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Coordination of NO_2 to Alkaline-Earth Metals. A Theoretical Study

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The structure and harmonic vibrational frequencies have been determined for the alkaline-earth metal MNO_2 systems (M = Be, Mg, Ca, and Sr) using the B3LYP method. Binding energies have also been calculated using conventional ab initio methods, CCSD(T), and MCPF, with different basis sets. Four different coordination modes of NO_2 to the metal have been considered. The C_{2v} η^2-O,O coordination mode is the most stable one for all metals. However, for $BeNO_2$ the ground state is a $^2B_1$ state while for the other metals the $^2A_1$ state is the most stable one. Our best estimates for the D_0 binding energies are 77 kcal mol^{-1} for $BeNO_2$, 53 kcal mol^{-1} for $MgNO_2$, 69 kcal mol^{-1} for $CaNO_2$, and 71 kcal mol^{-1} for $SrNO_2$.

Introduction

The study of the bonding in metal−ligand systems is a very active area of research,[1] owing to their applications in many fields, such as homogeneous and heterogeneous catalysis, environmental chemistry or biochemistry. In particular, the study of alkaline-earth metals interacting with different kind of ligands has been the subject of many studies.[2−11] Nitrogen oxides are unwanted pollutants that take part in important chemical reactions in the atmosphere. Because metal−NO_2 systems are known to be involved in the decomposition of nitrogen oxides, the study of the coordination of NO_2 to metals is important for understanding these processes.

Experimental studies of alkali[12−16] and alkaline-earth[17−20] metals with NO_2 suggest the existence of a long-lived $M^+NO_2^-$ complex. For alkali metals, the IR data are consistent with a planar ring structure of C_{2v} symmetry with an η^2-O,O bidentate coordination.[15,16] The IR data for the alkaline-earth metal nitrites suggest a similar structure or a nonplanar one with a poorly defined position of the metal lying above NO_2.[18]

From a theoretical point of view, few calculations have been reported for MNO_2 systems.[16,21−24] In agreement with the experimental results, the calculations for alkali metals show that the C_{2v} cyclic and the C_s *trans*-ONO structures are energy minima, the C_{2v} being the most stable one. For the transition metal systems Cu−NO_2 and Ag−NO_2, the C_{2v} η^2-O,O coordination mode was also found to be the ground-state structure.[24] Calculations on $[MNO_2]^+H_2O$ systems for alkaline-earth metals[25] have also recently been reported. To our knowledge no theoretical study has been performed for the neutral alkaline-earth−NO_2 complexes.

In this work we study the bonding in the MNO_2 systems for M = Be, Mg, Ca, and Sr. Calculations are done using both conventional ab initio methods and the density functional approach. One of the goals of the present work is to determine the ground-state structures and the vibrational frequencies for these systems. For this purpose we have studied four different coordination modes: the bidentate C_{2v} η^2-O,O and C_s η^2-N,O and the monodentate C_{2v} η^1-N and η^1-O modes. The nature of the different bonding mechanisms and the relative stabilities of the different isomers are analyzed as well as the trends in the group. Another important goal of these studies is to provide accurate binding energies for the alkaline-earth metal nitrites.

Computational Details

Molecular geometries and harmonic vibrational frequencies have been determined using the density functional approach. In these calculations we have used the hybrid Becke's three-parameter exchange functional[26] with the correlation functional of Lee, Yang, and Parr[27] (B3LYP). This functional has proved to provide reliable geometries and harmonic vibrational frequencies compared to more computational demanding ab initio correlated methods.[28−30] However, to confirm the reliability of the B3LYP binding energies, we have also done single-point calculations at the coupled cluster level with single and double excitations with a perturbative estimate of the triple excitations (CCSD(T))[31] at the B3LYP equilibrium geometries. In the calculations at the CCSD(T) level we have correlated all the electrons of Be and 10 electrons for Mg, Ca, and Sr. For N,O we have correlated the 2s and 2p electrons.

