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The vibrational frequencies of CaO_2, ScO_2, and TiO_2: a comparison of theoretical methods

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Abstract. The vibrational frequencies of several states of CaO_2, ScO_2, and TiO_2 are computed using density functional theory (DFT), the Hartree-Fock approach, second-order Møller-Plesset perturbation theory (MP2), and the complete-active-space self-consistent-field theory. Three different functionals are used in the DFT calculations, including two hybrid functionals. The coupled cluster singles and doubles approach including the effect of connected triples, determined using perturbation theory, is applied to selected states. The Becke-Perdew 86 functional appears to be the most cost-effective method of choice, although even this functional does not perform well for one state of CaO_2. The MP2 approach is significantly inferior to the DFT approaches.

Key words: Harmonic frequencies – Density functional theory – Coupled cluster singles and doubles

1 Introduction

There is a great interest in the ability to compute accurate vibrational frequencies and intensities of molecules in a cost-effective manner. In addition to helping identify bands observed in experiments, they are needed in the calculation of thermodynamic data; for example in the calculation of the zero-point energies and the temperature dependence of the heat of formation and entropy. Finally we should note that the efficient calculation of second derivatives makes the location of transition states much easier.

While scaled Hartree-Fock (HF) frequencies have been found to be reliable for many molecules [1], especially closed-shell organic systems, it has been found that the addition of electron correlation is very important for the calculation of accurate frequencies for many classes of compounds. Density functional theory (DFT) has been found to be a very cost effective method to study transition metal systems, see for example Ref. [2]. While second-order Møller-Plesset (MP2) perturbation theory works well for many systems, the DFT approach has been found to yield accurate frequencies even in cases where the MP2 is not accurate [3]. In addition, the calculation of the DFT frequencies requires significantly smaller computer resources than the calculation using the MP2 approach.

For the determination of equilibrium geometries and the calculation of vibrational frequencies, we observed that the hybrid [4] B3LYP [5] and Becke-Perdew 86 [6, 7] (BP86) functionals are of approximately equal accuracy, but that the B3LYP is superior in most cases for energetic properties [8]. However, we have recently found that for the metal dioxides, MO_2, these two functionals yield very different results [9, 10]. The results also vary significantly for the more traditional methods. For these systems, the method that yields the most accurate results varies from system to system and from state to state. That is, the metal dioxides appear to be very good systems to test the accuracy of methods for the calculation of equilibrium geometries and vibrational frequencies.

In this manuscript we report on the application of several methods to the metal dioxides. The methods include DFT (with several choices of functional), HF, MP2, the complete-active-space self-consistent-field (CASSCF) approach, and the coupled cluster singles and doubles approach [11] including the effect of connected triples determined using perturbation theory [12], CCSD(T). The CCSD(T) is the most accurate treatment considered in this work, but its high computational cost means that it is not practical for many systems, however it serves to calibrate the more approximate methods. For these systems it is possible to make all of the valence orbitals and electrons active in the CASSCF calculations, thus allowing us to address the importance of near degeneracy effects. However, it should be noted that it is difficult to apply the CASSCF to larger systems because large numbers of valence orbitals and electrons can lead to prohibitively large CASSCF calculations.

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2 Methods

A variety of methods are used to optimize the geometry and compute the harmonic frequencies of the MO_2 systems considered in this work. HF is the simplest approach and it does not include any electron correlation; we use a spin-unrestricted approach for the open-shell systems. MP2 is one of the simplest approaches to add electron correlation to the HF reference. The metal 1*s*–3*p* and oxygen 1*s* orbitals are not correlated at the MP2 level. Unlike the HF and MP2 calculations, which are spin-unrestricted for the open-shell systems, the CCSD(T) calculations are performed using the restricted open-shell approach [13, 14]. The metal 1*s* – 2*p* and oxygen 1*s* orbitals are not correlated at the CCSD(T) level.

