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STUDIU TEORETIC AL CEI MAI STABILI IZOMERI AI MOLECULELOR IO_3^- ȘI HIO_3

THEORETICAL STUDY OF THE MOST STABLE ISOMERS OF THE IO_3^- AND HIO_3 MOLECULES

*Natalia Gorincioi, dr., cercet. șt. coord., USM, Institutul de Chimie
Iolanta Bălan, dr., cercet. șt. superior, lector univ., USM, Institutul de Chimie
Ion Arsene, dr., cercet. șt. superior, USM, Institutul de Chimie
conferențiar universitar, UPS „Ion Creangă” din Chișinău*

*Natalia Gorinchoy, PhD, leading researcher, MSU, Institute of Chemistry
ORCID: 0000-0003-4529-9061, ngorinchoy@yahoo.com
Iolanta Balan, PhD, senior researcher, lecturer, MSU, Institute of Chemistry
ORCID: 0000-0002-8704-1344
Ion Arsene, PhD, senior scientific researcher, MSU, Institute of Chemistry
associate professor UPS “Ion Creanga” from Chisinau
ORCID:0000-0003-3102-3507*

Rezumat. În lucrarea de față, caracteristicile calitative ale structurii electronice a moleculelor XO_3^- și HXO_3 , posibilele structuri spațiale și forma suprafețelor de energie potențială adiabatică (SEPA) ale acestor sisteme în vecinătatea configurațiilor nucleare cu simetriile înalte D_{3h} și C_{3v} sunt considerate din punctul de vedere al teoriei vibronice. Calculele structurii electronice au fost efectuate prin metoda ab initio SCF CI cu utilizarea seturilor de baze extinse. Parametrii pseudo-efectului Jahn-Teller au fost estimați prin fitarea datelor calculate ab initio pentru SEPA ale XO_3^- și HXO_3 la formula generală a teoriei vibronice. S-a arătat că cauza instabilității configurațiilor lor nucleare cu simetrie înaltă este cuplarea PEJT între stările lor de bază și potrivite prin simetrie stările electronice excitate.

Cuvinte cheie: Izomerii ale XO_3^- și HXO_3 , Pseudo Efectul Jahn-Teller, suprafețe de energie potențială adiabatică, parametrii interacțiunii vibronice.

Abstract. In the present work the qualitative features of the electronic structure of the XO_3^- and HXO_3 molecules, their possible spatial structures and the form of the adiabatic potential energy surfaces (APES) of these systems in the neighborhood of their high-symmetry D_{3h} and C_{3v} nuclear configurations are considered from the vibronic theory point of view. The electronic structure calculations were carried out by ab initio SCF CI method with the use of the extended basis sets. Parameters of the pseudo Jahn-Teller effect were estimated by fitting the ab initio calculated data for the APES of the XO_3^- and HXO_3 to the general formula of the vibronic theory. It is shown that the reason of the instability of their high-symmetry nuclear configurations is the PJT coupling between the ground and appropriate by symmetry excited electronic states.

Keywords: XO_3^- and HXO_3 isomers, Pseudo Jahn-Teller Effect, adiabatic potential energy surfaces, parameters of the vibronic interaction.

Introduction

It is known that halogens can participate in numerous gas-phase ozone-depleting catalytic cycles. These cycles have been shown to involve the formation of bound (HXO_3) isomeric forms, which, through cyclic-type transition state configurations, proceed to different pathways of formation.

A number of experimental and theoretical studies have been devoted to the detection of these particles, finding their most stable isomers, and their possible participation in various reaction channels [1-4]. However, the question of the origin of the stability or instability of one or another nuclear configuration of the compounds under consideration remains out of consideration.

In the present work the qualitative features of the electronic structure of the XO_3^- and HXO_3 molecules, their possible spatial structures and the form of the adiabatic potential energy surfaces (APES) of these systems in the neighborhood of their high-symmetry D_{3h} and C_{3v} nuclear configurations are considered from the vibronic theory point of view. Electronic structure calculations of all the considered systems were performed using the GAMESS quantum chemistry package [5], and the TZV and MIDI basis sets. The geometry optimization was carried out in the frame of the *ab initio* SCF-HFR method.

