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Association of metal cations with alkanes: $Na(CH_4)^+$ versus $Cu(CH_4)^+$ as molecular models*

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Summary. *Ab initio* molecular orbital calculations give small stabilization energies for the various $Na(CH_4)^+$ adducts (less than 4 kcal mol^{-1}), but predict a stronger binding for the copper compounds (about 13 kcal mol^{-1}). The different behaviour of Na^+ and Cu^+, already present at the SCF level, is reinforced by electron correlation. This can be attributed to an important contribution of the dispersion energy to the binding energy of the copper ion: about 40% of the total, including basis set superposition corrections.

Key words: $Na(CH_4)^+$ – $Cu(CH_4)^+$ – Adducts – Binding energy – Bonds

A number of theoretical works has been devoted to adducts resulting from the association of a metal cation and an ordinary neutral compound, especially in connection with biological problems involving water [1]. The study of paraffinic hydrocarbons, however, has attracted much less attention, except in the case of complexes with the Li^+ cation [2]. Limited data are also available for the $CuCH_4{}^+$ system [3]. Experimentally, gaseous transition-metal cations, bearing ligands or not, have been shown to be extremely reactive with a variety of hydrocarbons; for instance, metals whose cations are unreactive under monocollisional conditions, as Cr, Mn, Cu or Zn, yield metal-alkane complexes under multicollisional conditions taking place in multiquadrupole devices [4] or in fast flow-reactors [5]. Since these complexes are probably the first intermediates formed in the reaction of alkanes with metal ions, the study of their electronic structures and geometries may be a key for understanding the alkane activation challenge [6].

First, let us mention some deficiencies of the usual electrostatic interpretation for the formation of fairly stable adducts with alkanes (see [7]): such a simple model fails to explain striking differences between the behaviour of apparently related metal cations, for instance the pair Cu^+ and Na^+ whose ionic radii are almost identical (Cu^+: 0.96 Å, Na^+: 0.95 Å). Actually, the compound formed by the Cu^+ ion and isobutane has a lifetime long enough to make its experimental study possible, whereas no trace of a corresponding product can be found with

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Na^+ (or, similarly, with K^+ and Ca^+) under the same conditions [4, 8]. In both cases, the metal-ligand interaction involves two closed-shell systems, Na^+ or Cu^+, and the hydrocarbon. We have tried to estimate the importance of these bonds using quantum chemistry methods.

1. $Na(CH_4)^+$ and $Cu(CH_4)^+$ molecular complexes

In this paper, we have studied the formation of adducts with the simplest alkane CH_4 as a model system for which detailed molecular orbital calculations can be performed at the *ab initio* level. In a first step, the self-consistent field (SCF) treatment was carried out, then electron correlation was introduced through the standard perturbation (PRT) theory. The geometries of the $Na(CH_4)^+$ and $Cu(CH_4)^+$ systems were optimized at the SCF and second-order perturbation level, and their binding energies computed by going up to the fourth-order perturbation level. The search for the optimal geometries was achieved by minimizing the total energy for each internal coordinate separately and reiterating the whole process till convergency; a step-by-step procedure was found to be necessary in order to avoid artefacts occurring sometimes for highly symmetrical structures when global gradient methods are used. The calculations have been performed using extended versions of the standard GAUSSIAN [9] and HONDO [10] programs.

The atomic orbitals chosen for this work are derived from the "MIDI" Gaussian sets given by Huzinaga [11]. They are split-valence bases whose last components are left free, increased by two *p* diffuse functions for sodium or two *p* and one *d* diffuse functions for copper whose exponents are the values recommended in [11]. Writing the Gaussians in the *s*, *p*, *d* descending order they are expressed as follows:

$$\mathrm{H}\ (4s) \rightarrow (2s);$$

$$\mathrm{C}\ (6\ \ 3/5) \rightarrow (6\ \ 2\ \ 1/3\ \ 2);$$

$$\mathrm{Na}\ (5\ \ 3\ \ 3/5) \rightarrow (5\ \ 3\ \ 2\ \ 1/5\ \ 1\ \ 1);$$

$$\mathrm{Cu}\ (5\ \ 3_3\ \ 3/5\ \ 3/5) \rightarrow (5\ \ 3\ \ 3\ \ 2\ \ 1/5\ \ 3\ \ 1\ \ 1/3\ \ 2\ \ 1)$$

