

Ab initio* study on the methanol–water cation radical potential energy surface

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Summary. Potential energy surface for reaction of $\text{CH}_3\text{OH}^{+\cdot}$ and H_2O was investigated at MP2/3-21G*(O) and MP2/6-31G* levels. Six minima and four saddle points were localized. The three deepest minima are of H-bond type while the fourth one possesses the three-electron hemibond.

Key words: *Ab initio* study – Methanol–water cation radical – H-bonded and hemibonded structures

1 Introduction

Intermolecular interactions between closed-shell systems in their ground electronic states have been studied in our laboratory during the past 20 years [1–3]. It is well known that removing or adding an electron from a molecule (i.e. passing to cation or anion radical) changes the properties of systems completely. The question arises whether the complexes between a closed-shell system and an open-shell system will be also different from their parent (closed-shell) complexes. The study of interaction between closed-shell and open-shell systems is therefore very tempting, and from the point of view of theory, quite challenging. Besides this we have one very practical reason to investigate the closed-shell–open-shell interaction. This is an existence of the very accurate data on intermolecular frequencies detected by zero-electron kinetic energy (ZEKE) spectroscopy [4] for cation radical derived from molecular complexes, particularly for phenol–water cation radical [5]. Let us remind that the complete set of intermolecular vibrations is available only for a very limited number of simple closed-shell complexes.

Complexes between closed-shell and open-shell systems are known for a long time and the first theoretical discussion was made by Pauling in thirties [6]. One interesting feature of these complexes is the fact that besides the classical structure (e.g. the hydrogen-bonded one) also an unusual structure with three-electron bond with bond order of 1/2 can be formed. While the former structure is clearly of

* Dedicated to Professor W. Kutzelnigg on the occasion of his 60th birthday

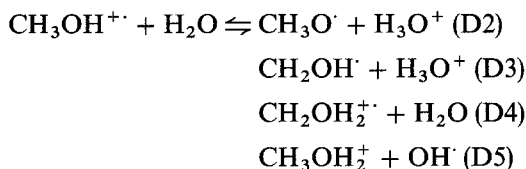
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a non-covalent origin, the three-electron bond mentioned, called also the hemibond, is more of a covalent origin. Gill and Radom have shown in their excellent paper [7] that a high level *ab initio* theory with inclusion of correlation energy is essential for a theoretical study of these type of complexes.

As mentioned above our final goal is a theoretical study of phenol–water cation radical. This complex is, however, rather large what prevents its investigation at higher theoretical level. We have decided, therefore, to study first a suitable model system: methanol–water cation radical. Calculations for this complex could be performed at both the lower and higher levels with the aim to test the reliability of the lower theoretical level which will be later applied to phenol–water cation radical.

Various cation radical complexes were studied theoretically; the literature is summarized in [7]. We are not aware of any study of the present system, however.

From the values of ionization potential of methanol and water it is clear that the cation radical from the former system is formed more easily. Reaction between $\text{CH}_3\text{OH}^{+\cdot}$ and H_2O (this pair of dissociation products will be labelled D1) can proceed through the four dissociation channels D2–D5:



2 Calculations

The spin-unrestricted methods (UHF, UMP2) were used for all the open shell systems.

Geometry optimizations of all the systems and complexes under study was performed at the MP2 level using smaller (3-21G*(O)) and larger (6-31G*) basis sets. In the first basis set the *d*-functions are localized only at the oxygens. The reason for inclusion of *d*-function on oxygens is the fact that hemibond (in this particular case the O–O three-electron hemibond) is satisfactorily described only by basis sets containing the *d*-functions.

With the smaller basis set a detailed search on the potential energy surface (P.E.S.) was carried out. All the minima found were later reoptimized with the larger basis set. The convergence criterion for gradient optimization was equal to 0.00045 hartree/a.u. resp. rad.

