## ESF Grant, Ref. 1280. Final Report

## Project of collaboration Toulouse – Liverpool. Stay of Dr. Teobaldi in Toulouse: Vibrational lifetime evaluation of adsorbates on solid surfaces, an *ab-initio* study.

### 1 Purpose of the visit.

The stay of Dr. Teobaldi (Liverpool) in Toulouse will permit to create a collaboration between the Toulouse (Prof. Lorente) and the Liverpool (Prof. Hofer) groups. The aim of the collaboration is to create *ab-initio* based tools in order to analyze the vibration of molecular systems on solid surfaces. The excitation of molecular vibrations is of great importance for the understanding of molecule-surface interactions, molecular manipulations, molecular reactivity and eventually catalysis. Hence, The Toulouse-Liverpool collaboration is based on the numerical evaluation of molecular processes at surfaces in order to achieve physical insight as well as predictive accuracy.

Recent experiments have permitted to manipulate molecules on the atomic scale.[1] The experiments are based on scanning tunnelling microscopy (STM) techniques. Typically, tunnelling electrons are injected on top of adsorbed molecules, and the resulting electron current excites vibrations. Depending on the electron fluency the molecules are excited to different degrees. Hence, the parameters of the STM permit to scan the full phase space from low excitations, where spectroscopic measurements are possible, to high excitations where the molecule can undergo severe transformations.[1,2] A key ingredient in the manipulation process is the vibrational lifetime. If the excited vibration is long lived, a second tunnelling electron might be able to excite again the molecule, increasing in this way the degree of excitation even in the low fluency regime. On the other hand, if the lifetime is very short, the molecule will be quickly damped to its ground state and no possible manipulation will ever take place. In order to achieve the degree of accuracy this combined project aims at, the accurate evaluation of vibrational lifetimes is of uttermost importance.

The project is based on density functional theory (DFT) calculations as implemented in the VASP package. Vibrations are described by diagonalizing the dynamical matrix obtained from VASP by introducing displacements on the molecular degrees of freedom. In the same way, the electron-vibration coupling can be obtained.[1] Hence, the application of Fermi's golden rule provides a simple way of using information obtained from VASP to evaluate the damping rate of molecular vibrations in contact with an electron continuum, permitting the excitation of electron-hole pairs. Indeed, on a metal surface, the first source of vibrational damping is due to the electronic excitations available in this system. Hence, the vibrational energy is dissipated in the excitation of the metallic electrons above the metal's Fermi level creating holes. This approach has been very successful in the past, and has been showed to give quantitative estimates of the vibrational damping rate when used with DFT tools.[1-3]

The situation changes when the substrate is non-metallic. In this case, electronic excitations are not possible because the vibrational energy is typically much smaller than the minimum energy required to induce an electronic excitation in the substrate. In the case of semiconductors this minimum energy is in the range of ~1 eV while the highest molecular vibrations are rarely above 0.2 eV. Hence, the only de-excitation mechanism is via the excitation of extended vibrations: phonons. Indeed, a molecular vibration will couple to the substrate phonons and disappear after a certain time. This type of damping mechanism has received some attention recently, showing that again, DFT can be valuable in predicting the right trends and the actual vibrational lifetimes of $H_2$ on Si surfaces.[4] The existing calculations make use of molecular dynamics simulations where the vibration is monitored against time, and a lifetime is obtained from the classical decay of the vibration. In contrast, we propose to use a quantum approach based on phonon Green's functions. Indeed, VASP can furnish us with all the data needed to calculate the full Green's function of the vibration. From the Green's function we can obtain the vibrational spectra, where the lifetime is associated with the full width at half maximum of the spectral features. Hence, we propose to create a new software tool that will read the vibrational data calculated from DFT simulations, and translate it into the spectral function of the interesting vibrations.

These two approaches will also permit us to compare the role of electrons and phonons in the actual lifetime of adsorbate vibrations. Indeed, there are open questions to the actual damping mechanism in low-frequency modes on metal surfaces where both electron excitation and phonon damping may compete hand in hand in the limitation of vibrational lifetimes.

