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Advantages and Drawbacks of Quantum Mechanical Static and Dynamic Approaches to Modelling Infrared Spectra[†]

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We present quantum mechanical vibrational computations beyond the harmonic approximation from effective second order perturbative and variation perturbation treatments defined as static approaches, as well as vibrational analysis from density functional theory molecular dynamics trajectories at 300 and 600 K. The four schemes are compared in terms of prediction of fundamental transitions, and simulation of the corresponding medium infrared spectrum at the same level of theory using the B3LYP/6-31+G(d,p) description of the electronic structure. We summarize conclusions about advantages and drawbacks of these two approaches and report the main results obtained for semi-rigid and flexible molecules.

Key words: Anharmonic vibrations, Vibrational configuration interaction, Perturbative approach, *Ab initio* molecular dynamic treatment

I. INTRODUCTION

Vibrational spectroscopies (infrared and Raman) provide fundamental informations about the structure of a given chemical system, often including the effects of its close chemical environment [1]. Nevertheless, the interpretation (band assignment) of an experimental spectrum is not trivial or straightforward, since multiple effects (for instance, anharmonicity, overtones, combinations band, and environmental effects) can play a relevant and intermingled role. As in the case of other spectroscopic investigations (such as UV-Vis, NMR or EPR), theoretical approaches provide useful tools to complement the experimental information. In this context, the computation of harmonic force fields by quantum mechanical methods has provided an invaluable aid due to the development of more and more reliable computational methods [2]. Currently, harmonic vibrational frequencies can be straightforwardly determined for isolated molecules, condensed phases or solid state systems. The discrepancy with respect to the experimental data, arising from both methodological errors and the lack of anharmonicity treatment, can be then reduced by introducing suitable scaling factors [3].

Furthermore several models have been developed and implemented to explicitly take into account anharmonicity. In particular, for small molecules converged rovibrational levels can be obtained by fully variational

treatments, as the vibrational configuration interaction (VCI) method [4-7]. However, to treat large systems it becomes unavoidable to introduce some approximations concerning both the form of the potential and the rovibrational treatment. Recently, the most successful approaches are based on truncated three-mode potentials. A perturbative approach (VPT2) often is proposed to solve the vibrational problem. Easy to implement and fast this treatment which presents numerical instabilities due to the presence of random degeneracy can be improved by tacking into account these latter through a variational scheme (VPT2-D) [8]. The vibrational self-consistent field approach (VSCF), although less accurate, is found to be the most stable with respect to the small variations of the potential energy and it also provides the anharmonic part of the vibrational energies with a relatively low computational effort. An alternative approach to overcome the size problem, is to consider a VCI method where a smaller CI matrix is built with the most relevant configurations estimated by a PT2 procedure [9]. This CI guessed by a perturbative treatment will be denoted as variation-perturbation (VCI-P). A second issue consists to build the vibrational Hamiltonian over several spectral areas, each called a "window", in parallelizing the corresponding algorithm. This method, called variational multiwindows configuration interaction P-VMWCI [10,11] and just recently proposed is known to give the same results as that the vibrational mean field configuration interaction VMFCI [10] treatment .

As matter of fact, such well-tested approaches, when coupled to reliable electronic structure calculations, allow for very accurate treatment of the vibrational problem, leading to typical errors of just a few tenths

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of wavenumber with respect to experimental data. Such vibrational approaches give rise to a well-defined methodological hierarchy where the numerical performances are systematically improved in going from one method to another (VSCF<VPT2<<VCI-P=VCI). This ladder resembles the similar order obtained for electronic methods (SCF<MBPT2<CI) and, in similar manner, VCI or VCI-P results can be considered as reference values, as it is often done with electronic CI results, in absence of experimental information.

Furthermore, when electronic structure methods such as density functional theory (DFT) are considered, the vibrational calculations of relatively large systems (up to 60 atoms) become feasible. As matter of fact, such vibrational approaches provide accurate predictions of band origin already with medium size polarized basis sets and without any ad hoc scaling.

Beside these static approaches, vibrational spectra can be calculated in an alternative way using dynamic approaches and statistical mechanic models based on the Fourier transform analysis of the time correlation function of atomic velocities or dipole moments. These approaches in principle yield a full description of the modes activated at a given temperature and naturally describe their coupling and anharmonicity, that is they practically allow for the complete description of the spectral properties. Indeed, for chemically interesting (i.e. large) systems the potential energy surface considered for molecular dynamics (MD) approaches is computed at classical mechanics level since a full quantum (i.e. nuclear and electronic) treatment is often unfeasible due to the size of the systems considered. Although several different quantum corrections to the classical time-correlation functions have been proposed, they do not affect the calculated frequencies but only the shape and width of the bands [12].

