A Study of the $\tilde{X}^2A_2$ State of KO_2 Using Ab Initio and Density Functional Theory: The Equilibrium Geometry and Vibrational Frequencies

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Geometry optimization and harmonic vibrational frequency calculations at the CASSCF, CISD, UMP2, QCISD, CCSD(T), and B3LYP levels of theory were performed on the ground $\tilde{X}^2A_2$ state of KO_2. Various augmented effective core potential and all-electron basis sets were employed, with the largest being the LANL2DZ effective core potential augmented by [6s6p3d1f], the all-electron basis set, [11s10p5d3f] for potassium, and aug-cc-pVTZ for oxygen. These calculations lead to the conclusion that the C_{2v} $\tilde{X}^2A_2$ state of KO_2 has an equilibrium bond angle of 32.3 ± 0.5°, a K−O bond length of 2.410 ± 0.005 Å, and an O−O bond length of 1.341 ± 0.001 Å. The B3LYP density functional method is also employed for NaO_2 and LiO_2, and it appears that this method does not suffer from symmetry breaking; a similar conclusion is reached for the QCISD method. Isotopic shifts for all three molecules are also reported and compared to available experimental values.

I. Introduction

The alkali metal oxides are of great importance in the chemistry of the upper atmosphere[1] and also in fuel applications.[2] For this reason many studies, both theoretical and experimental have been performed on these species. In this paper, we concentrate on the potassium superoxide molecule KO_2 whose equilibrium geometry has been the subject of some disagreement recently. In particular, the equilibrium bond angle of the C_{2v} molecule was derived as 37 ± 2° in a matrix-isolation far-infrared study[3] by Tremblay et al., with a K−O internuclear distance of 2.10 ± 0.14°. The obtained molecular parameters were noted[3] as being in some disagreement with the results from ab initio molecular orbital calculations, where the bond angle has been consistently calculated as 31.5 ± 1.0°, with a K−O internuclear distance of 2.45 ± 0.05 Å, at the highest levels of theory used (vide infra). (Clearly, the values for the bond angle and the K−O distance are interrelated.) In the present work, we perform state-of-the-art calculations in order to clarify the situation. As will be seen, we conclude that the bond angle is 32.3 ± 0.5°, and that the K−O internuclear distance is 2.410 ± 0.005 Å. The discrepancy between experiment and theory is addressed.

Background. Andrews[4] recorded the infrared spectrum of KO_2 in a solid argon matrix and assigned a band at 307.5 cm^{-1} to the symmetric K−O stretch (ν_2) of KO_2. Later, Raman studies by Smardzewski and Andrews[5] allowed the observation of the $^{16}O{-}^{16}O$ stretch (ν_1) at 1108 cm^{-1}. The more-recent study by Tremblay et al. (ref 3) allowed the confirmation of the assignment of the above two bands, with the positions measured with greater precision; in addition, the identification of the K−O asymmetric stretch (ν_3) at 304.3 cm^{-1} was also reported—very close to the ν_2 frequency. The observation of all of the vibrational frequencies, for a number of isotopomers, allowed the calculation of the force constants, under the assumption of a harmonic force field. Variation of the molecular geometry and comparison with experimental vibrational frequencies allowed the reported geometry to be obtained.

On the theoretical front, Plane and co-workers[6] have performed UHF calculations, yielding a bond angles of *ca.* 30.7° and K−O bond lengths of 2.4−2.55 Å. Partridge et al.[7] used the MCPF method to yield a calculated bond angle of 32.4° and a K−O bond length of 2.415 Å. Wright et al.[8] used ROHF, UHF, and UMP2 methods, with the latter yielding a bond angle of 32.4° and a K−O bond length of 2.46 Å. Thus all of the theoretical methods give reasonably consistent results for the molecular geometry. The latter study also calculated vibrational frequencies, and although the asymmetric K−O stretch frequency (ω_3) was affected by symmetry breaking, the symmetric vibrational frequencies were successfully calculated as 1007 cm^{-1} (O−O, ω_1) and 331.0 cm^{-1} (K−O, ω_2), at the UMP2 level of theory, using a triple-ζ plus polarization basis set. From the above, the following points need to be addressed: (i) would the use of higher levels of theory and/or larger basis sets than those employed in the previous studies have any effect on the calculated geometry? (ii) can the vibrational frequencies be calculated more reliably, especially the ω_3 frequency, so that comparison with experiment may be made?