The potential energy profiles along the normal distortion coordinates for the molecules in their ground and lowest excited states as the functions of corresponding low-symmetry displacements were calculated taking into consideration configuration interaction with single and double excitations (CISD). The numerical values of the parameters of the PJTE: vibronic coupling constants F , the primary force constants K_0 , and the resulting force constants for the curvature of the ground-state adiabatic potential K_{gr} were calculated by numerical fitting of the calculated energy profiles to the general Equation (1) for the energy obtained from the vibronic theory (see, for example, Refs. [6-9], and references herein):

$$\varepsilon_{1,2} = \frac{1}{4}(K_0)Q^2 + \frac{\Delta}{2} \mp \frac{1}{2} \sqrt{\left[\frac{1}{2}(K_{01})Q^2 - \Delta\right]^2 + 4F^2Q^2}, \quad (1)$$

where

$$F_{\Gamma\Gamma'} = \langle \Gamma | (\partial H / \partial Q)_0 | \Gamma' \rangle \quad (2)$$

is the vibronic coupling constant,

$$K_0 = \langle \Gamma | (\partial^2 H / \partial Q^2)_0 | \Gamma \rangle \quad (3)$$

is the primary force constant, H is the adiabatic electronic Hamiltonian of the system.

Results and discussion

The stereochemistry of molecular systems is determined by their electronic structure and the permutation symmetry of identical atoms. The latter means that from the viewpoint of symmetry any molecule must possess the spatial structure with the highest possible symmetry.

Therefore, we began the study of considered XO_3^- and HXO_3 molecules with their high-symmetry nuclear configurations, namely, the planar configuration of D_{3h} symmetry for XO_3^- anions and bipyramidal structures of C_{3v} symmetry for HXO_3 molecules.

The geometry optimization and vibration frequencies analysis of planar XO_3^- anions indicate the presence of one imaginary frequency corresponding to distortion of the system of a_2'' -symmetry which transforms the planar nuclear configuration into the pyramidal one of C_{3v} symmetry (Figure 1).

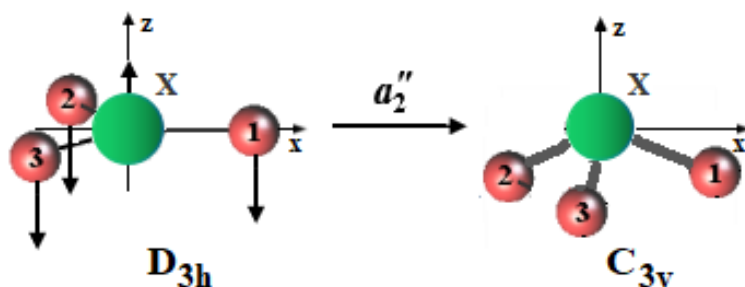


Fig. 1. Low-symmetry a_2'' -type distortion of the XO_3^- systems, which transforms the symmetric D_{3h} nuclear configuration into the C_{3v} one

The corresponding values of geometry parameters of XO_3^- compounds in both the planar (D_{3h}) and equilibrium pyramidal (C_{3v}) structures and the values of imaginary frequencies in the reference nuclear configurations are presented in Table 1.

Table 1. Optimized geometry parameters in the planar D_{3h} and pyramidal (equilibrium) C_{3v} configurations of XO_3^- compounds and the imaginary (a_2'') frequency in their planar geometry

Geometry parameters	Molecules					
	ClO_3^-		BrO_3^-		IO_3^-	
	D_{3h}	C_{3v}	D_{3h}	C_{3v}	D_{3h}	C_{3v}
R_{X-O} (Å)	1.92	1.90	1.99	1.87	1.97	1.91
R_{O-O} (Å)	3.33	3.07	3.45	3.07	3.30	3.17
$R_{X-O_3 \text{ plane}}$ (Å)	0.00	0.70	0.00	0.68	0.00	0.74
imaginary frequency a_2'' (cm^{-1})	160.71	-	173.12	-	220.87	-

As a reference nuclear configuration of XHO_3 molecules, a trigonal-bipyramidal (TBP) structure was taken, the base of which is formed by three oxygen atoms and the hydrogen and halogen atoms are located at the pyramid vertices (Figure 2). Calculations have shown that such a configuration is unstable with respect to the e-type distortion of the system, which mainly corresponds to the displacement of the hydrogen atom towards one of the oxygen atoms, thus leading to a structure of C_s -symmetry (Figure 2).

