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Ground Electronic States of RbO_2^+, CsO_2^+ and FrO_2: The Ionization Energies of RbO_2 and CsO_2

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Calculations are performed to establish the ground electronic states of RbO_2^+, CsO_2^+, and FrO_2. In the case of the cations, both linear and C_{2v} orientations were considered; for FrO_2, the two lowest electronic states, $^2A_2$ and $^2B_2$, were considered in C_{2v} symmetry. In addition, calculations were also performed on the $\tilde{X}^2A_2$ ground states of RbO_2 and CsO_2 to derive ionization energies. Binding energies and heats of formation are also derived. The bonding in FrO_2 is found to be less ionic than that of RbO_2 and CsO_2.

I. Introduction

The alkali metal dioxides, MO_2, are largely ionic and so may be thought of as M^+ interacting with O_2^-. The latter has a $^2\Pi$ ground state, with an unpaired "hole". Previous calculations have shown that the geometry of MO_2 is of C_{2v} symmetry, and so whether the "hole" is in-plane or out-of-plane determines whether the ground state is $^2A_2$ or $^2B_2$. Bauschlicher et al. have shown[1] that the ground electronic state of LiO_2−CsO_2 is $^2A_2$ and have calculated the $^2B_2$−$^2A_2$ separations for these species. CsO_2 had an unexpectedly high separation, which was attributed to core relaxation effects. The dissociation energies of LiO_2−RbO_2 were also calculated in a slightly earlier paper,[2] with the value for CsO_2 being reported in the aforementioned article.[1] RbO_2 and CsO_2 have also been produced in matrix isolation experiments, and studied by infrared and Raman spectroscopy. In the first study,[3] RbO_2 was produced by the co-deposition of Rb atoms and O_2, and infrared spectra were recorded. A weak absorption at 1097 cm^{-1} could not conclusively be assigned to ν_1, but a band at 255 cm^{-1} was confidently assigned to the symmetric interionic vibration, ν_2. Two years later, Raman studies by Smardzewski and Andrews[4] on both RbO_2 and CsO_2 identified the ν_1 vibration at 1110 and 1114 cm^{-1}, respectively. Other features were present, but these were not assigned to the superoxide species. The missing study − the infrared spectrum of CsO_2 − was reported almost immediately afterward by Andrews et al.[5] They identified the symmetric interionic vibration, ν_2 at 236.5 cm^{-1}, as well as a weak band at 1115.6 cm^{-1}, assigned to ν_1 (the O−O stretch). For the first time, the asymmetric interionic vibration, ν_3, was identified at 268.6 cm^{-1}. This observation prompted the reexamination of previous spectra and led to the identification of the ν_1 and ν_3 vibrations for RbO_2 also. Isotopic shifts and splitting patterns led to the conclusive determination of the geometry as C_{2v}, as well as estimates of the geometric parameters. RbO_2 and CsO_2 were also identified as products from reactions of the metal atoms with ozone in separate studies.[6]

Recently, we have calculated the structure and energetics of the alkali metal dioxide molecules NaO_2[7] and KO_2[8,9] and their cations.[7,9] These calculations allowed the ionization energies to be determined, as well as heats of formation of the neutrals and cations. The neutrals were found to have a C_{2v} geometry, whereas the cations were found to have a $C_{\infty v}$ geometry, and, consequently, there is a large geometry change upon ionization. In the present work, we extend these calculations, first to the calculation of the geometries of the lowest energy states for RbO_2^+ and CsO_2^+, since there are a number of possibilities, and we then perform calculations on the neutrals, so that ionization energies may be calculated at a consistent level of theory. We finish off by performing calculations on FrO_2 in order to confirm its ground electronic state.