In the DFT calculations we use BP86 and hybrid B3LYP and B3PW91 [15] functionals. In the CASSCF approach, we have all of the valence orbitals as active, namely the metal 3*d* and 4*s* orbitals and the oxygen 2*p* orbitals. Some test calculations using different active spaces are discussed as well.

The oxygen 6-31+G* basis set [16] is used in the HF, MP2, DFT, and CASSCF calculations. The oxygen augmented-correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) set [17, 18] is used in the CCSD(T) calculations. The Sc and Ti basis sets used in conjunction with the 6-31+G* oxygen basis set are a [8*s* 4*p* 3*d*] contraction of the (14*s* 9*p* 5*d*) primitive set developed by Wachters [19]. The *s* and *p* spaces are contracted using contraction number 3, while the *d* space is contracted (311). To this basis set two diffuse *p* functions are added; these are the functions optimized by Wachters multiplied by 1.5. A diffuse *d* function [20] is also added. The Ca basis set is the (12*s* 8*p* 5*d*)/[8*s* 6*p* 3*d*] modified [21] basis set of Roos et al. [22] used in our previous study [23] of CaO_2.

We should note that in a recent study [10] we observed that deleting the most diffuse *p* function on Sc did not significantly affect the BP86 geometries or frequencies of ScO_2 or ScO_2N_2, but improved the convergence of the orbital optimization, especially for ScO_2N_2. In addition, polarization functions are, in general, less important in DFT calculations than in traditional ones. However, for simplicity we use the same basis in the DFT, HF, MP2, and CASSCF calculations.

The Sc and Ti basis sets used in conjunction with the aug-cc-pVTZ oxygen basis set are derived from the averaged atomic natural orbital (AANO) set [24, 25] described in Ref. [26]; they have been modified to allow 3*s*3*p* correlation. The first 17*s* functions are contracted to three functions using the AANO orbitals while the four most diffuse *s* primitives are uncontracted. The first ten *p* functions are contracted to 2 functions, while the six most diffuse primitives are uncontracted. The four *d* AANOs are supplemented by uncontracting two *d* functions in the region of the 3*p* orbital, namely those with exponents of 1.342621 and 0.561524 for Sc and 1.6892689 and 0.7156706 for Ti. The unmodified three *f* and two *g* polarization sets are used, yielding final basis sets of the form (21*s* 16*p* 9*d* 6*f* 4*g*)/[7*s* 8*p* 6*d* 3*f* 2*g*]. The Ca set is the (20*s* 15*p* 9*d* 5*f* 2*g*)/[8*s* 7*p* 7*d* 5*f* 2*g*] developed by Partridge [27]. This set is sufficiently flexible to describe the ground and low-lying states of Ca and Ca^+ and to allow 3*s*3*p* correlation. While this basis set was developed by Partridge, it is described in the Appendix since this set has not been published. Only the spherical harmonic components of the basis sets are used.

The frequencies are computed using analytic second derivatives for all methods except for the CCSD(T) approach, where harmonic frequencies are computed using only energies. The HF, MP2, and DFT calculations are performed using Gaussian 94 [28]. The CCSD(T) calculations are performed using MOLPRO 96 [29]. The CASSCF calculations are performed with SIRIUS/ABACUS [30]. The CCSD(T) vibrational frequencies are computed using SPECTRO [31].

3 Results and discussion

3.1 CaO_2

The results for CaO_2 are summarized in Table 1. We consider the same three states as in previous work [23], where a subset of these methods was applied using a slightly different basis set. The three states are:

1. The $^3B_2$ state in which the O-O bonds are broken, two Ca-O single bonds are formed and there is one open-shell electron on each O atom.
2. The $^3A_2$ state, where there is a single electrostatic bond between Ca and O_2; that is, a superoxide species, $Ca^+O_2^-$, is formed. There is one open-shell electron on Ca^+ and one on O_2^-.
3. The $^1A_1$ state, where two Ca-O_2 bonds are formed and polarized strongly towards the O_2, so that the system contains significant $Ca^{+2}O_2^{2-}$ and peroxide character.