The interaction energy (ΔE) is determined as the difference between energy of methanol–water supersystem (E^{MW}) and the sum of energies of methanol and water ($E^{\text{M}}, E^{\text{W}}$):

$$\Delta E = E^{\text{MW}} - (E^{\text{M}} + E^{\text{W}}) \quad (1)$$

The interaction energies (ΔE) of the complexes were evaluated at the MP2 level. The ΔE term consists of SCF and electron correlation (COR) contributions:

$$\Delta E = \Delta E^{\text{SCF}} + \Delta E^{\text{COR}} \quad (2)$$

Because the finite basis sets were used, it was necessary to eliminate basis set superposition error (BSSE). The counterpoise method of Boys and Bernardi [8] was used for both ΔE^{SCF} and ΔE^{COR} contributions. All the occupied and virtual

orbitals of the “ghost” system were used. Interaction energy defined by Eq. (1) contains the deformation energy, i.e. energy needed to deform the subsystems from their optimum geometry to the geometry they have in a supersystem. Thus the geometry of the “ghost” system was taken from the supersystem and not from the respective isolated subsystems. The interaction energy corrected for BSSE ($\Delta E(\text{BSSE})$) is evaluated as follows:

$$\Delta E(\text{BSSE}) = \Delta E + \text{BSSE} \quad (3)$$

Harmonic vibrational frequencies were computed for each stationary point by evaluating the second derivatives of the energy with respect to the nuclear coordinates.

Enthalpies at 298 K were calculated with GAUSSIAN 90 set of programs [9].

3 Results and discussion

The degree of spin contamination for all the systems studied was rather small (lower than 0.76). The only exception represents the hemibonded M4 structure and the respective transition structure T2 (cf. Fig. 1) where the spin contamination was slightly higher (0.77–0.78).

3.1 Geometry of methanol cation radical

The geometry of the methanol cation radical and in particular the C–O bond is sensitive to the basis set and level of correlation [10]. The QCISD (T)/6-311G(2df, 2pd) value of $R(\text{C–O})$ is 1.31 Å, that evaluated at MP2/6-311G(2df, 2pd) level amounts to 1.287 Å. Our MP2/6-31G* and especially MP2/3-21G*(O) C–O bond lengths (1.383 and 1.447 Å) are longer but still better than that evaluated at HF/3-21G, HF/6-31G*(O) or MCSCF/6-31G* levels [10]. The O–H bond length calculated at MP2/6-31G* and MP2/3-21G*(O) levels (0.998 and 1.016 Å) are again longer than that evaluated at MP2/6-311G(2df, 2pd) level (0.971 Å [10]). The C–O–H bond angle is not so sensitive to the theoretical level: MP2/6-311G(2df, 2pd) 115° [10]; MP2/6-31G* 114°, MP2/3-21G*(O) 112°. We are aware of the unbalanced character of 3-21G*(O) basis set but we would like to stress again that for larger complexes we can hardly use higher level calculations. For our purposes the relative changes of the geometry are more important than the absolute values.

3.2 Dissociation channels

The energy and enthalpy changes for processes $\text{D1} \rightleftharpoons \text{D2–D5}$ are summarized in Table 1. The lower and higher level results indicate that products of reaction of $\text{CH}_3\text{OH}^{+\cdot}$ with H_2O are $\text{CH}_2\text{OH}^\cdot$ and H_3O^+ , and CH_2OH_2^+ and H_2O . This is confirmed by theoretical ΔH_{298}^0 values evaluated at the higher level. Theoretical ΔH_{298}^0 values agree qualitatively with experimental data. Despite the fact that channels D3 and D4 are comparably favored by ΔE and ΔH we expect that due to the geometry of most stable complex (see later), the D4 channel will be preferred.

3.3 Stationary points on the P.E.S.

The six minima (*M*) and four transition states (*T*) were found on the 3-21G*(O) P.E.S.; their geometries are displayed in Fig. 1. We are certainly not sure whether all the minima were localized; we hope, however, that at least these energetically most stable were found. The situation with transition structures is more difficult. Our aim was to find at least one *T* for each pair of minima, i.e. to be able to suggest the reaction path for a transition of one minimum to the other. Even in this way the number of *T* is enormous. We have finally tried to localize only these *T* separating M1, M2 (T1); M2, M4 (T2); M3, M6 (T3) and M5, M1 (T4). The fifth one, separating M3 and M4, were, despite large effort, not localized. The nature of all

