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
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## **Ab initio STUDY OF THE STRUCTURE, FORCE FIELD, AND VIBRATIONAL SPECTRUM OF THE LiClO<sub>3</sub> MOLECULE**

V. G. Solomonik, T. P. Pogrebnaya, and V. V. Sliznev

UDC 539.194

The geometrical structure and the vibrational spectrum of the LiClO<sub>3</sub> molecule are studied by the Hartree-Fock-Roothaan (HF) and configurational interaction (CI) methods taking into account single and double excitations and Davidson's correction for quadruple excitations. Double-zeta basis sets of Huzinaga-Dunning and McLean-Chandler complemented with polarization and diffuse functions are used. Potential surface sections corresponding to migration of the Li<sup>+</sup> cation around the ClO<sub>3</sub><sup>-</sup> fragment are investigated. It was found that the LiClO<sub>3</sub> molecule has a single stable configuration of C<sub>s</sub> symmetry with the bidentate coordination of the Li<sup>+</sup> cation by the ClO<sub>3</sub><sup>-</sup> anion. The cyclic fragment  is nonplanar (the dihedral angle  $\theta(\text{LiO}_2\text{Cl}) = 173^\circ$ ). The tridentate configuration of C<sub>3v</sub> symmetry lies higher than the equilibrium configuration by 24.5 (HF) or 18.3 (CI) kJ/mole and is not an isomer. The *ab initio* force field of the molecule was refined by the scaling method. Some assignments of the IR bands of the matrix-isolated molecular forms existing in vapor over lithium chlorate are corrected. The vibration frequencies (cm<sup>-1</sup>) and IR intensities (km/mole; in parentheses) are calculated with the refined force field: A' type 1099(236), 856(81), 630(73), 557(119), 481(87), 156(66); A'' type 887(229), 459(35), 367(23).

The IR spectra of alkali chlorates, MClO<sub>3</sub>, isolated in inert gas matrices were investigated in [1-6]. The spectra were interpreted [2-4] on the assumption of the tridentate coordination of the M<sup>+</sup> cation by the ClO<sub>3</sub><sup>-</sup> ion (C<sub>3v</sub> symmetry). In [5] the spectra of LiClO<sub>3</sub> and NaClO<sub>3</sub> molecules are explained on the assumption that each of these molecules has tridentate (t) and bidentate (b) isomers. The IR studies of hydrated LiClO<sub>3</sub> and NaClO<sub>3</sub> molecules [6] confirmed the structure of NaClO<sub>3</sub> suggested in [5] and showed that the bidentate coordination in the LiClO<sub>3</sub> molecule is preferable. *Ab initio* calculations of the properties of LiClO<sub>3</sub> and NaClO<sub>3</sub> molecules were published [7, 8]. They indicate that the bidentate coordination is preferable and that there is one more minimum (corresponding to the tridentate structure) on the potential energy surface (PES) of these molecules. However, the minimal energy path of the C<sub>3v</sub>(t) → C<sub>s</sub>(b) rearrangement and the value of the potential barrier between the minima were not investigated.

This paper deals with the *ab initio* calculations of the structure and properties of the ClO<sub>3</sub><sup>-</sup> ion and LiClO<sub>3</sub> molecule and studies the intramolecular rearrangement in LiClO<sub>3</sub>. The calculations employ wider basis sets than those used previously and adequately takes into account the electron correlation. Based on the results of calculations, the available experimental data are analyzed, and new interpretation is suggested for the IR spectra of LiClO<sub>3</sub> published in [1-6].

### **DETAILS OF CALCULATIONS**


The calculations were performed using the GAMESS program [9]. We employed the double-zeta basis sets of Huzinaga-Dunning [10-12] and McLean-Chandler [13] complemented by the polarization *d*-functions on oxygen


and chlorine atoms: Li(9s4p/4s2p), O(9s5p1d/4s2p1d), Cl(12s9p1d/6s4p1d) ( $\zeta_d(\text{O}) = 0.85$  [11],  $\zeta_d(\text{Cl}) = 0.68$  [14]). Below the basis set used here is denoted as DZP. A wider basis set, DZPD, was derived from the first basis set by adding diffuse functions on oxygen ( $\zeta_p(\text{O}) = 0.059$  [11]) and chlorine (the values of  $\zeta_s(\text{Cl}) = 0.063$  and  $\zeta_p(\text{Cl}) = 0.044$  were optimized in the Hartree-Fock calculations of the free  $\text{ClO}_3^-$  ion). In order to clarify the reasons for the contradictions between the results of our calculations and those of [8] in which the 6-31G\* basis set was used, we reinvestigated some sections of the potential energy surface of the  $\text{LiClO}_3$  molecule with the 6-31G\* basis set.