II. Computational Details

Calculations were performed using a variety of basis sets and levels of theory, in order to ascertain the effect of each of these on the calculated molecular geometric parameters and vibrational frequencies. The methods used were UMP2, CISD, UQCISD, and UCCSD(T), in order to investigate the effect of including dynamic electron correlation; and CASSCF, in order to investigate the effect of nondynamic electron correlation. The basis set effect was investigated both using ab initio methods up to the QCISD level, and also employing the B3LYP density functional method. In the case of the ab initio calculations, except for the CISD calculations, the basis sets were based on an effective core potential (ECP) for K in which the 1s, 2s, and 2p orbitals were included; for the B3LYP method both ECP and all-electron basis sets were employed, so as to establish

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TABLE 1: Calculated Geometric Parameters and Vibrational Frequencies of the $\tilde{X}^2A_2$ State of the KO$_2$ Molecule

method	r_{K-O}/Å	θ/deg	r_{O-O}/Å	ω_1/cm^{-1}	ω_2/cm^{-1}	ω_3/cm^{-1}
UMP2/TZ+P (ref 8)	2.459	32.4	1.372	1007	331	*a*
MCPF (ref 4)	2.415	32.4	1.346	*b*	*b*	*b*
CASSCF(7,8)/A	2.394	31.1	1.284	*b*	*b*	*b*
CISD/midi4+diff s,p+2d	2.495	31.5	1.356	*b*	*b*	*b*
UMP2/A	2.394	33.3	1.372	1040	361.9	*a*
UQCISD/A	2.403	32.7	1.352	1137	359.1	311
UQCISD/B	2.436	32.0	1.341	1173	330.9	306
UCCSD(T)/C	2.388	32.8	1.347	*b*	*b*	*b*
UB3LYP/A	2.380	32.8	1.343	1175	362	327
UB3LYP/B	2.413	32.2	1.340	1180	339	315
UB3LYP/D	2.411	32.3	1.341	1172	337	312
UB3LYP/E	2.410	32.3	1.341	1172	338	312
exptl[c]	2.28,[d] 2.10 ± 0.14[e]	33,[d] 37 ± 2[e]	1.33[f]	1108.9[e]	306.98[e]	304.3[e]

[a] Value not reported, as affected by symmetry breaking—see text. [b] Value not calculated. [c] Values given here are for the ^{39}K, ^{16}O, and ^{16}O isotopomer. [d] References 4 and 5. [e] Reference 3. [f] Fixed at the value found from X-ray crystallographic data[18] for NaO$_2$.

the reliability of both the augmented ECP basis sets and the density functional theory (DFT) method used.

Six basis sets are used in this work:

(i) midi4[9]+diff s,p + 2d: K (s, 0.015; p, 0.1143; d, 2.5, 0.8), O (s, 0.0933; p, 0.09; d, 2.314, 0.645).

(ii) Basis Set A: K LANL2DZ effective core potential,[10] augmented with even-tempered, uncontracted functions (s, 3.0,1.0, 0.3333, 0.1111, 0.037, 0.01233; p, 8.0, 4.0, 1.0, 0.25, 0.0625, 0.015625; d, 4, 1.3333, 0.4444) (i.e., [LANL2DZ + 6s6p3d]; O aug-cc-pVDZ[11]).

(iii) Basis Set B: K, LANL2DZ effective core potential,[10] augmented with even-tempered, uncontracted functions (s, 6.4, 2.56, 1.024, 0.4096, 0.1638, 0.065 536, 0.0262 144, 0.010 485 7; p, 10, 3.7037, 1.3717, 0.5081, 0.1882, 0.069 69, 0.025 81, 0.009 56; d, 5, 1.66 67, 0.5556, 0.1852) (i.e. [LANL2DZ + 8s8p4d]; O 6-311+G(3d).

