

# Vibrational and Electronic Oscillator Strengths of LiO\*

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Electronic energies and wave functions of ground and excited states of LiO are calculated in the Hartree-Fock approximation. The vibrational oscillator strengths of the  $X^2\Pi$  and  $A^2\Sigma^+$  valence states are calculated for  $v=0$  to 1 and 1 to 2 transitions. Electronic oscillator strengths are also presented for transitions to the quantum number two Li Rydbergs. Reasons are presented to support the use of the Hartree-Fock approximation.

Key words:  $A^2\Sigma$ ; electronic transition probabilities; Hartree-Fock; LiO, vibrational transition probabilities;  $X^2\Pi$ .

## 1. Introduction

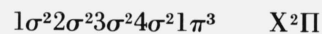
Refractory metal oxides have proved to be difficult experimental subjects. For even one of the simplest, LiO, little is known about the system beyond the ground state properties of the  $X^2\Pi$  state. In particular there is no experimental information on the infrared intensities and the ultraviolet spectrum. Interest in the radiative properties of LiO has prompted a number of theoretical calculations. Accurate Hartree-Fock (H-F) and configuration interaction (CI) results [1]<sup>1</sup> have been reported for the  $X^2\Pi$  and the low-lying  $^2\Sigma^+$  excited states. These results show that the properties of this molecule are accessible to theoretical calculation. This paper will apply the Hartree-Fock technique to some remaining problems of the properties of LiO.

The Hartree-Fock self-consistent-field variational calculations are based upon an anti-symmetrized product of one-electron orbitals that are determined by the averaged field of all the other electrons. The lack of correlation in this model leads to large absolute errors in the energy. But the applicability of the Hartree-Fock technique must not be rejected out of hand without an examination of the problem at question since correlated wave functions are obtained at high cost. There are four calculations considered in this paper: (1) the energy curve of the ground state and the vertical excitation energies of the low-lying excited states, (2) the infrared intensities of the  $X^2\Pi$  and  $^2\Sigma^+$  states, (3) the oscillator strengths for excitation from the ground state to all the low-lying excited states, and (4) the  $\Lambda$  doubling matrix elements.

The limitations of the Hartree-Fock method can lead to significant and unknown errors in the calculation of excitation energies when the correlation energies are very different in the ground and excited states. However, it is clear from the monovalent character of the Li and the ionic behavior of the molecule in the neighborhood of the equilibrium internuclear separation, that the  $X^2\Pi$  and  $A^2\Sigma^+$  states are best described as different orientations of the  $O(^2P)$  orbital angular momentum relative to the molecular axis. Hartree-Fock and correlated results should agree for relative energies and this is found in the recent accurate CI results [1b]. The present study supplements this work done on the  $X^2\Pi$  and  $A^2\Sigma^+$  states and repeats sufficient work to show substantial agreement in the areas that overlap.

## 2. Self-Consistent-Field Solutions

The present calculations were performed with a Gaussian-type function (GTF) constructed by augmenting the 9/5 basis of Huzinaga [3] with three  $2p$  Li functions that are suitable for representing the  $^2P$  excited state of Li. The configurations can be represented:



The  $X^2\Pi$  and  $A^2\Sigma^+$  were calculated at five distances for which the energies and dipole moments are given in table 1. There is a crossing of these states near

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. LiO Energy as a function of internuclear separation<sup>a</sup>

R(a.u.)	X <sup>2</sup> Π		A <sup>2</sup> Σ <sup>+</sup>	
	-E	μ	-E	μ
2.7	82.2493	2.49	82.2586	2.19
2.9	82.2706	2.63	82.2699	2.37
3.184	82.2817	2.84	82.2716	2.64
3.4	82.2815	2.99	82.2668	2.85
3.6	82.2774	3.14	82.2598	3.04

<sup>a</sup>Energy and dipole moment given in atomic units:  $E$ , 1 a.u. = 27.2097 eV;  $\mu$ , 1 a.u. = 2.54158.10<sup>-18</sup> esu cm.

