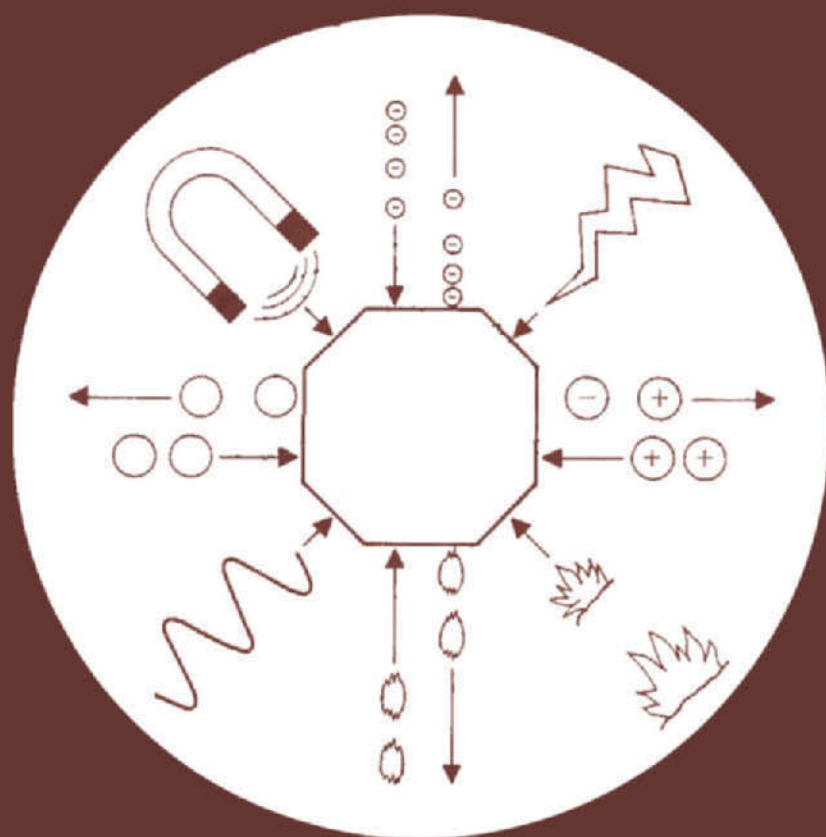


studies in surface science and catalysis



14

VIBRATIONS AT SURFACES

C.R. Brundle
and
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Asilomar, California, U.S.A., 1–4 September 1982

Editors

C.R. BRUNDLE and H. MORAWITZ

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FOREWORD

The third International Conference on " Vibrations at Surfaces " (VAS III) was held at Asilomar, California, from September 1-4, 1982. It followed its two forerunners held in Juelich, West Germany in 1978 and Namur, Belgium in 1980 with clear indications of continuing and increasing growth in both experimental and theoretical activities, sophistication and understanding.

Almost all of the 102 papers presented at the meeting are published in this volume. A few papers appear as abstracts only due to prior commitment to other publication channels or choice of authors and/or editors.

The conference attracted about 165 participants active in the field, and was organized by a group of scientists from the IBM Research Laboratory in San Jose, California acting as local committee. The hard-working members of this group included:

D. Auerbach	F. Houle
P. Bagus	A. Luntz
J. Barker	H. Morawitz (Chairman)
I. Batra	M. Philpott
R. Brundle	J. Rabolt
T. Chuang	H. Seki
F. Herman	J. Swalen

To cover the range of work relevant to the theme of the meeting, a set of eight session topics were chosen with the help of an International Advisory Committee consisting of :

S. Anderson, Sweden	B. Lundquist, Sweden
G. Boato, Italy	D. Menzel, Germany
E. Burstein, U.S.A.	A. Otto, Germany
C. Imbert, France	J. E. Rowe, U.S.A.
H. Ibach, Germany	W. Suetaka, Japan
D. King, England	P. Toennies, Germany
J. Kirtley, U.S.A.	R. Van Duyne, U.S.A.
A. Lucas, Belgium	H. Weinberg, U.S.A.

