

Quantum chemical calculations of coupled vibrations of adsorbates: A comparative study of CO/Cu(1 1 0) and O/diamond (1 0 0)

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Abstract

We have performed quantum chemical calculations for coupled oscillations examining CO adsorbed on Cu(1 1 0) and atomic oxygen on the (1 0 0) diamond face. For CO, we find that our calculations show coupling consistent with a dynamic dipole–dipole interaction. In the case of the adsorbed oxygen atoms the dominant coupling seems to be mechanical. The limits of the semiempirical method SAM1 are tested for consistency and precision. Our model gives accuracy within 10% when compared to experiment and works well with near neighbor adsorbates.

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1. Introduction

We report the results of our quantum chemical calculations for adsorbed species on metallic and insulating clusters. Our earlier work [1] showed that semiempirical wave functions give reasonable comparisons to experiment for chemisorbed systems when applied to local properties at the low coverage limit. Here, we use the cluster method

to investigate coupled oscillations between neighboring co-adsorbed molecules and atoms. Our results on coupled oscillations will test the numerical precision of our computational procedures.

Vibrational spectroscopy studies of adsorbates on surfaces often consider the effects of increasing coverage. Frequencies frequently shift as coupled oscillations occur within adsorbate islands. When two identical oscillators couple the normal modes of oscillation exhibit a symmetric mode when both oscillators vibrate in-phase and an asymmetric mode when they vibrate 180° out-of-phase. These modes of oscillation generally do not have the

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same frequency and their differences in frequency indicate the nature of the coupling. When the coupling is mechanical, i.e., through a rigid connection or springs (chemical bonds produce effective springs constants) the frequency of the symmetric mode is lower than that of the asymmetric mode. When oscillators couple electronically through fields generated by the dynamic dipole moments, the frequency of the symmetric mode is higher than that of the asymmetric mode. On the surfaces of many metals adsorbed CO molecules causes a shift of the C–O stretching frequency to lower wavenumbers. This is believed to be due to a chemical effect, first discussed by Blyholder [2]. The bonding of CO molecules to a metal surface is generally due to the two highest electron orbitals. The doubly occupied 5σ level and the unoccupied antibonding $2\pi^*$ level are the principal molecular orbitals used in the chemisorbed bond. The metal shares an electron to the $2\pi^*$ antibonding orbital often called back-bonding. This process tends to soften the CO bond and lowers the frequency slightly. More recent studies support this view [3–6] and in addition show some rehybridization of CO.

Experimental studies by Ryberg [7–9] on the coupling of CO/Pt(111) and atomic O/Pt(111) chemisorbed on transition metals have given us a comprehensive review of the contemporary field and theoretical studies of Persson [10,11] have given a solid basis for these same systems.

The question asked in these studies is: are semiempirical methods at a sufficiently advanced stage to be able to produce results which are in qualitative if not quantitative agreement with experimental results? To study such systems, fairly large clusters must be used. Furthermore, the calculations must be able to create within themselves a high degree of consistency. For example, when two adsorbate atoms are placed in mirror symmetric adsorption sites on a mirror symmetric cluster, the calculations should result in optimized structures where the two adsorbates have identical bond distances and mirror symmetric bond angles.

Our calculations examine coupled oscillations in linear arrays of CO molecules on Cu(110) surfaces and oxygen atoms on diamond (100) sur-

faces. This choice of adsorbates was led by systems where there exists a number of experimental studies. CO and O as adsorbates are prototypical of a great amount of investigation in surface science. The study of coupled oscillators in chemisorbed systems has a rich history. Treating the system as classical oscillators on flat metal surfaces was studied by Hammaker et al. [12] and expanded by Greenler et al. [13–16] to stepped surfaces. Quantum mechanical treatments have been given by Jacob et al. [17,18] and Tully et al. [19–21] for metals, semiconductors and insulator surfaces. We choose to use a finite linear array of the adsorbates. This allows one to explore the effects of distance between the adsorption sites and to study the end of a finite array providing the effects of island edge and steps, since some substrate systems have shown step edges as preferential adsorption sites [22].

