The bees killer imidacloprid insecticide: a vibrational characterization

Antônio A. G. Moreira[1](PG); Pedro de Lima-Neto[1]* (PQ); Valder N. Freire[2](PQ)

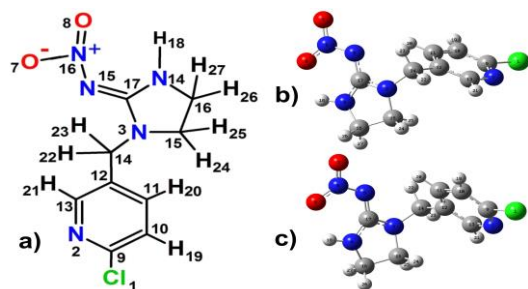[1]*Analytical and Physical-Chemistry Department, Federal University of Ceará – Fortaleza, Brazil.*
[2]*Physics Department, Federal University of Ceará – Fortaleza, Brazil.*
Keywords: *Vibrational spectra, Imidacloprid, Raman, Infrared, DFT, Insecticide*

Introduction

Imidacloprid (Fig. 1) is the most used insecticide in the world, being responsible for the Colony Collapse Disorder syndrome (CCD), which is affecting the honey bees (*Apis melífera*) colonies[1,2]. However, this compound is not well characterized in term of its vibrational properties. Here we present imidacloprid IR and Raman measurements (E) in powder from Sigma-Aldrich; the vibrational modes are assigned through state of the art density functional theory calculations, Gaussian 09 package, basis set 6-311++G(d,p), M06-2X functional within the vacuum (V) and PCM model (P) framework. The most stable conformers were obtained scanning the dihedrals C11C12C14N3 and C17N3C14C12 in 30º steps, after which a structure optimization was performed and used for IR and Raman calculations of the harmonic frequencies. The DFT results P and V are in very good agreement with the measurements.

Fig. 1 - Imidacloprid: (a) its planar structure; (b) its converged PCM and (c) vacuum structures.

Results and Discussion

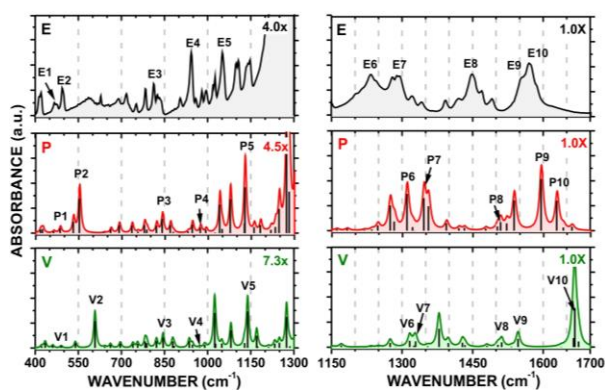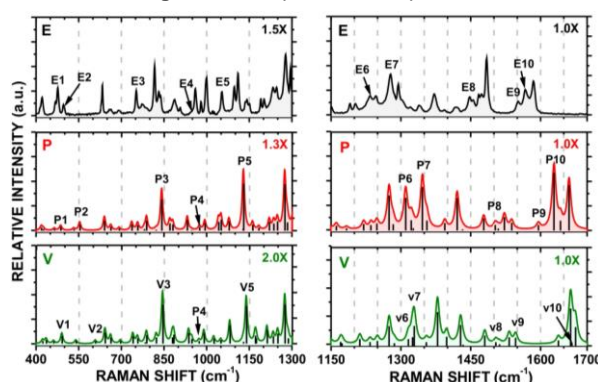**Fig.2** - Imidacloprid Infrared spectra.

Fig. 2 and 3 depicts ten of the most important imidaclopride vibrational modes, whose assignments are in Table 1. Most of the Cl vibrational modes are below 400 cm^{-1} (not shown here) due to its heavier atomic mass. In the small wavenumber region, the most important mode is E2, which is due to a N4H18 deformation; in the mean wavenumber region, the stronger modes are E3, E4, and E5, which are assigned as ring modes; in the high wavenumber region, there are five important modes E6-E10 – see assigments in Table 1.

Fig.3- Imidacloprid Raman spectra.

Tab. 1- Imidacloprid vibrational modes assignment.

Mode	ω_E (cm^{-1})	ω_P (cm^{-1})	ω_V (cm^{-1})	Assignment
1	467	486	490	βN3C14C17
2	493	553	608	δN4H18
3	818	842	845	CCC in-pl. ben.6a*
4	943	975	973	CH out-of-pl.tri-5*
5	1052	1129	1139	CCC tri.ben.12*
6	1232	1310	1316	βN4C17H18
7	1289	1346	1329	βN4C17H18
8	1449	1509	1512	CH in-pl.ben.3*
9	1551	1596	1547	νaO7O8N6
10	1571	1629	1667	νaN3N4N5C17

δ=deformation; ν=stretching; a=asymmetric; β=bending; * benzene ring naming.

Conclusion

The agreement of the calculations within the PCM level is better than in vacuum, reflecting the existence of few quantity of water molecules in the imidacloprid powder. Improvement of the results will be obtained considering DFT calculations in imidacloprid crystals.

Acknowledgment

[1]B. P. Oldroyd. *PloS Biol*. **2007**, 5, 168.
[2]M. Henry et all. *Science*. **2012**, 336, 348.