ADVANCES IN CHEMICAL PHYSICS – VOLUME LXXVI

I. Prigogine and Stuart A. Rice – Editors

MOLECULE SURFACE INTERACTIONS

Edited by

K. P. LAWLEY

Department of Chemistry
Edinburgh University

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Block B, Union Industrial Building, Singapore 2057

British Library Cataloguing in Publication Data:

Molecule surface interactions.
1. Molecules. Interactions
I. Lawley, K.P. (Kenneth Patrick) II.
Series
539'.6
ISBN 0 471 91782 6

Typeset by Thomson Press (India) Ltd, New Delhi
Printed and bound in Great Britain by Courier International, Tiptree, Essex

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE

STUART A. RICE

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Advances in Chemical Physics
Edited by K. P. Lawley
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INFRARED SPECTROSCOPY OF MOLECULES ADSORBED ON METAL SURFACES

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Abbreviations

EELS	Electron energy loss spectroscopy
FTIRS	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
IRS	Infrared spectroscopy
LEED	Low energy electron diffraction
NEXAFS	Near edge X-ray absorption fine-structure spectroscopy

NMR	Nuclear magnetic resonance
UHV	Ultrahigh vacuum
UPS	Ultraviolet photoemission spectroscopy
cm^{-1}	Wavenumbers; $8.065 cm^{-1} = 1 meV$, $2000 cm^{-1}$ at a wavelength of $5 \mu m$

1. INTRODUCTION

During the present century infrared spectroscopy (IRS) has been used as one of the main tools for studying molecules in the gas phase. It was therefore quite natural when modern surface physics started to evolve some twenty years ago, that one wanted to use the same approach also for studies of molecules adsorbed on a solid surface. However, when using the same type of spectrometers the experimentalists faced a sensitivity problem, which could not be overcome by simply increasing the number of molecules, as one was restricted to study one monolayer or less. This led to the development of dedicated spectrometers taking advantage of the special boundary conditions set up by the surface and also using some kind of modulation technique to increase the sensitivity. Today, infrared spectroscopy is able to detect submonolayers even for very weakly absorbing vibrational modes with energies above $2000 cm^{-1}$, of rather strongly absorbing modes above $800 cm^{-1}$, but has until now only been able to detect low energy substrate-molecule modes under very special conditions.

Although infrared spectroscopy has suffered from a somewhat limited energy range compared to the competing technique of electron energy loss spectroscopy, due to its inherent high resolution it has had a great success in studies of the fine structure of the vibrational spectra. It is the purpose of this review to summarize the present picture of fundamental processes in adsorption systems as they are revealed by the infrared spectra. This incorporates different kinds of vibrational coupling and the transfer and dissipation of the vibrational energy. We will also discuss how infrared spectroscopy can be used to study surface reaction intermediates and outline its use in high pressure situations. As we will discuss fundamental processes, we will mainly consider studies made on single crystalline metal surfaces under well characterized (often ultrahigh vacuum) conditions and for the same reason we will consider small molecules and frequently carbon monoxide will be our test molecule.

It is not the purpose of this chapter to describe the evolution of the spectroscopy. For such a historical background we refer the reader to the reviews by Hoffmann[1], Hollins and Pritchard[2] and Ueba[3]. Neither do we attempt to give references to all works in the field. This is done in the proceedings of the Conferences on Vibrations at Surfaces, where Darville[4-6] has presented careful and very useful tabulations of all systems investigated by

IRS. References in this chapter are only given to either the most relevant or latest works and the interested reader is referred to these papers for the appropriate background. The literature has been searched until the end of 1987.

2. EXPERIMENTAL ASPECTS

The fact that the molecules are adsorbed on a solid surface gives rise to a number of new effects compared to the gas phase situation. The experimental situation consists of a monolayer of molecules adsorbed on a metal surface, on which we shine infrared radiation and then detect the reflected light. The macroscopic theory for the electromagnetic response of such a system is reproduced in the previous reviews[1-3]. A more microscopic treatment has been given by Persson[7], showing that the integrated infrared absorptance for p-polarized light is given by;

$$\int (I_0 - I)/I_0 \, d\omega = (8\pi^2/hc)(N/A)\mu^2 \Omega G(\alpha) \qquad (1)$$

where N/A is the number of molecules per unit area, $G(\alpha)$ is a constant depending on the dielectric properties of the substrate and the angle of incidence α and Ω is the vibration frequency. How the dynamical dipole moment μ of the vibrational mode should be interpreted for adsorbed molecules was for a long time debated and we will try to clarify this in section 3.

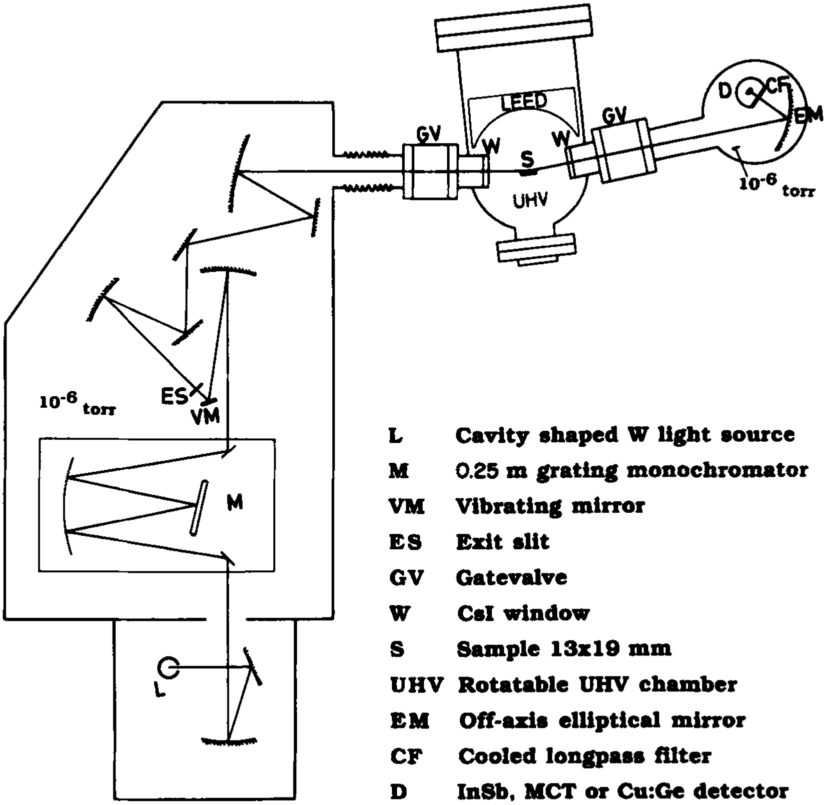
An important consequence of the presence of the metal surface is the so-called *infrared selection rule*. If the metal is a good conductor the electric field parallel to the surface is screened out and hence it is only the p-component (normal to the surface) of the external field that is able to excite vibrational modes. In other words, it is only possible to excite a vibrational mode that has a nonvanishing component of its dynamical dipole moment normal to the surface. This has the important implication that one can obtain information by infrared spectroscopy about the orientation of a molecule and definitely decide if a mode has its dynamical dipole moment parallel with the surface (and hence is undetectable in the infrared spectra) or not. This strong polarization dependence must also be considered if one wishes to use Eq. (1) as an independent way of determining μ. It is necessary to put a polarizer in the incident beam and use optically passive components (which means polycrystalline windows and mirror optics) to avoid serious errors. With these precautions we have obtained pretty good agreement[8] for the value of μ determined from Eq. (1) and by independent means as will be discussed in section 3.2.

Over the last decade there have been great developments of the infrared spectrometers used in surface science. One has moved from simple, single beam reflectometers to different kinds of modulation setups, from dispersive to multiplex Fourier transform infrared spectrometers and in addition to reflexion also tried direct absorption or emission spectroscopy. One has tested other light sources than blackbodies, like lasers[9] and synchrotron radiation[10]. Richards and Tobin[11] have critically discussed in an excellent way the present status of spectroscopy. They conclude that for a reflexion setup with proper, modern technology and careful design the sensitivity will be limited by the stability of the background. The reason is that in an optical reflexion measurement one is always, in one way or another, looking at a small difference between two large signals, i.e. in the present case with and without molecules adsorbed on the surface. This important conclusion, which is supported by my own practical experience, shows that from a sensitivity point of view there is nothing to gain in using other light sources than blackbody radiators, as they will only increase the source noise and the use of multiplex spectrometers can even be disadvantageous. Therefore, if one attempts to achieve maximum sensitivity and wants to study small molecules with few vibrational modes, the best solution is still a dispersive spectrometer, probably using the wavelength modulation technique which at present has shown the best reported signal/noise[12]. The main efforts should be made in designing an instrument as stable as possible, with special attention to temperature stability of all parts, repeatability of the grating motion, minimizing electronic drift and with special care to positional stability of the sample whilst cooling and heating during the actual experiment. If one is looking for very weak structures it is also important that one has the necessary dynamical response in the signal processing system (the lock-in amplifier and signal averager).