The topics chosen for the eight sessions held over a span of 3 days were: (I) Vibrational Frequency Shifts and Widths-Lateral Interactions; (II) Dynamical Processes at Surfaces; (III) and (IV) Electron Loss Spectroscopy; (V) Raman and Surface Enhanced Raman Scattering; (VI) Infrared Absorption and Reflection Spectroscopy; (VII) Beam Surface Scattering - Surface Phonons; (VIII) Electron Tunnelling Spectroscopy - Surface Enhanced Raman Studies in Electrochemistry. In addition, C. B. Duke presented an introductory keynote surveying progress in the field since the last meeting. In the final session H. Ibach and T. Grimley presented conference overviews and future prospects for the field from an experimental and theoretical perspective.

Also included in the Proceedings are four literature surveys on Energy Loss, Inelastic Tunnelling, Infrared and Raman (SERS) papers. The ones on EELS and Infrared are updates of similar surveys appearing in the Proceedings of VAS II, the remaining two are new additions.

A striking aspect of the meeting was the presence of much work related to dynamical effects occurring in atom and molecule-surface interactions. While the static properties of both surface and adsorbate define the zero order response, it is clear that many of the techniques used and properties determined in vibrational surface spectroscopy in fact depend on dynamical changes in both surface and adsorbate behavior. Typical examples are the various enhancement mechanisms proposed in SERS, the effect of substrate phonon and electronic excitations in atom and molecule scattering experiments and the interplay of local and collective modes in overlayer vibrations to mention a few.

The conference proved the timeliness of a two year period and provided a convenient geographical locus for the Pacific sector of surface vibrational spectroscopy given the European locations of VAS I and II. The conference organizers gratefully acknowledge generous support from the IBM Research Laboratory at San Jose, the National Science Foundation, the Air Force Office of Scientific Research, The Office of Naval Research, the International Union of Pure and Applied Physics and the American Physical Society for sponsorship and financial aid. Finally, Mrs. Beth MacQuiddy as conference secretary did a superb job keeping track of the myriad of logistical details and deserves the full gratitude of the organizing committee and all participants.

C. R. Brundle and H. Morawitz
(Guest Editors)

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Vibrations at Surfaces

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Part A

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HOT ATOMS AND COLD FACTS: MYSTERIES AND OPPORTUNITIES IN
VIBRATION-ASSISTED SURFACE CHEMISTRY

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ABSTRACT

This paper is a synopsis of the keynote lecture at the Third International Conference on Vibrations at Surfaces. The science of hot atoms at surfaces is divided into three broad areas: spectroscopy, theory, and process dynamics. A brief overview of each area is given in which the main advances and mysteries which have emerged during the past few years are noted. The resolution of such mysteries provides the traditional type of opportunity for scientific discovery. Most of the currently visible frontiers lie in the development of applications of the techniques of vibrational spectroscopy, however, so that these scientific opportunities tend to be different in kind than they were a decade ago.

Another type of opportunity is the development of hot-atom process technologies. Inspection of current activity reveals that a gap exists between the development of the techniques of vibrational spectroscopy as applied to well-defined model systems and the systematic application of these techniques to examine and extend process technologies based on surface chemistry. Radiation-induced surface chemistry is an example of an area which affords a unique opportunity for surface vibrational spectroscopy and theoretical chemistry to play a significant role in the development of fabrication technologies for electronic devices. This type of opportunity is shown to be particularly important for the future of surface vibrational spectroscopy in the current economic climate for research and development.

INTRODUCTION

During the past decade surface vibrational spectroscopy has come of age as a methodology for the characterization of molecules and atoms adsorbed on solid surfaces. A variety of specific spectroscopic techniques have emerged for the examination of adsorbed species in different environments. For example, infrared transmission-adsorption spectroscopy (ITAS) is utilized to study finely divided samples at "high" (e.g., atmospheric and higher) pressures characteristic of operating catalysts. Inelastic Electron Tunneling Spectroscopy (IETS) deals with samples prepared by adsorption of various species from solution on an insulating layer deposited or grown on a metal film. Electron Energy Loss Spectroscopy (EELS) consists of the use of high resolution inelastic electron scattering from carefully prepared surfaces, typically in ultrahigh vacuum ($p \leq 10^{-10}$ Torr), to examine the vibrations of ordered and disordered adsorbates on single crystal surfaces. The literature on surface vibrational spectroscopy is immense, several books having been published [1,2] since the previous (i.e., Second) International Conference on Vibrations at Surfaces [3]. An indication of the scope of current utilizations of vibrational

spectroscopies for surface analysis is given in Table I, which is adapted from a recent review [4] to which the reader is referred for a more systematic introduction to the subject. Also, the acronyms which I use in this article for the various spectroscopies are defined in Table I.