To refine the results of Hartree-Fock calculations in the DZPD basis set, we calculated the relative energies of different structures of the molecule by the configurational interaction (CI) method taking into account the singly and doubly excited configurations and introducing Davidson's correction for quadruple excitations (CISD + Q). When constructing configurations, we refined electron transitions from 13 highest occupied MOs to 35 lowest unoccupied MOs. The resulting wave function includes 52,501 configurations.

The geometrical parameters of the molecule were optimized by the gradient method. The force constants were calculated analytically, and the derivatives of the dipole moments were calculated by the numerical method described in [15]. Tables 1-4 represent the calculated parameters of the molecule. The results of calculations depend weakly on the basis expansion (6-31G\*  $\rightarrow$  DZP  $\rightarrow$  DZPD) and are therefore reliable. Below we discuss the results obtained in the widest, DZPD, basis set (unless specified otherwise).

### GEOMETRICAL STRUCTURE OF THE $\text{LiClO}_3$ MOLECULE

We consider the structures of the  $\text{LiClO}_3$  molecule shown in Fig. 1. The bidentate  $C_s$  structure (I) possesses the lowest energy. The cyclic fragment  is nonplanar: the lithium atom deviates from the  $\text{ClO}_2$  plane by an angle  $\gamma = 7^\circ$  (Fig. 1).

We studied an intramolecular rearrangement corresponding to migration of the  $\text{Li}^+$  cation around the  $\text{ClO}_3^-$  fragment. Figure 2 depicts the dependence of the relative energy  $\Delta E = E - E_{\min}$  on the  $\gamma$  angle, defining the deformation of the  ring. All other geometrical parameters of the molecule were optimized for the  $C_s$  structure at certain values of the  $\gamma$  angle. The highest point of the potential curve  $\Delta E(\gamma)$  corresponds to configuration III (Fig. 1). The minimum of the potential function  $\Delta E(\gamma)$  corresponds to bidentate structure I. The second minimum, which is due to the tridentate structure (structure II, Fig. 1), is very shallow: the barrier between the  $C_{3v}(t)$  and  $C_s(b)$  configurations is only  $0.9 \cdot 10^{-7}$  au ( $0.2 \text{ cm}^{-1}$ ). Consequently, the tridentate isomer of the  $\text{LiClO}_3$  molecule is nonexistent. The frequency of the corresponding normal vibration [ $\omega_6(A') = 57 \text{ cm}^{-1}$ ] is very high compared to the barrier of the  $C_{3v}(t) \rightarrow C_s(b)$  rearrangement, indicating that the harmonic approximation is inappropriate for calculating the vibrational

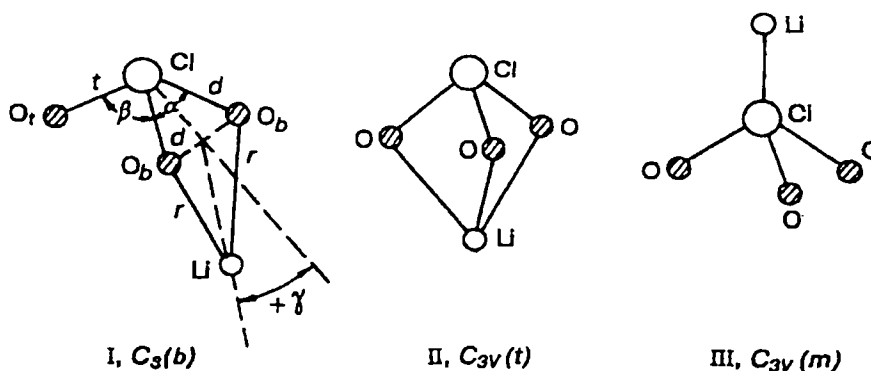


Fig. 1. Structures of the  $\text{LiClO}_3$  molecule.

