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REGULAR ARTICLE

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Vibrational analysis beyond the harmonic regime from ab-initio molecular dynamics

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Abstract The characterization of fundamental vibrational levels from the analysis of ab-initio dynamics is discussed. Results from test calculations are compared with those obtained by a second-order perturbative procedure to include anharmonicity exploiting the same ab-initio potential. The influence of the single molecular modes on vibrationally averaged properties calculated on the fly during the dynamics is also analyzed. Formaldehyde, both in the gas phase and in acetonitrile solution, and the vinyl radical in the gas phase have been chosen as test molecules, while the hyperfine coupling constants of the open shell system is computed as an example of molecular properties. Results allow for a quantitative comparison with experimental data.

Keywords Vibrational analysis · ESR hyperfine coupling constants · Vinyl radical

1 Introduction

The solution of the vibrational problem for polyatomic molecules and the theoretical determination of the infrared (IR) spectrum are among the most important applications in computational chemistry. Methods based on a quantum mechanical/ stationary-state picture of the system provide accurate energy levels by the solution of the ro-vibrational Hamiltonian $\mathbf{H}_{\text{ro-vib}}$. Variational [1–3], self-consistent [4–8] and perturbative [9–17] treatments can be exploited to account for anharmonic effects. However, these so-called 'Hessian-based' methods are computationally prohibitive for large systems, e.g. molecules in condensed phases or biomolecules.

Infrared spectroscopic data can be obtained by an alternative route based on a dynamic picture of the system. In this case the standard statistical mechanics formalism relies on Fourier transform analysis of the time correlation of atomic velocities or dipole moment. In principle these approaches can provide a complete description of the experimental spectrum, i.e. the characterization of the real molecular motion consisting of many degrees of freedom activated at finite temperature, often strongly coupled and anharmonic in nature.

However, computation of the exact quantum dynamics evolution of the nuclei on the ab-initio potential surface is as prohibitive as the quantum/stationary-state approaches. As a matter of fact, even a semiclassical description of the time evolution of quantum systems is usually computationally expensive. Therefore, time-correlation methods for realistic systems are usually carried out by sampling of the nuclear motion in the classical phase space [molecular dynamics (MD) techniques]. In this connection the basic issue is the extent to which a classical sampling of the nuclear motion can be used to characterize vibrational states that are quantum mechanical in nature.

Many efforts during the past decades have aimed at defining quantum corrections to the classical time-correlation function either in the time or in the frequency domain. Such corrections introduce frequency and/or temperature factors which take into account important symmetry properties absent in the classical picture. However, the corrections cannot be defined in a universal way, since they arise from comparison of several possible quantum-correlation functions with the single classical counterpart.

Recently, different quantum corrections have been compared on a theoretical basis and with respect to the performance on different kind of intramolecular and intermolecular motions [18]. However, all the proposed corrections only affect the width and the shape of the IR bands, while the accuracy of the calculated frequencies still relies on the ability of the classical approach to describe the fundamental vibrations.

Comparisons of spectra computed by classical, semiclassical and quantum approaches have been presented in few recent papers [18–21] focusing mainly on time-correlation functions, [18] intensities [20] and peak positions [19–21]. While the use of quantum-corrected time-correlation functions can indeed improve the accuracy of the computed intensities, the agreement between quantum and classical approaches in the frequency values is satisfactory only within

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the harmonic regime, i.e. when molecular motions correspond to the normal modes.

As a matter of fact, it is reasonable to expect that the classically determined frequencies will underestimate anharmonic shifts, since the classical amplitudes of the motion are smaller than their quantum counterparts at the same temperature [19]. Furthermore, the classical time-correlation function computed at 300 K for a stiff anharmonic mode in a single well reproduces the oscillating behavior of quantum counterpart, but within a smaller amplitude scale [18].

However, the actual performance of classical methods in reproducing frequency values is often difficult to evaluate beyond the harmonic regime. This is mainly due to the different physical pictures on which are based the quantum/stationary-state methods (which would provide the reference results) and the MD approaches. Furthermore, standard time-correlation methods provide a global description of the spectrum, i.e. with no detailed separation in terms of underlying molecular motions.

Normal modes-like analysis can actually be performed on MD trajectories. These methods are usually based on a quasi-harmonic model of the systems and have been extensively used in classical MD applications [22]. However, they show practical limitations when applied to ab-initio dynamics trajectories (vide infra).