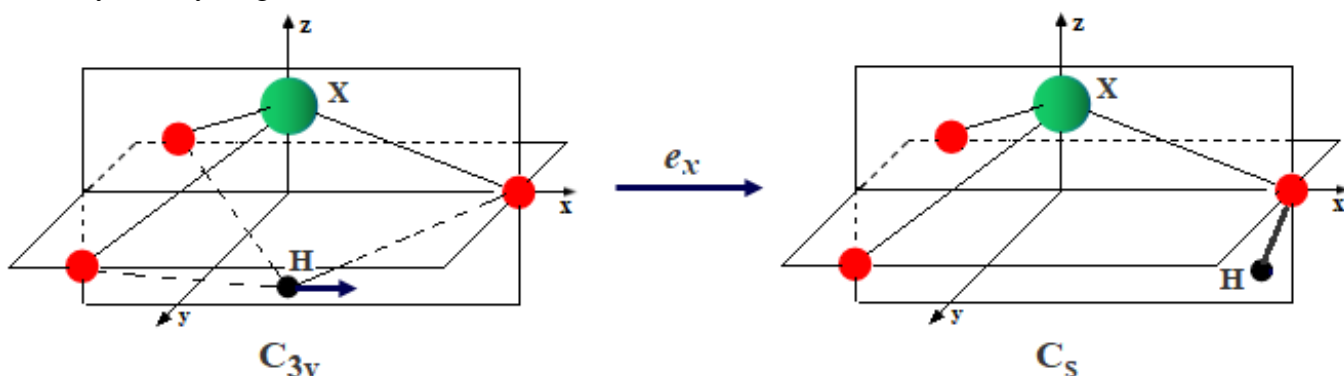


Fig. 2. Low-symmetry e_x -type distortion of the HXO_3 system, which transforms the symmetric C_{3v} nuclear configuration into the C_s one

Table 2 lists the corresponding values of the geometry parameters of HXO_3 molecules in both TBP (C_{3v}) and equilibrium (C_s) structures, as well as the values of imaginary frequencies in the reference C_{3v} nuclear configurations.

Table 2. Selected optimized structural parameters (Å) of the HXO₃ molecules in their bipyramidal C_{3v} and equilibrium C_s nuclear configurations and the imaginary *e*-type frequency in the C_{3v} structure

Parameters	Molecules					
	HClO ₃		HBrO ₃		HIO ₃	
	C _{3v}	C _s	C _{3v}	C _s	C _{3v}	C _s
R (X-O ₁)	1.97	1.75	1.95	1.89	2.05	1.95
R (O ₁ -H)	1.49	0.96	1.53	0.96	1.55	0.96
imaginary frequency <i>e</i> (cm ⁻¹)	1851.81	-	1884.55	-	1910.89	-

The ground electronic state wave function of XO₃⁻ anions transforms according the ¹A₁' representation of D_{3h} symmetry point group. Since the distortion is of the a₂'-symmetry, only the excited states of ¹A₂' symmetry are involved in the vibronic mixing with the ground state. In the case of HXO₃ molecules the ground state wave function is the ¹A₁ one. The instability coordinate is of *e*-symmetry. Therefore, the vibronic coupling only with the excited states of ¹E symmetry can contribute to the instability of the ground state TBP nuclear configurations. The main electronic configurations, total energies E (hartree) and relative energies ΔE (eV) of the ground and excited electronic terms of all the considered compounds in their optimized nuclear configurations are presented in Table 3.

Table 3. Main electronic configurations, total energies E (hartree) and relative energies ΔE (eV) of the ground and excited electronic terms of the XO₃⁻ and HXO₃ molecules in their optimized nuclear configurations

