

Theoretical Interpretation of the IR Spectrum of Propyne on Cu(111)

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The IR spectrum of propyne adsorbed on Cu(111) has been analyzed using first-principles density functional periodic slab calculations. The agreement between experimental reflection absorption infrared spectra data and the present results is almost quantitative. This permits an unambiguous assignment for the band appearing at 1361 cm⁻¹, thus solving some controversy in the existing literature. This band was previously assigned either to the C₁C₂ stretching or to CH₃ symmetric deformation modes whereas the present work shows that, as a matter of fact, it involves a strong coupling between the two corresponding group frequencies. This is an important result because it shows that, to properly assign IR bands in polyatomic adsorbed molecules, the coupling between different group frequencies has to be taken into account.

1. Introduction

A detailed knowledge of the chemistry of hydrocarbons adsorbed on transition metal surfaces is of fundamental importance in basic research on heterogeneous catalysis but it is also relevant to the chemical industry. To establish and understand the microscopic mechanisms of these surface reactions requires the determination of the structure of the adsorbed molecules. Among the large number of surface analytical methods, infrared spectroscopy (IR) and related techniques are widely used in heterogeneous catalysis research.^{1–23} This is because of their ability to provide quite detailed information about the interaction between the surface and the adsorbed molecules under reaction conditions. The analysis of IR spectra, in particular, the assignment of the adsorbate vibrational modes, provides valuable information regarding the adsorbate structure, bonding modes, and adsorption sites.^{4,5} This information largely contributes to establish a first step toward the understanding of the elementary reaction steps occurring at the surface.

The assignment of vibrational frequencies in terms of group functional frequencies is claimed to be very valuable⁶ although one must realize that this kind of analysis is based on rather classical arguments.⁷ For adsorbates that retain most of their gas phase geometric and electronic structure, the assignment of vibrational frequencies is straightforward; it just requires direct comparison with available data for gas phase molecules. However, when the interaction between the adsorbate and the surface implies a largely distorted structure for the adsorbate, with concomitant changes in its electronic structure, the assignment becomes much more difficult. In some cases it is possible to extract information from the IR spectra of the corresponding molecule obtained in different but related chemical environments such as inorganic complexes.⁸ Nevertheless, this may lead to serious errors because the surface may strongly influence some particular normal mode.⁹ Often, arguments based on Fermi

resonances are to be invoked when a given band cannot be directly assigned. Once vibrational bands are assigned, several hypotheses about the adsorption geometry are made, usually by applying the “metal surface selection rule” (MSSR).^{10,11} This selection rule is based on classical arguments and does not take into account the atomic nature of the surface or of the adsorbate. Despite this limitation, the MSSR has been very successful in helping to determine the bonding mode of adsorbates, very often without further theoretical support. For a given gas phase species with no formal symmetry, all vibrational modes are symmetry allowed and their observed relative intensity is related to the change of the dipole moment for the corresponding transition. However, when this species is adsorbed on a surface, the MSSR states that only those modes with significant change on the dipole moment in the direction perpendicular to the surface carry noticeable intensity and hence determines the bands that are observed in reflection absorption infrared spectroscopy (RAIRS) experiments. The MSSR is also widely used to interpret in situ RAIRS spectra in electrochemistry.¹² The analysis of stretching frequencies of the adsorbed molecule provides information about the bonding mode. Assuming the validity of the MSSR, it is normal to predict whether a given bond is parallel or not to the surface, on the basis of the presence or absence of the corresponding stretching band on the spectrum. Moreover, when various stretching modes appear in the same region of the IR spectrum, it is possible to identify each individual mode through a proper analysis of the spectra of some isotopic substituted species.

Nowadays, theoretical calculations have reached the point where molecular structures are predicted with accuracy comparable to the most sophisticated experiments.^{13,14} Moreover, calculated vibrational spectra are usually close enough to the experimental values and thus offer a rigorous way to assign all the observed frequencies in an unambiguous way. The advent of accurate density functional theory (DFT) methods, parallel supercomputers, and efficient computational codes^{15–19} have permitted us to reach a similar level of accuracy also for molecules adsorbed on metal surfaces.^{20–24} In addition, the

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modern theoretical methods of electronic structure applied to surface science phenomena permit one to obtain all frequencies and, which is more important, their relative intensities without further assumptions. In particular, one can determine if a given mode can be considered active or not according to the MSSR. Likewise, spectra for different isotopic substituted species—complicated and expensive to produce experimentally—can easily be obtained from theory with no significant additional cost. Despite the potential of this sophisticated computational machinery in predicting vibrational spectra of adsorbed molecules, practical applications have been quite limited and mainly addressed simple diatomic molecules or hydrocarbons with at most two carbon atoms.^{25–29} Recently, the vibrational spectrum of larger molecules such as adenosine adsorbed on silver surfaces,³⁰ cyanopyridine on Au(111),³¹ or hydrocarbons like 1,4-cyclohexadiene³² and benzene³³ on Pt(111) have been reported, although the later studies are carried out using a cluster model approach. Periodic models based on the repeated slab approach have also been used to study the EELS spectra of butadiene adsorbed on Pt(111),³⁴ several unsaturated hydrocarbons up to benzene on Pt(111) and Pd(111),³⁵ and benzene on Pt(111), Pd(111), and Rh(111).³⁶ Moreover, although applications involving such rather large molecules are sparse, there are no studies involving more than one molecule per unit cell. Indeed, frequency calculations considering more than one hydrocarbon molecule per unit cell would allow one to examine possible coupling of nuclear motion involving two neighboring molecules. In the forthcoming sections, we will show that these couplings are present in the propyne–Cu(111) system, and that they have to be explicitly considered to properly assign its RAIR spectrum.

Propyne, CH_3CCH , is one of the simplest hydrocarbons with more than two carbon atoms and an ideal candidate to study the structure and bonding mode of alkynes. The carbon skeleton of propyne adsorbed on Cu(111) was established by means of quantitative surface structure analysis based on the C(1s) photoelectron diffraction, PhD, technique.³⁷ Likewise, low energy electron diffraction (LEED) studies have also unambiguously established the long-range periodicity of propyne and 3,3,3-trifluoropropyne adsorbed on Cu(111).³⁷ A very important conclusion of this experimental study is that the long-range periodicities for ethyne and propyne on Cu(111) are different. This structural information is complemented by RAIRS studies for propyne on various metal surfaces including Cu(111),⁸ Ni(111) and Cu(110),³⁸ and Pd(100).³⁹

Recently, the reactivity and structure of propyne on Cu(111) have been studied theoretically by means of the cluster model and periodic approaches within a density functional based method.^{40,41} These studies established that adsorbed propyne is strongly distorted, in agreement with the PhD predicted structure. Moreover, it appears that the molecular structure of propyne adsorbed on Cu(111) is reminiscent of the gas phase molecule but in the first triplet excited state. The excellent agreement between the experimental and calculated structures for adsorbed propyne strongly suggests extending the theoretical study with the aim to provide an unbiased interpretation of the vibrational spectrum of this molecule, which is rather more complex than that of ethyne, the simplest alkyne. The need for such theoretical study is evidenced by the existing disagreement in the literature regarding band assignment. Some of the bands in the mid-IR zone, in particular the band at 1361 cm^{-1} , are attributed either to the $\text{C}_1\text{--C}_2$ stretch⁸ or to the CH_3 symmetric deformation.³⁸ Therefore, the main purpose of the present study is a detailed study of the vibrational spectrum of propyne on Cu(111) by

