Vibrational spectroscopy of adsorbates

O. M. Braun, A. I. Volokitin, and V. P. Zhdanov

Institute of Physics, Academy of Sciences of the Ukrainian SSR, Kiev; Kuĭbyshev Polytechnical Institute; and, Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk

Usp. Fiz. Nauk **158**, 421–450 (July 1989)

Present-day understanding of the nature of formation of vibrational spectra of adsorbates is examined. Particular attention is paid to the theoretical side of the problem. A comparison is made of the relative roles of T_1 (dissipative damping) and T_2 (pure dephasing) processes, and also of electron-hole pairs, phonons and photons in T_1 processes. The problem is discussed of separating out the mechanism dominating the determination of line shape. It is noted that inhomogeneous broadening which undoubtedly plays an important role in many cases has received little theoretical attention. An analysis is given of recent experimental data on the basis of modern theoretical concepts.

1. INTRODUCTION

Experimental methods for studying the vibrational spectra of adsorbates are an important part of surface physics. These methods include: inelastic scattering of neutrons and electrons, inelastic scattering of molecular beams, reflective IR spectroscopy, spectroscopy of surface polaritons, surface-enhanced Raman scattering, and time-resolved spectroscopy employing ultrashort pulses. The experimental methods of vibrational spectroscopy (VS) of adsorbates are described in detail in the collective monograph of Ref. 1. Vibrational spectroscopy has traditionally been employed for identifying the types of bonds in molecules. Since the characteristic frequencies of the bonds depend on the situation of the adsorbed molecule, in particular, to which of the atoms of the substrate this molecule is bound, there open up ways for analyzing the states, positions, and orientations of the molecules on the surface. In the process the spectral distribution of the intensity makes it possible to form estimates of the concentrations of particular adsorbed molecules. For example, when the H_2O molecule is adsorbed on the Si(100)—(2×1) surface frequencies characterizing the Si=H and O=H bonds are observed; this indicates that the H_2O molecule dissociates on adsorption.[2] The number of vibrational modes indicates the location at which the molecule is adsorbed. For example, for the system H/W(100) with coverage $\theta = 2$ there are three different modes,[3] which indicates unequivocally that the adsorption is of the B type, when the H atom lies between the two surface atoms of the substrate. On the other hand, for the system H/Ru(100) there are two different vibrational modes, indicating adsorption of the *c* type (centered).[4] The dependence of the vibrational frequency on the wave vector gives information about the force constants of the interaction between the adsorbed molecules. A shift of the frequency relative to its value in the gas phase indicates that the chemical bonds change as a result of chemisorption on the surface. Numerous examples illustrating how information about properties of adsorbates is obtained from frequency measurements are presented in Ref. 1.

A great deal of attention is now being devoted to the analysis of the shape of spectral lines. This is because the line shape contains important information about the lifetime of vibrations, the mechanisms of energy transfer, the inhomogeneity of the locations of adsorption, the mechanisms of interaction between adatoms, and the process of dephasing of the vibrations. Information on the vibrational relaxation of adsorbates is, in its turn, useful for interpreting other dynamic surface processes, such as diffusion, adsorption, and desorption. A detailed understanding of the nature of vibrational spectra of adsorbates is of fundamental importance for many areas of the physics and chemistry of surfaces, in particular, for heterogeneous catalysis. Over the last ten years extensive information has been accumulated in the field of interpretation of the shape of spectral lines, and the purpose of this review is to describe this information. The existing review articles[5] do not give a complete idea about this rapidly developing field.

2. THE SHAPE OF A SPECTRAL LINE

In this section we derive and discuss an expression for the reflecting power of an adlayer. Let *p*-polarized light with frequency ω, field strength $E(t) = E \cdot \mathrm{Re}\exp(i\omega t)$, and intensity $I_0 = cE_0^2/8\pi$, be incident on a surface at an angle β to the normal to the surface (Fig. 1). For the lowest-order nonadiabatic response of the electrons of the metal the action of the *p*-polarized incident and reflected waves is described by the quasistatic field $E_\perp(t)$, which at large distances from the surface is perpendicular to the surface. To calculate the reflecting power of the adlayer it is necessary to know how the electrostatic field varies in the space near the surface. To lowest order in $q = \omega/c$ it can be assumed that

$$E_\perp(t) = 2E_0 \sin\beta\ \mathrm{Re}\exp(i\omega t).$$

This expression holds for angles $\beta < 85°$; for $\beta > 85°$ the interference of the incident and reflected waves must be taken into account.[6] The energy of interaction of the external field with the dipole moment of the adsorbate equals $H_{\mathrm{int}} = -\hat{\mu}E_\perp(t)$, where $\hat{\mu}$ is the dipole-moment operator. According to the linear-response theory the energy adsorbed by vibrations per unit time per unit surface area equals[7]

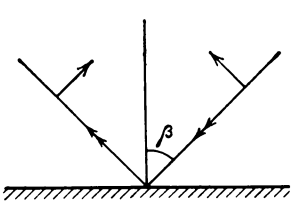

FIG 1 Incidence of light on a surface.

 0038-5670/89/070605-17$01.80

$$W = -\frac{1}{2}(2E_0 \sin\beta)^2\,\omega N \operatorname{Im}\alpha(\omega), \tag{2.1}$$

where N is the number of adsorbate molecules per unit area, while the generalized susceptibility $\alpha(\omega)$ is given by the expression

$$\alpha(\omega) = -i\int_0^\infty \exp(i\omega t)\,\langle[\hat{\mu}(t)\,\hat{\mu}(0)]\rangle\,dt, \tag{2.2}$$

where $\hat{\mu}(t)$ is the dipole-moment operator in the Heisenberg representation and $\langle\ldots\rangle$ indicates averaging over the grand canonical ensemble. Taking into account the fact that the intensity of the reflected light is reduced by an amount $W/\cos\beta$ we obtain for the reflecting power of the adlayer

$$\delta R = \frac{I_0 - I}{I_0} = -\frac{16\pi}{c}\frac{\sin^2\beta}{\cos\beta}N\omega \operatorname{Im}\alpha(\omega). \tag{2.3}$$