Our project addresses at the same degree of accuracy, the evaluation of vibrational lifetime of adsorbates on all types of solid surfaces. We aim at creating new computational tools for the standard VASP package and hence contribute to the study an understanding of many processes where vibrations are of fundamental importance, ranging from friction to heterogeneous catalysis.

## 2 Description of the work carried out during the visit

### 2.1 Implementation of the electron-hole damping theory within the VASP framework

During the first part of the stay of Dr Teobaldi in Toulouse a fully first principles method of electron-phonon interactions has been implemented in order to determine the electron-vibration coupling on the basis of DFT information from VASP according to the same theoretical approach as reported in [1]. Once the electron-vibration coupling matrix elements are known, it is possible to calculate the damping rate of molecular vibrations by mean of Fermi's golden rule. Within the computational VASP planewave framework, the general eigenfuctions of the Hamiltonian are Bloch states $|nk>$ where $n$ is the band index and $k$ is the wave vector of the Brillouin zone. Within this formalism, the general expression of the vibrational lifetime reads:

1) $$\frac{1}{\tau}=\frac{2\pi}{\hbar}\frac{1}{N_{kp}}\sum_{k}^{N_{kp}}\sum_{n}^{N_{bands}}\sum_{m\neq n}^{N_{bands}}\left(1-f_m\right)f_n\left|\left\langle mk\right|\frac{\partial \mathrm{H}}{\partial Q_\lambda}\cdot Q_\lambda\left|nk\right\rangle\right|^2\delta\left(\varepsilon_{mk}-\varepsilon_{nk}-\hbar\omega_\lambda\right)$$

where $Q_\lambda$ is the eigenvectors of the dynamical matrix for the optimized system of adiabatic Hamiltonian, $H$. The electron-vibration coupling is expressed by $\left(\partial H/\partial Q_\lambda\right)\cdot Q_\lambda$: it does not mix different k-points but only different bands $n$ and $m$ ($n\neq m$). The Fermi factors ($f_m$, $f_n$) account for the different occupation of the $n$ (occupied) and $m$ (unoccupied) states, hence the term *electron-hole excitation* for the damping mechanism of the vibrational excitation $\hbar\omega_\lambda$. The energy conservation is taken into account by the $\delta$-function, modelled by mean of a Gaussian function of width $\sigma$. Due to the use of a discrete k-point grid, the final result has to be normalized with respect to the number of k-points ($N_{kp}$) used in VASP calculations.

### 2.2 Intermode coupling: implementation of a variable step finite-difference approach to sample the potential energy surface close (and also not so close) to the computed VASP minimum

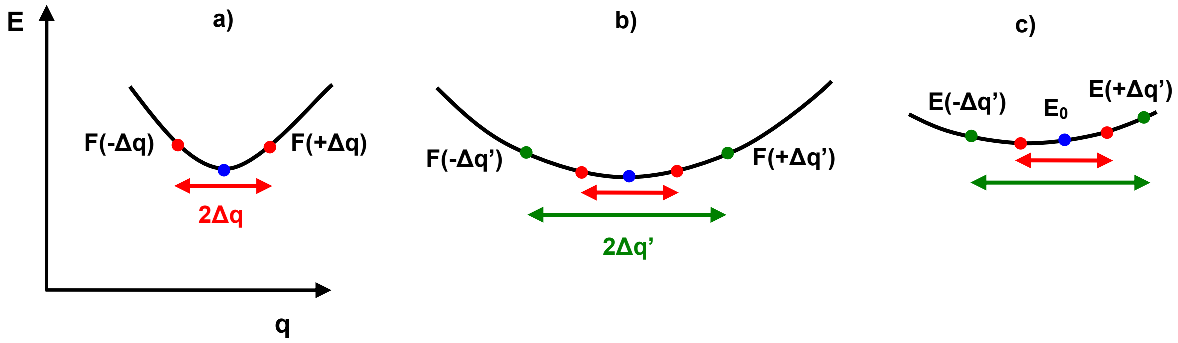
Vibrations are described by diagonalising the dynamical matrix (alias Hessian matrix) i.e. the matrix containing the second derivatives of the forces as obtained from VASP. The second derivatives of the forces are computed by introducing finite small displacements on the atomic degrees of freedom. According to the standard VASP implementation,[6] two (four) finite displacements (of step $\Delta q$) centred around the VASP optimised geometry (blue point in Scheme 1) are symmetrical produced for each active atom along the three Cartesian directions in turn. The wavefunction is then calculated for each displaced configuration and the ensuing atomic forces (from now on “displaced forces”) stored. Once all the displaced forces have been calculated, the dynamical matrix can be numerically determined according to eq. 2):