2.9 a.u. which is in accord with the united atom character of these states. At large internuclear separation the <sup>2</sup>Σ<sup>+</sup> state correlates with O(<sup>3</sup>P) + Li(<sup>2</sup>P) while the <sup>2</sup>Π state correlates with ground state atoms. Since the SCF configurations do not go correctly asymptotically there is little point in determining dissociation energies.

The Rydberg orbitals were obtained by direct variation at  $R=3.184$  a.u. of the Rydberg states to the <sup>3</sup>Σ<sup>-</sup> and <sup>1</sup>Σ<sup>+</sup> ions. These states were chosen as representative by consideration of the ion atom interaction at long distance. Adiabatic correlation rules predict that the interaction of Li+(<sup>1</sup>S) and O(<sup>3</sup>P) yields <sup>3</sup>Σ<sup>-</sup> and <sup>3</sup>Π states for which the <sup>3</sup>Σ<sup>-</sup> is attractive and <sup>3</sup>Π repulsive with respect to the ion-quadrupole interaction. Similarly, the interaction of Li+(<sup>1</sup>S) and O(<sup>1</sup>D) yields <sup>1</sup>Δ, <sup>1</sup>Π, and <sup>1</sup>Σ<sup>+</sup> for which only the <sup>1</sup>Δ state is attractive with respect to the ion-quadrupole interaction. The most attractive ion states were considered with 2s and 2p Rydberg Li electrons as given in the list above. Analysis of the wave functions shows very little difference between Rydberg orbitals obtained between the Rydbergs for the <sup>3</sup>Σ<sup>-</sup> and <sup>1</sup>Σ<sup>+</sup> states. The different orientation of the quadrupole of the oxygen atom will affect the energy position but the transition probabilities for a number of Rydberg transitions can be estimated from the orbitals calculated from a few representative states.

### 3. Discussion

#### A. X<sup>2</sup>Π and A<sup>2</sup>Σ<sup>+</sup> Energies

Polarization functions were not included in the present calculation. Comparison with the accurate Hartree-Fock results of Yoshimine [1b] show that the error increases to smaller internuclear separation as expected. Polarization is more important as the atoms approach each other. However, the error induced in the spectroscopic properties is not substantial. This calculation obtained  $\omega_e=804.4$  cm<sup>-1</sup>,  $R_e=3.275$  a.u., and  $\omega_e x_e=6.1$  cm<sup>-1</sup> for X<sup>2</sup>Π and  $\omega_e=877.5$  cm<sup>-1</sup>,  $R_e=3.076$  a.u., and  $\omega_e x_e=10.5$  cm<sup>-1</sup> for A<sup>2</sup>Σ<sup>+</sup>. The largest error is about 5 percent in the  $\omega_e$  of X<sup>2</sup>Π. Note that the accurate CI spectroscopic constants are in very close agreement with the H-F results [1b]. Fortunately, the present results are in better agreement

with the reported experimental results [2] for the X<sup>2</sup>Π state. The  $\omega_e$  for <sup>2</sup>Σ<sup>+</sup> is within 7 cm<sup>-1</sup> of the H-F value and the improved shape is related both to the fact that the asymptote of the <sup>2</sup>Σ<sup>+</sup> H-F state is not ionic which diminishes the asymptotic error and to the  $\sigma$  character of the open shell orbital. The GTF basis is more flexible for the  $\sigma$  orbitals and the polarization error is accordingly less.

#### B. Infrared Intensities

The dipole moment values are within 10 percent at worst in absolute agreement with the accurate CI values [1]. More important all the curves are very ionic and linear. The slopes of the present results agree with the CI results to within 2 to 3 percent.

