Born Oppenheimer Molecular Dynamics calculation of the $\nu_{O-H}$ IR spectra for acetic acid cyclic dimers

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Abstract. Both \textit{ab initio} molecular dynamics simulations based on the Born-Oppenheimer approach calculations and a quantum theoretical model are used in order to study the IR spectrum of the acetic acid dimer in the gas phase. The theoretical model is taking into account the strong anharmonic coupling, Davydov coupling, multiple Fermi resonances between the first harmonics of some bending modes and the first excited state of the symmetric combination of the two $\nu_{O-H}$ modes and the quantum direct and indirect relaxation. The IR spectra obtained from DFT-based molecular dynamics is compared with our theoretical lineshape and with experiment. Note that in a previous work we have shown that our approach reproduces satisfactorily the main futures of the IR experimental lineshapes of the acetic acid dimer [Mohamed el Amine Benmalti, Paul Blaise, H. T. Flakus, Olivier Henri-Rousseau, Chem Phys, 320(2006) 267-274].

1. Introduction
The linear infrared (IR) $\nu_{X-H}$ spectroscopy of absorption spectra is an important method to understand the physical informations on the dynamics of weak hydrogen bonds (H-bonds). This spectroscopy has been the object of considerable experimental and theoretical works in the literature [1, 2] Numerous studies on hydrogen bonded systems such as water molecule, biological molecules and carboxylic acid dimers is now studied using Density Functional Theory (DFT) techniques [3, 4]. There is also new methods such as Car Parrinello Molecular Dynamics (CPMD) program which is used to understand the dynamics of the hydrogen bond in cyclic dimers and to obtain vibrational spectra of such molecules. The calculation of infrared spectra through Molecular Dynamics (MD) relies on dipole time correlation functions recorded along the trajectory [5]. This is well established in the context of classical MD [6], but is much more recent in the ab initio MD community.
The vibrational properties of acetic acid dimer (A.A.D.) were studied many times, either experimentally [7, 8] or theoretically [9]. In a recent paper Piotr Durlak and Zdzisław Latajka [10] have studied Acetic acid monomer, dimer and its deuterated using ab initio Car-Parrinello molecular dynamics. They have demonstrated that the IR spectra calculated by CPMD method show a good agreement with the experimental Infrared spectrum and reproduces well isotopic effects. We have shown in a recent work [11, 12] how quantum theories are used to explain the changes in the infrared spectrum induced by the formation of the H-bond bridge, i.e. the: (i) large increase in the band width, (ii) band asymmetry, (iii) fine structure, (iv) temperature and isotopic effects. These theories were able to reproduce the IR spectra from some physical basic accessible parameters.

Recently [9, 11], we have proposed a quantum approach of the $\nu_s(X - H)$ IR spectra of the acetic acid dimer. This approach involves (i) the adiabatic approximation (allowing to separate the high frequency mXH motion from that of the H-bond bridge), for each separate part of the dimer, (ii) a strong non-adiabatic correction via the resonant exchange between the excited states of the two fast mode moieties (Davydov coupling), (iii) quantum direct damping taking into account the relaxation of the high frequency modes, (iv) quantum indirect damping taking into account the relaxation of the Hbond bridges.

The present paper aims at demonstrating the applicability of ab initio molecular dynamics simulations based on the Born Oppenheimer approach for the calculation of infrared spectra of the A. A. D in the gas phase. This method and its application to vibrational infrared spectroscopy has been described in details in previous papers [13, 14]. The main advantages of the molecular dynamics approach for the calculation of infrared spectra in comparison with a static ab initio calculations is: (i) Dynamics simulations are performed at finite temperature. (ii) When calculating IR spectrum from the dipole time correlation function, all anharmonic effects are naturally described. The calculated spectrum from the dynamics is compared with experiment typically done at room temperature.

2. Computational methods

The initial structure of the A.A.D. (figure.1) for which the trajectories are performed in the present work has been taken from optimized geometry obtained at the B3LYP with sddall (5d,7f) level by using Gaussian 03 program package [15]. DFT-based Born Oppenheimer Molecular Dynamics (BOMD) simulation were performed on this initial structure as a starting for the dynamics with Cp2k package. The calculated parameters concern an isolated dimer of acetic acid.

