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2. REPORT DATE April 22, 1994		3. REPORT TYPE AND DATES COVERED TECHNICAL REPORT	
4. TITLE AND SUBTITLE Anionic and Neutral States of Li ₃ O		5. FUNDING NUMBERS G N00014-89-J-1497 R&T 4131050	
6. AUTHOR(S) Maciej Gutowski and Jack Simons			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF UTAH DEPARTMENT OF CHEMISTRY SALT LAKE CITY, UTAH 84112 U.S.A.		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 45	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) OFFICE OF NAVAL RESEARCH CHEMISTRY PROGRAM 800 NORTH QUINCY ST. ARLINGTON, VIRGINIA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Submitted for publication in the Journal of Chemical Physics			
12a. DISTRIBUTION / AVAILABILITY STATEMENT THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE AND SALE; ITS DISTRIBUTION IS UNLIMITED		12b. DISTRIBUTION CODE UNLIMITED	
13. ABSTRACT (Maximum 200 words) The ground state of the cation, three lowest electronic states of the neutral, and two anionic states of Li ₃ O were studied using different ab initio techniques. Stationary points on the potential energy surfaces were determined both at complete active space (CAS) self-consistent field (SCF) and at second-order Møller-Plesset (MP2) levels of theory. Excited states were approached using the single-excitation configuration interaction (CIS) method. Electron detachment energies for the anionic and neutral states were calculated at the quadratic configuration interaction (QCI) level with single, double, and approximate triple excitations (SD(T)) included. The calculations indicate that Li ₃ O ⁺ possesses two bound electronic states. The ground ¹ A ₁ ' state has an equilibrium D _{3h} structure and a vertical electron detachment energy (VDE) of 0.66 eV. The ³ E' bound state pseudorotates through ³ A ₁ and ³ B ₂ stationary points. The barrier for pseudorotation was found to be less than 0.002 eV at the QCISD(T) level. Two VDE peaks for the ³ E' anion were predicted to be at 0.45 and 1.15 eV, for transitions to the ground and the first excited state of the neutral, respectively. The ground state of the cation and the first three electronic states of the neutral Li ₃ O were also considered and the vertical ionization potential for the ground neutral state was found to be 3.60 eV. Li ₃ O and Li ₃ O ⁺ are thermodynamically stable with respect to the unimolecular decompositions Li ₃ O ⁽⁺⁾ → Li ₂ O + Li ⁽⁺⁾ . Hence the species should be amenable to experimental studies.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
20. LIMITATION OF ABSTRACT			

OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1497

R&T Code 4131050
Scientific Officer: Dr. R. Nowak

Technical Report No. 45

"Anionic and Neutral States of Li_3O "

by

Maciej Gutowski and Jack Simons

Prepared for Publication in

The Journal of Chemical Physics

The University of Utah
Department of Chemistry
Salt Lake City, Utah 84112-1194

April 22, 1994

Accession For	
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Anionic and Neutral States of Li_3O

Maciej Gritowski[@] and Jack Simons

Chemistry Department
University of Utah
Salt Lake City, UT 84112

Abstract

The ground state of the cation, three lowest electronic states of the neutral, and two anionic states of Li_3O were studied using different ab initio techniques. Stationary points on the potential energy surfaces were determined both at complete active space (CAS) self-consistent field (SCF) and at second-order Møller-Plesset (MP2) levels of theory. Excited states were approached using the single-excitation configuration interaction (CIS) method. Electron detachment energies for the anionic and neutral states were calculated at the quadratic configuration interaction (QCI) level with single, double, and approximate triple excitations (SD(T)) included. The calculations indicate that Li_3O^- possesses two bound electronic states. The ground $^1\text{A}_1$ state has an equilibrium D_{3h} structure and a vertical electron detachment energy (VDE) of 0.66 eV. The $^3\text{E}'$ bound state pseudorotates through $^3\text{A}_1$ and $^3\text{B}_2$ stationary points. The barrier for pseudorotation was found to be less than 0.002 eV at the QCISD(T) level. Two VDE peaks for the $^3\text{E}'$ anion were predicted to be at 0.45 and 1.15 eV, for transitions to the ground and the first excited state of the neutral, respectively. The ground state of the cation and the first three electronic states of the neutral Li_3O were also considered and the vertical ionization potential for the ground neutral state was found to be 3.60 eV. Li_3O and Li_3O^- are thermodynamically stable with respect to the unimolecular decompositions $\text{Li}_3\text{O}^{-(0)} \rightarrow \text{Li}_2\text{O} + \text{Li}^{-(0)}$. Hence the species should be amenable to experimental studies.

