Interactions between Neutral Molecules and Ca²⁺: An Assessment of Theoretical Procedures

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The performance of a selection of theoretical procedures in describing the binding of Ca²⁺ to ammonia and formaldehyde has been assessed. Geometries and vibrational frequencies were obtained using the density functional theory procedures, B3-LYP and G96-LYP, as well as with CCSD(T) with a variety of basis sets, with the CCSD(T)/cc-pWCVQZ-optimized structures being used as a reference. Binding energies, including the consideration of basis set superposition errors, were additionally obtained with variants of the G3, W1C, and W2C methods, with the W2C values providing benchmark values in this case. We find that Ca–X (X = N, O) bond lengths for the $[Ca–NH_3]^{2+}$ and $[Ca–OCH_2]^{2+}$ complexes show some sensitivity both to the size of the basis set and to the theoretical procedure employed. In general, the Ca–X lengths decrease as the basis set is systematically enlarged. The B3-LYP and G96-LYP methods yield Ca–X distances that are slightly shorter than the CCSD(T) values obtained with the same basis set. As a consequence of these two factors, B3-LYP/cc-pWCVTZ and B3-LYP/6-311+G(3df,2p) give very reasonable geometries for the two complexes. The B3-LYP/cc-pWCVTZ and G96-LYP/cc-pWCVQZ approaches provide a good compromise between accuracy and computational cost in the calculation of binding energies. Ca²⁺ is predicted to bind more strongly to formaldehyde than to ammonia, in contrast to the ordering of proton and Li⁺ affinities for the two molecules.

Introduction

The important role of the interaction between metal dications and neutral molecules in chemical and biochemical processes, both in solution and in the gas phase, has been recognized for a long time.[1] It is well established, for instance, that the characterization of biopolymers depends on the generation of long-lived multiply charged ions.[2] The interaction of neutral systems with dications is also crucial in many biochemical processes. For example, the formation of polypeptides from amino acids is enhanced by the presence of divalent metal ions.[3] Similarly, a significant enhancement of base pairing has also been observed through the interaction of metal dications with DNA bases.[4,5] Multiply charged ions, and in particular dications, are also assumed to be important in extreme environments, such as the upper planetary atmospheres.[6,7] Dications are also of fundamental interest, often exhibiting unusual bonding properties that have intrigued chemists for many years.[8–14] Despite this interest and importance, the number of studies devoted to the investigation of the interactions between neutral molecules and metal dications are significantly less than those devoted to the investigation of similar interactions with monocations. The situation has been changing since the early 1990s with the development of electrospray ionization techniques that opened up the possibility of being able to readily produce clusters involving metal dications in the gas phase from aqueous solution.[15] Indeed, the past decade has witnessed a significant increase in the number of studies dealing with the solvation of metal dications and, in particular, with the possibility of generating monosolvated dications.[16–19] Other studies have focused on the structures and stabilities of complexes of metal dications with a variety of biomolecules.[5,20]

As noted above, molecular dications formed by attachment of a metal dication M²⁺ to a neutral base often show significant bonding peculiarities, associated with the strong polarization effects that accompany the formation of an M²⁺–molecule cluster, and the large electrostatic strain effects associated with the large Coulombic repulsion. A crucial aspect, from the theoretical point of view, is whether the standard approaches used in the study of neutral systems and monocations perform equally well when dealing with dications. An assessment of the theoretical models available is therefore needed. Initial studies in this direction have been carried out by Petrie and Radom[21] and by Alcamí et al.[22]

A primary constraint in assessment studies of complexes with metal dications is the almost complete lack of experimental information on the structures and stabilities of these species. In such circumstances, an alternative approach is to use high-level theoretical results as the benchmark. We have taken such an approach in the present study, in which we examine the performance of a number of levels of theory in describing the interaction of Ca²⁺ with two small model bases, ammonia and formaldehyde. Thus, we have used the W2C method of Martin et al.[23,24] (which approximates the limit of CCSD(T) calculations with an infinite basis set) to provide reliable reference values for binding energies. For the geometries, we have used the structures obtained through CCSD(T) calculations with the cc-pWCVQZ basis set as the reference. Results obtained with a number of simpler theoretical methods are assessed through comparison with the benchmark values.

Theoretical Procedures

Conventional ab initio[25,26] and density functional theory[27] calculations were performed on the complexes $[Ca–NH_3]^{2+}$ and

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TABLE 1: Frozen and Active Orbitals in CCSD(T) Calculations

	frozen	active
	rv (Relaxed Valence)	
Ca	1s, 2s, 2p, 3s, 3p	4s, 4p
C, O, N	1s	2s, 2p
H		1s
	riv (Relaxed Inner Valence)	
Ca	1s, 2s, 2p	3s, 3p, 4s, 4p
C, O, N	1s	1s, 2s, 2p
H		1s
	riiv (Relaxed Inner Inner Valence)	
Ca	1s	2s, 2p, 3s, 3p, 4s, 4p
C, O, N		1s, 2s, 2p
H		1s

[Ca—OCH$_2$]$^{2+}$, as well as for the neutrals NH$_3$ and O=CH$_2$, using the GAUSSIAN 98[28] and MOLPRO 2000[29] suites of programs. Optimized geometries and harmonic vibrational frequencies were obtained with the B3-LYP,[30,31] G96-LYP,[31,32] and CCSD(T) procedures, combined with basis sets ranging from 6-31G(d)[33] and 6-31G*(C)[34a,35] to cc-pWCV5Z.[23] The choice of functionals was directed by widespread use in the case of B3-LYP, and preliminary indications of good performance in the case of G96-LYP.[22] The notation aug′ in the basis set descriptions indicates that diffuse functions are included on C, N, and O but not on Ca or H.