2. Method

In an earlier paper [1], we discussed the advantages and problems of using the AMPAC [23] semiempirical package as used for cluster models of chemisorption [24] in a comparative study with density functional theory and Hartree Fock methods. The method we are using is fully quantum mechanical. There are no classical potentials involved. With a minimal basis set, the SAM1 Hamiltonian produces reasonable results for the local properties of the chemisorbed molecules studied. The cluster model has difficulties accounting for the many-body effects in the substrate model of the crystal. All such cluster approaches traditionally give adsorbate bonding to the crystal that is much greater than experiment. We have had some success in using the Birge–Spencer extrapolation in estimating the adsorption energies. The semiempirical method succeeds as a computational tool for surface studies of sp elements, in that it predicts with reasonable accuracy the correct reaction site, the structure of the adsorbate molecule, vibrational frequencies, charge distributions, molecular orbitals, and an estimate of the adsorption energies. The SAM1 option is essentially a reduced Hartree–Fock (RHF)

method whose main advantage is its computational efficiency [1]. We assume the atoms of the substrate cluster are placed in their crystallographic positions whereas the location and structure of the adsorbates are optimized.

The SAM1, like the earlier AM1 [25], method was used for these quantum mechanical calculations as implemented in the program *AMPAC with Graphical User Interface* [23]. Considerable effort was invested to locate the lowest energy conformer in the gas phase by extensive torsional investigation. While the gas phase geometry may not be representative of the molecules geometry in the chemisorbed state, it does provide a reference point to which all compounds in the study can be tied. Ground state species were optimized with respect to a minimum energy geometry and were then characterized by frequency calculations from the quantum mechanical derived Hessian matrix made up of the second derivatives of the energy with respect to all pairs of atoms. The Hessian is diagonalized giving the force constants for the system and the force matrix [26–28] which is used to calculate the vibrational frequencies.

At some points in our report, we make use of Mulliken population analysis [29]. All such methods in computational chemistry are arbitrary but one of the most common in assigning charges to individual atoms within a molecular cluster, is based upon the Mulliken's approach. This method is based on the density matrix and on the overlap integrals. The remaining electron density is associated with the overlap population. Since the density matrix and the overlap integrals have been calculated in our optimization, the assignment of Mulliken charges is readily available.

3. Results

The numerical computations (see Fig. 1 and Table 1) with the SAM1 Hamiltonian begin with a CO molecule. Since the C–O stretching frequency is involved in both of our adsorption computations, the shift in this frequency is a primary goal. The vibrational stretching frequency for gas phase CO is found to be 2143 cm^{-1} [30] with a bond energy of 257.3 kcal/mol. For comparison, our computed the frequency is 2358 cm^{-1} at a bond distance of 1.16 Å. Our results are 9% greater than experiment.

4. Results for CO chemisorbed on Cu(110)

The chemisorption of CO is a favorite candidate for many studies [31–34] in surface science and it serves as our test for our semiempirical method in the coupling of adsorbate oscillators.

4.1. Results for a single CO/Cu(110)

A single CO optimizes on an atop site on the Cu(110) (see Table 1). The clean face of Cu has, by Mulliken analysis, a charge of +0.94e and in the case of CO/Cu(110) the charge has increased to +1.02e. The oxygen has a charge of $-0.07e$ and the carbon has a charge of +0.045e. We found that the $\nu(\text{CO})$ by SAM1 [1] was 2374 cm^{-1} compared to 2090 cm^{-1} experimental [32]. Our computation is 13% too large. The bonding energy was estimated from the frequency of the CO–Cu stretch. Using the Birge–Spencer extrapolation method for anharmonic oscillations:

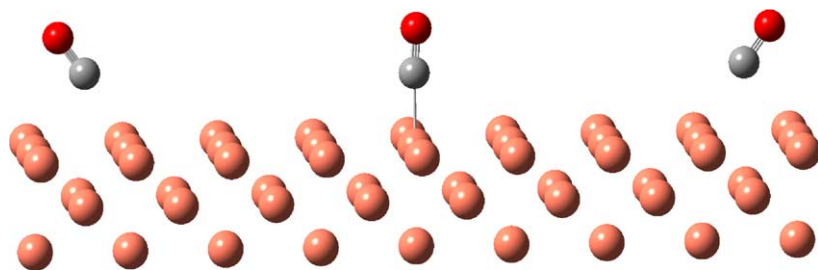


Fig. 1. Three CO molecules optimized on a Cu(110) surface of a cluster of 52 copper atoms.