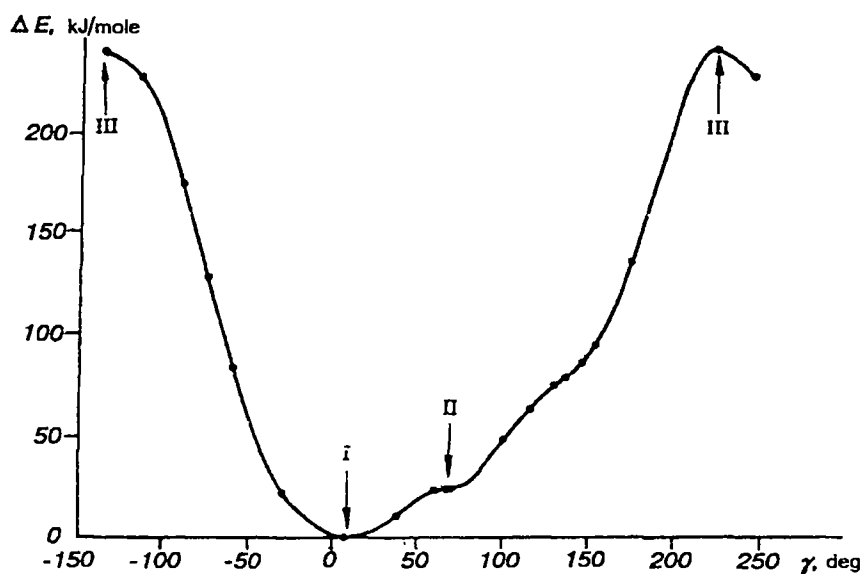



Fig. 2. Dependence of the energy  $\Delta E = E(\gamma) - E_{\min}$  of the  $\text{LiClO}_3$  molecule on the  $\gamma$  angle (the  $\gamma$  angle is shown in Fig. 1).

spectrum corresponding to this normal coordinate. It is interesting to note that in the 6-31G\* basis set the  $C_{3v}(t)$  configuration does not correspond to the energy minimum on the PES.

Inclusion of the electron correlation leads to a slight decrease in the relative energy of the tridentate structure:  $\Delta E(\text{II} - \text{I}) = 24.5$  (HF), 18.3 kJ/mole (CISD+Q) and to an increase in the relative energy of structure III:  $\Delta E(\text{III} - \text{I}) = 241$  (HF), 251 kJ/mole (CISD+Q).

Analysis of Mulliken populations ( $q(\text{Li}) = +0.73, +0.62$ , and  $+0.68$  e for structures I, II, and III, respectively) and comparison of the geometrical parameters of the  $\text{ClO}_3$  fragment of  $\text{LiClO}_3$  with the parameters of the free  $\text{ClO}_3^-$  ion confirm the conclusions of previous papers that the structure of the molecule may be described by the scheme  $\text{Li}^+ \text{ClO}_3^-$ . Nevertheless, there is pronounced distortion of the configuration of the  $\text{ClO}_3^-$  ion in the field of the  $\text{Li}^+$  cation (Table 1). The force constants of the  $\text{ClO}_3^-$  fragment also change considerably as a result of its coordination by the  $\text{Li}^+$  ion (Table 2).

The results of our calculations show some discrepancies from the data of the previous theoretical investigation (HF/6-31G\*) [8].

1. According to our calculations, in the equilibrium  $C_s(b)$  configuration of the  $\text{LiClO}_3$  molecule, the  fragment is nonplanar, whereas the authors of [8] postulated the planar structure of this ring.

2. The calculated potential curve  $\Delta E(\gamma)$  (Fig. 2) shows that in going from configuration II to the top of the barrier of III (region of monodentate configurations with Li-O bonds), the energy smoothly increases. This result conflicts with the data of [8], according to which the energy of the molecule with the angle  $\varphi(\text{LiOCl}) = 128^\circ$  (corresponding to  $\gamma = 154^\circ$ ) is lower than that of the structure with a linear LiOCl segment ( $\gamma \approx 130^\circ$ ). Our calculation in the 6-31G\* basis set gave the values of energies at these points that coincide with the curve  $\Delta E(\gamma)$  calculated in the DZPD basis set (Fig. 2). Evidently, the energy of the  $\text{LiClO}_3$  molecule obtained in [8] for  $\varphi(\text{LiOCl}) = 128^\circ$  is erroneous.