The same basis set has been used in these two levels of calculation. The N and O basis set is the (9s 5p)/[4s 2p] set developed by Dunning,[32] supplemented with a valence diffuse function ($\alpha_{sp} = 0.0639$ for nitrogen and $\alpha_{sp} = 0.0845$ for oxygen) and one d polarization function ($\alpha = 0.80$ for nitrogen and $\alpha = 0.85$ for oxygen). This basis set is referred to as D95+* in the Gaussian 94[33] program. The Be basis set is the (11s 5p)/[4s 3p] set given by Krishnan et al.[34] supplemented with a valence diffuse function ($\alpha_{sp} = 0.0207$) and one d polarization function ($\alpha = 0.255$). The Mg basis set is the (12s 9p)/[6s 5p] set of McLean and Chandler[35] supplemented with a d polarization function ($\alpha = 0.28$). The Ca basis sets is the (12s 6p)/[8s 4p] set given by Roos, Veillard, and Vinot[36] supplemented with two diffuse p functions (0.09913 and 0.03464) and five d functions contracted (311) to three functions.[37] For Sr we have used the relativistic effective core potential (RECP) of Hay and Wadt[38] in which the 4s, 4p, and 5s orbitals are included in the valence space. We have used their (5s 6p) valence basis set. With use of a general contraction, the inner three s functions are contracted to two functions, the outermost two s functions are uncontracted, and the six p functions are contracted (321). Five d functions contracted (311) to three functions have been added.[7] The final basis sets are

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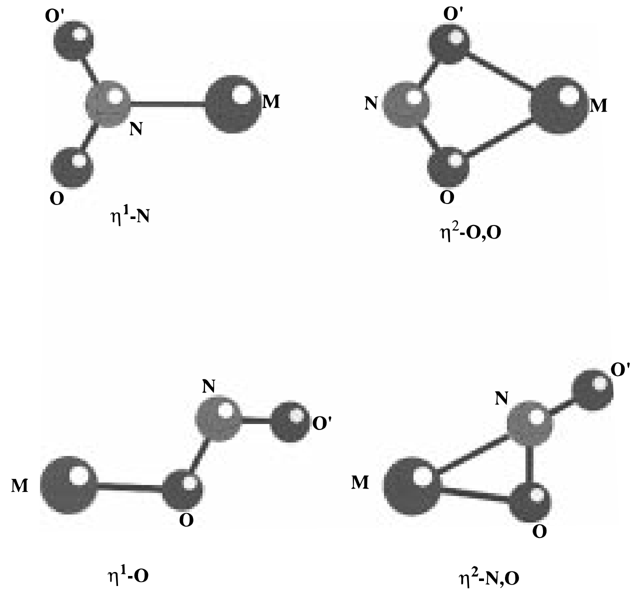

Figure 1. Studied coordination modes of NO_2 to the metal.

of the form (10s 6p 1d)/[5s 3p 1d] for N and O, (12s 6p 1d)/[5s 4p 1d] for Be, (12s 9p 1d)/[6s 5p 1d] for Mg, (12s 8p 5d)/[8s 6p 3d] for Ca, and (5s 6p 5d)/[4s 3p 3d] for Sr.

Single-point calculations using a larger atomic natural orbital (ANO) basis set have been carried out for the most stable isomer of each compound. These calculations have been performed using the modified coupled pair functional (MCPF)[39] method. The same electrons as in the CCSD(T) calculations have been correlated. For N and O we have used the (10s 5p 2d 1f)/[4s 3p 2d 1f] basis set of Dunning augmented with one diffuse s and one diffuse p functions.[40] This basis set, augmented with one diffuse d and one diffuse f functions, is referred to as aug-cc-pVTZ in the Gaussian 94 program.[33] For Be and Mg we have used the (14s 9p 4d 3f)/[5s 4p 3d 2f] and the (17s 12p 5d 4f)/[6s 5p 4d 3f] ANO basis sets of Widmark et al.,[41] respectively. For Ca and Sr we have used the (20s 15p 8d 6f)/[8s 7p 5d 3f] and (26s 19p 14d 4f)/[10s 10p 7d 3f] ANO basis set described in detail in reference 9.

The B3LYP and CCSD(T) calculations were performed using the Gaussian 94 program,[33] and open shell calculations were based on a spin-unrestricted treatment. The MCPF all-electron calculations were performed using the MOLCAS program,[42] while those calculations with Sr using pseudopotentials were performed using the SWEDEN-MOLECULE program.[43] In the MCPF case, the open shell calculations were based on a spin-restricted formalism.