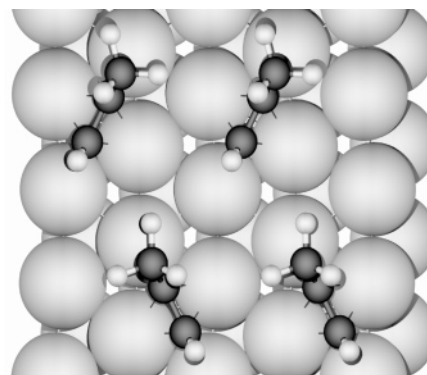


Figure 1. Schematic representation of the long-range structure of propyne adsorbed on Cu(111).

means of density functional theory (DFT) applied to suitable slab models. The present results will reconcile the contradictory assignments made above. In addition, the theoretical assignments will be completed by the analysis of the spectra for the deuterated species allowing a direct comparison with experiment.

2. Surface Models and Computational Details

The Cu(111) surface has been modeled by the repeated slab approach; this is an infinite two-dimensional slab in a three-dimensional periodic cell generated by introducing a sufficiently large vacuum width ($\sim 12\text{ Å}$) in the direction perpendicular to the surface. The slab contains four atomic metal layers with the hydrocarbon molecules adsorbed on one side of the slab. The Cu–Cu interatomic distances have been optimized for the bulk; the resulting calculated value being 2.57 Å which is very close to the experimental value of 2.55 Å .⁴² The $4\times\sqrt{3}$ -rect surface unit cell (0.29 monolayer (ML)), which is the one experimentally determined by LEED,³⁷ has been used. This model contains two adsorbed propyne molecules and thirty-two Cu atoms per unit cell. The propyne molecules are placed in a criss-cross fashion with the center of the $\text{C}_1\text{--C}_2$ bond nearly above a bridge site. Two different orientations can be distinguished for the adsorbed molecules, named P and twisted-P (t-P). P corresponds to a situation in which C_1 is nearly above the hcp site whereas in the t-P orientation the C_1 atom is nearly above the fcc site (Figure 1). The geometry optimization includes all degrees of freedom of the two adsorbed molecules and of the two uppermost atomic metal layers. The two lower metal planes are kept fixed at the optimized bulk geometry. Notice that the present model is slightly different from the one utilized in previous work, where the experimental Cu–Cu distance was used.⁴¹

Additionally, we have computed the structure and spectrum of a single propyne molecule adsorbed on a $2\times\sqrt{3}$ unit cell (0.29 ML). In this smaller unit cell, the two orientations, P and t-P, have also been explored. It is important to notice that only one propyne molecule is taken into account in each one of these calculations, and as a consequence, the interaction among adsorbed molecules is not explicitly included. Therefore, the purpose of these calculations is to artificially eliminate the coupling between molecules and thus give additional evidence of this important effect.

The calculations have been performed in the framework of DFT using the Vienna Ab Initio Simulation Program (VASP).^{17–19} This program solves the Kohn–Sham equations of the density functional theory with the development of the one-electron wave function in a basis set of plane waves. The electron–ion

interactions are described by the projector augmented wave (PAW) method developed by Blöchl.⁴³ The PAW is essentially an all electron frozen core method that combines the accuracy of all electron methods and the computational simplicity of the pseudopotential approach; especially in the implementation of Kresse and Joubert.⁴⁴ A tight convergence of the plane-wave expansion was obtained with a cutoff of 500 eV; grids of $3 \times 7 \times 1$ and $5 \times 7 \times 1$ Monkhorst–Pack special k points have been used for the $4\sqrt{3}$ and $2\sqrt{3}$ unit cells, respectively. The generalized gradient approximation (GGA) has been used with the functional of Perdew and Wang.⁴⁵ The vibrational frequencies and the corresponding normal modes have been calculated within the harmonic approach. The block of the Hessian matrix corresponding to adsorbate atomic displacements has been obtained by numerical differences of the analytical gradients. Only second derivatives of the energy are taken into account, and as a consequence, one must keep in mind this approximation when comparing with the experimental spectrum (anharmonic effects are especially important in the CH stretching modes). To investigate the effect of metal surface atoms displacements from equilibrium positions (phonons) on the vibrational frequencies of the adsorbate, test calculations have been carried out on the $2\sqrt{3}$ unit cell including also the first metallic layer on the construction of the Hessian matrix. As expected, the mixing of adsorbate vibrational modes above 600 cm^{-1} with phonons is negligible on both frequencies and intensities, the frequency changes with respect to a calculation with the substrate atoms frozen at their equilibrium positions are always less than 10 cm^{-1} . Only the propyne frustrated translation in z direction changes from 325 to 361 cm^{-1} . Therefore, the rest of calculations for the vibrational frequencies of adsorbed propyne using either the $4\sqrt{3}$ and $2\sqrt{3}$ unit cells were carried out by ignoring the coupling between molecular vibrations and surface phonons.

The IR intensities were calculated by using the IRIAN external code especially developed for this purpose.⁴⁶ The VASP code already computes the dipole moment components at each nuclear configuration used for the construction of the Hessian matrix. The IRIAN code computes a numerical estimate of the dipole moment derivatives, $d\mu_z/dz$, on the basis of the atomic Cartesian displacements. Note that, because only those vibrational modes that give rise an oscillating dipolar moment perpendicular to the surface are active, we have considered only the z component of the dipole moment. The calculated $d\mu_z/dz$ values are then projected onto the basis of normal modes to obtain the dynamic dipole moments of the vibrational normal modes, $d\mu_z/dQ_k$. The square of the latter is directly related to the IR intensities of fundamental bands. It is important to point out that vibrational frequencies for the normal modes are mass sensitive and, consequently, the intensities of IR bands may also change when substituted isotopic species spectra are examined. Nevertheless, intensity bands are not normally recalculated when changing atomic masses.³³ Because the overall calculation involves numerical derivatives, to provide accurate results for both frequencies and intensities, it is important to control several parameters. First, it is necessary to determine the single point geometries to be used and whether they must be the same or not for frequencies and intensities. Next, one needs to establish the step length for the numerical differences. Extensive tests have been performed with various single point samples; the optimal one being two atomic displacements of 0.02 Å in the three directions of the space for both type of derivatives. These displacements should be taken as large as possible to have