(iv) Basis Set C: K - as for basis set A, but augmented with an additional f function (1.1) (i.e., [LANL2DZ + 6s6p3d1f]; O aug-cc-pVTZ[11]).

(v) Basis Set D: K, the Wachters (14s9p) basis set[12] was used uncontracted, and was augmented with a diffuse s function (0.005 505) and a diffuse p function (0.076245), and then four even-tempered, uncontracted d functions (5.0, 1.6667, 0.5556, 0.1852) and two even-tempered, uncontracted f functions (1.1, 0.37) *i.e.* [15s10p4d2f]; O, aug-cc-pVTZ.

(vi) Basis set E: K, was obtained in the following fashion: three contracted s functions were based on the Huzinaga (26s16p) basis set expansion coefficients,[13] corresponding to the 1s, 2s, and 3s orbitals, and then eight even-tempered uncontracted *s* functions were added (6.4, 2.2857, 0.8163, 0.2915, 0.1041, 0.037 18, 0.013 28, 0.004 743); two contracted p functions were also formed from the Huzinaga 26s16p basis set, corresponding to the 2p and 3p orbitals augmented by eight even-tempered uncontracted p functions (13.0, 4.6428, 1.658 16, 0.5922, 0.2115, 0.075 53, 0.026 97, 0.009 634); five d functions (5.0, 1.667, 0.5556, 0.1852, 0.061 73); and three f functions (1.1, 0.37, 0.122 22). This gives an overall (17, 19, 22, 8 × 1/16, 16, 8 × 1/5 × 1/3 × 1) basis set, where for the 17 primitive s contraction, the nine most diffuse functions of the Huzinaga (26s16p) basis set were excluded, for the 19 primitive s the most tight and the six most diffuse functions were excluded and for the 22 primitive s the two most tight and the two most diffuse functions were excluded; the 16 primitive p contractions were used with the expansion coefficients as given by Huzinaga[13] (i.e., [11s10p5d3f]; O, aug-cc-pVTZ).

We believe that the above six basis sets cover the important aspects of the possible basis set variation, such as the effect of contractions in the core, flexibility in the valence region (including the diffuse region), and d and f polarization functions.

All of the calculations were performed using the Gaussian suite of programs,[14] except for the CISD calculations, which were performed using GAMESS-UK.[15]

III. Results

The results of all the calculations, as well as a selection of the previous calculations, are shown in Table 1. As may be seen, at all levels of theory, the calculated bond angle is in the region of 31.1−33.3°, with the higher levels of theory favoring 32.3 ± 0.5°. In a similar way, the K−O bond length is consistently calculated to be between 2.38 and 2.44 Å. This good agreement is shown using methods which account for dynamic and non-dynamic correlation, as well as using large, flexible basis sets, and so it seems unlikely that any further calculations would lead to a different conclusion concerning the geometry. We also note here that in the CASSCF calculations the coefficient of the dominant configuration was >0.999 and in the CISD calculation it was >0.96, showing that it is a single reference that is dominating here, giving extra weight to the conclusions of the QCISD and CCSD(T) calculations. Additionally, in all cases where unrestricted wavefunctions were used in the present work, the $\langle S^2 \rangle$ value was <0.77, showing that spin contamination was negligible for these calculations. Thus, taking into account the results of all the calculations, it can be confidently concluded that the equilibrium bond angle of KO$_2$ is 32.3 ± 0.5°, the K−O equilibrium internuclear distance is 2.410 ± 0.005 Å, and the O−O internuclear distance is 1.341 ± 0.001 Å.

