A GENERAL AUTOMATED AND USER-FRIENDLY TOOL FOR THE ACCURATE SIMULATION OF VIBRATIONAL SPECTRA[*]

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In this work the basic theory and computational strategies for the simulation of the vibrational spectra at the full anharmonic level using the vibrational perturbative (VPT2) approach will be first reported. Then, the Virtual Spectroscopic Laboratory (VSL) software package, a program recently developed in order to assist the interpretation of the vibrational spectra using graphical and user-friendly tools will be presented.

Nowadays computer science and computational methodologies provide increasingly powerful tools to assist the research, in both industrial and scientific chemical investigation fields. In fact, as far as the complexity of the molecular systems under study increases, the combination of experimental and computational methodologies is often required for a complete understanding of the phenomena and for the development of new technological applications. The computer simulations can be also used in the first stages of the research in order to obtain useful suggestions at a relatively low budget, being feasible and affordable for small and medium size enterprises. In such a scenario the combination of different know-how and competences plays a fundamental role and the data sharing between people with different scientific backgrounds is a key step for the development of effective and synergic research strategies and for the transferability of the knowledge.

Among the different areas, this point is extremely important especially when spectroscopic processes are under study. In fact, from one side the spectroscopic techniques are very useful and largely employed in many fields, ranging from the most subtle scientific investigations, to the routine chemical analysis required by the characterization of the products of a synthetic procedure. From the other side the spectroscopic processes are quite difficult to be studied, due to the intricate underlying theoretical background and to the complexity of the chemical-physical effects contributing to the spectral signal. Even in the case of small molecules in the gas-phase[1,2,3,4,5], the interaction between the species in the sample can be rather complex, and can strongly affect the features of the spectra. Analogously, the spectra of flexible molecules can be composed by separate contributions originating from the different conformers, thus increasing the difficulty of interpretation[4,5]. An additional source of complexity originates from environmental

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effects, such as the interaction between the sample and the solvent[6,7] or the matrix medium[5]. In such circumstances, *in silico* modeling is an unvaluable tool in order to assist the interpretation of the experimental measurements. In order to integrate the specialistic knowledge of the scientists working on the simulation and the analysis of the spectra, with the simplicity required by the communication of the results to a wider community, in the past years we followed two main guidelines. The first one is the development of computational approaches for the simulation of vibrational spectra aiming to produce reliable and robust scientific codes for the calculation of the relevant spectroscopic quantities[8]. The second one is the integration of such codes in user-friendly software packages, able to visualize in an intuitive way the results of the calculations, allowing the comprehension of the numerical data also by a non-specialistic audience. Our target is to encourage the communication between people with different backgrounds, increasing the interconnection between different areas and allowing an easy and fast sharing of the results, which is often a critical point in the scientific research.

The simulation of vibrational spectra requires the solution of the complete (electronic and nuclear) Schrödinger equation for polyatomic molecules, and the treatment of the light-matter interaction in an effective way, in order to determine the position and intensities of the peaks, respectively[9,10,11,12,13,14,15]. Although both time-dependent and time-independent routes have been proposed to this end[11]. we will refer only to time-independent approaches in view of their efficiency and ease of use. Within the Born-Oppenheimer approximation, the electronic problem is first solved, and then the nuclear motion is treated in the force field generated by the electrons, which is usually referred to as the intramolecular potential (V). The intramolecular potential is usually represented as a fourth-order Taylor expansion on the normal coordinates[8,12,16,17,18,,19,20,21,22] (**q**) of the type[10,11,18]:

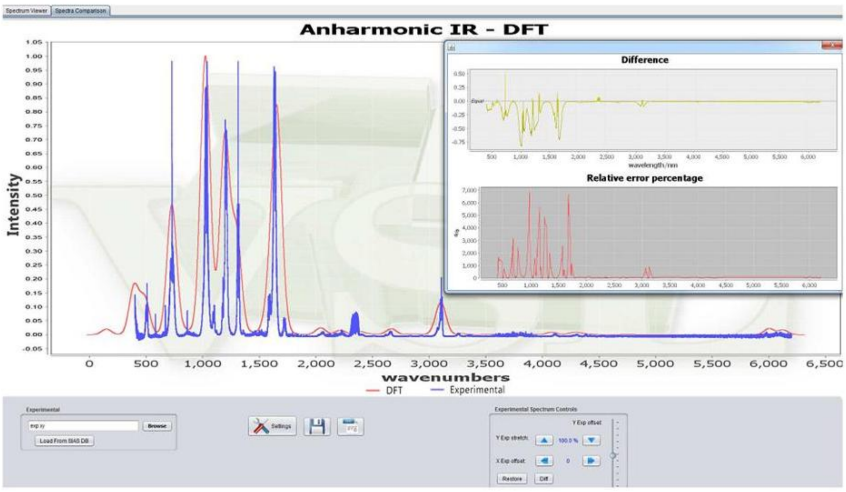
$$V = \frac{1}{2}\sum_{i}^{3N-6} \omega_i\, q_i^2 + \frac{1}{6}\sum_{ijk}^{3N-6} k_{ijkq_iq_jq_k} + \frac{1}{24}\sum_{ijkl}^{3N-6} k_{ijkl} q_i q_j q_k q_l$$