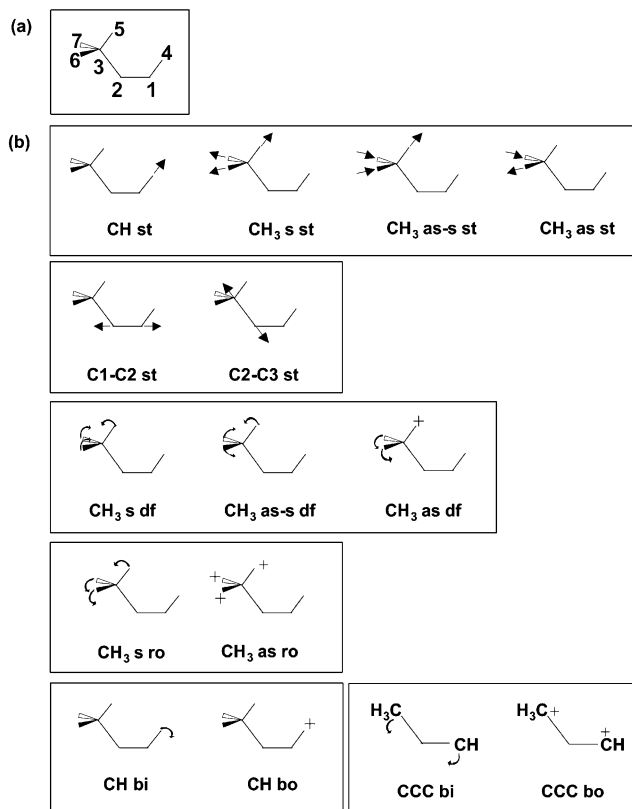


Figure 2. (a) Notation used for atom labeling in the adsorbed molecule. (b) Notation used for the group frequency modes. Key: *as*, asymmetric; *s*, symmetric; *st*, stretching (bond with the smallest atom numbers is elongated); *bi*, bending in-plane (angle with the smallest atom numbers is opened); *bo*, bending out-of-plane (atoms with the smallest atom numbers go away from the plane); *ro*, rocking; *df*, deformation; *to*, torsion (atoms with the smallest atom numbers move clockwise).

meaningful numerical values but small enough to avoid going beyond the harmonic region.

To translate the vibrational normal modes to the current analysis in terms of group functional frequencies, the following notation will be used. First of all, atoms are labeled as displayed in Figure 2a. Next, for each group frequency the “positive” direction (see below) is as in Figure 2b. This definition was chosen by taking into account the convention described in the following. For stretching movements, the “positive” sense corresponds to a motion where the bond with the two smallest atom numbers is elongated. For bending modes, the positive sense corresponds to the motion where the angle with the three smallest atom numbers is opened. For out of plane bending modes, atoms with smallest atom numbers moving away from bonding plane mark the positive sense. Although they are not explicitly displayed, torsion modes would be defined as the clockwise motion of atoms with smallest atom numbers. This notation is obviously unnecessary when each normal mode could be associated with a unique group frequency, but when different group frequencies contribute to a given vibrational normal mode this simple notation helps to decide a given assignment. This notation is also useful to avoid the usual in-phase and out-of-phase terms, which are not always univocal. When two (or more) group frequencies are coupled as the superposition of the two movements displayed in Figure 2b, the coupling is indicated by a plus sign. On the other side, a minus sign is used to indicate the situation where two modes are coupled but one in the sense displayed in Figure 2b and the other one in the opposite sense (i.e., all displacement vectors in opposite direction). Moreover, the approximate contribution of each group frequency to a given

mode is indicated by λ and μ coefficients (λ indicates a contribution less than $\sim 10\%$ and μ a contribution of $\sim 20\%$ at most). Coupling coefficient less than $\sim 2\%$ have been neglected; these coupling coefficients are estimated from the square of the coefficients appearing in the normal mode.

Finally, all simulated spectra have been obtained using Lorentzian functions, with a bandwidth of 20 cm^{-1} and a resolution of 0.5 cm^{-1} .

3. Results and Discussion

3.1. Structure. As reported previously,^{40,41} propyne adsorbs on the Cu(111) surface in a di- σ /di- π mode. Both the $4\times\sqrt{3}$ and the $2\times\sqrt{3}$ unit cell predict identical structures. The adsorbed geometry is highly distorted with the methyl group tilted away from the surface. The molecular $\text{C}_1\text{--C}_2\text{--C}_3$ plane is perpendicular to the surface and the center of the $\text{C}_1\text{--C}_2$ bond is found to be almost above the bridge site with the $\text{C}_1\text{--C}_2$ bond along the long bridge direction. The $\text{C}_1\text{--C}_2\text{--C}_3$ angle becomes close to 120° as expected from a sp^2 to sp^3 hybridization change. The $\text{C}_1\text{--C}_2$ and $\text{C}_2\text{--C}_3$ distances are predicted to be 1.38 and 1.51 Å, respectively. Both close enough to the experimental value.³⁷ The C–H distances, which cannot be predicted by PhD experiments, are all within $1.100 \pm 0.005\text{ Å}$ and one of the hydrogen methyl atoms is in an *eclipsed* orientation with the H atom bonded to C_1 (see Figure 1). The $\text{H--C}_1\text{--C}_2$ angle, which also provides a measure of the C_1 hybridization, is 123° and adds further support to a di- σ /di- π adsorption mode with C_1 and C_2 both on a $\text{sp}^2\text{--sp}^3$ like hybridization. This bonding geometry is reminiscent of the one proposed for acetylene on Cu(111).^{47,48} It should be pointed out that the lack of enough accuracy on the PhD experiments leads to predictions of the bond distances that are nearly parallel to the surface. Therefore, it is very difficult to distinguish between sp^2 and sp^3 hybridization on the C_1 and C_2 atoms, although the $\text{C}_1\text{--C}_2\text{--C}_3$ angle indicates that the former is more likely. A similar claim was raised from Chesters and McCash from the vibrational analysis.⁸ The vertical distances of C atoms to the surface in both P and t-P orientations are 1.41 (C_1) and 1.51 (C_2) Å to be compared with the experimental values, 1.44 ± 0.04 and $1.45 \pm 0.04\text{ Å}$, respectively.³⁷ Minor changes are observed on the Cu(111) surface upon adsorption of the propyne molecule. The three Cu atoms surrounding the C_2 move upward (1%) whereas the one directly under the acetylene hydrogen moves inward, causing a slight corrugation of the metallic surface. The changes on the second metal layer are even smaller. Only the hcp Cu atoms in the adsorption site move down (1%), away from the carbon atom directly above.

3.2. IR Spectra. Gas Phase Propyne. The computed frequencies and assignments for gas phase propyne are displayed in Table 1 where experimental results⁴⁹ have also been included for comparison. The agreement between experimental and calculated data is fairly good. In fact, the average deviation for the PW91 harmonic calculated vibrational frequencies with respect to the fundamental experimental values, ν_i , is of $\sim 30\text{ cm}^{-1}$.