In previous calculations, the parameter which changed the most with respect to changes in level of theory and basis set, has been the calculated O−O bond distance. KO$_2$ has been shown in previous studies,[8] as well as confirmed in the present work, to be very ionic, with a charge of >+0.9e on K, and thus −0.9e on the O$_2$ moiety. Since isolated O$_2^-$ has a degenerate $^2\Pi$ state, the degeneracy of the π-orbitals is broken by the presence of the K$^+$ cation nearby, and this situation is not facile to describe. From Table 1, however, it can be seen that the QCISD, CCSD(T), and B3LYP methods are able to describe this bonding, giving very consistent results for the O−O bond length, which are also in good agreement with the gas-phase value of the O$_2^-$ bond length (vide infra); this good performance of the B3LYP method is confirmed by similar calculations on NaO$_2$ and LiO$_2$ (vide infra).

With regard to the vibrational frequencies, the UMP2 method has been noted by Wright et al. (ref 8) as being affected by

TABLE 2: Calculated Geometry and Vibrational Frequencies for the $\tilde{X}^2A_2$ state of LiO_2

method	r_{Li-O}/ Å	θ/ deg	r_{O-O}/ Å	ω_1/ cm^{-1}	ω_2/ cm^{-1}	ω_3/ cm^{-1}
CISD-π (ref 16)	1.794	43.9	1.340	1263	740	519
B3LYP/6-311+G(2*df*)	1.757	45.0	1.348	1168.0	752.3	525.7
B3LYP/6-311+G(3*df*)	1.755	44.9	1.350	1172.4	751.5	526.6
exptl (ref 27)	1.77	44.1	1.33[a]	1097	699	492

[a] Fixed at the value found from X-ray crystallographic data[18] for NaO_2.

TABLE 3: Calculated Geometry and Vibrational Frequencies for the $\tilde{X}^2A_2$ state of NaO_2

method	r_{Na-O}/ Å	θ/ deg	r_{O-O}/ Å	ω_1/ cm^{-1}	ω_2/ cm^{-1}	ω_3/ cm^{-1}
CISD-π (ref 17)	2.139	36.5	1.340	1284	434	364
B3LYP/6-311+G(2*df*)	2.138	36.8	1.350	1161.1	421.3	349.0
B3LYP/6-311+G(3*df*)	2.129	36.8	1.345	1166.3	426.0	350.0
exptl. (refs 5 and 28)	2.07	37.5	1.33[a]	1094	391	333

[a] Fixed at the value found from X-ray crystallographic data[18] for NaO_2.

symmetry breaking for KO_2, in a similar manner to that observed by Allen et al. in calculations on LiO_2 (ref 16) and NaO_2 (ref 17), using a variety of methods. In the present work, the ω_3 value of KO_2 calculated at the UMP2/A level of theory was 791 cm^{-1}, clearly far away from both the experimental value and that of the other methods (Table 1); this value is disregarded in the following. The conclusion that the B3LYP method is able to describe these species, and is not subject to the symmetry-breaking problem to any great extent, is confirmed by performing B3LYP calculations on NaO_2 and LiO_2. The values obtained using this method are in good agreement, both with experiment and previous CISD-π calculations (which are able to deal with the symmetry problem), for both the geometry and the vibrational frequencies, in particular the ω_3 value—see Tables 2 and 3, as well as Discussion below. Consequently, it is concluded that the ω_3 value calculated for KO_2 in the present work is also reliable.

IV. Discussion

(a) Comparison with the Experimental Values for KO_2. *(i) Geometry*. Since the ab initio calculations appear to be unambiguous in their conclusions regarding the molecular geometry, another source must be searched for the disagreement between theory and experiment. First, it should be restated that the bond angle and K−O bond length reported in ref 3 were derived from a fit of observed frequencies as a function of bond angle, while the O−O distance was fixed at the X-ray crystallographic value[18] of 1.33 Å (although a different value for KO_2 of 1.28 ± 0.02 Å is also available[19]). It was noted therein that a small variation in the O−O bond distance should not affect the derived bond angle greatly. Our calculated value of 1.341 Å is larger than the crystallographic value, but it is in excellent agreement with the gas-phase value for the bond length of O_2^- of 1.341 ± 0.010 Å (ref 20), as is expected, since the bonding in this molecule is very ionic;[8] we believe the theoretical value of 1.341 Å calculated here to be more reliable than the assumed value of 1.33 Å. A similar fit to that performed in ref 3 of experimental matrix isolation vibrational data for the K−O stretch by Andrews[4] yielded a bond angle of 33°. Given the greater precision of the measurements of ref 3, it might be expected that the derived molecular geometry from that work ought to be the most reliable, but this does not appear to be the case. Our conclusions in this respect are that the good agreement of the bond angle from ref 4 is probably fortuitous, since the derived bond length of 2.28 Å reported therein, is far from the calculated value of 2.410 Å obtained here. The poor agreement between the computed geometry obtained here, as well as the experimentally derived values of ref 3, is rather surprising, but can most easily be attributed to the use of a harmonic force field (see next subsection).