We present here a discussion of some test calculations aimed at evaluating the accuracy of vibrational analysis of ab-initio trajectories. We moved from the consideration that a vis-a-vis comparison between results from ab-initio dynamics and sophisticated pertubative/variational treatments of the anharmonicity is now feasible. In particular, the quantum/stationary-state and the classical/ab-initio dynamics approaches can be performed using exactly the same, accurate ab-initio potential. Furthermore, a general mode formalism [23] has been recently proposed, which allows for the separation of molecular motions in the anharmonic regime and at finite temperature, thus representing a useful tool for the analysis of ab-initio trajectories.

Time-correlation functions can also be exploited to study fluctuations of specific properties computed on the fly during the dynamics. After transformation in the frequency domain, a comparison with fundamental frequencies can reveal the relative influence of molecular modes on the averaged property. In this connection we have explored the possibility to combine the vibrational analysis with the study of properties of interest computed on the fly along the trajectory.

The atom-centered density matrix propagation (ADMP) dynamics considered here presents several advantages that have been discussed in detail elsewhere [24–26]. The most important feature in the present context is the high quality of the adiabatic control afforded by the method. In particular it has been demonstrated [26] that even in critical cases, e.g. the treatment of ionic systems, any variation of the fictitious electronic mass over a wide range of values does not affect the molecular mass and therefore it does not affect the sampled vibrational frequencies either. Furthermore, with this method we can employ gaussian basis sets together with a wide variety of exchange-correlation functionals, including hybrid and kinetic energy functionals. These features allow us to perform dynamical sampling on the same potential employed in the quantum/stationary-state approach and consequently a direct comparison of the results.

The reference vibrational treatment is provided by a second-order perturbative (PT2) model recently implemented to take into account anharmonicity [17]. This is based on quadratic, cubic and semidiagonal quartic force constants. When combined with accurate hybrid functionals and medium-sized basis sets, the method has provided accurate frequencies, thermodynamic and kinetic quantities, in good agreement with experimental results [27–31].

As an example of vibrational analysis from ab-initio dynamics, we have characterized fundamental levels and the vibrational influence on the ESR hyperfine coupling constants for the vinyl radical in the gas phase. We also performed the vibrational analysis of formaldehyde both in the gas phase and in acetonitrile solution. This latter application exploits the combination of the ADMP dynamics with potential energy including solvation effects by the polarizable continuum model (PCM) [32].

Results show that vibrational anharmonic frequencies can be calculated with accuracy comparable to the quantum level. In perspective, the present analysis can also be combined with quantum-correction techniques to calculate IR intensities.

We recall that ab-initio dynamics belongs to the category of computational strategies aiming to join the detail of quantum approaches and the feasibility for realistic systems. As a matter of fact, the present vibrational analysis becomes an alternative to quantum Hessian-based methods for applications to liquids or complex molecules, and is even more promising when considering mixed classic-quantum potentials and/or strategies to include solvent effects. Such combinations are already possible, [33] and the quality of induced solvent shifts calculated in the present tests appears to be promising in this respect.

A study of complex systems can take advantage of the detailed analysis of the molecular motion in the interpretation of complex spectra and in the characterization of modes promoting reactivity or involved in conformational transitions. We show here that it is also possible, to sample electronic properties on the fly, allowing for a direct characterization of properties like magnetic constants on the potential energy surface. This provides an alternative to applications in which averaging of frames from MD dynamics is exploited to compute properties by quantum techniques, like those performed in order to parametrize force fields.

Section 2 describes the methods of the computational strategy; Sect. 3 gives the technical details of test calculations discussed in Sect. 4 while the last section gives the conclusion.

2 Methods

2.1 Vibrational analysis from ab-initio trajectories

We give here a sketch of the methods employed to extract normal-like modes from classical dynamics. Most of these methods refer to a quasi-harmonic model of the molecular motion and relate normal modes directions to the principal components of the fluctuations of nuclear configurations in the NVT ensemble. The basic idea is that the variation of nuclear coordinates can be related to an effective force constant matrix, from which quasi-normal modes can be extracted. These modes are anharmonic in nature.

In the quasi-harmonic model for an NVT ensemble, the distribution $P(\mathbf{x})$ of configurations $\mathbf{x}$ is determined by an effective quadratic potential $(\mathbf{x^T F x})/2$, sampled according to a Boltzmann distribution, where $\mathbf{F}$ is the effective force constant matrix.