The dimer was located in a simple cubic box of dimension 13.0 Å. Gaussian basis sets and pseudo-potentials are used. We have used the Becke, Lee, Yang and Parr (BLYP) gradient-corrected functional [16, 17] for the exchange and correlation terms. The calculations are performed with Goedecker-Teter-Hutter (GTH) pseudopotentials [18] and large Gaussian basis sets (in this work (aug-TZV2P) from the CP2K library). We have performed five trajectories (250K, 270K, 300K, 302K and 305K). The average temperature of the dynamics is 285,4K. Our dynamics are strictly microcanonical (NVE ensemble) with a time step of 0,4 fs. In order to eliminate the effect of the periodic images of the charge density we have used the decoupling technique of Martyna and Tuckerman [19]. The data was visualized using the VMD [20] program. The vibrational spectrum has been calculated using the Fourier transformation of the dipole autocorrelation function obtained from dipole trajectories generated by the Cp2k simulation through the following expression.

$$I(\omega) = \frac{2\pi\beta \omega^2}{3cV} \int_{-\infty}^{\infty} dt <M(t).M(0)> exp(i\omega t) \quad (1)$$

Where $\beta = 1/kT$, $c$ is the speed of light in vacuum, $V$ is the volume. $M$ is the total dipole moment of the system.
3. Results and discussion

Figure 2 presents the comparison between the experimental and theoretical IR spectrum extracted from Ref [12] and the present final IR spectrum extracted from an average of five trajectories of A. A. D. Typical broad band shape for the $\nu(O-H)$ mode is presented. One can see that the Born-Oppenheimer Molecular Dynamics (BOMD) simulated IR spectrum in the range of O–H stretching mode reproduce correctly complicated bands shape observed in both experimental [21] and theoretical spectrum for the nondeuterated acetic acid dimer [9]. The main reason of it is that during the *ab initio* molecular dynamics simulations all possible coupling of modes are taken into accounts due to the oscillations of atoms in molecules and in this approach there is no limitation due to inclusion of only specific coupling between modes. It should be noted that no scaling factors to the vibrational band positions are applied in our BOMD calculations. The sampling of anharmonicities (potential energy surface, dipole anharmonicity, mode couplings, anharmonic modes) being included in our simulations. It is clear that the lineshape obtained by our BOMD calculated spectrum (black line in figure 2) reproduce satisfactorily almost all the experimental features. The shoulder seen at 2900 cm$^{-1}$ is present in the calculation but smaller. The shoulder located at 3150 cm$^{-1}$ is also present in both experimental and theoretical spectrum. As expected the vibrational spectrum obtained by our simulation is very sensitive to the temperature effect and the anharmonicities, all these parameters are responsible for band broadenings. This result is in agreement with the band shapes obtained in the experimental spectra.

![Figure 1. Structure of the acetic acid dimer.](image1)

![Figure 2. Comparison between the infrared spectra](image2)

In table 1 are given the calculated bonds lengths as a function of the temperature of the simulation. These values are taken for only one moiety of the dimer, the values of the other moiety of the dimer are almost the same. The average distance between the two oxygens O....O of the A. A. D in the gaseous phase is 2.66Å. The calculated values are in a good agreement with experimental data 2.684 Å[22]. It should be noted that the hydrogen bond distance is modulated by the coupling mechanism between the bending modes of the hydrogen bond and the stretching...
Table 1. Calculated average bond lengths at each trajectories for acetic acid dimer at different temperature.

| T(K) | 250 | 270 | 300 | 302 | 305 |
|------|-----|-----|-----|-----|-----|
| d_{O-H}(Å) | 1.00 | 1.05 | 0.99 | 0.99 | 0.99 |
| d_{O...O}(Å) | 2.64 | 2.72 | 2.66 | 2.67 | 2.61 |
| d_{H...O}(Å) | 1.67 | 1.67 | 1.66 | 1.69 | 1.63 |

modes

In figure 3 are represented the time evolution of interatomic distances of atoms involved in intramolecular H-bonds of A. A. D. at 300K from the BOMD calculation. Analysis of the trajectories of the atoms during the BOMD simulation shows that there is a proton transfer, which is occurring at 16000 step (6.4 Ps) of the simulation. This proton transfer is also observed by Durlak [23] in the case of propinoic acid dimer in a PIMD (Path Integral Molecular Dynamics).

Figure 3. Time evolution of interatomic distances of atoms involved in intramolecular H-bonds of A. A. D. at 300K

4. Conclusion
In this paper, we report ab initio molecular dynamics simulations of acetic acid cyclic dimer in order to reproduce experimental infrared spectra. We have shown that vibrationnal properties can be obtained by using Molecular Dynamics within a DFT framework. The results we have obtained are in a good agreement with experiments. Such agreement can not be obtained in the case of static harmonic calculations. We think that our MD IR spectrum will match the experimental one if we increase the temperature of the dynamics and better resolution can be reached if we perform more tarjectories. The MD calculated spectra is better in comparison to that calculated with CPMD method by Durlak et al [23]. If we compare our MD spectrum with that obtained by the quantum approach the calculations reproduces satisfactorily the main features of the experimental spectrum. However, the theoretical model reproduce the main features of the lineshape of the ν(OH), but the use of approximations in the quantum approach
such as adiabatic separation between the vibrational modes (high frequency and the H-bond bridge), Davydov coupling and Fermi resonances make reaching the experimental IR spectra a very hard task.

Acknowledgments
Acknowledgments: This study was granted access to the HPC ressources of IDRIS made by GENCI (Grand Equipement National de Calcul Intensif) in France.

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