Table 1

A summary of the results of our calculations on CO/Cu(110)

<i>CO molecule</i>								
Experiment [30]			SAM1					
D_0	ν_{CO}		ν_{CO}	d_{CO}				
257.3 kcal/mol	2143 cm^{-1}		2358 cm^{-1}	1.16 Å				
<i>CO/Cu₂₈(110)</i>								
Experiment [32]			SAM1					
D_0	ν_{CO}		D_0	ν_{CO}	d_{CO}			
−14.6 kcal/mol	2090 cm^{-1}		−15 kcal/mol (0.65 eV)	2374 cm^{-1}	1.82 Å			
<i>2CO/Cu₃₄(110)</i>								
Experiment [32]		SAM1						
θ	$\nu_{\text{CO}}^{\text{sym}}$	$\nu_{\text{CO}}^{\text{asym}}$	θ	$d_{\text{C-O}}$	$d_{\text{C-Cu}}$			
77°	2341 cm^{-1}	2288 cm^{-1}	60°	1.16 Å	2.34 Å			
<i>3CO/Cu₅₂(110)</i>								
Outer pair			Middle molecule					
$\nu_{\text{CO}}^{\text{sym}}$	$\nu_{\text{CO}}^{\text{asym}}$	$\nu_{\text{CO-Cu}}^{\text{sym}}$	$\nu_{\text{CO-Cu}}^{\text{asym}}$	θ	$d_{\text{C-Cu}}$	ν_{CO}	$\nu_{\text{CO-Cu}}$	$d_{\text{C-Cu}}$
2379 cm^{-1}	2376 cm^{-1}	425 cm^{-1}	423 cm^{-1}	60°	2.32 Å	2389 cm^{-1}	292 cm^{-1}	1.82 Å
<i>4CO/Cu₅₈(110)</i>								
Outer pair				Inner pair				
$\nu_{\text{CO}}^{\text{sym}}$	$\nu_{\text{CO}}^{\text{asym}}$	$\rho_{\text{C-O-Cu}}^{\text{wsym}}$	$\rho_{\text{C-O-Cu}}^{\text{wasym}}$	$\nu_{\text{CO}}^{\text{sym}}$	$\nu_{\text{CO}}^{\text{asym}}$	$\nu_{\text{CO-Cu}}^{\text{sym}}$	$\nu_{\text{CO-Cu}}^{\text{asym}}$	
2693.9 cm^{-1}	2693.9 cm^{-1}	334.2 cm^{-1}	334.5 cm^{-1}	2525 cm^{-1}	2525 cm^{-1}	240.4 cm^{-1}	240.2	

$$D_0 = \frac{(\omega_e + x_0\omega_0)^2}{4x_0\omega_0} \quad (1)$$

with ω_e the computed frequency and $x_0\omega_0$ as the first-order correction for the anharmonic effects [1,30]. The computed enthalpy of absorption is 0.65 eV or 15 kcal/mol.

4.2. Results for 2CO/Cu(110)

Our investigation as to whether SAM1 calculations will show couple oscillations for adsorbate systems begins with two CO molecules adsorbed on a Cu(110) cluster of 34 atoms. The optimized positions are atop sites with a C–O bond distance of 1.16 Å and the C–Cu distance at 2.34 Å, the molecules are found to be in line with the (110) short bridge rows and at an angle of 60° to the plane of the substrate. The tilt is caused by the repulsive interaction of the CO ions. Based on Mullikan analysis, the oxygen and carbon atoms have partial

charges of −0.23e and +0.13e, respectively. This tilt is exaggerated since only the two molecules are placed on this cluster precluding interaction with other CO molecules as might be expected in an experimental system. The experimental tilt measured by Ahner et al. [32] is only 77° with the coverage at one half of a monolayer. The charges on the individual atoms of the two CO molecules results in an intermolecular repulsion that does not allow the molecules to find a stable geometry any closer than three ⟨011⟩ lattice constants (2.55 Å) away. The strong repulsion will not allow the molecules to find a stable geometry any closer to one another in this low coverage limit. At higher coverage, there is a symmetry as the adsorbate molecules are crowded into a tighter overlayer.

Calculations performed for this system do show coupling between the two molecules that is in qualitative agreement with experiments (see Table 1). The calculations show the two molecules vibrating in-phase with a frequency of 2341 cm^{-1} , the asym-

metric mode of vibration has a frequency of 2288 cm^{-1} . The frequency of the symmetric mode is higher than that of the asymmetric mode is consistent with dipole–dipole coupling. That both vibrational frequencies are lower than the calculated frequency of a single CO molecule may be regarded as being consistent with chemical effects (i.e., Blyholder backbonding [2–11]).