II. Calculational Details

Geometry optimizations and harmonic vibrational frequency calculations were performed using Gaussian03.[10] The methods employed were B3LYP, MP2, QCISD, and CCSD(T), where unrestricted wave functions were used for the open-shell species; but in these cases the $\langle S^2 \rangle$ values being less than 0.78 indicated that the spin contamination was minimal. Single-point RCCSD(T) calculations were also performed, in this case employing MOLPRO.[11] The basis sets employed for oxygen were the standard versions of the aug-cc-pVXZ basis sets ($X = Q$ and 5). For the alkali metals, we used ECP basis sets that had been augmented with a large, flexible valence space. We give summaries of the molecular basis sets below; the full details of the alkali metal basis sets may be found in the report of our previous work on the heaviest alkali metal hydroxides[12] and alkali metal monoxides.[13] The basis sets are labeled A−C, depending on which combination of O atom basis set and alkali metal basis set has been employed.

Basis Set A	LANL2[7s6p3d] for Rb LANL2[9s8p3d] for Cs CRENBL78[9s8p4d] for Fr 6-311+G(3d) for O
Basis Set B	ECP28MWB[10s8p5d4f3g] for Rb ECP46MWB[10s8p5d4f3g] for Cs CRENBL78[11s10p5d4f3g] for Fr aug-cc-pVQZ for O
Basis Set C	ECP28MWB[10s8p5d4f3g] for Rb ECP46MWB[10s8p5d4f3g] for Cs aug-cc-pV5Z (no h) for O

The LANL2 ECP is from ref 14, the ECPXXMWB (XX = 28, 46) and CRENBL78 ECPs are from Dolg and co-workers,[15,16]

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TABLE 1: Geometries, Energies, and Harmonic Vibrational Frequencies for the Lowest Energy States of RbO_2^+

structure	state	R_{RbO}/Å	R_{OO}/Å	θ_{ORbO}/°	frequencies/ cm^{-1}	energy/E_h	relative energy/ kcal mol^{-1} [a]
B3LYP/A							
linear RbOO	$^1\Delta$ (π^2)	3.143	1.202		71*i*;83 (π); 69(σ); 1641(σ)	−174.03530	38.6
C_{2v}	$^1A_1$	3.253	1.206	21.4	62(b_2); 78(a_1); 1618(a_1)	−174.03716	37.5
C_{2v}	$^3B_1$ ($4b_2^1 1a_2^1$)	3.546	1.207	19.6	61*i*(b_2); 46(a_1); 1629(a_1)	−174.09490	1.24
linear RbOO	$^3\Sigma^-$(π^2)	3.140	1.203		32(π); 69(σ); 1650(σ)	−174.09688	0.00
MP2/A							
C_{2v}	$^1A_1$	3.220	1.253	22.4	89(a_1); 107(b_2); 1237(a_1)	−173.57551	32.3
C_{2v}	$^3B_1$ ($4b_2^1 1a_2^1$)	3.415	1.227	20.7	57(a_1); 62(b_2); 1443(a_1)	−173.62630	0.42
linear RbOO	$^3\Sigma^-$(π^2)	3.139	1.219		28(π); 69(σ); 1529(σ)	−173.62697	0.00
QCISD/A							
C_{2v}	$^1A_1$	3.238	1.214	21.6	84(a_1); 93(b_2); 1564(a_1)	−173.57768	32.1
C_{2v}	$^3B_1$ ($4b_2^1 1a_2^1$)	3.464	1.206	20.0	60*i*(b_2); 54(a_1); 1632(a_1)	−173.62710	1.10
linear RbOO	$^3\Sigma^-$(π^2)	3.119	1.202		29(π); 73(σ); 1648(σ)	−173.62884	0.00
CCSD(T)/A							
C_{2v}	$^1A_1$	3.231	1.228	21.9	86(a_1); 96(b_2); 1562(a_1)	−173.59870	28.9
C_{2v}	$^3B_1$ ($4b_2^1 1a_2^1$)	3.446	1.215	21.3	54*i*(b_2); 56(a_1); 1568(a_1)	−173.64316	0.97
linear RbOO	$^3\Sigma^-$(π^2)	3.117	1.211		34(π); 73(σ); 1593(σ)	−173.64472	0.00
CCSD(T)/B							
C_{2v}	$^1A_1$	3.076	1.223	22.9		−174.01947	27.6
C_{2v}	$^3B_1$ ($4b_2^1 1a_2^1$)	3.239	1.211	21.6		−174.06144	1.25
linear RbOO	$^3\Sigma^-$(π^2)	2.991	1.205			−174.06344	0.00