Results and Discussion

Figure 1 shows the four different coordination modes of NO_2 to the metal that we have studied. For the η^2-O,O structures we have considered two different electronic states, the $^2A_1$ and the $^2B_1$ states. For the other coordinations we have only considered the ground state, that is, the $^2A_1$ state for the C_{2v} structures and the $^2A'$ for the C_s structures. The B3LYP optimal geometries and the B3LYP and CCSD(T) relative energies for the MNO_2 complexes are shown in Tables 1and 2, respectively.

Table 2 shows that in all cases the most stable coordination mode is the η^2-O,O one. For $BeNO_2$ the ground state is the $^2B_1$ state, while for the other metals the $^2A_1$ state is the most stable one. The computed B3LYP relative energies are in quite good agreement with the CCSD(T) values, the only exception being the $^2B_1$ state for all metals due to the different nature of the bonding (see below). The ordering of stabilities between the different isomers is the same for Mg, Ca, and Sr, while for Be the η^1-O structure is more stable than the η^2-N,O one.

TABLE 1: B3LYP Optimal Geometries[a]

η^1-N Coordination ($^2A_1$)

	M−N	N−O	N−O′	MNO	ONO′
Be	1.634	1.246	1.246	118.0	124.1
Mg	2.085	1.247	1.247	118.7	122.5
Ca	2.273	1.252	1.252	119.0	122.1
Sr	2.427	1.253	1.253	119.1	121.7

η^1-O Coordination ($^2A'$)

	M−O	N−O	N−O′	MON	ONO′
Be	1.449	1.434	1.182	125.5	111.6
Mg	1.840	1.351	1.206	171.1	113.6
Ca	2.035	1.351	1.210	179.0	113.6
Sr	2.193	1.347	1.211	168.0	113.9

η^2-O,O Coordination ($^2A_1$)

	M−O	N−O	N−O′	OMO	ONO′
Be	1.680	1.283	1.283	76.3	107.9
Mg	2.089	1.275	1.275	61.1	112.7
Ca	2.311	1.278	1.278	54.9	112.9
Sr	2.477	1.277	1.277	51.0	113.2

η^2-O,O Coordination ($^2B_1$)

	M−O	N−O	N−O′	OMO	ONO′
Be	1.463	1.436	1.436	100.4	103.0
Mg	1.882	1.376	1.376	74.2	111.3
Ca	2.044	1.407	1.407	68.2	109.0
Sr	2.195	1.399	1.399	62.5	109.0

η^2-N,O Coordination ($^2A'$)

	M−O	M−N	N−O	N−O′	MON	ONO′	N−O	ONO
Be	1.529	1.800	1.361	1.196	76.8	118.6		
Mg	1.974	2.177	1.330	1.210	79.8	117.9		
Ca	2.192	2.365	1.317	1.215	80.5	118.7		
Sr	2.361	2.530	1.313	1.218	81.7	118.4		
NO_2 ($^2A_1$)							1.208	133.7
NO_2^- ($^1A_1$)							1.270	116.4
NO_2^{2-} ($^2B_1$)							1.380	113.7

[a] Bond lengths are in angstroms and bond angles in degrees.

The bonding mechanism between an alkaline-earth metal and NO_2 is believed to be initiated by long-range electron transfer from the metal to the NO_2 ligand, which leads to a charge-transfer $M^+NO_2^-$ complex.[17,19] Our calculations show an important ionic character for the MNO_2 complexes studied. In all cases except the $^2B_1$ state of the η^2-O,O structure, the last doubly occupied orbital of the complex is mainly the $6a_1$ orbital of NO_2. This orbital, which is schematically represented in Figure 2, is the single occupied orbital in the $^2A_1$ ground state of NO_2. The open shell orbital of the complex mainly corresponds to the s orbital of the metal. This orbital polarizes away from the ligand to reduce repulsion. This polarization takes place through sp hybridization for Be and Mg and through spd hybridization for Ca and Sr. The nature of these molecular orbitals is consistent with a bond with an important ionic $M^+NO_2^-$ character. Mulliken population analysis indicates that there is also some back-donation from the occupied orbitals of the ligand to the empty p and d orbitals of the metal. This back-donation is more important for Be complexes than for the other metal complexes studied. This view of the bonding is supported by the geometrical parameters shown in Table 1. The geometry of the NO_2 fragment in the η^2-O,O coordination ($^2A_1$ state) is in all cases very similar to that obtained for free NO_2^-. In the η^1-N coordination the geometrical parameters of the ligand are between those obtained for free NO_2^- and NO_2,