For the $^3B_2$ state, the CCSD(T) approach is highly accurate because it is well described by a single reference, as shown by the small norm of the singles amplitudes (0.015). Thus the CCSD(T) approach should yield the most accurate harmonic frequencies available to date, and therefore we compare the other methods to this approach. Consistent with this expectation, the CCSD(T) ω_3 harmonic frequency is in reasonable agreement with the ν_3 fundamental observed in solid argon [32]. The HF, B3LYP, B3PW91, and CASSCF approaches are in good agreement with the CCSD(T). The HF frequencies, without any scaling, are in the best agreement with the CCSD(T) results, but its geometry differs more with the CCSD(T) than the DFT approaches. At the CASSCF level, the angle agrees the best with the CCSD(T), but the bond length has an error even larger than the HF approach. The B3LYP and B3PW91 approaches are quite acceptable for this system. The MP2 approach yields very reasonable stretching frequencies, but the bending frequency is much too small and the angle is significantly too large. The BP86 results are unacceptable. We obtain a solution with C_s symmetry instead of C_{2v}, which occurs even starting from the B3LYP orbitals. Apparently the BP86 prefers to make one stronger bond and one weaker bond, but the energy lowering associated with this distortion is very small (0.01 kcal/mol).

For the $^3A_2$ state ($Ca^+O_2^-$), all the methods are in reasonable agreement except for the MP2 approach. The HF has a somewhat higher ω_1 (mostly the O-O stretch) than the other approaches, but this can be traced to the HF result for the O_2 stretch, which is also significantly higher than that obtained using the other approaches; the harmonic frequencies for free O_2 are: 1978(HF), 1643(B3LYP), 1685(B3PW91), 1547(BP86), 1410(MP2), and 1542 cm^{-1} (CASSCF). The MP2 approach yields unacceptable results, the b_2 mode has a frequency that is much too high. This combined with the very large intensity indicates that the MP2 is near a symmetry breaking point [33] and hence is unreliable.

For the $^1A_1$ state, the results for all of the methods are in reasonable agreement with those obtained using the CCSD(T) approach, which is expected to be accurate based on the norm of the singles amplitudes (0.03). This state has $Ca^{2+}O_2^{2-}$ character and therefore might have been expected to be the most difficult to describe. However, this state has the advantage that there are no low-lying singlet states that can be described using these orbitals. It is especially pleasing that the three DFT

Table 1. Computed geometries, harmonic frequencies and intensities at different levels of theory for selected states of CaO_2. Bond lengths are in Å, angles are in degrees, harmonic frequencies in cm^{-1}, intensities are in km/mol, and energy separations are in kcal/mol

	a_1		a_1		b_2		Geometry		ΔE
	ω_1	I	ω_2	I	ω_3	I	r(Ca-O)	∠(OCaO)	
$CaO_2(^3B_2)$									
HF	469	29	73	113	552	266	2.151	150.1	−54.6
B3LYP	468	53	97	71	514	160	2.100	134.1	13.0
B3PW91	474	54	101	72	522	174	2.090	134.1	15.9
BP86	477	1	74	82	100i		2.006	171.9	24.7[a]
BP86 (C_s)	490	2	68	82	182	71	1.975, 2.044	173.0	24.7
MP2	434	2	29	120	549	384	2.212	170.4	11.2
CASSCF	436	29	80	96	518	229	2.177	144.7	7.2
CCSD(T)	467		88		550		2.116	141.2	15.7
Expt.[b](ν)					516			140 ± 10	
$CaO_2(^3A_2)$									
HF	1424	1	444	99	346	4	2.232	33.7	−27.9
B3LYP	1185	8	444	68	370	0	2.207	35.4	9.7
B3PW91	1225	9	450	70	380	0	2.193	35.3	10.5
BP86	1127	11	443	57	372	0	2.199	35.9	16.3
MP2	846	48	395	33	1312	7729	2.254	36.8	18.4
CASSCF	1058	1	420	84	373	0	2.269	35.3	−5.2
CCSD(T)[c]							(2.207)	(35.4)	10.2
$CaO_2(^1A_1)$									
HF	915	42	667	183	536	28	1.988	43.7	0.0
B3LYP	814	67	617	82	506	43	1.981	45.2	0.0
B3PW91	847	66	633	90	516	46	1.969	44.8	0.0
BP86	797	61	599	63	502	45	1.984	45.4	0.0
MP2	744	71	545	114	494	65	2.070	45.9	0.0
CASSCF	692	108	574	58	521	2	2.029	46.1	0.0
CCSD(T)	755		617		529		1.977	46.1	0.0
Expt.[d](ν)	742	44	556	100	501	33			