The correlation spaces used in the various CCSD(T) calculations are defined in Table 1.[24] If only the valence orbitals among the occupied orbitals are included in the correlation space, we use the notation *rv* standing for relaxed-valence. This is often referred to alternatively as frozen-core. If the next set of orbitals, the inner-valence orbitals, are included in the correlation space, we refer to this as relaxed-inner-valence or "riv". Relaxing the subsequent set of orbitals leads to the riiv correlation space. If all the orbitals on all atoms are included in the correlation space, this is referred to as "full", in line with common usage. If different types of correlation space are used for the metal and carbon, oxygen or nitrogen atoms, they are specified in the order (metal, [carbon, oxygen or nitrogen]), e.g., (riv, rv).

Zero-point vibrational energies (ZPVEs) were obtained by scaling the calculated harmonic vibrational frequencies. Unless otherwise noted, the scale factors used were the values required to reproduce the experimental ZPVE for the neutral component of the complexes (i.e., either NH$_3$ or O=CH$_2$).[36] This ensures the correct ZPVE for the complex at infinite separation, i.e., for separated Ca^{2+} and NH$_3$ or separated Ca^{2+} and OCH$_2$.[37] For the highest-level calculations, we use ZPVEs that are standard for W2C, i.e., B3-LYP/cc-pWCVTZ scaled by 0.985.[23,24]

Binding energies were calculated in the first place at the same levels of theory as those used for geometry optimizations. In addition, binding energies were calculated at the G3[CC](direct,-full),[24] W1C,[23,24] and W2C[23,24] levels. Corrections for basis set superposition errors (BSSEs), evaluated using the counterpoise method of Boys and Bernardi,[38] were incorporated into the final binding energies.

G3[CC](direct,full)[24] denotes a CCSD(T) energy calculation in which the additivity approximation of standard G3[39] is removed (direct), all the occupied orbitals are included in the correlation space (full), and CCSD(T) is used in place of QCISD(T) due to the poor behavior of the QCISD(T) method in obtaining reliable thermochemical data for molecules involving third-row atoms such as CaO and K$_2$O.[24,34a,40] Thus G3-[CC](direct,full) corresponds to CCSD(T)(full) calculations with the G3 large basis set. The latter is a modification of 6-311+G-

(3df,2p) that includes (3d2f) polarization functions for second-row atoms, (2df) polarization functions for first-row atoms, and the addition of core polarization functions. CCSD(T)/cc-pWCVQZ geometries are used in the G3[CC](direct,full) calculations. Higher-level corrections (HLCs), given by $-An_\beta - B(n_\alpha - n_\beta)$ for molecules and $-Cn_\beta - D(n_\alpha - n_\beta)$ for the Ca dication (with $A = 6.597$, $B = 1.934$, $C = 5.895$, and $D = 1.107$ mhartrees,[24] and n_α and n_β being the number of α and β electrons, respectively), are added to take into account the remaining deficiencies in the energy calculations. ZPVE corrections were obtained using B3-LYP/cc-pWCVTZ frequencies, scaled by 0.985.[36]

Martin's W1C and W2C methods[23,24] attempt to approximate CCSD(T) calculations with an infinite basis set. They represent variants of the standard W1 and W2 procedures[36,41] and were introduced[23,24] to obtain more reliable thermochemistry for molecules containing alkali metal and alkaline earth metal atoms. In W1C and W2C, the cc-pVnZ basis sets of W1 and W2 are replaced for Ca by recently developed cc-pWCVnZ sets.[23] W1C and W2C procedures use B3-LYP/cc-pWCVTZ and CCSD(T)-(riv,rv)/cc-pWCVQZ optimized geometries, respectively. The valence correlation contribution to the energy is evaluated by considering two-point extrapolations of the SCF, CCSD, and (T) component energies, with an (riv, rv) correlation space and aug′-cc-pWCVnZ basis sets being used. The core-correlation contribution is evaluated from CCSD(T) energies calculated using the Martin–Taylor core-correlation basis sets,[42,43] with and without the core orbitals frozen. Scalar relativistic corrections were calculated using the ACPF method.[44] Note that the deep-lying 1s orbital on Ca was held frozen in the core-correlation and scalar relativistic calculations; i.e., the "unfrozen" calculations are (riiv, riv). ZPVE corrections were obtained using B3-LYP/cc-pWCVTZ frequencies, scaled by 0.985.[36]

The density functional theory results reported in this paper correspond to the use of scf=tight and the default grid in GAUSSIAN 98. We have also carried out a selection of the calculations using the ultrafine grid and find that the consequent changes are generally small, though they can be up to 0.004 Å in Ca—X bond lengths, 0.1 kJ mol^{-1} in ZPVEs, 0.3 kJ mol^{-1} in BSSEs, and 0.3 kJ mol^{-1} in binding energies.