According to the model, the distribution can also be expressed as a multivariate gaussian function modulated by the covariance matrix of configurations σ with elements $\sigma_{ij} = \left\langle (x_i - \langle x_i \rangle) \left(x_j - \langle x_j \rangle\right)\right\rangle$. Comparing the two expressions of $P(\mathbf{x})$ in terms of $\mathbf{F}$ and σ we obtain the simple connection $\mathbf{F} = k_B T \sigma^{\mathbf{-1}}$. The matrix $\mathbf{F}$ and the fluctuation matrix σ share the same eigenvectors, i.e. the quasi-normal directions. Thus, it is sufficient to diagonalize the mass-weighted fluctuation matrix to obtain normal modes and frequencies $\nu_i = \sqrt{k_B T / \lambda_i^x}$, where the eigenvalues λ_i^x give the expansion of each coordinate in the configurational distribution.

The method sketched above has been introduced by Karplus [34,35] and is similar to the principal modes analysis presented by Wheeler et al. [36]. The quasi-harmonic model is also the basis for methods of essential modes searching in proteins [22] and has been extensively adopted in applications to biomolecules.

The equipartition of the kinetic energy among the normal modes dictated by the thermal equilibrium allows one to focus on the configurational distribution $P(\mathbf{x})$ and to identify the normal mode vectors with the directions issuing from the decomposition of the covariance between coordinates.

Thermal equilibrium among modes is an essential assumption. Thus a problem arises when the simulation time required to get energy equipartition among internal modes is computationally too expensive as is the case for ab-initio dynamics. Indeed, even the simultaneous excitation of all the intramolecular modes can be an issue when gas-phase molecules are considered in ab-initio trajectories.

From a practical point of view the accuracy can be improved by carrying out the time evolution analysis in the momenta sub-space instead of the configuration space.

This choice has been recently advocated by Strachan [23]: the basic consideration is that, at any temperature, generalized normal modes q_i correspond to uncorrelated momenta, such that

$$< \dot{q}_i(t) \dot{q}_j(t) > \approx \delta_{ij} \tag{1}$$

The directions of these generalized modes compose the unitary trasformation matrix which diagonalizes the covariance matrix of the mass weighted velocities $\mathbf{K}$, with elements

$$K_{ij} = \frac{1}{2} < (m_i m_j)^{1/2} v_i v_j > \tag{2}$$

The eigenvalue λ_i^v of $\mathbf{K}$ represents the average kinetic energy associated with the single mode i. Frequencies associated with each mode can be obtained by Fourier transform of the autocorrelation function of normal modes velocities $\dot{\mathbf{q}}$.

The definition in (1) is more general than that provided by the quasi-normal model, because equipartition of thermal energy among modes is not required, and an effective quadratic shape of the potential is not assumed. Strachan showed that normal mode directions obtained from velocities and coordinate fluctuations are very similar. Comparing the expressions for the spectral distribution $P(\nu)$ as function of velocity and coordinates respectively an approximate expression for the frequencies has been obtained: $2\pi\nu_i \approx (\lambda_i^v / \lambda_i^x)^{1/2}$, where λ_i^v and λ_i^x are eigenvalues of the covariance matrix of velocities and coordinates, respectively. Note that this espression relates the averages kinetic energy and the spreading in the configurations space of each mode.

A very similar connection has been obtained by Schmitz and Tavan [19,21], starting from the consideration that kinetic and potential energy are equally partitioned within each normal mode (virial theorem). From the harmonic hamiltonian expressed in normal coordinates they showed the relationship $2\pi\nu_i = \left(\langle \dot{q}_i \rangle^2 / \left\langle (q_i - \langle q_i \rangle)^2 \right\rangle\right)^{1/2}$. The latter expression allows to compute frequencies, once normal modes directions have been obtained as eigenvectors of the coordinate fluctuation matrix, according to the quasi-normal analysis prescription. However, the expression is rigorous only in the harmonic approximation.

Thus, the calculation of generalized normal modes from unitary transformation of velocity matrix $\mathbf{K}$ and the computation of frequencies by the power spectra of velocities projected along the generalized modes, appear to be the most general choice to perform vibrational analysis of fundamental anharmonic modes from ab-initio trajectories at finite temperature.

Some more general considerations on the use of a classical sampling of the phase space to characterize properties that are intrinsically quantum mechanical in nature, e.g. vibrational states, are also in order. From the quantum point of view, frequencies are constants of motion of the ground vibrational state. This state is of course populated even at 0 K and corresponds to a configurational distribution that in the harmonic approximation is a gaussian-like function centered on the minimum of each single normal mode, with $(h\nu)/2$ as the zero-point energy.