[a] The C_s structure is 0.01 kcal/mol below the C_{2v}

[b] Ref. [32]

[c] The geometry is taken from the B3LYP approach

[d] Ref. [23], the most intense absorbance has been set to 100

methods are in good agreement with the CCSD(T), as these methods are quite inexpensive and can be applied to large systems.

On the basis of the results for three states of CaO_2, one would probably pick one of the two hybrid approaches as the method of choice, as they work for all three states and are in good agreement with the available CCSD(T) and experimental fundamentals in solid argon [32] or nitrogen [23]. The failure of BP86 for the $^3B_2$ state and MP2 for the $^3B_2$ and $^3A_2$ states would appear to make these approaches less desirable for these systems. While the CASSCF works well, it should be remembered that it is difficult to perform analogous calculations for larger systems. We should also note that the HF and CASSCF approaches, which include no or limited electron correlation, incorrectly order the states. This arises because O_2^{2-} (i.e., the peroxide) has more electron correlation than O_2^-. The hybrid DFT results are in good agreement with the CCSD(T) for the relative energetics.

3.2 ScO₂

We next consider four states of ScO_2, which are summarized in Table 2. We should note that for ScO_2 (and TiO_2, discussed below) we considered many states, but only report the results for a few of the most interesting ones. The $^2B_2$ state is analogous to the $^3B_2$ state in CaO_2, with an extra electron added to a metal-O bonding orbital. As in CaO_2, the bonds are strongly polarized toward O. The addition of one more bonding electron dramatically changes the accuracy of the methods for ScO_2 relative to CaO_2. The B3LYP and B3PW91 methods, which worked well for CaO_2, fail for ScO_2, producing a symmetry broken solution with unequal Sc-O bond lengths. The energy associated with this distortion is very small – see Table 2. At the HF level we find two solutions; the one with C_{2v} symmetry has an S^2 value of 1.75, showing that it is highly contaminated. The C_s solution is 8.6 kcal/mol lower in energy and has an S^2 value of 0.76. Both solutions yield frequencies that differ greatly with the CCSD(T) approach. At the MP2 level we find three solutions. The first is similar to the C_{2v} HF solution. The second also has C_{2v} symmetry and has a very large imaginary frequency; NB we are unable to find a HF solution corresponding to this MP2 solution. The third MP2 solution has C_s symmetry, as found for the hybrid functionals; however the MP2 stabilization energy is quite large, if computed with respect to either C_{2v} solution. While the CASSCF yields a C_{2v} solution, the large frequency and intensity for the b_2 mode indicates that it is near a symmetry breaking point and therefore is not reliable. The BP86 approach, which broke symmetry