TABLE 2: Relative Energies of MNO_2 Complexes Computed at Several Levels of Calculation[a]

	Be		Mg		Ca		Sr	
structure	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)	B3LYP	CCSD(T)
η^1-N	25.6	28.5	22.6	26.2	20.8	24.2	18.8	21.2
η^1-O	1.9	3.2	13.9	15.0	8.8	11.6	8.5	8.8
η^2-O,O($^2A_1$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
η^2-O,O($^2B_1$)	−13.7	−7.8	24.9	31.4	7.3	22.4	11.4	22.2
η^2-N,O	6.5	8.2	10.8	11.8	6.2	8.9	6.1	7.2

[a] Relative to the $^2A_1$ state of the η^2-O,O structure. In kcal mol^{-1}.

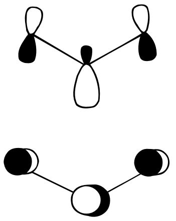

Figure 2. Schematic representation of the monooccupied $6a_1$ and first virtual $2b_1$ orbitals of NO_2.

indicating that for this coordination the covalent interaction between the metal and the ligand is larger than in the bidentate η^2-O,O structure. In the C_s structures the interpretation of the geometrical parameters is more difficult because the symmetry between the two NO bonds has been broken. However, it can be observed that the ONO angle is much closer to NO_2^- than to NO_2.

The ionic interaction is maximized in the η^2-O,O coordination mode by the approach of the metal atom along the C_{2v} axis between the two oxygen atoms. Thus, this coordination is the most stable one. The second most favorable ionic interaction takes place in the η^1-O structure. For the η^2-N,O structure the ionic stabilization is somewhat less favorable owing to the M−N interaction, and for the η^1-N isomer the ionic interaction is very inefficient. This is the order observed for Be complexes, since the differences between the ionic interactions are more important when the metal−ligand distances are smaller. However, in the case of Mg, Ca, and Sr, the η^2-N,O structure is slightly more stable than the η^1-O one. In these cases the more favorable overlap between the $6a_1$ orbital of NO_2 (see Figure 2) and the orbitals of the metal determines the order of stability of the η^1-O and η^2-N,O isomers.

The bonding mechanism corresponding to the $^2B_1$ state of the η^2-O,O coordination is different. The Mulliken population analysis shows that the charge over the metal is always larger than in the $^2A_1$ state. In this complex the last doubly occupied molecular orbital is mainly the $6a_1$ orbital of free NO_2 (as in the $^2A_1$ state) but now the open shell corresponds to an orbital that is mainly the $2b_1$ orbital of NO_2 (see Figure 2). This $2b_1$ orbital would be the first virtual orbital in free NO_2. Consistent with this, the Mulliken population analysis shows that in the $^2B_1$ state the unpaired electron is completely located in the NO_2 fragment of the complex. The nature of these orbitals shows that in the $^2B_1$ state there is some ionic $M^{2+}NO_2^{2-}$ contribution to the bonding. As in the case of the $^2A_1$ state, in addition to the electron-transfer mechanism there is also important back-donation from the occupied orbitals of NO_2 to the empty p and d orbitals of the metal atom. It can be observed in Table 1 that the geometrical parameters of the NO_2 fragment in the $^2B_1$ state are now more similar to those obtained at the same level of calculation for NO_2^{2-}. The M−O distances are shorter than in the $^2A_1$ state because the s orbital of the metal is empty and the repulsion with the ligand is smaller. The N−O distances are larger because now the antibonding $2b_1$ orbital of NO_2 is occupied.

Table 2 shows that the energy difference between the $^2A_1$ and the $^2B_1$ states of the η^2-O,O coordination varies significantly with the level of calculation. It is observed that the $^2B_1$ state is more stabilized with respect to the $^2A_1$ one at the B3LYP level than at the CCSD(T) one, the largest difference being determined for Ca and Sr. The use of the larger basis set reduces the difference between B3LYP and CCSD(T) results. However, for Ca both methods still differ by 9.1 kcal mol^{-1}. Part of this error may arise from the fact that the s−d excitation in Ca^+ is underestimated at the B3LYP level compared to CCSD(T). Considering that the d population is larger in the $^2B_1$ state than in the $^2A_1$ one, it is not surprising that Ca and Sr, which have low-lying d orbitals, show the largest differences.

