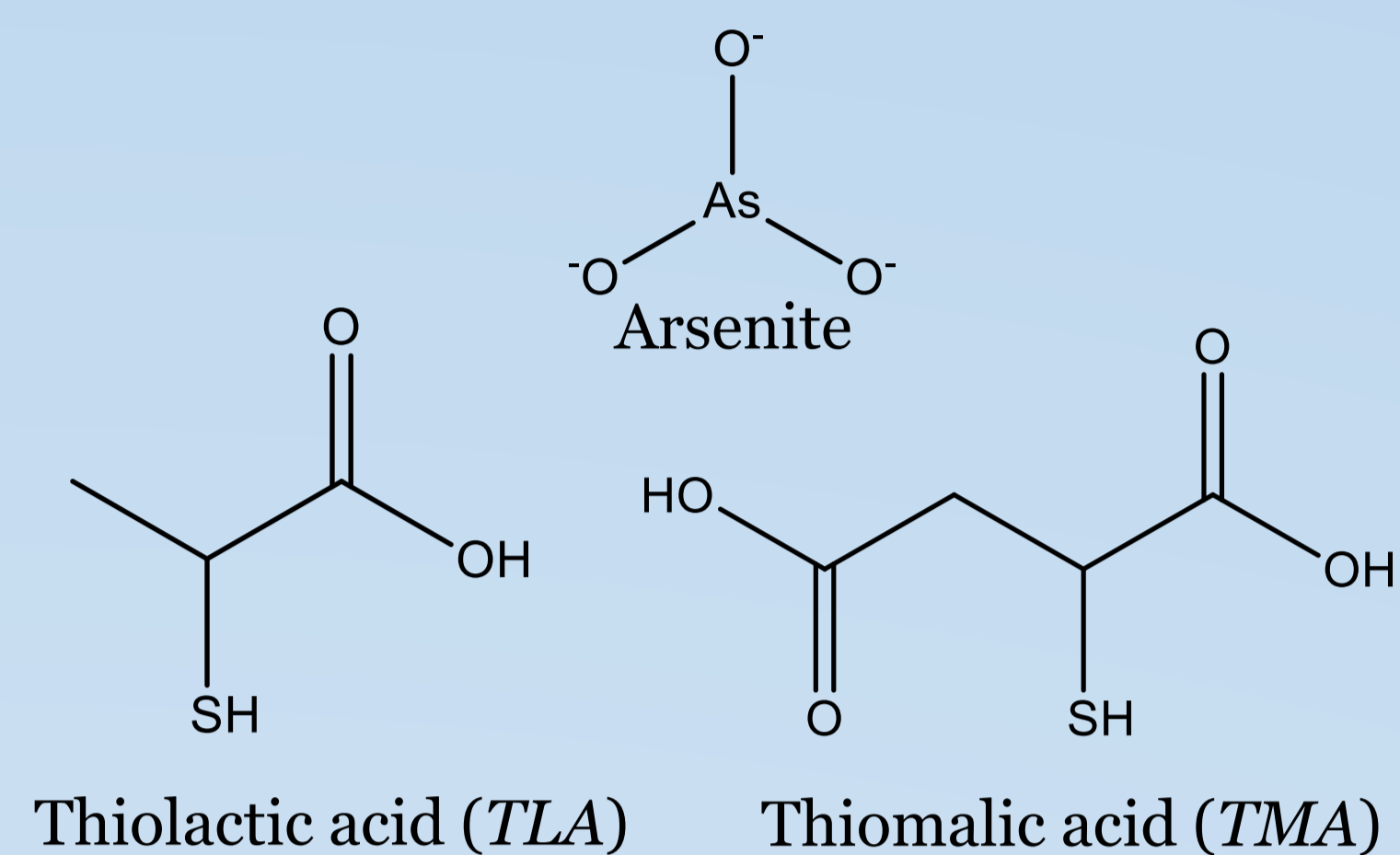


# DFT calculations and Raman spectroscopy of As(III) complexation with thiol ligands

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The extensive arsenic contamination is considered one of the most important toxicological problem [1]. Its poisonousness is mainly due to the high affinity for the sulfhydryl groups present in active biomolecules, such as enzymes and proteins [2]. The significance of the metal pollution, as well as its mobility and bioavailability, depends on arsenic speciation, which represents the distribution of the different chemical species in a given system. The study here reported was based on a previous speciation analysis on As<sup>3+</sup>-TLA and As<sup>3+</sup>-TMA systems and subsequently on Raman spectroscopic investigations combined with density functional calculations (DFT). The results obtained by means of Raman spectroscopy combined with data provided by DFT calculations give information about the molecular mechanisms of chelation of arsenic with these S-donor ligands.