TABLE I

List of major vibrational spectroscopies, their spectral ranges and resolutions, and the nature of the samples used therein.

Vibrational spectroscopy	Sample	Resolution (cm^{-1})	Spectral Range (cm^{-1})
Infrared Transmission-absorption (ITAS)	10-100 mg, pressed powder, solution	1-10	1250-4000
Infrared Reflection-absorption (IRAS)	polycrystalline foil, single crystal	1-10	400-4000
Raman Scattering	100 mg powder, some-times single crystals	1-10	200-4000
Surface Enhanced Raman Scattering (SERS)	roughened single crystal, polycrystalline electrode	1-10	200-4000
Inelastic Electron Tunneling (IETS)	1-10 mm Al or other metal oxide (20 Å thick supported on metal film)	10-50	10-4000
Electron Energy loss (EELS)	single crystal	30-90	30-4000
Neutron Inelastic Scattering (NIS)	50-100 g of powder	5-50	20-1600
Photoacoustic (PAS)	100 mg powder	1-10	400-4000

My purpose in this keynote lecture at the Third International Conference on Vibrations at Surfaces is not to provide a survey or review of the enormous literature on surface vibrational spectroscopy, but rather to stimulate thought on the future prospects for this field by virtue of a somewhat unconventional overview of its past presented within the context of current trends in surface chemistry process research and US national science policy. The central theme of the lecture is that the field of surface vibrational spectroscopy seems to be at or near an inflection point in its growth and development. Following a decade of rapid improvement in instrumentation, technique and theoretical modelling, the performance and interpretation of measurements of the vibrational spectra of surface species has reached a point of considerable refinement at which the major physical phenomena and consequently the limitations of the individual techniques are recognized. Thus, current efforts center around elucidating the details of comparisons between measurements on exemplary systems and various theoretical models of the phenomena involved. Good examples of this process may be found in recent articles on

several of the spectroscopies emphasized at this conference, including surface enhanced Raman scattering [5], electron energy loss spectroscopy [6], and inelastic tunneling spectroscopy [7]. One might expect, therefore, that continued growth will require linking surface vibrational spectroscopy with studies of specific surface chemical processes of technological significance. Such processes, e.g., those in chemical vapor deposition, plasma processing, and industrial catalysis, presently are described at best by empirical kinetic models [8-10]. Consequently, an opportunity exists for the application of surface vibrational spectroscopies to make major advances in the quantitative description and control of technologically important processes, especially in the fabrication of electronic devices. Moreover, capitalizing on this opportunity seems uniquely compatible with current trends in US science policy [11-13].

I proceed by indicating initially a taxonomy which I found useful for organizing the diverse contributions to the field of surface vibrational spectroscopy. This classification scheme leads naturally to the identification of recent advances, mysteries and opportunities in each of the three major three streams of endeavor: i.e., spectroscopy, theory, and process dynamics. The presentation concludes with a brief consideration of the current climate for surface chemistry research and development, and of the consequences of this climate for the future of surface vibrational spectroscopy.

SCOPE AND ORGANIZATION OF THE LITERATURE

It is convenient to divide the literature on surface vibrational spectroscopy into three broad areas: spectroscopy, theory, and process dynamics. The area of spectroscopy encompasses the development and utilization of instrumentation to perform the measurements listed in Table I as well as atomic and molecular beam scattering from surfaces. The vast majority of the literature falls into this category, as may be ascertained from inspection of recent books and reviews [1-4, 6]. Theoretical work in vibrational spectroscopy encompasses three generic types of activity: the construction of models of surface vibrational modes [3,14], the evaluation of the interaction of electrons, photons and atomic species with these modes [3,6], and the model calculation of various spectra for comparison with the experimental measurements [3, 6-7]. Process dynamics refers to the study of energy transfer, surface atomic motion and chemical reactions (including adsorption and desorption) at surfaces, especially reactions induced by external radiation (e.g., LASERS, plasmas, electron and ion beams). Much of the current work in this area is either highly theoretical [15, 16] or rather applied [10, 17-19] in nature. Indeed, using the tools developed in the first two areas to bridge the gap between theory and practice in studies of process dynamics is one of the main future opportunities in surface vibrational spectroscopy.