Vibrational oscillator strengths were calculated from the equation

$$f = \frac{2}{3} \Delta E |\langle \Psi_{v'} | \mu(R) | \Psi_v \rangle|^2$$

$$= \frac{2}{3} \Delta E I^2.$$

The vibrational energies and  $f$  numbers for the 0→1 and 1→2 transitions are given in table 2. The infrared

TABLE 2. LiO vibrational oscillator strength

State	Vibrational transition	ΔE(cm <sup>-1</sup> )	Band strength (I <sup>2</sup> )	f · 10 <sup>5</sup>
X <sup>2</sup> Π	0-1	792	0.0082	2.0
	1-2	780	.0165	3.9
A <sup>2</sup> Σ <sup>+</sup>	0-1	856	.0128	3.3
	1-2	836	.0260	7.4

transitions are strong for both states as expected for an ionic system. These values are in moderate agreement [4] with values obtained from the CI calculation. Since the dipole moment function is linear the 0→2 transition is very weak.

The vibration-rotational levels of the X<sup>2</sup>Π state are perturbed by the A<sup>2</sup>Σ<sup>+</sup>. The Λ-doubling matrix element is readily evaluated since the electronic matrix element  $\langle \Psi(\pi) | L^+ | \Psi(\Sigma^+) \rangle$  does not vary with internuclear separation and is equal in magnitude to the pure precessing value. The matrix element  $\langle \Psi_v(^2\Pi) | V | \Psi_{v'}(^2\Sigma^+) \rangle$ , where

$$V = \frac{1}{\sqrt{2}\mu R^2},$$

is given in table 3. The sensitivity of these values with vibrational quantum number would caution that they be considered quite approximate considering the level of accuracy of the energy curves.

TABLE 3. LiO  $\Lambda$ -doubling matrix element <sup>a</sup>

$v(^2\Pi) v'(^2\Sigma^+)$	0	1	2	3	4
0	1.25	1.03	0.69	0.43	0.25
1	-0.96	0.47	.90	.83	.62
2	0.40	-0.99	-0.008	.65	.81
3	-0.09	0.57	-.89	-0.29	.39
4	0.0007	-0.14	0.67	-.77	-0.44

<sup>a</sup> Matrix element  $\langle \psi_v(^2\Pi) | \hbar^{-2} / \sqrt{2} \mu R^2 | \psi_{v'}(^2\Sigma^+) \rangle$  in  $\text{cm}^{-1}$ .

### C. Electronic Oscillator Strengths

The low-lying ion states of  $\text{LiO}^+$  can be represented:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^2 \quad {}^3\Sigma^-, {}^1\Delta, {}^1\Sigma^+$$

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^3 \quad {}^3\Pi, {}^1\Pi$$

Rydberg Li  $2s$  and  $2p$  orbitals were generated in the field of the  ${}^3\Sigma^-$  and  ${}^1\Sigma^+$  SCF approximations to the ions. Since these states are most widely separated in energy and the Rydberg orbitals were determined to be substantially the same for both ion cores, the Rydberg  $5\sigma$  (Li  $2s$ ),  $6\sigma$  (Li  $2p$ ), and  $2\pi$  (Li  $2p$ ) orbitals were used to determine oscillator strengths for the  ${}^3\Sigma^-$ ,  ${}^1\Delta$ ,  ${}^3\Pi$ , and  ${}^1\Pi$  Rydbergs. The  ${}^1\Sigma^+$  state will require substantial mixing of the  $4\sigma^2 1\pi^2$  and  $1\pi^4$  configurations and, in any case, is the highest energy of these ion states.

Asymptotic correlations are given in table 4 for

TABLE 4. Adiabatic correlation of molecular states of LiO

Molecular states <sup>a</sup>	Atomic states <sup>b</sup>	Asymptotic energy (eV)
${}^2, {}^4\Sigma^+, \Sigma^-(2), \Pi(2), \Delta$	$\text{Li}({}^2P_u) + 0({}^3P_g)$	3.83
${}^2, {}^4\Sigma^-, \Pi$	$\text{Li}({}^2S_g) + 0({}^3P_g)$	3.37
${}^2\Pi(3), \Sigma^-, \Sigma^+(2), \Phi, \Delta(2), \Phi$	$\text{Li}({}^2P_u) + 0({}^1D_g)$	2.57
${}^2\Delta, \Sigma^+, \Pi$	$\text{Li}({}^2S_g) + 0({}^1D_g)$	1.97
${}^2, {}^4\Sigma^-(2), \Pi(2), \Delta, \Sigma^+$	$\text{Li}({}^2P_u) + 0({}^3P_g)$	1.85
${}^2, {}^4\Sigma^-, \Pi$	$\text{Li}({}^2S_g) + 0({}^3P_g)$	0

