

**On the "Expanded Local Mode" Approach  
Applied to the Methane Molecule:  
Isotopic Substitution  $\text{CH}_3\text{D} \leftarrow \text{CH}_4$  and  $\text{CHD}_3 \leftarrow \text{CH}_4$**   
O. N. Ulenikov<sup>a,b,c</sup>, E. S. Bekhtereva<sup>a,b,c</sup>, A. L. Fomchenko<sup>c,d</sup>,  
A.G. Litvinovskaya<sup>c</sup>, C. Leroy<sup>d</sup>, and M. Quack<sup>a</sup>

<sup>a</sup>Physical Chemistry, ETH-Zürich, CH-8093 Zürich, Switzerland; <sup>b</sup>Department of General Physics, Institute of Physics and Technology, National Research Tomsk Polytechnic University, Tomsk, 634050, Russia; <sup>c</sup>Laboratory of Molecular Spectroscopy, Physics Department, National Research Tomsk State University, Tomsk, 634050, Russia; <sup>d</sup>Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 5209, Université de Bourgogne, 21078, Dijon, France.

The operator perturbation theory and symmetry properties of an axially symmetric  $\text{XYZ}_3$  ( $\text{C}_{3v}$ ) type molecule are used to determine of its spectroscopic parameters in the form of functions of structural parameters and parameters of the intramolecular potential function. On that basis, different relations between sets of spectroscopic parameters of a molecule are obtained. Compilation of the "expanded local mode" model and the general isotopic substitution theory is used for the estimation of relations between spectroscopic parameters of the  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$  molecules, on the one hand, and their mother isotopic species,  $\text{CH}_4$ , on the other hand. Test calculations with the isotopic relations derived show that, even with a total absence of initial information about the  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$  species, numerical results of our calculations are in a good agreement both with experimental data for these molecules, and with results of *ab initio* calculations.