Symmetry		State	E	ΔE	Electronic configuration
ClO ₃ ⁻	D _{3h}	¹ A ₁ '	-683.75	0	[... (e') ⁴ (a ₂ '') ² (a ₁ ') ⁰ (e') ⁰ ...]
		¹ A ₂ '	-683.60	4.24	[... (e') ⁴ (a ₂ '') ¹ (a ₁ ') ¹ (e') ⁰ ...]
	C _{3v}	A ₁	-683.76	0	[... (e) ⁴ (a ₁) ² (a ₁) ⁰ (e) ⁰ ...]
HClO ₃	C _{3v}	A ₁	-684.16	0	[... (a ₁) ² (e) ⁴ (e) ⁰ (a ₁) ⁰ ...]
		E	-683.96	5.59	[... (a ₁) ² (e) ³ (e) ¹ (a ₁) ⁰ ...]
	C _s	A'	-684.25	0	
BrO ₃ ⁻	D _{3h}	¹ A ₁ '	-2786.53	0	[... (e') ⁴ (a ₂ '') ² (a ₁ ') ⁰ (e') ⁰ ...]
		¹ A ₂ '	-2786.40	3.38	[... (e') ⁴ (a ₂ '') ¹ (a ₁ ') ¹ (e') ⁰ ...]
	C _{3v}	¹ A ₁	-2786.55	0	[... (e) ⁴ (a ₁) ² (a ₁) ⁰ (e) ⁰ ...]
HBrO ₃	C _{3v}	A ₁	-2786.93	0	[... (a ₁) ² (e) ⁴ (e) ⁰ (a ₁) ⁰ ...]
		E	-2786.73	5.55	[... (a ₁) ² (e) ³ (e) ¹ (a ₁) ⁰ ...]
	C _s	A'	-2787.04	0	
IO ₃ ⁻	D _{3h}	¹ A ₁ '	-7120.37	0	[... (e') ⁴ (a ₂ '') ² (a ₁ ') ⁰ (e') ⁰ ...]
		¹ A ₂ '	-7120.25	3.03	[... (e') ⁴ (a ₂ '') ¹ (a ₁ ') ¹ (e') ⁰ ...]
	C _{3v}	A ₁	-7120.38	0	[... (e) ⁴ (a ₁) ² (a ₁) ⁰ (e) ⁰ ...]
HIO ₃	C _{3v}	A ₂	-7120.78	0	[... (a ₁) ² (e) ⁴ (e) ⁰ (a ₁) ⁰ ...]
		E	-7120.59	5.05	[... (a ₁) ² (e) ³ (e) ¹ (a ₁) ⁰ ...]
	C _s	¹ A ₁	-7120.91	0	

Figures 3 and 4 show the molecular orbitals diagram for XO₃⁻ ions and HXO₃ molecules in their ground electronic states in the optimized D_{3h} and C_{3v} configurations, respectively, and the cross-sections of the adiabatic potential energy surfaces (APES) for their ground and corresponding excited states.

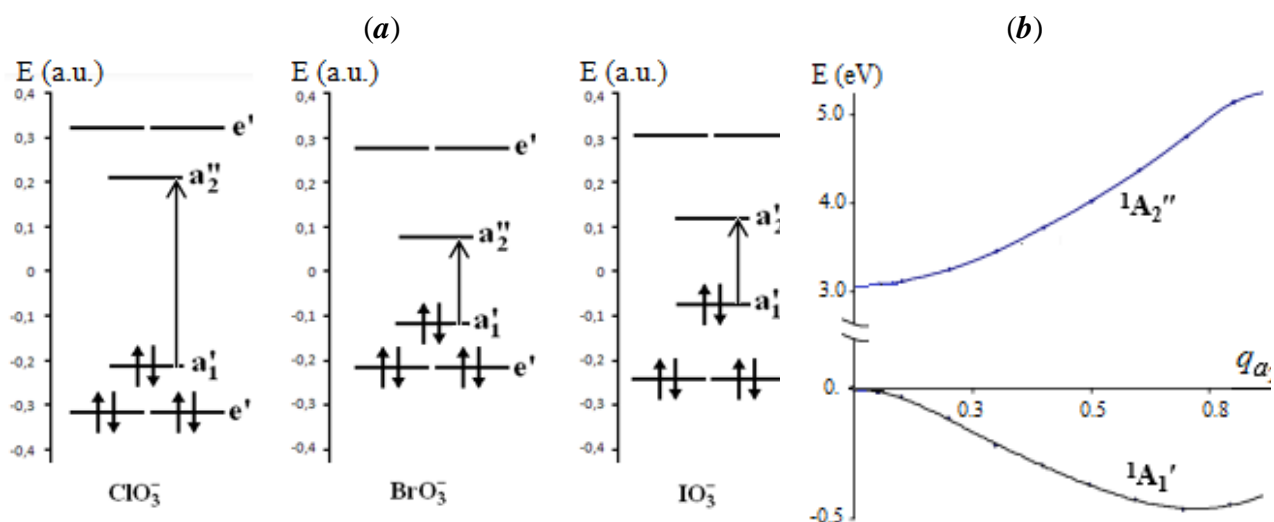


Fig. 3. (a) The MO energy level scheme for XO_3^- systems in their ground $^1\text{A}_1'$ electronic states in optimized D_{3h} nuclear configurations with indication of the one-electron excitations to the excited $^1\text{A}_2''$ terms; (b) APES cross-sections along the a_2'' -coordinate of instability for the IO_3^- anion.