The expression (2.3) holds in the limit of low coverage. For high coverage the value of N in the formula (2.3) must be set equal to unity, and $\alpha(\omega)$ must be interpreted as the generalized susceptibility of the entire system. Since $\mu = e^*Q$, where e^* is the dynamic charge of an admolecule and Q is the normal coordinate of the vibrations, $\alpha(\omega) = \mu^2 D^R(\omega)$, where μ is the dynamic dipole moment of the admolecule, which, generally speaking, can be a complex quantity,[8] i.e., $\mu = \mu_1 + i\mu_2$. The imaginary part μ_2 is related to the nonadiabaticity of the response of the electrons to the motion of the nuclei. $D^R(\omega)$ is the retarded phonon Green's function, which can be written in the form[9]

$$D^R\,\omega = 2\omega_0(\omega^2 - \omega_0^2 - 2\omega_0\Pi(\omega))^{-1}, \tag{2.4}$$

where ω_0 is the frequency of the vibrations neglecting the interaction, which is included in the polarization operator $\Pi(\omega)$. The real part of the polarization operator determines the frequency shift while the imaginary part determines the FWHM:

$$\Delta\omega = \omega - \omega_0 = \operatorname{Re}\Pi(\omega_0), \tag{2.5}$$

$$\Gamma = 2\operatorname{Im}\Pi(\omega_0). \tag{2.6}$$

By virtue of the causality principle $\operatorname{Im}\Pi(\omega)$ and $\operatorname{Re}\Pi(\omega)$ are related by the Kramers–Kronig relation, so that any level-broadening mechanism will also lead to a frequency shift. If the linewidth is determined by energy transfer processes, then $\Gamma = 1/\tau$, where τ is the lifetime of the vibrations. Purely, phase relaxation processes could also be important. Elastic scattering of electrons and phonons by local vibrations of admolecules can lead to interruption of the phase of the vibrations, i.e., to dephasing of the vibrations. If at $t = 0$ all oscillators, which are assumed to be identical, have the same phase, then after a time t the phases of their vibrations will be different owing to random phase interruption. On time averaging the correlation function $\langle Q(t)Q(0)\rangle$ will be a decaying function of time. If this decay is exponential

$$\langle Q(t)\,Q(0)\rangle \sim \exp\left[-i(\omega_0 + \Delta\omega)t - \frac{\Gamma}{2}t\right], \tag{2.7}$$

then the line shape

$$L(\omega) \sim \operatorname{Re}\int_0^\infty \exp(i\omega t)\,\langle Q(t)\,Q(0)\rangle\,dt \tag{2.8}$$

will be Lorentzian with width Γ. It is important to note that in the process the energy of the vibrations does not change, i.e., the amplitude of the vibrations remains constant. The line broadening associated with decay and dephasing of vibrations is often termed, respectively, longitudinal and transverse relaxation or T_1 and T_2 processes.

Line broadening also arises when the system is spatially disordered. For example, the surface of a crystal usually contains defects—steps, vacancies, impurity atoms, etc. The interaction between a defect and admolecules located near it brings about a change in the frequency of the vibrations of the admolecules, and averaging over an ensemble gives broadening of the vibrational line. The mechanism of line broadening owing to interaction between admolecules in the presence of structural defects in the adfilm is analogous. In an experiment it is important to know how to distinguish the

TABLE I. Vibrational frequency, line width, and dynamic charge for vibrations of adsorbed hydrogen (deuterium in parentheses).

Substrate	Mode	ω_0, MeV	Γ, MeV	e^*/e	Method	Reference
Ni (111)		88 (67)			EELS*)	[105]
		139 (90)			—	—
Ni (110), θ=1		76		0.025	EELS	[106]
		117			—	—
		140			—	—
Ni (100)-c (2×2)	⊥	74 (52)			EELS	[107]
Ru (100), θ=1	⊥	141 (101)	20—30		EELS	[108]
	∥	102 (74)	20—30		—	—
Pd (100)-c (2×2)	⊥	64			EELS	[109]
W (111)		160			EELS	[110]
W (110)		95			EELS	[110]
		157			—	—
W (100), θ=2	⊥	133 (95)	11	0.053	IR	[65]
	∥	80			EELS	—
	∥	118			—	—
Pt (111)		68			EELS	[111]
		153			—	—
Si (111)-(7×7)	⊥	257		0.02	IR	[112]
Si (100)-(2×1)		258		0.04	IR	[2]

*) EELS—electron energy-loss spectroscopy

TABLE II. Frequency and line width of C=O vibrations accompanying adsorption of the CO molecule on the surface of some metals with low coverage (the results of measurements by the method of high-resolution IR spectroscopy (1 cm = 0.124 meV).

Metal	Coverage	ω_0, cm^{-1}	Γ, cm^{-1}	Reference
Ni (111)	0.16	1838	25	[113]
Ni (100)	<0.2	2030	50	[114]
Cu (111)	<0.2	2080	15	[115]
Cu (110)	0.1	2090	15	[116]
Cu (100)	0.17	2077	5	[117]
Ru (100)	0,05	1992	12	[118]
Pd (100)	0.14	1920	25	[119]
Pt (111)	0.32	2105	25	[120]
Pt (110)	0.1	2080	10	[121]
Pt (100)	<0.2	2082	7	[122]

contributions of different mechanisms to the measured width of a line. For this it is necessary to know the characteristic features of spectral lines associated with each specific mechanism of broadening. These features are studied in the following sections of this review.

The lifetime can be measured directly by the method of induced laser fluorescence, employing picosecond laser pulses.[10] The sensitivity of this method now permits studying adsorption only on colloidal silicon oxide, which has a large surface area. It has been found that for adsorption of the radicals OH, OD, BOH, and OCH_3 $\Gamma\tau$ equals 200–2000. For example, for the system OH/SiO_2 $\Gamma \approx 8$ cm^{-1} and $1/\tau \approx 2.6\times 10^{-2}$ cm^{-1}.