Table 2. Computed geometries, harmonic frequencies and intensities at different levels of theory for selected states of ScO_2. Bond lengths are in Å, angles are in degrees, harmonic frequencies in cm^{-1}, intensities are in km/mol, and energy separations are in kcal/mol

	a_1		a_1		b_2		Geometry		ΔE
	ω_1	I	ω_2	I	ω_3	I	r(Sc-O)	∠(OScO)	
$ScO_2(^2B_2)$									
HF	594	55	142	16	640	253	1.959	125.5	0.0
HF(C_s)	1021	473	168	94	575	164	1.678, 2.025	128.4	−8.6
B3LYP	755	45	113	69	166i		1.778	129.3	0.4
B3LYP(C_s)	886	97	133	51	413	14	1.704, 1.913	117.2	0.0
B3PW91	762	43	121	71	126i		1.767	131.0	0.6
B3PW91(C_s)	914	123	142	49	447	25	1.691, 1.917	116.3	0.0
BP86	740	44	116	55	542	6	1.783	125.9	0.0
MP2′	485	1124	157	79	469	257	1.936	121.6	69.4
MP2	1065	175	143	110	***[a]		1.726	146.3	28.0
MP2(C_s)	912	202	158	46	540	141	1.718, 2.038	119.7	0.0
CASSCF	729	21	103	112	5833	> 99999	1.800	148.1	0.0
CCSD(T)	745		121		604		1.776	138.2	0.0
Expt[b](ν)					722			128 ± 4	
$ScO_2(^2A_1)$									
HF	980	106	739	109	572	0	1.852	46.4	35.6
B3LYP	899	127	658	37	574	8	1.862	47.2	32.7
B3PW91	926	129	676	44	585	8	1.853	46.8	31.5
BP86	880	92	634	26	569	7	1.870	47.1	33.1
MP2	868	97	650	24	1140	10081	1.886	47.9	34.1
CASSCF	819	121	614	17	544	0	1.883	48.8	12.3
CCSD(T)	879		654		592		1.853	47.9	26.5
Expt[b,c] (ν)	842	100	615	86	603	57			
$ScO_2(^2A_2)$									
Peroxide									
HF	924	45	675	159	980	2180	1.939	45.0	68.4
B3LYP	836	64	626	77	507	251	1.928	46.5	66.3
B3PW91	865	63	641	85	509	255	1.917	46.1	65.0
BP86	817	59	610	65	459	207	1.928	46.8	70.0
MP2	775	73	605	88	7730i		1.976	46.9	75.6
CASSCF	717	105	588	53	319i		1.968	48.0	69.4
Superoxide									
HF	1425	2	466	97	332	5	2.148	35.0	43.2
B3LYP	1200	24	490	59	392	2	2.081	37.3	74.4
B3PW91	1241	23	494	59	403	2	2.071	37.1	74.6
BP86	1146	34	488	57	387	1	2.078	37.7	80.6
MP2	1083	61	519	88	3438	> 99999	2.097	38.5	83.3
CASSCF	1105	15	507	89	395	5	2.093	37.9	58.8
$ScO_2(^4A_2)$									
HF	1429	2	466	95	311	9	2.153	34.9	39.0
B3LYP	1196	18	474	61	349	2	2.117	36.8	74.5
B3PW91	1205	18	422	93	387	6	2.172	35.7	100.4
BP86	1141	24	472	48	349	3	2.108	37.3	82.9
MP2	1111	71	449	104	6885	> 99999	2.212	36.8	80.6
CASSCF	1094	2	445	79	368	1	2.183	36.5	48.4

[a] The imaginary frequency is so large that it is not printed by the program

[b] Ref. [10]

[c] The most intense absorbance has been set to 100

for CaO_2, yields a C_{2v} solution, with vibrational frequencies in reasonable agreement with the CCSD(T); the biggest difference being that the BP86 frequency for the b_2 mode is 62 cm^{-1} lower than the CCSD(T), and both are much lower than the 722 cm^{-1} experimental value [10]. The disagreement between the CCSD(T) and experimental value is disappointing, since the CCSD(T) was expected to be accurate based on the norm of the single amplitudes (0.053). Given the BP86 relative intensities and the apparent agreement of the CCSD(T) and BP86 ω_1 values and the experimental fundamental, it is tempting to reassign the experimentally observed band as ν_1, but the results of isotopic substitution supports [10] its assignment as ν_3; the CCSD(T) isotopic ratios for $^{16}O/^{18}O$ are 1.0554 and 1.0362 for the a_1 and b_2 modes, respectively, compared with the experimental value of 1.0367.