The aim of this work is to compare the advantages and the drawbacks of QM static and MD approaches for the calculation of medium infrared red (MIR) spectra when using the same level of theory, i.e the same electronic Hamiltonian and the same basis set.

In this work, DFT has been applied for the description of the electronic structure using the very popular Becke three parameter hybrid functional (B3LYP) [13] and a localized Gaussian type basis set. At this level of theory, we discuss also the results previously obtained using two different static approaches, namely the VPT2 and VCI-P treatments, and a DFT MD approach based on the propagation of the density matrix [14-16] for semi-rigid H₂CN [17] and flexible systems NH₂CHO [18], NH₂CHCOOH [19].

After a brief description of the computational methods applied, the main results will be discussed and compared.

II. COMPUTATIONAL DETAILS

Structural optimization, harmonic frequencies, and IR intensities, anharmonic frequencies issuing from second order perturbative approach and *ab initio* molecular dynamic simulations were performed with the Gaussian 03 program [20]. Variational treatment of the anharmonicity and spectral analysis from the MD simulations were obtained using purposely developed programs.

Electronic structure calculations were performed at the DFT level B3LYP [13] and a valence double zeta Pople basis set including diffuse and polarization functions, 6-31+G(d,p). This model chemistry was chosen since it has been previously shown that, for the prediction of harmonic and anharmonic force constants and in the case of small organic [21-25] and radical systems [26], it is able to recover the results obtained using the more expensive CCSD(T) [27]/cc-pVTZ [28] approach.

A. Vibrational analysis from QM static methods

Here, the two static approaches used to compute anharmonic effects, namely VPT2 and VCI-P treatments are briefly recalled. In the first case (VPT2, implemented in the Gaussian code [20]), from a minimum energy structure of a given system, a quartic force field is built in which the third and fourth derivatives are computed by $6N-11$ (N =number of atoms) numerical differentiation of analytical second derivatives. This method is only suitable for computational models for which analytical second derivatives are available. In all cases, a complete quartic force field can be determined by conjointly using molecular energies and analytical successive derivatives for several nuclear configurations in a least square fitting procedure [29]. In the quartic approximation, the potential provided by the Gaussian code is given by :

$$V = \frac{1}{2!} \sum_i \omega_i q_i^2 + \sum_{i,j,k} k_{ijk} q_i q_j q_k + \sum_{i,j,k,l} k_{ijkl} q_i q_j q_k q_l \quad (1)$$

where q_i the i -th dimensionless normal coordinate, and ω_i , k_{ijk} , k_{ijkl} are the harmonic, cubic, and quartic force constants respectively, expressed in cm⁻¹. Note that only the anharmonic force constants involving the tri-mode interactions ($k=1$) are determined by numerical differentiation.

Next, the vibrational frequencies can be evaluated in the VPT2 approach by using the well-know formula of Miller and coworkers [30] derived from second order perturbation theory:

$$E_{\psi_i}^P = \langle \psi_i^0 | \hat{H} | \psi_j^0 \rangle + \sum_{i \neq j} \frac{\langle \psi_i^0 | \hat{H} | \psi_j^0 \rangle^2}{E_i^0 - E_j^0} \quad (2)$$

where $E_{\psi_i}^P$ corresponds to the energy of the vibrational state i ; ψ_a^0 is the vibrational configuration “ a ” which is an eigenvector of the zero-order vibrational treatment; E_a^0 is the corresponding energy, and $\langle \psi_i^0 | \hat{H} | \psi_j^0 \rangle$ is a term of the Hamiltonian matrix representation coupling the i -th and j -th configurations.

From a technical point of view, it can be shown [31] that the best setup is obtained using a step size of 0.01 Å for the numerical differentiation of harmonic frequencies, tight convergence criteria for structural optimizations, and fine grids for integral evaluation (that is at least 99 radial and 590 angular points). Finally, it is well known that VPT2 computations are plagued by Fermi resonances; however, the Gaussian implementation neglects nearly singular contributions, thus effectively removing the strongest interactions in the second order treatment, which are more properly treated at first order. This is accomplished by direct diagonalization of the corresponding part of the Hamiltonian matrix.