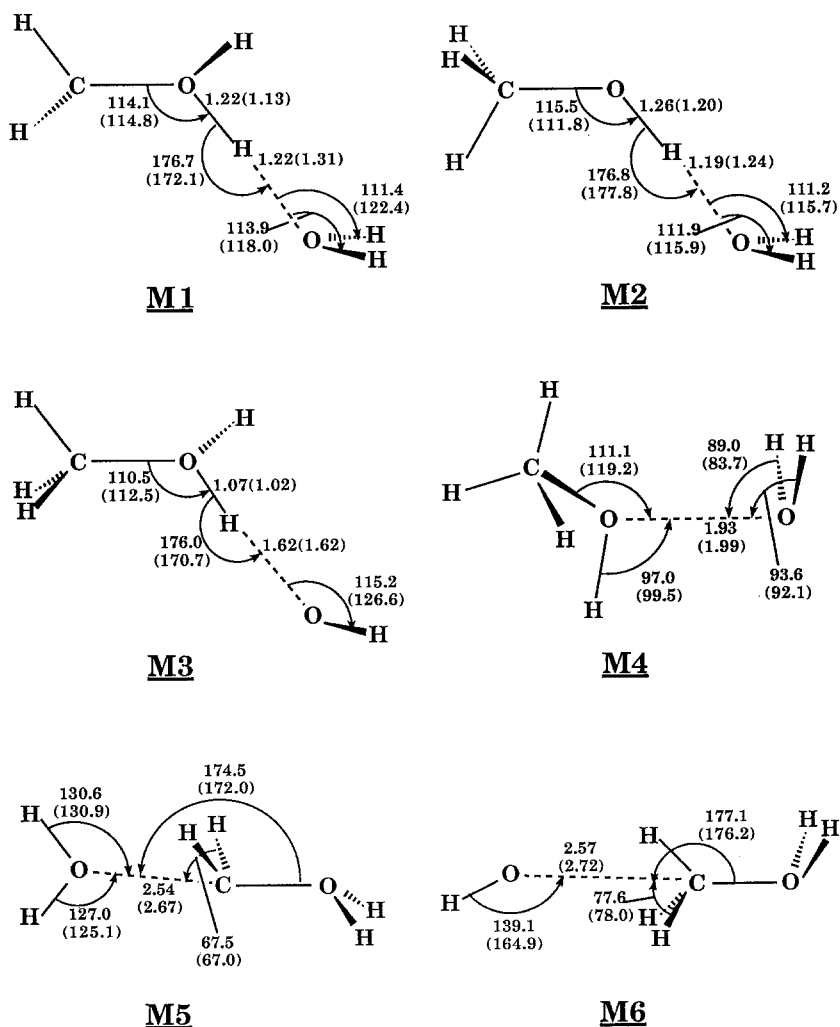


Fig. 1. Continued

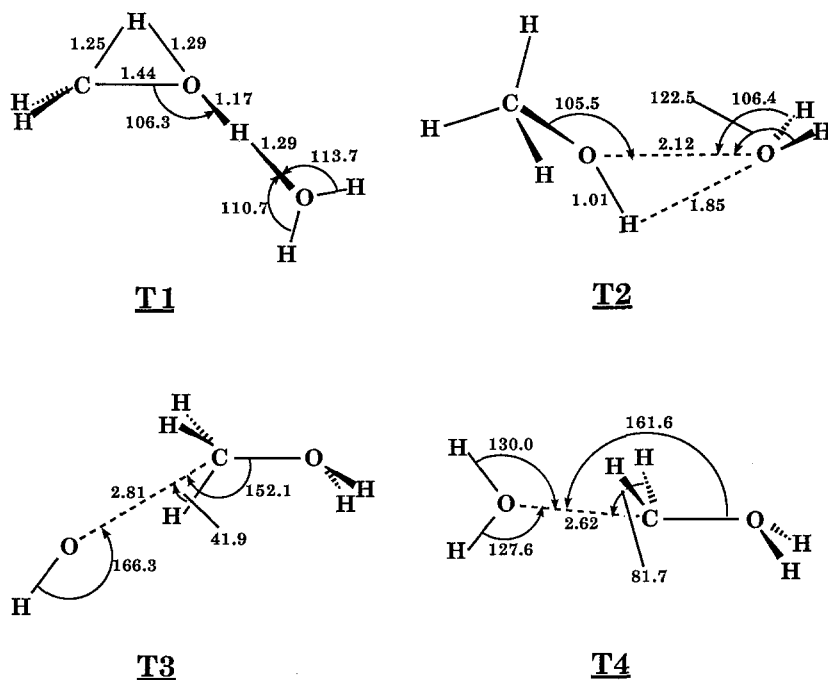


Fig. 1. The most important bond lengths (in Å) and bond angles (in degree) for all the minima and transition structures evaluated at MP2/3-21G*(O) level. Values in parentheses corresponds to MP2/6-31G* level. The remaining coordinates will be supplied on request