Infrared radiation can excite only dipole-active modes, to which the transverse (perpendicular to the surface) vibrations refer. The longitudinal (parallel to the surface) vibrations usually are not dipole active; this is attributable to the fact that in the IR region of the spectrum the electric field is perpendicular to the surface, and the dipole moment of an admolecule is screened by the dipole moment of its mirror image. For this reason, for longitudinal vibrations the absorption peak at the fundamental frequency $\omega = \omega_0$ cannot be observed using IR spectroscopy. However the peak at the overtone frequency can be observed.[11]

The most extensive spectral data have been collected for vibrations of adsorbed H atoms and CO molecules. These data are summarized in Tables I and II.

3. ENERGY TRANSFER ACCOMPANYING VIBRATIONS OF ADSORBATES

In a vacuum the damping of the vibrations of a molecule occurs by means of a single mechanism—the radiation mechanism (with emission of a photon), for which, as is well known, $\tau^{-1} \approx \mu^2(\omega_0/c)^3$. On adsorption the lifetime of the vibrations decreases by many orders of magnitude; this indicates that the main mechanisms for the damping of the vibrations in this case are associated with excitation of quasiparticles of the substrate—phonons, electron-hole pairs, plasmons, etc. If the frequency of the vibrations of the molecules $\omega_0 > \omega_m$, where ω_m is the maximum frequency of the vibrational spectrum of the substrate, then damping of the vibrations of the admolecule owing to excitation of phonons is possible only owing to the anharmonicity of the vibrations. The electron-hole pairs are generated in the process of inelastic scattering of conduction electrons by the oscillating potential of a molecule. This potential can be separated into short- and long-range parts. The mechanism of damping associated with scattering by the short-range potential is simply called electron-hole damping. This mechanism can play the main role in chemisorption. Scattering of electrons by the long-range potential leads to the electromagnetic mechanism of damping, which plays an important role in physical adsorption. For metals the plasmon frequency is $\omega_p \gg \omega_0$, so that the plasmon mechanism of damping is inefficient for adsorption on metals. This mechanism can, however, be efficient for adsorption on semiconductors, for which it can happen that $\omega_p \approx \omega_0$.[12]

3.1. The phonon mechanism. In the case when the anharmonicity of the vibrations of the adsorbate is weak the diagram technique for temperature Green's functions can be employed to calculate the susceptibility $\alpha(\omega)$.[9] We shall write the total Hamiltonian of the anharmonic crystal in the form[1)]

$$H = H_0 + H_{\text{int}}, \tag{3.1}$$

where H_0 is the Hamiltonian in the harmonic approximation and H_{int} denotes the anharmonic part of the potential. We shall illustrate the Green's functions technique using the simplest example—perpendicular surface vibrations of an adatom for A-type adsorption, when the interaction only with the nearest atom of the substrate is taken into account. In this case H_{int} depends only on the difference $u = Q_A - Q_S$, where Q_A and Q_S are the displacements of an adatom and an atom of the substrate from the position of equilibrium, so that H_{int} can be expanded in a power series in u:

$$H_{\text{int}} = \sum_{s=3}^{\infty} \lambda_s u^s. \tag{3.2}$$

We introduce the temperature Green's function[9]

$$D(\omega_n) = \int_0^{\beta} \exp(i\omega_n \tau) D(\tau)\, d\tau,$$
$$D(\tau) = -\langle T_\tau u(\tau) u(0)\rangle, \quad \omega_n = \frac{2\pi n}{\beta}, \tag{3.3}$$

where T_τ is the time-ordering operator and $\beta = 1/k_B T$. The Green's function satisfies Dyson's equation[9]

$$D = D_0 + D_0 \Pi D, \tag{3.4}$$

where $\Pi(\omega)$ is the polarization operator, determined by dia-

grams with no external lines, to calculate which the following rules are applicable:

1) to each phonon line there corresponds the function $D_0(\omega_n)$;

2) a factor λ_k is assigned to each vertex at which k phonon lines converge; and,

3) summation is performed over the free energy parameters $(\beta^{-1}\sum_{n=-\infty}^{\infty})$.

In the harmonic approximation Green's function $D_0(\omega_n)$ is given by the formula[12]

$$D_0(\omega_n)=\frac{1}{m_A}\frac{1-m_A\omega_n^2 D_s(\omega_n)}{\omega_n^2+\omega_A^2-m_A\omega_A^2\omega_n^2 D_s(\omega_n)}, \tag{3.5}$$

where $D_s(\omega_n)$ is the Green's function for a substrate atom

$$D_s(\omega_n)=-\int_0^\beta \exp(i\omega_n\tau)\langle T_\tau Q_s(\tau)Q_s(0)\rangle\,d\tau, \tag{3.6}$$

where ω_A is the vibrational frequency of an adatom on a rigid substrate. The retarded Green's function $D^R(\omega)$ can be found by analytical continuation of the function $D(\omega_n)$ from a discrete set of points $z_n=2\pi ni/\beta$ onto the real axis in the upper complex half-plane.[9] It follows from the formula (3.5) that taking into account the vibrations of substrate atoms leads to renormalization of the frequency of the vibrations, so that

$$\omega_0^2=\omega_A^2(1+m_A\omega_0^2\,\mathrm{Re}\,D_s^R(\omega_0)). \tag{3.7}$$

For $\omega_0<\omega_m$ the vibrations of the adatom are virtual and are characterized by the width

$$\Gamma=-\omega_0\omega_A^2 m_A\,\mathrm{Im}\,D_s^R(\omega_0)=\frac{\pi}{2}\frac{m_A}{m_s}\omega_A^2\rho_s(\omega_0), \tag{3.8}$$

where $\rho_s(\omega)$ is the surface density of phonon states. The diagram technique is convenient in that it permits writing out any term in the perturbation theory. It was employed in Refs. 13 and 14 to describe the vibrations of adsorbates. At high temperatures, however, it becomes too cumbersome, since many terms of the perturbation series must be taken into account. For this reason, a different approach,[15,18] which permits taking into account in a compact manner the most important terms in the perturbation series to all orders, is presented below.

