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NOTES

Alkali oxide diatomics: Explanation of the change in ground state symmetry from LiO($^2\Pi$) to CsO($^2\Sigma^+$)^a

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Generally, there is close correspondence in the ground symmetries of molecules as an atom is replaced by others in the same column of the periodic table. An exception to this occurs with the alkali oxides where LiO has a $^2\Pi$ ground state,¹ whereas CsO has a $^2\Sigma^+$ ground state.² In this paper we report a series of *ab initio* calculations [including extensive configuration interaction (CI)] designed to elucidate the bonding in these systems and to explain this reversal.

We find that the wave functions can be accurately characterized in terms of an ionic description M^+O^- . There are two ways of orienting the O^- , leading to $^2\Pi$ and $^2\Sigma^+$ states that are within 0.3 eV of each other for all alkali metals M. In contrast, for a covalent bond as in HO, the ground state would clearly be $^2\Pi$, with the $^2\Sigma^+$ state very high in energy (4.05 eV for HO).

For the $^2\Pi$ and $^2\Sigma^+$ states, we carried out CI calculations allowing all single and double excitations (to *all* virtual orbitals) from the seven valence electrons of the self-consistent HF wave functions at each internuclear separation (*R*). The basis set³ was of optimized valence double zeta form for M and O but with optimized polarization functions (3*d*) and diffuse functions on the O. The results are summarized in Table I.

For LiO and NaO we find that the $^2\Pi$ state is much more stable than $^2\Sigma^+$ (by 2634 and 2177 cm^{-1} , respectively). This is consistent with electric deflection and magnetic deflection scattering experiments, also indicating a $^2\Pi$ ground state.^{1,4}

For CsO we find that the $^2\Sigma^+$ state is 846 cm^{-1} below $^2\Pi$, in agreement with ESR and reactive scattering

studies that also lead to a $^2\Sigma^+$ ground state. We also find RbO to have a $^2\Sigma^+$ ground state; however, the energy splitting is small, 114 cm^{-1} . ESR studies were consistent with RbO; however, the spectra were too weak for a clear-cut assignment.²

For KO we find a $^2\Pi$ ground state (by 831 cm^{-1}). This is also consistent with experiment since no ESR signal was observed.²

Previous calculations on the $^2\Pi$ - $^2\Sigma^+$ splitting of alkali oxides have been carried out mainly at the HF level. For LiO, Yoshimine,⁵ and Grow and Pitzer⁶ find the $^2\Pi$ state to be favored by 2330 cm^{-1} (CI) and 3065 cm^{-1} (HF), respectively. For NaO, O'Hare and Wahl⁷ report a $^2\Pi$ ground state with $^2\Sigma^+$ at 1613 cm^{-1} (HF). So and Richards⁸ reported HF calculations on NaO, KO, and RbO. They find a $^2\Pi$ ground state for NaO by 1236 cm^{-1} but $^2\Sigma^+$ ground states for KO (by 347 cm^{-1}) and for RbO (by 606 cm^{-1}). Our calculations differ from these in that we use highly correlated wave functions and that we include diffuse functions on the O^- . Omitting the diffuse functions on the O causes the bond distance to decrease and the vibrational frequency to increase.

Singles and doubles CI calculations do not yield reliable values for homolytic bond energies; however, for an ionic species such as M^+O^- , this type of calculation should yield quite reliable values for the heterolytic bond energy to M^+ and O^- . Consequently, the homolytic bond energies quoted in Table I are based on the calculated dissociation energy to M^+ and O^- corrected by the experimental electron affinity of O and ionization potential for M. An illustration of the accuracy of this cor-

TABLE I. Spectroscopic properties (ground state denoted by †). Experimental values are from Refs. 9–12.