On the other hand, in the classical picture, vibrational motions are characterized by frequencies activated only at finite temperature. We recall that for an isolated oscillator, i.e. corresponding to a microcanonical thermodynamic ensemble NVE, the classical and the quantum zero-point configurational distributions are different also in the analytical form [$P(\mathbf{x})$ shows a minimum and a maximum at the minimum of the potential, respectively, in the two cases]. For the harmonic oscillator coupled to a bath (NVT ensemble), the unormalized classical distribution

$$P(\mathbf{x}) = \exp\left(\frac{-\mathrm{m}\,(2\pi\nu)^2\,\mathbf{x}^2}{2k_BT}\right) \tag{3}$$

and the unnormalized quantum ground-state distribution

$$P(\mathbf{x}) = \exp\left(\frac{\text{-m}\,(2\pi)^2\,\nu\mathbf{x}^2}{\mathrm{h}}\right) \tag{4}$$

correspond to the classical limit $k_BT = h\nu$, i.e. at the vibrational temperature.

Let us consider the collection of velocities and positions in the classical phase space for a NVT ensemble starting from a minimum of the potential energy. The potential energy that is accessible to the sampling is limited by the virial theorem, namely the maximum value of the potential is related to k_BT for each internal mode. Because at room temperature $k_BT \ll h\nu$, the exaustive sampling of the potential shape in order to reproduce the quantum distribution is precluded. This can be problematic when we wish to include with a good accuracy the anharmonic contributions to frequency values. For instance frequencies of about $3000\,\mathrm{cm}^{-1}$, i.e. in the range of the stretching motions involving hydrogen atoms, correspond to a vibrational temperature of about 5000 K. However, when the energy potential is expanded in powers of the nuclear displacements, the anharmonicity contributions decrease markedly in magnitude with the order of the power. On this ground, one could hypothesize that anharmonicity of motions of interest can be captured with acceptable accuracy already by amplitudes of nuclear motion allowed at temperatures below the classical limit. We investigate this hypothesis through test calculations discussed in Sect. 4

2.2 Calculation of molecular properties from ab-initio dynamics

In principle, ab-initio dynamics allows for on-the-fly computation of molecular properties that depend upon the electronic density.

When extended-Lagrangian approaches are considered, the electronic density does not converge at each point of the configurational space; instead, the Born Oppenheneimer (BO) surface is mimicked in an averaged way. However, when the dynamics is characterized by a good adiabatic control, averaging of electronic properties on an extended Lagrangian-based trajectory can be acceptable. In particular, the ADMP formalism allows us to employ values of the fictitious mass for the electronic variables (the elements of the density matrix **P**) compatible with a reasonable separation between the time scales of the electronic and nuclear motion. Furthermore, the adiabaticity can be rigorously monitored on-the-fly evaluating of those quantities which give a measure of the deviation from the true BO surface, i.e. the Frobenius norm of the Fock and density matrices commutator, $\|[\mathbf{F},\mathbf{P}]\|_F$, and the derivative with respect to the time of the fictitious Hamiltonian, $\mathrm{d}\mathcal{H}_{\mathrm{fict}}/\mathrm{d}t$ [26,37].

Fluctuations of a molecular property can be investigated in the frequency domain by a simple Fourier transform of the property autocorrelation function. Peaks in this power spectrum can be related to the influence of single modes on the vibrationally averaged value of the property under study.

In the stationary-state picture offered by the quantum perturbative approach, vibrationally averaged values can be calculated at a specific temperature T assuming a Boltzmann population of the vibrational levels, and contributions of single modes to the averaged value can be obtained according to the procedure described, for example, in Ref. [17,38]. Thus, analysis of molecular properties by means of the ab-initio dynamics approach can be validated by comparison with the quantum mechanical result.

As an example we consider the characterization via ab-initio dynamics of the isotropic component of the hyperfine coupling between unpaired electrons and nuclei with nonzero spins in open shell systems. The isotropic coupling constant for the nucleus M located at $\mathbf{x_M}$ [39] is

$$a(M) = \frac{8\pi}{3}\beta_e\beta_M g_M \sum_{m,n} P^{\alpha-\beta}_{m,n}\left\langle\phi_m\left|\delta\left(\mathbf{x}-\mathbf{x_M}\right)\right|\phi_n\right\rangle, \tag{5}$$

where β_e, β_M and g_M are the electronic and nuclear magnetons and the nuclear magnetogiric ratio, $\delta\left(\mathbf{x}-\mathbf{x_M}\right)$ is the Dirac delta, and the indices m and n run over the orthogonal basis functions. $\mathbf{P}^{\alpha-\beta}$ is the spin density matrix, i.e. the difference between the density matrices for α and β spin electrons.