[a] Energy relative to that of $RbOO^+$ ($^3\Sigma^-$), π^2 state at the corresponding level of theory.

all obtained from the Gaussian basis set order form (GBSOF).[16] In each case, the standard valence basis sets associated with the ECP were removed and replaced with our own versions, which were derived for the alkali metal cations (see our previous references for fuller descriptions of the derivation of these basis sets). In the correlated treatments, the O 1s orbital was kept frozen and all other electrons (except those described by the ECP) were correlated.

In some of the thermodynamic calculations below, heats of formation have been obtained from the JANAF tables,[17] with much of the data also available on the NIST Webbook site (webbook.nist.gov). The latter site also contains spectroscopic data for O_2 and O_2^-, cited in the sections below.

III. Results

(a) Geometries and Vibrational Frequencies. First we note that symmetry breaking at the MP2 level is known to be a problem with the neutral species and has been investigated in the cases of LiO_2[18] and NaO_2.[19] We have also noted this problem previously for KO_2 (ref 8). The effect of the problem is manifested in the value for the asymmetric (b_2) vibration, which is calculated to have nonsensical values: consequently the UMP2 values (although reported in the tables) should be disregarded. We also showed in ref 8 that the B3LYP method did not appear to suffer from the symmetry breaking problem.

(i) RbO_2^+. This species is expected to be composed largely of an Rb^+ ion interacting with O_2. Since O_2 has a ground electronic state of $^3\Sigma_g^-$, then the lowest energy, linear $RbOO^+$ state is expected to be $^3\Sigma^-$, with the next highest state being a $^1\Delta$ state arising from Rb^+ interacting with the metastable $^1\Delta_g$ state of O_2. If M^+ approaches $O_2(X^3\Sigma_g^-)$ perpendicular to the intermolecular bond, then a C_{2v} structure is expected, which will be a $^3B_1$ state. If Rb^+ interacts with $O_2(a^1\Delta_g)$, then two $^1A_1$ states result and the lowest is expected from the calculations. The question is whether the linear or the C_{2v} structure is the lowest in energy. We study these three states and present the results for the geometry optimization and harmonic vibrational frequency calculations in Table 1. As may be seen, the results are consistent across a range of methods and show conclusively that the lowest energy state is the linear $^3\Sigma^-$ state of RbO_2^+, which is in line with our previous results for NaO_2^+ [7] and KO_2^+.[9] That said, the energy difference between the $^3\Sigma^-$ state and the C_{2v} structure is very small at < 1 kcal mol^{-1}; note that the C_{2v} structure ($^3B_1$) is a saddle point and corresponds to the rotation of the O_2 from linearity by $\pi/2$. This indicates that the O_2 is very loosely bound to the Rb^+ (see binding energy calculations below). A similar observation is found for the first excited state, composed of Rb^+ interacting with $O_2(a^1\Delta_g)$, in the B3LYP calculations, except that in this case it is the C_{2v} structure that is the minimum and one component of the $^1\Delta$ state is lower in energy. This state is therefore Renner−Teller split, with the $\cdots 4b_2^2 1a_2^0$ state lying lower in energy than the $\cdots 4b_2^0 1a_2^2$ state. We have not, however, characterized this in any further detail; other techniques such as CASSCF are required for a balanced consideration of the states involved here.

The vibrational frequencies are also indicative of a weak interaction in these states, with the intermolecular bend and stretch frequencies being extremely low: their values are therefore only indicative, since anharmonicity is expected to affect them significantly. The highest frequency corresponds essentially to the O−O stretch, and for the $^3\Sigma^-$ state is close to the known frequency of $O_2(X^3\Sigma_g^-)$, 1580.2 cm^{-1}, especially at the CCSD(T) level of theory.