ADVANCES, MYSTERIES AND OPPORTUNITIES

Spectroscopy

Steady improvements in instrumentation and sample handling technique during the past few years have led to important new discoveries. Increases in resolution of EELS together with the introduction of low-temperature sample manipulators resulted in the measurement of rotational excitations of H_2 and D_2 on Ag films [20] and Cu(100) [21]. Improvements in sensitivity (and angular resolution) permitted the systematic study of EELS angular distributions, thereby enabling the observation of surface phonon dispersion relations [22], the identification of the detailed nature of vibrational modes of adsorbed species [6, 23–25], and the examination of surface-phonon overtone and combination bands [26, 27]. The variation of the incident electron energy in EELS yielded the observation of both molecular [28,29] and surface-state [6, 23, 30] resonances in the electron loss cross sections. Increases in the sensitivity of IRAS as well as the construction of instruments in which it is used in concert with other surface analytical techniques permitted detailed studies of interactions between adsorbed molecules [31–34] as well as of the mechanisms of surface-phonon damping [35]. A trend in the development of new instrumentation has been the construction of high sensitivity spectrometers for the examination of transients in real time [4]. These spectrometers represent the initial stages of the transition of vibrational spectroscopy from a tool for surface characterization to one for the study of process dynamics.

As succeeding generations of new instruments have been constructed and utilized the nature of the remaining mysteries has changed profoundly. Early questions concerning the nature of photon-solid [36] and electron-solid [6, 37–41] interactions, the consequences of interactions between adsorbates [31–34, 42], and the relative merits of the various spectroscopies [4] have largely been resolved, although the details must be determined and examined in each individual case. Issues of current interest concern the continuing refinement of each separate technique to achieve, e.g., more sensitivity or better resolution, and the application of these techniques to examine particular systems of interest. Indeed, recent tabulations for IETS [43], EELS [44] and IR spectroscopies [45] reveal graphically the extensive scope of systems studied by vibrational spectroscopy. Mysteries remain, of course, like the insensitivity of the IR spectrum of CO on Cu(III) [31] and Cu(100) [34] to the magnitude of the CO coverage, the microscopic through-space or through-substrate origin of interactions among adsorbates [33], the mechanism of SERS [5,46], and the unexpectedly large damping of certain adsorbate vibrational modes [35]. Nevertheless, resolving these mysteries seems largely a matter of the patient pursuit of details, and the current main thrusts of vibrational spectroscopy are primarily the development of new applications of existing techniques and secondarily the continuing extension of the capabilities of these techniques.

Theory

Three topics loomed large during the past few years on the landscape of the theory

of surface vibrational spectroscopy. Recent calculations of the vibrational spectra [14, 47, 48] and IR absorption [34, 49] of adsorbed species are extensions of decades of work on this topic [49, 50]. Evaluations of EELS cross sections were performed for both dipolar [51] and deformation-potential [52] electron-phonon coupling, and the former were compared exhaustively with measurements for CO on Cu(100) [6, 22, 42, 53]. In IETS, three detailed applications (and extensions) of the partial charge model [54] were attempted [7, 55, 56], and a model of the non-linear dependence of the IETS intensities on the adsorbate coverage was proposed [57]. All of these calculations are phenomenological in character: i.e., the experimental data with which they are compared are utilized to fix the values of model parameters. They illustrate well the nature of work in the main stream of current theoretical research in vibrational spectroscopy.

The major remaining area of mystery is electron-phonon coupling. Analyses of both EELS and IETS spectra require a model which is valid for both dipolar and resonant-scattering ("impact") process. In spite of a growing body experimental data on resonant scattering in EELS [20, 21, 28-30] no quantitative analyses of these data have been given. There are comparable mysteries in IETS. For example, the unusual selection rules exhibited by adsorbed TCNQ [58] suggest the occurrence of resonant ("two-step") tunneling [59, 60] via TCNQ anions: a process known to require extension of the traditional transfer-hamiltonian models of IETS. The construction of a suitably general model applicable to both resonant and non-resonant electron scattering processes remains, therefore, a major opportunity in the theory of vibrational spectroscopies. Another one is the development of a theory of SERS. Although many candidates have been presented [5], the subject remains in confusion [5, 46] which must be resolved if SERS is to become a broadly useful technique for the analysis of interface composition.

