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A theoretical study of the interaction between Ni^+ and small oxygen- and nitrogen-containing bases

Alberto Luna[a], Manuel Alcamí[a], Otilia Mó[a], Manuel Yáñez[a,*], Jeanine Tortajada[b]

[a] *Departamento de Quimica, C-9 Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*
[b] *Laboratoire Analyse et Environnement, UMR CNRS 8587, Université d'Evry Val d'Essonne Institut des Sciences, Boulevard François Mitterrand, 91025 Evry Cedex, France*

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This paper is dedicated to the memory of Prof. Pierre Longevialle.

Abstract

The complexes between Ni^+ and a series of small nitrogen and oxygen-containing bases, namely NH_2, NH_3, CH_3NH_2, CH_2=NH, HCN, OH, H_2O, CO, CO_2, CH_2=O, and $NH_2C(H)$=O were investigated by means of high-level G2(MP2) ab initio method and B3LYP density functional approach. The former formalism exhibits systematically a pathological behavior associated with high spin contamination of the unrestricted wave function and with convergency problems of the MP*n* series. Conversely, the B3LYP method exhibits a much regular behavior. With the only exception of the NH_2, the Ni^+ binding energies evaluated at the B3LYP/6-311+G(2df,2p) level are in good agreement with the experimental values, and with other theoretical estimates obtained through the use of multireference or CCSD(T) formalisms, when available. The behavior of the bases investigated with respect to Ni^+ resembles closely the one they exhibit when the reference acid is Cu^+ or H^+. This can be taken as an indication of the non-negligible covalent character of the base–Ni^+ interactions. Consequently, there is a rough linear correlation between Ni^+ binding energies and both proton affinities and Cu^+ binding energies. (Int J Mass Spectrom 217 (2002) 119–129) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ni^+ binding energies; Density functional theory; Convergency; Spin contamination

1. Introduction

The important role played by computational chemistry in the extraordinary development of the gas-phase ion chemistry is well documented in the literature [1,2]. The availability of new theoretical schemes as the G2 [3] or G3 [4] theories which yield results within the so-called chemical accuracy ($\approx$1 kcal mol^{-1}) permitted not only to establish relative trends in gas-phase reactivity, but also to accurately determine absolute values for ionization potentials, electron affinities [5], dissociation energies, proton affinities or cation binding energies [6].

However, in most of these ab initio theoretical schemes, at least part of the electron correlation contributions to energy are estimated by using the MP*n* perturbation series, so they can exhibit, in some specific cases, a pathological behavior associated with convergency problems of that series [7–9]. On the other hand, these single-reference methods can also

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* Corresponding author. E-mail: manuel.yanez@uam.es

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fail when the zeroth order wave function has a clear multireference character. Unfortunately, alternative multireference procedures as the CASSCF [10] or the CASPT2 [11] methods are difficult to apply to large systems of chemical interest, specially when dealing, for example, with complexes involving large neutral compounds and transition metal cations, which are already systems with many electrons.

An alternative theoretical scheme is provided by the density functional theory (DFT) [12], which permits to take into account dynamical correlation effects at a quite low cost. On the other hand, for some challenging cases it has been shown, that most of the DFT approaches available, and in particular the B3LYP method [13,14], present less instabilities than the usual ab initio methods [15]. Although, strictly speaking, the B3LYP method does not account for non-dynamical correlation, it exhibits a quite regular behavior when dealing with systems which present nearly degenerate states. For instance, while Cu^+ binding energies are very well reproduced by B3LYP/6-311+G(2df,2p) calculations [16], many high-level ab initio procedures, such as G2 predict some complexes to be unbound [16]. Even at CCSD(T)/6-311+G(3df,2p) level, the calculated binding energies are, in some cases, off the experimental values by more than $20\,kcal\,mol^{-1}$. This pathological behavior is due to a lack of convergency of the MP*n* series, and to the instability of the HF wave function, because although Cu^+ is formally a closed shell system, the d^{10} and the d^9s configurations are rather close in energy [17].

One of the aims of this paper is to investigate the performance of the G2(MP2) ab initio molecular orbital method and the B3LYP DFT approach when the transition metal cation is not a closed-shell but an open-shell system such as Ni^+. For this purpose we have chosen a series of small nitrogen- and oxygen-containing bases, namely NH_2, NH_3, CH_3NH_2, $CH_2{=}NH$, HCN, OH, H_2O, CO, CO_2, $CH_2{=}O$, and $NH_2C(H){=}O$. On the other hand, the information on Ni^+ binding energies is rather scarce, therefore a second goal of our study is to provide information on the structures and binding energies of these Ni^+ complexes.