<sup>a</sup>  ${}^2, {}^4\Sigma^-, \Pi$  signifies  ${}^2\Sigma^-, {}^4\Sigma^-, {}^2\Pi, {}^4\Pi$ .

<sup>b</sup> Atomic states and energies, from C. E. Moore, Atomic Energy Levels, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 35, Vol. 1, 359 pages (Dec. 1971).

several of the lower asymptotes that can correlate with the valence and quantum number 2 Rydbergs. It is apparent that the asymptotic behavior of the Rydberg states is complicated since a sizable fraction must become valence. However, at the  $R_e$  of the ground state the single Rydberg configuration should be a good approximation to the true wave function.

From the asymptotic behavior and the calculated energies at  $R=3.184$  a.u., we can deduce that these Rydberg states will probably be photodissociated. Both the  ${}^4\Sigma^-$  and  ${}^2\Sigma^-$  that arise from the ground state atoms will correlate with the  $1\pi^2 5\sigma$  configuration and the  ${}^4\Sigma^-$  state is at least 0.6 eV above the asymptote. The  ${}^2\Delta$  state correlates to  $\text{Li}({}^2P) + \text{O}({}^3P)$  and is calculated to be about 1.0 eV above this asymptote. The ion states go formally correctly to the asymptote, and the configuration mixing required to insure that the excited valence asymptotes are correctly obtained should only be important at large internuclear separation. The excitation energy is, therefore, meaningful within the error due to the lack of polarization functions. The error in the  $X^2\Pi$  state at  $R_e$  is about 0.027 a.u. and the  ${}^2\Delta$  state would still be repulsive at this distance. The  ${}^2\Sigma^-$  and  ${}^2\Pi$  Rydbergs that can go asymptotically to  $\text{Li}({}^2P) + \text{O}({}^3P)$  should be above the  ${}^4\Sigma^-$  in energy and, even with the polarization error, would be photodissociated. Without a configuration mixing calculation it is impossible to be certain but the present analysis would indicate that the vertical excitation of LiO from either  $X^2\Pi$  or  $A^2\Sigma^+$  would lead to dissociation throughout the Rydberg region.

Transition probabilities are calculated from both the  $X^2\Pi$  and  $A^2\Sigma^+$  states by forming the appropriate symmetry-adapted linear combination of determinants. In order to avoid estimating the excitation energy, the oscillator strengths were obtained with an expression using the product of the dipole length and velocity matrix elements [5],

$$f = \frac{2}{3} | \langle \mathbf{r} \rangle \langle \mathbf{p} \rangle |^{1/2} (2 - \delta_{0\Lambda_i} \delta_{0\Lambda_f}) / (2 - \delta_{0\Lambda_i}),$$

after summing over all initial and final state degeneracies, averaging over the degeneracies of the initial state, including the  $\Lambda$ -doublet substates [6], and using the fact that the sum of Franck-Condon factors to final vibrational states is unity.

There are no strong transitions apparent in table 5. The strong  $2s \rightarrow 2p$  resonance transition of Li is not involved here since the ground state is so ionic that all low-lying transitions originate on the O<sup>-</sup> atom and the overlap through the dipole operator is relatively small.

The electronic oscillator strength for the transition from the ground  $X^2\Pi$  state to the  $A^2\Sigma^+$  state is calculated to be about  $4 \cdot 10^{-7}$ . This extremely small value reflects the ionic character of the two states. The transition is between different orientations of the O<sup>-</sup> ion which has no dipole moment.