Process Dynamics

Historically, most work in this area has concerned the kinetics of adsorption, desorption and surface diffusion [61], with much recent activity being focussed on the role of precursor states in adsorption and surface chemical reactions [62, 63]. Interest in such topics has been increasing [64, 65], in part because of their pertinence for molecular beam epitaxy [66], chemical vapor deposition [8,9], and heterogeneous catalysis [67]. Typically, three rather independent types of activity are reported in the literature: studies of the structures of model systems [3, 6, 48, 66,67], studies of the kinetics of model systems [61-63, 66-68], and empirical process studies which may or may not be rationalized by detailed kinetic models [8-10, 66, 69, 70]. Only in a few selected examples of heterogeneous catalysis [67] (e.g., the oxidation of CO and synthesis of ammonia) and of molecular beam epitaxy [66] has a systematic effort been made to link quantitatively the process studies with structural and kinetic results obtained on model systems.

During the past few years the microelectronics industry has stimulated increasing activity in radiation-assisted surface chemistry utilizing lasers [17-19, 71], electron beams [72, 73], ion beams [74-76] and plasmas [10, 70]. Current indications suggest that growth

in these areas will continue for over a decade [77]. Therefore one of the major opportunities in surface science will be the provision of a sound technical foundation for the present largely empirical process chemistry involved in the fabrication of microelectronics and thin films.

Considerable work has been reported on radiation-stimulated desorption. A useful modern review of photodesorption is available [78], and a synopsis of developments during the past few years in both photodesorption (PSD) and electron stimulated desorption (ESD) has just appeared [79]. One important new development is the discovery of the Auger decay mechanism of desorption following core-hole excitation by electrons, photons or ions [79, 80]. Another is the observation of desorption stimulated by the resonant absorption of multiple IR photons [81]. A third is the construction of elaborate (but largely untested) theoretical models of laser-induced surface processes, including desorption [15, 16, 82, 83]. One current challenge is the critical evaluation of these models via confrontation with an adequate set of experimental measurements. Another, probably more enduring, opportunity is the development of a sound microscopic (i.e., quantitative) basis for the largely empirical beam and plasma processing technologies [10, 17-19, 66, 70, 71, 74-76] currently being developed for the fabrication of electronic devices.

COLD FACTS

Science in the USA is in the doldrums. While I defer to others the task of speculating about the nature and causes of this observation [11, 84], one fact reveals its reality to the audience of this conference: The average salary in constant 1967 dollars of a Ph.D. chemist in the USA has declined from \$16,000 in 1973 (\$20,000 in 1973 dollars) to \$13,000 in 1982 (\$37,000 in 1982 dollars) [85]. The wages of production workers have consistently risen faster (by roughly 30% on average) than the salaries of Ph.D. chemists [85]. Moreover, salaries have been rising in current dollars much more rapidly than equipment expenditures. Research during 1972-1982 was no longer a growth industry in the USA [86]. Different circumstances prevailed in many other countries during the past decade, although most western economies are now experiencing similar phenomena. The present discussion is limited to the USA because I lack data on other countries.

The surface chemistry community prospered in this difficult decade. The reason, in large part, resides in the rapid increase of research and development (R&D) activities in the petroleum and chemical industries during a period of rapidly rising prices. Both the rapid price increases and the build up in R&D have ended. Indeed during the past six months both prices and R&D employment have declined. The 1980's will not be a repeat of the relatively prosperous 1970's for surface chemists. Only sustained growth of its industrial base will induce growth of surface chemistry research.

The major presently perceived engines of sustained growth in the 1980's are the information and communications industries with their dependence on electronic devices as

the raw materials of their hardware. Suppliers of these devices will face increasing pressure on the price and performance of their products, both of which are critically influenced by the surface chemistry of microelectronics and thin-film fabrication [77]. Ultimately, biotechnology will be another important growth area, but its prospects during the 1980's are uncertain at this time. Moreover, biotechnology competes with process chemistry, so that its growth may not affect the surface science community favorably.