4.3. Results from 3CO/Cu(110)

To further study the usability of the SAM1 package, we considered three CO molecules chemisorbed in a linear array on a Cu(110) cluster composed of 52 atoms (see Fig. 1 and Table 1). The center CO is optimized to the Cu(110) rows with a C–Cu bond length of 1.89 \AA and the two adjacent molecules optimize with a bond distance of 2.32 \AA . These molecules are also tilted in opposite directions at angles of 60° to the surface. The outer oxygens have a Mulliken charge of $-0.24e$ and oxygen atom of the center molecule has a charge of $-0.10e$. The adsorbate carbons are $+0.05e$ for the center and $+0.23e$ for the outer atoms.

While the two outer molecules are tilted and stretched (Table 1), the center molecule has a shorter C–Cu bond length (1.82 \AA). One expects this adsorbed molecule to have a slightly greater vibrational frequency than the outer pair. Physically, one expects that the normal modes of oscillation will consist of a mode in which the center molecule vibrates with little motion of the other two and then a symmetric and asymmetric vibrational mode for the two outer molecules with the center molecule remaining nearly motionless. The increased distance between the two outer molecules should result in a lower degree of coupling, we computed a small difference in frequency between the symmetric and asymmetric modes.

The first-order symmetric mode for the C–O stretch is 2389 cm^{-1} with the displacement in a vertical direction. The second-order symmetric mode is 2379 cm^{-1} and the first-order asymmetric mode at only 2376 cm^{-1} . This shows the level of our limitations in computational consistency from site to site using this semiempirical approach. These frequencies are nearly the same, differing by only 3 cm^{-1} . One might reasonably expect re-

versed order for second-order symmetric vs asymmetric frequencies. Our method has enough precision to show the effects of coupling but when the differences are as close as these values, the systematic order cannot be properly judged.

For the CO–Cu stretch, the symmetric frequency is 425 cm^{-1} and the asymmetric is 423 cm^{-1} . This coupling is very weak and is only observed in the normal coordinates. The derivative of the dipole moment in this case (CO–Cu) is only $0.215\text{ debye/angstrom}$ whereas for the C–O stretch it is 3.676 .

4.4. Results for 4CO/Cu(110)

We also considered four CO molecules chemisorbed in a linear array on Cu(110) cluster containing 58 atoms (see Table 1). In this linear array, the carbon to copper distance was optimized to 1.89 \AA for the two inner CO molecules and the outer CO's optimized at 2.33 \AA . The outer pair is, as before, tilted in opposite directions along the (110) rows toward the outer edge of the substrate cluster at an angle of 60° to the Cu(110) base. The inner oxygens have a Mulliken charge of $-0.08e$ and the carbons $+0.05e$. The outer oxygens have a $-0.18e$ and the carbons have $+0.15e$ for their charges.

One expects that the inner pair should couple strongly with symmetric and asymmetric modes. The outer pair should couple weakly but still have a symmetric and asymmetric vibrational modes. The highest C–O stretching frequencies involve the outer pair, and they have the nearly same frequency at 2623.9 cm^{-1} . Two modes can be observed but the order of the modes is beyond our computational accuracy. The inner pair of CO's also have the nearly the same C–O stretching frequency at 2525 cm^{-1} . Our computations allow us to distinguish that there are two modes but again not the order. There is a waggle of carbon about the oxygen of the outer pair, the symmetric mode is 334.2 cm^{-1} and the asymmetric mode is 334.5 cm^{-1} . The stretching frequency for the CO–Cu again has two frequencies but they are also very close at 292.8 cm^{-1} . The inner pair of CO molecules have a symmetric 240.4 cm^{-1} and asymmetric 240.2 cm^{-1} CO–Cu stretch, but again, the

frequencies are too close to judge with confidence the systemic order.

4.5. Results for oxygen chemisorbed on the (100) face of diamond

The chemisorption of oxygen on (100) face of diamond starts with a single O atom optimized to be on an atop site of a forty four atom cluster of carbons in the diamond structure (see Fig. 2 and Table 2). The diamond cluster is a line of three fcc cubes with each side measuring 3.567 Å. No reconstruction of the surface was included. The atomic oxygen is chemisorbed at an atop site. The O–C stretching frequency is found to be 1991 cm^{-1} at a bond distance of 1.24 Å. Using HREELS, Laikhtman et al. [34] measured a peak at 220 meV (1774 cm^{-1}), and by comparison, our calculation is 11% too large. Again the Birge–Spencer method for anharmonic oscillations Eq. (1) estimates [19,1] the enthalpy of absorption to be 9.25 eV or 213.3 kcal/mol. For comparison, the HREELS data by Laikhtman, et al. [23] found the EDS peak to be 8.5 eV. Considering that the SAM1 method is 9% greater for the CO molecule, this result seems consistent with a single oxygen chemisorbed on a cluster of diamond like carbons.