To facilitate the forthcoming discussion, it is important to point out that some mixing between different group functional frequencies appears in some normal modes (see Table 1). El Idrissi et al.⁵⁰ (using the second-order Møller Plesset, MP2, level of theory and augmented cc-pVTZ basis set) were the first to report the corresponding nuclear displacements and to recognize that some normal modes involve a noticeable mixing of stretching group frequencies corresponding to adjacent bond in the linear carbon chain skeleton; mainly $\text{C}_1\text{--C}_2\text{ st}$ and $\text{C}_2\text{--C}_3$

TABLE 1: Calculated PW91 Frequencies for the Free Propyne Molecule; Frequencies Have Been Obtained by Carrying out the Calculation of the Molecule in a Sufficiently Large Cubic Box^a

vibrational mode	PW91	exp ⁴⁹	$\Delta\nu_{\text{PW91}}$
CH <i>st</i>	3398	3334	64
CH ₃ <i>as st</i>	3019	3008	−11
CH ₃ <i>s st</i>	2976	2918 ^b	58
$\text{C}_1\text{--C}_2\text{ st} - \lambda\text{ CH st}$	2172	2142	30
CH ₃ <i>as df</i>	1424	1452	−28
CH ₃ <i>s df</i>	1359	1382	−23
CH ₃ <i>ro</i> + $\lambda\text{ CCC } b$	1001	1053	−52
$\text{C}_2\text{--C}_3\text{ st}^d$	958	931	27
CH <i>b</i>	619	633	−14
CCC <i>b</i>	325	328	−3

^a Differences with respect to the experimental values are also shown ($\Delta\nu_{\text{PW91}}$). All values in cm^{-1} . ^b Selected value. Fermi resonance with first CH₃ *as df* overtone. Experimental bands at 2941 and 2881 cm^{-1} . ^c $\text{C}_1\text{--C}_2\text{ st}$ causes $\text{C}_2\text{--C}_3\text{ st}$ (only C_2 moves against C_3). ^d This vibrational normal mode is not like that in Figure 2b. The acetylene group, CH, goes away; C_2 (which does not move practically) and methylene H atoms move like C_3 .

TABLE 2: Experimental⁴⁹ (f_{exp}) and Calculated PW91 (f_{T}) Isotopic Factors for the Free Propyne Molecule

CH ₃ CCH assignment	CH ₃ CCD		CD ₃ CCH		CD ₃ CCD	
	f_{exp}	f_{T}	f_{exp}	f_{T}	f_{exp}	f_{T}
CH <i>st</i>	1.27	1.28 ^a	1.00	1.00	1.27	1.28 ^a
CH ₃ <i>as st</i>	1.00	1.00	1.35	1.35	1.35	1.35
CH ₃ <i>s st</i>	1.00	1.00	1.38 ^b	1.39	1.38 ^b	1.39
$\text{C}_1\text{--C}_2\text{ st} + \lambda\text{ CH st}$	1.04	1.08 ^c	1.00	1.00	1.07	1.08 ^c
CH ₃ <i>as df</i>	1.00	1.00	1.39	1.39	1.39	1.39
CH ₃ <i>s df</i>	1.00 ^d	1.00	1.24	1.24 ^e	1.25	1.24 ^e
CH ₃ <i>ro</i> + $\lambda\text{ CCC } b$	1.00	1.00	1.26 ^f	1.24 ^g	1.26	1.24 ^g
$\text{C}_2\text{--C}_3\text{ st}$	1.05 ^h	1.01	1.12 ⁱ	1.12 ^j	1.15 ^h	1.13 ^j
CH <i>b</i>	1.27	1.29 ^k	1.00	1.00	1.29	1.29 ^k
CCC <i>b</i>	1.04	1.05 ^l	1.08	1.08 ^l	1.12	1.13 ^l

^a Assigned to $\text{CD st} + \mu\text{ C}_1\text{--C}_2\text{ st}$; C_1 moves against C_2 . ^b Selected value (2110 cm^{-1}). Fermi resonance with first CD_3 *as df* overtone. Experimental bands at 2121 and 2077 cm^{-1} . ^c Assigned to $\text{C}_1\text{--C}_2\text{ st} + \mu\text{ CD st}$. The movement of D atom versus C_1 increases, and the displacement of C_2 versus C_3 decreases. ^d Overlap with CH₃ *s df*. ^e Assigned to $\text{CD}_3\text{ s df} + \lambda\text{ C}_1\text{--C}_2\text{ st}$. The displacement of C_3 against C_2 increases considerably, causing the $\text{C}_2\text{--C}_3$ stretch. ^f Overlap with $\text{C}_2\text{--C}_3\text{ st}$. ^g Assigned to $\text{CD}_3\text{ s ro} + \mu\text{ CCC } b$. The displacement of C_2 , C_3 , and H_4 out of molecular axis enlarges. ^h Calculated frequency. ⁱ Overlap with $\text{CD}_3\text{ s ro}$. ^j Assigned to $\text{C}_2\text{--C}_3\text{ st} + \text{CD}_3\text{ s df}$. ^k Assigned to $\text{CD } b + \lambda\text{ CCC } b + \lambda\text{ CH}_3$ (or CD_3) *ro*. ^l Displacements of H methylene atoms decrease and displacement of acetylene H increases as the number of D atom increases.

st. Unfortunately, the assignment of experimental bands usually neglects these couplings.

With the aim of proposing some general rules that can be helpful to carry out the experimental assignment of the bands arising from adsorbed species, especially when the couplings above commented need to be explicitly considered, the isotopic factors of the bands for the free molecule have also been calculated. Table 2 reports the experimental isotopic factors and the PW91 calculated values. The latter have been evaluated as the quotient between the frequency for CH_3CCH and the corresponding frequency for the isotopic substituted species. From simple reduced mass arguments a factor between 1.35 and 1.39 is to be expected for the bands, implying the motion of one D atom whereas a factor 1.0 corresponds clearly to the case where the D atom does not participate in that particular nuclear motion. In some cases, the calculated values differ significantly from this simple estimate (Table 2). This is a clear indication that the corresponding normal mode involves coupling

TABLE 3: Computed Frequencies for Propyne on Cu(111) in the Range 3000–1300 cm⁻¹ ^a

vibrational mode	4x√3				2x√3	
	ν	I^b	% P	% t-P	ν	I^b
P (CH ₃ <i>as st</i>)	3018	0	100	0	3020	0
t-P (CH ₃ <i>as st</i>)	3008	0	0	100	3024	0
t-P (CH ₃ <i>as-s st</i>)	2992	2	0	100	2997	1
P (CH ₃ <i>as-s st</i>)	2989	1	100	0	3004	1
t-P (CH <i>st</i>)	2935	7	2	98	2944	4
P (CH <i>st</i>)	2930	4	98	2	2944	3
P (CH ₃ <i>s st</i>) + μ t-P (CH ₃ <i>s st</i>)	2920	26	84	16	2923	18
t-P (CH ₃ <i>s st</i>) - μ P (CH ₃ <i>s st</i>)	2918	5	17	83	2927	14
P (CH ₃ <i>as-s df</i>)	1477	0	100	0	1427	0
t-P (CH ₃ <i>as-s df</i>)	1429	0	0	100	1430	0
P (CH ₃ <i>as df</i>)	1422	0	99	1	1410	0
t-P (CH ₃ <i>as df</i>)	1413	0	1	99	1413	0
t-P (C ₁ –C ₂ <i>st</i> + CH ₃ <i>s df</i>) + μ P (C ₁ –C ₂ <i>st</i> + CH ₃ <i>s df</i>)	1354	1	8	92	1356	2
P (C ₁ –C ₂ <i>st</i> + CH ₃ <i>s df</i>) + μ t-P (C ₁ –C ₂ <i>st</i> + CH ₃ <i>s df</i>)	1350	6	84	16	1357	2
t-P (CH ₃ <i>s df</i> + μ C ₁ –C ₂ <i>st</i>)	1330	0	1	99	1327	0
P (CH ₃ <i>s df</i> + μ C ₁ –C ₂ <i>st</i>)	1325	1	99	1	1328	0