Results and Discussion

Geometries. The optimized geometries of the complexes [Ca—NH$_3$]$^{2+}$ and [Ca—OCH$_2$]$^{2+}$ are displayed schematically in Figure 1, with the geometric parameters of the neutrals (NH$_3$ and O=CH$_2$) and the complexes summarized in Tables 2–4, respectively. Our best geometries correspond to the CCSD(T)/cc-pWCVQZ values.

For ammonia and formaldehyde (Table 2), we see that the CCSD(T)/cc-pWCVQZ geometries are in good agreement with experiment (Table 2).[45–47] When B3-LYP and G96-LYP are used with identical basis sets (e.g., cc-pWCV5Z), the computed geometries show only small differences, the most notable being 0.008 Å for the N—H bond length for NH$_3$ and 0.010 Å for the C—O length for O=CH$_2$. For basis sets larger than 6-31G(d), the variation in geometric parameters with basis set is relatively small.

Formation of the [Ca—NH$_3$]$^{2+}$ complex is accompanied by an elongation of the N—H bonds and a narrowing of the ∠HNH angles (by 0.010 Å and 2.6°, respectively, at the CCSD(T)/cc-pWCVQZ level) (Table 3). Results for the Ca—N distance with the cc-pWCVQZ basis set show slightly shorter lengths with B3-LYP and G96-LYP than with CCSD(T). Increasing the size of the cc-pWCVnZ basis set leads to a shortening of the Ca—
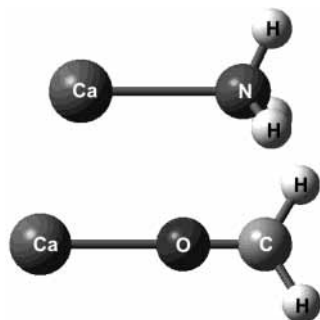
10458 *J. Phys. Chem. A, Vol. 107, No. 48, 2003*

Corral et al.

Figure 1. Schematic representation of [Ca−NH₃]²⁺ and [Ca−OCH₂]²⁺ complexes.

TABLE 2: Optimized Geometric Parameters (Å, Degrees) for the Neutrals NH₃ and OCH₂

level of theory	r(N−H)	∠HNH	r(O=C)	r(C−H)	∠HCO
B3-LYP					
6-31G(d)	1.019	105.7	1.206	1.110	122.4
6-311G(d)	1.015	106.7	1.199	1.110	122.2
6-311+G(3df,2p)	1.013	107.3	1.198	1.107	122.0
cc-pWCVTZ	1.014	106.5	1.198	1.107	122.1
aug′-cc-pWCVTZ	1.013	107.2	1.200	1.106	122.0
cc-pWCVQZ	1.013	106.8	1.198	1.106	122.0
aug′-cc-pWCVQZ	1.013	107.2	1.198	1.106	122.0
cc-pWCV5Z	1.012	107.2	1.198	1.106	122.0
aug′-cc-pWCV5Z	1.012	107.2	1.198	1.106	122.0
G96-LYP					
6-31G(d)	1.028	105.1	1.217	1.120	122.5
6-311G(d)	1.023	106.2	1.209	1.119	122.3
cc-pWCVTZ	1.021	105.9	1.209	1.115	122.2
cc-pWCVQZ	1.020	106.3	1.208	1.114	122.1
cc-pWCV5Z	1.020	106.6	1.208	1.114	122.1
CCSD(T)					
6-31G(d)	1.022	105.8	1.220	1.108	122.1
6-311G(d)	1.015	106.7	1.211	1.110	122.0
6-311+G(3df,2p)	1.015	106.5	1.208	1.104	121.8
cc-pWCVTZ	1.014	105.7	1.209	1.103	121.9
aug′-cc-pWCVTZ	1.014	106.4	1.211	1.103	121.7
cc-pWCVQZ	1.013	106.2	1.206	1.102	121.8
exp[a]	1.011	106.7	1.203	1.101	121.7

[a] From refs 46 (NH₃) and 47 (O=CH₂).

N bond length, particularly in going from TZ to QZ but much less so from QZ to 5Z. As a consequence of these two effects, the B3-LYP/cc-pWCVTZ and B3-LYP/6-311+G(3df,2p) methods provide reasonably reliable and cost-effective predictions of the geometry of the [Ca−NH₃]²⁺ complex.

Formation of the [Ca−OCH₂]²⁺ complex is accompanied by a lengthening of the O=C bonds, shortening of the C−H bonds and a narrowing of the ∠HCO angles (by 0.031 Å, 0.010 Å, and 1.8°, respectively, at the CCSD(T)/cc-pWCVQZ level) (Table 4). The Ca−O distance calculated with the cc-pWCVQZ basis set is again slightly shorter with B3-LYP and G96-LYP than with CCSD(T). There is again a significant shortening in the Ca−O distance as the size of the basis set is increased, particularly in going from TZ to QZ. Inclusion of diffuse functions on all atoms except hydrogen and Ca (aug′-cc-pWCVTZ) leads to a decrease in the Ca−O bond length of 0.016 Å for the [Ca−OCH₂]²⁺ complex, compared with a corresponding decrease of 0.009 Å for the [Ca−NH₃]²⁺ complex. The B3-LYP/cc-pWCVTZ and B3-LYP/6-311+G-(3df,2p) methods again provide reasonably reliable and cost-effective predictions of the geometry of the [Ca−OCH₂]²⁺ complex.