Once the density matrices $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ have been obtained at each ADMP step, the calculation of $a(M)$ is achieved in a straightforward way and with no increasing of the computational cost.

2.3 Ab-initio dynamics in solvent

The energy in solution according to the PCM is the free energy of a molecular solute in equilibrium with respect to the solvation process [32]. We recall that, beside the electrostatic contribution, the thermodynamic work involved in such a process is constituted by the cavitation and dispersion contributions. The ab-initio dynamics on the PCM potential provides a sampling in a phase space in which the self consistent reaction field due to the solvent is equilibrated to the electronic density at each time step. Therefore, nonequilibrium effects involving solute–solvent interactions are not described, and the accuracy of the present approach strictly depends upon the amount of solvation dynamical effects affecting the property or the process under study. The latest version of the PCM routines in the Gaussian [40] suite of programs allow for the analytic definition of an energy potential in solution and the performance of a conservative dynamics. In practice, the machinery of the ADMP ab-initio dynamics including the treatment of the solvation trough the PCM approach is the same as in gas phase. In particular, the

Table 1 Frequencies (cm^{-1}) obtained from generalized modes analysis of atomcentered density matrix propagation (ADMP) trajectories performed at different temperatures

Mode	Harmonic	150 K	300 K	450 K	600 K	PT2
1.CH stretch	3,256.42	3,161	3,156	3,150	3,150	3106.32
2.CH$_2$ asymmetric stretch	3,165.79	3,058	3,045	3,015	3,012	3003.37
3.CH$_2$ symmetric stretch	3,063.58	2,995	2,937	2,911	2,911	2894.06
4.CC stretch	1,654.78	1,608	1,607	1,608	1,601	1622.44
5.CH$_2$ bend	1,396.20	1,378	1,371	1,362	1,361	1362.55
6.CH's wag in phase	1,052.88	1,014	1,016	1,008	1,008	1002.40
7.CH's wag out of phase	717.84	706	692	687	683	681.40
8.CH$_2$ out of plane	922.60	912	911	908	910	907.50
9.CH out of plane	810.60	798	796	795	795	791.99

Values are compared with harmonic analysis (second column) and with anharmonic perturbative analysis (last column). Both the static and the dynamics approaches refer to B3LYP/6-31+G(d, p) level of the theory for the calculation of the potential

expression of the nuclear forces as described in Refs. [24,25] includes further terms taking into account the PCM derivatives as described in the Ref. [41]. The modular routines in the Gaussian package allow for the performance of ADMP dynamics on PCM potentials with no further modification in the implementation of both the techniques. As expected, energy conservation and adiabatic control observed in test calculations not reported here show the same behavior of dynamics performed for isolated systems.

3 Computational details

Spectral analysis have been carried out from ADMP ab-initio trajectories. The core and valence orbitals were weighted differently during the dynamics with $\mu_{\mathrm{valence}}=0.1$ amu bohr^2 $\approx 180\,A^{\circ}$ for the valence electrons, using the tensorial fictitious mass scheme described in Ref. [25] to obtain improved adiabatic control. We performed dynamics of a canonical ensemble integrating a time step of 0.2 fs over a period of 12 ps, the nuclear velocities being scaled in order to obey to a Boltzman distribution at the desired temperature with a frequency chosen in order to sample the slowest motions properly. The total angular momentum and the motion of the center of nuclear masess were projected out at each step of the trajectory, according to the default setting of ADMP routines. The dynamics for molecules in the gas phase ran over potentials calculated at the B3LYP/6-31G(d, p) and B3LYP/6-31+G(d, p) level of theory, starting from structures optimized at the corresponding level.

In order to perform the spectral analysis of the trajectories we adopted the generalized normal modes procedure described in Sect. 2.1. The vibrational analysis for the vinyl radical has been compared with both the standard harmonic and the PT2 treatment.

We considered the solvation effects running the dynamics over a potential calculated at the B3LYP/6-31G(d, p) level of theory and including a self-consistent reaction field. In order to do that, we exploited the latest version of the PCM [41, 42]; we adopted in particular the CPCM [41] approach with a modified version of the UA0 [43] model for the molecular cavity. This choice was motivated for reasons of efficiency.

4 Discussion of test calculations

4.1 Vinyl radical in the gas phase

In Table 1 we report frequency values (cm^{-1}) for the vinyl radical in gas phase obtained by different approaches on a potential calculated at the B3LYP/6-31G+(d, p) level of theory. The harmonic values refer to the standard Hessian-based analysis of the structure that is a minimum on the potential surface, while the anharmonic analysis refers to the PT2 approach to include anharmonicity. The latter is our reference to test the accuracy of the vibrational analysis of MD trajectories. In order to gauge the capability of the classical sampling in reproducing anharmonic frequencies, we choose to perform dynamics at different increasing temperatures. In the table we include the results of generalized modes analysis of the ADMP trajectories obtained for an NVT ensemble at 150, 300, 450, and 600 K. In Fig. 1 we also report power spectra of the generalized modes obtained at 450 K.

