

## PICVib: An Accurate, Fast and Simple Procedure to Investigate Selected Vibrational Modes at High Theoretical Levels

Marcus Vinicius Pereira dos Santos<sup>a</sup> (PQ), Yaicel G. Proenza<sup>b</sup> (PG), Eduardo C. Aguiar<sup>b</sup> (PQ), João Bosco P. da Silva<sup>b</sup> (PQ), Ricardo Luiz Longo<sup>b</sup> (PQ)

<sup>a</sup>Centro Acadêmico do Agreste, Universidade Federal de Pernambuco

<sup>b</sup>Departamento de Química Fundamental, Universidade Federal de Pernambuco

Keywords: energy only, normal modes, frequencies, high level *ab initio*, large molecules, DFT, MP2, CCSD(T), vibration.

### INTRODUCTION

Vibrational spectroscopy is a well-known technique for structural characterization and quantitative analysis. From the theoretical point of view, the development of analytical gradients and Hessians for electronic structure methods has enabled the application of these methods to a wide range of molecular systems. However, the computational demand (RAM memory, hard disks access and CPU time) for calculating the Hessian matrix is very high compared to the geometry optimization and has become the source of frustration for studying systems at higher levels or studying large systems.

Hence, we have devised an alternative procedure denoted PICVib<sup>1</sup> (Procedure for Investigating Categories of Vibrations) that computes the vibrational normal modes at higher theoretical levels using energy only (single-point) calculations.

### METHODS

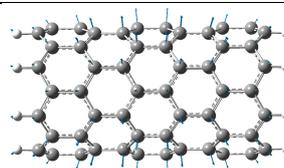
This procedure was applied to a wide class of molecular systems and vibrational modes using computational methods ranging from semiempirical to high level *ab initio* such as CCSD(T). All calculations were performed with ACESIII, CFOUR and Gaussian 09 programs.

### RESULTS AND DISCUSSION

To illustrate the PICVib results, we predicted the radial breathing mode (RBM, Figure 1) vibrational frequencies of three (8,0) single wall carbon nanotubes (SWCNTs): pristine, C<sub>2</sub>H<sub>2</sub>@NT and HCN@NT. RBM frequencies are useful for (*n,m*) assignments<sup>1</sup>. In Table 1, we present the vibrational frequency and the percentage difference in relation to the analytical calculation in parenthesis. It can be seen good agreement between the analytical and PICVib calculated values for all SWCNTs.

**Table 1.** Vibrational frequencies (cm<sup>-1</sup>) of the RBM for pristine SWCNTs, with C<sub>2</sub>H<sub>2</sub> (C<sub>2</sub>H<sub>2</sub>@NT) and HCN (HCN@NT) molecules inside its cavity at B3LYP/6-31G(d):AM1 level.

Pristine	C <sub>2</sub> H <sub>2</sub> @NT	HCN@NT
370 (+0.5)	371 (-0.5)	373 (0.0)



**Figure 1.** RBM Mode of pristine (8,0) SWCNTs.

Noteworthy that using PICVib, only one normal mode (RBM) was calculated, instead of 330 modes (in pristine case) in traditional calculation.

### CONCLUSIONS

The PICVib has an excellent performance (errors smaller than ca. 0.5%), at only a small fraction of the computational demand required for a complete analytical calculation of the vibrational frequencies. The approach is quite general because it can use practically any quantum chemical program and electronic structure method. In addition, it has been generalized for infrared intensities.<sup>2</sup>

### ACKNOWLEDGMENTS

The authors would like to thank the SINAPAD, FACEPE, CAPES and CNPq for the grant and scholarships.

<sup>1</sup> M. V. P. D. Santos et al., *J. Comput. Chem.*, 34, 611–621, 2013.

<sup>2</sup> M. V. P. D. Santos et al., *Phys. Chem. Chem. Phys.*, 16, 17670–17680 (2014).