Examination of the results in Tables 3 and 4 shows that even B3-LYP/6-31G(d) provides reasonable geometries for the [Ca−

TABLE 3: Optimized Geometric Parameters (Å, Degrees) for the [Ca−NH₃]²⁺ Complex

level of theory	r(Ca−N)	r(N−H)	∠HNH
B3-LYP			
6-31G(d)	2.369	1.031	103.8
6-31G*(C)	2.366	1.030	103.6
6-311G(d)	2.385	1.026	103.7
6-311+G(3df,2p)	2.372	1.025	104.1
cc-pWCVTZ	2.395	1.024	104.0
aug′-cc-pWCVTZ	2.392	1.025	104.0
cc-pWCVQZ	2.363	1.024	104.0
aug′-cc-pWCVQZ	2.363	1.024	104.0
cc-pWCV5Z	2.361	1.025	104.0
aug′-cc-pWCV5Z	2.361	1.025	104.0
G96-LYP			
6-31G(d)	2.373	1.038	103.8
6-31G*(C)	2.370	1.038	103.6
6-311G(d)	2.390	1.033	103.6
cc-pWCVTZ	2.403	1.031	103.8
cc-pWCVQZ	2.369	1.031	104.1
cc-pWCV5Z	2.367	1.031	104.1
CCSD(T)			
6-31G(d)	2.425	1.032	103.4
6-31G*(C)	2.400	1.032	103.1
6-311G(d)	2.411	1.025	103.5
6-311+G(3df,2p)	2.396	1.025	103.6
cc-pWCVTZ	2.411	1.023	103.5
aug′-cc-pWCVTZ	2.402	1.024	103.5
cc-pWCVQZ	2.374	1.023	103.6

TABLE 4: Optimized Geometric Parameters (Å, Degrees) for the [Ca−OCH₂]²⁺ Complex

level of theory	r(Ca−O)	r(O=C)	r(C−H)	∠HCO
B3-LYP				
6-31G(d)	2.132	1.243	1.098	120.0
6-31G*(C)	2.127	1.242	1.098	120.0
6-311G(d)	2.149	1.237	1.096	120.0
6-311+G(3df,2p)	2.135	1.233	1.095	120.1
cc-pWCVTZ	2.157	1.235	1.094	120.1
aug′-cc-pWCVTZ	2.151	1.235	1.095	120.1
cc-pWCVQZ	2.129	1.234	1.094	120.1
aug′-cc-pWCVQZ	2.129	1.234	1.094	120.1
cc-pWCV5Z	2.129	1.234	1.094	120.1
aug′-cc-pWCV5Z	2.128	1.234	1.094	120.1
G96-LYP				
6-31G(d)	2.134	1.254	1.105	119.9
6-31G*(C)	2.132	1.252	1.105	120.0
6-311G(d)	2.154	1.247	1.103	119.9
cc-pWCVTZ	2.165	1.245	1.101	120.1
cc-pWCVQZ	2.134	1.244	1.101	120.0
cc-pWCV5Z	2.132	1.244	1.101	120.0
CCSD(T)				
6-31G(d)	2.183	1.249	1.098	120.0
6-31G*(C)	2.174	1.247	1.098	120.1
6-311G(d)	2.189	1.241	1.098	120.0
6-311+G(3df,2p)	2.162	1.236	1.095	120.1
cc-pWCVTZ	2.181	1.238	1.093	120.1
aug′-cc-pWCVTZ	2.165	1.240	1.094	120.0
cc-pWCVQZ	2.145	1.237	1.092	120.0

NH₃]²⁺ and [Ca−OCH₂]²⁺ complexes, with a largest deviation from CCSD(T)/cc-pWCVQZ bond lengths of just 0.013 Å.

Zero-Point Vibrational Energies (ZPVEs). The ZPVE values for NH₃ and O=CH₂, calculated at a variety of levels of theory, are shown in Table 5. Also included are the scaling factors at the various levels required to reproduce the experimental ZPVEs for NH₃ and O=CH₂. These scale factors are applied to the directly calculated ZPVEs for the complexes [Ca−NH₃]²⁺ and [Ca−OCH₂]²⁺, to produce scaled ZPVEs that are suitable for use in the calculation of binding energies.