CONCLUSIONS

By now the themes of this lecture are self-evident. First, the major unresolved mysteries in the surface science of the early 1970's are gone, having been replaced by less fundamental, more intricate matters of detail in specific applications of surface sensitive spectroscopies. Second, there remains a yawning chasm between the process technologies of industrial use and most surface science studies of model systems. This chasm has been bridged in at least one case (CO oxidation) of interest in heterogeneous catalysis, but the chemical process industries as a whole have lost their steam as significant driving forces for growth in surface chemistry research. Only the information and communications industries seem likely to assume this status in the 1980's. I close, therefore, by suggesting that the broad implications of these themes are clear. The next decade is likely to be rather more applications oriented than the last, and the "customer" (i.e., source of funding) is critical. If vibration-assisted surface chemistry chooses growth-engine customers it will prosper. If not it will decline. Growth during the past decade occurred via surface chemistry for catalysis. Growth during the next one is likely to occur in surface chemistry for electronics, with more industrial and less federal funding. Thus, a central theme emerges: The future will not be like the past. It seems probable that surface vibrational spectroscopy is approaching an inflection point in its growth and development beyond which its future depends critically on the judgement and skill with which its practitioners apply their techniques successfully to contribute to technological advance in the electronics and other growth industries. The days of ever increasing government funding of basic research in the physical sciences are over in the USA. I suspect that they are numbered, if not over, elsewhere as well. Industrial funding of R&D is increasing, however, especially in the growth areas noted above. Surface vibrational spectroscopy has much to offer these areas. The opportunities of the past decade are by no means over, but they are changing in character. The most successful groups of the coming decade will be those which exploit these changes adroitly.

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PHASE AND BONDING TRANSITIONS IN CHEMISORBED LAYERS STUDIED BY VIBRATIONAL FREQUENCY SHIFTS

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ABSTRACT

Coverage-dependent frequency shifts have been observed for a wide variety of adsorbates on metal single crystal surfaces. In some cases, these shifts are attributable to changes in bonding coordination to surface metal atoms, or to alterations in the geometry of the chemisorbed complex. The major part of this review is concerned with the information that can be obtained from shifts which have been observed, both upward and downward in frequency, when bonding coordination or geometric effects do not occur. It is shown that when the observation of frequency shifts is combined with the measurement of singleton frequencies using the dilution limit isotopic mixing method of Crossley and King (now applied to CO adsorption on a variety of metal single crystals), shifts due to dipole coupling in the overlayer can be deconvoluted from shifts due to chemical (bonding) effects. A review of recent data for CO adsorption on Pt{111}, {100} and {110}, Cu{111}, {100} and {110}, Pd{100} and Ru{100} is presented which illustrates the information available from such data concerning phase boundaries between lattice gas, island and condensed phases, and also subtle changes in adsorbate bonding.

COVERAGE-DEPENDENT FREQUENCY SHIFTS FROM ADSORBATES

Vibrational spectroscopy has proved to be a powerful tool for the determination of the structure of adsorbate complexes, strengthened by analogies drawn from inorganic complexes and matrix-isolated species. For example, it is now widely accepted that for CO adsorption on metals the assignment of observed C-O stretching frequencies, ω_{CO} , can be made on the basis of the scheme originally proposed by Eischens and coworkers (ref.1) and recently modified by Sheppard and Nguyen (ref.2): for linear species (bonded to one metal atom) ω_{CO} is in the range 2000 to 2130 cm^{-1} ; for CO bridged to two metal atoms, $1880 \text{ cm}^{-1} < \omega_{\text{CO}} < 2000 \text{ cm}^{-1}$; while for CO bridged to three or four metal atoms, the range ω_{CO} is 1650 to 1880 cm^{-1} . One coverage-dependent effect quite frequently observed is the appearance of species with different metal atom coordination at specific coverages; for example, when CO is chemisorbed on Pt{111}, occupation occurs initially into linear sites, with bridged sites of coordination 2 being filled at higher coverages in addition to the linear species. Another effect is illustrated by the chemisorption of hydrogen on W{100} at 300 K (ref.3,4). Hydrogen atoms are chemisorbed into bridged sites of coordination 2 at all coverages; but

at low fractional coverages the surface W atoms are laterally displaced to form a dimer structure, with the W^H-W bond angle 80° , while at saturation coverage the W atoms return to bulk lattice sites and the W^H-W bond angle opens up to $\sim 100^\circ$. This change in bond angle produces a shift in the symmetric stretching frequency of the complex, from 1250 cm^{-1} to 1040 cm^{-1} , as the hydrogen coverage is increased. Phase transitions involving changes in the adsorbate coordination or in the structure of the chemisorption complex can therefore be readily followed by vibrational spectroscopies.