It has already been mentioned that for all the alkaline-earth metals considered the most stable structure corresponds to the η^2-O,O coordination. However, although for Be the ground state is the $^2B_1$ state, for the rest of the metals the $^2A_1$ state is the lowest one. The Be atom has the smallest atomic radius; its inner electron shell contains only the 1s electrons, and so the closed shell repulsion with the ligand is smaller than in the rest of the alkaline-earth metals considered. This fact allows Be to get closer to the ligand, and thus, the stabilizing interactions are stronger for the Be complexes. Therefore, in the case of Be the $^2B_1$ state becomes more stable than the $^2A_1$ state because these strong interactions compensate the cost of transferring a second electron to the ligand. This is not the case with the other alkaline-earth metals studied, where the metal−ligand distances are larger than for Be complexes. For the other coordination modes of the $BeNO_2$ complex, the electronic state equivalent to the $^2A_1$ state is always more stable than the one involving the occupation of the $2b_1$ orbital of NO_2.

The harmonic vibrational frequencies computed for the most stable electronic state of each coordination are presented in Table 3. All coordination modes have been found to be minima on the potential energy surface except the η^1-N structure for all metals and the η^1-O isomer of $MgNO_2$. The η^1-N structure is a transition state connecting two equivalent η^2-N,O minima. For $MgNO_2$, the η^1-O transition state connects the η^2-O,O and the η^2-N,O minima. It can be observed in Table 3 that the first frequency of the η^1-O coordination, which corresponds to the bending of the MON angle, is very low for all metals except Be, indicating that the potential energy surface is very flat. Therefore, the only structures that one would expect to detect in experiments are the η^2-N,O and η^2-O,O structures.

Let us consider the largest three frequencies of each case that correspond to the vibrations of the NO_2 fragment. If one compares the frequencies associated with the NO_2 fragment of the same coordination mode but for the different metals, it can be observed that they are always very similar, especially for Mg, Ca, and Sr compounds. This indicates that the nature of the NO_2 fragment remains more or less the same regardless of

TABLE 3: Harmonic Vibrational Frequencies[a] Computed at B3LYP Level

η^1-N Coordination

	$M-NO_2$ in-plane wag (b_2)	$M-NO_2$ out-of-plane wag (b_1)	$M-NO_2$ stretch (a_1)	NO_2 bend (a_1)	NO stretch (b_2)	NO stretch (a_1)
Be ($^2A_1$)	190i	403	621	896	1516	1438
Mg ($^2A_1$)	116i	311	344	790	1486	1368
Ca ($^2A_1$)	180i	214	288	790	1462	1406
Sr ($^2A_1$)	165i	173	231	784	1452	1401

η^1-O Coordination

	$M-NO_2$ in-plane wag (a′)	$M-NO_2$ out-of-plane wag (a″)	$M-NO_2$ stretch (a′)	NO_2 bend (a′)	NO stretch (a′)	NO stretch (a′)
Be ($^2A'$)	186	125	579	828	1136	1746
Mg ($^2A'$)	87i	39	447	813	1035	1620
Ca ($^2A'$)	83	62	386	801	1006	1612
Sr ($^2A'$)	35	57	298	793	1018	1603

η^2-O,O Coordination

	$M-NO_2$ in-plane wag (b_2)	$M-NO_2$ out-of-plane wag (b_1)	$M-NO_2$ stretch (a_1)	NO_2 bend (a_1)	NO stretch (b_2)	NO stretch (a_1)
Be ($^2B_1$)	581	333	633	965	1174	1121
Mg ($^2A_1$)	293	217	388	864	1285	1333
Ca ($^2A_1$)	243	149	314	823	1249	1339
Sr ($^2A_1$)	219	143	253	821	1257	1341