[@]Present address: IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099.

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I. Introduction

Recent theoretical studies indicate that neutral molecular radicals containing alkali metal atoms can accommodate more than one bound anionic state. The simple alkali metal oxide diatomic molecules possess electronically bound anionic states of $^3\Pi$, $^1\Pi$, $^1\Sigma^+$, and $^3\Sigma^+$ symmetry [1]. Experimental [2,3] and theoretical [4] studies on alkali metal trimer anions (M_3^-) have concentrated primarily on the lowest $^1\Sigma_g^+$ isomer. Recently, we demonstrated that one triplet ($^3A_2'$) and two quintet ($^5A_1'$ and $^5A_2'$) states of Li_3^- and Na_3^- are also electronically stable for a wide range of molecular geometries [5]. Also $LiFLi^-$ possesses two electronically bound states of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetry [6].

The neutral Li_3O has already been studied both experimentally [7] and theoretically [8-11]. Wu et al. identified Li_3O in the course of their study on the nature of gaseous species over solid lithium oxides [7]. The values of the ionization potential, atomization energy, and dissociation energy to produce $Li + Li_2O$ were found to be 4.54 ± 0.2 eV, 228.7 ± 2 kcal/mol, and 50.7 ± 10 kcal/mol, respectively [7,12].

Li_3O is an example of a "hypermatalated" molecule with a stoichiometry which violates the octet rule [8]. In addition, it is a promising candidate for being a "superalkali", (i.e., a molecular system whose first ionization potential is smaller than that of the Cs atom [9-11]). Both of these unusual chemical features are related to the nature of the highest occupied molecular orbital (HOMO). It displays bonding interactions between pairs of Li "ligands" which help to offset the octet-rule-violating structure and antibonding Li-O interactions.

Early predictions of a C_{2v} equilibrium structure for Li_3O [8] have not been confirmed in more advanced calculations [13,10] which indicated a D_{3h} structure, similar to that of Li_3O^+ . Theoretical predictions of the adiabatic and vertical ionization potential produced 3.55 and 3.45 eV, respectively [10,11], far outside the range of experimental values [7], although the theoretical dissociation energy of 47.1 kcal/mol [10] agrees well with the experimental prediction.

To the best of our knowledge, neither the excited electronic states of the neutral nor the anionic states of Li_3O have yet been experimentally studied.

II. Computational Aspects

For the lithium atom, we used the Dunning (9s5p/3s2p) one-electron basis set [14] supplemented with diffuse s and p functions with the same exponent 0.0074 [15] and one d function with the exponent 0.2 [16]. This basis set is detailed in Ref. [5]. For the oxygen atom we employed Dunning's aug-cc-pVDZ basis set which was designed to describe anionic species [17]. Cartesian d functions were used throughout the calculations and the full basis set for the molecule consists of 82 contracted gaussian functions.

Potential energy surfaces were explored within a complete active space (CAS) self-consistent field (SCF) formalism as well as at the second-order Møller-Plesset (MP2) theory level.

In CAS SCF calculations we imposed a constraint that molecular orbitals which result from the core 1s atomic orbitals were doubly occupied in every configuration state function (CSF). The neglected core-core and core-valence correlation effects are negligible for the lithium and oxygen atoms due to the low polarizability of the 1s cores. The remaining eight (cation), nine (neutral) or ten (anion) electrons were distributed in all possible ways among four a_1 , two b_1 , and two b_2 molecular orbitals (the C_{2v} symmetry labeling is used). This choice of the active space led to 1764, 2352, 1176, and 1512 CSF's for the cation, neutral, singlet and triplet anion, respectively. The CAS SCF calculations were performed with the Utah MESS-KIT modular electronic structure codes [18] which generate analytical second geometrical derivatives. Stationary points on the potential energy surfaces were determined using our automated surface walking algorithm [19].