3. The energy and the geometrical parameters of structure III calculated by us in the 6-31G\* basis set disagree with the data of [8]. Our calculations showed that the calculations of [8] for structure III were performed without using standard scale factors for the Gaussian exponents of the 6-31G\* basis set.

4. The value of the vibration frequency  $\omega_6$  obtained by us in the 6-31G\* basis set for the  $C_{3v}(t)$  structure disagrees with the value given in [8] (Table 3). The reason for this discrepancy is unknown to us.

**TABLE 1.** Results of *ab initio* Calculations of the Geometrical Parameters, Total and Relative Energies, and Dipole Moments of the  $\text{LiClO}_3$  Molecule and  $\text{ClO}_3^-$  Ion ( $R_e$  in Å,  $\alpha_e$  in deg,  $E$  in au,  $\Delta E$  in kJ/mole,  $\mu_e$  in D)

Property	HF/6-31G*		HF/DZP	HF/ZPD
	[8]	Our calculation		
LiClO <sub>3</sub> , C <sub>s</sub> (b)				
R <sub>e</sub> (ClO <sub>t</sub> )	1.4498	1.4510	1.4562	1.4567
R <sub>e</sub> (ClO <sub>b</sub> )	1.5199	1.5197	1.5231	1.5232
R <sub>e</sub> (LiO <sub>b</sub> )	1.8697	1.8730	1.8990	1.8932
α <sub>e</sub> (O <sub>b</sub> ClO <sub>b</sub> )	100.1	100.1	99.5	99.5
β <sub>e</sub> (O <sub>b</sub> ClO <sub>t</sub> )	109.5	109.3	109.1	109.2
θ <sub>e</sub> (LiOOCl)	(180)	173.4	171.6	173.1
−E	691.27858	691.278812	691.359417	691.363616
μ <sub>e</sub>		5.82	6.11	6.16
LiClO <sub>3</sub> , C <sub>3v</sub> (t)				
R <sub>e</sub> (ClO)	1.4982	1.4982	1.5027	1.5024
R <sub>e</sub> (LiO)	2.1083	2.1084	2.1390	2.1293
α <sub>e</sub> (OCIO)	103.2	103.2	103.1	103.1
−E	691.26953	691.269534	691.350953	691.354271
ΔE	23.8	24.4	22.2	24.5
μ <sub>e</sub>		3.49	3.83	3.75
LiClO <sub>3</sub> , C <sub>3v</sub> (m)				
R <sub>e</sub> (ClO)	1.4667	1.4671		1.4725
R <sub>e</sub> (LiCl)	2.2782	2.2733		2.2860
α <sub>e</sub> (OCIO)	111.4	111.3		110.9
−E	691.17838	691.180567		691.271960
ΔE	263.2	233.6	240.6	
μ <sub>e</sub>		11.93		12.38
ClO <sub>3</sub> <sup>−</sup> , C <sub>3v</sub>				
R <sub>e</sub> (ClO)	1.4866		1.4925	1.4946
α <sub>e</sub> (OCIO)	108.6		108.4	108.3
−E			683.89336	683.887598

### VIBRATIONAL SPECTRUM OF THE $\text{LiClO}_3$ MOLECULE

Let us compare the theoretical vibrational spectrum with the available experimental data. To eliminate the errors of theoretical force constants that are due to the incomplete basis set and neglect of electron correlation, we performed empirical scaling of the force field of the molecule by a standard method [17]. The force field of the molecule was refined in four steps. The vibration frequencies and IR intensities calculated during the sequential refinement of the force field are represented in Table 4.

In the first step ( $M1$ ), the estimated values of scale indices transferred from the  $\text{ClO}_3^-$  ion and the  $\text{LiNO}_3$  molecule were used:  $c_r(\text{Cl-O}) = 0.895$ ,  $c_\alpha(\text{OCiO}) = 0.947$ ,  $c_r(\text{Li-O}) = 0.809$ . The *ab initio* force fields of the  $\text{ClO}_3^-$

TABLE 2. *Ab initio* (AI) and Scaled (M) Force Fields of the  $\text{ClO}_3^-$  Ion and the  $\text{LiClO}_3$ ,  $C_s(b)$ , Molecule