2) $$\frac{\partial F_{ij}}{\partial q_{ij}}\approx\frac{F\left(+\Delta q\right)-F\left(-\Delta q\right)}{2\Delta q}$$

In general, for a given system and its corresponding Potential Energy hyper-surface (from now on “PES”), the energy minimum is characterized by different curvatures for atomic displacements along different directions. As a consequence, any generic polyatomic (bound) system is characterized by the existence of both high energy *hard* modes of small vibrational amplitudes (see Scheme 1.a) and low energy *soft* modes of larger vibrational amplitude (see Scheme 1.b). The size of the displacement is very important with respect to a homogeneous numerical accuracy across all the calculated modes. In order to account for the existence of hard and soft vibrational modes the finite difference VASP standard approach (main.F, finite_diff.F) has been modified to provide an internal automatic check over the applied displacement for a given atomic degree of freedom. The implemented modifications account for the possibility to (automatically) increase or reduce the displacement till the energy of the displaced configuration or the very same displaced forces lie within a range entered by the user from standard input (INCAR file). At the present stage, when computing the dynamical matrix, the enforced displacement are smaller for hard than soft modes ($\Delta q < \Delta q'$ according to Scheme 1) to better account for the specific flatness of the energy profile along the considered degree of freedom.

A subtler drawback affecting fixed step finite difference approaches is that for soft degrees of freedom (i.e. those characterized by flat potential energy profiles), grid based DFT optimisations may converge on a geometry that does not correspond strictly to a minimum due the adopted computational accuracy (blue point in Scheme 1.c). If the applied displacement is too small (red points in Scheme 1.c) then it may happen that the energy of a displaced configuration is lower than the current minimum(!). This aspect heavily lowers the accuracy of computed vibrational frequencies in that the computed dynamical matrix is no longer positive defined (all positive eigenvalues except 6, or 5 if the system is linear, null eigenvalues) as it should be for a minimum point. Consequently, too large imaginary frequencies may appear and make the description of low energy frequencies worse, above all in terms of the corresponding eigendisplacements. According to the implemented modifications, this problem can be overcome by increasing the displacement in order to have a displaced configuration (green points in Scheme 1.c) whose energy is higher than that of the computed minimum.

Even though the implemented modifications do increase the computational cost when evaluating frequencies, in the present context they represent a step forward. In fact, the multi-step automatic approach here presented, accounts for a user-controlled automatic sampling of the PES near the computed minimum in terms of geometries, energies and forces, thus providing information necessary for a description of local anharmonicities and inter-modes coupling which in the end is the second final target of the currently running collaboration between the groups of Prof. Lorente in Toulouse and Prof. Hofer (Dr. Teobaldi) in Liverpool.



**Scheme 1.** Potential energy profiles along hard (a) and soft (b,c) degrees of freedom, q. Blue points represents VASP optimised geometries; red and green points refer to ±Δq and ±Δq' displaced configurations, respectively (see text for discussion).

## 3 Description of the main results obtained

### 3.1 Vibrational damping rates for CO/Cu(100) and CO/Cu(110)

CO chemisorption on Cu(100) and Cu(110) has been studied within the density functional projected augmented wave (DFT-PAW) approach within a PW91-GGA approximation for the exchange and correlation functional as currently implemented in the VASP program.[7] The Cu(100) and Cu(110) surfaces have been modelled by mean of four and six layers slab, respectively. The simulated slabs have been defined on the basis of the optimised bulk lattice parameter for Cu (fcc) i.e. 3.66 Å. In order to simulate an adsorbate density low enough to account for single molecule properties, one molecule of CO has been optimized on top of Cu(100)-(4x4) and Cu(110)-(2x3) super cells (see Fig. 1). The molecule and the two [three] topmost Cu(100) [Cu(110)] layers have been fully optimized adopting a 0.01 eV Å$^{-1}$ convergence threshold for the atomic forces. Optimisations and vibrational frequency evaluations have been carried out using a 4x4x1 k-points sampling that has been increased to 6x6x1 in order to evaluate converged lifetimes (see eq. 1) and reference [5]). All the calculations have been carried out with a planewave energy cutoff of 400 eV. Since all common GGA approximations to the exchange and correlation functional fail to determine the correct adsorption site for CO/Cu(110),[5] the on top adsorption geometry was enforced as in ref. [5] by constraining the CO optimisation just to the direction perpendicular to the Cu(110)-2x3 slab.