For the *X* $^3\Sigma^-$ state, the geometry indicates a fairly long Rb^+−O_2 bond length, with our best value being 2.991 Å; the O−O bond length is very close to that of $O_2(X^3\Sigma_g^-)$, which has an r_e value of 1.2075 Å.

(ii) RbO_2 $\tilde{X}^2A_2$. Bauschlicher and co-workers[1,2] have already shown that the ground state of RbO_2 is $\tilde{X}^2A_2$, and hence in the present work we only performed calculations on this state, using the same levels of theory as employed for the cation. The results are given in Table 2 and may be seen to be in good agreement of the geometric parameters with the previous MCPF values from ref 1, and also with the geometric parameters estimated from the matrix isolation studies. It is perhaps noteworthy that it requires the better basis set B to obtain this good agreement, in part due to the demands of O_2^- (note that this basis set also employs a different ECP for Rb). The vibrational frequencies are reported here for the first time, and we note first that the O−O stretch frequency is close to that of O_2^- (1090 cm^{-1}), as would be expected for an ionic species, $Rb^+\cdots O_2^-$. In turn, this agreement is good when compared to the matrix isolation

TABLE 2: Geometries, Energies and Harmonic Vibrational Frequencies for $RbO_2(\tilde{X}^2A_2)$

method	R_{RbO}/ Å	R_{OO}/Å	θ/°	frequencies/ cm^{-1}			energy/E_h
				$\nu_1(a_1)$ O−O stretch	$\nu_2(a_1)$ interionic stretch	$\nu_3(b_2)$ interionic bend	
MCPF[a]	2.542	1.347	(30.7)[c]				
MCPF + Rel[b]	2.538	1.342	30.7				
B3LYP/A	2.695	1.344	28.9	1176	261	278	−174.29996
MP2/A	2.696	1.362	29.3	1071	262	474[d]	−173.81696
QCISD/A	2.695	1.344	28.9	1167	262	279	−173.81909
CCSD(T)/A	2.697	1.358	29.2	1106	262	293	−173.83722
RCCSD(T)/B	2.567	1.348	30.4				−174.27285
matrix isolation[4,5]	2.57	(1.24)[c]	28	1110	255	282.5	

[a] Modified coupled-pair functional, employing a [10s10p7d4f] all-electron basis set, from ref 1. [b] As for footnote (a), except that mass-velocity and Darwin relativisitic terms were included perturbatively. [c] Calculated based on the other reported parameters. [d] Possibly affected by symmetry breaking − see text.

TABLE 3: Geometries, Energies, and Harmonic Vibrational Frequencies for the Lowest Energy States of CsO_2^+