For transition metal systems convergence to a local minimum is a common problem, and this appears to be quite common at the CASSCF level. This does not appear to be the origin of the problem for this system. In this regard we note that MOLPRO and SIRIUS/ABACUS yield the same CASSCF solution starting from several choices of orbitals, including the natural orbitals from a multirefence configuration interaction calculation. A state-averaged CASSCF calculation shows that the origin of the problem at the CASSCF level is that the $^2B_2$ and $^2A_1$ states are close in energy at the $^2B_2$ equilibrium geometry. At the CCSD(T) level, the $^2B_2$ is significantly stabilized relative to the $^2A_1$ state and hence this symmetry breaking does not occur.

For the CASSCF approach, changing the active space should change the separation of the $^2B_2$ and $^2A_1$ states and hence yield accurate results. However for all practical choices of the active space that we tried, the CASSCF approach yielded either an imaginary frequency for the b_2 mode or a very large frequency and intensity. We should also note that increasing the size of the basis set did not improve the CASSCF results.

While the CASSCF results show that the origin of the problem is due to two close lying states, it does not help predict other cases where this problem might occur. For this it is better to think of the problem in terms of the two possible bonding mechanisms. In the first, there are two equivalent bonds with a bond order of 1.5 while in the second there is one double bond and one single bond. It is unfortunate that some methods favor one bonding mechanism and others incorrectly favor the other.

The next three states are of the cyclic Sc–O_2 variety. The states fall into two categories, the first has a bond angle of about 45° and the second has a bond angle of about 37°. The states with the large angle tend to have shorter Sc-O bond lengths and are peroxide-like states, $M^{2+}O_2^{2-}$, while the smaller angle structures are superoxide states, $M^+O_2^-$. For the $^2A_2$ state both solutions are found. In addition to the geometry, the O-O stretching frequency differentiates between the peroxide and superoxide states.

The MP2 approach fails for all three of these states, which when combined with its failure for the $^3A_2$ state of CaO_2 and for similar states in TiO_2 (discussed below), suggests that MP2 is unable to treat the M–O_2-like states. All of the other methods yield similar results for the $^2A_1$ state, which is a peroxide species, $Sc^{2+}O_2^{2-}$, like the $^1A_1$ state of CaO_2. The DFT frequencies are in good agreement with experimental data and with the CCSD(T) results, but the DFT relative intensities are only in qualitative agreement with experimental values.

For the $^2A_2$ state of ScO_2, we find both the superoxide and peroxide solutions. HF and CASSCF favor the superoxide, but with electron correlation, the peroxide structure becomes more favorable; this is similar to CaO_2. Excluding the MP2, all methods yield similar results for the superoxide. For the larger angle peroxide structure, the HF, MP2, and CASSCF are unacceptable. Displacing the MP2 peroxide structure in the direction of the imaginary frequency results in a collapse to the $^2B_1$ state. This lower lying state is probably the origin of the failure of the HF and CASSCF approaches as well.

For the $^4A_2$ state all the methods agree reasonably well, except for the MP2 approach. The ω_1 (O-O stretch) indicates that this is a superoxide state, like the $^3A_2$ state of CaO_2. The HF approach yields an ω_1 that is too large, as observed for several other states and, as noted above, is related to the HF's treatment of free O_2.

3.3 TiO_2

The three most interesting states of TiO_2 are summarized in Table 3. The ground $^1A_1$ state is analogous to the $^3B_2$ state of CaO_2 and $^2B_2$ state of ScO_2. For Ti with four valence electrons, two double bonds are formed. With no low-lying singlet states that can be described with these orbitals, all of the methods yield reasonable results. The agreement of the BP86 and CASSCF with the CCSD(T) is exceptionally good. The MP2 frequencies are too small, but part of this could be the use of the small basis set. Thus the DFT methods perform significantly better than the MP2 approach with the same quality basis set. The computed harmonic frequencies are in good agreement with the two observed fundamentals [34]. The computed relative intensities are in reasonable agreement with experiment.