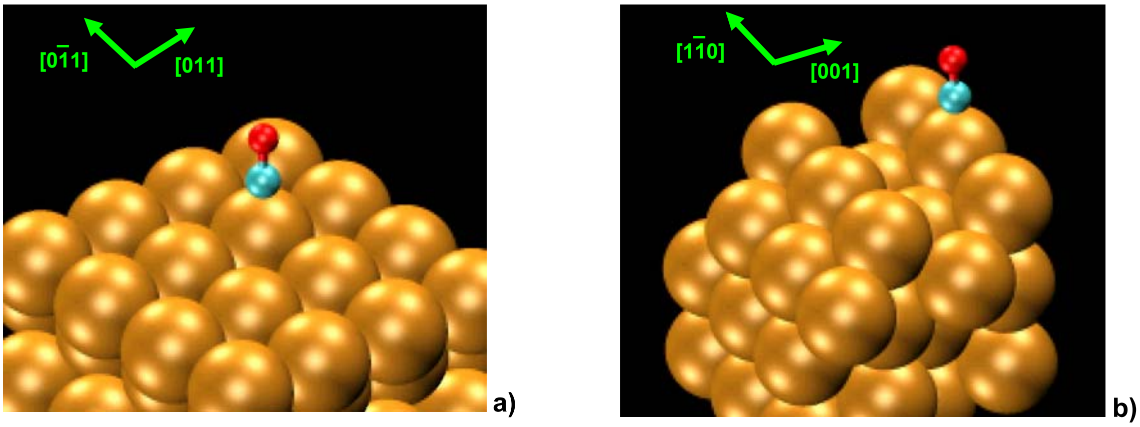


**Figure 1.** CO/Cu(100)-(4x4) (a) and CO/Cu(110)-(2x3) (b) simulation cell. O, C and Cu atoms are displayed in red, cyan and ochre, respectively.

The optimised adsorption distances (see Tab. 1) are found to be in agreement with previously published (ultra-soft pseudopotentials ) DFT data within deviations of less than 1%. The calculated adsorption energies, defined as the difference between the total energy of the full optimised system minus the sum of the non-interacting relaxed molecule and surface, are also reported in Tab. 1.

**Table 1.** CO/Cu(100) and CO/Cu(110) adsorption data. Previously published DFT data are reported within parenthesis.

| **Distance** | **Cu(100)** | **Cu(110)** |
|---|---|---|
| **C−O (Å)** | 1.20 Å (1.17 Å)[3] | 1.155 Å (1.166 Å)[5] |
| **C−Cu (Å)** | 1.84 Å (1.86 Å)[3] | 1.843 Å (1.860 Å)[5] |
| **$E_{ads}$ (eV)** | -0.96 (-0.77)[3] | -0.97 eV (-0.95)[5] |

The calculation of the vibrational frequencies has been performed according to the two-steps approach currently implemented in the VASP program: first the dynamical matrix is computed on the basis of small finite atomic displacements (here 0.02 Å) along the three Cartesian axes; then the dynamical matrix is diagonalized yielding the vibrational eigendisplacements and frequencies (eigenvalues). For computational reasons the dynamical matrix has been determined displacing only CO and the topmost metallic layer from the optimised positions. Tab. 2 reports the results for some selected modes of CO/Cu(100) and CO/Cu(110). The adopted labelling is the following: **I** for the C−O stretching, **M** for the molecular bouncing on the surface (motion of the molecular centre of mass along the direction perpendicular to the surface plane), **R** for the frustrated rotation i.e. motion of the C and O atoms nearly parallel to the surface but in opposite directions. While the two calculated frustrated rotations result degenerate for CO/Cu(100), this is not the case for CO/Cu(110). This aspect can be rationalized in terms of surface symmetry. In fact, while for a fcc (100) surface the geometrical corrugation is the same for both $[011]$ and $[0\bar{1}1]$ crystal directions, this is not true for a fcc(110) surface where the corrugation along $[001]$ is not the same as along $[1\bar{1}0]$ (see Fig. 1).