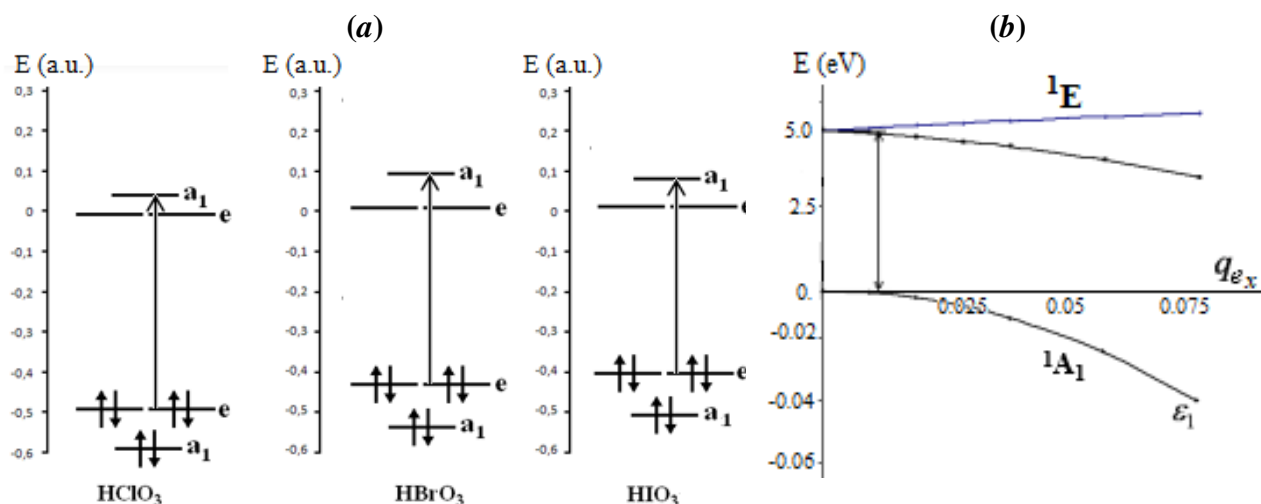


Fig. 4. (a) The MO energy level scheme for HXO_3 systems in their ground $^1\text{A}_1$ electronic states in the optimized C_{3v} nuclear configuration with indication of the one-electron excitations to the excited ^1E terms; (b) APES cross-sections along the e_x -coordinate of instability for HIO_3 molecule

The calculated two-dimensional and three-dimensional ground-state surfaces for the HXO_3 molecules as the functions of $\mathbf{r}(\text{H})$ are presented in Figure 5. It is seen that there are three type of extreme points on the surface: point 1 (C_{3v} configuration) is a maximum on the APES, three equivalent minima of C_s symmetry (points 3) correspond to the bonding of the hydrogen atom with one of the oxygen atoms, and three saddle points of C_s symmetry (points 2) between the minima. Calculated energies of the systems in these extreme points are in Table 4. Obtained data demonstrate that the TBP configuration of all HXO_3 molecules is unstable with respect to the e -type displacement corresponding to the motion of the H atom towards one of the oxygens.