Much of the effort in recent years has been devoted to the development of spectrometers that are able to detect low frequency modes, such as the metal-molecule stretch at energies below 500 cm^{-1}. This has turned out to be a very difficult problem, because the integrated absorptance (1) suffers from an Ω dependence and the dynamical dipole moment μ normally is smaller for these modes than for the intramolecular high frequency ones. If we consider the CO/Cu(100) system and use the dynamical dipole moments of the two stretch modes as obtained from electron energy loss spectroscopy (EELS)[13], we find that the integrated infrared absorptance is about 90 times smaller (assuming constant $G(\alpha)$) for the low frequency mode. In this context we can mention that the energy loss peaks in EELS do not suffer from the Ω dependence in (1), which here makes a difference by a factor of 6, and that many EELS spectrometers enhance low energy modes as the angular distribution for dipole excitation losses narrows[13].

Furthermore, if one uses the wavelength modulation technique, which is strictly not surface sensitive but only enhances sharp structures and as the bandwidth of a grating monochromator decreases with decreasing energy, the low frequency peak will appear broad for reasonable slit widths. The solution to this problem is to use special gratings with very low dispersion, decrease the angle of incidence and use larger samples to enable an increase of the slit width. There exists in the literature no report that it has been possible to detect such a low frequency mode in a reflexion configuration, despite several attempts both with dispersive and multiplex spectrometers[14]. However, Chiang *et al.*[15] in a very nice experiment used a quit different approach with a new design of infrared *emission* spectrometer. The sample is surrounded by liquid nitrogen-cooled baffles and the emitted light is measured by a liquid helium-cooled grating spectrometer. With this technique they were able to detect the very weak absorption of the low frequency stretch mode of CO—Ni[15] and CO—Pt[16].

However, during the last three to four years, I have in several stages improved on my infrared spectrometer along the lines discussed above.



L	**Cavity shaped W light source**
M	**0.25 m grating monochromator**
VM	**Vibrating mirror**
ES	**Exit slit**
GV	**Gatevalve**
W	**CsI window**
S	**Sample 13x19 mm**
UHV	**Rotatable UHV chamber**
EM	**Off-axis elliptical mirror**
CF	**Cooled longpass filter**
D	**InSb, MCT or Cu:Ge detector**

Fig. 1. Schematic drawing of the wavelength modulation spectrometer setup. The spectrometer keeps the throughput ($f/3.6$) of the monochromator through the whole optical path.

Figure 1 shows this latest version of the experimental setup with the wavelength modulation spectrometer, where emphasis has been put on stability of all parts. During the course of writing this paper I was finally able to detect the low frequency metal-molecule stretch of CO/Pt(111), as will briefly be discussed in section 4.

It is often stated that one of the advantages of infrared spectroscopy is the possibility to work under high ambient pressures. This is certainly true if one studies a vibrational mode of a surface intermediate, which is well away in energy from any of the modes of the gasphase molecules. When this is not the case, the strong gasphase absorption with the broad rotational bands will interfere with the spectrum of the adsorbed molecules. The straightforward approach is of course just to take the difference of two spectra in the ordinary way, but this demands high spectrometer stability and dynamical range. The second possibility is to take advantage of the infrared selection rule and make some kind of a polarimetric setup. The third way is to make a true double beam spectrometer, with the reference beam not striking the sample. Even though some work has been done in this field along these lines, one is still waiting for the development of a dedicated high pressure spectrometer. This would be important in bridging the so-called pressure gap and connecting the ultrahigh vacuum studies with investigations on real heterogeneous catalytic reactions.

3. HIGH FREQUENCY INTRAMOLECULAR MODES

In this section we will discuss the properties of high frequency intramolecular modes carrying a large dynamical dipole moment. Most conclusions in this section are general but we will for the sake of clarity exclusively deal with the C—O stretch vibration of adsorbed carbonmonoxide. This is by far the most studied object in surface science and from the huge amount of information we will try to extract a coherent picture. When a CO molecule is adsorbed on a metal surface, the conduction electrons in the vicinity of the adsorption site are affected. The molecule carries both a small statical and a large dynamical dipole moment, the latter being the derivative of the former with respect to the C—O distance. If we represent the adsorbed molecule by a point dipole and place it above a metal surface, the conduction electrons will rearrange themselves to screen the dipole field. This can be represented by placing an image of the dipole inside the metal, mirrored at an image plane, as schematically shown in Fig. 3a. When considering the vibrational properties of an adsorbed molecule it is this whole object of the molecule and the induced charges that should be regarded as the chemisorbed species.

Ideally, one would like to study one single adsorbed molecule at 0 K but for practical reasons one has to study an ensemble of molecules at finite temperatures. Even if it is feasible to cool the sample to very low temperatures,

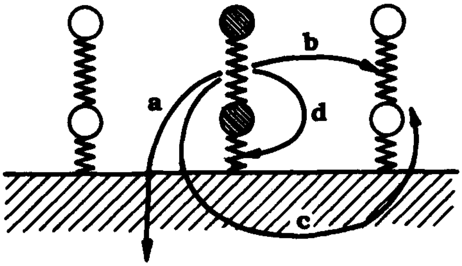


Fig. 2. The different kinds of interactions of the intramolecular high frequency mode that may be seen in the infrared spectra. Interactions with the substrate (a) will both affect the vibration frequency and the lifetime of the vibrational excitation. Molecule–molecule interactions can be direct (b) or mediated via the substrate (c). There may also be a substantial interaction with thermally excited, low frequency modes (d).

studies of very dilute overlayers are seldom meaningful. Even for the best prepared metal surface there is a defect concentration of the order of 1%, so even if one has the sensitivity to record 1/1000 of a monolayer, at very low coverages one will often mainly probe molecules sitting at these defects. Therefore, considering rather dense overlayers we have to take into account the different kinds of interaction that can occur, as indicated in Fig. 2. For a chemisorbed molecule there is of course an interaction with the substrate, which will affect the vibration frequency. The vibrational energy can be dissipated by different kinds of excitations in the metal. We can imagine different kinds of molecule–molecule interactions, direct or mediated via the substrate. The high frequency mode can couple to other, thermally excited low frequency modes. All these kinds of interactions will in principle affect the infrared spectrum in one way or another, so it is essential to sort these things out to be able to give a correct interpretation of the measured data and we will discuss each phenomenon in the following sections.

3.1. Metal–molecule interaction

It is a well known fact that the vibration frequency of the internal stretch mode of CO decreases from its gas phase value of 2143 cm^{-1} on chemisorption onto a metal surface. In general terms, depending on the adsorption site it takes values between 2000–2100 cm^{-1} in the ontop position, 1900–2000 cm^{-1} when bridgebonded and 1800–1900 cm^{-1} for molecules in the hollow site[1–3]. The vibration frequency of a particular system is of course the total effect of the different kinds of interactions sketched in Fig. 2. For example, simply the fact that the oscillator is attached to a more or less rigid substrate so that the

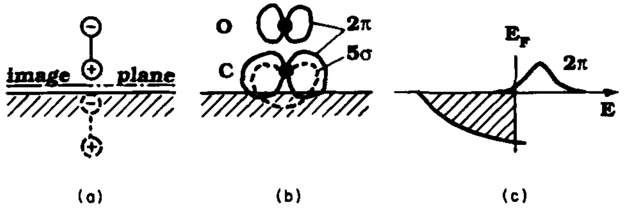


Fig. 3. Schematic picture of a chemisorbed CO molecule. (a) As a point dipole with its image, representing the screening by the conduction electrons. (b) The spatial extension of the two molecular orbitals involved in the chemisorption bond, the highest occupied 5σ and the lowest unoccupied 2π orbital. (c) The density of states of the conduction electrons and the 2π orbital, which by interaction with the metal electrons has broadened into a resonance and shifted down in energy.

carbon atom cannot oscillate freely gives rise to a *mechanical shift*. This has been estimated by a simple masses and springs model[1] to give an increase in frequency by $\sim 50\,\mathrm{cm}^{-1}$.

Furthermore, as mentioned above the screening of the dipole field by the conduction electrons can be represented by an image dipole inside the metal. This complex of the chemisorbed molecule and its image has a vibration frequency different from that of the free molecule. The *electrodynamic interaction between a dipole and its image* has been discussed in many works[17]. The theoretical problem is that the calculated frequency shift is extremely sensitive to the position of the image plane (Fig. 3a). One can with reasonable parameter values obtain a downward frequency shift of the order of 5–50 cm^{-1}, but the latest work[17] indicates that the shift due to this interaction is rather small.