structure	state	R_{CsO}/Å	R_{OO}/Å	θ_{OCsO}/°	frequencies/ cm^{-1}	energy/E_h	relative energy/ kcal mol^{-1} [a]
				B3LYP/A			
C_{2v}	$^1A_1$	3.546	1.206	19.6	$62(b_2)$; $78(a_1)$; $1618(a_1)$	−170.06302	37.6
C_{2v}	$^3B_1$ $(4b_2{}^1 1a_2{}^1)$	3.854	1.206	18.0	$61i(b_2)$; $46(a_1)$; $1629(a_1)$	−170.12150	0.93
linear CsOO	$^3\Sigma-(\pi^2)$	3.455	1.203		$32(\pi)$; $69(\sigma)$; $1650(\sigma)$	−170.12298	0.00
				MP2/A			
C_{2v}	$^1A_1$	3.471	1.253	20.8	$89(a_1)$; $107(b_2)$; $1237(a_1)$	−169.59389	32.7
C_{2v}	$^3B_1$ $(4b_2{}^1 1a_2{}^1)$	3.674	1.226	19.2	$57(a_1)$; $62(b_2)$; $1443(a_1)$	−169.64544	0.35
linear CsOO	$^3\Sigma^-(\pi^2)$	3.407	1.220		$28(\pi)$; $69(\sigma)$; $1529(\sigma)$	−169.64601	0.00
				QCISD/A			
C_{2v}	$^1A_1$	3.494	1.213	20.0	$84(a_1)$; $93(b_2)$; $1564(a_1)$	−169.59539	32.3
C_{2v}	$^3B_1$ $(4b_2{}^1 1a_2{}^1)$	3.725	1.206	18.6	$60i(b_2)$; $54(a_1)$; $1632(a_1)$	−169.64550	0.88
linear CsOO	$^3\Sigma^-(\pi^2)$	3.385	1.203		$29(\pi)$; $73(\sigma)$; $1648(\sigma)$	−169.64690	0.00
				CCSD(T)/A			
C_{2v}	$^1A_1$	3.491	1.227	20.3	$86(a_1)$; $96(b_2)$; $1562(a_1)$	−169.61623	29.1
C_{2v}	$^3B_1$ $(4b_2{}^1 1a_2{}^1)$	3.704	1.215	18.9	$54i(b_2)$; $56(a_1)$; $1568(a_1)$	−169.66139	0.78
linear CsOO	$^3\Sigma^-(\pi^2)$	3.385	1.211		$34(\pi)$; $73(\sigma)$; $(1593(\sigma)$	−169.66263	0.00
				CCSD(T)/B			
C_{2v}	$^1A_1$	3.250	1.226	21.7		−170.07897	27.7
C_{2v}	$^3B_1$ $(4b_2{}^1 1a_2{}^1)$	3.421	1.210	20.4		−170.12138	1.05
linear CsOO	$^3\Sigma^-(\pi^2)$	3.191	1.206			−170.12307	0.00

[a] Energy relative to that of $CsOO^+$ $(^3\Sigma^-)$, π^2 state at the corresponding level of theory.

studies,[3−5] especially noting that we are comparing harmonic values with fundamentals and that matrix shifts may well be present. The interionic vibrational frequencies are also in excellent agreement with the calculated values, and in particular confirm the ν_3 value, which was not assigned in the initial work.

(iii) CsO_2^+. Table 3 shows the results of the series of calculations on CsO_2^+. Essentially the conclusions are very similar to those for RbO_2^+: the ground electronic state is the $^3\Sigma^-$ state, with the C_{2v} structure ($^3B_1$) being a saddle point lying ~1 kcal mol^{-1} higher in energy and corresponding to rotation of the O_2 by $\pi/2$. Higher in energy (~28 kcal mol^{-1}) is the $\cdots 4b_1{}^2 1a_2{}^0$ ($^1A_1$) state, which is one component of the $^1\Delta$ Renner−Teller components. The weakly bound nature of these states is indicated by the low vibrational frequencies, as before. In addition, the Rb^+-O_2 nature of the $X^3\Sigma^-$ species is confirmed by the calculated values for the O−O bond lengths, and the calculated O−O stretch vibrational frequency, both being close to that expected for $O_2(X^3\Sigma_g{}^-)$. The consistency of the calculated vibrational frequencies and geometric parameters is noteworthy, although basis set B leads to a slightly shorter Cs−O bond length compared to the results using basis set A.

(iv) $CsO_2\tilde{X}^2A_2$. The ground state of CsO_2 has again been established previously[1,2] as $^2A_2$, and so again, we concentrated on this state, using the same levels of theory as for the cation. The results are given in Table 4. As with RbO_2, good agreement is obtained with the previous MCPF study[2], with again the larger basis set B being required to obtain the best agreement. Confirmation is again obtained for the ionicity of this species, as the O−O bond length and the ν_1 vibrational frequency are both close to that expected for O_2^-. The calculated vibrational frequencies are reported here for the first time, and again we have very good agreement between the calculated values and those from the matrix work, with the same caveats regarding harmonic values and matrix shifts mentioned for RbO_2 above.