From the same quartic force field, a direct VCI computation could be performed using a locally developed Fortran 90 code [32] which allows, in its most advanced version, the treatment of molecular systems approaching 15 atoms. This and will be dealt with in a forthcoming work [33]. The general method, described in detail elsewhere [34], consists in the diagonalization of the Watson Hamiltonian matrix representation-CI matrix-including [35] the most pertinent configurations for the description of the vibrational states of interest. Note that the strength of the interactions stemming from each configuration is estimated by the PT2 formula. The procedure is iterative since each upcoming configuration generates its own multiexcitations and is completed when the vibrational states under investigation converge to less than 0.1 cm^{-1} .

The VCI-P procedure starts from the same basis as its VCI counterpart except that the contribution of the discarded configurations is taken into account by a subsequent PT2 treatment. In all cases in the electric harmonic approach the computation of the IR intensities for fundamentals frequencies needs only the knowledge of the configuration coefficients in the description of the vibrational states.

B. Vibrational analysis from *ab initio* MD

Ab initio MD simulations were performed using the atom-centered density matrix (ADMP) formalism [14-16] which uses localized Gaussian basis sets, thus allowing for sampling on the same potential employed for the static methods. This is of particular importance when both the potential energy surface and the observables are sensitive to the choice of the DFT computational level and, in particular, it allows for the use of hybrid functionals [21,36-38]. Furthermore, in our case, this choice led to a direct comparison of the re-

sults of anharmonic calculations obtained from static and dynamic approaches. Molecular dynamic simulations were performed in the microcanonical ensemble [39] for a NVE ensemble with a time-step of 0.2 fs over an overall period of 10 ps, the initial nuclear velocities being set to perform simulations averaging the temperatures around 300 and 600 K. A suite of programs developed locally was then used to perform the spectral analysis from ADMP *ab initio* trajectories [40]. Several papers report in detail a simple procedure [39,41-47] to get the IR spectrum as Fourier transform of the dipole autocorrelation function [48,49] that is :

$$I(\bar{\nu}) \propto \int dt \langle \dot{M}_0 \dot{M}_t \rangle e^{i\omega t} \quad (3)$$

M being the total dipole, \dot{M} the derivative dM/dt and $I(\bar{\nu})$ the intensity at the $\bar{\nu}$ frequency. However, the attribution of the vibrational bands to molecular motions is less trivial. This fact led to the proposal of several methods particularly well documented in the works of Tavan and Schmitz [46,47].

Starting from a set of mass-weighted atomic velocity issuing from a simulation ($V(t)$), we used the fourier transform of time correlation function (FTTCF) method that consists in the Fourier transformation of the corresponding autocorrelation function projected along the normal modes (NMs). This gives rise to a set of power spectra of the generalized modes $\hat{V}_j(\bar{\nu})$ where the position of the main peak corresponds to the wavenumber of the mode j .

$$\hat{V}_j(\bar{\nu}) = \int dt \langle V_{j0} V_{jt} \rangle e^{i\omega t} \quad (4)$$

with V_j the velocity of the normal coordinate j .

In this work, the eigenvectors $\langle \tilde{c}_j \rangle$ corresponding to the NMs were calculated in two different ways: (i) by diagonalization of the Hessian matrix at the minimum energy structure, that is using the harmonic normal modes (NMH); (ii) by extracting them from MD simulations diagonalizing the covariance matrix of mass-weighted velocities K (hereafter NMVC) defined as:

$$K_{ij} = \frac{1}{2} \langle (m_i m_j)^{1/2} v_i v_j \rangle \quad (5)$$

where the associated eigenvalues (λ_i^v) represent the average kinetic energy associated with the single mode i . It should indeed be noticed that velocity autocorrelation function can be projected on any internal coordinate [48] or related local modes for a more comprehensive assignment of the peaks.

III. RESULTS AND DISCUSSION

Table I reports the fundamental vibrational wavenumbers obtained at different levels of theory from

TABLE I Vibrational frequencies (cm^{-1}) computed at B3LYP/6-31+G(d,p) level, for methylene-amino radical, formamide and glycine using static and dynamic approaches.