Even if the distance of the molecule above the image plane varies with adsorption site, most of the observed site dependence of the frequency must come from changes in the *electronic structure*. The present, somewhat revised picture of the CO chemisorption stems from recent cluster calculations by Bagus and coworkers[18]. The lowest unoccupied 2π molecular orbital in free CO is, due to the interaction with the metal electrons, broadened and pulled down in energy close to the Fermi level, as sketched in Fig. 3. The chemisorption bond is formed by transfer of charge from the metal into this 2π resonance, while the 5σ molecular orbital interacts with the conduction band with little net charge transfer. Since the 2π orbital has an antibonding character with respect to the C—O bond, the filling of this resonance lowers the vibration frequency. The 2π resonance has also been observed experimentally a few eV above the Fermi level by inverse photoemission. Its position in energy varies somewhat for different adsorption sites and metal substrates. For some systems the lower energy is found for the more strongly bonded species[19], quite in line with the picture above. However, a critical review of all present data[20] shows that the problem is not yet completely understood.

Within the same cluster calculation approach, attempts have also been made to mimic the vibrational motion of the chemisorbed molecule. If the cluster gives a good representation of the metal, the different interactions above should be included. For the internal stretch mode of CO in the ontop position on Cu(100) Müller and Bagus[21] obtain a downward frequency shift of 40–50 cm^{-1}, depending on the cluster size. This rather close to the observed value[8] of 67 cm^{-1}. Even if this good agreement may be rather fortuitous, they obtain the correct trends of the shifts for CO bonded on different metals. In the ontop position at low coverages IRS data give for Cu(100)[8] 2076 cm^{-1} and for Ni(100)[11] 2020 cm^{-1}, which gives a ratio of 1.03, which is just the same as for the calculated values[21]. Hopefully, larger clusters or complementary calculation techniques in the future will be able to predict the vibration frequencies of molecules chemisorbed at different sites and on different metals.

The situation is quite different for *physisorbed* molecules. In that case, there is no transfer of charge, the mechanical renormalization is weaker due to a much weaker metal–molecule bond and also the image interaction is smaller as the molecule probably is adsorbed further out from the surface. In a recent IRS investigation of CO physisorbed on Al(100)[22] the measured frequency is only shifted down a few cm^{-1} from the gasphase value. However, there is for this system also a short range intermolecular interaction that certainly will affect the vibrational frequency. As yet there exist no theoretical calculations for the van der Waals interaction between a CO molecule and a metal.

3.2. Molecule–molecule interaction

When a dipole is placed above a metal surface, the conduction electrons rearrange themselves to screen the dipole field as discussed above. This charge redistribution is found mainly in the very vicinity of the adsorption site but a small tail extends over several angstroms as so-called Friedel oscillations. When the adsorbed molecule is vibrationally excited, this will also give rise to a time-dependent variation in these oscillations. In principle these could affect the nearest neighbours and give rise to a *short range electronic interaction mediated via the substrate*. Treating the metal in the jellium model (that is neglecting the localized d-electrons), Persson[23] has estimated that the effect on the high frequency intramolecular modes should be negligible for $R > 4/k_F$, where R is the molecule–molecule distance and k_F is the Fermi wavenumber of the metal. This corresponds for copper to a distance of 2.9 Å. CO on close packed metal surfaces forms structures with a nearest neighbour distance larger than 3.5 Å and one has not seen any effect of this interaction in the infrared spectra. The main reason is that it is only in special cases that one can obtain the densely packed overlayers that produce the necessary short intermolecular distance. The situation for atomic adsorbates is different; one has found, in closed packed overlayers of hydrogen on Pd(100)[24] and Ni(100)[25], by EELS a very strong vibrational coupling, which has to be attributed to this electronic interaction through the substrate.

When the chemisorbed molecule is vibrationally excited this influences not only the metal electrons but also the ion cores in the neighbourhood. The vibrating ion cores can then in turn couple to other molecules and give rise to a *short range interaction mediated via the substrate lattice.* However, as Ω is much larger than the highest substrate phonon frequency the effect of this interaction is very small[26], but it can be important for low frequency modes[27].

CO chemisorbed on a metal surface often occupies distinct adsorption sites, giving at certain coverages ordered structures in phase with the substrate. On fcc(100) and (111) surfaces saturation occurs at coverages well below 1, the molecules are chemisorbed in an upright position with the oxygen end pointing outwards and with a molecule–molecule distance larger than 3 Å. However, it is now well established that on the (110) surfaces of Ni, Pd and Pt it is possible to obtain a coverage of 1, that is one adsorbed molecule on every metal surface atom. The surface consists of close packed, well separated rows of surface metal atoms. The most studied system is CO/Ni(110)[28] and at coverages less than 0.8 the molecules have the normal orientation but at higher coverages one obtains a CO–CO separation of only 2.5 Å. At such a short distance there is a *direct short range interaction* between the molecular orbitals of neighbouring molecules, which forces them to tilt away from each other to increase the intermolecular distance. The situation is similar for CO/Pt(110), where an angular resolved ultraviolet photoemission spectroscopy (UPS) study[29] has shown that at a coverage of 1 the molecules are tilted with about 25° away from the surface normal. This is confirmed by an infrared investigation of this system by Hayden *et al.*[30]. They find a decrease in the integrated absorptance for coverages above 0.5, reflecting how the component normal to the surface of the dynamical dipole moment decreases when the molecules tilt away from each other. One could expect that the onset of this molecule–molecule interaction also would show up in the infrared spectrum as a frequency shift and/or a change in the line shape. However, the data show a monotonous coverage-dependent frequency shift solely caused by the dipole–dipole interaction discussed below and the peak has a width of about 20 cm^{-1} at all coverages, probably caused by inhomogeneous broadening[30].

If the interaction with the substrate is weaker the situation becomes different. For a chemisorbed molecule an electronic rearrangement or even charge transfer between the substrate and the molecule has taken place, as discussed in the previous section. Physisorbed molecules on the other hand are only bonded via the fluctuating polarization, that is the van der Waals interaction. The problem when investigating physisorbed or weakly chemisorbed molecules is that as the interaction with the substrate is so weak they do not form any ordered structures and one does not get from the low energy electron diffraction (LEED) pattern any information about the nearest neighbour distance. This was seen in the infrared study on CO physisorbed on an Al(100) surface[22]. As much of the binding energy comes from the molecule–molecule interaction they form close packed clusters on the surface at all coverages and it is not possible to observe the onset of the direct short range interaction. This interaction manifests itself in the infrared spectrum as a relatively large inhomogeneous broadening and asymmetry of the infrared absorption peak (see Fig. 10).

The vibrational interaction that by far gives the strongest influence on the vibrational spectra is the *long range dipole–dipole interaction.* It originates from the fact that the vibrating molecule in Fig. 3a gives rise to a long range dipole field which oscillates in time and which is felt by the other adsorbed molecules. Already from the beginning of the infrared studies of adsorbed molecules one often found an upward frequency shift of 5–50 cm^{-1} as the coverage increased up to a full monolayer[1–3]. It was discussed how much of this shift was due to a vibrational coupling and how much was caused by changes in the electronic environment of the molecules, the 'chemical shift'. Hammaker *et al.*[31] early realized that the two effects could be separated by studies of mixtures of two different isotopes of the molecule. If the study is made at a constant coverage, the chemical environment in the different mixtures is the same, while the vibrational properties are varied. However, it was only after one had obtained enough sensitivity/resolution in IRS that one realized how strong the effect of the interaction could be. Figure 4 shows the infrared spectra of different mixtures of $^{12}C^{16}O/^{12}C^{18}O$ on a Cu(100) surface in the ordered *c*(2 × 2) structure[32]. The difference in vibration frequency for the two isotopes in the gas phase is 50 cm^{-1}, so for noninteracting molecules we would expect two absorption peaks, each with a height proportional to the concentration of the corresponding isotope. However, we observe one absorption peak dominant for nearly all concentrations and we find two peaks of equal height not at a 50/50 concentration but for 5% of the light isotope and 95% of the heavy one. Obviously, the overlayer must be regarded as a strongly coupled system and at that time the existing theories of the dipole–dipole interaction were unable to explain such a strong intensity transfer.

