MODELING OF LOW-TEMPERATURE TORSIONAL SPECTRA OF THE DOOOH AND DOOOD MOLECULES

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Large amplitude motions (LAM) in molecules and complexes had been attracting the attention of the researchers for a long time. At the same time, the technique of analysis of such vibrations was constantly improved. Torsional vibrations in molecules undoubtedly belong to the LAM. Recently [1] we have analyzed torsional vibrations in the hydrogen trioxide (HOOOH) molecule. The purpose of this study is getting the torsional spectra of DOOOH and DOOOD molecules. There are at least two reasons to analyze the torsional spectra of these molecules. First of all, it is reasonable to expect that replacing the hydrogen atoms with deuterium ones should lead to a decrease of all tunneling frequencies. Secondly, replacing only one hydrogen atom with deuterium in DOOOH molecule should lead to the changing of the symmetry properties in comparison with those for HOOOH and DOOOD molecules. Actually, assuming tunneling is prohibited, the DOOOH molecule will have no symmetry elements. However, since tunneling still takes place DOOOH molecule belongs to the $C_S(M)$ molecular symmetry group which is isomorph to the C_S point group symmetry. This fact changes the restrictions on the transition between torsional levels what affects the form of the spectrum. The values of the kinematic coefficients are changing for both considered molecules too.

To find the splitting of the torsional energy levels due to tunneling the stationary vibrational Schrödinger of the following form

$$\left[-F_{\gamma\gamma}(\gamma,\varphi)\frac{\partial^2}{\partial\gamma^2} - G_{\varphi\varphi}(\gamma,\varphi)\frac{\partial^2}{\partial\varphi^2} - S_{\gamma\varphi}(\gamma,\varphi)\frac{\partial^2}{\partial\gamma\partial\varphi} + U(\gamma,\varphi)\right]\Psi(\gamma,\varphi) = E\Psi(\gamma,\varphi);$$

was solved using the Fourier method. Here $F_{\gamma\gamma}$ (γ, φ), $G_{\varphi\varphi}$ (γ, φ) are the kinematics coefficients for the O-H, O-D groups, $S_{\gamma\varphi}$ (γ, φ) - kinematics coefficients for the interaction between O-H, O-D groups, and U (γ, φ) - potential energy. The calculated values of the tunneling frequencies in the ground states of the DOOOH and DOOOD are equal to $2.22\cdot10^{-10}$ and $6.67\cdot10^{-11}$ cm^{-1} respectively, what is less than in the case of HOOOH molecule. Some information about calculated values of torsional states energies of the DOOOH molecule represented in Table 1.

Table. 1. The calculated at MP2/cc-pVQZ level of theory values of torsional states energies of the DOOOH molecule and their assignments.

	DOOOH					
Energy level number	Confomation	Energy[cm^{-1}]	Energy splitting [cm^{-1}]	n_{OH}	n_{OD}	Symmetry species
1	trans	0	$2.22\cdot10^{-10}$	0	0	A'
2	trans	$2.22\cdot10^{-10}$		0	0	A''
3	trans	286.625	$1.93\cdot10^{-11}$	0	1	A'
4	trans	286.625		0	1	A''
5	trans	378.873	$5.50\cdot10^{-10}$	1	0	A'
6	trans	378.873		1	0	A''
7	trans	559.773	$1.49\cdot10^{-10}$	0	2	A'
8	trans	559.773		0	2	A''
9	trans	666.981	$2.54\cdot10^{-10}$	1	1	A'
10	trans	666.981		1	1	A''
11	trans	730.245	$2.26\cdot10^{-9}$	2	0	A'
12	trans	730.245		2	0	A''

Based on calculated data the low-temperature torsional spectra of the DOOOH and DOOOD were predicted too.

[1] G.A. Pitsevich, A.E. Malevich, U.U. Sapeshka, Chem.Phys., 530 (2020) 110633.