4.6. Results for 2O/C(100) diamond

Our test for the coupled oscillation begins with two oxygen atoms adsorbed on a diamond cluster of 33 atoms in a pair of fcc cubes (see Table 2). The optimized adsorbate atoms prefer an atop site and

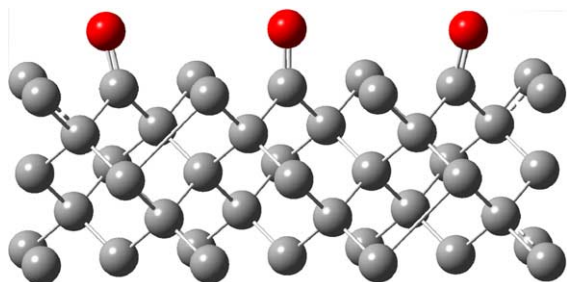


Fig. 2. Three oxygen atoms optimized on the C(100) face of diamond containing 44 carbon atoms.

a C–O bond distance of 1.24 Å. The two adsorbate oxygen atoms are optimized on the face centered positions (atop site) and they are tilting in opposite directions toward the open corners of the cluster at an angle of 73° to the fcc base. The oxygen atoms have $-0.26e$ for their Mulliken charges. The tilt caused by the repulsive interaction of the oxygen ions would not necessarily be the case in surface with a symmetric geometry for the overlayer. As one might expect from classical coupled oscillators, the coupling between the two oxygen atoms is largely mechanical and thus the asymmetric mode should have the higher frequency. The asymmetric C–O stretch mode is computed to be 1929 cm^{-1} and the symmetric mode is found to be 1904 cm^{-1} .

4.7. Results for 3O/C(100) diamond

The next study involved the coupling between adsorbates was to considered three oxygen atoms chemisorbed on the face centers of three linear fcc cubes containing forty four carbon atoms in the diamond structure (see Fig. 2 and Table 2). Again, the atoms optimized to the face centered positions with a bond length of 1.24 Å. The outer pair are tilted in opposite directions toward outer cube corners at an angle of 75° to the fcc base. The oxygen ions have $-0.26e$ for their Mulliken charges. The center oxygen is vibrating at $\nu_{OC} = 1997\text{ cm}^{-1}$ vertically and the outside oxygens are computed to be 1964 and 1923 cm^{-1} . This shows the limitations of our semiempirical approach. These frequencies should be nearly the same but they differ by 41 cm^{-1} . Our method does not have the precision to show the effects of coupling of the outer pair. In this case the outer ions are so far apart which may also contribute to the lack of coupling of the model.

4.8. Results for 4O/C(100) diamond

The last attempt to find coupling between the adsorbate molecules was to consider four oxygen atoms chemisorbed on the face centers of four linear fcc cubes containing fifty seven carbon atoms in the diamond structure (see Table 2). As found

Table 2

A summary of the results of our calculations on O/C(100) diamond

<i>O/C₄₄(100) diamond</i>				
Experiment [34]				
D_{O}	$\nu_{\text{O-C}}$	D_{O}	$\nu_{\text{O-C}}$	$d_{\text{O-C}}$
8.5 eV	1774 cm ⁻¹	9.25 eV (213.3 kcal/mol)	1991 cm ⁻¹	1.24 Å
<i>2O/C₃₃(100) diamond</i>				
θ	$d_{\text{O-C}}$	$\nu_{\text{O-C}}^{\text{sym}}$	$\nu_{\text{O-C}}^{\text{asym}}$	
73°	1.24 Å	1904 cm ⁻¹	1929 cm ⁻¹	
<i>3O/C₄₄(110) diamond</i>				
Middle atom		Outer pair		
$d_{\text{O-C}}$	$\nu_{\text{O-C}}$	θ	$\nu_{\text{O-C}}^{\text{sym}}$	$\nu_{\text{O-C}}^{\text{asym}}$
1.24 Å	1997 cm ⁻¹	75°	1964 cm ⁻¹	1923 cm ⁻¹
<i>4O/C₅₇(100) diamond</i>				
Inner pair		Outer pair		