2. Computational details

The Ni^+ binding energies were evaluated using the G2(MP2) method. Although the standard procedure is based on the use of MP2(full)/6-31G* optimized geometries, in our case we have used MP2(full)/6-311G(d,p) optimized geometries, because in general transition metals are highly correlated systems and the 6-311G(d,p) basis [18] is better suited to describe these systems than the smaller 6-31G* expansion. It is worth mentioning that most of the attempts to optimize the geometries of the complexes under investigation at the MP2(fc)/6-311G(d,p) level failed due to convergency problems along the optimization process. This may indicate that core electron correlation effects can be important for these systems. Similar convergency problems were found, for many of the systems investigated, in the QCISD(T)/6-311G(d,p) calculations which impede to get a final G2(MP2) energy. For the particular case of nitrogen-containing compounds only for methyl amine and HCN, the convergence of this step was possible, but as we shall discuss later the results obtained are physically meaningless.

The DFT geometry optimizations were carried out by using the B3LYP method, together with the 6-311G(d,p) all electron basis sets and with the LANL2DZ expansion [19–22], which uses an effective core potential (ECP) for Ni. In both cases, the final energies were evaluated using the 6-311+G(2df,2p) all electron basis set. It must be noted that for Ni this basis includes two sets of ‘f’ functions (rather than ‘d’) and one set of ‘g’ (rather than ‘f’) functions as polarization components. Furthermore, for this atom this basis includes one set of ‘s, p and d’ diffuse functions.

In all cases, the harmonic vibrational frequencies and the zero point energies were evaluated at the same level of theory used in the geometry optimization. The latter were scaled by the empirical factor 0.9646, when obtained at the MP2 level [23].

All these calculations have been carried out by means of the Gaussian 98 suite of programs [24].

3. Results and discussion

3.1. Geometries

The optimized geometries of the different complexes investigated are schematized in Fig. 1. It can be observed that MP2 and B3LYP geometries are reasonably close if we consider the base subunit exclusively. However, they provide a quite different description of the interaction of this subunit with the metal monocation, as reflected in differences of the X–Ni bond lengths that can be as large as 0.1 Å. In general, the B3LYP/6-311G(d,p) approach leads, in average, to X–Ni bond lengths shorter than the MP2 ones, with the only exceptions of the $[Ni–NH_3]^+$ and the $[Ni–CO]^+$ complexes. It must be indicated however that for the $[Ni–NH_3]^+$ complex the MP2 values should be taken with caution due to convergency problems, also manifested in the fact that for this system the QCISD(T) calculation does not converge.

It is also worth noting that the X–Ni bond distances obtained at the B3LYP/LANL2DZ are sizeably longer than those obtained with the all electron basis set. Actually the B3LYP/LANL2DZ Ni–X distances are also much longer than the MP2/6-311G(d,p) ones. This clearly indicates the need of including polarization functions in the basis set used. The structures of the $Ni^+–CO_2$, $Ni^+–H_2O$ complexes were reported in the literature at different levels of accuracy [25,26]. In all cases our B3LYP optimized geometries do not differ significantly from the previous reported values, although, for the $Ni^+–CO_2$ complex, our Ni–O distance (1.924 Å) is slightly shorter than the one obtained at the CCSD(T) level (2.01 Å) [25].

3.2. Binding energies

The total energies of the different systems investigated are summarized in Table 1, together with the zero point energies and the binding energies. Since most of the experimental binding energies are given at 0 K we have evaluated them as:

$$\mathrm{BE} = E(\mathrm{Ni}^+\text{–base complex}) - E(\mathrm{base}) \qquad (1)$$

where the energies of the complex and the base include the ZPE correction. Only for the case of $[Ni–NH_3]^+$ where also the binding enthalpy is experimentally known we have evaluated it by including, in Eq. (1) the thermal corrections and the $P\,\Delta V$ term evaluated at 298 K.