We shall write the Hamiltonian of the system in the form

$$H=H_l+H_p+H_{\mathrm{int}}, \tag{3.9}$$

$$H_l=\sum_\lambda \omega_\lambda b_\lambda^+ b_\lambda, \tag{3.10}$$

$$H_p=(P^2/2m)+\langle V(Q,Q_A)\rangle, \tag{3.11}$$

$$H_{\mathrm{int}}=V(Q,Q_A)-\langle V(Q,Q_A)\rangle, \tag{3.12}$$

where H_l is the Hamiltonian of the lattice, H_p is the Hamiltonian describing the motion of an adparticle in the averaged potential $\langle V(Q,Q_A)\rangle$, H_{int} is the interaction Hamiltonian, Q_A is the coordinate of an adatom, Q is the set of phonon coordinates of the crystal, and m is the reduced mass. Averaging over the phonon coordinates of the substrate is performed:

$$\langle V(Q,Q_A)\rangle=\mathrm{Sp}_l(\rho_l V(Q,Q_A)), \tag{3.13}$$

$$\rho_l=\exp(-\beta H_l)Z_l^{-1},\quad Z_l=\mathrm{Sp}[\exp(-\beta H_l)]. \tag{3.14}$$

In the case when the anharmonicity of the potential $\langle V(Q,Q_A)\rangle$ is weak the Hamiltonian H_p can be written in the harmonic approximation

$$H_p=\omega_0 b^+ b, \tag{3.15}$$

and only the terms that are linear in the vibrational coordinate of the adatom need be included in H_{int}:

$$H_{\mathrm{int}}=Q_A V'(Q). \tag{3.16}$$

In this case the linear-response theory[7] gives the following result for the polarization operator:

$$\Pi(\omega)=-i\int_0^\infty \exp(i\omega t)\langle[(H_{\mathrm{int}}(t))_{01}(H_{\mathrm{int}}(0))_{10}]\rangle\,dt, \tag{3.17}$$
$$(H_{\mathrm{int}})_{01}=\langle 0|H_{\mathrm{int}}|1\rangle,\quad H_{\mathrm{int}}(t)=\exp(iH_l t)H_{\mathrm{int}}\exp(-iH_l t),$$

where $|0\rangle$ and $|1\rangle$ denote the ground and first excited state for vibrations of an adatom. The width of the level is given by the formula

$$\Gamma=(1+n(\omega_0))^{-1}\int_{-\infty}^{+\infty}\exp(i\omega_0 t)c(t)\,dt, \tag{3.18}$$

$$c(t)=\langle(H_{\mathrm{int}}(t))_{01}(H_{\mathrm{int}}(0))_{10}\rangle,\quad n(\omega)=[\exp(\beta\omega_0)-1]^{-1}.$$

If the Morse potential is employed for $V(Q,Q_A)$ and the interaction with the nearest substrate atoms only is taken into account (in this case Q is the coordinate of the vibrations of a surface substrate atom in the direction normal to the surface), then the function $c(t)$ has the form[16]

$$\begin{aligned}c(t)=D^2\{&B^2[\exp(4\alpha^2\langle Q(t)Q(0)\rangle)-1]\\&+4A^2[\exp(\alpha^2\langle Q(t)Q(0)\rangle)-1]\\&-4AB[\exp(2\alpha^2\langle Q(t)Q(0)\rangle)-1]\},\end{aligned} \tag{3.19}$$

where D is the energy of adsorption, $\alpha^2=m\omega_0^2/2D$, $A=(1/2k)(2k-3)^{1/2}$, $B=A(2k-1)/k$, and $k=(2mD)^{1/2}\alpha^{-1}$. In the harmonic approximation the correlation function of the substrate $\langle Q(t)Q(0)\rangle$ is determined by the expression

$$\begin{aligned}\langle Q(t)Q(0)\rangle=&\\&=\frac{1}{2m_s}\int_0^{\omega_M}\frac{\rho_s(\omega)}{\omega}[(1+n(\omega))\exp(-i\omega t)\\&\qquad+n(\omega)\exp(i\omega t)]\,d\omega,\end{aligned} \tag{3.20}$$

where m_s is the mass of a substrate atom and $\rho_s(\omega)$ is the density of the phonon states for transverse vibrations of a surface substrate atom. Since the term $\langle Q(t)Q(0)\rangle$ stands in the exponent of the expression (3.19) the formula (3.18) for Γ takes into account all multiphonon processes to second order in H_{int}, which corresponds to summation of the most important diagrams to all orders. The one-, two-, and three-phonon contributions to the level width can be obtained by expanding the function $c(t)$ in a series in $\langle Q(t)Q(0)\rangle$. For $\omega_0\gg\omega_m$ the integral (3.18) can be approximately calculated by the saddle-point method.[18,19] For this the contour of integration over t must be shifted into the upper half of the complex plane, where there is an infinite number of saddle points. Taking into account only the saddle point closest to the real axis and lying on the imaginary axis for Debye's model gives[18]

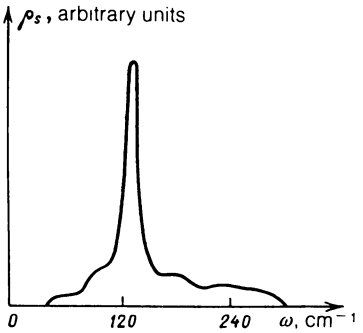

FIG. 2. The spectral density of the motion of atoms normal to the Ni(111) surface.

$$\Gamma = \frac{2\pi D^2}{(\omega_D \omega_0)^{1/2}} \exp\left[-\frac{\omega_0}{\omega_D}(y-1)\right], \tag{3.21}$$

where $z = iy = i\omega_D \tau$ is the coordinate of the saddle point, which is determined from the equation

$$\frac{\exp y}{y} = \frac{1}{3}(1 + n(\omega_D))^{-1} \frac{m_s D}{m\omega_0}. \tag{3.22}$$