	$\text{ClO}_3^-$			$\text{LiClO}_3$			$\text{LiClO}_3$	
	AI	M		AI	M4		AI	M4
$f_t$	6.533	5.845	$\{f_t$	7.949	7.541	$f_{rr}$	0.168	0.136
			$f_d$	5.913	5.041	$f_{rr'}$	-0.053	-0.046
$f_\alpha$	2.443	2.313	$\{f_\alpha$	3.738	3.281	$f_{dr}$	0.091	0.076
			$f_\beta$	2.074	1.790	$f_{dr'}$	-0.133	-0.111
$f_{tt}$	0.062	0.055	$\{f_{td}$	-0.019	-0.018	$f_{ra}$	-0.379	-0.319
			$f_{dd}$	0.224	0.191	$f_{r\beta}$	0.034	0.028
$f_{ra}$	0.103	0.094	$\{f_{t\beta}$	0.204	0.185	$f_{r\beta'}$	-0.039	-0.033
			$f_{d\alpha}$	0.616	0.533	$f_\gamma$	0.156	0.156
			$f_{d\beta}$	0.152	0.131	$f_{t\gamma}$	0.082	0.080
$f_{t\alpha'}$	-0.266	-0.244	$\{f_{t\alpha}$	-0.252	-0.230	$f_{d\gamma}$	-0.008	-0.007
			$f_{d\beta'}$	-0.168	-0.144	$f_{r\gamma}$	0.037	0.033
$f_{\alpha\alpha}$	0.790	0.748	$\{f_{\alpha\beta}$	0.585	0.509	$f_{\alpha\gamma}$	-0.042	-0.039
			$f_{\beta\beta}$	0.513	0.443	$f_{\beta\gamma}$	-0.051	-0.047
			$f_r$	0.822	0.622			

Notes: The natural coordinates  $r$ ,  $d$ ,  $t$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are shown in Fig. 1. The force constants  $f_{t\alpha}$ , etc., define the interactions of the  $t$  and  $\alpha$  coordinates with two common atoms; the force constants with primed coordinates (e.g.,  $f_{t\alpha'}$ ) define the interactions of the  $t$  and  $\alpha$  coordinates with one common atom. The dimensionalities are: for the force constants of bond stretching ( $f_r$ ,  $f_d$ ,  $f_t$ ) and bond interaction ( $f_{rr}$ ,  $f_{rr'}$ , etc.),  $\text{mdyn}/\text{\AA}$ ; for the force constants of the deformations of angles ( $f_\alpha$ ,  $f_\beta$ , and  $f_\gamma$ ) and interactions ( $f_{\alpha\beta}$ ,  $f_{\beta\beta}$ , etc.),  $\text{mdyn} \cdot \text{\AA}$ ; for the coefficients of  $f_{t\alpha}$ ,  $f_{t\beta}$ , etc., types,  $\text{mdyn}$ .

ion and the  $\text{LiNO}_3$  molecule that we calculated in the HF/DZPD approximation were preliminarily scaled using the vibration frequencies of the  $\text{ClO}_3^-$  ion in an aqueous solution (933, 608, 977, and  $477 \text{ cm}^{-1}$  [16]) and the vibration frequencies of the  $\text{LiNO}_3$  molecules isolated in argon matrices [18] (the frequency of the stretching vibration  $\nu(\text{Li-O}) = \nu_4(A_1) = 528 \text{ cm}^{-1}$  [18]). The calculations confirmed the assignment of two intense IR bands, 1099 and  $887 \text{ cm}^{-1}$  ( $\Delta\nu(^{35}\text{Cl} - ^{37}\text{Cl}) = 12$  and  $9 \text{ cm}^{-1}$ , respectively), to the  $\text{LiClO}_3$  molecule of  $C_s$  symmetry made in [5, 6]. According to theory, the IR spectrum of  $\text{LiClO}_3$  must primarily show two vibrations:  $\nu_1(\text{Cl-O}_t) = 1073$ ,  $\Delta\nu = 11 \text{ cm}^{-1}$  and  $\nu_7(\text{Cl-O}_b) = 909$ ,  $\Delta\nu = 9 \text{ cm}^{-1}$ . The minor deviations of the values of  $\nu_1$  and  $\nu_7$  calculated with the force field M1 from the experimental values are explained by the rough estimation of the scale indices  $c_r(\text{Cl-O})$ , which disregards the difference between the bridging and terminal bonds leading to different values of the  $c_r(\text{Cl-O}_b)$  and  $c_r(\text{Cl-O}_t)$  coefficients.