It can be observed that in many cases, it was not possible to obtain the G2(MP2) value due to the lack of convergence of the QCISD calculation. Nevertheless, in two of the cases where this convergence was achieved the results obtained were meaningless. For methyl amine an unbound complex is predicted. Furthermore, in this case the spin contamination of the QCISD calculation was very large (the expectation value of $S^2 = 1.658$), but even larger in the MP2/6-311+G(3df,2p) calculation with a value of $\langle S^2 \rangle$ of 2.729. The large value of $\langle S^2 \rangle$ indicates a stronger mixing with some quartet states. In fact, the ^{4}F excited state of Ni^+ is only about 32 kcal mol^{-1} above the ground state [26] and very likely, by enlarging the basis set the contamination by quartet multiplicities is artificially enhanced. The pathological consequence is that in the standard G2(MP2) calculation the MP2/6-311+G(3df,2p) term provides a second-order energy contribution *smaller* than the one obtained with the 6-311G(d,p) basis set, for which the spin contamination was much smaller. This result is in-line with the conclusions of Olsen et al. [27] who showed that divergences in the MP*n* series may appear, even for well-behaved systems, when the basis set expansion used is augmented with diffuse functions. These divergences are due to very diffuse intruder states, which usually lie very high in energy relative to the ground state. However, when the basis set used is very flexible these high-lying intruder states are quite well described, and the coupling with the ground state is unphysically exaggerated. Consistently, this unphysical result is not corrected when using projected energies. For HCN, although the complex is predicted to be bound at the G2(MP2) level, the binding energy is clearly too small (vide infra). Since in many cases the convergency problems were found in the QCISD calculation we have considered it of interest to use for the evaluation of the BE the