It follows from the formulas (3.21) and (3.22) that at high temperatures $\Gamma \sim T^n$, where $n = \omega_0/\omega_D$.[18,20] Calculations[18] using the formula (3.21) for transverse vibrations S ($\omega_0 = 360$ cm^{-1}) and O ($\omega_0 = 430$ cm^{-1}) on the Ni(100) surface at $T = 80$ K give $\Gamma_s = 34$ cm^{-1} and $\Gamma_0 = 30$ cm^{-1}, which agrees well with the experimental value of the linewidth obtained at the same temperature $\Gamma \approx 40$ cm^{-1}.[21]

Numerical calculation of the integrals (3.18) and (3.20) using a realistic function $\rho_s(\omega)$ (Fig. 2) for transverse vibrations of a CO molecule as a whole on the Ni(100) surface with A type adsorption was performed in Ref. 17 (Fig. 3). At room temperature ($T = 300$ K) the theoretical value of Γ (13.7 cm^{-1}) agrees well with the experimental value (15.3 cm^{-1}).[22] It is interesting that although decay into two phonons is possible ($\omega_0/\omega_D \approx 1.6$) the three-phonon process makes the main contribution to the linewidth. This is explained by the fact that the function $\rho_s(\omega)$ has a sharp peak at ≈ 135 cm^{-1}.

In the case of strong anharmonicity the shift in the positions of equilibrium of the atoms of the lattice accompanying the relaxation of the vibrations of the adsorbed particle must

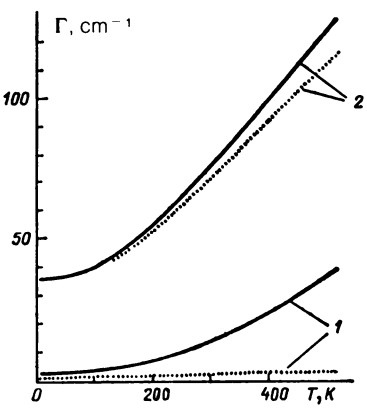

FIG. 3 The line width for CO=Ni vibrations for the system CO/Ni(111).[17] *1*—taking into account the spectral density $\rho_s(\omega)$ calculated in Ref 26, *2*—Debye model. The dotted lines show the contribution of two-phonon processes

be taken into account in order to describe the vibration. relaxation. The standard perturbation theory is not convenient in this case; generally speaking, many terms must be included in the perturbation series. To describe the "shift" adiabatic perturbation theory is traditionally employed.[23] The standard and adiabatic perturbation theories are sometimes contrated with one another on the grounds that they lead to different results.[23] As shown in Refs. 24 and 25, however, this difference is only apparent and is attributable to the fact that in the standard perturbation theory and the adiabatic perturbation theory different terms of the anharmonic potential coupling the oscillations are traditionally taken into account. Calculations[25] show that it is important to take into account the "shift" already for $n \geqslant 3$.

Summarizing the results presented we note that the rate of decay of a local vibration into substrate phonons is determined primarily by the ratio $n = \omega_0/\omega_m$, as well as by the degree of anharmonicity of the vibrations. The phonon mechanism is characterized by a strong temperature dependence and a positive frequency shift $\Delta\omega > 0$. The contribution of multiphoton processes increases rapidly as the temperature increase $\Gamma \sim T^n$. There is also a strong isotopic effect. The phonon mechanism of decay is the main mechanism for $n \leqslant 3$. For high-frequency vibrations $n > 3$ the electron-hole mechanism studied below is more efficient.

3.2. The electromagnetic mechanism. If a molecule is physically adsorbed or is located quite far from the surface of the metal, the electric field from the oscillating dipole of the molecule penetrates into the bulk of the metal, and this generates electron-hole pairs. The Hamiltonian for the interaction of the vibrations of the molecule and the electrons of the metal has the form

$$H_{\text{int}} = Q_A \int g(\mathbf{r})\, \hat{\rho}(\mathbf{r})\, d^3\mathbf{r}, \tag{3.21'}$$

where Q_A is the normal coordinate of the vibrations, $Q_A g(\mathbf{r})$ is the change in the potential energy of the molecule accompanying a displacement of the normal coordinate from the position of the equilibrium by an amount Q_A, and $\hat{\rho}(\mathbf{r})$ is the electron density operator for the metal. In the linear-response approximation the polarization operator can be represented in the form

$$\Pi(\omega) = \int d^3\mathbf{r}' \int d^3\mathbf{r} \varphi(\mathbf{r})\, \chi(z, z', \mathbf{x} - \mathbf{x}', \omega)\, \varphi(\mathbf{r}'), \tag{3.23}$$

where $\varphi(\mathbf{r})$ is the potential of a point dipole with the dipole moment

$$\mu = e^* Q_0 = e^* (2m\omega_0)^{-1/2}.$$

The charge-density response function for a semiinfinite metal [$\mathbf{r} = (\mathbf{x}, z)$; the metal is assumed to occupy the half-space $z < 0$] is given by the formula

$$\chi(z, z', \mathbf{x} - \mathbf{x}', \omega) = \sqrt{-i} \int_0^\infty \exp(i\omega t) \langle [\hat{\rho}(\mathbf{r}, t),\ \hat{\rho}(\mathbf{r}', 0)] \rangle\, dt. \tag{3.24}$$

