

Vibrational Spectra of Thiametoxam: Experimental and DFT studies

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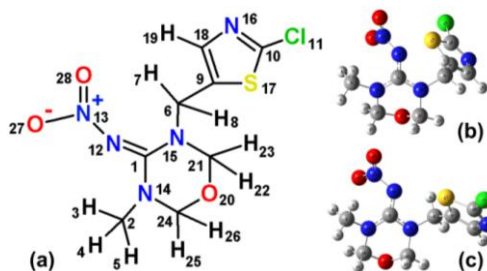
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Introduction

Neonicotinoids are insecticides that have structures similar to nicotine. They interact with nicotinic acetylcholine receptors (nAChR)¹ of mammals and insects. Thiametoxam (Fig.1) is a representative of the second-generation pesticide class. However, it is toxic for mammals and, therefore, it is relevant to know its chemical structure in order to study its interaction with nAChR. Here, we have measured the IR and Raman spectra of thiametoxam powder (Sigma-Aldrich) for the sake of comparison with first principles computations.

Fig. 1 - (a) Planar structure, (b) converged PCM, and (c) vacuum structures of thiametoxam.

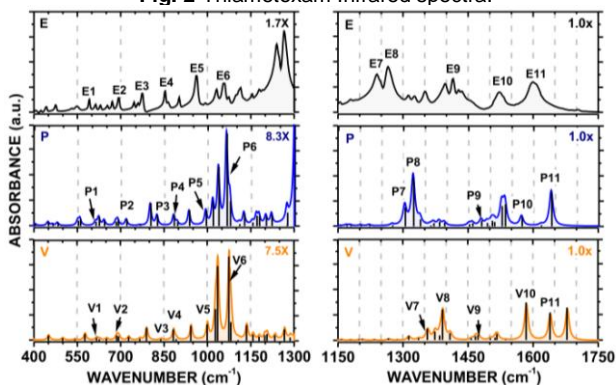


Density functional theory (DFT) calculations were performed with the Gaussian 09 package, basis set 6-311++G(d,p), M06-2X functional with vacuum (V) and PCM (P) modeling. The most stable conformers were obtained by scanning the C18C9C6N15 and C9C6N15C1 dihedrals in 30° steps, which was followed by structure optimization and infrared and Raman harmonic frequencies calculation.

Results and Discussion

Fig. 2 and 3 show eleven of the most important thiametoxam vibrational modes, whose assignments

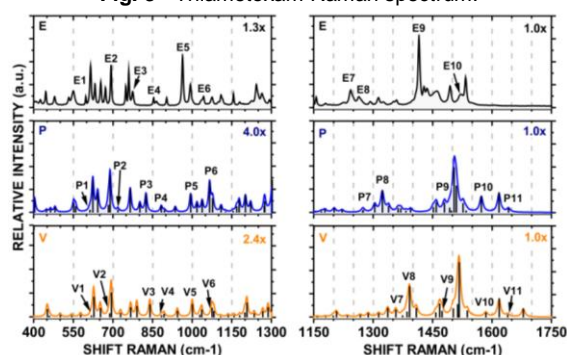
Fig. 2-Thiametoxam Infrared spectra.



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are in Table 1, which shows clearly that the PCM frequencies are close to the experimental ones than the vacuum calculated. The CI vibration modes in the wavenumber depicted region are P1, P6 in PCM and V1, V6 in vacuum which are due to, respectively, a S17C916C10C11 torsion and a S17C10C11 stretching.

Fig. 3 - Thiametoxam Raman spectrum.



In the small wavenumber region, the most important mode is E2, which is due to a N14C1C2C24 out-of-plane vibration. In the median wavenumber region, the stronger modes E3, E4, and E5 are due to torsions and stretchings of the six member ring, while E6 is due to the stretching of the five members ring. In the high wavenumber region, there are four important modes, E7-E10, being E8 the most intense, which is assigned to a stretching of the nitro group - see Table 1.

Tab. 1 - Thiametoxam vibrational modes assignments.

Mode	ω_E (cm ⁻¹)	ω_P (cm ⁻¹)	ω_V (cm ⁻¹)	Assignment
1	592	613	617	τS17C916C10C11
2	693	719	687	φN14C1C2C24
3	775	825	840	τN15N14C1C21
4	853	883	893	νS114C1C24
5	962	994	1000	νN12N14C1C24
6	1059	1066	1075	νS17C10C11
7	1240	1304	1357	νN16C18
8	1264	1323	1392	νaO27O28N13N12
9	1415	1480	1473	βC6H7H8
10	1523	1573	1584	νN12N15C1
11	1599	1642	1679	νN14N15C1

v=stretching; φ=out-of-plane; β=bending; a=asymmetric; τ=torsion.

Conclusion

As measured thiametoxam vibrational bands were identified/explained through DFT computations. A better measurement-calculation agreement was obtained within the PCM modelling framework.

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¹ J. P. Cerón-Carrasco, *J. Phy. Chem.* **2013**, 117, 3944.

² P. Maiefisch *et al.*, *Pest Manage. Sc.* **2001**, 57, 165.