Table 1. The energy and enthalpy changes (in kcal/mol) for reactions $D1 \rightleftharpoons D2$ – $D5$ taken from MP2 calculations with 3-21G*(O) and 6-31G* basis sets and from experiment

Products ^a	ΔE		ΔH_{298}^0	
	3-21G*(O)	6-31G*	6-31G*	exp. ^b
D2	– 10.27	– 6.13	– 4.43	0.5 ± 0.7
D3	– 19.46	– 12.60	– 10.69	-9 ± 2
D4	– 16.06	– 12.47	– 11.06	-7 ± 2
D5	– 13.89	– 9.56	– 7.19	1

^a For definition see text

^b Taken from [11]

the stationary points is convincingly supported by the calculated harmonic frequencies of the normal vibration modes (see later). The intermolecular distances with all the complexes are smaller than in the closed shell complexes. This is especially true with minima M1 and M2 where intermolecular H...O distance amounts to 1.31 Å and 1.24 Å, respectively.

The intramolecular geometry of methanol cation radical is influenced by complexation. The most important changes concern the OH and CO bonds. In

case of H-bonded structures the former bond is, as expected, prolonged, this prolongation being most important for the M2. The MP2/6-31G* CO bond lengths (in Å) for M1–M6 are 1.430, 1.401, 1.498, 1.447, 1.482 and 1.528. This bond length evaluated at the MP2/3-21G*(O) level for M1–M6 and T1–T4 amount to 1.437, 1.432, 1.508, 1.468, 1.503, 1.548 and 1.436, 1.464, 1.539, 1.498. The CO bond is in all the minima prolonged, this effect is most important in M6, where the CO bond directly participate in the intermolecular bonding. In case of transition structures the CO bond is slightly shorter for T1 and larger for remaining structures. The prolongation is most important for T3, having similar structure as M6.

Relative energies with respect to isolated CH_3OH^+ and H_2O for all the stationary points (cf. Fig. 1) evaluated at MP2/3-21G*(O) level are depicted in Fig. 2. Relative energies, again with respect to isolated CH_3OH^+ and H_2O obtained with larger 6-31G* basis set, are available for energy minima only and are presented also in Fig. 2.

Interaction energies (ΔE) and their components, corrected for the BSSE for all the stationary points, are summarized in Table 2. The numbers in the BSSE column represent the sum of BSSE(SCF) and BSSE(COR).

Results obtained at the lower level will be discussed first. Minima M1, M2 and M3, which are of H-bond type, are mutually separated by rather high barriers. This supports the fact that these minima may be detectable at experimental conditions. From the Table 2 it is evident that structures M1 and M2 are bound very strongly (more than 30 kcal/mol), while structure M3 is much weaker. Minimum M4 is of unusual type – it possess the three-electron hemibond and it is again rather strong (cf. Table 2). This suggest that the hemibond system could be observed. Unfortunately this minimum is separated from the minimum M2 by a relatively low barrier (3.7 kcal/mol) and there exists a possibility of internal rearrangement to a more stable isomer. The chance to experimentally detect the hemibonded structure is therefore not high and it could be done only in an experiment of a sufficiently small

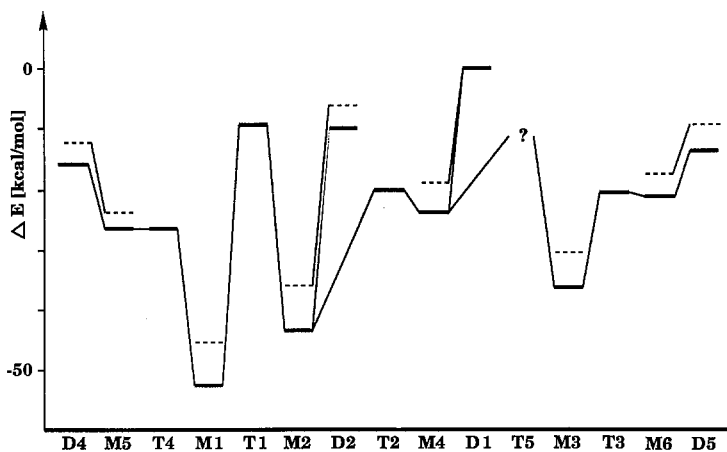


Fig. 2. Relative energies with respect to isolated systems CH_3OH^+ and H_2O (in kcal/mol) for all the stationary points evaluated at the MP2/3-21G*(O) level (full line); these energies for all the minima evaluated at the MP2/6-31G* level are depicted by a dashed line. The energy values were corrected for the BSSE