Introducing the function

$$g(q_\parallel, \omega) = \frac{2\pi}{q_\parallel} \int dz \int dz' \exp[q_\parallel (z + z')]\, \chi(z, z', \mathbf{q}_\parallel, \omega), \tag{3.25}$$

where

$$\chi(z, z', \mathbf{q}_\parallel, \omega) = \int \exp(i\mathbf{q}_\parallel \mathbf{x})\, \chi(z, z', \mathbf{x}, \omega)\, d^2\mathbf{x}, \qquad (3.26)$$

and carrying out the two-dimensional Fourier transform in the integrand in (3.23) gives[27,28]

$$\Pi(\omega) = \left(\frac{\mu_\parallel^2}{2} + \mu_\perp^2\right) \cdot \frac{1}{2} \int_0^\infty q_\parallel^3 \exp(-2q_\parallel d)\, g(q_\parallel, \omega)\, dq_\parallel, \qquad (3.27)$$

where d is the distance between the point dipole and the surface of the metal; $\mu_\parallel$ and $\mu_\perp$ are the components of the dipole moment parallel and perpendicular to the surface; $g(q_\parallel,\omega)$ is the linear-response function employed for describing many processes at a surface, including the van-der-Waals force between an atom and the surface of a metal, the surface photoeffect, friction for motion of charged particles near the surface,[29] etc. As shown in Ref. 30 the function $g(q_\parallel,\omega)$ can be determined experimentally with the help of inelastic scattering of slow electrons.

A large number of publications,[28,31-35] in which the electromagnetic mechanism of damping is analyzed differ by the form of the approximation employed for the function $g(q_\parallel,\omega)$. If spatial dispersion is neglected, i.e., the metal is described by a local permittivity, equal to the bulk value of $\varepsilon(\omega)$ for $z<0$ and unity for $z>0$, then the response function can be expressed in terms of the permittivity[36]

$$g(q_\parallel, \omega) = (\varepsilon(\omega) - 1)(\varepsilon(\omega) + 1)^{-1}. \qquad (3.28)$$

In Drude's approximation $\varepsilon(\omega) = 1 - [\omega_p^2/\omega(\omega + i\tau)]$, where ω_p is the bulk plasma frequency, $\tau = l/v_F$, where l is the mean-free path of an electron with velocity v_F at the Fermi surface. For $\omega_0 \ll \omega_2$ ($\omega_s = \omega_p/\sqrt{2}$ is the surface plasmon frequency) we obtain

$$\Gamma = \frac{2\mu^2}{d^3} \frac{\varepsilon_F}{\omega_p} \frac{1}{k_F l} \frac{\omega_0}{\omega_p}, \qquad (3.29)$$

where it is assumed that $\mu_\parallel = 0$. The formula (3.29) describes damping not only of the vibrational but also the electronic excitations of the molecule. According to (3.29) $\Gamma \sim d^{-3}$; this prediction was checked experimentally.[37] The described bulk contribution to Γ corresponds to excitation of an electron-hole pair in the bulk of the metal, and in addition the excess momentum $\Delta k = k_f - k_i \sim k_F(\omega_0/2\varepsilon_F)$ is absorbed when electrons are scattered by phonons, impurities, or the crystalline potential (interband transitions) of the metal.

There also exists a purely surface contribution to Γ. First of all, the excess momentum can be adsorbed when an electron is scattered by the surface (S_1 process). Second, when the distance between the oscillator and the surface is small

$$d < \frac{2\varepsilon_F}{k_F \omega_0}$$

direct excitation of electron-hole pairs (Landau damping) is possible, since the field of the oscillator contains components with wave vectors right up to $1/d$ (S_2 process). The calculation turns out to be quite complicated because of the need to take into account spatial dispersion,[31-35] and the results are sensitive to the model employed (the selected profile of the electron distribution). In particular, for the jellium model it was found[33] that

$$\Gamma_{S_1} = \frac{3[(\mu_\parallel^2/2) + \mu_\perp^2]}{2d^3} \frac{\omega_0}{\omega_p} \frac{1}{k_F d}, \qquad (3.30)$$

$$\Gamma_{S_2} = \frac{9[(\mu_\parallel^2/2) + \mu_\perp^2]}{2d^3} \frac{\varepsilon_F \omega_0}{\omega_p^2} \frac{1}{k_F d}, \qquad (3.31)$$

where ξ_F is a constant (≈ 1). It follows from the expressions (3.30)–(3.31) that $\Gamma_s \sim d^{-4}$. Since for a metal substrate $l \sim 100$ Å in the infrared region the "surface" makes the main contribution to Γ. Calculations[28,32] show that when CO and N_2 molecules are adsorbed on the surface of the metals Cu and Pt the electromagnetic broadening of the spectral line is less than 10% of the experimentally observed value. The electromagnetic mechanism also leads to a small frequency shift. For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface $\Delta\omega_{el} = -2$ cm^{-1}.[35] The foregoing theory is, generally speaking, limited by processes which include small values of $q_\parallel$ (and thus large d, since $q_\parallel \lesssim 1/d$). The corrections arising from components with large $q_\parallel$ were evaluated in Ref. 38.

The electromagnetic mechanism can play an important role in adsorption on the surface of a semiconductor or semimetal, when the frequency ω_0 is close to one of the characteristic frequencies of the collective excitations of the substrate, in particular, the surface plasmon frequency ω_s (for the surface of a semiconductor $\omega_s = (4\pi e^2 n/(\varepsilon_0 + 1)m^*)^{1/2}$, where n is density of conduction electrons (holes) with effective mass m^* and ε_0 is the static permittivity). In this case[12]

$$\Gamma = \frac{\mu^2 \omega_s \delta_s^{-1}}{8(\varepsilon_0 + 1) d^3}, \qquad (3.32)$$

where δ_s is the damping decrement of surface plasmons. If $\delta_s \lesssim \omega_s$, damping will occur primarily by the electromagnetic mechanism.

In concluding this section we note that for the electromagnetic damping mechanism there is an isotopic effect ($\Gamma \sim m_A^{-1}$, since $\mu^2 \sim m_A^{-1}$), but the temperature dependence turns out to be weak.