In the first treatment of this problem, taking up ideas from molecular crystal work, Hammaker *et al.*[31] considered only the direct interaction between the dipoles. Mahan and Lucas[33] made a substantial improvement by taking into account both the contribution from the images and the electronic polarizability of the molecules. Still they were not able to explain the observed coverage dependent freqency shifts. The reason for this became evident when Persson *et al.*[32,34] developed a new theory for the dipole–dipole interaction based on the old ideas but with several important new concepts. They showed

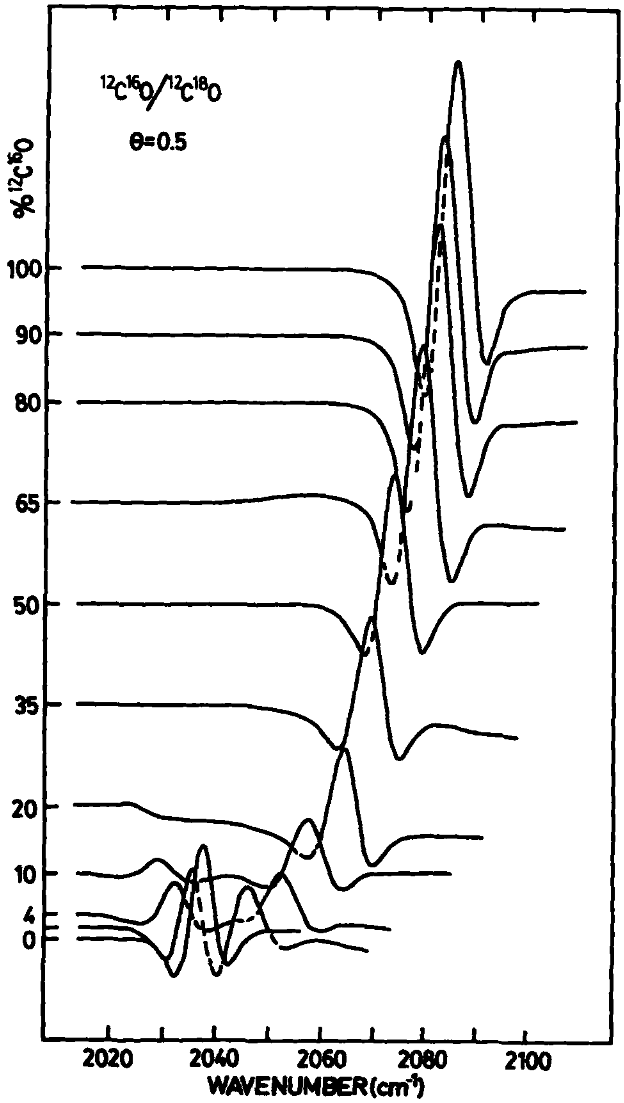


Fig. 4. Infrared derivative spectra for different isotopic mixtures of $^{12}C^{16}O/^{12}C^{18}O$ in the $c(2 \times 2)$ structure at 100 K on Cu(100). (*Reproduced by permission from Persson and Ryberg*[32].)

that the dynamical dipole moments that previously had been deduced from the strength of the IRS absorption or EELS loss peaks were incorrect, because earlier theories had neglected the screening of the external field by the electronic polarizability of the adsorbed molecules. Including this screening it was found that the dynamical dipole moment of chemisorbed CO is twice as large as for the free molecule. Using this new value in the previous theory[33] it was possible to explain the observed frequency shift. This result also solved an old problem as to why the dynamical dipole moment of the C—O stretch mode in carbonyls such as $Ni(CO)_4$ seemed to be about twice as large as for chemisorbed CO. With this new evaluation the values became about the same[32].

It was then possible to describe the behaviour of the frequencies but not the strong, anomalous intensity transfer. However, by using a theoretical approach called the coherent potential approximation it was possible to reproduce also these fine structures of the problem[32]. We ended up with a two-parameter theory, the parameters being the vibrational polarizability α_v (related to the dynamical dipole moment μ by $\alpha_v = 2\mu^2/\hbar\Omega$) and the electronic polarizability α_e of the adsorbed molecule. These quantities are attributed to a vibrationally excited object consisting of the *chemisorbed molecule and its image charge.* It has been argued that the molecule and its image should be treated separately and that the position of the molecule above the image plane could be used as a theoretical parameter[2, 35]. However, Persson and Liebsch[34] have shown that it is the whole object to which one should attribute the different measured quantities like the vibrational resonance frequency, the dynamical dipole moment and the electronic polarizability.

A best fit to the experimental data in Fig. 4 gave $\alpha_v = 0.25 \pm 0.02$ Å^3 and $\alpha_e = 2.5 \pm 0.5$ Å^3 (compared to 2.5 Å^3 for the free molecule)[34]. The vibrational polarizability can also be obtained in two independent ways, from the total infrared absorptance using Eq. (1), which gave $\alpha_v = 0.19$ Å^3 [8] and from EELS data, giving $\alpha_v = 0.23$ Å^3 [36], both assuming $\alpha_e = 2.5$ Å^3. These three values are in satisfactory agreement and give a dynamical dipole moment twice as large as for the free molecule. This increase is caused both by a polarization of the chemisorbed molecule and by the charge transfer to the 2π molecular resonance discussed in section 3.1, as charge is oscillating between this resonance and the metal during the vibration. Theoretical cluster calculations on CO/Cu(100)[37] also predict an enhancement in μ of this magnitude.

Using this theory of the dipole–dipole interaction it was then possible to get a good description of the experimentally measured integrated absorptance and vibration frequency as function of coverage. This is shown in Fig. 5 for CO/Ru(001). The solid lines are calculated using

$$(\Omega/\omega_1)^2 = 1 + c\alpha_v U(\mathbf{0})/[1 + c\alpha_e U(\mathbf{0})] \qquad (2)$$

$$\int (I_0 - I)/I_0 \, \mathrm{d}\omega \sim c\alpha_v U(\mathbf{0})/[1 + c\alpha_e U(\mathbf{0})]^2 \qquad (3)$$

where ω_1 is the vibration frequency when the coverage c goes to zero and $U(\mathbf{0})$ is the dipole sum for the actual adsorbate structure with the wavevector $\mathbf{q} = \mathbf{0}$.

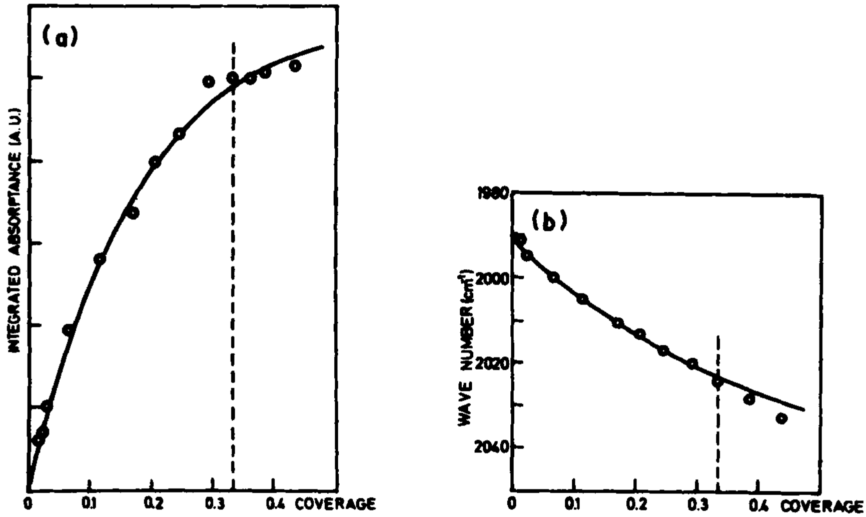


Fig. 5. The integrated infrared absorptance (a) and the vibration frequency (b) as function of converage for CO/Ru(001). The circles are experimental data from Pfnür *et al.*[38] and the solid lines are calculated using Eqs. (2) and (3), giving $\alpha_v = 0.28$ Å^3 and $\alpha_e = 2.8$ Å^3. (*Reproduced by permission from Persson and Ryberg*[32].)

From the fit one obtains values of α_v and α_e. Note how the electronic polarizability of the adsorbed molecules gives the absorptance a nonlinear coverage dependence. However, there exist several systems that do not follow Eqs. (2) and (3). This can be caused either by a coverage dependent change in the electronic structure, that is an additional chemical shift, or because the system exhibits clustering or the molecules occupy more the one adsorption site, since the theory assumes a random filling of the adsorbate lattice.