(v) The Ground State of FrO_2. First we note that in the alkali monoxides there is a well-known switch of ground state from $^2\Pi$ (for LiO and NaO) to $^2\Sigma^+$ (for RbO, CsO, and FrO), with KO having the states so close together that spin−orbit coupling causes the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}{}^+$ states to mix.[20] Bauschlicher et al.[2] raised the question of whether such a switch in ground electronic state occurred for the superoxides. As mentioned in the preceding sections, Bauschlicher et al.[2] have determined that the ground state of the alkali superoxides is $^2A_2$ for LiO_2-CsO_2 in a series of high-quality calculations. This confirmation of ground electronic state was important, as ESR experiments had noted that CsO_2 had a larger than expected $^2B_2-^2A_2$ splitting,[21,22] and it was hypothesised that this might have been due to a switch in ground state. The final member of the series is FrO_2 which, for obvious reasons, has not been studied experimentally. It is, however, amenable to theoretical study, and we in fact confirmed that the ground state of FrO was $^2\Sigma^+$ very recently.[13] In Table 5 are presented our results on FrO_2. We calculate the geometry and vibrational frequencies for the two lowest states, at three levels of theory. It may be seen that the ground state is

TABLE 4: Geometries, Energies, and Harmonic Vibrational Frequencies for $CsO_2(\tilde{X}^2A_2)$

				frequencies/ cm^{-1}			
method	R_{CsO}/ Å	R_{OO}/ Å	θ/°	$\nu_1(a_1)$ O−O stretch	$\nu_2(a_1)$ interionic stretch	$\nu_3(b_2)$ interionic bend	energy/E_h
MCPF[a]	2.678	1.340	(29.0)[b]				
B3LYP/A	2.877	1.342	27.0	1179	233	262	−174.29996
MP2/A	2.875	1.361	27.4	1076	235	437[c]	−173.81696
QCISD/A	2.875	1.344	27.0	1172	235	262	−173.81909
CCSD(T)/A	2.877	1.356	27.3	1110	234	276	−173.83722
RCCSD(T)/B	2.651	1.343	29.4				−174.27285
matrix isolation[4,5]	2.67			1115.6	236.5	268.6	

[a] Modified coupled-pair functional, employing a [10s10p7d4f] all-electron basis set, from ref 1. [b] Calculated based on the other reported parameters. [c] Possibly affected by symmetry breaking − see text.

TABLE 5: Geometries, Energies and Harmonic Vibrational Frequencies for $FrO_2(\tilde{X}^2A_2)$ and $FrO_2(\tilde{A}^2B_2)$

				frequencies/ cm^{-1}				
method	R_{FrO}/ Å	R_{OO}/ Å	θ/°	$\nu_1(a_1)$ O−O stretch	$\nu_2(a_1)$ interionic stretch	$\nu_3(b_2)$ interionic bend	energy/E_h	E_{rel}/ kcal mol^{-1} [a]
				$\tilde{X}^2A_2$				
B3LYP/A	2.750	1.337	28.1	1184	241	266	−169.68277	0.00
MP2/A	2.738	1.358	28.7	1078	245	538[b]	−169.21621	0.00
QCISD/A	2.751	1.339	28.2	1175	240	251	−169.21720	0.00
RCCSD(T)/B	2.691	1.344	28.9				−169.43006	0.00
				$\tilde{A}^2B_2$				
MP2/A	2.770	1.366	28.6	1464	218	127	−169.20465	7.25
QCISD/A	2.794	1.342	27.8	1048	231	2595[b]	−169.20546	7.37
RCCSD(T)/B	2.728	1.348	28.6	1168	223	115	−169.41776	7.72

[a] Energy relative to the $\tilde{X}^2A_2$ state at the corresponding level of theory. [b] Possibly affected by symmetry breaking − see text.