3.3. The electron-hole mechanism. In the process of chemisorption the interaction of vibrations of the adsorbate with the electrons of the metal is described by the well developed theory of electron-phonon interaction.[39] The expression for the polarization operator is determined, as before, by the formula (3.2), in which $\varphi(\mathbf{r})$ represents the change in the potential of the adsorbate when the normal coordinate of the vibrations Q is increased by an amount equal to the transition matrix element $Q_0 = (1/2m\omega_0)^{1/2}$, i.e.,

$$\varphi(\mathbf{r}) = \frac{\partial V(Q, \mathbf{r})}{\partial Q} Q_0,$$

where $V(Q,\mathbf{r})$ is the potential of the adsorbate. For practical calculations it is convenient to rewrite the formula (3.3) in the form

$$\Pi(\omega) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \tilde{\varphi}(\mathbf{r})\, \tilde{\chi}(\mathbf{r}, \mathbf{r}')\, \tilde{\varphi}(\mathbf{r}'), \qquad (3.33)$$

where $\varphi(\mathbf{r})$ is the screened change in the potential and $\chi(\mathbf{r},\mathbf{r}')$ is the irreducible part of the charge-density response function, which determines the response of the electrons in the metal to the screened change in the potential (the irreducible part does not contain diagrams that can be divided into

two parts separated by one coulomb line). In the random-phase approximation

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}') = 2\sum_{k,k'} \frac{\psi_k(\mathbf{r})\,\psi_{k'}^*(\mathbf{r})\,\psi_{k'}(\mathbf{r}')\,\psi_k^*(\mathbf{r})}{\omega - \varepsilon_k - \varepsilon_{k'} + i\delta}$$

$$f(\varepsilon_k)(1 - f(\varepsilon_{k'})) + (\omega \to -\omega), \qquad (3.34)$$

where $\tilde{\psi}_k(\mathbf{r})$ and ε_k are the single-electron wavefunctions and energies, $f(\varepsilon_k)$ is the Fermi distribution function, and the factor of 2 arises owing to summation over the electron spins. Substituting (3.34) into the formula (3.31) gives the following expression for the width of a level[40]

$$\Gamma = \frac{2\pi}{m}\sum_{k,k'}\left|\int d^3\mathbf{r}\,\psi_k(\mathbf{r})\frac{\partial V(Q, r)}{\partial Q}\psi_{k'}(\mathbf{r})\right|^2, \quad \varepsilon_k = \varepsilon_{k'} = \varepsilon_F. \qquad (3.35)$$

For a homogeneous medium the formula for Γ can be presented in the form[40,43]

$$\Gamma = \left(\frac{9}{4\pi}\right)^{1/3}\frac{3}{mr_s^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_{l+1} - \delta_l), \qquad (3.36)$$

where δ_l are the phase shifts for scattering of an electron with the Fermi energy by the potential of the adatom and r_s is the electron density parameter ($4\pi r_s^3/3 = n$; n is the electron density). The expression (3.36) can be employed to make a rough estimate of Γ at the surface, if the local values of the phases are employed for δ_l.[41]

The formula (3.35) serves as a basis for numerical calculations of the rate of vibrational relaxation in the jellium model within the framework of the density functional method[40–42] (see, for example, Fig. 4). The width Γ has also been calculated by the method of linear combination of atomic orbitals (LCAO).[44]

In spite of the importance of calculations based on first principles the Anderson-Newns semiempirical model[14,17,45–48] plays a large role in elucidating the physical essence of the electron-hole mechanism of damping and establishing a correlation with the experimental data. The Anderson-Newns Hamiltonian has the form[49]

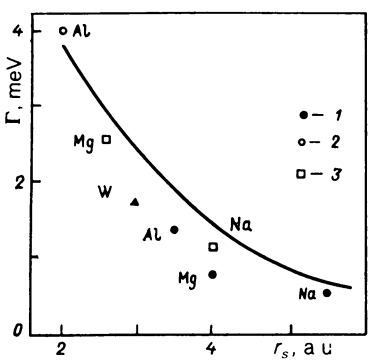

FIG. 4. The rate of relaxation of vibrations of a hydrogen atom normal to the surface as a result of the excitation of electron-hole pairs (calculation of Ref. 40 on the basis of the jellium model) The solid line shows the calculation for a uniform electron gas; the separate points correspond to different distances from the proton to the jellium boundary: 1) equilibrium distance; 2) $d = -2$ a.u., 3) $d = -14$ a u; for tungsten the experimental value is given

$$H = \sum_\sigma \varepsilon_a(Q)\,n_{a\sigma} + \sum_{k\sigma}\varepsilon_k n_{k\sigma} + \sum_{k\sigma}(V_{ak}(Q)\,c_{k\sigma}^+ c_{a\sigma} + \text{h.c.}) + Un_{a\sigma}n_{a-\sigma} + \omega_0 b^+ b, \qquad (3.37)$$

where $n_{k\sigma} = c_{k\sigma}^+ c_{k\sigma}$, $n_{a\sigma} = c_{a\sigma}^+ c_{a\sigma}$, and $c_{k\sigma}^+$ and $c_{a\sigma}^+$ are operators creating an electron in the states of the metal $|k\rangle$ and adatom $|a\rangle$ with energies ε_a and ε_k, V_{ak} is the hybridization matrix element, U is the coulomb repulsion energy between electrons with opposite spins σ on the adatom, $Q = (1/2m\omega_0)^{1/2}(b^+ + b)$, and b^+ is the phonon creation operator for local vibration of an adatom. In the presence of vibrations the position of the electronic level of the adatom ε_a and its width

$$\Delta = \pi\sum_k |V_{ak}|^2\,\delta(\varepsilon - \varepsilon_k),$$

change, and this in its turn leads to oscillations of the charge of the adatom. The nonadiabatic nature of the charge oscillations leads to damping of the oscillations. Expanding $\varepsilon_a(Q)$ and $V_{ak}(Q)$ up to terms linear in Q and applying the linear-response theory in the quasiadiabatic limit ($\Delta \gg \omega_0$) gives the following formula for the width of a vibrational level[17]

$$\Gamma = \frac{4}{\pi m}\left\{\sin^2\delta(\varepsilon_F)\left[\frac{\langle|V'_{ak}|^2\rangle_{\varepsilon_F}}{\langle|V_{ak}|^2\rangle_{\varepsilon_F}} - \left(\frac{\Delta'}{2\Delta}\right)^2\right] + \frac{1}{2}(\delta'_\varepsilon(\varepsilon_F))^2\right\}, \qquad (3.38)$$

where $\langle\ldots\rangle$ indicates averaging over a surface with constant energy with $\varepsilon = \varepsilon_F$ and $\delta(\varepsilon_F)$ is the phase shift which, even for the case $U \neq 0$, is given by the expression

$$\delta(\varepsilon) = \operatorname{arctg}\frac{\Delta(\varepsilon)}{\varepsilon_a - \varepsilon - \Lambda(\varepsilon)},$$

where

$$\Lambda(\varepsilon) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'}d\varepsilon'.$$