In the case of the neutral 2^2A_1 state, which correlates with the $2E'$ state, the CAS SCF optimization was hindered by the problem of "root-flipping" [20]. Since the MP2 approach is inapplicable for excited electronic states, we invoked single-excitation configuration

interaction (CIS) approach [21] to determine geometry and relative energy of the 2^2A_1 transition state. The CIS results for the doublet neutral state should be considered cautiously. In the CIS approach, creation of spin eigenstates relies on having an RHF ground state and non-interaction of singlets and triplets does not carry over to doublets and quartets with a UHF reference. The Gaussian 92 code [22] attempts to handle these doublet cases but the theory is not clean anymore [23]. In view of the above doubts, we "calibrated" the CIS approach on the 2^2B_2 electronic state which also correlates with $2^2E'$ but for which the CAS SCF and MP2 approaches are straightforwardly applicable.

In the MP2 geometry optimizations we allowed for the correlation of the core orbitals. In general, the structures corresponding to stationary points are quite similar at the CAS SCF and MP2 levels what suggests that the core-core and core-valence correlation effects are not important for geometrical predictions.

The restricted CAS SCF approach is capable to predict accurate geometries but it is inappropriate to accurately compare energies of species with a different number of electrons. Hence we employed the quadratic configuration interaction (QCI) approach with single, double and approximate triple excitations (SD(T)) [24] to determine relative energies and electron detachment energies. The QCISD(T) approach is size-extensive and takes into account dynamical correlation effects. In the QCI calculations, we kept the eight core electrons uncorrelated. We checked in our earlier study on $LiFLi^-$ [6] that such a restriction changes the vertical detachment energy for the ground state anion by less than 0.003 eV. The QCI results were obtained with the Gaussian 92 suite of codes [22].

III. Results

The stationary points on the potential energy surfaces of the cation, neutral, and anion determined at the CAS SCF and MP2 levels are characterized at Table 1 and the geometrical parameters used are defined in Fig. 1. The vibrational frequencies were calculated using analytical second derivatives. For the excited 2^2B_2 and 2^2A_1 states of

the neutral, stationary points are also reported at the CIS level. The spatial extents of the electronic charge distributions are characterized by the SCF values of $\langle R^2 \rangle$. The reported relative energies were obtained at the QCISD(T) level, as were our vertical (VDE) and adiabatic electron affinities (EA_a) presented in Tables 2 and 3 for the neutral and the anion, respectively.

A. The Cation and Neutral

The D_{3h} electronic configuration for the closed-shell cation involves an orbital occupation $3a_1'^2 2e' 21a_2''^2$ (the core $1s$ orbitals are not included in this labelling) which will be denoted (+). Our D_{3h} geometry and frequencies for the closed-shell cation are quite similar at the CAS SCF and MP2 levels. They are also in a good agreement with the results of Rehm et al. [10]. The pyramidization mode (a_2''), which lowers symmetry to C_{3v} , has the lowest frequency. Interestingly, the cation H_3O^+ , studied earlier [25] has a C_{3v} equilibrium structure with the D_{3h} barrier of only 1.07 kcal/mol [26].