TABLE 6: Calculated AIEs and VIEs of RbO_2 and CsO_2[a] (eV)

	RbO_2		CsO_2	
level of theory	AIE	VIE	AIE	VIE
RCCSD(T)/B	5.698		5.696	
RCCSD/C	5.610	6.788	5.591	6.893
RCCSD(T)/C	5.708	6.698	5.712	6.818

[a] All correspond to the process $MO_2^+(X^3\Sigma-) + e^- \leftarrow MO_2(\tilde{X}^2A_2)$, M = Rb, Cs. These calculations were all performed at the RCCSD(T)/B-optimized geometry, and the values in this table have not been corrected for zero-point vibrational energy.

the $^2A_2$, thus confirming that there is no switch in ground-state symmetry for the alkali metal superoxides. The $^2B_2-^2A_2$ splitting is rather consistently calculated, with our best T_e value being ca. 7.7 kcal mol^{-1} (2700 cm^{-1}). This value is smaller than that reported[2] for CsO_2 but larger than the values reported for KO_2 and RbO_2.

As with the other alkali metal superoxides, the O−O bond length and the O−O stretch vibrational frequency are consistent with a largely ionic character.

(b) Ionization Energies of RbO_2 and CsO_2. Table 6 presents the calculated adiabatic ionization energies of RbO_2 and CsO_2. The agreement between the RCCSD(T)/B and RCCSD(T)/C calculations is excellent and indicates that the basis set is close to saturation. Comparison of the RCCSD/C and RCCSD(T)/C results indicates that there is a small, but important contribution to the AIEs from the triple excitations. Our previous experience with calculations on the alkali metal monoxides and superoxides indicates that we would expect an accuracy around 0.05 eV for these calculations (a fairly conservative error estimate). Hence we cite AIE(RbO_2) = 5.71 ± 0.05 eV and AIE (CsO_2) = 5.72 ± 0.05 eV, after correction for zero-point vibrational energy. We note that within experimental error the AIEs for RbO_2 and CsO_2 are identical. These values may be compared with the AIEs of KO_2 and NaO_2 of 5.98 ± 0.05 eV[9] and 6.47 ± 0.03 eV.[7] Thus there is a convergence of the AIE for these species, similar to (but a little more pronounced than) that observed for the monoxides.[13] We note that the large change in geometry on going from the neutral (C_{2v}) to the cation ($C_{\infty v}$) will mean that there will only be very weak Franck−Condon factors accessing the ground state of the cation; this was discussed in ref 9 in the case of KO_2 in comparing to the published photoelectron spectrum.[23] In addition, the VIE (Table 6) is over 1 eV above the AIE for both RbO_2 and CsO_2. It is therefore possible to predict that any photoelectron band will be very broad, with a weak onset.

(c) Binding Energies. We calculated binding energies for RbO_2, CsO_2, and their cations employing RCCSD(T)/C energies calculated at the RCCSD(T)/B geometries. The energies were calculated with respect to the ionic limits ($M^+ + O_2^-$) in the case of the neutral, and then correcting this energy to neutral dissociation products (M + O_2) using the well-known values for the adiabatic electron detachment energy of O_2^-, and the ionization energies for Rb and Cs. Basis set superposition error (BSSE) was calculated in the usual way, employing the geometry of the fragments as they are in the complex.

We calculate a binding energy for $Rb^+\cdots O_2^-$ of 124.96 kcal mol^{-1}, which may be corrected to 38.8 kcal mol^{-1} for the binding energy of $Rb\cdots O_2$; correction for ZPVE energy yields $D_0(RbO_2)$ = 38.0 kcal mol^{-1}. The BSSE is calculated to be 0.4 kcal mol^{-1}, and we therefore cite a value of 38 ± 1 kcal mol^{-1}. For RbO_2^+, we calculate D_e = 2.7 kcal mol^{-1}, which yields D_0 = 2.5 kcal mol^{-1}, the BSSE is calculated to be 0.2 kcal mol^{-1}, and hence we cite $D_0(RbO_2^+)$ as 2.5 ± 0.5 kcal mol^{-1}.