ν	ω	VPT2	VCI-P	MD		Exp.
				300 K	600 K	
Methylene-amino radical						
ν_1	2989	2825	2830		2864	2820
ν_2	1726	1698	1704		1686	1725
ν_3	1386	1349	1349		1334	1337
ν_4	992	972	973		969	954
ν_5	3050	2874	2885		2890	3103
ν_6	940	920	920		906	913
Formamide						
ν_1	3733	3558	3567	3593	3542	3564
ν_2	3588	3422	3440	3455	3426	3440
ν_3	2977	2821	2841	2848	2817	2854
ν_4	1797	1774	1763	1733	1730	1754
ν_5	1621	1589	1565	1611	1597	1579
			1600		1632	
ν_6	1418	1395	1386	1370	1367	1391
ν_7	1270	1246	1242	1253	1241	1258
ν_8	1054	1040	1032	1060	1058	1046
ν_9	1035	1023	1007	1007	1003	1033
ν_{10}	637	591	606	596	596	602
ν_{11}	565	569	553	563	569	566
ν_{12}	257			288		289
					395	370
Glycine radical						
ν_1	3783	3584	3610	3659	3619	
ν_2	3735	3556	3589	3614	3585	
ν_3	3583	3406	3419	3481	3448	
ν_4	3258	3087	3141	3152	3124	
ν_5	1719	1682	1688	1652	1644	
ν_6	1649	1605	1600	1585	1578	
ν_7	1532	1464	1491	1481	1470	
ν_8	1333	1296	1291	1300	1281	
ν_9	1293	1255	1257	1256	1252	
ν_{10}	1146	1108	1110	1115	1111	
ν_{11}	1118	1091	1083	1096	1096	
ν_{12}	896	878	878	874	870	
ν_{13}	716	698	697	693	693	
ν_{14}	670	609	641	642	644	
ν_{15}	626	614	603	619	622	

a B3LYP/6-31+G(d,p) potential energy surface for methylene-amino radical, formamide and glycine. These three molecules appear as a prototype of a semi-rigid system for the former and a prototype of flexible systems for the two latter, formamide and glycine exhibiting a double well inversion mode not coupled or coupled with torsional modes at the low wavenumbers.

The harmonic values issue from the Hessian matrix determined at the minimum energy structure while the “static” anharmonic counterpart arises from VPT2 and VCI-P calculations. As reported by Burel and coworkers [50], the simplest VPT2 treatment provides, in absence of strong anharmonic couplings, reasonable vibrational wavenumbers of stretching motions, especially those containing hydrogen atoms exhibiting a well-defined Morse Potential. The calculated VPT2 values are 6 cm^{-1} to 33 cm^{-1} smaller than the experimental data for the NH and CH modes of formamide even though the corresponding VCI-P wavenumbers are in fair agreement with the experimental data for all modes greater than 3000 cm^{-1} . Concerning the FTTCF results issuing from MD simulation at $300 \pm 60 \text{ K}$, they underestimate the anharmonic shifts. This could be due to the exploration at this temperature of the potential surface, which is less anharmonic than the oscillation amplitudes stemming from excitation of the molecule by an IR quantum. When enlarging the exploration of the surface at $600 \pm 120 \text{ K}$, the MD transitions decrease and get closer to the VCI-P values; the anharmonicity is then fairly recovered for the NH and CH stretching modes. The main drawback of MD approach is the partial recovering of anharmonicity which seems to be artificially avoided by increasing the average temperature of the simulation. All non-coupled vibrations between 1800 and 1000 cm^{-1} are generally well reproduced by all approaches. Besides the X–H stretching, other motions difficult to reproduce are the so-called floppy modes, lying generally below 600 cm^{-1} . Among all these modes, torsions and angular deformations characterized by a double well potential are particularly challenging. As expected, the floppy out-of-plane motion NH_2 group, poorly evaluated if a fourth order polynomial potential is used in static anharmonic computations, is well reproduced from a MD approach in case of formamide

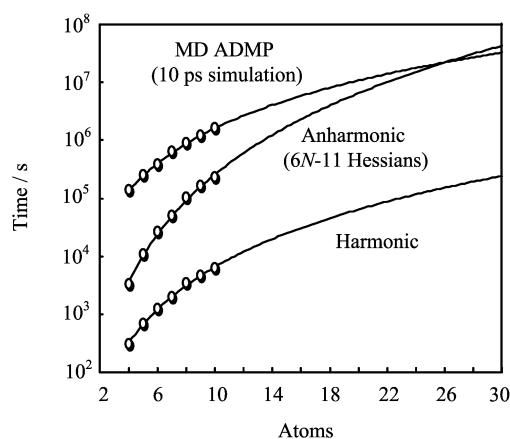


FIG. 1 Exploration time of molecular potential from static and dynamic process versus the size of the molecular system.