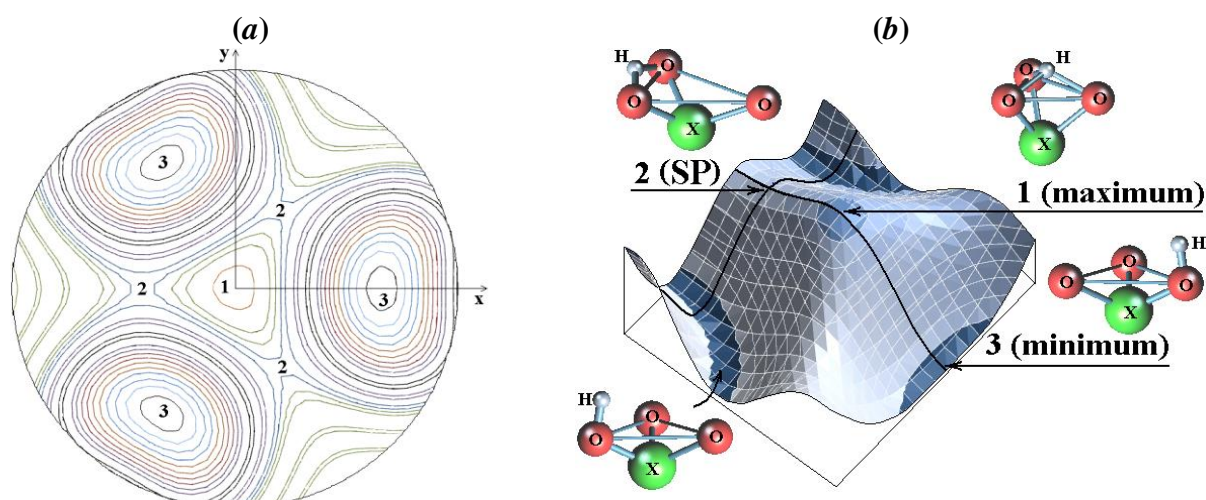


Fig. 5. Two-dimensional (a) and three-dimensional (b) ground-state surfaces for the HXO₃ molecules as a function of r(H)

Table 4. Energies (kcal/mol) of the HXO₃ molecules in the extreme points of their APESes

X	1	2	3
Cl	70.88	25.03	0
Br	79.17	27.85	0
I	89.13	32.62	0

The parameters of the PJTE: coupling constants F_{0i} , the primary force constants K_0 , and the resulting force constants for the curvature of the ground-state adiabatic potential K_{gr} were calculated by numerical fitting of the calculated energy profiles to the general equation (1) for the energy obtained from the vibronic theory:

$$\varepsilon_{1,2} = \frac{1}{4}(K_0)Q^2 + \frac{\Delta}{2} \mp \frac{1}{2} \sqrt{\left[\frac{1}{2}(K_{01})Q^2 - \Delta\right]^2 + 4F^2Q^2} \quad (1)$$

The obtained values of parameters K_0 , F and $K = K_0 - 2F^2/\Delta$ are presented in Table 5.

Table 5. Values of the PJTE parameters K_0 , F and $K_{\Gamma} = K_0^{\Gamma} - 2F_{\Gamma}^2/\Delta_{\Gamma}$

q_{Γ}	Δ_{Γ} (eV)	ΔE_{PJTE} (eV)	K_0^{Γ} (eV/Å ²)	F_{Γ} (eV/Å)	K_{Γ} (eV/Å ²)
ClO ₃ ⁻ $q_{a_2'} (D_{3h} \rightarrow C_{3v})$	4.24	0.14	4.48	3.68	-1.91
BrO ₃ ⁻ $q_{a_2'} (D_{3h} \rightarrow C_{3v})$	3.38	0.51	6.80	4.93	-7.58
IO ₃ ⁻ $q_{a_2'} (D_{3h} \rightarrow C_{3v})$	3.03	0.40	4.87	3.95	-8.19
HClO ₃ $q_e (C_{3v} \rightarrow C_s)$	5.59	0.11	1.78	5.61	-5.65
HBrO ₃ $q_e (C_{3v} \rightarrow C_s)$	5.55	0.25	3,23	4,87	-5.32
HIO ₃ $q_e (C_{3v} \rightarrow C_s)$	5.05	2.70	2.11	5.73	-10.89

It can be seen from Table 5 that the resulting values of the curvature of the adiabatic potential energy curves K_{Γ} are negative for all the studied compounds. It confirms that the symmetrical nuclear configurations (D_{3h} for XO_3^- and C_{3v} for HXO_3) for all the investigated systems are energetically unstable due to the PJT effect.

Conclusions

It is shown that the theory of the pseudo Jahn-Teller Effect is instrumental in the search for the most stable conformations of molecular systems.

On the base of the ab initio calculations of the electronic structure and the potential energy surfaces it was demonstrated that the only reason of instability of the most symmetrical planar equilateral (D_{3h}) configuration of XO_3^- anions and trigonal-bipyramidal C_{3v} geometry of HXO_3 molecules is the pseudo Jahn-Teller effect.

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