^a First five columns: assigned normal modes, vibrational frequency, relative intensity, and percentage of P and t-P structures adsorbed on the 4x√3-rect unit cell. Last two columns: vibrational frequency and intensity for the P or t-P orientation in the 2x√3-rect unit cell. Approximated coupling coefficients evaluated from VNM: $\lambda < 10\%$, $\mu < 20\%$. Additional couplings in the slab model appear in italics. Frequencies in cm⁻¹ and Intensities in km.mol⁻¹. ^b Intensity values smaller than 0.5 have been rounded to zero, the finite although small value arises from slight geometric distortions that remove the molecular symmetry plane.

between two or more group frequencies. Therefore, the accurate assignment of the corresponding bands requires special care. In fact, upon deuteration the couplings between group frequencies can appear, disappear, or change their relative percentage (see footnotes in Table 2). The experimental assignment of CH/CD *st* did not consider the coupling of the CD *st* motion with that of the C₁–C₂ *st*. Nevertheless, an additional indication of the importance of these group frequency couplings can be found in the spectrum of propyne physisorbed on Cu(111)—the random orientation of weakly physisorbed propyne molecules with the three carbon atoms in a collinear conformation—which closely resembles that of gas phase propyne.⁸ The effect of deuteration of the acetylene hydrogen on the CH *st* shows up an isotopic factor of 1.27. This downshift is not as large as the one predicted from a simple harmonic oscillator model on CD *st*. This led Chesters and McCash⁸ to assign this band of the CH₃CCD spectrum to the CD *st* coupled to the C≡C *st* and stated that the resulting mixing of group frequencies shifts the bands. Note that the experimental isotopic factor for C≡C *st* is 1.08, significantly larger than 1.00, which is the ideal value in the absence of group frequency coupling.

Propyne on Cu(111). The calculated frequencies for the adsorbed propyne species are summarized in Table 3. Notice that although the adsorbed molecule does not exhibit any particular symmetry and, hence, all vibrational modes could be observed in the IR spectrum, one must still take into account the MSSR. Therefore, only the vibrational modes implying a concomitant noticeable change of the dipole moment in the direction normal to the surface will be active in RAIRS. Because the adsorbed propyne molecules exhibit a near *C_s* local symmetry similar to that of the gas phase structure in the triplet state,⁴⁰ the group frequencies displayed in Figure 2b have been used to assign the bands. Hence, the *as* and *s* notation refers to the corresponding local symmetry plane. The *as-s* notation corresponds to nuclear displacements symmetric to this plane but arising from symmetry E in gas phase propyne. This kind of mode is usually referred to as *as*, asymmetric, because the *as* counterpart component is not observed (cf. Figure 2b).

The experimental spectrum of propyne adsorbed on Cu(111)⁸ is dominated by the CH stretching bands appearing in the 2900–3000 cm⁻¹ region and by a quite strong feature showing up around 1350 cm⁻¹. It is important to note that the experimental

resolution of the spectrum reported by Chesters and McCash a long time ago was quite low.⁸ Moreover, the experimental assignment was carried out on the basis of one adsorbed propyne per unit cell with the C–C axis lying parallel to the surface, with an overall 4-fold coordination to the surface and with the methyl group and the acetylene hydrogen tilting away from the surface. However, because of the rather low resolution in the experiment, the propyne–surface bonding model was only used to assign the main features with no attempt to resolve the numerous shoulders accompanying the main bands. Nevertheless, these shoulders could also be ascribed to the presence of molecules on the surface on a different adsorption mode or even to intra- or intermolecular couplings.

To provide some evidence in favor of or against these possibilities, we first analyze the results obtained with the 2x√3-rect unit cell for both P and t-P orientations. In this case there is only one adsorbed molecule over the model. In the 2900–3100 cm⁻¹ region, this model predicts the same fundamental bands as assigned experimentally, i.e., CH₃ *as-s st* (3004–2997 cm⁻¹), CH *st* (2944–2944 cm⁻¹), and CH₃ *s st* (2923–2927 cm⁻¹), where the values in brackets correspond to the P and t-P orientations. Concerning the CH *st* mode some variation in the order is observed (see the two rightmost columns of Table 3 and the experimental assignments in Table 4). This order is the same obtained for propyne in the triplet state [CH₃ *as-s st* (2977), CH *st* (2946), and CH₃ *s st* (2862)], indicating that the activation of the molecule produces the shift down in the CH *st* frequency. Apart from that, the relative band intensities are well reproduced, the CH₃ *s st* being the most intense one. For the two possible orientations of the molecule above the surface (P and t-P) the intensity of this band changes slightly (20%). The simulated spectrum for the 2x√3 unit cell is reported in Figure 3a and has been obtained by putting together the frequencies and intensities of the two orientations. Hence, one may find a larger number of fundamental frequencies than plotting only those corresponding to one orientation only. This strategy permits a representation of the simulated spectrum when intermolecular couplings are neglected but considering simultaneously both the P and t-P orientations. In the 1300–1500 cm⁻¹ region, a very weak feature at 1427–1430 cm⁻¹ shows up and is assigned to the CH₃ *as-s* deformation. The two bands immediately below (1357–1356 and 1328–1327 cm⁻¹) cor-

TABLE 4: Main IR Peaks for Propyne (CH_3CCH) on Cu(111) and Their Assignment^a

vibrational mode	Cu(111) ^b	Cu(111) ^c	Cu(110) ^d	Ni(111) ^d	Pd(100) ^e
CH <i>st</i>	2930–2935	2855	2751	2871	2862
CH ₃ <i>as st</i>	3008–3018				
CH ₃ <i>as-s st</i>	2989–2992	2923			2934
CH ₃ <i>s st</i>	2918–2920	2883	2875	2888	2885
C ₁ –C ₂ <i>st</i> (– CH ₃ <i>s df</i>)	1350–1354	1361			
CH ₃ <i>as-s df</i>	1429–1477				1420
CH ₃ <i>s df</i> (+ C ₁ –C ₂ <i>st</i>)	1325–1364		1358	1354	1344

^a Experimental results on different metal surfaces have also been included for comparison. ^b Theory, present (slab) results. ^c Reference 8. ^d Reference 38. Bands at 2815 and 2826 cm^{-1} were also assigned as the first overtone of CH₃ asymmetric deformation for Cu(110) and Pd(100), respectively. ^e Reference 39.