TABLE 5: Zero-Point Vibrational Energies (kJ mol^{-1}) for NH$_3$ and OCH$_2$ and the Complexes [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$

level of theory	calcd ZPVE NH$_3$	scaling factor[a,b]	scaled ZPVE [Ca−NH$_3$]$^{2+}$	calcd ZPVE O=CH$_2$	scaling factor[b,c]	scaled ZPVE [Ca−OCH$_2$]$^{2+}$
B3-LYP						
6-31G(d)	90.68	0.984	98.90	70.44	0.982	74.83
6-31G*(C)	90.68	0.984	99.13	70.44	0.982	74.91
6-311G(d)	91.36	0.977	99.09	69.78	0.991	75.34
6-311+G(3df,2p)	89.86	0.993	98.51	69.53	0.995	75.23
cc-pWCVTZ	89.82	0.994	98.45	69.57	0.994	75.09
cc-pWCVTZ[d]	89.82	0.985	97.60	69.57	0.985	74.40
aug′-cc-pWCVTZ	89.68	0.995	98.53	69.54	0.995	75.16
cc-pWCVQZ	89.84	0.993	98.40	69.65	0.993	75.04
G96-LYP						
6-31G(d)	88.06	1.013	99.26	67.91	1.018	75.21
6-31G*(C)	88.06	1.013	99.45	67.91	1.018	75.29
6-311G(d)	88.83	1.005	99.32	67.31	1.028	75.74
cc-pWCVTZ	87.57	1.019	98.61	67.22	1.029	75.50
cc-pWCVQZ	87.62	1.019	98.50	67.32	1.027	75.37
CCSD(T)						
6-31G(d)	91.23	0.978	98.85	70.58	0.980	75.15
6-31G*(C)	91.23	0.978	99.44	70.58	0.980	75.24
6-311G(d)	92.24	0.968	99.08	69.78	0.991	75.47
cc-pWCVTZ	90.61	0.985	98.23	70.05	0.987	

[a] Experimental ZPVE for NH$_3$ (from ref 36) is 89.24 kJ mol^{-1}. [b] Scale factor = experimental ZPVE/calculated ZPVE. [c] Experimental ZPVE for O=CH$_2$ (from ref 36) is 69.16 kJ mol^{-1}. [d] Results obtained using standard W1C and W2C scaling factor of 0.985.

The scaled ZPVEs for [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$ are not very sensitive to either the level of theory employed or to the basis set. They span a range of just 2 kJ mol^{-1} for [Ca−NH$_3$]$^{2+}$ and 1 kJ mol^{-1} for [Ca−OCH$_2$]$^{2+}$. For the G3 and W methods, and for CCSD(T) calculations with larger basis sets, we have used the B3-LYP/cc-pWCVTZ ZPVEs scaled by 0.985 (the standard for W1C and W2C) in the calculation of binding energies, as explicitly noted.

Basis Set Superposition Errors (BSSEs). Basis set superposition errors, calculated using the counterpoise method and a variety of theoretical procedures and basis sets, are summarized in Table 6. Large BSSEs (5−20 kJ mol^{-1}) are found with the 6-31G(d), 6-31G*(C), 6-311G(d), and cc-pWCVTZ basis sets, presumably reflecting significant incompleteness in these sets in their description of the [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$ complexes. The values generally follow the expected trend, in the sense that the BSSE diminishes as the basis set becomes larger. An exception is seen for the 6-311G(d) basis set for which the estimated BSSE is larger than the values for the 6-31G*(C) basis in all cases, and larger than for the 6-31G(d) basis set for the [Ca−NH$_3$]$^{2+}$ complex. The BSSEs are slightly larger (by 3−6 kJ mol^{-1}) with CCSD(T) than with B3-LYP or G96-LYP for the same basis sets. The G3(direct,full) procedure has moderately large BSSEs, but both W1C and W2C, which attempt to approximate CCSD(T) energies at the infinite basis set limit, yield very small BSSEs.

Binding Energies. The calculated binding energies of the [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$ complexes, including ZPVE and BSSE corrections, are compared in Table 7. The benchmark W2C values are 266.4 ([Ca−NH$_3$]$^{2+}$) and 274.7 ([Ca−OCH$_2$]$^{2+}$) kJ mol^{-1}, respectively.

Figure 2 shows the variation with cc-pWCVnZ basis set (n = T, Q, 5) of the binding energies, calculated both without and with the inclusion of BSSE corrections. It can be seen that, for both the [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$ complexes, the CCSD-(T) binding energies are smaller than the W2C values. As a consequence, the binding energies improve with increasing basis set size but become slightly worse with the inclusion of BSSE. On the other hand, the B3-LYP binding energies are larger than the W2C values. As a consequence, the results improve with the inclusion of the BSSE corrections. Results with the Pople

TABLE 6: Basis Set Superposition Errors (kJ mol^{-1}) for the Complexes [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$

level of theory	BSSE [Ca−NH$_3$]$^{2+}$	BSSE [Ca−OCH$_2$]$^{2+}$
B3-LYP		
6-31G(d)	13.69	17.58
6-31G*(C)	12.01	6.07
6-311G(d)	15.22	8.42
6-311+G(3df,2p)	0.71	0.82
cc-pWCVTZ	7.72	5.35
aug′-cc-pWCVTZ	0.32	0.34
cc-pWCVQZ	3.08	1.72
aug′-cc-pWCVQZ	0.14	0.07
cc-pWCV5Z	0.71	0.33
aug′-cc-pWCV5Z	0.14	0.14
G96-LYP		
6-31G(d)	13.52	17.06
6-31G*(C)	11.92	6.16
6-311G(d)	14.77	7.69
cc-pWCVTZ	7.08	4.59
cc-pWCVQZ	2.45	1.17
cc-pWCV5Z	0.92	0.59
CCSD(T)		
6-31G(d)	18.77	20.40
6-31G*(C)	17.68	10.35
6-311G(d)	20.11	11.77
6-311+G(3df,2p)	2.21	2.52
cc-pWCVTZ	8.36	7.16
aug′-cc-pWCVTZ	1.51	2.21
cc-pWCVQZ	3.12	2.48
G3[CC](direct,full)	3.92	4.71
W1C	0.31	0.04
W2C	0.03	0.07

basis sets, not surprisingly, show a less smooth variation with basis set (Figure 3). However, it is still found that the limiting values (corresponding to the 6-311+G(3df,2p) basis set) are smaller than W2C for CCSD(T) and larger than W2C for B3-LYP.