The MP2 equilibrium structure of the ground state neutral with the electronic configuration (+) $4a_1'$ is again D_{3h} and similar to that of the cation. Because the $^2A_1'$ wavefunction is found to have a single configuration character, the MP2 prediction should be quite accurate. Unexpectedly, the e' (in-plane) vibrational mode has an imaginary frequency at the CAS SCF level. Doubting whether the CAS SCF e' imaginary frequency is physically meaningful, we carried out a CAS SCF search for a new stationary point in C_{2v} symmetry and found a structure with $R_1=1.683$ Å, $R_2=1.731$ Å, $\vartheta=133^\circ$ and an energy 0.06 eV lower than at the D_{3h} stationary point. However, the QCISD(T) energy is lower by 0.02 eV at the D_{3h} than at the C_{2v} CAS SCF stationary point. Hence, we conclude that the D_{3h} structure corresponds to a genuine minimum and the CAS SCF approach suffers for symmetry breaking artifacts [27]. Even though this $^2A_1'$ state has a D_{3h} equilibrium structure, the MP2 vibrational frequencies of the a_2'' and e' modes are much softer than in the underlying cation which implies that C_{3v} , C_{2v} , and C_s symmetries are easily accessible by vibrational movement.

The $4a_1'$ HOMO of the neutral is dominated by Li 2s orbitals which interact constructively with each other and destructively with small s-type contributions from the central O atom, as observed in Refs. [8-10]. The Mulliken-population atomic charges are +0.20 and -0.60 for Li and O, respectively. Our values for the VDE and EA_a of this ground state of Li_3O are 3.60 and 3.59 eV, respectively, in a good agreement with the electron propagator theory VDE of 3.45 eV [11]. However, these results disagree with the experimental estimation of 4.54 ± 0.2 eV [7]. The theoretical VDE for Li_3O is lower than that of alkali metal atoms, so our result support the claimed "superalkali" nature of Li_3O [9-11].

The first excited state for the neutral of $2E'$ symmetry has a dominant orbital occupancy of $(+)3e'$ and is subject to first-order Jahn-Teller (FOJT) distortion. Geometry optimization for the resulting $2B_2$ component of this state is straightforward and the resulting CAS SCF and MP2 geometries and frequencies are quite similar. Due to problems with "root-flipping" at the CAS SCF level, geometry optimization for the 2^2A_1 component of this $2E'$ state was performed at the CIS level. The reliability of the CIS approach was tested on the $2B_2$ state where the stationary point characteristics were found to be similar for the CIS, CAS SCF, and MP2 approaches. We therefore believe that application of the CIS approach to the 2^2A_1 state is justified.

Pseudorotation in the $2E'$ state is depicted in Fig. 2. Estimating the pseudorotation barrier requires a consistent calculation of the 2^2A_1 and $2B_2$ energies. A QCISD(T) estimate for the 2^2A_1 energy was obtained using the following approximation: $E_{QCI}(2B_2) - E_{CIS}(2B_2) + E_{CIS}(2^2A_1)$, because only the CIS method could be applied directly to the 2^2A_1 state. The barrier for pseudorotation thus found was less than 0.04 eV.

The CIS oscillator strength for the $2E' \leftarrow 2^2A_1'$ transition is 0.48 and the QCISD(T) vertical excitation energy is 0.728 eV. Interestingly, the neutral $2E'$ state thus produced would be in the neighborhood of its conical intersection. This fact could be reflected in the dynamics of the $2E'$ state, which might be studied using time dependent two-photon ionization techniques [28].

The next excited state of Li_3O has $^2A_2''$ symmetry and $(+)2a_2''$ orbital occupancy and an equilibrium D_{3h} structure. In comparison with the cation, the vibrational frequencies are quite similar and the equilibrium R is somewhat shorter. These features are consistent with the "out-of-the-plane" nature of the $2a_2''$ orbital and similar trends were observed in the alkali metal trimers with the unpaired electron in an a_2'' orbital [5,29]. In Li_3O , the $2a_2''$ orbital is dominated by the Li 2p atomic orbitals with constructive Li-Li and destructive Li-O interactions. The CIS oscillator strength for the $^2A_2'' \leftarrow ^2A_1'$ transition is 0.32 and the QCISD(T) vertical excitation energy is 1.551 eV.

B. The Anion

The ground electronic state of Li_3O^- has a D_{3h} equilibrium structure with a geometry close to that of the cation and that of the ground state neutral. There is again a significant difference between the a_2'' out-of-plane vibrational frequency calculated at the MP2 and CAS SCF levels, but this time both approaches predict a D_{3h} minimum. The MP2 frequencies are quite similar for the anion and the $^2A_1'$ neutral.