	${}^2\Pi$ to ${}^2\Sigma^+$ excitation energy (cm^{-1})		Bond energy (eV) of ground state			Vibrational frequency (cm^{-1})			Bond distance (\AA)	
			Theory ^a		Experiment	Theory ^a		Experiment ^d	Theory	
	Theory	Experiment	${}^2\Pi$	${}^2\Sigma^+$		${}^2\Pi$	${}^2\Sigma^+$		${}^2\Pi$	${}^2\Sigma^+$
LiO	2634	> 0	3.40 [†]	3.08	3.49 ± 0.06 ^b	772 [†]	824	(752) ^f	1.76 [†]	1.65
NaO	2177	> 0	2.55 [†]	2.28	2.61 ± 0.20 ^c	464 [†]	493		2.09 [†]	2.00
KO	831	...	2.03 [†]	1.93	...	363 [†]	403	(384) ^e	2.52 [†]	2.34
RbO	-114	...	2.15	2.16 [†]	...	399	452 [†]		2.67	2.52 [†]
CsO	-846	< 0	2.06	2.14 [†]	...	236	286 [†]	(314) ^e (322) ^f	2.84	2.67 [†]

^aBased on singles plus doubles CI and including zero point energy.

^bReference 9.

^cReference 10.

^dFirst vibrational transition ω_0 . All experimental values are based on matrix studies.

^eReference 11.

^fReference 12.

^gCurvature at R_e from cubic spline fit to potential curve.

rection is that for CsO the total energy drops 4.25 eV from HF to CI, whereas the predicted bond energy (using the above procedure) decreases only 0.15 eV.

Calculated bond distances, vibrational frequencies, and bond energies are shown in Table I and compared with experimental values.^{9–12}

The essence of our explanation of the shift in ground state symmetry can be grasped by considering the energy curves for purely ionic wave functions, as shown in Fig. 1 for LiO and CsO. In all cases, ${}^2\Pi$ is favored at longer distances, while ${}^2\Sigma^+$ is favored at shorter distances, leading always to a crossing of the

${}^2\Sigma^+$ and ${}^2\Pi$ states. The reason that ${}^2\Pi$ is lower at larger R is the greater electrostatic attraction caused by the orientation of the oxygen ion. In the ${}^2\Sigma^+$ state,¹ the orientation of the oxygen ion is such that the quadrupole terms are repulsive (the hole is in the p_v orbital). However, in the ${}^2\Pi$ state,² the quadrupole terms are attractive (the hole is in the p_r orbital); thus lowering this state relative to the ${}^2\Sigma^+$ state.

The reason that ${}^2\Sigma^+$ is lower than ${}^2\Pi$ at shorter R is due to Pauli repulsion effects arising from orthogonalizing the Op_v orbital to the M^* core. This term becomes important for small R and is roughly twice as large for ${}^2\Pi$ than for ${}^2\Sigma^+$ due to the presence of two electrons in the p_v orbital for ${}^2\Pi$ and only one for ${}^2\Sigma^+$.

The equilibrium bond distance is determined by a balance of the attractive $1/R$ electrostatic term and the repulsive Pauli orthogonality term. As we move down the periodic table, the M core becomes larger, leading to a larger bond distance and hence a smaller bond energy. Indeed, the total bond energy scales roughly as $1/R_e$, so that the effective Pauli repulsion term (at R_e) scales as $1/R_e$. However, the ${}^2\Sigma^+ - {}^2\Pi$ splitting involves a balance between Pauli repulsion (scaling as $1/R_e$) and a quadrupole term that scales as $(1/R_e)^3$. Thus, at R_e the ${}^2\Sigma^+$ state should be stabilized with respect to ${}^2\Pi$ as we move down the column.

Summarizing, the change in stability of ${}^2\Sigma^+$ with respect to ${}^2\Pi$ occurs because the balance between Pauli repulsion (favoring ${}^2\Sigma^+$) and quadrupole interactions (favoring ${}^2\Pi$) is shifted toward the Pauli repulsion terms (and hence ${}^2\Sigma^+$) as we go to metal ions with larger cores.