**Table 2.** Calculated vibrational energies $\hbar\omega_\lambda$ (meV) for some selected modes of CO adsorbed on Cu(100) and Cu(110). Experimental value (when available) are reported within parenthesis.

| **Mode** | **Cu(100)** | **Cu(110)** |
|---|---|---|
| **I** | 246.1 (259)[3] | 253.0 (257)[5] |
| **M** | 47.1 (43)[3] | 52.8 (//) |
| **R** | 36.1 (35)[3] | 36.6 (36.3)[5] |
| **R** | 36.0 (35)[3] | 34.9 (36.3)[5] |

On the basis of the vibrational eigenvectors $Q_\lambda$ and implementing eq. 1) into a VASP based program, the vibrational lifetimes for selected modes of CO/Cu(100) and CO/Cu(110) have been calculated. Electron-hole lifetimes are quite dependent on fineness of the k-point sampling: as reported in ref. [5] for Cu(110) they can change by a factor of 3 going from a 4x4x1 to a 6x6x1 k-point sampling grid. Consequently, the k-points sampling has been performed with an augmented 6x6x1 k-points grid in order to evaluate converged lifetimes. A comparison between the calculated lifetimes and previously reported experimental and DFT data for some selected modes of CO/Cu(100) is presented in Tab. 3. As previously found,[1,3,5] the agreement between the present theory and the experiment is quite good with deviations that lie within a few percent from the experiments for the considered modes.

**Table 3.** Lifetimes ($10^{12}$ $s^{-1}$) of selected CO vibrations on Cu(100). The calculated values are shown as a function of the gaussian broadening σ. Previously published DFT data are reported within parenthesis.

| **Mode** | **σ = 0.20** | **σ = 0.30** | **σ = 0.40** | **Experimental[3]** |
|---|---|---|---|---|
| **I** | 0.33 (0.76)[3] | 0.45 (0.70)[3] | 0.51 (0.63)[3] | 0.5 |
| **R** | 0.27 (0.47) [3] | 0.36 (0.52)[3] | 0.40 (0.52)[3] | 0.33 |

The present VASP approach is found to yield results in accordance with previously reported data also for CO/Cu(110) (see Tab. 4). In agreement with previous findings[3,5] the vibrational lifetimes are found to follow the same trend marked by the mode energy: the higher the vibrational frequency, the longer the lifetime. As already suggested in [5], this trend can be understood assuming that the available phase-space of electron excitation is given by $\hbar\omega_\lambda$, provided that the electron-vibration couplings are constant across the considered modes.

**Table 4.** Lifetimes ($10^{12}$ $s^{-1}$) of selected CO vibrations on Cu(110). The reported error bar has been estimated by varying the Gaussian broadening, σ, from 0.1 eV to 0.4 eV.

| **Mode** | **Present study** | **Previous DFT study** [5] |
|---|---|---|
| **I** | 0.57±0.04 | 0.45±0.03 |
| **M** | 0.077±0.010 | 0.093±0.005 |
| **R** | 0.32±0.03 | 0.37±0.03 |

In line with previous experimental and theoretical data, the electron-vibration coupling is found to loosely depend on the geometrical corrugation of the adsorption substrate as long as the nature of the bonding to the surface does not change: it has been already reported that the calculated lifetimes for a given mode of CO do not to change drastically going from Cu(100) to Cu(110). An aspect fully recovered by the data presented in Tab. 3 and 4 which have been calculated on the basis of a VASP based implementation of the electron-hole vibrational damping mechanism.