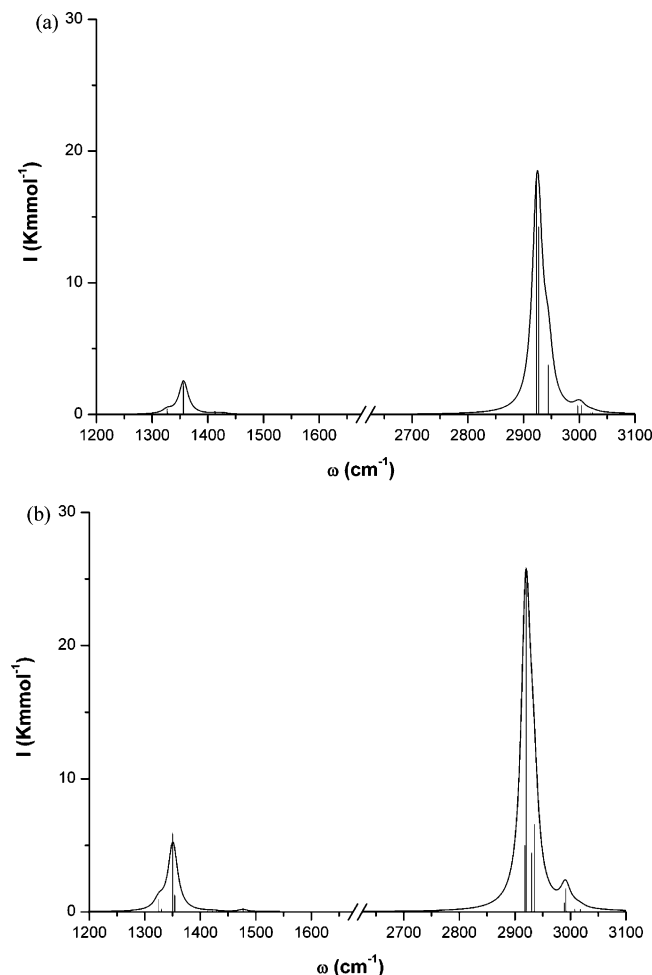


Figure 3. Simulated vibrational spectrum of propyne adsorbed on Cu(111) as obtained from: (a) merging the P and t-P $2\times\sqrt{3}$ calculations; (b) the $4\times\sqrt{3}$ slab model calculation.

respond to the negative and positive coupling (in the sense of Figure 2b) of C₁–C₂ *st* and the CH₃ *s df* (i.e., umbrella mode) group modes. Interestingly enough, this coupling causes two bands with very different intensities, the C₁–C₂ *st* + CH₃ *s df* being the most intense band in this region of the spectrum and having the same intensity in P and t-P orientations. The frequency calculations for free propyne in the triplet state predict a C₁C₂ *st* at 1664 cm^{-1} (corresponding to a double CC bond) and not coupled with any CH₃ deformation. The use of the frequency values of the triplet state to assign the spectrum of the adsorbed molecule is not straightforward because of the different character of the C₁C₂ bond. This difference supports the sp²–sp³ hybridization inferred from structural data. After the analysis of the local modes, we turn our attention to the results emerging from calculations including explicitly two propyne molecules per unit cell and isotopic effects. The

assignment of the vibrational peaks in the two important regions of the spectrum will be explained in detail in the forthcoming discussion and with the help of Tables 3–6.

In the CH stretching region, the 2989–2992 cm^{-1} feature is assigned to the CH₃ *as-s* stretching; upon methyl deuteration it shifts down to 2210–2212 cm^{-1} , with a calculated isotopic factor of 1.35. In agreement with the experimental work, the most intense peak appears at 2918–2920 cm^{-1} and is assigned to the CH₃ *s* stretching. In contrast to the case of CH₃ *as-s st* (and to CH₃ *as st*, which has intensity zero), there is a coupling between the CH₃ *s st* of both molecules present in the unit cell. As in the case of the intramolecular coupling described in the discussion of the $2\times\sqrt{3}$ cell results, this coupling causes two bands with very different intensities. In one of the bands the H atoms of the methyl group of two molecules move in the same sense and hence the dipole moment change is larger than in the case that they move in opposite directions. One may interpret this result by stating that one band borrows intensity from the other. Unfortunately, the resolution of the experimental spectrum does not allow us to firmly confirm this interpretation. Upon methyl deuteration this feature shifts to 2097–2098 cm^{-1} , with a calculated isotopic factor of 1.39. The CH *st* mode appears now at 2930–2935 cm^{-1} . This is characteristic of a rehybridization of the triple C–C bond from sp to somewhat between sp² and sp³ in character. Upon deuteration of the acetylene hydrogen a shift of $\sim 800\text{ cm}^{-1}$ is observed for this CH *st* mode. A similar shift has also been reported for ethyne on Cu(111).⁴ All theoretical frequencies have isotopic factors between 1.35 and 1.39 and 1.00 depending on whether deuteration affects or not the corresponding group mode. Unfortunately, there are only available experimental data concerning the deuterated spectrum of the acetylene hydrogen on Cu(111). From assigned values, the experimental isotopic factor is 1.33,⁴ only slightly different from the one obtained theoretically, 1.36.⁴⁷ The present results are in very good agreement with the experimental ones,⁸ although we must admit that a reverse order between calculated results and the experimental assignment is found for the methyl symmetric stretching and the CH stretching bands. This reversal in the CH₃ *s st* and CH *st* group frequencies in the simulated spectrum, in either the $2\times\sqrt{3}$ or $4\times\sqrt{3}$ system, could be ascribed to the presence of a peak corresponding to the first overtone of the CH₃ asymmetric deformation in the experimental spectrum, which, obviously, is not explicitly included in the calculations. Moreover, a clear shoulder can also be observed in the experimental spectrum on the CH *st* band and still another one on the overtone of the CH₃ asymmetric deformation. From the present results one could tentatively assign these shoulders either to the modes of other orientations of adsorbed propyne or to some combination of all of them. Additionally, on CH₃CCD two clear bands with similar intensities and at 2158 and 2117 cm^{-1} , respectively, can be observed in the experimental spectrum. These have been assigned to CD *st* and to the first

TABLE 5: Main IR Peaks (cm⁻¹) for Propyne (CH₃CCD) on Cu(111) and Their Assignment, Intensities (km mol⁻¹), and Isotopic Factors^a

modes	Cu(111) ^b	<i>I</i> ^b	<i>f</i> _T	Cu(111) ^c	<i>f</i> _{exp}	Pd(100) ^d	<i>f</i> _{exp}
CD <i>st</i>	2157–2161	1.3–1.6	1.36	2157 ^e	1.32	2151	1.33
CH ₃ <i>as st</i>	3008–3017	0.1–0.2	1.00				
CH ₃ <i>as-s st</i>	2989–2992	0.6–1.6	1.00	2922	1.00	2947	1.00
CH ₃ <i>s st</i>	2918–2921	5–29	1.00	2883	1.00	2883	1.00
C ₁ –C ₂ <i>st</i> (– CH ₃ <i>s df</i>)	1342–1347	6–2	1.01	1353	1.01		
CH ₃ <i>as df</i>	1413–1422	0–0	1.00				
CH ₃ <i>as-s df</i>	1429–1477	0–0.2	1.00			1422	1.00
CH ₃ <i>s df</i> (+ C ₁ –C ₂ <i>st</i>)	1323–1328	0.4–0	1.00			1343	1.00