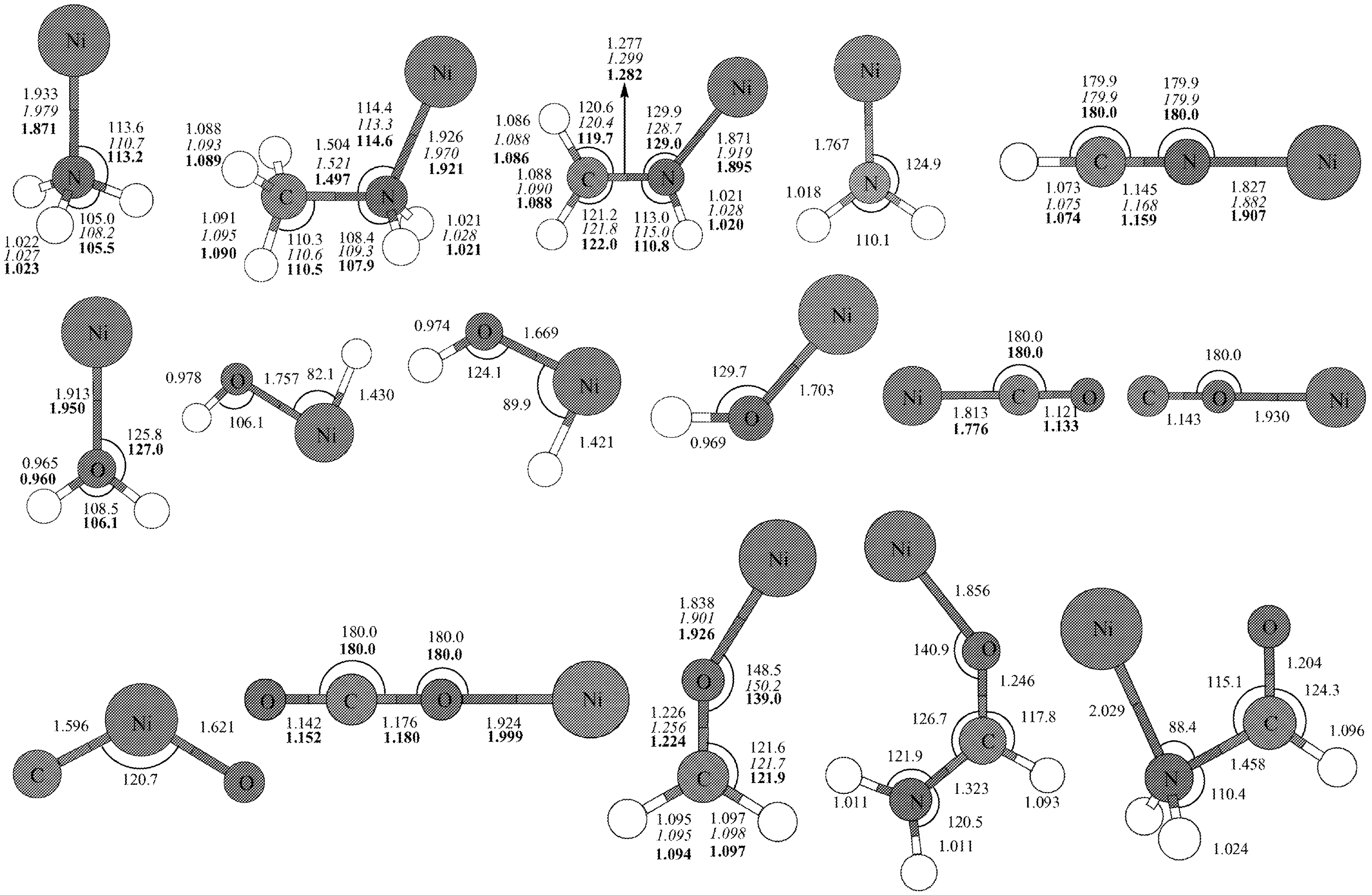

Fig. 1. Optimized geometries for the different Ni$^+$ complexes included in this study. Bond angles (°) and bond lengths (Å). Numbers in normal case were obtained at the B3LYP/6-311G(d,p) level, values in italic were obtained at the B3LYP/LANL2DZ level and values in bold were obtained at the MP2/6-311G(d,p) level.

Table 1
Total energies (*E*, Hartree), zero point energies (ZPE, Hartree) and Ni^+ binding energies (BE, kcal mol^{-1}) calculated at different levels of theory

System	B3LYP			G2(MP2)			MP2/6-311G(d,p)		Experimental value
	E	ZPE	BE	*E*	BE	*E*	ZPE	BE	BE
$[Ni–NH_3]^+$	−1564.63927	0.03889	55.2	–	–	−1563.20435	0.03906	51.5	51.2^{b}, 56.9^{c}
	−1564.64424^{a}	0.03931^{a}	60.5^{a}	–	–	–	–	–	–
$[Ni–CH_3NH_2]^+$	−1603.95780	0.06791	58.8	−1602.17851	−212.7	−1602.35815	0.06913	36.1	–
	−1603.95490^{a}	0.06809^{a}	58.0^{a}	–	–	–	–	–	
$[Ni–CH_2NH]^+$	−1602.72580	0.04322	58.8	–	–	–	0.04412	–	–
	−1602.68809^{a}	0.04342^{a}	63.3^{a}	–	–	–	–	–	–
$[Ni–HCN]^+$	−1601.48310	0.01789	50.0	−1600.15633	12.7	−1599.94195	0.01765	38.8	–
	−1601.48120^{a}	0.01794^{a}	50.1^{a}	–	–	–	–	–	–
$[Ni–H_2O]^+$	−1584.49376	0.02445	42.5	−1583.24506	39.3	−1583.03948	0.0219	39.5	36.5 ± 3^{d}, 39.7^{e}, 43.1 ± 0.7^{e}
$[Ni–CO]^+$	−1621.37620	0.00753	36.8	−1620.07608	29.8	−1619.85503	0.0074	3.9	38 ± 3^{f}, 41.7 ± 2.5^{g}
$[Ni–CO_2]^+$	−1696.65290	0.012409	21.7	–	–	–	–	–	24.9 ± 0.2^{h}
	−1622.58245	0.02875	45.1	−1621.25551	41.5	−1621.00339	0.0295	35.3	–
$[Ni–NH_2C(H)O]^+$ (O–attached complex)	−1678.01228	0.04817	53.2	–	–	–	–	–	–
$[Ni–NH_2C(H)O]^+$ (N–attached complex)	−1677.99515	0.04735	43.0	–	–	–	–	–	–
$[Ni–OH]^+$	−1583.82339	0.011601	59.5	–	–	–	–	–	56.3 ± 4.6^{i}
$[Ni–NH_2]^+$	−1563.97184	0.024242	64.1	–	–	–	–	–	53.2 ± 1.8^{b}

[a] Values obtained using the B3LYP/LANL2DZ optimized geometries.
[b] Value taken from [28].
[c] Binding enthalpy value taken from [30].
[d] Value taken from [32].
[e] Value taken from [33].
[f] Value taken from [36].
[g] Value taken from [37].
[h] Value taken from [38].
[i] Value taken from [40].