In the second step of the force field refinement (M2), this difference was taken into consideration: the values of the coefficients  $c_r(\text{Cl-O}_b) = 0.851$  and  $c_r(\text{Cl-O}_t) = 0.948$  were found by fitting the calculated frequencies  $\nu_1$  and  $\nu_7$  and their isotopic shifts to the observed values [5, 6].

The frequency  $\nu_3 = 651 \text{ cm}^{-1}$ ,  $\Delta\nu(^{35}\text{Cl} - ^{37}\text{Cl}) = 3.7 \text{ cm}^{-1}$ , calculated with the refined force constants is in good agreement with the frequency  $630.5 \text{ cm}^{-1}$ ,  $\Delta\nu(^{35}\text{Cl} - ^{37}\text{Cl}) = 4.8 \text{ cm}^{-1}$ , assigned in [1] and [3] to the  $\text{LiClO}_3$

\* The parameters of the  $\text{LiNO}_3$  molecule obtained in the HF/DZPD approximation are:  $R_e(\text{NO}_t) = 1.1808 \text{ \AA}$ ,  $R_e(\text{NO}_b) = 1.2581 \text{ \AA}$ ,  $R_e(\text{LiO}_b) = 1.8790 \text{ \AA}$ ,  $\alpha(\text{O}_b\text{NO}_b) = 114.7^\circ$ ;  $\omega_i$ :  $A_1$  type 1828, 1192, 842, 590;  $B_1$  type 939, 183;  $B_2$  type 1497, 783,  $414 \text{ cm}^{-1}$ .

**TABLE 3.** Results of *ab initio* Calculations of the Frequencies of Normal Vibrations  $\omega_i$  ( $\text{cm}^{-1}$ ) and IR Intensities  $A_i$  ( $\text{km/mole}$ ) of the  $\text{LiClO}_3$  Molecule and  $\text{ClO}_3^-$  Ion

Assignment		HF/6-31G*		HF/DZP	HF/DZPD	
		[8]	Our calculation	$\omega_i$	$\omega_i$	$A_i$
$\text{LiClO}_3, C_s(b)$						
$A'$	$\omega_1$	1176	1171	1139	1133	243
	$\omega_2$	942	942	927	923	73
	$\omega_3$	694	696	679	676	91
	$\omega_4$	635	630	611	607	119
	$\omega_5$	532	529	528	523	68
$A''$	$\omega_6$	167	156	157	157	68
	$\omega_7$	984	983	963	960	230
	$\omega_8$	529	521	498	498	39
	$\omega_9$	429	434	403	406	19
$\text{LiClO}_3, C_{3v}(t)$						
$A_1$	$\omega_1$	941	941	919	918	28
	$\omega_2$	697	687	690	691	23
	$\omega_3$	509	509	491	495	206
$E$	$\omega_4$	1037	1037	1014	1013	429
	$\omega_5$	536	536	536	534	71
	$\omega_6$	187	9.41	45	57	92
$\text{ClO}_3^-, C_{3v}$						
$A_1$	$\omega_1$	993		964	949	60
	$\omega_2$	640		625	620	46
$E$	$\omega_3$	1105		1066	1044	581
	$\omega_4$	507		502	498	42

molecule. Therefore in the third step of the scaling (*M3*), we used the coefficient  $c_\alpha(\text{OClO}) = 0.876$  found from the experimental frequency  $\nu_3 = 630.5 \text{ cm}^{-1}$  (the value of  $c_\alpha$  was taken the same for the  $\text{O}_t\text{ClO}_b$  and  $\text{O}_b\text{ClO}_b$  angles).