Table 2. Interaction energies and their components (for the definition see text) evaluated with 3-21G*(O) and 6-31G* basis sets for all the stationary points; the dissociation channel considered is depicted in parenthesis. Energies are in kcal/mol

Stationary point ^a	Basis set	ΔE^{SCF} (BSSE)	ΔE^{COR} (BSSE)	BSSE	ΔE (BSSE)
M1 (D4)	3-21G*(O)	- 31.39	- 5.32	10.69	- 36.71
M2 (D2)		- 28.33	- 4.62	8.58	- 32.95
M3 (D5)		- 18.61	- 3.63	7.44	- 22.24
M4 (D1)		- 4.54	- 19.30	10.31	- 23.84
M5 (D4)		- 9.85	- 0.48	6.03	- 10.33
M6 (D5)		- 6.15	- 0.47	4.77	- 6.62
T1 (D4)		+ 17.98	- 11.83	10.54	+ 6.15
T2 (D1)		- 15.85	- 4.31	8.39	- 20.16
T3 (D5)		- 6.22	- 0.39	3.75	- 6.61
T4 (D4)		- 9.83	- 0.54	5.86	- 10.37
M1 (D4)	6-31G*	- 27.22	- 5.57	2.98	- 32.79
M2 (D2)		- 22.77	- 5.95	3.07	- 28.72
M3 (D5)		- 15.85	- 2.93	1.98	- 18.78
M4 (D1)		- 0.87	- 18.32	4.59	- 19.19
M5 (D4)		- 10.93	- 0.63	1.52	- 11.56
M6 (D5)		- 7.46	- 0.36	1.08	- 7.82

^a Cf. Fig. 1

time scale. Minima M5 and M6 are separated from minima M1 and M3 by very low barriers and probability for their rearrangement is therefore high. The qualitative picture of the P.E.S. is not changed when passing to the higher level. At the higher level we have optimized only the minima and not the transition structures. We cannot therefore estimate the changes in rearrangement barriers. Figure 2 contains relative energies of all the stationary points with respect to $\text{CH}_3\text{OH}^{+\cdot}$ and H_2O . To discuss a composition of stabilization energy for these stationary points it is necessary to consider each of them with respect to its dissociation products.

From Table 2 it is evident that there exist three very stable minima, M1–M3, stabilized by formation of the strong hydrogen bond. These H-bonds are considerably stronger and shorter (cf. Fig. 1) than the H-bonds formed between neutral systems. The ionic character of these complexes is clearly responsible for the stability of structures M1–M3 (cf. values of ΔE^{SCF} in Table 2).

Minimum M4 is stabilized by 3-electron hemibond. Because such a bond is a special type of covalent bond, it is not surprising that in this case the ΔE^{COR} term is decisive. Optimizing the structure at the HF level no minimum even exits.

The stabilization of the M5 and M6 minima originates almost completely from the ΔE^{SCF} term; the role of electron correlation is almost negligible. In both complexes there exists an electrostatic stabilization between negatively charged oxygens of H_2O or OH^- , and positively hydrogens of CH_2 or CH_3 groups.

Transition structure T1 has a positive stabilization energy due to the large positive ΔE^{SCF} term. The fact that stabilization energy is positive cannot be exaggerated. This energy is evaluated with respect to $\text{CH}_2\text{OH}_2^{+\cdot}$ and H_2O ; more appropriate dissociation product could be instead of $\text{CH}_2\text{OH}_2^{+\cdot}$, the transition state between $\text{CH}_2\text{OH}_2^{+\cdot}$ and $\text{CH}_3\text{OH}^{+\cdot}$. Use of the latter transition state as the

Table 3. Intermolecular harmonic vibrational modes (in cm^{-1}) evaluated at the MP2/3-21G*(O) level for saddle points and at the 6-31G* level for minima