The wavefunction for the anionic $^1A_1'$ state is dominated by the $(+)4a_1'^2$ configuration, but two equivalent contributions from the $(+)3e'^2$ configuration are also important and have CI coefficients of 0.30 each. This feature is consistent with the low separation between the $^2A_1'$ and $^2E'$ states of the neutral (0.7 eV) and suggests that $^3E'$ anionic state may be also electronically stable. The VDE for the $^1A_1'$ anion state is 0.656 eV and the electron detachment peak is expected to be sharp because the anion and neutral equilibrium structures are very similar.

In addition to the ground $^1A_1'$ state, the anion Li_3O^- possesses a second electronically bound state of $^3E'$ symmetry with the dominant electronic configuration $(+)4a_1'3e'$. Due to FOJT distortion, stationary points develop on 3B_2 and 3A_1 surfaces. Both CAS SCF and MP2 approaches locate a transition state on the 3B_2 surface with negative curvature along the b_2 distortion mode. The surface must, however,

be extremely flat since at the QCISD(T) level the relative order of the 3B_2 and 3A_1 stationary points is changed, giving 3B_2 lower than 3A_1 by 0.001 eV, whereas the difference at the MP2 level was 0.011 eV with the opposite order. Clearly, the pseudorotation, as depicted on Fig. 2, is practically free and the numerical values of the b_2 mode frequency are probably of little reliability.

The electron detachment energies for the pseudorotating $^3E'$ state were calculated at both daughter-state stationary points (see Table 3). The detachment energies to the ground $^2A_1'$ state of the neutral are predicted to lie in the range 0.43-0.46 eV. The detachment energies to the higher pseudorotating $^2E'$ state of the neutral lie within 1.1-1.2 eV. We thus conclude that the electron detachment peaks from the $^3E'$ anion state would bracket the anion's ground state detachment peak at 0.66 eV. Hence, the $^3E'$ state may be amenable to experimental detection, providing a significant concentration of the triplet can be produced in the source.

Another feature which makes Li_3O and Li_3O^- suitable for experimental studies is their thermodynamic stability. The energy barrier (corrected for zero-point vibrations) for the decomposition $Li_3O(+0-) \rightarrow Li_2O + Li(+0-)$ is predicted to be 84.40, 44.54, and 46.03 kcal/mol for the cation, neutral, and anion, respectively. The increased stability of the anion compared to that of the neutral reflects the fact that the electron affinity is larger for Li_3O than for Li. Our decomposition energy for the neutral is within the range of experimental data 50.7 ± 10 kcal/mol [7,12].

IV. Conclusions

Theoretical calculations indicate that Li_3O^- can possess more than one bound electronic state. The fully symmetric singlet state is the ground state, but a triplet state is also electronically bound. Although only the anionic states of Li_3O^- were studied in this work, the preliminary results for the isoelectronic Li_4N^- produce a VDE from the 1A_1 state of ca. 0.51 eV. For the 3T_2 state of Li_4N^- , the VDE is ca. 0.17 eV, whereas detachment to the 2T_2 state of the neutral Li_4N would require ca. 0.98 eV.

For the ground $^1A_1'$ state of Li_3O^- , the electron detachment energy is 0.66 eV. The cation, ground state neutral, and the anion all have the equilibrium D_{3h} geometries, with the O-Li distances in the range 1.71-1.69 Å (MP2 level).

The pseudorotating anionic $^3E'$ state is electronically stable with respect to the $^2A_1'$ and $^2E'$ states of the neutral by ca. 0.4 and 1.1 eV, respectively. The geometrical features of the daughter-state 3A_1 and 3B_2 stationary points are consistent with the bonding/antibonding interactions among the atomic orbitals contributing to the anion's singly occupied molecular orbitals. The QCISD(T) energies of the two stationary points are the same to within 0.002 eV. Hence, the pseudorotation is practically free.