A comparison of the calculated (*M3*) vibration frequencies with the published IR spectra [1, 3, 5, 6] shows that the  $557 \text{ cm}^{-1}$  [1] and  $481 \text{ cm}^{-1}$  [1, 3] bands may be assigned to vibrations of the  $\text{LiClO}_3$  molecule. As follows from our calculations, these are the  $\nu_4$  and  $\nu_5$  vibrations (*M3* calculation:  $559$  and  $482 \text{ cm}^{-1}$ ), whose modes are mixed: the coordinates  $r(\text{Li-O})$ ,  $\alpha(\text{O}_b\text{ClO}_b)$ , and  $\beta(\text{O}_t\text{ClO}_b)$  make approximately the same contributions to these vibrations. The assignments of the bands at  $972$ ,  $961$ ,  $904$ , and  $896 \text{ cm}^{-1}$  [3] to  $\text{LiClO}_3$  are not confirmed. These assignments were also doubted in [6]. Evidently, the  $533 \text{ cm}^{-1}$  [1] and  $891 \text{ cm}^{-1}$  [6] bands do not belong to  $\text{LiClO}_3$  either. In the fourth step (*M4*), the theoretical force field was refined using the experimental frequencies  $\nu_1$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ , and  $\nu_7$  for the isotopic varieties  $\text{Li}^{35}\text{ClO}_3$  and  $\text{Li}^{37}\text{ClO}_3$ . The following scale factors were obtained:  $c_t(\text{Cl-O}_t) = 0.9487$ ,  $c_d(\text{Cl-O}_b) = 0.8528$ ,  $c_\alpha(\text{O}_b\text{ClO}_b) = 0.8776$ ,  $c_\beta(\text{O}_t\text{ClO}_b) = 0.8632$ ,  $c_r(\text{Li-O}) = 0.8062$ . The  $c_\gamma$  factor was again estimated at unity.

Thus the IR spectrum of  $\text{LiClO}_3$  has: a) two intense bands:  $\nu_1(A') = 1099 \text{ cm}^{-1}$  [potential energy distribution (PED) in coordinates:  $0.89t + 0.07d$ ] and  $\nu_7(A'') = 887 \text{ cm}^{-1}$  ( $0.96d$ ); b) five medium-intensity bands:  $\nu_2(A') = 856 \text{ cm}^{-1}$  ( $0.85d + 0.06\alpha$ ),  $\nu_3(A') = 630 \text{ cm}^{-1}$  ( $0.18r + 0.68\alpha + 0.08\beta$ ),  $\nu_4(A') = 557 \text{ cm}^{-1}$  ( $0.41r + 0.13\alpha + 0.40\beta$ ),  $\nu_5(A') = 481 \text{ cm}^{-1}$  ( $0.40r + 0.27\alpha + 0.30\beta$ ), and  $\nu_6(A') = 156 \text{ cm}^{-1}$  ( $0.83\gamma + 0.14\beta$ ); c) two weak bands:  $\nu_8(A'') = 459 \text{ cm}^{-1}$  ( $0.78\beta + 0.20r$ ) and  $\nu_9(A'') = 367 \text{ cm}^{-1}$  ( $0.76r + 0.23\beta$ ). In the experimental works [1, 3, 5, 6], both intense

**TABLE 4.** Frequencies of Vibrations  $\nu_i$  ( $\text{cm}^{-1}$ ) and IR Intensities  $A_i$  ( $\text{km/mole}$ ) of the  $\text{LiClO}_3$  ( $C_s$ ,  $b$ ) Molecule Calculated with the Scaled<sup>a</sup> Force Field

Isotopomer	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	$\nu_8$	$\nu_9$
$M1 \nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}_3)$	1073	876	653	570	490	157	909	477	371
$A_i$	245	77	63	105	106	67	229	31	28
$M2 \nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}_3)$	1099	860	651	570	491	157	887	476	371
$M3 \nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}_3)$	1099	887	630.5	559	482	156	887	462	368
$M4$									
$\nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}_3) \left\{ \begin{array}{l} 1098.5 \\ 1099^b \end{array} \right.$	1098.5 1099 <sup>b</sup>	856.4	630.0 630.5 <sup>b</sup>	557.0 557 <sup>b</sup>	481.1 481.2 <sup>b</sup>	156.0	886.9 887 <sup>b</sup>	458.8	367.2
$\nu_i (^7\text{Li}^{37}\text{Cl}^{16}\text{O}_3) \left\{ \begin{array}{l} 1987.5 \\ 1087^b \end{array} \right.$	1987.5 1087 <sup>b</sup>	849.2	626.3 625.7 <sup>b</sup>	555.1	479.8	156.0	878.1 878 <sup>b</sup>	457.7	366.8
$\nu_i (^7\text{Li}^{35}\text{Cl}^{18}\text{O}_3)$	1059.3	823.6	601.8	541.1	470.1	152.5	855.4	437.6	358.3
$\nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}^{18}\text{O}_2)$	1096.8	826.5	604.6	544.7	474.6	154.3	855.5	446.4	361.0
$\nu_i (^7\text{Li}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2)$	1061.6	853.0	627.8	552.3	477.3	154.1	886.9	450.3	354.6
$\nu_i (^7\text{Li}^{35}\text{Cl}^{16}\text{O}^{16}\text{O}^{18}\text{O})$	1097.7	835.1	617.3	551.1	478.5	155.2	877.6	451.8	364.0
$\nu_i (^7\text{Li}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}^{18}\text{O})$	1960.4	832.5	614.8	546.9	474.4	153.3	877.0	443.2	361.3
$\nu_i (^6\text{Li}^{35}\text{Cl}^{16}\text{O}_3)$	1098.6	856.5	631.3	575.5	499.0	163.4	887.2	463.4	382.5
$A_i$	236	81	73	119	87	66	229	35	23