Line missing

previously, the oxygen ions are optimized to the face centered position at a bond length of 1.24 Å. The outer pair are also tilting in opposite directions toward and outer cube corners at an angle of 74° to the fcc base. These oxygen ions have -0.26e for their Mulliken charges. The two inner oxygens have a symmetric stretch at $\nu_{\text{O-C}}^{\text{sym}} = 2000 \text{ cm}^{-1}$ vertically and we calculate the inner oxygens to have an asymmetric stretching frequency of 1995 cm^{-1} . The outside oxygens are at 1950 and 1906 cm^{-1} and separated by 10.7 Å . Our computation shows a difference of 44 cm^{-1} . The distances and lack of precision are too great to demonstrate higher ordered coupling. We obtain the symmetric and the asymmetric frequencies, but the numerical precision is insufficient to assign the order reliably.

5. Discussion

Our calculations give a qualified answer to the coupling of adsorbate oscillations. When we consider only two CO molecules chemisorbed on the Cu(110) surface, it is clear that the coupled oscillation occur and the symmetric mode has the higher

frequency. This is in agreement with the classical prediction by Leibsle [14,15] for dynamic dipole coupling. The $2\text{CO}/\text{Cu}_{34}(110)$ system gives a reduction in the frequency of 33 wave numbers in the $\nu_{\text{CO}}^{\text{sym}}$ symmetric mode. Although our computed frequencies are too high, they do follow the classical model [15] in the order of symmetric over the asymmetric modes.

By adding a third CO to the linear array of adsorbates, we see the middle molecule in the same position and at nearly the same frequency as in the single CO model. The center CO represents the structure that one would expect from an experimental system with balanced adsorbate geometry. The outer pair represents the structure of molecules on the edges of an adsorbed island. Our computed coupling is quite weak but it can be detected in the listing of the normal coordinates. The coupling is between the outer pair is notably weaker because of tilt and the distance one from another (six lattice constants). We find what one might expect from classic prediction, the symmetric mode has the higher frequency.

When the fourth CO is added to the line of adsorbates, the limits of our model become clearer.

Coupled modes in the outer pair are apparent, but their value is the same for both modes making the judging of the order impractical. It is the same for the CO–Cu stretch modes; there are two modes but no basis for ordering them. In the inner pair, the situation is the same.

Our comparative computations used the O/C(100) diamond as an example of atomic oxygen adsorbed on an insulator. There exists experimental data [34] which allow us to judge the nature of the adsorbate coupling and the level of error of our calculations. This system is interesting when contrasted with the CO molecule to metal example. The classical model of adsorbate coupling would indicate that the interaction of the oscillations is “mechanical”, in that the asymmetric mode is anticipated to be higher in frequency than the symmetric modes.

Our estimate the bond energy is 0.75 eV higher than the Laikhtman experiment [34]; resulting in our semiempirical model being 8.8% too high. In general, all of our comparisons with experiment tend to be about 10% high. It is interesting that the scaling factor for frequencies ab initio RHF is usually about 0.9. We do see a similar behavior for our model.

We next use two oxygen atoms on the diamond surface. In this case the coupling is mechanical and the asymmetric mode is higher at $\nu_{\text{O-C}}^{\text{asym}} = 1929 \text{ cm}^{-1}$ whereas the symmetric mode is $\nu_{\text{O-C}}^{\text{sym}} = 1904 \text{ cm}^{-1}$. The coupled frequencies are lower than the gas phase molecule of CO with experiment at 2143 cm^{-1} and SAM1 at 2358 cm^{-1} . This is our clearest case for the coupling for an insulator as a substrate.

The least demonstrative cases for coupling we considered are those with three adsorbate units. The repulsion between the atoms or molecules cause the end pair to experience a significantly different environment resulting in tilted geometries. This kept us from achieving a first-order asymmetric mode. Only the center atom is involved. With three O's, the middle O has nearly the same frequency as the single oxygen adsorbate described above.

Four oxygens are an informative case, with the inner pair clearly showing coupling with the expect order of the symmetric mode being slightly higher.

The frequencies are close to the uncoupled single atom. The method is unable to detect the coupling, since the outer atoms are three cubic lattice constants apart and are 44 wave numbers different in frequency even though they have a presumably identical substrate environment. This indicates that the numerical precision of this method has been exceeded.

Our model and our computation accuracy allows for the physical coupling in all of our cases. The frequencies are of the order of 10% greater than the points that can be compared to experiment and our numerics are not effective when the oscillators are some distance apart. The approach works well within these limits and can provide the physical mechanism for the coupling.

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