(ii) Vibrational Frequencies. The vibrational frequencies calculated in the present work are summarized in Table 1. The ω_1 vibration (O−O stretch) requires the use of correlated methods as has been reported in ref 21. At the highest levels of theory used, QCISD/B and B3LYP/A-E, the agreement between theory and experiment is very good, considering that the calculated values are harmonic frequencies, whereas the experimental value is a fundamental. As far as the ω_3 frequency is concerned, very pleasing agreement is seen for the QCISD and B3LYP methods with all basis sets used (except for B3LYP/A). This is the vibrational mode that has been noted as being subject to symmetry breaking in previous studies,[16,17] and indeed, we observed the same effect here at the MP2 level. The consistency of the QCISD and B3LYP results, and the close agreement with experiment implies that these theoretical methods are not so prone to the symmetry breaking phenomenon. In order to confirm this, we performed calculations using the B3LYP method with the 6-311+G(2d) and the 6-311+G-(3df) all-electron basis sets on the LiO_2 and NaO_2 molecules: the results are shown in Tables 2 and 3. These molecules have been subjected to a rigorous theoretical study by Allen and coworkers.[16,17] They concluded that many theoretical methods are affected by symmetry breaking of the O_2^- electronic wave functions during the ω_3 asymmetric stretch vibration, where the two oxygen atoms lose their equivalency. In order to achieve a good description of the electronic wavefunction throughout the ω_3 vibration, it was necessary to use a selected active space of the molecular orbitals in a CASSCF calculation; the effects of dynamic electron correlation energy were then accounted for by CI calculations using the natural orbitals of the CASSCF calculation. In this way it was possible to obtain good

TABLE 4: Calculated Vibrational Frequencies of Various Isotopomers of KO_2. Calculations Performed at the QCISD/B Level of Theory[a]

	ω_1/cm^{-1}		ω_2/cm^{-1}		ω_3/cm^{-1}	
isotopomer	theory	exptl	theory	exptl	theory	exptl
39-16-16	1172.5 (1.000)	1108.9 (1.000)	330.9 (1.000)	306.98 (1.000)	306.1 (1.000)	304.3 (1.000)
39-16-18	1139.4 (0.972)	1078 (0.972)	327.1 (0.989)	305.78 (0.996)	296.6 (0.969)	292.68 (0.962)
39-18-18	1105.3 (0.943)	1046.2 (0.943)	320.6 (0.969)	297.48 (0.969)	289.6 (0.946)	288.29 (0.947)
39-17-18	1121.5 (0.957)		323.4 (0.977)	300.61 (0.979)	293.3 (0.958)	
41-16-16	1172.5 (1.000)		327.3 (0.989)	303.7 (0.989)	305.7 (0.999)	
41-16-18	1139.4 (0.972)		323.5 (0.978)	303.1 (0.987)	295.9 (0.967)	
41-18-18	1105.3 (0.943)		316.9 (0.958)	294.09 (0.958)	289.2 (0.945)	

[a] Values in parentheses are the ratio of the isotopic frequency relative to the 39-16-16 values. Experimental values from ref 3.