However, for a number of chemisorption systems relatively large coverage-induced frequency shifts have been observed even where structural evidence indicates no change in either the adsorbate coordination to the surface or the geometry of the chemisorption complex. This effect was recorded some years ago by transmission infrared spectroscopy from CO chemisorbed on supported Pt catalysts (ref.1), and has since been reproduced on metal single crystals by both reflection-absorption infrared spectroscopy (RAIRS) and high resolution electron energy loss spectroscopy (HREELS). In general, the C-O stretching frequency is found to shift upwards with increasing coverage, from $\sim 9\text{ cm}^{-1}$ on Cu{100}(ref.5,6), through $\sim 35\text{ cm}^{-1}$ on Pt single crystals (ref.7,10) to 100 cm^{-1} on Pd{100}(ref.11). In some instances the shift $\Delta\omega$ is towards lower frequencies, ranging from $\Delta\omega = -10\text{ cm}^{-1}$ on Cu{111}(ref.12) to $\Delta\omega = -30\text{ cm}^{-1}$ on Au and Ag films (ref.5). It is the information content of these shifts that is the subject of the remainder of this review.

FREQUENCY SHIFTS INDUCED BY DIPOLE COUPLING

Frequency shifts induced by dipole coupling between molecules, first discussed by Decius (ref.13) in relation to carbonate and nitrate crystals and by Eischens and coworkers (ref.1,14) in relation to chemisorbed CO, can be understood within a very simple conceptual framework. We consider an isolated molecule (singleton), such as CO, oriented in space and with a stretching frequency ω_{CO} , and then bring up to it a second oriented CO molecule, its axis aligned parallel to the first, with a separation distance R . Due to dipole-dipole coupling between the two molecules, the two stretching modes of the molecules become non-degenerate as R is decreased, producing an in-phase mode $\begin{smallmatrix} \text{O} & \text{O} \\ | & | \\ \text{C} & \text{C} \end{smallmatrix}$, at a frequency $\omega_0 + \Delta\omega$, and an out-of-phase mode $\begin{smallmatrix} \text{O} & \text{O} \\ | & | \\ \text{C} & \text{C} \end{smallmatrix}$, at a frequency $\omega_0 - \Delta\omega$. Only the in-phase mode is infrared (or dipole) active. Thus, as R is decreased, $\Delta\omega$ becomes larger and a continuous upward shift in the infrared absorption band frequency should be observed. This decrease in R simulates, in a simple manner, increasing coverage of adsorbates. In the absence of any other effect, therefore, the observed band should increase with frequency as the coverage is increased, provided that dipole selection rules are operative. Thus, with RAIRS and with HREELS in the specular direction (where dipole selection rules

dominate) the dipole coupling shift should be observed, while with off-specular HREELS where the selection rules are relaxed, both in-phase and out-of-phase modes should be active and no shift in the centre of gravity of the band components should be observed.

In the derivation of a theoretical expression (refs.14-18) for the dipole-dipole coupling shift, account must be taken of:

(i) the molecular environment of an infinite array of oscillating dipoles (ref.14), expressed through the vibrational polarizability α_v and the adsorbate site lattice sum $T = \sum (1/R_k^3)$;

(ii) the screening influence of the adlayer (ref.16), which introduces the electronic polarizability of the adsorbed molecule, α_e ;

(iii) the interaction between a dipole and the images of the other adlayer dipoles (ref.16), expressed through the image lattice sum V ; and

(iv) the interaction between a dipole and its own image (ref.17), expressed through a term $1/4d^3$, where $2d$ is the distance between the image plane and the dipole.