The effect on the calculated binding energies of including diffuse functions in the basis set at the CCSD(T)/cc-pWCVTZ level is rather small for the [Ca−NH$_3$]$^{2+}$ complex but is more than 6 kJ mol^{-1} for [Ca−OCH$_2$]$^{2+}$. The B3-LYP results indicate a markedly decreasing effect of diffuse functions in going from TZ to QZ to 5Z basis sets, amounting to less than 0.1 kJ mol^{-1} in the last case.

10460 *J. Phys. Chem. A, Vol. 107, No. 48, 2003*

Corral et al.

TABLE 7: Binding Energies (kJ mol^{-1}) for the Complexes [Ca−NH$_3$]$^{2+}$ and [Ca−OCH$_2$]$^{2+}$

level of theory	BE [Ca−NH$_3$]$^{2+}$	BE [Ca−OCH$_2$]$^{2+}$
B3-LYP		
6-31G(d)	290.8	282.5
6-31G*(C)	287.9	284.0
6-311G(d)	279.3	278.0
6-311+G(3df,2p)	269.2	283.2
cc-pWCVTZ	264.6	272.7
aug′-cc-pWCVTZ	262.4	275.4
cc-pWCVQZ	272.7	284.7
aug′-cc-pWCVQZ	271.7	285.0
cc-pWCV5Z	272.5	285.7
aug′-cc-pWCV5Z	272.4	285.7
G96-LYP		
6-31G(d)	286.0	272.2
6-31G*(C)	283.2	274.4
6-311G(d)	273.7	267.6
cc-pWCVTZ	256.2	259.5
cc-pWCVQZ	267.2	274.8
cc-pWCV5Z	266.9	275.8
CCSD(T)		
6-31G(d)	265.6	254.8
6-31G*(C)	265.7	256.1
6-311G(d)	260.8	250.6
6-311+G(3df,2p)^a	253.5	261.6
cc-pWCVTZ^a	251.5	254.1
aug′-cc-pWCVTZ^a	251.7	260.9
cc-pWCVQZ^a	261.2	268.4
composite methods		
G3[CC](direct,full)^a	263.7	268.9
G3[CC](direct,full)^{a,b}	267.6	273.6
W1C^a	266.0	274.6
W2C^a	266.4	274.7

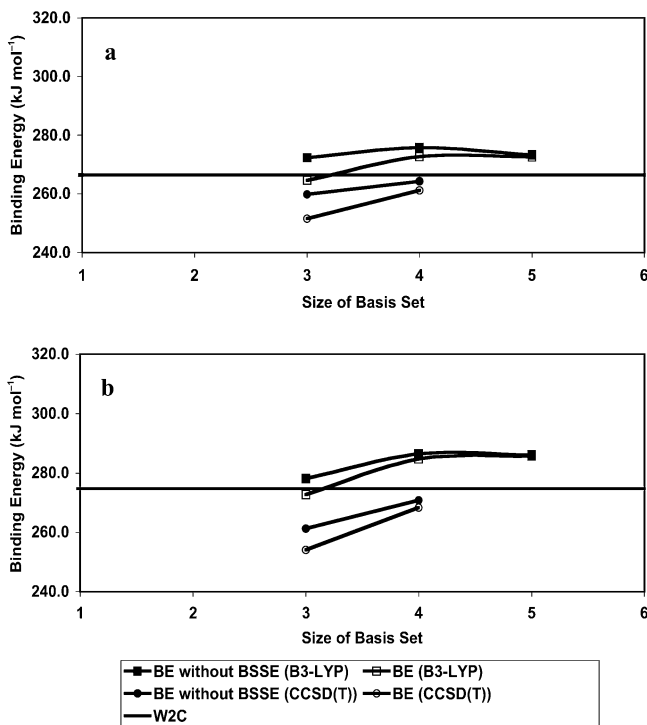^{a} Calculated using B3-LYP/cc-pWCVTZ ZPVEs scaled by 0.985, from Table 5. ^{b} Calculated without including BSSEs.

Figure 2. Variation of binding energies calculated with cc-pWCV*n*Z basis sets (*n* = 3−5), without and with corrections for BSSEs for (a) [Ca−NH$_3$]$^{2+}$ and (b) [Ca−OCH$_2$]$^{2+}$.

