications* **45**, 41 (1985)
- [3] J. H. Callomon and F. Creutzberg, *Phil. Trans. Roy. Soc. Ser. A* **277** (1974) 157.
- [4] S. Abed, M. Broyer, M. Carré, M. L. Gaillard and M. Larzillière, *Chem. Phys.* **74**, 97 (1983).
- [5] M. Larzillière and C. Jungen, *Mol. Phys.* **67**, 807 (1989).
- [6] M. Chafik el Idrissi, M. Larzillière, M. Carreé, *J. Chem. Phys.* **100**, 204 (1994).
- [7] C. E. Fellows and M. Vervloet, *Chem. Phys.* **264**, 203 (2001).
- [8] M. A. Gharaibeh and D. J. Clouthier, *J. Chem. Phys.* **136**, 044318 (2012).
- [9] C. E. Fellows, *J. Chem. Phys.* **138**, 164316 (2013)

¹E-mail: laisll@fisica.if.uff.br

²E-mail: asmartins73@gmail.com

³E-mail: cefellows@id.uff.br