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Variational Calculations of IR Ro-Vibrational Spectra for Nitric Acid

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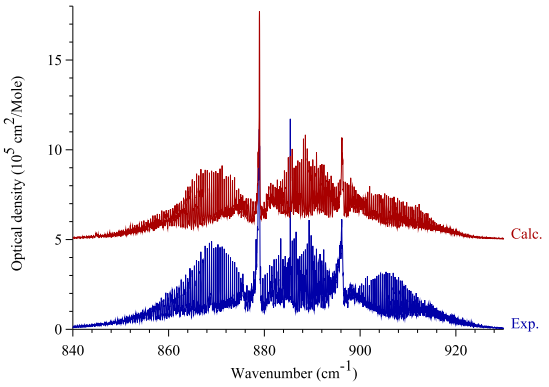
To model the atmospheric composition of the potentially habitable planets, it is essential to have comprehensive data on the spectroscopic properties of the main molecular absorbers. This is especially true in the infrared region which is dominated by transitions of polyatomic molecules [1]. Nitric acid (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 $x_i = 1 - e^{-\alpha_i q_i}$ 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 Taylor series of the 2nd order in terms of q_i. The parameters of the potential energy and the dipole moment functions of HNO_3 were calculated by the quantum chemical method 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. The figure shows an example of the simulated spectra of HNO_3 in the area of the strong Fermi resonance between the ν_5 and $2\nu_9$ bands along with an experimental counterpart. The resulting line list can be used for modelling atmospheres of (exo)planets at elevated temperatures.



References

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