The use of the B3-LYP approach together with the 6-311+G-(3df,2p) basis set yields binding energies that are quite close to our reference value for the [Ca−NH$_3$]$^{2+}$ complex but about 8 kJ mol^{-1} greater than W2C for the [Ca−OCH$_2$]$^{2+}$ complex. B3-
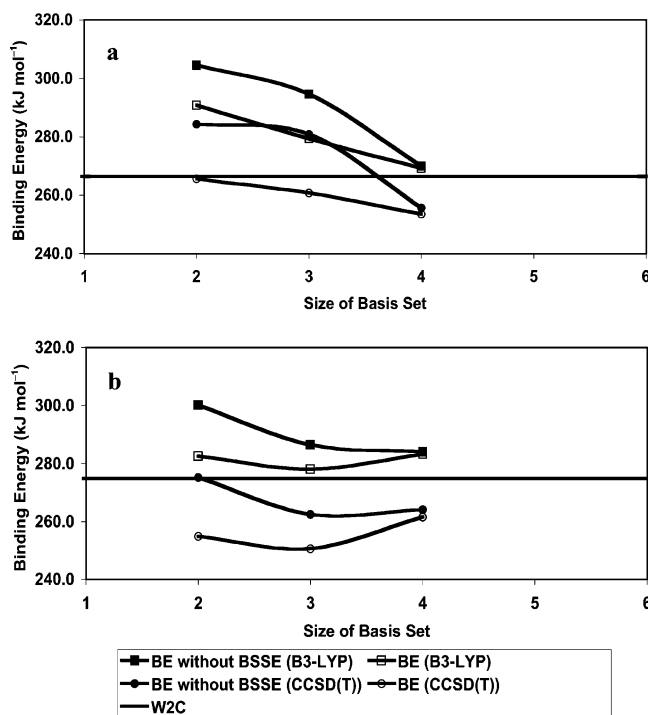
Figure 3. Variation of binding energies calculated with Pople basis sets (6-31G(d), 6-311G(d,p), and 6-311+G(3df,2p)), without and with corrections for BSSEs for (a) [Ca−NH$_3$]$^{2+}$ and (b) [Ca−OCH$_2$]$^{2+}$.

LYP/cc-pWCVTZ performs better, giving binding energies to within 2 kJ mol^{-1} of the benchmark values, though the agreement worsens for B3-LYP when larger cc-pWCV*n*Z basis sets are used. G96-LYP shows a large change in binding energies in going from TZ to QZ but very small further changes in going to 5Z. The G96-LYP/cc-pWCVQZ binding energies are remarkably close (within 1 kJ mol^{-1}) to the W2C values. CCSD(T) calculations with the 6-311+G(3df,2p) basis set yielding binding energies for both complexes that are approximately 13 kJ mol^{-1} lower than the W2C benchmarks.

G3[CC](direct,full) yields binding energies that are lower than the W2C values by 3−6 kJ mol^{-1}. Intriguingly, if the BSSE correction is not included, the agreement between G3[CC]-(direct,full) and W2C is improved significantly (to within 1.2 kJ mol^{-1}). For the [Ca−NH$_3$]$^{2+}$ complex, the G3[CC](direct,-full) binding energy is in close agreement with the G2(QCI) value reported previously.[21] The W1C binding energies are very similar to the W2C reference values for both systems.

An important result is the prediction by all the theoretical methods, when basis sets larger than 6-311G(d) are used, that the binding energy of Ca^{2+} to formaldehyde is greater than that to NH$_3$. This is the reverse of the ordering of proton and Li$^+$ affinities of the two molecules. Further work to explore this intriguing observation is in progress.

Concluding Remarks

In this study, we have investigated the influence of the size of the basis set as well as the theoretical procedure employed on the geometries, zero-point vibrational energies, and binding energies of the complexes of Ca^{2+} with NH$_3$ and O=CH$_2$. We find that the Ca−X (X = N, O) bond lengths show some sensitivity to both factors. Compared with benchmark CCSD-(T)/cc-pWCVQZ values, these distances are slightly underestimated by B3-LYP and G96-LYP. In general, the Ca−X bonds become shorter as the size of the cc-pWCV*n*Z basis is systematically increased, particularly in going from TZ to QZ.

Both B3-LYP/cc-pWCVTZ and B3-LYP/6-311+G(3df,2p) provide cost-effective means of determining the geometries of these complexes.

As far as binding energies are concerned, and taking the W2C values as the benchmark, we find that the CCSD(T) values are generally slightly too small, whereas the B3-LYP values are slightly too large. For CCSD(T), the binding energy increases with the size of the cc-pWCVnZ basis set, leading to improved binding energies with increasing basis set size. For the B3-LYP method, however, the best agreement is attained with a cc-pWCVTZ basis set, the values obtained being approximately 2 kJ mol^{-1} lower than the W2C results for both complexes. B3-LYP/cc-pWCVTZ thus provides a good compromise between accuracy and computational cost in the calculation of binding energies. G96-LYP/cc-pWCVQZ also performs very well for binding energies and appears to be close to the G96-LYP basis set limit. The G3[CC](direct,full) composite method gives binding energies approximately 3−6 kJ mol^{-1} smaller than the reference W2C values for both complexes. Interestingly, the results are improved if BSSE corrections are not included.

Quite intriguingly, all the larger basis set calculations predict Ca^{2+} to bind more strongly to formaldehyde than to ammonia, which is the reverse of the ordering of proton and Li^{+} affinities.

References and Notes

(1) See, for example: Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385−7394 and references therein.