The formation energy of the metal complex is defined at each step of the theoretical calculation by the energy balance of the reaction:

$$M(CH_4)^+ \rightarrow CH_4 + M^+$$

each species being taken in its own optimized geometry. It is well known that a formula like:

$$D_e = E^0(\mathrm{AB}) - (E^0(\mathrm{A}) + E^0(\mathrm{B}))$$

where the superscript 0 means lowest-energy structures, may involve rather large "basis set superposition errors" (BSSE) due to the limited size of the atomic bases. The theoretical binding energies D_e can be corrected from the main part of their BSSE's if one replaces $E^0(\mathrm{A})$ and $E^0(\mathrm{B})$ by the values $E^1(\mathrm{A})$ and $E^1(\mathrm{B})$ computed for A and B by using all the atomic orbitals used in the calculation of AB energy at the same places in the adduct [12]. However, this procedure may be biased by the geometry changes occurring for each fragment when the structure of AB is optimized. So, we have used a slightly modified procedure by putting:

$$D_e = E^0(AB) - (E^0(A) + E^0(B)) - \Delta E(A) - \Delta E(B)$$

$$\Delta E(A) = E^1(A) - E^2(A)$$

$$\Delta E(B) = E^1(B) - E^2(B)$$

the superscript indices 1 and 2 mean that the energy of one fragment, in its distorted geometry, is computed in the presence of the orbitals of the other (index 1), or not (index 2) [13].

For a monoatomic ion M^+, $E^0(M^+)$ and $E^2(M^+)$ are identical, and we have in this particular case:

$$D_e = E^0(M(CH_4)^+) - E^1(M^+) - E^1(CH_4) - (E^0(CH_4) - E^2(CH_4))$$

The first three terms give the evaluation of D_e with the correction of substantial part of the BSSE error and the two last terms take into account the CH_4 geometry distortion in the adduct. The BSSE corrections computed in this way are listed in Table 1 for the ground-state geometries of the (C_{3V} 3H ligands) $Na(CH_4)^+$ and $Cu(CH_4)^+$ adducts. They are smaller in the case of sodium than in the case of copper and are respectively equal to about one quarter and one half of the stabilization energy of the adduct with respect to its fragments. Basis superposition effects were found to have a comparable importance in early studies of hydrogen-bonded systems using limited basis sets [14].

Complete minimization of energy with respect to the geometry parameters of the adduct suggests that the symmetrical structures with 1, 2 or 3 hydrogens serving as ligands of the metal ion (Fig. 1) are preferred. As indicated in Table 2 for $Na(CH_4)^+$, the greater the number of H ligands is, the more stable the adduct is (less symmetrical structures are found to have higher energy), in accordance with simple electrostatic models.

By comparing the BSSE-corrected D_e values of Table 3, it appears that the copper adduct should have some stability, whereas its sodium analogue remains weakly bonded at every step of theory. Moreover, the dispersion effects introduced by correlation at the perturbation level are of trifling importance for $Na(CH_4)^+$, in contrast with $Cu(CH_4)^+$ for which they amount to 40% of the binding energy [15].

Table 1. BSSE corrections of fragments for 3H ligand adducts in C_{3V} symmetry (in kcal mol^{-1})

	$Cu(CH_4)^+$(I)			$Na(CH_4)^+$(II)		
ΔE	a	b	c	a	b	c
(CH_4)	−0.692	−3.493	−3.689	−0.336	−0.821	−0.878
(M^+)	−0.733	−3.913	−4.245	−0.028	−0.144	−0.149
Total	−1.425	−7.406	−7.934	−0.364	−0.965	−1.027