TABLE 5: Calculated Vibrational Frequencies of Various Isotopomers of LiO$_2$. Calculations Performed at the B3LYP/6-311+G(3*df*) Level of Theory[a]

	ω_1/cm^{-1}		ω_2/cm^{-1}		ω_3/cm^{-1}	
isotopomer	theory	exptl	theory	exptl	theory	exptl
7-16-16	1172.4 (1.000)	1097 (1.000)	751.5 (1.000)	699 (1.000)	526.6 (1.000)	
6-16-16	1173.0 (1.001)		800.8 (1.065)		544.0 (1.033)	
7-18-18	1105.6 (0.943)	1035 (0.943)	743.7 (0.990)	690 (0.987)	508.8 (0.966)	
6-18-18	1106.4 (0.944)		793.2 (1.055)		526.9 (1.000)	
7-17-17	1137.5 (0.970)		747.4 (0.994)		517.3 (0.982)	
7-17-18	1121.7 (0.957)		745.6 (0.992)		513.0 (0.974)	
7-16-18	1139.6 (0.972)	1067 (0.973)	747.7 (0.995)	695 (0.994)	517.6 (0.983)	
6-16-18	1140.3 (0.973)		797.1 (1.061)		535.3 (1.017)	
6-17-17	1138.2 (0.971)		796.8 (1.060)		535.0 (1.016)	
7-16-17	1155.1 (0.985)		749.5 (0.997)		521.9 (0.991)	
6-16-17	1155.8 (0.986)		798.8 (1.063)		539.5 (1.024)	

[a] Values in parentheses are the ratio of the isotopic frequency relative to the 7-16-16 values. Experimental values from ref 27.

TABLE 6: Calculated Vibrational Frequencies of Various Isotopomers of NaO$_2$. Calculations Performed at the B3LYP/6-311+G(3*df*) Level of Theory[a]

	ω_1/cm^{-1}		ω_2/cm^{-1}		ω_3/cm^{-1}	
isotopomer	theory	exptl	theory	exptl	theory	exptl
23-16-16	1166.3 (1.000)	1080 (1.000)	426.0 (1.000)	391 (1.000)	349.9 (1.000)	333 (1.000)
23-18-18	1099.5 (0.943)	1019 (0.944)	415.9 (0.976)	382 (0.977)	332.5 (0.950)	318 (0.955)
23-17-17	1131.4 (0.970)		420.7 (0.988)		340.8 (0.974)	
23-16-18	1133.4 (0.972)	1050[b] (0.972)	421.4 (0.989)	387 (0.990)	340.7 (0.974)	325 (0.976)
23-16-17	1149.0 (0.985)		423.5 (0.994)		345.2 (0.987)	
23-17-18	1115.5 (0.956)		418.4 (0.982)		336.5 (0.962)	

[a] Values in parentheses are the ratio of the isotopic frequency relative to the 23-16-16 values. Experimental values from refs 5 and 28. [b] Value estimated in ref 28.

agreement between the calculated ω_3 frequency and that of the experiment (although the O−O stretch frequency obtained was not in such good agreement with experiment). As may be seen from Tables 2 and 3, the B3LYP method is adequate for these species, and unrealistic values of the ω_3 vibrational frequency are not occurring here. From this we conclude that the B3LYP density functional is able to describe the electronic wave function well throughout the ω_3 vibration. In addition, the good agreement between the QCISD and B3LYP results for KO$_2$ (Table 1) suggests that the QCISD method is also able to cope with this situation.

Both ω_1 and ω_3 are found to be in very good agreement with experiment at the B3LYP level with the large basis sets D and E. The ω_2 (K−O symmetric stretch) is in slightly poorer agreement (the ω_1 value is 6% too high, the ω_2 is 10% too high, and the ω_3 value is 3% too high). Since we have exhausted the basis set effect, shown that single-reference methods are adequate, and shown that the B3LYP method is yielding results close to the QCISD method, we conclude that anharmonicity is the major contributor to the remaining discrepancy between theory and experiment. The bonding in KO$_2$ is rather weak, as evinced by the low vibrational frequencies for ν_2 and ν_3 and the relatively low dissociation energy of 40.6 kcal mol^{-1} (ref 7), and so it is reasonable to expect that anharmonicity might be significant.