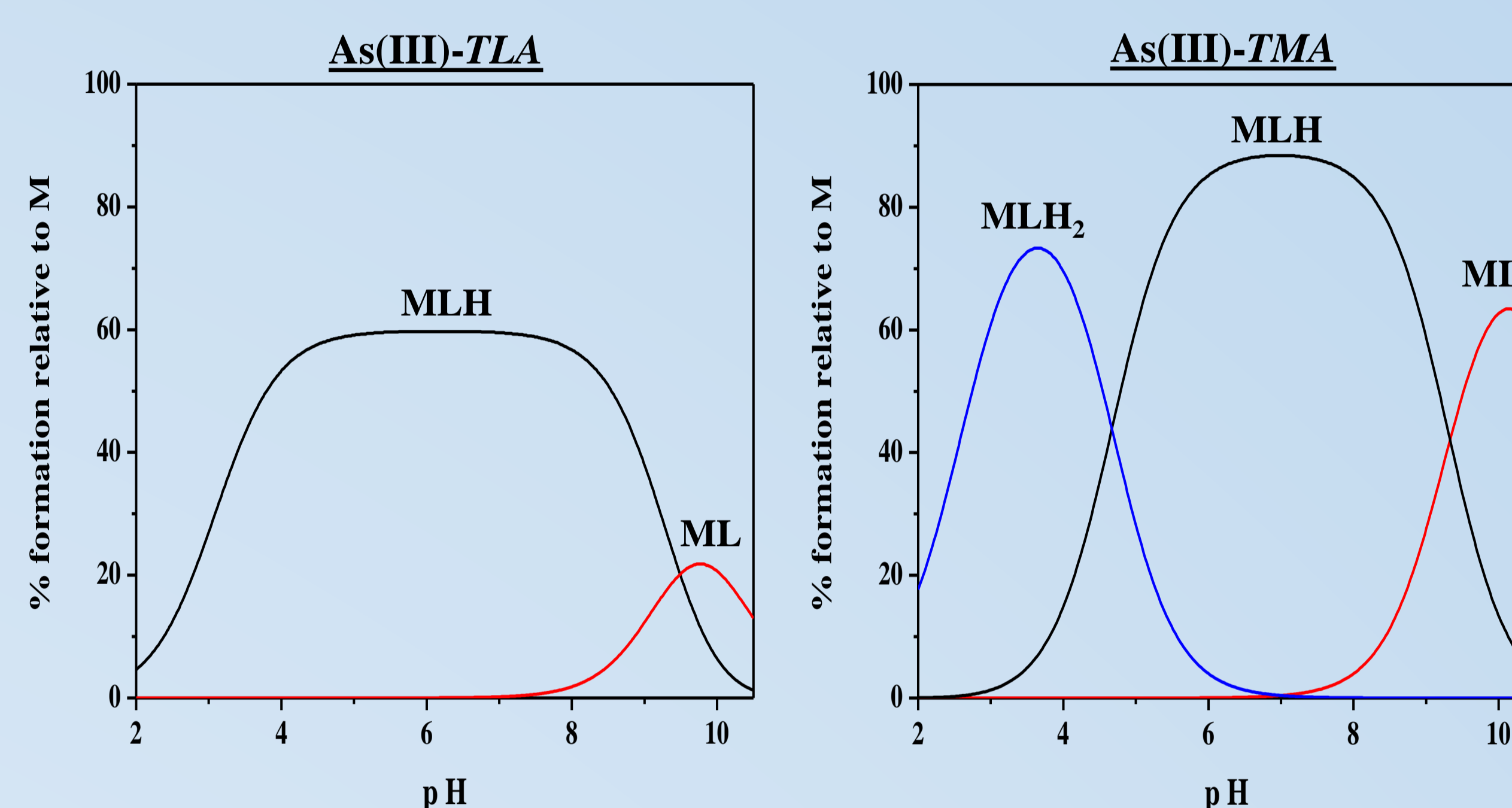
## Speciation Study

Experimental formation constant values for As(III) -TLA (L<sup>2-</sup>), -TMA (L<sup>3-</sup>) species in NaCl at  $I = 0.15 \text{ mol L}^{-1}$  and  $t = 25 \text{ }^\circ\text{C}$

Ligand	Species <sup>a)</sup>	log $\beta$
TLA	MLH	12.22±0.03 <sup>b)</sup>
	ML	2.73±0.05
TMA	MLH <sub>2</sub>	17.86±0.01
	MLH	13.19±0.02
	ML	3.86±0.03

<sup>a)</sup> according to the reaction:  $M^{3+} + qL^{z-} + rH^+ \rightleftharpoons ML_qH_r^{(3-qz+r)}$ ; <sup>b)</sup> ± standard deviation.