Previously it has been suggested that the reversal of ${}^2\Pi - {}^2\Sigma^+$ ordering from LiO to CsO might be the result² of interactions of the alkali inner shell electrons with the O^- or might be due³ to the more polarizable nature of the core electrons of Cs and Rb. The fact that we

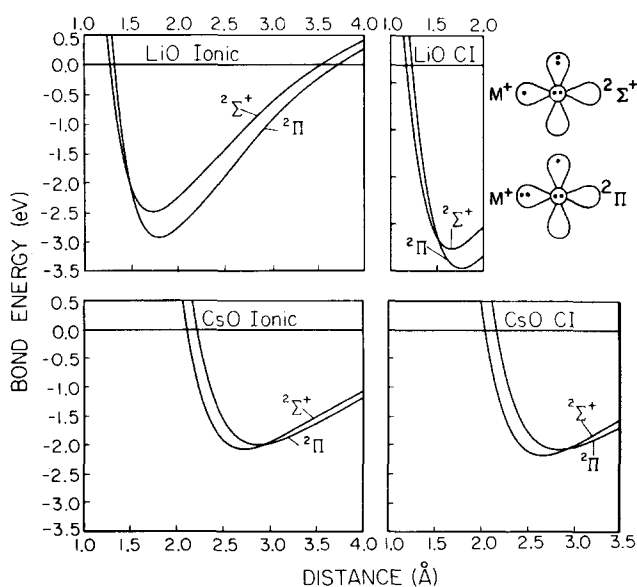


FIG. 1. Potential curves for the ${}^2\Pi$ and ${}^2\Sigma^+$ states of LiO and CsO. The ionic wave function is constructed from atomic M^* and O^- wave functions.

obtain the same results for ionic wave functions obtained from atomic M^+ combined with atomic O^- shows that these effects cannot be responsible for the reversal.

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Millimeter and submillimeter spectrum of NO^+

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In this letter we report the detection of the pure rotational absorption spectrum of the molecular ion NO^+ by means of millimeter and submillimeter microwave spectroscopy. This species is one of a very small class of molecular ions that have been detected by high resolution microwave techniques.¹ This class would be even smaller if those species originally identified and measured by radioastronomical techniques were excluded. The detection of NO^+ was made possible by the combination of the high sensitivity of our experimental technique and the development of a new molecular ion production method that increases ion concentrations by two orders of magnitude. Also of considerable value were the excellent frequency predictions derived from the optical work of Alberti and Douglas.²

We have previously reported the details of our millimeter and submillimeter spectroscopic techniques.³ For this experiment NO^+ was produced in a 5 ft long, 1½ in. diameter glass tube cooled to liquid N_2 temperature. In this cell a discharge current of ~5 ma was maintained by a potential of 5 kV applied to a mixture (5:1) of NO and Ar at a total pressure of a few mTorr. A solenoid was wrapped around the cell so that axial magnetic fields of up to 200 G could be applied. In the initial testing of the cell, we found that signals from the previously observed ions HCO^+ , HN_2^+ , and CO^+ were enhanced by a factor of 100 upon the application of the magnetic field. Although NO^+ is much weaker (HCO^+ is several hundred times stronger⁴), it appears to experience a similar enhancement. This enhancement is strongly dependent on the discharge mode. Part of the reduced signal strength of NO^+ can

be attributed to its substantially smaller dipole moment, which Jungen and Lefebvre-Brion⁵ calculate to be 0.66 ± 0.38 D and Billingsley⁶ calculates to be 0.31 D. With this range of values, an estimated fractional NO^+ concentration in our cell of 10^{-4} can be obtained.

Figure 1, a tracing of the $J=1 \rightarrow 2$ transitions of NO^+ at 238 381–238 386 MHz, clearly shows the quadrupole structure due to the nitrogen nucleus. The transition frequencies measured in this experiment are contained



FIG. 1. The $J=1 \rightarrow 2$ transitions of NO^+ . Frequency increases from right to left.