For the interpretation of infrared spectra of molecules adsorbed on a metal surface the dipole-dipole interaction have the following important implications:

1. An *ordered* monolayer of molecules having a large dynamical dipole moment must not be regarded as an ensemble of individual oscillators but a strongly coupled system, the vibrational excitations being collective modes (phonons) for which the wavevector $\mathbf{q}$ is a good quantum number. The dispersion of the mode for CO/Cu(100) in the $c(2 \times 2)$ structure has been measured by off-specular EELS[36], while the infrared radiation of course only excites the $\mathbf{q} = \mathbf{0}$ mode.
2. One must account for the screening of the external field by the electronic polarization of the adsorbed molecules. This screening gives rise to a reduced infrared absorption. Taking it into account in a proper way shows

that the dynamical dipole moment of chemisorbed CO is roughly twice as large as for the free molecule.

3. The anomalous strong transfer of intensity to the high frequency mode that is seen in Fig. 4 arises from the fact that high frequency modes can screen low frequency ones but not vice versa. If this screening effect is overlooked it can give rise to a significant misinterpretation when one tries to use the peak height as a measure of the concentration as is done in gas phase spectroscopy. This is particularly important when one considers two or more modes separated by less than a hundred cm^{-1}. This intensity transfer to the high frequency mode has been shown to give an apparently too low concentration of a surface species[39], too small intensity from molecules chemisorbed in the bridge position[40] and even missing peaks in some structures[8].
4. It has turned out to be important to use the full theory[32] of the dipole–dipole interaction also when calculating other vibrational properties of an adsorbate layer. It was important for the interpretation of the coupling to the low frequency modes[41], the so-called dephasing discussed in the next section. Further, it had drastic effects on the calculated shape of the infrared absorption peak[42], as discussed in section 3.4.

All this work on the dipole–dipole interaction has been made for modes oriented normal to the surface or for the normal component of μ and they predict an upward frequency shift for increasing coverage. Hayden *et al.*[43] suggested that a downward shift could occur for modes oriented parallel to the surface and this idea has also been used to assign modes of H/W(100)[44]. However, it should be clear that the interaction must be much weaker for modes parallel to the surface, as the dipole field in accordance with the infrared selection rule mentioned in section 2 is screened by the metal surface. At least, in a theoretical model this has to be taken into account.

In conclusion, the effects of the dipole–dipole interaction cause the greatest difference between the interpretation of infrared spectra of gas phase and adsorbed molecules and if the mode has a large dynamical dipole moment this interaction is always in operation.

3.3. Interaction with low frequency modes

Consider the possible normal modes of a diatomic molecule oriented with the axis normal to the surface. If we neglect the surface structure, we get starting from the lowest energy as schematically shown in Fig. 6;

(a) a *frustrated translation* consisting mainly of translational but also some rotational motion, because the molecule has its highest binding energy at a certain site;

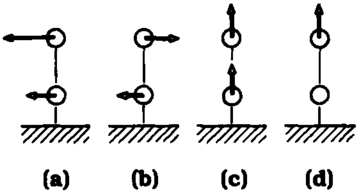


Fig. 6. Schematic representation of the normal modes of an adsorbed diatomic molecule neglecting the surface structure, after Richardson and Bradshaw[45]. In parentheses the experimentally measured values for CO in the ontop position on Pt(111). (a) A frustrated translation (60 cm^{-1})[46]. (b) A frustrated rotation (not yet detected). (c) The metal–molecule stretch (460 cm^{-1})[16]. (d) The intramolecular stretch model (2100 cm^{-1})[14].

(b) a *frustrated rotation* consisting mainly of rotational but also some a translational motion;
(c) a mainly *metal–molecule stretch* mode; and finally
(d) a mainly *intramolecular stretch* mode.

The C—O stretch vibrational mode of a free molecule is almost a perfect harmonic oscillator and if the interaction with the substrate were negligible this would also hold for an adsorbed molecule. However, we know that for a chemisorbed molecule there is a substantial molecule–substrate interaction which manifests itself, for example, as a dependence of the vibration frequency on the binding position on the surface. The trend is that the vibration frequency decreases as we go from ontop to bridge site and from bridge to hollow site, the difference being about 100–200 cm^{-1} in each step. Intuitively we feel that if the whole molecule is making any motion with respect to the surface described by the low frequency modes above, this will affect the high frequency mode and should in principle be seen in the infrared spectrum. Such effects of an anharmonic coupling (which does not exist for a perfect harmonic oscillator) gives rise to vibrational phase relaxation of the C—O stretch mode, a process often called *dephasing*. There is no transfer of vibrational energy but the high frequency mode, after a certain time due to this anharmonic coupling will be out of phase compared with an unperturbed harmonic oscillator. Characteristic for this kind of interaction would be a strong temperature dependence, because the low frequency modes are thermally excited and the effect should vanish at low temperatures. Gadzuk and Luntz[47] have reviewed the different kinds of phase relaxation mechanisms that may be applicable to adsorption systems. On the other hand there exist other temperature dependent effects such as phase transitions, increased surface mobility causing disorder in the overlayer and so on. Experimentally we find for some systems, like CO/Cu(100)[12], almost no temperature dependence at all, while for other systems drastic temperature effects have been reported.

Rather strong temperature variation has been seen in the infrared spectra of CO/Ni(111)[48,49]. Figure 7 shows the peak width and position as a function of substrate temperature for the c(4 × 2) structure, where all molecules are chemisorbed in the bridge position. As seen in the figure the peak width increases strongly with increasing temperature and there is also a small upward shift of the peak position. We observe that both the peak width and position reaches a constant value for very low temperatures, so it could be possible that the behaviour can be explained in terms of an anharmonic coupling. Persson *et al.*[40,41] developed a new theory for this problem, partly

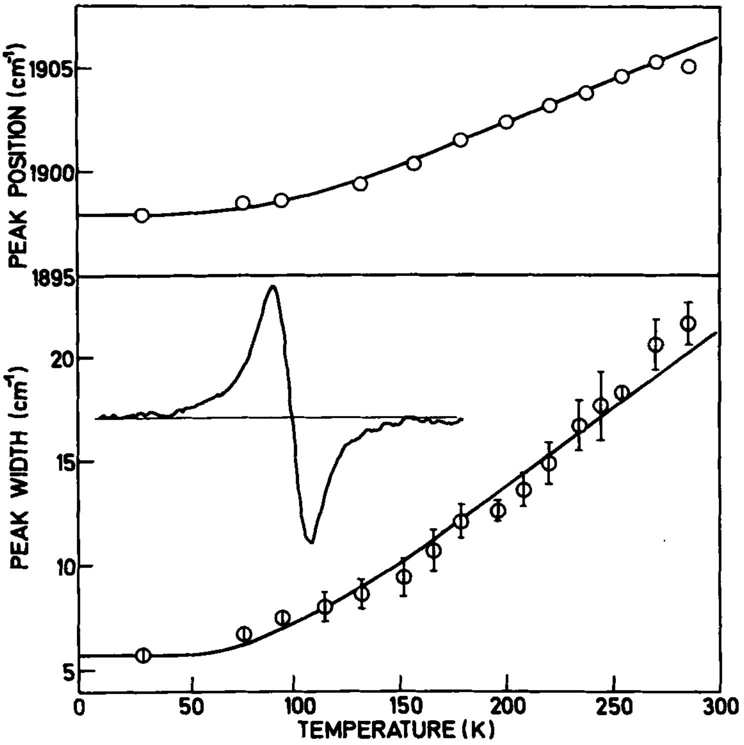


Fig. 7. The position and width of the infrared absorption peak as function of substrate temperature for the c(4 × 2) structure of CO on Ni(111). All molecules are chemisorbed in the bridge position and the solid lines are calculated within the theory describing the anharmonic coupling to a low frequency mode. (*Reproduced by permission from Persson and Ryberg*[40].)

based on older work[50] but incorporating new important concepts, in particular the lateral dipole–dipole interaction. The theory contains three parameters, which describe the dephasing mechanism:

1. The frequency ω_0 of the low energy mode. This frequency must of course be low enough to give a reasonable population at temperatures where the adsorption system is stable.
2. The coupling strength $\delta\omega$, which is the shift in frequency of the high energy mode when the low frequency mode is in its first excited state. $\delta\omega$ has to be large enough to give a measurable effect. It can take both positive and negative values, e.g. a frustrated translation for ontop bonded molecules gives a negative $\delta\omega$, as the frequency decreases when going away from the ontop position.
3. The damping rate η of the low energy mode. These modes are predominantly damped by excitations of substrate phonons. If the damping rate is very large, there will of course be little effect on the high frequency mode. On the other hand if the damping is very weak, we will observe a two-peak spectrum with one peak for the molecules where the low energy mode is in its ground state and one peak for molecules where it is in its first excited state (naturally, if ω_0 is low enough we can get a number of peaks).