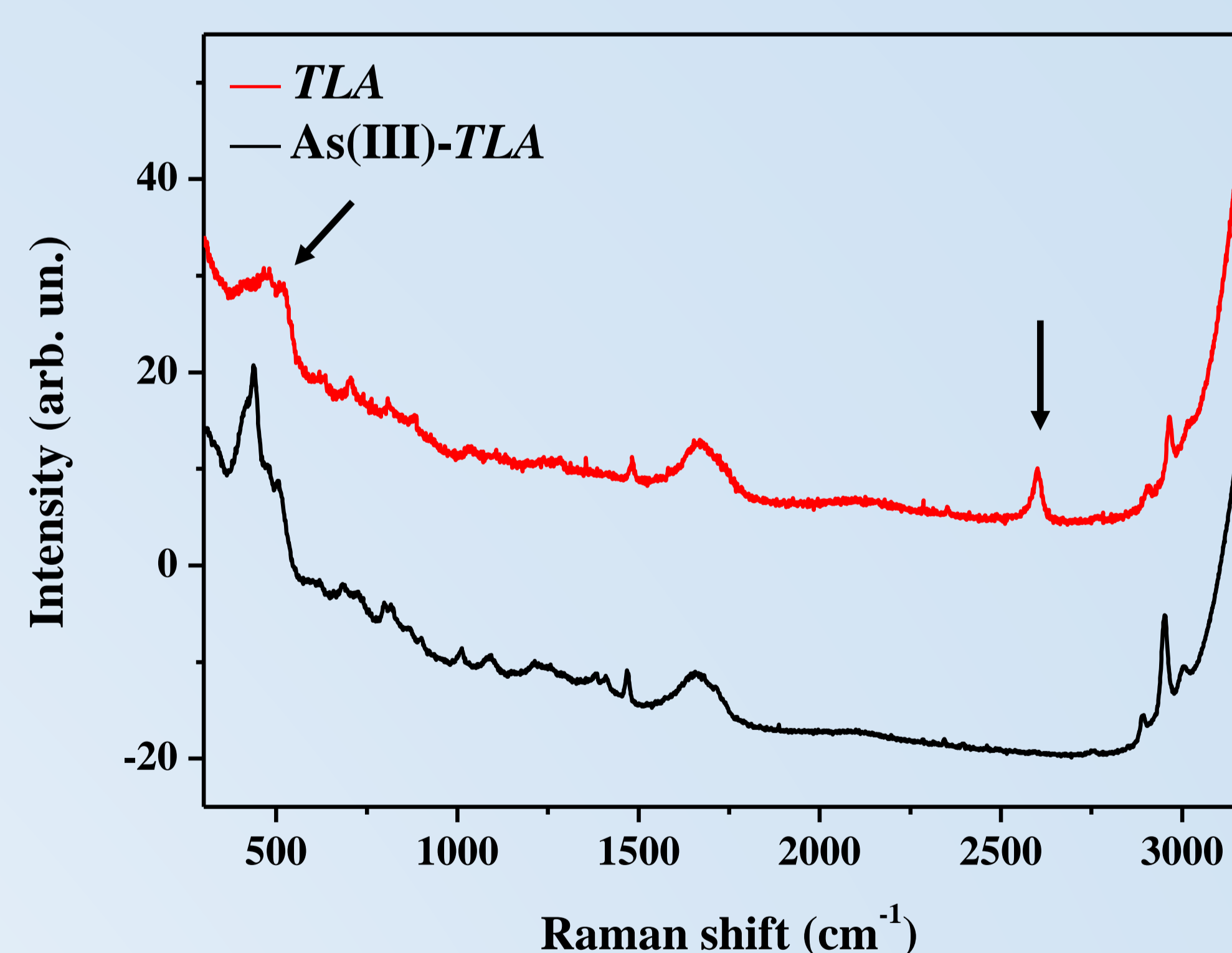
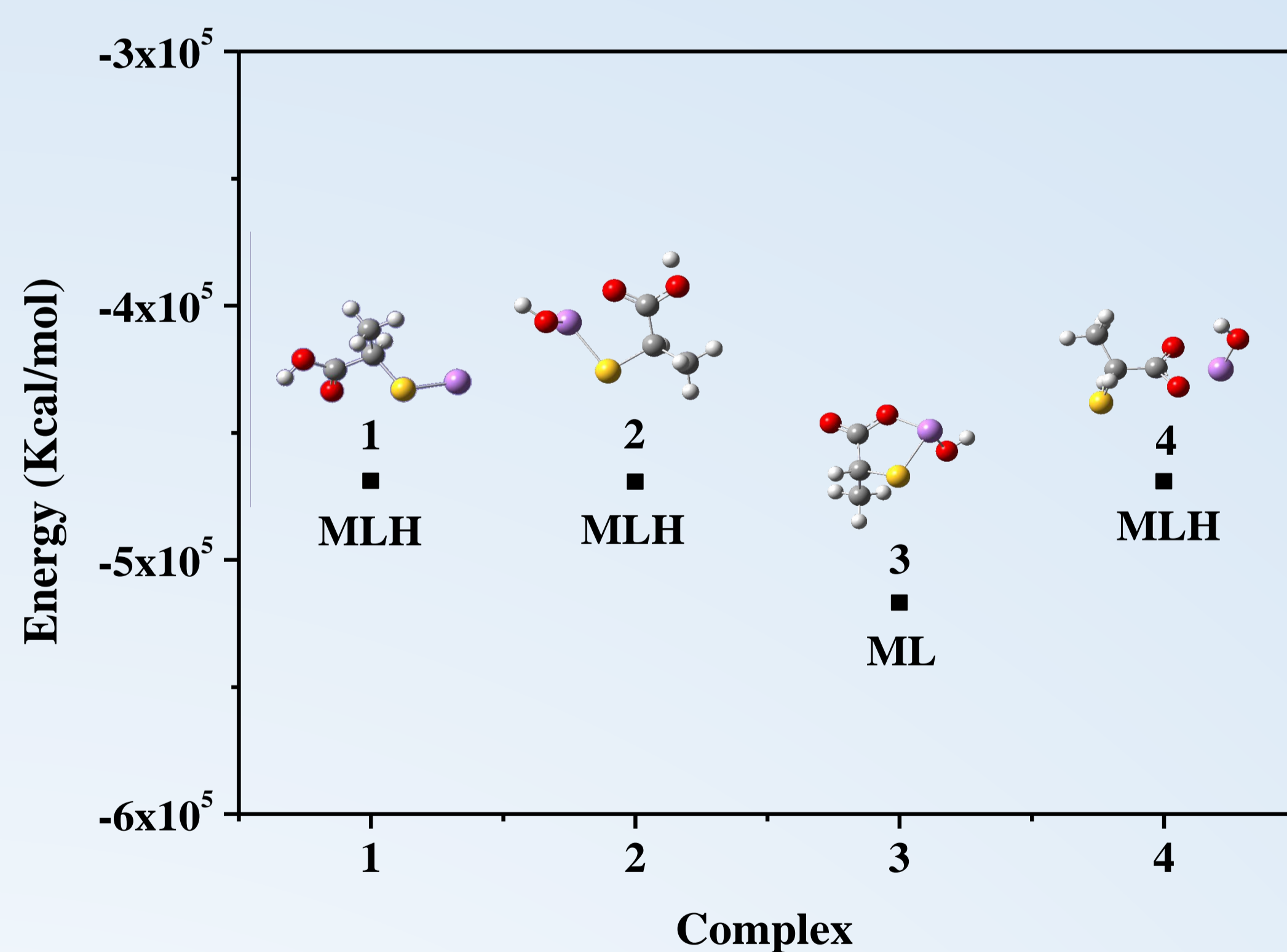
Distribution diagrams of As(III)-TLA and -TMA species vs. pH. Conditions:  $C_M = 1 \text{ mM}$ ,  $C_L = 10 \text{ mM}$ ,  $I = 0.15 \text{ mol L}^{-1}$  in NaCl,  $t = 25 \text{ }^\circ\text{C}$