In a similar vein, we find $D_e(CsO_2)$ = 44.7 kcal mol^{-1}, $D_0(CsO_2)$ = 44.0 kcal mol^{-1}, with a BSSE value of 0.95 kcal mol^{-1}. We therefore cite $D_0(CsO_2)$ = 44 ±1 kcal mol^{-1}.

Similarly, $D_e(CsO_2^+) = 2.3$ kcal mol^{-1}, $D_0(CsO_2^+) = 2.1$ kcal mol^{-1}, with a BSSE value of 0.4 kcal mol^{-1}. We therefore cite $D_0(CsO_2^+) = 2.1 \pm 0.5$ kcal mol^{-1}.

For completeness, we also calculate $D_e(FrO_2) = 40.5$ kcal mol^{-1}, $D_0(FrO_2) = 39.8$ kcal mol^{-1}, with a BSSE value of 0.97 kcal mol^{-1}. We therefore cite $D_0(FrO_2) = 40 \pm 1$ kcal mol^{-1}.

(d) Heats of Formation. By making use of the dissociation energies above and heats of formation of Rb, Rb^+, Cs, and Cs^+, it is then straightforward to derive the $\Delta H_f(0\ K)$ values for $RbO_2^{(+)}$ and $CsO_2^{(+)}$. We derive values of $\Delta H_f[RbO_2(\tilde{X}^2A_2)] = -18.4 \pm 0.5$ kcal mol^{-1}, $\Delta H_f[RbO_2^+(X^3\Sigma^-)] = 113.5 \pm 0.5$ kcal mol^{-1}, $\Delta H_f[CsO_2(\tilde{X}^2A_2)] = -25 \pm 1$ kcal mol^{-1}, $\Delta H_f[CsO_2^+(X^3\Sigma^-)] = 106 \pm 1$ kcal mol^{-1}.

(e) Bonding in FrO_2. When the charge density of the neutral species is examined using Mulliken population analysis, it is found that although RbO_2 and CsO_2 are very ionic with the charge on the metal being 0.93 e and 0.95 e, respectively, the charge on the francium atom in FrO_2 is 0.84 e. We have noted that FrO and FrOH exhibit an increased covalency over the rubidium and cesium counterparts,[12,13] and we have attributed this to the increased interaction of the 6s and 6p orbitals of francium with the oxygen orbitals. Note that formally the $n = 6$ shell of francium is core, but it becomes valence with the removal of the 7s electron in Fr^+. Analysis of the wave function shows that indeed the HOMOs of a_1 symmetry have contributions from both O_2 in-plane orbitals, as well as the 6s and $6p_z$ orbitals of francium. In addition, the highest b_1 and b_2 orbitals also have contributions from combinations of the francium 6p orbitals. It is therefore important to include valance basis functions that describe the occupied $n = 6$ orbitals of francium, since these should be considered valence in the largely ionic species.

IV. Conclusions

We have completed the set of calculations on the alkali metal superoxides, NaO_2−FrO_2, and for the cations NaO_2^+−CsO_2^+. We have shown that there is no switch in the ground state of the neutral, with all superoxides having a $^2A_2$ ground state. For the cations, we have confirmed that for NaO_2^+−CsO_2^+ the ground state is a linear $^3\Sigma^-$ state with $M^+\cdots O_2$ character, but that the O_2 is weakly bound with a barrier to rotation of only ∼1 kcal mol^{-1} for the two species studied herein. We have also calculated binding energies and heats of formation for these species and determined the AIE of the neutrals. We note that experimentally the AIE will be hard to observe, owing to the expected weak Franck−Condon factors, and hence the weak onset for the ionization process. We note that the expected increasing ionicity of the superoxides as one descends the group is not continued at francium, where some increased covalency is found, in agreement with our previous work on FrO and FrOH. We have found similar behavior in other ionic species where the formally valence electrons are lost and the next shell becomes the highest occupied. For example, in RaF_2 we found that this was largely $Ra^{2+}(2F^-)$ but that there is mixing between the radium 6s and 6p electrons and the various combinations of the fluorine 2p orbitals.[24]

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