Notes. <sup>a</sup>The refinement of the force field was carried out in four steps  $M1 \rightarrow M4$  (see text). <sup>b</sup>Experimental values of the frequencies of vibrations  $\nu_1$  [6],  $\nu_3$ ,  $\nu_5$  [1, 3],  $\nu_4$  [1],  $\nu_7$  [6].

bands ( $\nu_1$ ,  $\nu_7$  [5, 6]) and three of the five medium-intensity bands ( $\nu_3$  [1, 3],  $\nu_4$  [1],  $\nu_5$  [1, 3]) were observed. The band  $\nu_6 = 156 \text{ cm}^{-1}$ , corresponding to the ring-puckering vibration, lies in the spectral region that has not yet been studied experimentally. Among the medium-intensity bands, the band  $\nu_2 = 856 \text{ cm}^{-1}$  was not observed in the experimentally studied region of the IR spectrum. According to the calculations, this band is nearly three times less intense than the strong band  $\nu_7 = 877 \text{ cm}^{-1}$ .

The calculated isotopic shifts agree with the experimental ones. An exception is the  $\nu_3(A')$  frequency. Some details of the isotopic structure of this band observed in [3] for the  $^{16}\text{O} \rightarrow ^{18}\text{O}$  isotopic substitution do not quite agree with theory:

Experiment [3]	Calculation (M4)	Isotopomer
630.5	630.0	$^7\text{Li}^{35}\text{Cl}^{16}\text{O}_3$
625.5	$\left\{ \begin{array}{l} 627.8 \\ 626.3 \end{array} \right.$	$^7\text{Li}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2$ $^7\text{Li}^{37}\text{Cl}^{16}\text{O}_3$
622.1	...	?
615 $\pm$ 1	$\left\{ \begin{array}{l} 617.3 \\ 614.8 \end{array} \right.$	$^7\text{Li}^{35}\text{Cl}^{16}\text{O}^{16}\text{O}^{18}\text{O}$ $^7\text{Li}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}^{18}\text{O}$
604 $\pm$ 1	$\left\{ \begin{array}{l} 604.6 \\ 601.8 \end{array} \right.$	$^7\text{Li}^{35}\text{Cl}^{16}\text{O}^{18}\text{O}_2$ $^7\text{Li}^{35}\text{Cl}^{18}\text{O}_3$



All observed components of the multiplet in the region of  $630\text{ cm}^{-1}$  may be assigned to different isotopic varieties of the  $\text{LiClO}_3$  ( $C_s$ ) molecule if we assume that the frequencies of vibrations of some isotopomers overlap in the spectrum. An exception is the observed frequency  $622.1\text{ cm}^{-1}$ ; it may not be assigned to any of the isotopomers.

To further clarify peculiarities of the vibrational spectrum of the  $\text{LiClO}_3$  molecule, it would be useful to carry out additional spectral investigations, including studies of IR and Raman spectra using the  $^{16}\text{O} \rightarrow ^{18}\text{O}$ ,  $^{35}\text{Cl} \rightarrow ^{37}\text{Cl}$ , and  $^7\text{Li} \rightarrow ^6\text{Li}$  isotopic substitutions. We hope that our calculations will be helpful for future studies of the  $\text{LiClO}_3$  molecule.

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