For the neutral Li_3O , we studied the $^2E'$ and $^2A_2''$ excited states in addition to the $^2A_1'$ ground state. The $^2E'$ state pseudorotates through a 2B_2 minimum and a 2A_1 transition state with a pseudorotation barrier of ca 0.04 eV. The oscillator strength for the $^2E' \leftarrow ^2A_1'$ transition is 0.48 and the corresponding vertical excitation energy is 0.728 eV.

The $^2A_2''$ neutral, with a D_{3h} equilibrium structure, is separated from the ground state neutral by 1.551 eV, and is easily accessible since the oscillator strength is 0.32.

Our vertical and adiabatic ionization potentials for Li_3O of 3.60 and 3.59 eV, respectively, disagree with the experimental value of 4.54 ± 0.2 eV [7], yet agree with other theoretical predictions [10,11].

All of the species discussed in this study are thermodynamically stable with respect to unimolecular decomposition. Hence, the neutral and the anion are more amenable to experimental studies than their hydrogen-substituted analogs H_3O and H_3O^- , which are thermodynamically unstable [25].

Acknowledgments

This work was supported by the Office of Naval Research and National Science Foundation Grant CHE9116286.

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Captions for Figures

Figure 1. Geometrical parameters for the C_{2v} structure of the Li_3O neutral and anionic species.

Figure 2. Graph representing the pseudorotation for anionic or neutral Li_3O .

Table 1. Stationary points (distances R in Å, ϕ in degrees) and harmonic frequencies (cm^{-1}) for different electronic states of the cation, neutral, and anion of Li_3O . The spatial extent of the SCF electronic charge distribution $\langle R^2 \rangle$ is given in a.u., and the relative energies (QCISD(T) level) are in eV. The dominant electronic configurations (DEC) are given with respect to the closed-shell cationic core $3a_1'^2 2e'^2 1a_2'^2$, which is denoted (+).

Species	Symmetry	State	DEC	Method	Geometry	Vibrational Frequencies ^a	$\langle R^2 \rangle$	EqQ
Li_3O^+	D_{3h}	$1A_1'$	(+)	CAS	R=1.726	a_2'' 244, e' 265, a_1' 655, e' 806	91	0.0
				MP2	R=1.708	e' 270 (73), a_2'' 291 (270), a_1' 687 (0), e' 853 (290)		
Li_3O	D_{3h}	$2A_1'$	(+)4 a_1'	CAS	R=1.707	e' 251i, a_2'' 77, a_1' 669, e' 767	141	-3.593
				MP2	R=1.694	e' 135 (462), a_2'' 180 (2), a_1' 699 (0), e' 869 (109)		
Li_3O	C_{2v}	$2B_2$	(+)3 b_2	CAS	R1=1.705 R2=1.707 ϕ =114.58	b_1 193, b_2 215, a_1 219, a_1 679, a_1 801, b_2 871	153	-2.890
				MP2	R1=1.690 R2=1.707 ϕ =114.96	b_2 202 (9250), a_1 213 (87), b_1 243 (1), a_1 687 (52), b_2 844 (148), a_1 849 (16)		
				CIS	R1=1.662 R2=1.699 ϕ =117.96	b_1 210, b_2 229, a_1 244, a_1 697, b_2 814, a_1 903		
Li_3O	C_{2v}	2^2A_1	(+)7 a_1	CIS	R1=1.718 R2=1.671 ϕ =121.08	b_2 132i, b_1 211, a_1 424, a_1 702, b_2 745, a_1 1025		-2.854b)

Table 1. (continued)