^a Experimental results on different metal surfaces have also been included for comparison. The experimental isotopic factors have been evaluated from the corresponding experimental assigned values. ^b Theory, present (slab) results. ^c Reference 8. Two bands, at 2827 and 2117 cm⁻¹, were also assigned as the first overtones of CH₃ asymmetric deformation and CH₃ methyl rocking. ^d Reference 39. A band at 2821 cm⁻¹ was also assigned as the first overtone of CH₃ asymmetric deformation. ^e Coupled with first overtone of CH₃ methyl rocking (2117 cm⁻¹).

overtone of the CH₃ rocking.⁸ This overtone is not observed on the undeuterated case and its corresponding fundamental band is found experimentally at 1039(H)–1035(D) cm⁻¹. The present slab model calculations show that both symmetric and asymmetric CH₃ rocking are strongly coupled with CH bending in-plane (and in a minor extent to C₂–C₃ *st*) and out-of-plane modes, respectively, and the normal mode that presents a major contribution on both CH₃ rocking lies just below 1000 cm⁻¹. For the singly deuterated propyne these frequencies are not coupled with CD *bi* and *bo*; the CH₃ *as ro* features lie below 1000 cm⁻¹ and the CH₃ *s ro* modes appear at 1040–1050 and 905–915 cm⁻¹ (in this case it increases the coupling with C₂–C₃ *st*). Except in the unlikely case that the CH₃ rocking has a very small or even negative anharmonicity constant, it seems clear that these two bands should be ascribed to CD *st* of propyne and twisted-propyne molecules and, perhaps, they are coupled with some overtone. This might be clarified experimentally over the CD₃CCH or CD₃CCD spectra on the same copper surface.

For the features appearing in the 1300–1500 cm⁻¹ region the two unit cells provide similar results (see Table 3). The very weak feature above 1400 cm⁻¹ (Figure 3b) in the simulated spectrum corresponds to the CH₃ *as-s* deformation. For the two differently oriented adsorbed molecules, both deformation modes are not coupled. These four normal modes have isotopic factors of 1.39 and 1.00 upon methyl and acetylene deuteration, respectively. As in the case of considering only one adsorbed molecule, the C₁–C₂ *st* and CH₃ *s df* group frequencies are strongly coupled, indicating that this result is not an artifact of the model. The (C₁–C₂ *st* + CH₃ *s df*) mode appears higher in frequency and intensity (1350–1354 cm⁻¹) than the positive coupling (1325–1330 cm⁻¹). For the most intense peaks, the agreement between computed (1350 cm⁻¹) and experimental values (to 1361 cm⁻¹) is excellent. Notice that this is precisely the band with a controversial assignment in the literature. Chesters and McCash⁸ assigned the peak at 1361 cm⁻¹ to the supposedly MSSR inactive C₁–C₂ stretching mode (Table 4). However, upon deuteration of the acetylene hydrogen this peak shifts to 1353 cm⁻¹ (Table 5), indicating that the previous assignment is perhaps incomplete and also rules out, in principle, its assignment to the CH₃ symmetric deformation. Indeed, the EELS⁵¹ and RAIR⁸ spectra of acetylene on Cu(111) exhibits a strong peak at 1307 and 1294 cm⁻¹, which is also assigned to the C≡C stretch. In these studies, the presence of the MSSR-inactive CC stretch is justified in terms of changes in dipole moment perpendicular to the surface arising from modification of the electron density near the C≡C bond region produced by the vibrational mode parallel to the surface. However, McCash⁴ suggested that this electron density change is enough to make this vibrational mode MSSR active and so intense. Still, for

TABLE 6: Main IR Peaks (cm⁻¹) for Propyne (CD₃CCH) on Cu(111) and Their Assignment, Intensities (km mol⁻¹), and Isotopic Factors^a

modes	Cu(111) ^b	<i>I</i> ^b	<i>f</i> _T	Cu(110) ^{c,d}	<i>f</i> _{exp}	Ni(111) ^c	<i>f</i> _{exp}
CH <i>st</i>	2930–2935	3–5	1.00	2751	1.00	2869	1.00
CD ₃ <i>as st</i>	2224–2232	0.1–0.2	1.35				
CD ₃ <i>as-s st</i>	2210–2212	1–2	1.35			2202 ^e	
CD ₃ <i>s st</i>	2097–2098	2–12	1.39	2031	1.42	2032	1.42
C ₁ –C ₂ <i>st</i>	1345–1351	2–1.6	1.00				
CD ₃ <i>as df</i>	1014–1017	1–0.1	1.39				
CD ₃ <i>as-s df</i>	1021–1060	0–0.3	1.39	1030		1030	
CD ₃ <i>s df</i>	1046–1052	3–0	1.26	1072	1.26	1074	1.26

^a Experimental results on different metal surfaces have also been included for comparison (experimental isotopic factors evaluated from the corresponding experimental assigned values). ^b Theory, present (slab) results. ^c Reference 38. ^d A band at 2078 cm⁻¹ was also assigned as the first overtone of CD₃ asymmetric deformation. ^e Coupled with 2 CD₃ asymmetric deformation (2147 cm⁻¹).

propyne on Cu(110)/Ni(111), Roberts et al.³⁸ assigned the features at 1358–1354 cm⁻¹ (Table 4) to the methyl deformation mode and hence did not refer at all to a possible band corresponding to the C₁C₂ stretch. Their assignment is based on the fact that methyl group deuteration produces a significant shift of these bands toward lower frequencies (Table 6). In a similar way, Camplin et al.³⁹ found that deuterium substitution on the acetylene hydrogen (Table 5) did not affect the position of the 1343 cm⁻¹ band on Pd(100) and thus assigned this peak to the methyl symmetric deformation (Table 4), although the same authors admit that the corresponding feature for propyne on Cu(111) could indeed correspond to the C₁C₂ stretching mode. They proposed that in the latter case the unit cell dimensions are such that the distance between two adjacent hollow sites matches that of the C≡C bond of the chemisorbed propyne. This correspondence would allow the C₁C₂ stretch to become active at the expense of the methyl deformation. In the present study an unambiguous explanation emerges from the analysis of calculated values for propyne chemisorbed on Cu(111). The analysis of the calculated normal modes shows that this band exhibits a strong coupling of the C₁–C₂ stretch and CH₃ symmetric deformation group modes. This coupling results in a normal dipole moment in the direction perpendicular to the surface which varies due to the synchronized motion of the two groups. Therefore, the corresponding mode is MSSR active and results in a relatively intense band. Thus, the present theoretical study supports and reconciles all the experimental assignments, both are indeed correct but both are also incomplete because in the actual normal mode the two functional group motions are coupled. The main difference between the 2x√3 and 4x√3 slab calculations concerns the coupling of (C₁–C₂ *st* + CH₃ *s df*) group modes between the two species present in the unit cell. As in the CH₃ *s st* intermolecular coupling, the

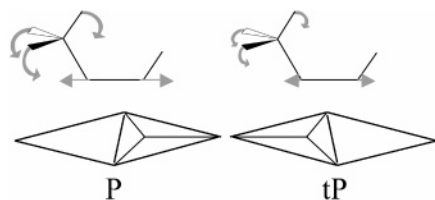


Figure 4. Vibrational normal mode corresponding to the band at 1350 cm^{-1} as obtained from the $4\times\sqrt{3}$ slab calculation. The scheme shows the coupling between the $\text{C}_1\text{--C}_2$ *st* and the CH_3 *sdf* group frequencies in the two orientations, P and t-P.