η^2-N,O Coordination

	$M-NO_2$ in-plane wag (a′)	$M-NO_2$ out-of-plane wag (a″)	$M-NO_2$ stretch (a′)	NO_2 bend (a′)	NO stretch (a′)	NO stretch (a′)	NO_2 bend (a_1)	NO stretch (b_2)	NO stretch (a_1)
Be ($^2A'$)	122	295	726	839	1102	1701			
Mg ($^2A'$)	169	236	480	766	1109	1630			
Ca ($^2A'$)	189	238	394	775	1135	1609			
Sr ($^2A'$)	167	225	319	775	1151	1589			
NO_2 ($^2A_1$)							741	1701	1387
NO_2^- ($^1A_1$)							780	1321	1338
NO_2^{2-} ($^2B_1$)							584	868	1004

[a] In cm^{-1}.

the metal considered. It can also be observed that for the η^2-O,O coordination in the $^2A_1$ state (Mg, Ca, and Sr) the frequencies resemble more those of free NO_2^- than those of free NO_2 or NO_2^{2-}, confirming again the $M^+NO_2^-$ character in these complexes. In the $^2B_1$ state of the η^2-O,O coordination of $BeNO_2$ the values of the two NO stretchings are smaller than in the rest of the η^2-O,O structures, approaching the values of NO_2^{2-}.

In the η^1-N coordination mode the two NO stretching values are always larger than in the η^2-O,O isomers, proving the larger covalent contribution to the bond in this coordination. Moreover, the relative ordering values in this coordination between the two NO stretchings are the same as in NO_2 and the opposite in NO_2^-. In the C_s structures, η^2-N,O and η^1-O, the values of the two NO stretching frequencies are very different. This is due to the fact that in this coordination the C_{2v} symmetry has been lost with a lengthening of the NO bond interacting with the metal and a shortening of the terminal NO bond compared to free NO_2^-.

Tevault and Andrews[18] reported an experimental value of 1244 cm^{-1} for the frequency corresponding to the asymmetric stretching of the NO_2 fragment in the $CaNO_2$ and $SrNO_2$ complexes in rare-gas matrixes and another value of 1223 cm^{-1} only for $SrNO_2$ complex. They suggested a nonplanar structure of the complex with a poorly defined position of M^+ above the plane of the ligand associated with the first value and a coplanar structure associated with the second one. All our attempts to calculate a nonplanar η^2-O,O structure collapsed to the planar one. In any case, both experimental values are in very good agreement with the values computed for the NO asymmetric stretching of $CaNO_2$ and $SrNO_2$ (1249 and 1257 cm^{-1}, respectively).

TABLE 4: D_e Binding Energies for the Ground States of the MNO_2 Complexes[a]

	Be	Mg	Ca	Sr
B3LYP[b]	80.8	47.2	70.1	67.9
CCSD[b]	70.2	50.4	68.1	71.3
CCSD(T)[b]	68.7	48.9	66.0	69.3
MCPF[b]	69.8	49.8	67.1	70.6
MCPF[c,d]	78.8 (77.2)	53.4 (52.6)	69.1 (68.7)	71.4 (71.1)

[a] In kcal mol^{-1}. [b] Smaller basis set. [c] Larger basis set. [d] In parentheses are shown the D_0 binding energies computed using the B3LYP harmonic frequencies.

Table 4 presents the bond dissociation energies, with respect to neutral M and NO_2, of the ground-state structure of each complex. These binding energies are computed at different levels of calculation and using different basis sets. By comparing the B3LYP values with the CCSD(T) ones, one can observe that for Mg, Ca, and Sr the computed binding energies are very similar while for $BeNO_2$ the difference is 12.1 kcal mol^{-1}.

The CCSD(T) calculations with the larger basis set were computationally too demanding, so we have done the calculations at the MCPF level, which provide results similar to those at CCSD and CCSD(T) levels with the smaller basis set (see Table 4). Thus, one can expect that with the larger basis set the MCPF and CCSD(T) values will also be similar. MCPF values show that the computed binding energy increases with the size of the basis set. For Mg, Ca, and Sr the differences are small, while in the case of Be the difference is more important (9.0 kcal mol^{-1}). It seems that at the CCSD(T) and MCPF levels with the smaller basis set, the binding energy of $BeNO_2$ is underestimated. The B3LYP dissociation energy is less sensitive to the basis set. The value computed with the larger basis set for $BeNO_2$ is 77.0 kcal mol^{-1}.