The solid lines in Fig. 7 are a best fit to the experimental data, giving the following values for the parameters above[42]:

$$\omega_0 = 235\,\mathrm{cm}^{-1} \quad \delta\omega = 20\,\mathrm{cm}^{-1} \quad \eta = 20\,\mathrm{cm}^{-1}.$$

The important conclusion is that we get a very good fit to the experimental data assuming an anharmonic coupling to one specific low frequency mode. The normal mode calculation of CO bridgebonded on Ni by Richardson and Bradshaw[45] estimates for the frustrated translation $\omega = 76\,\mathrm{cm}^{-1}$ and for the frustrated rotation $\omega = 184\,\mathrm{cm}^{-1}$, while it is known from EELS data[51] that the metal–molecule stretch is found at $400\,\mathrm{cm}^{-1}$. The calculated values should only be taken as rough estimates, because the frequencies of these frustrated modes have not yet been experimentally determined. However, it seems very likely that the temperature effects for the bridgebonded CO molecules on Ni(111) are caused by this anharmonic coupling and that the high frequency mode couples mainly to one specific mode, possibly the frustrated rotation. In a simple model it was possible to estimate the damping rate η for a mode at $235\,\mathrm{m}^{-1}$ to be of the order of $50\,\mathrm{cm}^{-1}$, while the coupling strength $\delta\omega$ is much more difficult to treat without an extensive chemisorption calculation.

It was interesting to compare these results for bridgebonded molecules with similar data of ontop bonded ones. Figure 8 shows the temperature dependence of CO on Ru(001)[42] in the $(\sqrt{3} \times \sqrt{3})\mathrm{R}30^\circ$ structure, with all molecules in the ontop position. In this case the temperature dependence on the peak width is small while there is a large downward frequency shift. Again

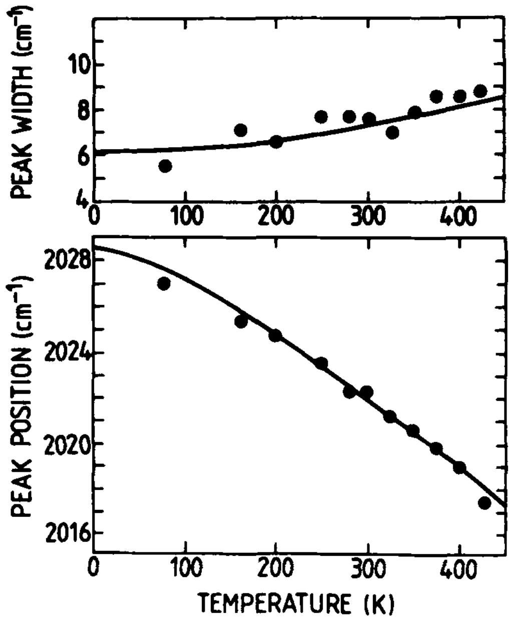


Fig. 8. The position and width of the infrared absorption peak as function of substrate temperature for the ($\sqrt{3} \times \sqrt{3}$)R30° structure of CO on Ru(001). All molecules are chemisorbed in the ontop position and the solid lines are calculated within the theory describing the anharmonic coupling to a low frequency mode. (*Reproduced by permission from Persson et al.*[41].)

the solid lines are best fits giving[42]:

$$\omega_0 = 105\,\mathrm{cm}^{-1} \quad \delta\omega = -6\,\mathrm{cm}^{-1} \quad \eta = 6\,\mathrm{cm}^{-1}.$$

Comparing with the normal mode calculation and the experimentally determined value for CO/Pt(111) below, it seems likely that for the ontop bonded molecules the anharmonic coupling is to the frustrated translation. As expected, $\delta\omega$ is then negative as the C—O stretch vibration frequency decreases when going away from the ontop position.

As we are dealing with an ensemble of molecules with a large dynamical dipole moment, we have to consider the dipole–dipole interaction. The strong intensity transfer to high frequency modes that was seen for two different species in the isotopic mixtures in the previous section will also affect the peak shape for this ensemble of slightly shifted oscillators. If there were no molecule–molecule interaction the anharmonic coupling would for the ontop bonded molecules give a broadened infrared absorption peak with a low frequency tail. However, when the dipole–dipole interaction is taken into account, there is an intensity transfer to the high frequency side, making the line narrow again. The effect may become reversed when $\delta\omega$ is positive, as this gives a peak with a high frequency tail[42,52]. These important effects on the lineshape due to the dipole–dipole interaction are discussed in the next section and are illustrated in Fig. 9.

That the parameter values obtained from this fit of the theory to experimental data are physically relevant was confirmed by a study on CO in the ontop position on Pt(111). In an IRS investigation of this system Schweizer[14] using the same theory obtained:

$$\omega_0 = 50\,\mathrm{cm}^{-1} \quad \delta\omega = 3\,\mathrm{cm}^{-1} \quad \eta = 4\,\mathrm{cm}^{-1}.$$

Lahee *et al.*[46] have studied CO on Pt(111) using inelastic scattering of He atoms and showed that they could detect adsorbate–metal modes at energies below $200\,\mathrm{cm}^{-1}$ (with a resolution of $4\,\mathrm{cm}^{-1}$), an energy range previously of course not accessible to IRS but also burried in the elastic peak in EELS. They found for this system an energy loss peak at $48\,\mathrm{cm}^{-1}$, which they assign to a frustrated translation and possibly a weak feature at $133\,\mathrm{cm}^{-1}$ due to a frustrated rotation. Furthermore, for such a low energy mode that lies well in the one-phonon band of the metal, one can rather accurately calculate[42] $\eta = 4\,\mathrm{cm}^{-1}$.

In principle, there exists an independent way of determining ω_0, $\delta\omega$ and η. The theory predicts the existence of sidebands at $\Omega \pm 2\omega_0$[49]. The strength of these combination bands should be $(\delta\omega/\omega_0)^2/8$ of the fundamental mode with a width equal to 2η[53]. We investigated very carefully the $c(4 \times 2)$ CO/Ni(111) system without being able to detect these bands. It is not clear whether this is because the bands are too weak (1×10^{-3}) and/or too broad ($40\,\mathrm{cm}^{-1}$) or that it has a more fundamental reason.

To conclude, it seems that the nature of the anharmonic coupling between a high frequency intramolecular mode and a thermally excited low frequency mode is understood. It turns out that the strength of the influence on the infrared spectrum critically depends on the values of ω_0, $\delta\omega$ and η. However, we have to wait for more experimental data on these low frequency modes, probably obtained with the helium atom scattering technique, before we can make more definite conclusions.

3.4. Vibrational energy dissipation

One of the main differences between a free and an adsorbed CO molecule is that whereas the vibrational energy of the gas phase molecule can only be transferred into a photon, giving the excitation a lifetime of 30 ms, the adsorbed molecule is able to dissipate the vibrational energy into the substrate, giving the mode a lifetime in the picosecond range. This is extremely important for the energy transfer in most dynamical processes at surfaces, as in many cases the molecules in an intermediate state are vibrationally excited. For a metal substrate there exist two fundamental processes that can accommodate the energy, excitation of phonons and of electrons, the latter mechanism often called creation of electron–hole pairs.

To study a dynamical phenomenon like the vibrational damping, the most direct way is to use some kind of time resolved spectroscopy. As we are dealing with processes on the ps scale, this calls for a pulsed laser experiment. The technique is to saturate by a pump beam all molecules in their first vibrationally excited state and then with a time delayed probe beam measure the relaxation. With this approach one has been able to determine both the vibrational lifetime and the influence of anharmonic coupling to other modes in molecular solids and other systems[54]. However, the experimental problem for studies of adsorbed molecules is the same as that encountered by ordinary infrared spectroscopy some twenty years ago, namely to obtain high enough sensitivity to detect a monolayer or less on the metal surface. Cavanagh and coworkers have made great efforts in creating such a laser system in the infrared and at the time of writing they have reached the 2000 cm^{-1} region with pulses of 10 ps width at a power of 15 μJ[55]. Previously, in a transmission experiment they have measured the lifetime of the O—H stretch mode at 3000 cm^{-1} on silica[54]. Despite these considerable achievements a lot of instrumental development has still to be done before the lifetime of a vibrational excitation of a molecule adsorbed on a metal surface can be unambiguously determined.

Another, less straightforward way to determine the vibrational lifetime is by studies of the infrared absorption peak shape. Consider a single adsorbed molecule at 0 K. The width of the peak is then determined by the lifetime broadening and in the first approximation it has a Lorentzian shape with a full width at half maximum (FWHM) $\Delta = (2\pi c\tau)^{-1}$, τ then being the lifetime. However, as usual we have to consider an ensemble of molecules at finite temperatures and then there exist other peak broadening mechanisms that must be taken into account.