and the numerical evaluation of the third (k_{ijk}) and fourth (k_{ijkl}) derivatives of the PES is required. Such a representation is especially suitable for small amplitude vibrations, and many methods are currently available for the accurate evaluation of the derivatives. Approaches based on the post Hartree-Fock theories are usually the methods of election when the accuracy of the results is a mandatory priority, and a quantitative agreement with the experimental measurements is nearly always obtained[20,23,24,25,26,27], provided that correlation and basis set completeness are taken into account in a proper and balanced way. Approximate approaches based on the Møller-Plesset[28] Density Functional Theory (DFT) or semi-empirical methods, must be employed in the case of larger systems. A particularly effective scheme is obtained when the PES at the DFT level is computed, employing hybrid (especially B3LYP[29]) or double-hybrid (especially B2PLYP[30,31,32]) functionals with medium-size (double- or triple-ζ , polarization augmented) basis sets[8,33,34,35,36]. Hybrid force fields based on the use of two different methods, one - more accurate - for the evaluation of the harmonic part, the other - less computationally demanding - for the calculation of the higher order derivatives can be also used[33-35,37,38,39,40,41]. Once the intramolecular potential is defined, the corresponding vibrational Schrödinger equation is solved

$$\left[-\frac{1}{2}\sum_{i}^{3N-6}\frac{\partial^2}{\partial q_i^2} + V(\boldsymbol{q})\right]|\Psi\rangle = E|\Psi\rangle$$

in order to obtain the vibrational wavefunction and energies, from which the frequencies and intensities of the spectrum can be computed. The vibrational second-order perturbation theory (VPT2[10,11,18]) is a well stated robust and reliable approach[8,26,35,42] which can be used to this aim, also in view of the recent development and implementation of automatic and system-independent schemes[18-20,43] able to treat the singularities that usually affect the perturbative approaches. Also an approximate version of VPT2, the Reduced Dimensionality VPT2 (RD-VPT2[44,45]), has been developed, in order to compute vibrational anharmonic spectra for large systems. Such an approach allows to focus the calculations on a selected frequency range of the IR spectrum, evaluating only the necessary derivatives and avoiding the calculation of the full k_{ijk} and k_{ijkl} matrices, and it was successfully applied for the interpretation of the HREEL spectrum of the glycine molecule adsorbed on the (100) Silicon surface[44,45].

Due to the high accuracy of the results obtained using the VPT2 approach, we integrated the code for the calculation of vibrational properties in a general purpose and user-friendly program, the Virtual Spectroscopic Laboratory (VSL) software package[46]. VSL is an application which guides the user to the interpretation and analysis of a number of different spectroscopic observables[47,48], providing an integrated environment able to easily handle and visualize the results of the calculations. In fact, most of the quantum-chemical packages usually provide vibrational frequencies and the infrared intensities as two separate quantities. The VSL code automatically performs the convolution of the stick spectrum using a pre-defined convolution function, usually Gaussian or Lorentzian with arbitrary full width at half maximum. Furthermore such a feature can be combined with the possibility to import digitized experimental spectra and to superimpose different spectra in one window, allowing an easy comparison between simulated and experimental spectra and between spectra related to different molecules or different conformers of a molecule. In Fig. 1 the infrared spectrum of the *cis*-CHFCHI molecule is shown, as computed at the full anharmonic level using the VPT2 approach in conjunction with the B3LYP/SNSD force field and as experimentally measured[33].



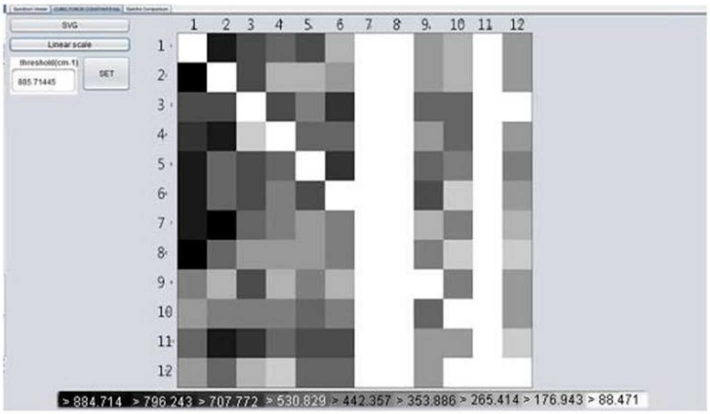
exp.xy

Y Exp stretch: 100.0 %

X Exp offset: 0

Fig. 1 - Experimental and simulated (B3LYP/SNSD) Infrared spectrum of cis-CHFCHI, as visualized in a working window of the VSL package

One important point when the vibrational anharmonic spectra are analysed, is the magnitude of the contribution of the third and fourth derivatives of the potential (see Eq. 1) to the vibrational frequencies. Such a contribution is usually described through the anharmonic matrices, in which the Coriolis, 3rd and 4th derivatives contributions are included. The analysis of such matrices plays a primary role when the approximate RD-VPT2 approach is applied or when hybrid force fields are employed. In the VSL program a specific feature assisting the analysis of such matrices with a graphical tool has been integrated. In Fig. 2 the semidiagonal matrix of the kiij force constants (see Eq. 1), is graphically represented for the cis-CHFCHI molecule and the most coupled vibrations are highlighted by a darker colour.



threshold(cm-1) 885.71445

Fig. 2 - Graphical representation of the semi-diagonal matrix of the k_{iij} *force constants, for the cis-CHFCHI molecule, visualized using the VSL package*

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