[a] SCF values

[b,c] 2nd and 4th order PRT values

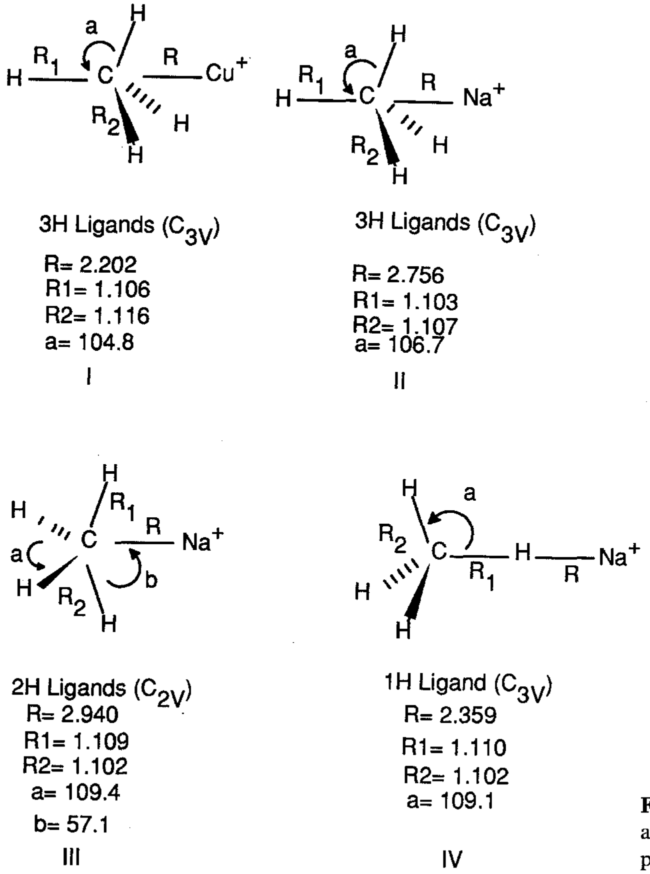

Fig. 1. Structures of adducts at the second-order perturbation level

According to an orbital hybridization analysis in terms of SCF Mulliken populations [16], the two metal cations may be described as follows:

Cu: $s^{6.072}$; $(p_x, p_y)^{8.032}$; $p_z^{4.072}$; $d_{z2}^{2.007}$; $(d_{xz}, d_{yz})^{4.032}$; $(d_{x2\text{-}y2}, d_{xy})^{4.000}$

and Na: $s^{4.019}$; $(p_x, p_y)^{4.010}$; $p_z^{2.022}$

The population of copper and sodium increase by, respectively, 21% and 5% of the formal electronic charge from $Cu^+(K, L, 3s^2, 3p^6, 3d^{10})$ and $Na^+(K, 2s^2, 2p^6)$. Although population analyses are only qualitative, this suggests that the formation of a one ligand adduct involves a not very significant orbital hybridization. The different values obtained for the binding energy of the Cu^+ and Na^+ compounds may be attributed to the presence of the wholly occupied *d*-shell of Cu^+ in agreement with the polarizabilities of the cations themselves about $1 \times 10^{-30}\,m^3$ and $0.2 \times 10^{-30}\,m^3$, respectively [17].

These conclusions are not substantially modified if the zero-point vibrational energy differences are considered, because of the three normal modes added by the metal to those of CH_4 should have low frequencies (less than $500\,cm^{-1}$); so, D_0 binding energies would be smaller than the preceding D_e values by about

Table 2. Energies E^0 of adducts and fragments in optimized geometries (in u.a.)

E^0	a	b	c	d
$Cu(CH_4)^+$				
I	−1678.43077	−1678.83077	−1678.77133	−1678.83567
$Na(CH_4)^+$				
II	−201.79398	−201.89483	−201.90772	−201.91483
III	−201.79300	−201.89402	−201.90695	−201.91405
IV	−201.79108	−201.89169	−201.90469	−201.91180
Fragments				
$[CH_4]$	−40.17422	−40.27188	−40.28495	−40.29188
$[Na^+]$	−161.61326	−161.61535	−161.61523	−161.61534
$[Cu^+]$	−1638.24195	−1638.53003	−1638.46214	−1638.51098

[a] SCF values
[b,c,d] 2nd, 3rd and 4th order PRT values, respectively

Table 3. BSSE-corrected binding energies D_e (in kcal mol^{-1})

Adduct	I	II	III	IV
a	7.74	3.72	3.25	2.05
b	10.70	3.80	3.35	2.50
c	12.65	3.75	3.32	2.56

[a] SCF D_e values
[b,c] 2nd and 4th PRT D_e values

2 kcal mol^{-1}; in case of the sodium adduct, D_0 is of the same order of magnitude as thermal energy at room temperature. The latter results are consistent with observation of copper compounds in mass-spectrometry experiments and lack of adducts with alkaline ions. The more important binding energies recently reported for Cu^+ and Na^+ water systems [18] are explained by the existence of lone-pairs on oxygen and OH bonds of water. Although the CH bonds of methane are far less polar, in both cases Cu^+ adducts are more stable than Na^+ adducts.

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