Speciation study in aqueous solution achieved a key role, with the aim of examining and predicting a molecule behaviour in a natural fluid (seawaters, freshwaters, blood, plasma, etc.). This is possible by taking into account the formation equilibria of all the chemical species, thus considering acid - base properties of ligand molecules, metal hydrolysis, temperature, ionic strength, ligand-metal concentration ratio and pH. Experimental potentiometric data were collected by varying the pH (from 2 to 10.5) and the  $C_M/C_L$  ratio (from 0.3 to 2) in order to promote the eventual formation of species with different stoichiometry. For each system, the speciation model was selected on the basis of several criteria, such as the best fit between experimental and calculated curves, simplicity, probability and species formation percentages.

## DFT Study and Raman spectroscopy

### As(III)-TLA system

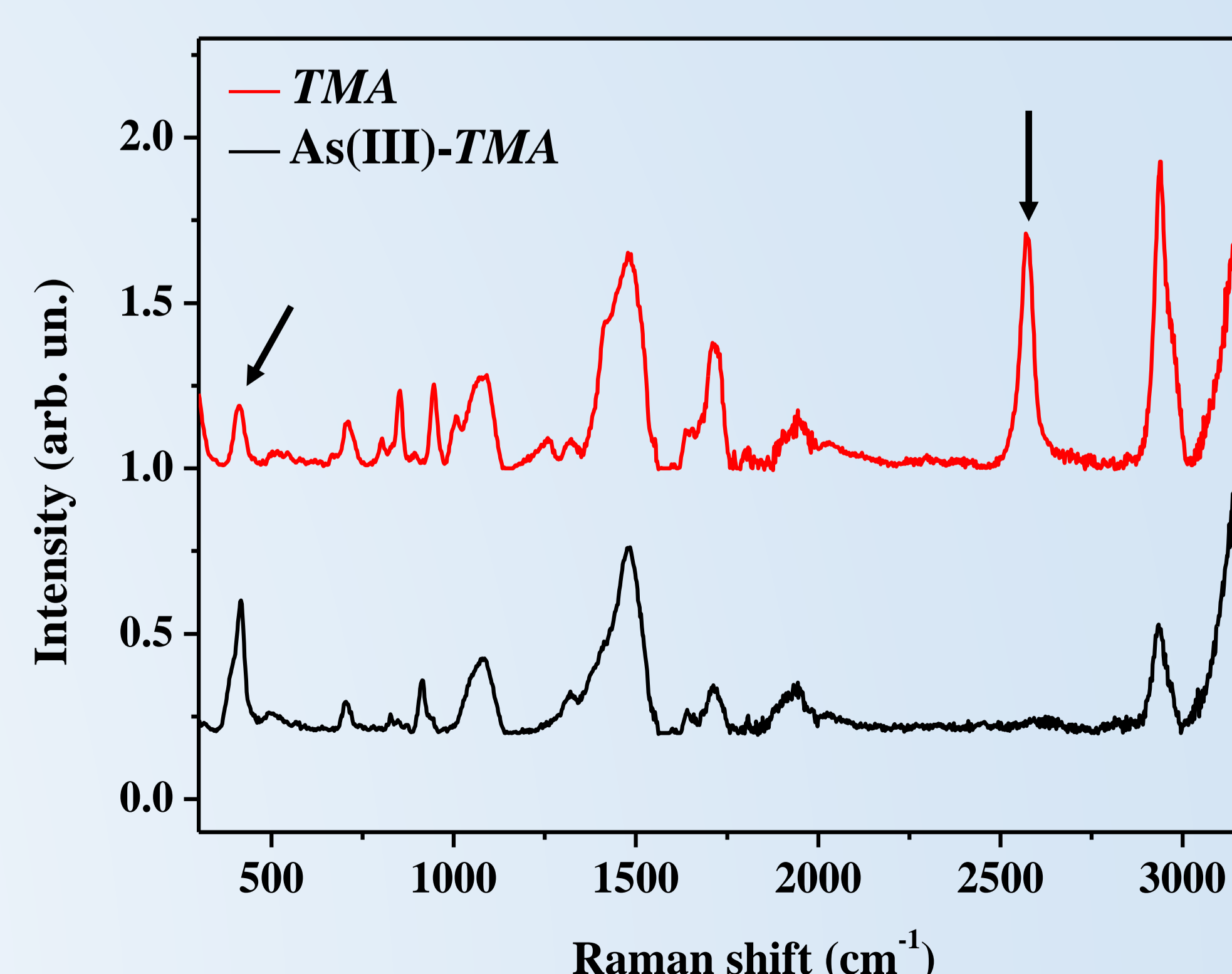
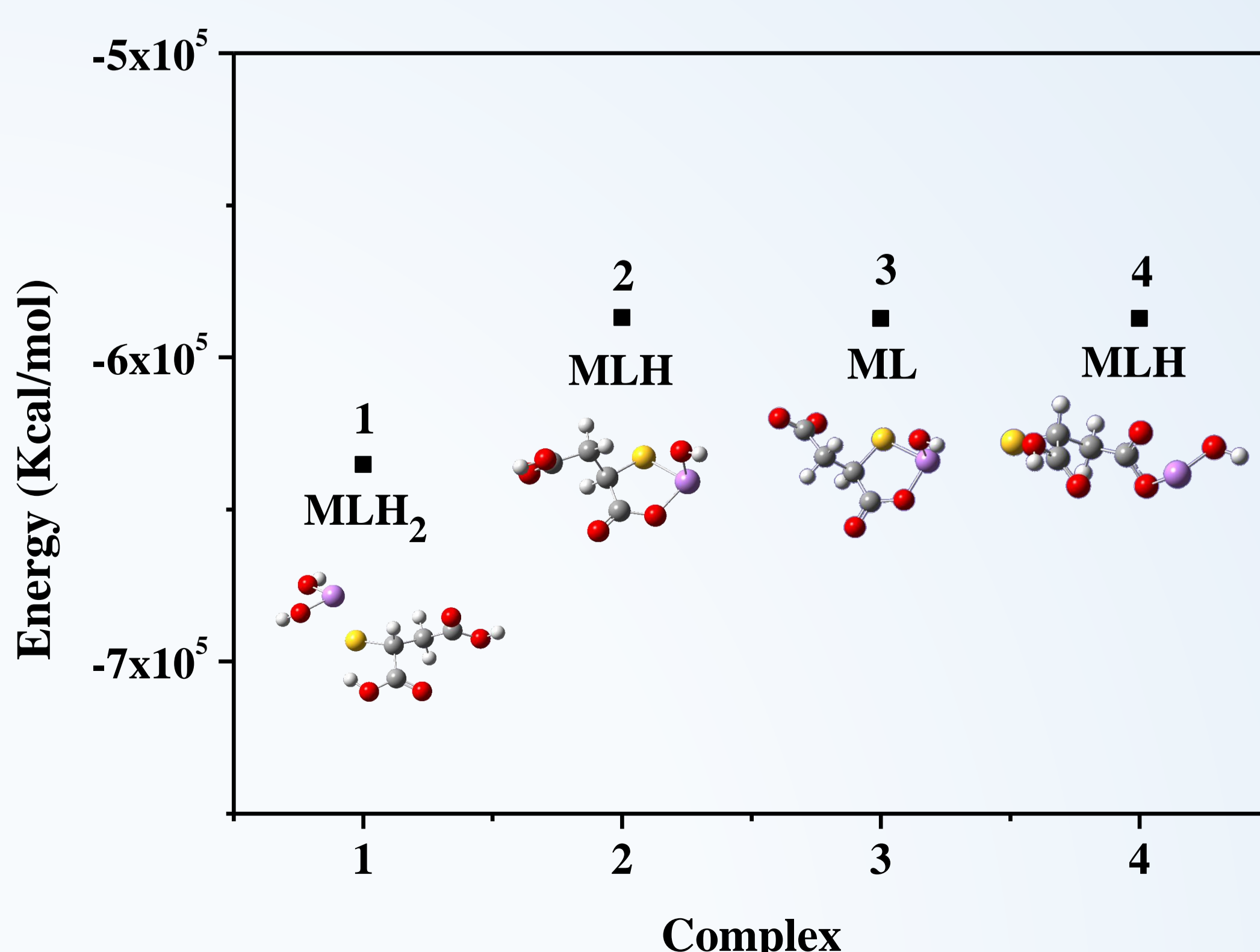