The out of plane of CHs, characterized by the lowest anharmonic red-shifts (≤ 20 cm^{-1}), are well reproduced at room temperature. Shifts of the order of magnitude up to 50 cm^{-1}, corresponding to the two wagging modes of the molecule and to the CH$_2$ bending, are in good agreement with the expected results only above the room temperature. Note, however, that no sensible variation in the analysis performed at 600 and 450 K can be appreciated. At 450 K, all the modes below 1400 cm^{-1} agree with quantum results within the spectral resolution (2.7 cm^{-1}).

The stretchings involving hydrogens are the modes characterized by the larger anharmonicity: the red-shifts are expected to have values of 169.52, 162.42 and 150.1 cm^{-1} for the symmetric and asymmetric CH$_2$, and the CH stretchings, respectively. While the analysis performed at 150 K reproduce the CHs' shifts with a loose agreement (40, 66 and 64%, respectively), the generalized modes at 450 K reproduce the 89.9, the 94.9 and the 70.9 % of the anharmonicity. However, we notice a general good agreement between the classical/ab-initio and the quantum/stationary-state approach.

Although the present example cannot be considered as a template for a general behavior, some considerations can be made. In principle, the quantum configurational distribution

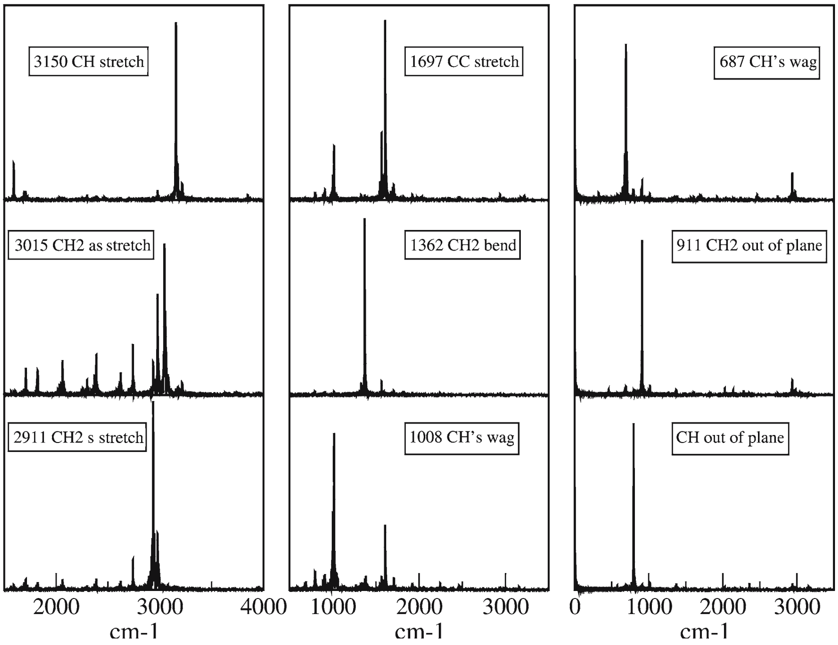

Fig. 1 Power spectra of the autocorrelation functions of generalized modes velocities obtained for the vinyl radical in gas phase from ADMP dynamics at 450 K. Potential calculated at the B3LYP/6-31+G(d, p) level of theory

Table 2 Hyperfine coupling constants (Gauss) for vinyl radical in gas phase

	Equilibrium structure	PT2 (0 K)	PT2 (298 K)	150 K	300 K	450 K
a(C_1)	− 6.08	− 7.56	−7.61	− 6.78	− 7.51	− 7.65
a(C_2)	112.71	110.38	110.16	111.32	109.21	110.08
a(H_3)	37.56	39.55	39.54	38.24	39.07	39.93
a(H_4)	59.83	61.83	61.83	59.91	60.75	61.41
a(H_5)	15.52	14.30	14.19	15.07	13.86	14.11

We compare values for the minimum structure (second column), values obtained averaging over quantum vibrational states obtained by perturbative anharmonic treatment at 0 K and room temperature (third and fourth columns), and values averaged from ADMP trajectories at different temperatures. All the approaches refer to the B3LYP/6-31+G(d, p) level of theory for the calculation of the potential

at 0 K can be approximatively mimicked through a classical sampling using T as a parameter, i.e. considering kinetic energy values large enough to take into account the real shape of the potential in a proper way.