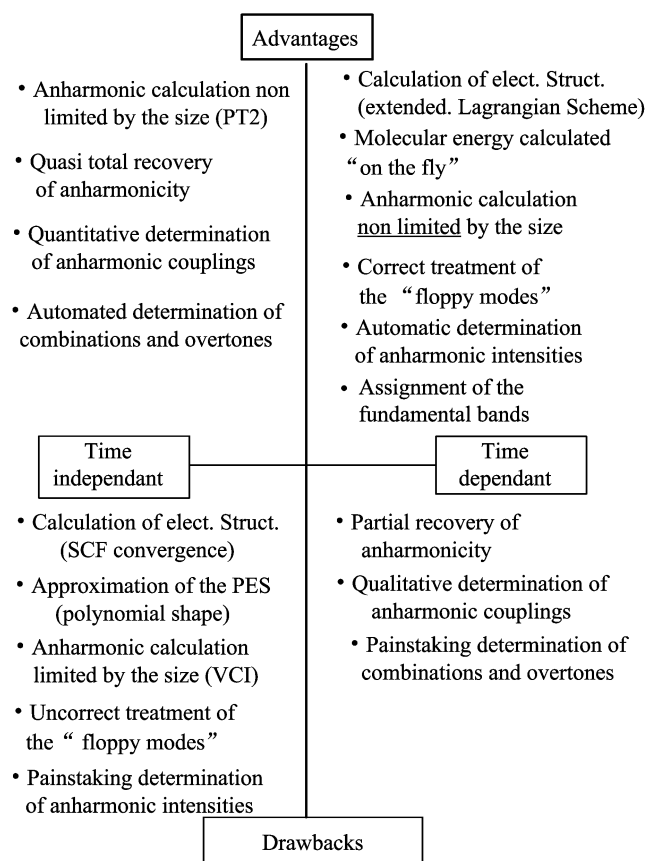


FIG. 2 Advantages and drawbacks of time-dependant and time-independant processes in modelling IR spectra.

and glycine.

We show in Fig.1 for H_2C_nO ($n=1-7$) molecular systems the time to explore the molecular potential from a DFT harmonic and anharmonic static approach compared to an MD approach when the simulation time is 10 ps with a time step of 0.2 fs. We can see the greater increase of the anharmonic curve relatively to the MD simulation. Extrapolation of our results shows that for molecular systems containing more than 25 atoms the MD simulation can be competitive in time to solve the vibrational problem.

To summarize the advantages and the drawbacks of the time dependant and time independant processes in modelling vibrational spectra are shown in Fig.2. Taking into account these conclusions we can propose a preferential static treatment to solve anharmonic vibrational problems for medium-sized semi-rigid molecules and an MD process for modelling large-sized molecular systems in which floppy vibrational motions are expected.

IV. CONCLUSION

In this work we compare the capabilities of first-principles static and dynamic DFT approaches for the computation of vibrational transitions beyond harmonicity. As test cases, we investigated the semi-rigid and flexible molecules, which present both torsional and double-well type modes, by effective VPT2 and VCI-P approaches, as well as doing a vibrational analysis of ADMP *ab initio* molecular dynamics trajectories computed at 300 ± 60 and 600 ± 120 K.

The VPT2 treatment is the fastest, followed by the VCI type computations and MD simulations, the last being extremely time consuming for small molecular systems. Furthermore, the MD based approach does not reproduce the total anharmonicity at ambient temperature, but has, in contrast, the advantage of being less hampered by the size of the system or by the shape of the molecular potential compared to the VCI approach. Thus, the soft modes are well described, even though their anharmonic values seem not very different from their harmonic counterpart at 300 ± 60 K, at least in the examples treated here. As a consequence, anharmonic static calculations for non-semi rigid systems could remain valid while considering a harmonic investigation on these modes. This suggests that the first-principle static computations could still be the method of choice for a satisfactory treatment of "medium size systems" (i.e. about twenty atoms).

In contrast, the determination of a simulated MIR spectrum from vibrational analysis of MD trajectory, anharmonic by nature, is an extremely easy task compared to the painstaking wave function analysis of static computations. This strategy deserves more interest when considering flexible molecular systems.

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