Species	Symmetry	State	DEC	Method	Geometry	Vibrational Frequencies ^a	$\langle R^2 \rangle$	EqQ
Li ₃ O	D _{3h}	2A ₂ ^{''}	(+)2a ₂ ^{''}	CAS	R=1.706	a ₂ ^{''} 215, e' 232, a ₁ ' 678, e' 804	189	-2.042
				MP2	R=1.697	e' 232 (403), a ₂ ^{''} 247 (4), a ₁ ' 702 (0), e' 839 (1353)		
Li ₃ O ⁻	D _{3h}	1A ₁ '	(+)4a ₁ ' ²	CAS	R=1.708	a ₂ ^{''} 85, e' 180, a ₁ ' 666, e' 748	274	-4.248
				MP2	R=1.697	e' 171 (77), a ₂ ^{''} 172 (179), a ₁ ' 693 (0), e' 856 (214)		
Li ₃ O ⁻	C _{2v}	3A ₁	(+)6a ₁ 7a ₁	CAS	R ₁ =1.709 R ₂ =1.707 ϕ=131.18	b ₂ 144, b ₁ 149, a ₁ 257, a ₁ 673, b ₂ 723, a ₁ 858	249	-4.023
				MP2	R ₁ =1.717 R ₂ =1.697 ϕ=129.23	b ₂ 101 (123), b ₁ 202 (166), a ₁ 235 (316), a ₁ 682 (5), b ₂ 806 (781), a ₁ 875 (458)		
Li ₃ O ⁻	C _{2v}	3B ₂	(+)6a ₁ 3b ₂	CAS	R ₁ =1.700 R ₂ =1.707 ϕ=109.43	b ₂ 270i, b ₁ 144, a ₁ 191, a ₁ 673, a ₁ 761, b ₂ 809	246	-4.024
				MP2	R ₁ =1.692 R ₂ =1.709 ϕ=109.81	b ₂ 154i (6108), a ₁ 176 (342), b ₁ 200 (162), a ₁ 682 (139), a ₁ 824 (439), b ₂ 845 (318)		

a) IR intensities (km/mol) in parenthesis

b) the energy of 2²A₁ is estimated as: EQCI(2B₂) + ECIS(2²A₁) - ECIS(2B₂)

Table 2. Electron vertical detachment energies (VDE) and adiabatic electron affinities (EA_a) (in eV) calculated at the QCISD(T) level for the transitions $Li_3O^+ + e \leftarrow Li_3O$.

Transition	VDE	EA_a
$^1A_1' + e \leftarrow ^2A_1'$	3.603	3.593
$^1A_1 + e \leftarrow ^2B_2$	2.933	2.890
$^1A_1 + e \leftarrow ^2^2A_1^a)$	2.954	2.909
$^1A_1' + e \leftarrow ^2A_2''$	2.052	2.042

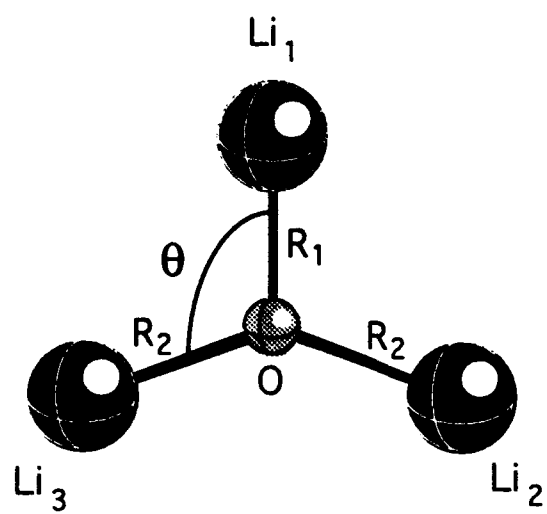
a) the energy of 2^2A_1 is estimated as in Table 1

Table 3. Electron vertical detachment energies (VDE) and adiabatic electron affinities (EA_a) (in eV) calculated at the QCISD(T) level for the transitions $Li_3O + e \leftarrow Li_3O^-$.