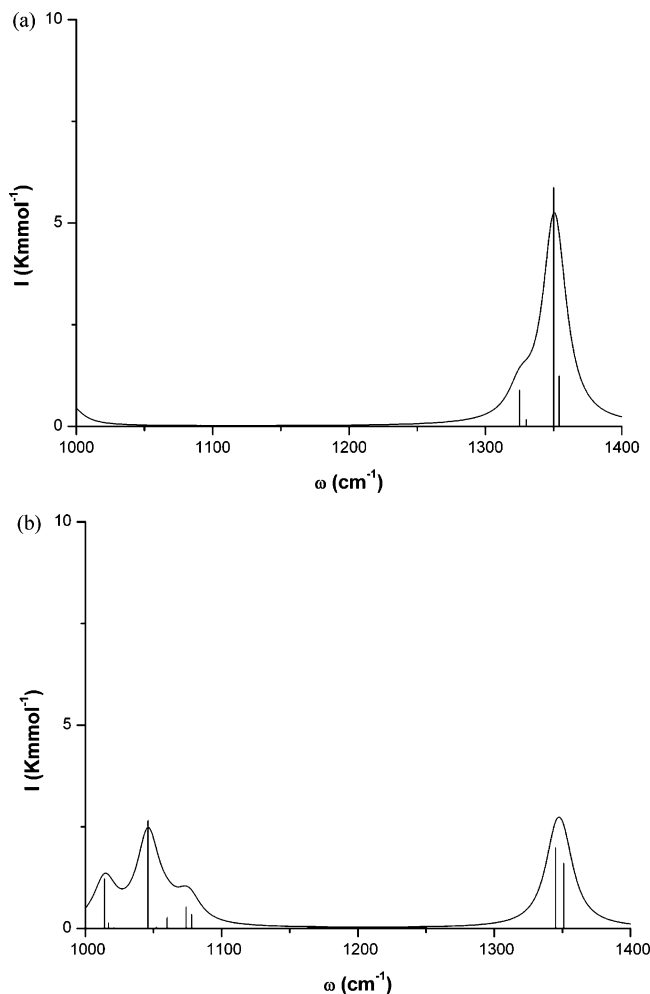


Figure 5. Isotopic effects on the simulated vibrational spectrum ($1000\text{--}1400\text{ cm}^{-1}$ region) of propyne adsorbed on Cu(111) as obtained from the $4\times\sqrt{3}$ slab model calculations. (a) CH_3CCH ; (b) CD_3CCH .

synchronized motion of the atoms of the two propyne molecules cause a major dipole moment change, leading to a more intense feature on the spectrum. This vibrational normal mode is displayed in Figure 4. In the $2\times\sqrt{3}$ model, the intensity of the $\text{C}_1\text{--C}_2$ *st* + CH_3 *sdf* band is almost the same for P and t-P orientations, whereas on the $4\times\sqrt{3}$ slab model the corresponding band for the positive coupling between P and t-P orientation has an intensity 6 times larger than that for the negative one. Deuteration of the acetylene hydrogen does not produce any noticeable change in this spectral region (see Table 5). However, deuteration of the methyl group shifts the CH_3 *sdf* to lower frequencies as expected, breaking the coupling with the $\text{C}_1\text{--C}_2$ *st* mode. Consequently, the intensity of the $\text{C}_1\text{--C}_2$ *st* band strongly decreases but it can still be observed, cf. Figure 5. This is an additional confirmation that the C_1C_2 stretch creates a significant dipole moment change normal to the surface.

Moreover, the C_1C_2 *st* modes are uncoupled between the P and t-P propyne molecules, and they exhibit similar intensities. On the contrary, the CH_3 *sdf* modes remain coupled between adjacent molecules (in fact, the degree of coupling increases), and new intermolecular couplings appear (the CH_3 *sdf* is strongly coupled with the CH *bi* and in some extension with the $\text{C}_2\text{--C}_3$ *st*). Therefore, an isotopic factor of 1.26 is obtained from the slab results instead of the common value between 1.35 and 1.39. Such a lower value, as observed for some modes on gas phase propyne and physisorbed propyne on Cu(111), is an indication of the change of the vibrational normal mode upon deuteration. Although the experimental spectrum for CD_3CCH on Cu(111) is not available, the same value of the isotopic factor of CH_3 *sdf* is obtained from the assigned values on Cu(110) and Ni(111), thus indicating changes on the normal mode upon methyl deuteration.³⁸

4. Conclusions

A thorough density functional theory study of the IR spectrum of propyne adsorbed on Cu(111) using a periodic slab model for the metal surface has been presented. The present results indicate that theoretical methods may be of great utility to interpret the vibrational spectra of adsorbed complex molecules and to confirm the validity of some assignments. The main difference between considering explicitly in the model one or two adsorbed molecules concerns essentially peaks that are simultaneously associated with couplings between group modes involving different adsorbed molecules. Nevertheless, one can conclude that the agreement between experimental RAIRS data and the present computed harmonic frequencies is almost quantitative. The main differences between experimental and calculated data concern the absence of overtones in the later. This leads to a concomitant absence of coupling between overtones and fundamental bands in the calculated spectrum.

The present work also proposes an unambiguous assignment of the 1361 cm^{-1} peak. This is based on a detailed analysis of first principle calculations that show that the normal mode responsible for this band involves a strong coupling between the C_1C_2 stretching and the CH_3 symmetric deformation modes and a weak coupling between the two species present on surface. Moreover, deuteration of the methyl group causes the breaking of this coupling with concomitant changes on the calculated frequencies and intensities. The intensity of the C_1C_2 *st* decreases but it is still observed in the simulated spectrum. The significant intensity of this band in the spectrum of the deuterated molecule confirms that for nonlinear adsorbed molecules, stretching frequencies of bonds lying parallel to the surface are active and therefore can be seen on the IR spectrum. A possible explanation has already been given by McCash⁴ as follows: For a nonlinear adsorbed molecule, a stretching motion parallel to the surface, the corresponding nuclear displacement may produce quite important changes of the dipole moment component perpendicular to the surface. Hence, the present results permit one to reconcile the different assignments proposed in the existing literature. In fact, the band at 1361 cm^{-1} , which has been previously assigned to the C_1C_2 *st*⁸ or to CH_3 *sdf*⁸⁸ deformation modes involves actually a strong coupling between them. Therefore, coupling between different group frequencies is important and must be taken into account.

To summarize, usual assignments of IR bands of polyatomic adsorbed molecules are often oversimplistic. The present paper strongly supports the idea that theoretical approaches provide a rigorous and univocal way to assign the vibrational spectra, which is indeed free of the inconveniences found when

extracting information from the vibrational frequencies of either gas phase or inorganic complexes.

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Supporting Information Available: A zip file of IR frequencies and intensities and xyz values of propyne on Cu(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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