First of all we must consider *inhomogeneous* broadening, which in the first approximation give a Gaussian shaped peak, but with modifications discussed below. Chemisorbed molecules tend to occupy distinct adsorption sites but if we have a large concentration of surface defects (steps, vacancies, adatoms, impurities and so on) the chemical environment will differ for the adsorbed molecules, which will give rise to a broadening of the peak. However, for the high purity materials used in surface science and with proper alignment and surface preparation the defect concentration should be less than 1%[56]. If we study a rather dense monolayer this effect should then be negligible, but it can be extremely important in studies in the low coverage regime.

Even for a high coverage monolayer on a perfect surface we can get additional inhomogeneous broadening. It should be clear from the discussion

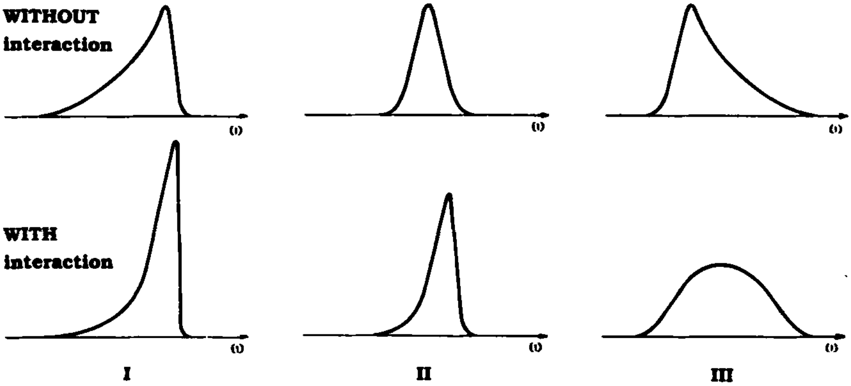


Fig. 9. The effect of the dipole–dipole interaction on inhomogeneously broadened infrared absorption peaks. Without and with the interaction turned on for peaks with I, a low frequency tail, II, a symmetric Gaussian distribution and III, a high frequency tail. (*Adapted from Persson and Hoffmann*[52].)

in section 3.2 that there can be a substantial molecule–molecule interaction. Disorder in the overlayer will then produce additional broadening, as the vibrational environment will differ among the sites. An interaction that gives rise to an upward coverage-dependent frequency shift (an increasing vibration frequency for increasing coverage) will give rise to a low frequency tail of the absorption peak (the local coverage is less than or equal to that of the full monolayer) and vice versa. However, a general effect of the dipole–dipole coupling is the intensity transfer to high frequency modes as discussed several times in the previous sections. This mechanism will push the intensity upwards, so a low frequency tail will be diminished, a symmetric absorption peak will get a low frequency tail, while a peak with a high frequency tail will be broadened[52]. These general effects are shown schematically in Fig. 9. Obviously, anyone who wants to interpret the shape of the infrared absorption peak of dense overlayers must take these effects into account and when calculating such shapes use the full theory of the dipole–dipole interaction[32].

An example of an inhomogeneously broadened peak is found for CO physisorbed on an Al(100) surface[22]. In addition to the dipole–dipole coupling there is a substantial short range interaction. The adsorbed molecules do not form any ordered structures and hence the overlayer contains a large degree of disorder. We find in Fig. 10 a spectrum with a rather Gaussian shaped peak with a high frequency tail. However, as the structure of this system is unknown it s not possible to make a more detailed interpretation of the peak shape.

From the discussion in section 3.3 it should be obvious that another peak broadening mechanism, at least at higher temperatures, is the *anharmonic coupling* to low energy modes. We discussed the origin of the broadening in that context and found in Fig. 7 that for $c(4 \times 2)$CO/Ni(111) this interaction

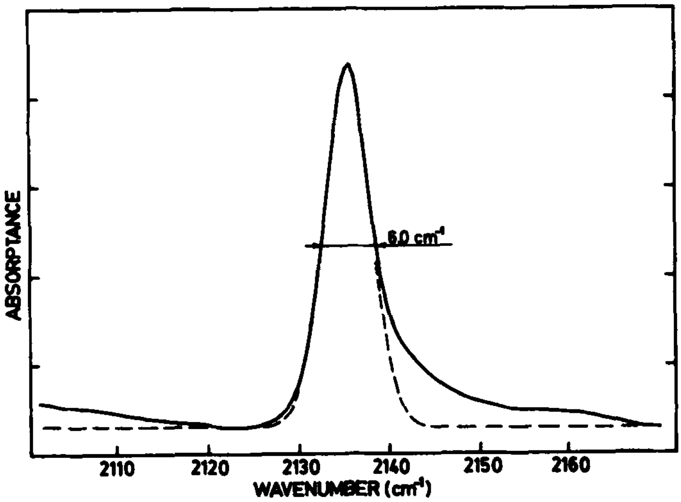


Fig. 10. The infrared absorption peak of a full monolayer of CO physisorbed on an Al(100) surface at 30 K. No ordered structures are formed and the peak is inhomogeneously broadened. The dotted line is a Gaussian distribution. (*Reproduced by permission from Ryberg*[22].)

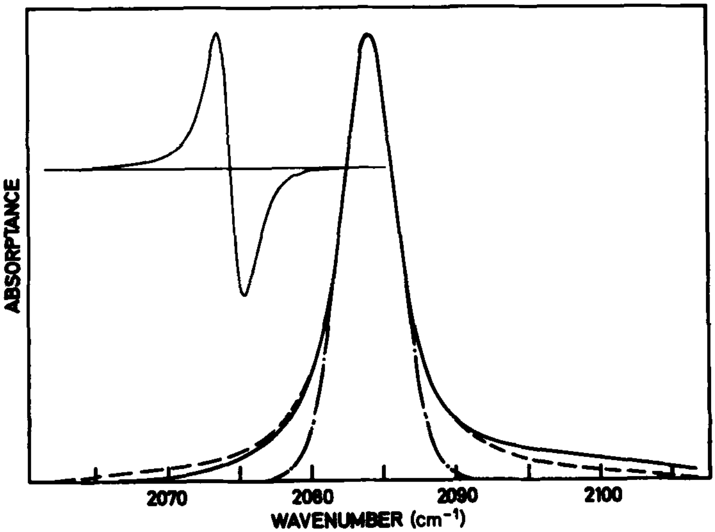


Fig. 11. The infrared absorption peak (solid line) of the ordered $c(2 \times 2)$ structure of CO on Cu(100) at 100 K. Shown also are Lorentzian (dashed) and Gaussian (dash-dotted) distributions. The recorded first derivative spectrum is shown in the inset. (*Reproduced by permission from Ryberg*[12].)

gave a considerable contribution to the width for temperatures above 70 K but also that it vanished at very low temperatures. It seems fair to say that if there is a negligible temperature dependence of the absorption peak, there is no dephasing contribution at least in that temperature region.

A system that seems free from the most obvious inhomogeneous or phase relaxation broadening is $c(2 \times 2)$CO/Cu(100)[12], where all molecules are bonded in the ontop position. Figure 11 shows the infrared absorption peak, which exhibits almost no temperature dependence in the range 20 to 130 K. The peak has a predominantly Lorentzian shape with a weak high frequency tail. The intrinsic line width $\Delta = 4.6\,\mathrm{cm}^{-1}$, which would correspond to a lifetime $\tau = 1.2$ ps if the width was caused solely by lifetime broadening. As stated above the influence of surface defects for a dense overlayer like this can be neglected. The effect of imperfections in the adsorbate layer was tested by measurements on an incomplete overlayer. This made the peak lose most of its Lorentzian shape and it was therefore argued[12] that the weak high frequency tail of the ordered structure in Fig. 11 sets an upper limit for the inhomogeneous broadening for this system. Another observation that speaks against inhomogeneous broadening is the fact that most recent infrared investigations made with high resolution spectrometers give similar values of the peak width: $5\,\mathrm{cm}^{-1}$ on Cu(100)[12], Cu(111)[57] and Pt(111)[14] and $6\,\mathrm{cm}^{-1}$ on Ni(111)[40] and Ru(001)[41].

There exists an extensive literature on theoretical calculations of the vibrational damping of an excited molecule on a metal surface. The two fundamental excitations that can be made in the metal are creation of phonons and electron–hole pairs. The damping of a high frequency mode via the creation of phonons is a process with small probability, because from pure energy conservation, it requires about 6–8 phonons to be created almost simultaneously.

The other excitation in the metal that can accommodate the vibrational energy is creation of electron–hole pairs. The theoretical aspects of this problem have been reviewed by Avouris and Persson[58]. For molecules with a large dynamical dipole moment the *long range in time-oscillating dipole field* will set up currents in the metal. The response of the metal and the damping rate for a vibrationally excited molecule placed well above the metal surface can be rather accurately calculated. However, for an adsorbed molecule which is sitting inside the metal charge distribution some serious assumptions have to be made. For CO on Cu the most detailed theoretical calculations[59,60] of this damping process predict a lifetime $\tau \approx 10$ ps.