The $^3B_2$ state of TiO_2 is related to the ground state by an excitation of a bonding electron into a non-bonding 4*s*4*p* hybrid on Ti pointing away from the O atoms. That is, this state can be viewed as starting from the $^2B_2$ state of ScO_2 and adding an electron into a non-bonding orbital. It is therefore not surprising to find that the same methods that fail for ScO_2 $^2B_2$ also fail for TiO_2 $^3B_2$. The only minor difference is that the failure of the CASSCF approach is more dramatic for TiO_2 $^3B_2$, as it yields an imaginary frequency rather than very large frequency and intensity.

The $^1A_1$ peroxide state of cyclic TiO_2 is 107.5 kcal/mol above the ground state at the BP86 level. This places the singlet state above the $^3A_1$ (peroxide) state. This is consistent with the expectation that the peroxide states of cyclic TiO_2 involve the formation of two Ti-O_2 bonds, and therefore high-spin coupling of the open-shells on Ti is favorable. We do not consider the $^1A_1$ state in detail.

Finally, we consider the $^3A_1$ state of cyclic Ti–O_2. As for the $^2A_2$ state of ScO_2, both the superoxide and peroxide solutions are found. As for CaO_2 and ScO_2, correlation favors the peroxide structure with the larger angle, thus the peroxide is the more stable at all levels except the HF. The CASSCF approach without extensive correlation has them much closer in energy than the DFT approaches, but unlike CaO_2 and ScO_2, the CASSCF has the states correctly ordered for the $^3A_1$ state of cyclic TiO_2. For the smaller angle superoxide structure, all of the methods are in reasonable agreement, excluding the MP2 approach. The HF has a higher O-O stretch as observed for other superoxide systems. For the larger angle peroxide structure, all of the methods are in reasonable agreement, excluding the MP2 where the frequency and amplitude of the b_2 mode is slightly large. That is, the MP2 appears to fail for both solutions, as found for many of the M–O_2 structures of CaO_2 and ScO_2, but unfortunately the frequency and intensity of the b_2 mode in the TiO_2 peroxide structure are not so large that they are immediately recognized as being due to symmetry breaking.

There is no experimental evidence for cyclic Ti–O_2 species, even in nitrogen matrix experiments [34], where Ca–O_2 and Sc–O_2 were formed [10, 23]. This is presumably due to the fact that the cyclic Ti–O_2 species are much higher in energy, relative to open TiO_2, than the

Table 3. Computed geometries, harmonic frequencies and intensities at different levels of theory for selected states of TiO_2. Bond lengths are in Å, angles are in degrees, harmonic frequencies in cm^{-1}, intensities are in km/mol, and energy separations are in kcal/mol