The results of the isotopic substitutions are shown in Tables 4−6, together with the experimental results, where available. As may be seen, the agreement between the calculated and experimental isotopic shifts for all three molecules is excellent in most cases. The only exception is for the ω_2 symmetric K−O stretch of the ^{41}K^{16}O^{18}O isotopomer; this weak feature may have been misassigned in ref 3, and may be due to, for example, a different matrix environment.

In summary, the calculated vibrational frequencies are in very good agreement with the experimental values, in the main, with the ω_2 value being the least accurate. The residual differences between theory and experiment are probably due to anharmonic effects, and these could be investigated by calculating full potential surfaces as a function of the internal coordinates and extracting the anharmonicity in that manner—these calculations are presently under consideration. The neglect of anharmonicity in ref 3 seems the most likely cause of inaccuracy in the derived geometry, which was based on the use of harmonic force fields.

(b) Some Comments about the Performance of the Theoretical Methods Employed. *(i) QCISD vs B3LYP.* As may be seen from Table 1, the calculated bond angle and O−O bond length using the QCISD and B3LYP methods are in very good agreement. The agreement for the O−O bond length between these methods, and the experimental value for O$_2^-$, is particularly encouraging, since the O$_2^-$ moiety has been noted as being difficult to describe[16,21] using the Hartree−Fock approach, as well as even correlated methods[16]. The K−O bond length is difficult to compare between the QCISD and B3LYP methods since this parameter appeared to be more basis set dependent than the bond angle and the O−O bond length. Unfortunately it was not possible to extend the basis set to saturation using the QCISD method, but it was possible to do so for the B3LYP method; as may be seen, the basis set is exhausted with the all-electron basis set E. With regard to the vibrational frequencies, again the QCISD and B3LYP methods lead to very good agreement, with the basis set effect appearing to be exhausted more quickly. The good agreement for all of the calculated values using different theoretical approaches and different basis sets gives us confidence that the calculated values are reliable.

The results obtained here are in agreement with those found by previous workers, where for tightly-bound molecules (as opposed to molecular complexes, where DFT methods are not necessarily accurate[22]) the B3LYP method has consistently been found to perform well,[23−25] in particular giving results close to CCSD(T) results,[24,25] when used with basis sets of a similar size to those used here. The reliability of the B3LYP method when used with ECPs, has been demonstrated elsewhere.[26]

(ii) The ECP versus the All-Electron Basis Sets: Basis Set Saturation. As noted in the preceding paragraph, the LANL2DZ effective core potential, when augmented by a set of flexible valence basis functions and polarization and diffuse functions, is able to cope with describing even a quite demanding molecule. This is very encouraging, since all-electron calculations on a molecule of this size are quite expensive. Of course, such all-electron calculations are viable using density functional theory, but the reliability of the latter method appears to be case dependent, and must be tested against ab initio calculations, whose performance is better documented. It is clear that basis set A, based on the LANL2DZ ECP is not sufficient for this molecule, since there are significant changes in the calculated parameters on extending the basis set to B; B appears to be close to saturation, but the K−O bond length seems to demand a very flexible basis set, as noted above. Finally, we note that, as here, the LANL2DZ ECP, suitably augmented, has been shown to perform with comparable reliability to all-electron basis sets in a study on the BBr_2 molecule.[26]

V. Conclusions

The KO_2 molecule has been studied at high levels of ab initio theory. A very consistent set of molecular parameters was obtained, which leaves the equilibrium geometry in little doubt. The poor agreement of the calculated geometry with that derived from a recent far-infrared study is attributed to the use of a harmonic force field therein. Thus it is concluded that KO_2 has an equilibrium bond angle of $32.3 \pm 0.5°$ and a K−O bond length of 2.410 ± 0.005 Å. The O−O bond length is calculated to be 1.341 ± 0.001 Å, in excellent agreement with a gas-phase determination of the bond length of O_2^-, which further supports the result that KO_2 is very ionic. A reliable set of harmonic vibrational frequencies were also calculated, and it was concluded that any remaining discrepancies between theory and experiment can be attributed to anharmonicity. The B3LYP density functional is found to perform very well for the alkali metal superoxides, as does the LANL2DZ effective core potential.

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