Writing the frequency of an isolated molecule in the absence of the surface, i.e. excluding the self-image term, as ω_0 , the frequency ω observed at a coverage θ relative to occupancy of an identical array of sites represented by the lattice sums T and V , assuming random occupation of these sites, is given by:

$$\omega = \omega_0 \left\{ 1 + \alpha_v \{ \theta(T + V) - 1/4d^3 \} / [1 + \alpha_e \{ \theta(T + V) - 1/4d^3 \}] \right\}^{\frac{1}{2}} \quad (1)$$

When $\theta \rightarrow 0$, the observed frequency for the adsorbed singleton species, ω_s , includes the self-image term, and is given by:

$$\omega_s = \omega_0 [1 - \alpha_v/(4d^3 - \alpha_e)]^{\frac{1}{2}}. \quad (2)$$

At infinite dilution the band should be observed at ω_s , increasing with coverage θ to values given by equation (1). There has been considerable discussion in the literature concerning the appropriate values for α_v , α_e and d , with particular relation to the sensitivity of the calculated shift to the value chosen for d (ref.19), but it is now generally accepted that the dipole-coupling-induced upward frequency shift for CO between infinite dilution and saturation coverage is in the range 30 to 40 cm^{-1} .

Here we draw attention to two factors arising from expressions (1) and (2).

(1) The shift in the singleton frequency induced by its own image, is downward, i.e. $\omega_0 > \omega_s$, and sensitive to the spacing d . For example, for CO on Pt{111}, Crossley and King estimate $\omega_0 - \omega_s$ to be $\sim 40 \text{ cm}^{-1}$, and conclude that the self-image interaction may account for as much as half of the total

shift from the gas phase frequency (2143 cm^{-1}) to the observed singleton frequency ω_s (2065 cm^{-1}). Any coverage-induced increase in d would, from equation (2), result in an increase in ω_s towards ω_0 , even with no change in the C-O force constant, and, from equation (1), this would increase the size of the overall coverage-induced shifts.

(2) If ω_s can be independently evaluated, the total lattice sum S pertaining to the actual arrangement of the adsorbate at a coverage θ can be determined from the observed frequency ω at this coverage. (Only when the adsorbate randomly occupies sites is $S = \theta(T + V)$). This means that the adsorbate environment can be probed; in particular, island formation can be detected and island dimensions evaluated, as described below.

EVALUATION OF SINGLETON FREQUENCY AND DIPOLE SHIFTS FROM ISOTOPIC MIXTURES

The dipole coupling theory was extended by Hammaker et al (ref.14) to include the case where a mixture of two isotopes, e.g. ^{12}CO and ^{13}CO , are adsorbed on the surface, and a more refined treatment has recently been given by Persson and Ryberg (ref.18). Two dipole-active bands are observed from the mixed layer, which can be simply understood in the two-body model: a high frequency band due to the in-phase ^{12}CO - ^{12}CO and ^{12}CO - ^{13}CO coupled modes, and a low frequency band composed of the in-phase ^{13}CO - ^{13}CO and the (very weak) out-of-phase ^{12}CO - ^{13}CO modes. The coupling interactions bring about a significant transfer of intensity into the high frequency band, which, as recently shown (ref.18), was underestimated in the original approximate procedure followed by Hammaker et al. (ref.14) Moreover, in a dilute isotopic mixture, where a molecule of one isotope is effectively surrounded by an environment of the other, the coupling of the first isotope into this environment is very weak. This led Crossley and King (ref.8) to design an experiment for the evaluation of the singleton frequency ω_s at high total adsorbate coverages. At constant total coverage, θ , spectra are obtained as a function of the composition of an isotopic mixture. The position of the band of the low partial coverage isotopic species then extrapolates, in the dilution limit, to the singleton frequency for that species, ω_s . The independent measurement of ω_s at finite coverage allows a distinction to be made between coupling-induced shifts and shifts which may be attributed to coverage-induced changes in bonding characteristics, i.e. chemical effects, since any variation in ω_s with total coverage must be ascribed to such chemical effects. Thus, Crossley and King (ref. 8,9) have demonstrated that the full 36 cm^{-1} shift observed for CO on Pt{111} as the coverage increases from $\theta = 0$ to saturation, at room temperature, can be attributed to coupling interactions. The method has now been applied to CO adsorption on a variety of metal single crystal planes; as shown in Table 1, the measured dipole coupling