	a_1		a_1		b_2		Geometry		ΔE
	ω_1	I	ω_2	I	ω_3	I	r(Ti-O)	∠(OTiO)	
$TiO_2(^1A_1)$									
HF	1126	75	330	44	1055	876	1.622	117.8	0.0
B3LYP	1017	38	339	14	976	446	1.647	111.4	0.0
B3PW91	1033	40	345	14	991	459	1.639	111.2	0.0
BP86	976	29	337	10	942	361	1.658	110.2	0.0
MP2	851	3	316	4	895	264	1.700	107.2	0.0
CASSCF	978	33	332	17	965	373	1.663	112.1	0.0
CCSD(T)	978		331		951		1.654	111.6	
Expt(v)[a]	947	16			917	100		113 ± 5	
$TiO_2(^3B_2)$									
HF	521	27	133	55	548	151	1.904	121.5	−3.0
B3LYP	883	294	201	4	391i		1.705	97.9	46.0
B3LYP(C_s)	957	248	162	0	512	92	1.633, 1.821	103.6	45.4
B3PW91	896	336	204	3	446i		1.696	97.1	48.5
B3PW91(C_s)	985	265	159	1	540	116	1.622, 1.823	104.1	47.5
BP86	881	9	205	5	501	0	1.708	96.6	49.0
MP2	877	6	180	72	4733i		1.718	138.7	132.6
MP2(C_s)	1042	381	155	52	543	132	1.651, 2.006	132.1	76.7
CASSCF	893	307	227	10	1238i		1.708	97.4	43.9
$TiO_2(^3A_1)$									
Peroxide									
HF	1027	74	737	97	474	10	1.816	46.4	39.0
B3LYP	935	206	689	87	503	8	1.833	47.0	89.3
B3PW91	968	206	699	101	521	9	1.823	46.6	88.6
BP86	920	124	664	49	477	2	1.838	47.0	95.9
MP2	916	52	710	71	637	50	1.840	47.8	123.0
CASSCF	875	96	664	17	445	1	1.848	47.9	73.8
Superoxide									
HF	1417	4	461	104	276	9	2.120	35.5	31.2
B3LYP	1184	59	482	34	355	2	2.057	37.8	128.0
B3PW91	1222	55	492	29	363	1	2.043	37.8	130.8
BP86	1138	18	499	37	298	0	2.036	38.6	146.0
MP2	1030	8	452	92	3930	> 99999	2.122	38.0	160.3
CASSCF	1057	9	401	87	353	11	2.098	38.4	90.0

[a] Ref. [34], the most intense absorbance has been set to 100

cyclic Sc–O_2 and Ca–O_2 species, relative to open ScO_2 and CaO_2.

4 Conclusions

The calculation of the vibrational frequencies for the MO_2 systems appears to be an interesting test of methods. Excluding the CCSD(T) approach on the basis of computational cost, the BP86 approach appears to be the best choice of a cost effective method to compute frequencies of these systems. However, even the BP86 does not work for all systems, failing for the $^3B_2$ state of CaO_2. The hybrid methods appear to have problems for cases with equivalent bonds with an order of 1.5, incorrectly preferring to break symmetry yielding one bond with order 2 and one with a bond order of 1. Even the CASSCF fails for these systems, because the two different bonding mechanisms result in two nearly degenerate states, which are of the same symmetry with a distortion of b_2 symmetry. The MP2 approach does not work very well for these systems. In fact, the HF approach appears to be superior to the MP2. The main problem with the HF is that it is unable to correctly position the relative energies of different structures or states with different bonding mechanisms.

Some of the problems observed in this work are not easy to predict and therefore one method of detecting them is to perform the calculations with both the B3LYP and BP86 approaches. When the results obtained with these two functionals agree, the calculations are probably accurate. When they disagree, other tests must be run to understand the origin of the difference between the two functionals. The ultimate test is, of course, comparison with experiments, and isotopic shifts are necessary to verify the vibrational assignments. While we do not consider isotopic shifts in this work, it is probably safe to assume that a method that consistently yields accurate harmonic frequencies will also yield accurate isotopic shifts.

Appendix

The large Ca basis set is derived [27] from the (20s 12p) set optimized by Partridge [35] for the ^1S state of Ca.

The three supplemental *p* functions, optimized for the ^3P state, are added. An even-tempered 4*d* 2*f* 2*g* polarization set, optimized in a configuration interaction (CI) calculation for the ^1S state correlating the two valence electrons, is added. The *d* and *f* spaces are supplemented with additional even-tempered functions to accurately describe the ^1D and ^3D states of Ca and the ^2D state of Ca^+. The extra functions include two tight *d*, three diffuse *d*, and three diffuse *f* functions. The tightest 15*s* functions are contracted to 3 functions and the tightest 10*p* functions are contracted to 2; both contractions are based on the HF orbitals. The three tightest *d* functions are contracted to one function using the natural orbital of a nine electron CI calculation on the ^2D state of Ca^+.

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