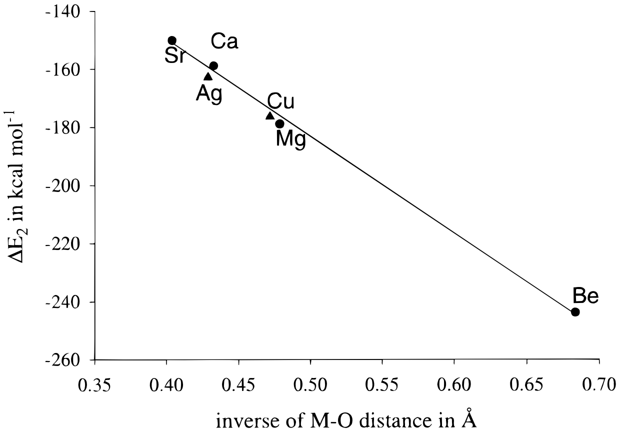

Figure 3. Energy of formation of MNO_2 relative to the ions (ΔE_2) plotted against the reciprocal of the M−O bond distance for the ground-state structure of each complex. The values corresponding to $CuNO_2$ and $AgNO_2$, taken from reference 24, are included for comparison.

In all cases, the MCPF binding energies computed with the larger basis set are in good agreement with the initial values obtained at the B3LYP level with the smaller basis set; the main difference can be observed in the case of the Mg complex (6.2 kcal mol^{-1}). Therefore, one can conclude that for these alkaline-earth metal complexes the values of the binding energies computed at the B3LYP level with a relatively small basis set seem to be good enough when compared with those values computed at the MCPF level using a large basis set.

Let us now consider the variation of the binding energy when changing the metal. The Be complex presents the strongest bond, while the binding energies corresponding to Mg, Ca, and Sr complexes increase when going down in the group. The values computed for Ca and Sr are very similar, while for Mg the binding energy is notably smaller. The binding energy of a complex with an important ionic nature can be formally decomposed into two contributions. The first one, ΔE_1, would involve the formation of the M^+ and NO_2^- ions from the neutral fragments. The second contribution, ΔE_2, would correspond to the interaction between both ions.

$$D_e = -(\Delta E_1 + \Delta E_2)$$

ΔE_1 includes the first ionization potential of the metal atom and the adiabatic electron affinity of NO_2. This second term remains constant along the group so that the variation of ΔE_1 is determined by the ionization potential of the metal. ΔE_2 is the formation energy of MNO_2 relative to the M^+ and NO_2^- ions. Figure 3 represents the variation of ΔE_2 with respect to the inverse of the M−O bond distance for the studied complexes. The observed linear variation corresponds to what is expected for complexes with an important ionic nature.[44,45] The variation of D_e for Mg, Ca, and Sr complexes is determined by the variation of the ionization potential of the metal (the computed MCPF values are 7.58 eV for Mg, 6.03 eV for Ca, and 5.55 eV for Sr). On the other hand, the difference between the values of D_e corresponding to Mg and Be is governed by the ΔE_2 term. ΔE_2 is extremely stabilizing in $BeNO_2$ owing to the small size of Be. This allows Be to have the largest binding energy despite its large ionization potential (the computed MCPF value is 9.29 eV). It can also be observed in Figure 3 that, although Cu and Ag are transition metals, the nature of the bonding in $CuNO_2$ and $AgNO_2$[24,46] is analogous to that found in the alkaline-earth nitrite complexes.

Conclusions

The structure, binding energies, and vibrational frequencies of different coordination modes have been determined for the MNO_2 system (M = Be, Mg, Ca, Sr). The η^2-O,O coordination is the most stable one for all the metals studied, as was previously found for the alkali and the Cu and Ag nitrite complexes. In the case of Mg, Ca, and Sr, the ground state is a $^2A_1$ state while for Be it is a $^2B_1$ state. This $^2B_1$ state presents a different bonding mechanism, and it is geometrically very different from the $^2A_1$ state. The B3LYP values for the binding energy obtained with a double-ζ plus polarization quality basis set are very similar to those obtained at the MCPF level with a large ANO basis set. Our best calculation for the D_0 binding energies are 77 kcal mol^{-1} for $BeNO_2$, 53 kcal mol^{-1} for $MgNO_2$, 69 kcal mol^{-1} for $CaNO_2$, and 71 kcal mol^{-1} for $SrNO_2$. The variation of the binding energies agrees with a metal−ligand bond of basically ionic character.

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