corresponding MP2/6-311G(d,p) energies, which does not include diffuse functions and which uses to converge in most cases. However, the values reported in Table 1, clearly show a quite erratic behavior of the estimated values. While for ammonia, for instance, the value is close to the B3LYP result and to other theoretical estimates [28], for methyl amine and for HCN the calculated values are more than 10 kcal mol^{-1} off with respect to the B3LYP/6-311+G(2df,2p) value. Also significantly, for CO the estimated MP2/6-311G(d,p) Ni^+ binding energy does not only differ by more than 30 kcal mol^{-1} from the B3LYP value and by more than 25 kcal mol^{-1} from the G2(MP2) estimate, but it is off the experimental value by 35 kcal mol^{-1}. This seems to indicate that for Ni^+, as it has been found before for Cu^+, the MP*n* series does not converge properly or it does slowly. This is indeed the case as illustrated in Fig. 2 where we have plotted the correlation energy corrections up to fifth order for water, Ni^+ and H_2O–Ni^+ complex. It can be observed that while the MP*n* series converges smoothly for the neutral water molecule it does not for Ni^+. The first conspicuous fact is that although the second-order corrections are of the same order of magnitude for Ni^+ and H_2O, the third, fourth and fifth order corrections are one order of magnitude larger for Ni^+. Furthermore, the oscillations of the series increase significantly when the basis set includes diffuse components and high angular momentum polarization functions. It is also worth noting that all these problems become

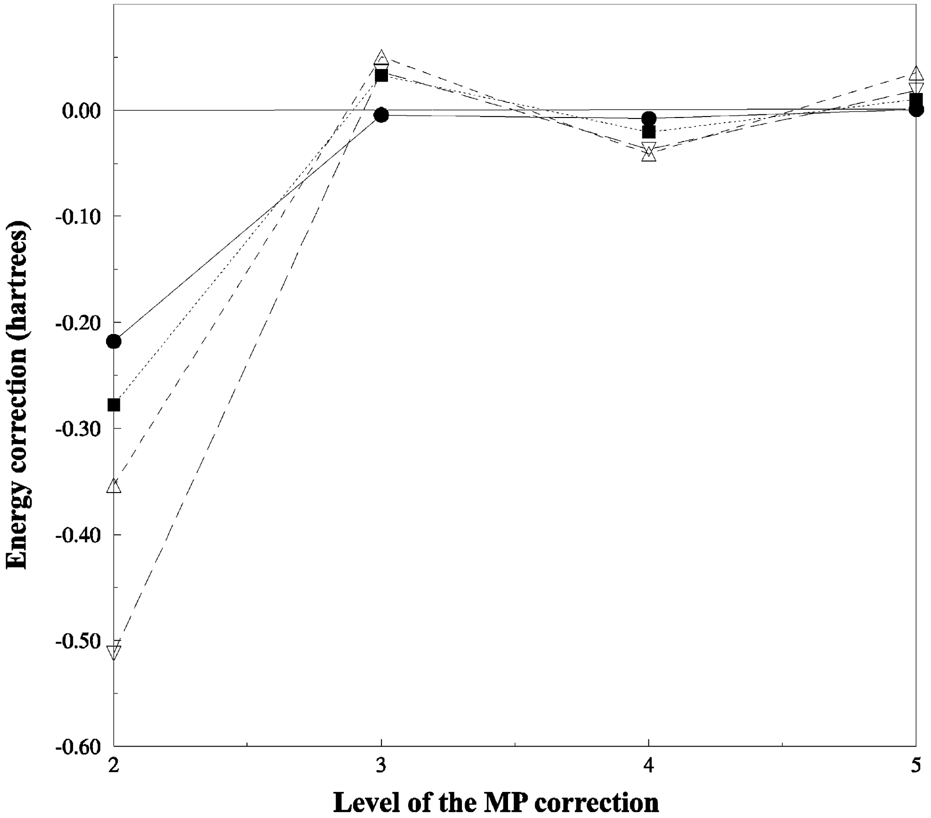

Fig. 2. Values of the second, third, fourth and fifth order contributions to the correlation energy of H_2O (●); Ni^+ ((■) when a 6-311G(d,p) basis set is used, (△) when a 6-311+G(3df) basis set is used); $[Ni–H_2O]^+$ complex (▽). For H_2O and $[Ni–H_2O]^+$ a 6-311G(d,p) basis set was used.