## 3.2 $H_2O$ frequencies: standard vs modified treatment

In order to test the implemented modification to the standard VASP finite difference treatment of vibrational frequencies a simple polyatomic molecular system has been considered i.e. one water molecule. In order to model a $H_2O$ in the vacuum, a cubic simulation cell of side 10 Å has been adopted. $H_2O$ has been optimised using a 0.01 eV $Å^{-1}$ atomic force converge threshold and a plane wave energy cutoff of 450 eV. The optimisation has been carried out within a PW91/PAW-GGA approach as currently implemented in the VASP package.[7] The accuracy of the calculation has been set to the highest possible level (PREC=HIGH in the INCAR file).[6] After full optimisation, $H_2O$ vibrational modes have been calculated according to the standard (NFREE=2, POTIM=0.02 Å) [6] and modified centred finite difference approach. For sake of comparison, the same system has been fully optimised and its vibrational modes evaluated by mean of the Gaussian package,[8] as currently licensed to Prof. F. Zerbetto, Dip.to di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40100 Bologna, Italy (email: francesco.zerbetto@unibo.it). Gaussian calculations have been carried at a relatively high level of computational accuracy adopting a hybrid B3LYP grid based DFT approach with a 6-31G* basis set and enforcing the default Gaussian grid fineness.[9] It is worthwhile to stress how the Gaussian treatment of vibrations has been thoroughly tested in the last years and nowadays it can be safely taken as a reference standard when evaluating vibrational frequencies and eigenvectors. Figure 2 report the vibrational VASP displacement together with the calculated frequencies.

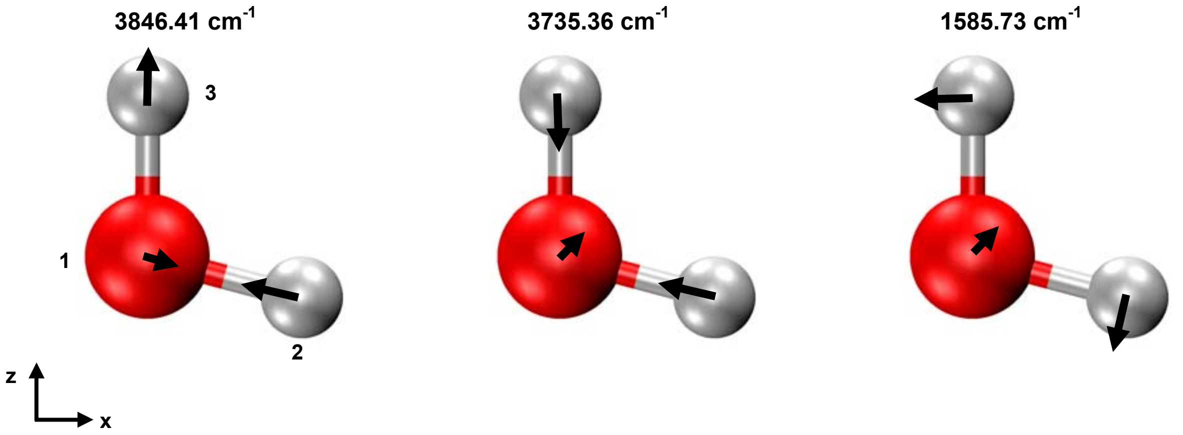


**Figure 2.** Calculated $H_20$ vibrational frequencies and eigendisplacement. The arrows representing the displacement are not in scale. O and H atoms are displayed in red and silver, respectively.

Tab. 5 reports the displacements enforced to scan the PES while looking for displaced configuration whose energies lie in between $E_0$ and 10xEDIFF, where $E_0$ is the energy of the computed minimum and EDIFF is the VASP convergence criterion on the wavefunction energy (here EDIFF=$0.5x10^{-7}$ eV).[6] It is worthwhile to remind that, while changing the displacements on the fly, information regarding the energy, wavefunction and forces for the intermediate steps has been produced and it could have been easily stored or outputted for post-processing purposes.