TABLE 5. LiO spectral distribution from X<sup>2</sup>Π and A<sup>2</sup>Σ<sup>+</sup> states

Transitions <sup>a</sup>			⟨r⟩	⟨∇⟩	f(r, ∇)
Final Ion Ryd- state	state	berg			
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>3</sup> Π, <sup>2</sup> Σ <sup>+</sup> )			0.0217	0.00271	3.94 × 10 <sup>-5</sup>
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>3</sup> Π, <sup>2</sup> Σ <sup>+</sup> )			.0193	.00639	8.26 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>1</sup> Π, <sup>2</sup> Σ <sup>+</sup> )			.125	.0156	1.31 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>1</sup> Π, <sup>2</sup> Σ <sup>+</sup> )			.111	.0368	2.75 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>1</sup> Π, <sup>2</sup> Π)			.0415	.0179	4.97 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>-</sup> ; <sup>1</sup> Π, <sup>2</sup> Π)			.0415	.0179	4.97 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>3</sup> Π, <sup>2</sup> Π)			.0239	.0103	1.65 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>-</sup> ; <sup>3</sup> Π, <sup>2</sup> Π)			.0239	.0103	1.65 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Δ; <sup>1</sup> Π, <sup>2</sup> Π)			.0587	.0254	9.94 × 10 <sup>-4</sup>
<sup>2</sup> Π → ( <sup>2</sup> Δ; <sup>3</sup> Π, <sup>2</sup> Π)			.0678	.0293	1.32 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>-</sup> ; <sup>3</sup> Σ <sup>-</sup> , <sup>2</sup> Σ <sup>+</sup> )			.207	.0209	2.89 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Σ <sup>-</sup> ; <sup>3</sup> Σ <sup>-</sup> , <sup>2</sup> Σ <sup>+</sup> )			.258	.0812	1.40 × 10 <sup>-2</sup>
<sup>2</sup> Π → ( <sup>2</sup> Δ; <sup>1</sup> Δ, <sup>2</sup> Σ <sup>+</sup> )			.254	.0256	4.34 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Δ; <sup>1</sup> Δ, <sup>2</sup> Σ <sup>+</sup> )			.316	.0995	2.10 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>3</sup> Σ <sup>-</sup> , <sup>2</sup> Π)			.243	.0279	4.52 × 10 <sup>-3</sup>
<sup>2</sup> Π → ( <sup>2</sup> Π; <sup>1</sup> Δ, <sup>2</sup> Π)			.297	.0342	6.79 × 10 <sup>-3</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Π; <sup>1</sup> Π, <sup>2</sup> Σ)			.308	.0548	2.26 × 10 <sup>-2</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Π; <sup>1</sup> Π, <sup>2</sup> Σ)			.236	.1012	3.18 × 10 <sup>-2</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>3</sup> Π, <sup>2</sup> Σ)			.0535	.0095	3.39 × 10 <sup>-4</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>3</sup> Π, <sup>2</sup> Σ)			.0409	.0175	4.79 × 10 <sup>-4</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>1</sup> Π, <sup>2</sup> Π)			.143	.0111	1.06 × 10 <sup>-3</sup>

TABLE 5. LiO spectral distribution from X<sup>2</sup>Π and A<sup>2</sup>Σ<sup>+</sup> states—Continued

Transitions <sup>a</sup>			⟨r⟩	⟨∇⟩	f(r, ∇)
Final Ion Ryd- state	state	berg			
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Σ <sup>+</sup> ; <sup>3</sup> Π, <sup>2</sup> Π)			0.248	0.0192	3.19 × 10 <sup>-3</sup>
<sup>2</sup> Σ <sup>+</sup> → ( <sup>2</sup> Π; <sup>1</sup> Σ <sup>+</sup> , <sup>2</sup> Π)			.0571	.0226	1.72 × 10 <sup>-3</sup>

<sup>a</sup> The transition <sup>2</sup>Π → (<sup>2</sup>Π; <sup>3</sup>Π, <sup>2</sup>Σ<sup>+</sup>) designates the following: initial state → (final state; ion state, Rydberg orbital symmetry).

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