Transition	VDE	EA_a
$2A_1' + e \leftarrow 1A_1'$	0.656	0.656
$1^2A_1 + e \leftarrow 3A_1$	0.450	0.430
$2^2A_1 + e \leftarrow 3A_1$	1.346 ^{a)}	1.074 ^{b)}
$1^2A_1 + e \leftarrow 3B_2$	0.459	0.431
$2B_2 + e \leftarrow 3B_2$	1.151	1.134

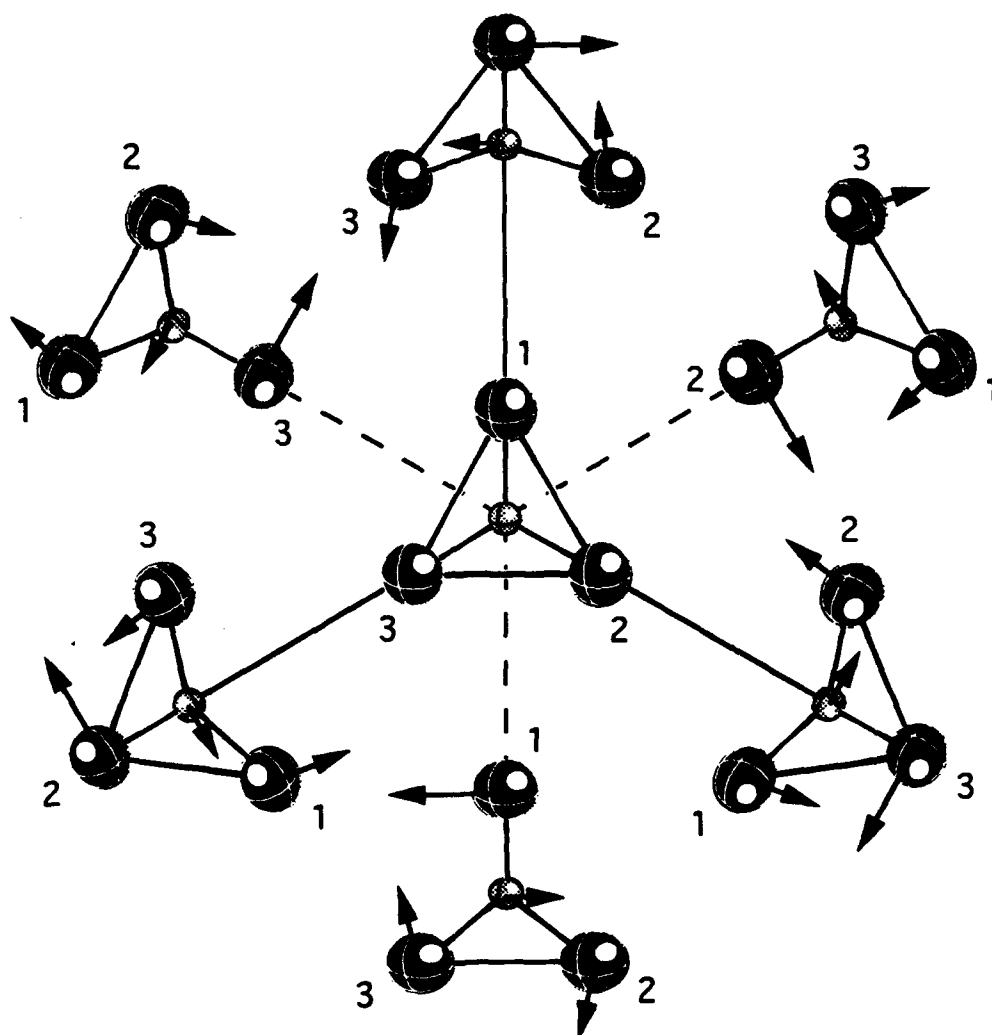
a) the VDE is estimated as: $E_{QCI}(^3A_1) - E_{QCI}(^2B_2) + E_{CIS}(^2B_2) - E_{CIS}(2^2A_1)$.

b) the EA_a is estimated as: $VDE + E_{CIS}(2^2A_1 \text{ at the } ^3A_1 \text{ geometry}) - E_{CIS}(2^2A_1 \text{ at its CIS stationary point})$.



Anionic and Neutral States of
 Li_3O
Gutowski, Simons

FIG. 1



Anionic and Neutral States of Li_3O

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FIG. 2