**Table 5.** Enforced $H_20$ atomic displacement. The atomic labelling is the same as in Fig.2

| **Degree of freedom** | **+Δq (Å)** | **-Δq (Å)** |
|---|---|---|
| **1x** | 0.02 | 0.02 |
| **1y** | 0.06 | 0.06 |
| **1z** | 0.02 | 0.02 |
| **2x** | 0.02 | 0.02 |
| **2y** | 0.06 | 0.06 |
| **2z** | 0.02 | 0.02 |
| **3x** | 0.02 | 0.02 |
| **3y** | 0.04 | 0.04 |
| **3z** | 0.02 | 0.02 |

In the present context our aim is to examine the calculated values for the 6 lowest energy mode for one optimised water molecule. Since $H_2O$ is a non-linear system, upon diagonalisation of the dynamical matrix, the six lowest vibrational frequencies should be zero or very close to it. As a rule of thumb, upon diagonalisation the lowest six frequencies of the dynamical matrix should be lower than 50 $cm^{-1}$ (6.20 meV) disregarding the sign.[9] Before discussing the presented results, a comment is necessary:

the fineness of the default grids implemented in Gaussian for DFT integrations is larger than those adopted by VASP even when the PREC=HIGH treatment is switched on.[6,9] Consequently, a coarser criterion of acceptance should be used to assess the quality of the vibrational treatment for the computed VASP minimum. The calculated frequencies for $H_2O$ with the modified VASP approach are reported in Tab. 6 and compared with standard VASP and Gaussian (B3LYP/6-31G*) data. While the implemented modifications do not significantly change the results for the three highest frequencies with respect to the standard fixed step approach, this is not the case for the six lowest energy modes that should correspond to three rotations and three translations of the considered system. In fact, due to the use of a different displacement for hard and soft modes, the description of the lowest six modes has been significantly improved with reduction up to ~ 68 $cm^{-1}$ (5th mode)! The new approach thus, globally accounts for an improved description of the computed frequencies and, above all, for a lower contamination of the vibrational eigenvectors by system translations and rotations. The next step of the Liverpool-Toulouse collaboration is the implementation of a computational procedure to project out the three system rotations and translations from the computed vibrational eigenvectors as currently implemented in Gaussian program.[8]

**Table 6.** Calculated $H_20$ vibrational frequencies ($cm^{-1}$). Imaginary frequencies are reported as negative.

| **Mode** | **Gaussian** | **Standard VASP** | **Modified VASP** |
|---|---|---|---|
| **1** | 3848.96 | 3843.62 | 3846.41 |
| **2** | 3727.01 | 3744.17 | 3735.36 |
| **3** | 1713.23 | 1589.63 | 1585.73 |
| **4** | 19.98 | 180.54 | 125.08 |
| **5** | - 0.0002 | 138.66 | 70.98 |
| **6** | - 0.0017 | 112.25 | 51.75 |
| **7** | - 0.0025 | -4.99 | -1.67 |
| **8** | - 37.18 | -51.99 | -34.60 |
| **9** | - 46.40 | -72.29 | -47.78 |

## 4 Projected publications/articles resulting or to result from the assigned grant

Since at the present stage the implementation of the electron-hole damping rate theory within VASP machinery can be considered finished and the computational approach working, the presented result for lifetimes of CO/Cu(100) and Cu(110) are going to be presented together with recently calculated Bardeen Inelastic Electron Tunnelling Spectroscopy data for CO adsorbed on Cu(100), Cu(110) and Cu(111):

G. Teobaldi, M. Peñalba, A. Arnau, W. A. Hofer and N. Lorente, *Tip effects in IETS: a first-principle study*, in preparation.

A second short-term application of the presented approach concerns the study of vibrational damping rates for Ce/Ag(110) and H-Ce/Ag(110), a computational study that has been recently started in Liverpool.

Concerning the second research theme considered during the stay of Dr. Teobaldi in Toulouse i.e. the intermode coupling evaluation in view of a theoretical description of phonon-phonon vibrational damping for adsorbates on semi-conducting surfaces, the computational tools necessary to collect DFT information for the PES around the computed minimum have been coded. Future work is going to be focused on the implementation of an enhanced vibrational treatment where rotations and translations are totally projected out from vibrational eigenvectors as currently implemented in the Gaussian package.[8] To our best knowledge, at the present stage such a treatment is not currently implemented in any solid state planewave simulation package. Consequently, documentation of our implementation could be of interest for the computational Solid State Physics community.

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