even more evident when dealing with the Ni^+–H_2O complex. In this case, not only the third, fourth and fifth order corrections are anomalously large, but the fourth order correction is even larger than the third order one in absolute value. This problem is observed also for other complexes. In this respect it must be mentioned that the fact that odd terms are positive and large uses to be a clear indication, as shown by Cremer and He [8], of erratic convergency of the MP*n* series. Although in general the spin contamination was not significantly large, in many cases, the HF wave function was found to present internal instabilities, so many of the ab initio calculations, including geometry optimizations were carried out by stabilizing first the HF wave function.

Conversely, no convergency problems have been observed when the B3LYP method is used and, in general, the spin contamination in these calculations is negligibly small, the values of $\langle S^2 \rangle$ being typically lower than 0.767. Nevertheless, the B3LYP calculations presented internal instabilities when dealing with the singlet states of the $[Ni–OH]^+$ and the $[Ni–NH_2]^+$ complexes. In those cases the geometry optimizations were carried out after stabilizing the wave function.

For ammonia the calculated binding energy is in fairly good agreement with the experimental value ($51.2\,kcal\,mol^{-1}$) [29] and in excellent agreement with previous theoretical calculations using multireference methods ($54.6\,kcal\,mol^{-1}$) [28]. More recently a new experimental binding enthalpy measured at 298 K ($56.9\,kcal\,mol^{-1}$) was reported by Walter and Armentrout [30]. When our calculated binding energy is converted to the corresponding enthalpy, the value obtained ($56.7\,kcal\,mol^{-1}$) is almost identical to the experimental one. For the other nitrogen bases there are neither experimental values, nor previous theoretical estimates, but the results obtain seem to be correct in the sense that methyl amine is predicted to be $3.6\,kcal\,mol^{-1}$ more basic than ammonia, as well as methyl imine. Conversely, HCN is predicted to be about $8\,kcal\,mol^{-1}$ less basic than ammonia, resembling closely the basicity trends exhibited by these compounds in protonation processes. It is also worth noting that these calculated Ni^+ binding energies compare very well with previous reported values for Cu^+ binding energies [16]. We will come back later to this point.

As far as the oxygen-containing bases are concerned, the water–Ni^+ binding energy is estimated to be, as expected, almost $13\,kcal\,mol^{-1}$ lower than that of ammonia and in nice agreement with previous theoretical estimates ($41.1\,kcal\,mol^{-1}$) [31]. We have found however three different experimental values ranging from 36.5 ± 3 [32] and $39.6\,kcal\,mol^{-1}$ [33] to $43.1 \pm 0.7\,kcal\,mol^{-1}$ [33]. Our estimate clearly supports the last value reported by Marinelli and Squires [33]. The value obtained for carbon monoxide is also in-line with its expected lower intrinsic basicity, and in good agreement with previous theoretical estimates (38 ± 5 [34], $36.7\,kcal\,mol^{-1}$ [35]). Also in this case two different experimental values can be found in the literature, which differ significantly. Our estimate is quite close to the values reported by Carpenter et al. [36] ($38 \pm 3\,kcal\,mol^{-1}$), while it differs more from the value reported by Armentrout and coworkers [37] ($41.7 \pm 2.5\,kcal\,mol^{-1}$). As it was found previously for Cu^+ complexes [16] and it is also the case for protonation, our results also indicate that carbon attachment is preferred over oxygen-attachment by $21.9\,kcal\,mol^{-1}$.

It is also worth to emphasize that the insertion of Ni^+ into the O–H bonds of water, is predicted to be endothermic processes by $19.6\,kcal\,mol^{-1}$, in fairly good agreement with previous theoretical estimates [26]. As expected, for carbon monoxide, the Ni^+ insertion into the $C{\equiv}O$ bond is much more endothermic ($181.3\,kcal\,mol^{-1}$).

For complexes between CO_2 and Ni^+ we have considered exclusively the linear arrangement, which was found to be the most stable conformation at the CCSD(T) level of theory [25]. The calculated binding energy is in fairly good agreement with the experimental value [38], although slightly smaller (see Table 1), but almost identical to the one estimated by Burda at the CCSD(T) level of theory ($22.2\,kcal\,mol^{-1}$) [25].