Unfortunately this cannot be performed in a rigorous way in that the classical limit can be reached at very high temperatures, where the molecular systems can be instable and the classical dynamics unphysical. Moreover, at each value of the temperature the classic MD samples a different shape of the potential, thus leading to different frequencies values.

Finally, the typical range of frequencies for internal molecular motions include vibrational temperatures of different orders of magnitude (hundreds to thousands of K). When soft modes are considered, the classical sampling at high temperatures could imply amplitudes of motions corresponding to those visited by vibrational excited states, thus introducing artifacts in the calculated frequencies.

However, the present test calculations show the encouraging result that the comparison with the quantum approach is satisfactory for typical ranges of frequencies and anharmonic shifts at room temperature.

In Table 2 we compare the hyperfine coupling constants calculated for the vinyl radical at the equilibrium structure, those averaged on vibrational quantum states (our reference values) at 0 and 298 K, and those averaged along the ab-initio dynamics at different temperatures.

Note that, when the quantum results are considered, no sensible variation can be appreciated when going from 0 K to room temperature. Furthermore, consistent with the results obtained in the frequency calculations, we observe a very close agreement between the quantum values averaged at 298 K and the classical values averaged at 450 K.

In Table 3 we collect the percent contribution of normal modes to the hyperfine coupling constants estimated from the relative height of the peaks in the power spectra of the hyperfine constants autocorrelation function. The power spectra for the hyperfine coupling constants are also drawn in Fig. 2. Those results are in good qualitative agreement with those obtained by the quantum analysis performed at 298 K. Note that the isotropic constants are not affected sensibly by the out-of-plane motions, due to the σ nature of the radical. Instead, vibrationally averaged values are influenced mostly by the wagging of CHs' in the molecular plane. The hydrogen coupling constants are also sensitive to stretching motions.

It is worth noting that the adiabaticity retained through the dynamics allows for a quantitative comparison between

Table 3 Percentage of relative contributions of generalized normal modes to the hyperfine coupling constants values obtained from ADMP dynamics performed at 450 K on a potential calculated at the B3LYP/6-31G(d, p) level of theory

Mode	a(C_1)	a(C_2)	a(H_3)	a(H_4)	a(H_5)
1. CH stretch	–	–	–	–	7(21)
2.CH_2 asymmetric stretch	24 (16)	–	26 (21)	8	–
3.CH_2 symmetric stretch	–	–	–	31 (45)	–
4.CC stretch	–	–	22 (20)	25 (22)	–
5.CH_2 bending	–	–	14 (8)	–	–
6.CH's wag in phase	40 (33)	52 (38)	–	25 (19)	56 (37)
7.CH's wag out of phase	17 (40)	18 (50)	24 (50)	–	28 (35)
8.CH_2 out of plane	–	–	–	–	–
9.CH out of plane	–	–	–	–	–

In parentheses we show values obtained from the PT2 analysis at 298 K. Values less than 5% are not reported

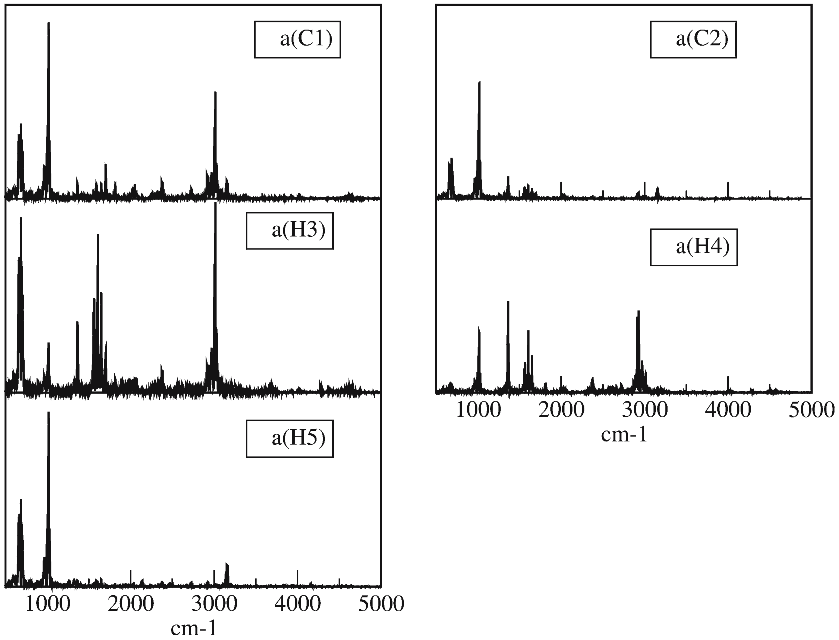

Fig. 2 Power spectra of hyperfine coupling constants autocorrelation functions obtained for the vinyl radical in gas phase from ADMP dynamics at 450 K. Potential calculated at the B3LYP/6-31+G(d, p) level of theory

