Ab initio Calculations of Infrared Ro-Vibrational Spectra for Nitric Acid

A.I. Pavlyuchko[a,b], S.N. Yurchenko[b], Jonathan Tennyson[b]

[a] Moscow State University of Civil Engineering (MGSU), Russia
[a] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

To model the atmospheric composition of the potentially habitable planets, it is essential to have comprehensive data on the spectroscopic properties of the main molecular absorbers. This is especially true in the infrared region which is dominated by transitions of polyatomic molecules [1]. Nitric acid (HNO_3) is an important constituent of the Earth atmosphere where it is a prominent bio-signature. Here we present simulations of the absorption spectra for HNO_3.

We have developed a variational method to solve the ro-vibrational Schrödinger equation for a general polyatomic molecule. The ro-vibrational Hamiltonian is given by [2]

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{i,j} t^{0.25}\frac{\partial}{\partial q_i}\tau_{ij}(q)t^{-0.5}\frac{\partial}{\partial q_j}t^{0.25} + V(q) - \frac{\hbar^2}{2}\sum_{a,b}\frac{\partial}{\partial \varphi_a}\mu_{ab}(q)\frac{\partial}{\partial \varphi_b},$$

where the internal curvilinear vibrational coordinates q_i are used to represent the displacements of the bond lengths and bond angles, $\tau_{ij}(q)$ are elements of the matrix of the kinematic coefficients, t is the determinant of this matrix, φ_a are the Euler angles, and $\mu_{ab}(q)$ is the inverse matrix of the tensor of inertia. The potential energy function, $V(q)$, is given by a fourth-order polynomial expansion in terms of Morse variables $x_i = 1 - exp(-a_i q_i)$ for the stretching coordinates and $x_i = q_i$ for the bending coordinates.

The dipole moment of the molecule is presented in the form of a second order Taylor series in terms of q_i. The parameters of the potential energy and the dipole moment functions of HNO_3 were calculated *ab initio* at the CCSD(T)/aug-cc-pVQZ level of theory. With this potential energy function, agreement between the calculated and experimental fundamental frequencies of vibrations is within 5 cm^{-1}.

The harmonic part of the potential function was then optimized by fitting to the experimental fundamental frequencies and used to simulate the IR spectra of HNO_3. The results are in good agreement with the experimental data. Our goal is to produce a comprehensive line list for this molecule which can be used for modelling atmospheres of (exo)planets at elevated temperatures.

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