(2) Vekéy, K. *Mass Spectrom. Rev.* **1995**, *14*, 195−225.

(3) Remko, M.; Rode, B. M. *Chem. Phys. Lett.* **2000**, *316*, 489−494.

(4) Anwander, E. H. S.; Probst, M. M.; Rode, B. M. *Biopolymers* **1990**, *29A*, 757−769.

(5) Burda, J. V.; Sponer, J.; Leszczynski, J.; Hobza, P. *J. Phys. Chem. B* **1997**, *101*, 9670−9677.

(6) Plane, J. M. C.; Helmer, M. *Faraday Discuss.* **1995**, *100*, 411−430.

(7) Witasse, O.; Dutuit, O.; Lilensten, J.; Thissen, R.; Zabka, J.; Alcaraz, C.; Blelly, P.-L.; Bougher, S. W.; Engel, S.; Andersen, L. H.; Seiersen, K. *Geophys. Res. Lett.* **2002**, *29*, 1041−1044.

(8) Bertrán, J.; Rodríguez-Santiago, L.; Sodupe, M. *J. Phys. Chem. B* **1999**, *103*, 2310−2317.

(9) Duflot, D.; Robbe, J.-M.; Flament, J.-P. *J. Chem. Phys.* **1995**, *102*, 355−363.

(10) Hill, Y. D.; Freiser, B. S.; Bauschlicher, C. W. *J. Am. Chem. Soc.* **1991**, *113*, 1507−1510.

(11) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1986**, *108*, 5808−5817.

(12) Wong, M. W.; Yates, B. F.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 3181−3187.

(13) Wong, M. W.; Baker, J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2245−2250.

(14) Wong, M. W.; Radom, L. *Int. J. Mass Spectrom. Ion Processes* **1988**, *86*, 319−327.

(15) Jayaweera, P.; Blades, A. T.; Ikonomou, M. G.; Kebarle, P. *J. Am. Chem. Soc.* **1990**, *112*, 2452−2454.

(16) El-Nahas, A. M.; Tajima, N.; Hirao, K. *Chem. Phys. Lett.* **2000**, *318*, 333−339.

(17) El-Nahas, A. M. *Chem. Phys. Lett.* **2001**, *348*, 483−490.

(18) Shvartsburg, A. A.; Siu, K. W. M. *J. Am. Chem. Soc.* **2001**, *123*, 10071−10075.

(19) Schröder, D.; Schwarz, H.; Wu, J.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001**, *343*, 258−264.

(20) Sponer, J.; Sabat, M.; Burda, J. V.; Leszczynski, J.; Hobza, P. *J. Phys. Chem. B* **1999**, *103*, 2528−2534.

(21) Petrie, S.; Radom, L. *Int. J. Mass Spectrom.* **1999**, *192*, 173−183.

(22) Alcamí, M.; González, A. I.; Mó, O.; Yáñez, M. *Chem. Phys. Lett.* **1999**, *307*, 244−252.

(23) Iron, M. A. O. M.; Martin, J. M. L. *Mol. Phys.* **2003**, *101*, 1345−1361. cc-pWCVnZ basis sets for calcium can be downloaded from: http://theochem.weizmann.ac.il/web/papers/group12.html.

(24) Sullivan, M. B.; Iron, M. A.; Redfern, P. C.; Curtiss, L. A.; Martin, J. M. L.; Radom, L. *J. Phys. Chem. A* **2003**, *107*, 5617−5630.

(25) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(26) Jensen, F. *Introduction to Computational Chemistry*; Wiley: New York, 1999.

(27) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, 2000.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; J. A. Montgomery, Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1999.

(29) Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schutz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J. *MOLPRO 2002.1*; University of Birmingham: Birmingham, U.K., 2002.

(30) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(31) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785−789.

(32) Gill, P. M. W. *Mol. Phys.* **1996**, *89*, 433−445.

(33) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976−984.

(34) (a) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016−5021. (b) Note that this basis set was originally referred to as 6-31G(d) but the 6-31G(d) description has subsequently been assigned to the set of Rassolov et al.[33] and the 6-31G*(C) label has been suggested as a replacement. [35]

(35) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287−9295.

(36) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843−1856.

(37) Hartmann, M.; Wetmore, S. D.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 4470−4479.

(38) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−566.

(39) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776.

(40) Schulz, A.; Smith, B. J.; Radom, L. *J. Phys. Chem. A* **1999**, *103*, 7522−7527.

(41) Martin, J. M. L.; Parthiban, S. In *Quantum-Mechanical Prediction of Thermochemical Data*; Cioslowski, J., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp 31−65.

(42) Martin, J. M. L. *Chem. Phys. Lett.* **1995**, *242*, 343−350.

(43) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473−479.

(44) Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413−420.

(45) A thorough discussion of the determination of molecular equilibrium structures using CCSD(T) procedures is given in: Bak, K. L.; Gauss, J.; Jorgensen, P.; Olsen, J.; Helgaker, T.; Stanton, J. F. *J. Chem. Phys.* **2001**, *114*, 6548−6556.

(46) Duncan, J. L.; Mills, I. M. *Spectrochim. Acta* **1964**, *20*, 523−546.

(47) Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177−1191.