In section 3.1 we discussed the present picture of the electronic arrangement of CO chemisorbed on a metal surface, which was schematically shown in Fig. 3. When the molecule is vibrationally excited charge is oscillating between the 2π resonance and the metal. This gives rise to the large increase in the dynamical dipole moment, as was discussed in that section. These *local charge* *oscillations* also cause vibrational damping and if one uses the increase in dynamical dipole moment due to the chemisorption as a measure of the oscillating charge, in a simple model[58] for CO/Cu one can estimate $\tau \approx 2$ ps.

Langreth[61] pointed out that if the energy relaxation originates from these local charge oscillations, then the infrared absorption peak will not have a Lorentzian shape. The oscillating charge will not be in phase with the external field, which will give the absorption peak a low frequency tail. This seems to be in contradiction with the data in Fig. 11. However, the calculation was made for a single adsorbed molecule and as discussed above influences on the line shape due to the vibrational interaction can be severe. In a later work Crljen and Langreth[42] incorporated the dipole–dipole interaction of the full monolayer using the theoretical approach introduced by Persson and Ryberg[32]. The result is reproduced in Fig. 12, showing that the low frequency tail of a single molecule due to the dipole–dipole interaction becomes a high frequency tail for the full monolayer. An important consequence of the theory is that the vibrational quantities that we have assigned to the adsorbed molecule (including its image) are renormalized. Fitting the theory to the experimental spectrum in Fig. 11 gives for a *single adsorbed molecule* a line width $\Delta = 2.8\,\text{cm}^{-1}$ (instead of the apparent width of $4.6\,\text{cm}^{-1}$), which then corresponds to a lifetime $\tau = 1.9$ ps. The polarizabilities are also renormalized to $\alpha_v = 0.31\,\text{Å}^3$ and $\alpha_e = 4.3\,\text{Å}^3$, compared to $\alpha_v = 0.25\,\text{Å}^3$ and $\alpha_e = 2.5\,\text{Å}^3$ obtained from the isotopic mixtures in section 3.2.

The theory reproduces the experimental line shape of the ordered overlayer very well but is unable to explain the more complicated spectrum of an incomplete layer. More important, using the same parameter values Crljen

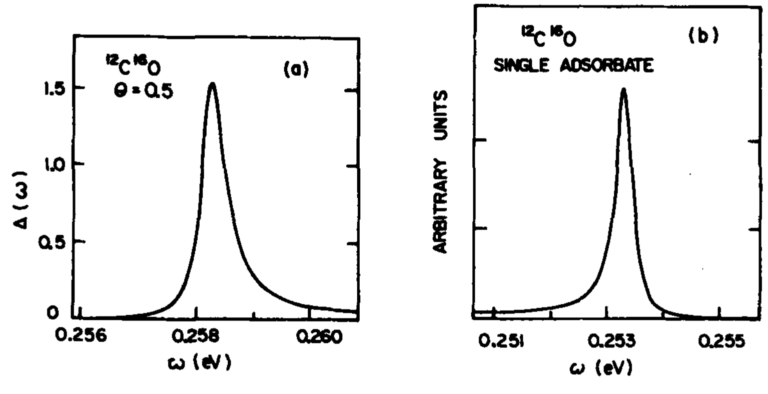


Fig. 12. The calculated infrared absorption peak, assuming lifetime broadening and vibrational damping via local charge oscillations. (a) Fitted to the experimental spectrum in Fig. 11 for an ordered overlayer incorporating the dipole–dipole interaction. (b) The same calculation for a single adsorbed molecule. (*Reproduced by permission from Crljen and Langreth*[42].)

and Langreth[42] were able to reproduce the asymmetry of the absorption peaks as function of composition of the isotopic mixtures in Fig. 4. This shows, in an independent way, both that we have a very good description of the dipole–dipole interaction and that the line width, to a significant degree, is caused by vibrational damping due to electron–hole pair excitations.

To conclude, even if there exist several processes that affect the vibrational line shape it seems probable that when most of them have been sorted out and with the good agreement between theory and experiment, the lifetime broadening for a chemisorbed CO molecule is of the order of a few cm^{-1}, corresponding to a lifetime of a few ps. The main vibrational energy relaxation mechanism is creation of electron–hole pairs caused by the local charge oscillations between the metal and the 2π molecular resonance crossing the Fermi level.

4. LOW FREQUENCY METAL–MOLECULE MODES

Studies of the metal–molecule stretch modes are very important for the understanding of adsorption systems as they are the vibrational levels in the binding energy potential. These modes will be highly excited during all kinds of surface processes like sticking, desorption and reactions. The damping rate of such a mode will definitely be important for the kinetics of the system and therefore the experimentalists have for a long time tried to extend the infrared measurements to this region below $500\,\mathrm{cm}^{-1}$. The associated experimental problems were discussed to some extent in section 2.

The only reported infrared measurements on metal–molecule modes on single crystalline surfaces have been carried out in very nice experiments by Tobin and Richards[15,16], using a dedicated emission spectrometer. Two systems have so far been investigated, CO chemisorbed on Ni and Pt surfaces. The initial study[15] of the $c(2 \times 2)$CO/Ni(100) system was made at room temperature and showed a weak absorption peak at $475\,\mathrm{cm}^{-1}$ and with a width of about $15\,\mathrm{cm}^{-1}$. The vibration energy lies in the two-phonon band of Ni, so the relatively large width could be caused by strong vibrational damping caused by two-phonon excitations. Such a mechanism should exhibit a strong temperature dependence and vanish at 0 K. However, the weak infrared signal did not permit a more detailed study of the temperature dependence of the system. Instead, the technique was applied to the CO/Pt(111) system[16], which gave one order of magnitude better signal/noise. In Fig. 13 emission spectra at different coverages are reproduced and they show for the $c(4 \times 2)$ structure at 200 K a peak at $460\,\mathrm{cm}^{-1}$ with a width of about $7\,\mathrm{cm}^{-1}$. The highest phonon frequency is much lower for Pt than for Ni, so here the vibrational mode is above the two-phonon band and the damping rate for three-phonon excitations should be at least one order of magnetic smaller[62]. Furthermore, for the Pt system they were able to study

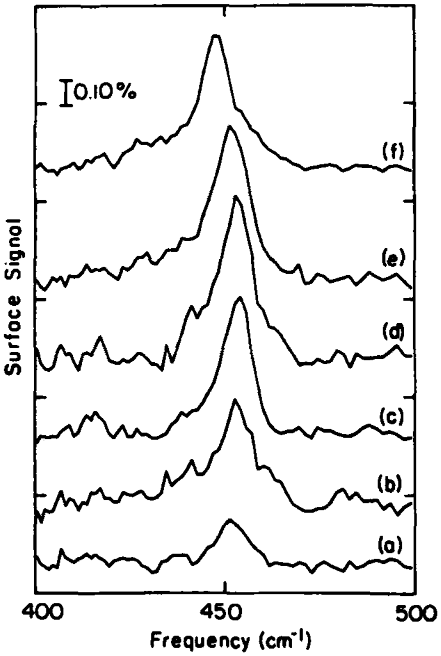


Fig. 13. Infrared emission spectra of the metal–molecule stretch mode for $^{13}C^{16}O$ on Pt(111) at 275 K. The different coverages are: (a) 0.07, (b) 0.14, (c) 0.27, (d) 0.31, (e) 0.50 (the *c*(4 × 2) structure) and (f) 0.55. (*Reproduced by permission from Tobin and Richards*[16].)

the temperature dependence above 200 K, which was found to be rather weak. Together with a large spread in the values of the widths this indicated that the peak width was determined by inhomogeneous broadening. It follows that for the Ni system there is a need for a temperature dependence study before anything more definite can be said about the damping mechanisms.

The inherent drawback of the emission technique is that the substrate, which acts as the light source, must be held at a relatively high temperature. This makes it difficult to make more definite studies on thermally excited modes, which often require rather low substrate temperatures. So the efforts to develop a more traditional reflection spectrometer for this region have continued, since much important information can be obtained if these thermally excited modes could be frozen out. As mentioned in section 2, during the time of writing this paper, for the first time I was able to detect the metal–molecule stretch mode in a reflection experiment, using a wavelength modulation spectrometer. Figure 14 shows preliminary spectra of $^{13}C^{18}O$ and $^{12}C^{18}O$ in the *c*(4 × 2) structure on Pt(111) at 100 K. The reproduced first