As expected from its intrinsic basicity, the formaldehyde–Ni^+ binding energy is higher than that of water and carbon monoxide. Also, the attachment of Ni^+ to formamide takes place preferentially on the oxygen atom of the carbonyl group, while the attachment to the amino group is predicted to be 10.7 kcal mol^{-1} less favorable. In both systems, formaldehyde and formamide, the CONi bond arrangement is far from linear, the bond angle being near 150°. This indicates that, as in the protonation process the association takes place on one of the lone pairs of the base. A purely electrostatic interaction, as the one taking place in Li^+ complexes [39–42] will lead to a linear arrangement, in which the cation locates along the axis of the dipole moment of the neutral. This can be taken as an indication of the non-negligible covalent character of the base–Ni^+ interaction. In this sense, Ni^+ resembles closely Cu^+, even if the latter is formally a closed-shell system. Actually, as illustrated in Fig. 3 there is an excellent correlation between calculated Ni^+ and Cu^+ binding energies for the set of bases considered in this work. The latter were evaluated at the same level of theory used to obtain the former and were taken from [16]. Also, there is a fairly good linear correlation between our calculated Ni^+ binding energies and the corresponding experimental proton affinities [43,44] (see Fig. 4), even though the former are about four times smaller than the latter. It can be also observed, that in spite of the reduced number of points, this linear correlation between proton affinities and Ni^+ binding energies is also observed when using experimental rather than calculated values (see Fig. 4b).

We have considered it of interest to include OH and NH_2 in the set of oxygen and nitrogen bases because they are radicals for which the Ni^+ binding energy has been measured [29,45]. In both cases the corresponding singlet and triplet states have been considered, and in both cases the triplet state was found to be significantly more stable than the singlet. The estimated binding energy for OH is slightly higher than the experimental value but lies within the error bars of the experiment (see Table 1). For NH_2, however, our

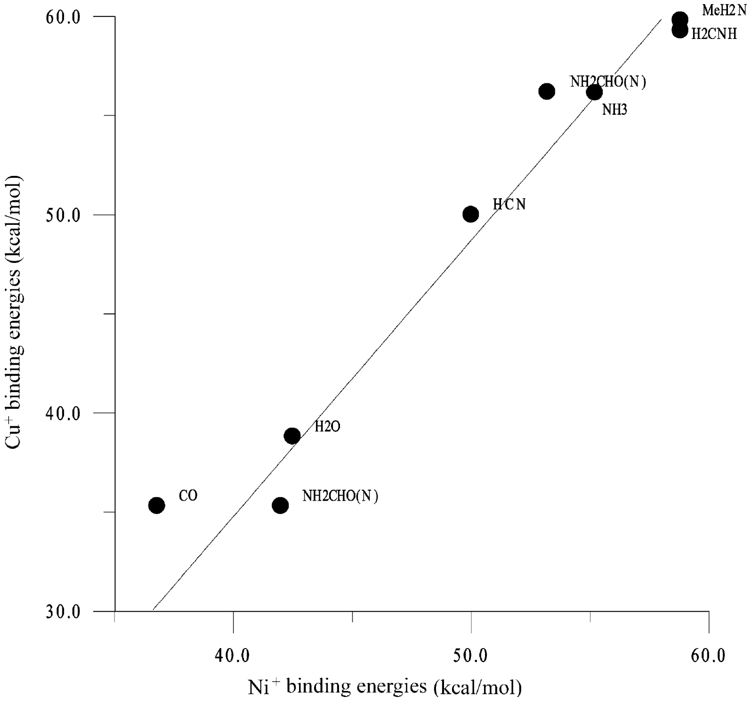

Fig. 3. Correlation between calculated Ni^+ and Cu^+ binding energies for the different bases under study.