Raman spectroscopy studies were performed to confirm the complex formation and to obtain information about the way of ligand chelation towards Arsenite. More in detail, these investigations allowed to understand which ligand-chelating group played a key role in the metal - ligand complexation.

The figures show the comparison between the Raman spectrum obtained on a free ligand solution ( $C_L = 300 \text{ mmol L}^{-1}$ ) and the one recorded for a metal - ligand containing solution, with a M:L ratio of 1:2 ( $C_M = 0.15 \text{ M}$  and  $C_L = 0.3 \text{ M}$ ). As it can be observed, the signal relative to the stretching of the S-H bond ( $\sim 2600 \text{ cm}^{-1}$ ), is not visible in the spectrum collected on the As(III)-L solutions. Moreover, an increase in intensity of the band at  $\sim 400 \text{ cm}^{-1}$  is observed in the spectrum of the As (III) - ligands systems, probably due to the metal interaction with the sulfur of the thiol group present on the given ligand. In the light of these considerations, it is possible to assert that SH group plays a key role in the complexation of arsenite.

DFT studies, as shown in the graphs alongside, provide an energetic study on the different possible complexes, showing which is the most stable in energy and therefore the one favored.

### As(III)-TMA system



## References

- [1] B.K. Mandal, K.T. Suzuki. *Talanta*, (2002), **58**, 201.
- [2] T. Kaise, et al. *J. Food, Hygien. Soc. Jpn.* (1996), **37**, 135.