properties calculated from unconverged electronic densities and the corresponding values obtained by the quantum/stationary-state approach. In particular, the analysis of all the trajectories for the open shell system showed a fictitious kinetic energy of about two orders of magnitute lower than the kinetic energy of the nuclei, while the Frobenius norm of the Fock and density matrix commutator maintained values of about 10^{-2} in order of magnitude, thus confirming the stability and the accuracy of the ADMP dynamics.

4.2 Formaldehyde in the gas phase and in acetonitrile solution

In Table 4 we report generalized normal modes frequencies (cm^{-1}) obtained from ADMP dynamics at 450 K on a potential at the B3LYP/6-31G(d, p) level for formaldehyde both in gas phase and in acetonitrile solution.

Regarding the vibrational analysis performed in the gas phase, the general comparison with the experimental results can be considered satisfactory. The CH_2 scissor and rocking motions are within 7 cm^{-1} of the experiment. The stretchings' frequencies suffer the most important discrepancies (they show a difference with the experiment of 42, 40 and 28 cm^{-1} for the asymmetric CH_2, symmetric CH_2, and CO stretchs, respectively). However, the overestimation of the stretching frequency when carbon and oxygen atoms are involved is a general trend of current density functionals [28–31]. Note that frequencies for asymmetric and symmetric stretchings are reversed and the first one shows the lowest discrepancy with the expected value. The underestimation of asymmetric stretchings has been observed previously for potentials of comparable accuracy, and it is expected that a more accurate basis set would remove this effect [30,31]. Therefore, it is reasonable that this effect combined with the underestimation of the anharmonic shift at 450 K leads to a value closer to the experiment than other frequencies in the same range.

We recall that the combination of the ADMP with the PCM as performed in the present work corresponds to a

Table 4 Generalized normal modes frequencies (cm^{-1}) obtained from ADMP dynamics at 450 K on a potential calculated at the B3LYP/6-31G(d, p) level for formaldehyde both in gas phase and in acetonitrile solution

Mode	ν_{vac}	^{a}Exp. ν_{vac}	ν_{solv}	^{a}Exp. ν_{solv}
CH_2 asymmetric stretch	2,815	2,843	2,855 (+40)	2,876 (+33)
CH_2 symmetric stretch	2,822	2,782	2,829 (+7)	2,797 (+15)
CO stretch	1,788	1,746	1,760 (−28)	1,723 (−23)
CH_2 bending	1,502	1,500	1,510 (+5)	1,503 (+3)
CH_2 rock	1,242	1,249	1,237 (−5)	1,247 (−2)
CH_2 wag	1,190	1,167	1,194 (+4)	

Corresponding experimental values are also reported. Induced solvent shifts are reported in parentheses. ^{a}See Ref. [44]

dynamics on a potential surface where the solute and the surrounding medium are equilibrated at each point. Thus the present vibrational analysis does not include dynamical solvation effects. Furthermore, possible influence of specific solute solvent interactions are not taken into account. However, this approximation is accurate enough in the present case in that solvent-induced shifts are in a very good agreement with the experimental results for all the frequencies.

5 Summary

We performed vibrational analysis from ADMP ab-initio dynamics based on the calculation of uncorrelated momenta (generalized mode analysis). The vinyl radical in the gas phase and formaldehyde, both in vacuum and in acetonitrile solution, have been chosen as benchmarks.

When compared with quantum results at PT2 level, the analysis from dynamics at 450 K for the vinyl radical show a satisfactory level of accuracy. Large anharmonic red-shifts ($\approx 170\,cm^{-1}$) for CHs' stretchings are reproduced within 70–90% of the amount. Consistently, vibrational averaged ESR hyperfine coupling constants obtained by the quantum approach are well reproduced by the collection on the fly during the dynamics at 450 K.

When compared to the experiment, vibrational analysis for formaldehyde shows an acceptable level of accuracy (the largest discrepancy is $40\,cm^{-1}$ for high anharmonic frequencies). Induced solvent shifts are in good agreement with the experimental results.

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