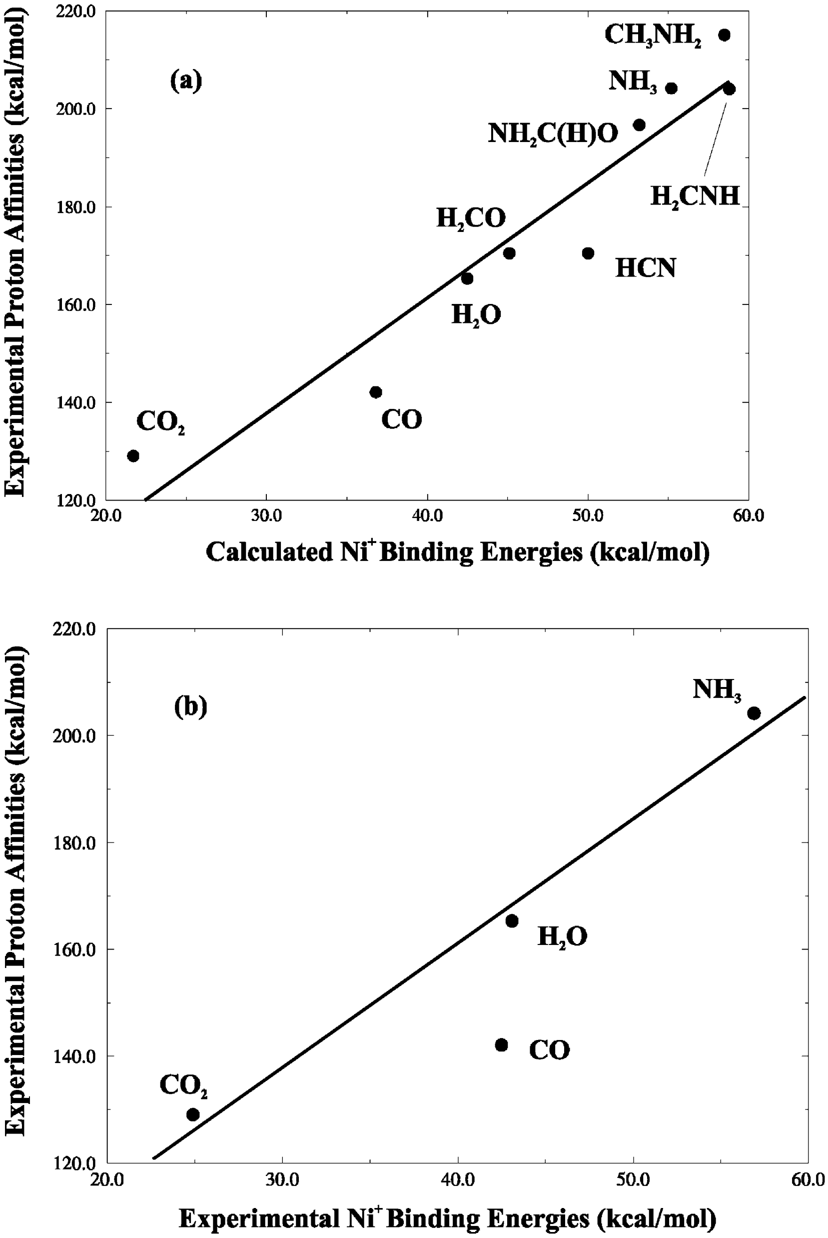

Fig. 4. Correlation between experimental proton affinities and (a) calculated Ni^+ binding energies; (b) experimental Ni^+ binding energies for the different bases under investigation.

estimated Ni^+ binding energy significantly overestimates the experimental value. We cannot offer any plausible explanation for this disagreement. If one considers that the intrinsic basicity of NH_2 is larger than that of OH, it would not be surprising to find, in agreement with our theoretical prediction, the Ni^+–NH_2 binding energy to be larger than the Ni^+–OH one. Hence, the fact that experimentally the Ni^+–NH_2 binding energy is smaller than the Ni^+–OH, is in our opinion an open question.

4. Conclusions

The description of Ni^+ complexes at the G2(MP2) level presents remarkable pathologies, rather similar to those described before in the literature for complexes of Cu^+. This pathological behavior is associated with high spin contamination of the unrestricted wave function and with convergency problems of the MP*n* series. As a consequence the results obtained in the framework of this formalism are physically meaningless. Conversely, the B3LYP method exhibits a much regular behavior. With the only exception of the NH_2, the Ni^+ binding energies evaluated at the B3LYP/6-311+G(2df,2p) level are in good agreement with the experimental values, and with other theoretical estimates obtained through the use of multireference or CCSD(T) formalisms, when available. The behavior of the bases investigated with respect to Ni^+ resembles closely the one they exhibit when the reference acid is Cu^+ or H^+. This can be taken as an indication of the non-negligible covalent character of the base–Ni^+ interactions. Consistently, for the set of bases investigated Ni^+ binding energies are linearly correlated with both proton affinities and Cu^+ binding energies.

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