System ^a	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
M1	143.3	149.2	347.0	444.4	499.8	558.2
M2	92.0	130.1	475.9	492.2	573.4	776.1
M3	82.6	114.9	302.6	437.7	498.2	–
M4	127.7	173.0	196.3	392.8	649.9	775.0
M5	64.7	90.5	160.8	180.4	297.6	316.9
M6	94.7	98.0	147.4	155.3	199.9	–
T1 ^b	125.9	153.9	304.3	537.6	605.1	621.1
T2	– 535.0	184.5	219.3	432.4	497.1	514.4
T3	– 101.9	122.2	198.9	238.1	269.2	288.4
T4	– 106.8	90.4	164.7	199.9	215.3	–

^a Cf. Fig. 1

^b Imaginary vibration mode has an intramolecular character; $\nu = -2090.1 \text{ cm}^{-1}$

dissociation product is supported by clearly intramolecular character of the imaginary vibration of T1 (cf. Table 3). In this case the stabilization energy of T1 should be negative. The important value to us is the relative height of T1 with respect to M1 and M2. Stabilization energies for T2, T3 and T4 are negative, and it is again the ΔE^{SCF} which is decisive.

Structures of hemibonded minimum M4 and transition structure T2 are rather similar what corresponds to the small energy difference between M4 and T2 (see Fig. 2). On the other hand structures of M1, M2 and T1 differ considerably what again agrees with large energy differences among M1, M2 and T1.

The BSSE values are, as expected, considerably larger with 3-21G*(O) than with 6-31G*. With some stationary points the BSSE (3-21G*(O)) values are comparable to the values of interaction energies. This is not surprising; it is known [12] that BSSE already for 3-21G basis set is large. In agreement with other conclusions of paper [12] the ΔE^{SCF} (BSSE) values are for both basis sets rather similar. This provides a support for future applications of 3-21G*(O) basis set for a study of larger cation radicals for which the use of 6-31G* basis set will be prohibitively expensive.

To demonstrate the usefulness of the 3-21G*(O) basis set we have used it for the well known complex, for the neutral water dimer. The MP2 stabilization energies evaluated with 3-21G, 3-21G*(O) and 6-311G** basis sets are 4.6, 3.6 and 4.2 kcal/mol, while the BSSE values are 7.7, 7.8 and 2.8 kcal/mol. Clearly the MP2/3-21G*(O) stabilization energy is reasonable despite the large BSSE. We would like to mention here the recent paper by Cybulski and Chalasinski [13]. On the basis of comparison of variation and perturbation interaction energies the authors [13] have concluded that there is not any overcorrection in the original function counterpoise correction by Boys and Bernardi [8].

Intermolecular harmonic vibrational modes, evaluated at the MP2/3021G*(O) level for transition states and the MP2/6-31G* level for minima are collected in Table 3. All the positive values indicate a minimum, while the one negative value gives an evidence of saddle point. Despite rather large values of stabilization energies (cf. Table 2) the values of respective intermolecular frequencies are comparable with these known for considerably weaker closed-shell H-bonded

complexes. To make the orientation easier we have calculated at the same level of sophistication (MP2/3-21G*(O)) the harmonic intermolecular frequencies for HOH...OH₂ neutral dimer as well as for the receptive cation radical. The following values (in cm⁻¹) were obtained: 143, 209, 258, 296, 555, 804; 132, 559, 674, 690, 841, 1132.

4 Conclusion

i) The six minima and the four saddle points were localized at the [CH₃OH...H₂O]⁺ P.E.S. The three deepest minima have a H-bonded character while the fourth possesses a three-electron hemibond.

ii) The barriers for interconversion are rather high for H-bonded minima, which offers a chance to detect them experimentally. The respective barrier for hemibonded structure is smaller and a chance to detect this structure is therefore lower.

iii) The qualitative picture of P.E.S. is not changed when passing from the lower, MP2/3-21G*(O), to the higher, MP2/6-31G* level. This gives us confidence to use smaller 3-21G*(O) basis set for extended cation radicals where the use of 6-31G* basis will be impracticable.

iv) The intramolecular geometry, especially the CO and OH bond lengths are sensitive to the level of calculation and at present levels they are overestimated. The relative changes of the geometry upon complexation, evaluated at MP2/6-31G* and MP2/3-21G*(O) levels, are similar. The stabilization energies are, due to the inclusion of BSSE, not too sensitive to the theoretical level and are close to the results obtained with larger basis sets.

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