The derivation of the formula (3.38)[17] employed the relation[17,41] between the linewidth and the coefficient of friction

$$\Gamma = \eta \qquad (3.39)$$

for excitation of electron-hole pairs, which is valid for $\Delta \gg \omega_0$, as well as the coefficient of friction calculated in Ref. 50.

The fact that the formula (3.38) for Γ is identical for both $U = 0$ and for $U \neq 0$ is linked with the fact that the imaginary part of the self-energy part of the electronic Green's function of the adatom, associated with the Coulomb interaction U, vanishes at the Fermi energy.[51]

The formula (3.38) contains two substantially different terms. For transverse oscillations the first term turns out to be small; in particular, the first term vanishes identically if $V_{ak}(Q) = f(Q)V_{ak}$. For longitudinal vibrations, for which $\varepsilon'_a = \Delta' = 0$, the second term vanishes. One can see that the first term is reminiscent of the well-known formula for the resistance of a metal.[52] Indeed, both formulas are equivalent, if the surface is smooth and scatters electrons specularly and

the Fermi surface is spherical. The mechanism for damping of oscillations associated with the second term is termed the mechanism with charge transfer, while the mechanism associated with the first term is termed the potential-scattering mechanism.

The formula (3.38) shows that the mechanism with charge transfer and the potential-scattering mechanism are related with the interaction of the orbitals of the adatom with the orbitals of the substrate atoms, whose symmetry is different. In particular, if the adatom orbital has σ symmetry, then the mechanism with charge transfer is related to the interaction with the orbitals of the substrate atoms, which also have σ symmetry, while the potential-scattering mechanism is related to the orbitals having π-symmetry, which do not participate in the formation of a chemisorption bond.

For noninteracting electrons ($U = 0$) the temperature dependence of Γ has the form

$$\Gamma(T) = \Gamma(0)\,(1 + O(k_B T \Delta^{-1}))^2,$$

i.e., it is weak when $k_B T \ll \Delta$.[17] The temperature dependence, however, can be strong, if the adatom is in a Kondo regime (U is large, the levels of the adatom are arranged symmetrically with respect to the Fermi level, and $T \approx T_K$, where T_K is the Kondo temperature). Calculations[14,17,47] show that for chemisorption of hydrogen on the surface of transition metals $\Gamma_\perp \approx \Gamma_\parallel \approx 275$ meV.

For transverse vibrations the formulas for the level width and the frequency shift can be written in the form[17,45,46]

$$\Gamma = 2\pi\omega_0 (\delta n)^2, \tag{3.40}$$
$$\Delta\omega = -\lambda\delta n, \tag{3.41}$$

where $\lambda = (1/2m\omega_0)^{1/2}|\varepsilon_a'|$, δn is the charge of an admolecule accompanying a shift in its position of equilibrium by an amount $Q_0 = (1/2m\omega_0)^{1/2}$, and m is the reduced mass. We note that the electron-hole mechanism is characterized by a "red" shift of the vibrational frequency ($\Delta\omega < 0$). For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface, according to the experimental data $\delta n = 0.3$,[46] $|\varepsilon_a'| = 11$ eV/Å,[53] and $\omega_0 = 2084$ cm^{-1}.[54] Using these values and taking into account the spin and orbital degeneracy of the $2\pi^*$ orbitals of the CO molecule we obtain $\Gamma = 3$ cm^{-1} (Ref. 46) and $\Delta\omega = -88$ cm^{-1} (Refs. 17 and 55). The theoretical value of Γ is in good agreement with experiment: $\Gamma_{exp} = 4.6$ cm^{-1}.[54] To calculate the total frequency shift it is also necessary to take into account the electromagnetic component of the shift $\Delta\omega_{el} = -2$ cm^{-1} (Ref. 35) owing to the interaction of the dipole of the CO molecule with its image, as well as the frequency shift owing to the interaction of the vibrations of the C=O bond with the vibrations of the CO molecule as a whole relative to the surface $\Delta\omega_{ph} = 33 \pm 6$ cm^{-1}.[56] From here the total shift $\Delta\omega_{tot} = -67 \pm 6$ cm^{-1},[17,55] which is also in good agreement with experiment: $\Delta\omega_{exp} = -60 \pm 10$ cm^{-1}.[57,76]

The formulas (3.38), (3.40), and (3.41) were derived in the quasiadiabatic limit, when $\Delta \gg \omega_0$. As the molecule moves away from the surface a transition occurs from the quasiadiabatic limit to the strong nonadiabatic limit $\Delta \ll \omega_0$. The formulas describing this transition were derived in Ref. 48. It follows from these formulas that in the quasiadiabatic limit $(\Delta \gg \omega_0)\,\Gamma \sim \Delta^{-2}$, $\Delta\omega \sim \Delta^{-1}$, if $|\varepsilon_a - \varepsilon_F| \ll \Delta$. In the opposite limit $(\Delta \ll \omega_0)\,\Gamma \sim \Delta$, $\Delta\omega \sim \Delta^2$. In this limit polaron narrowing of the electronic level must be taken into account. The theory of polaron narrowing can be constructed by analogy to the theory of the image potential for the fluctuation charge of the adatom.[58] As the distance from the surface increases the width Δ decreases rapidly, so that for small distances between the admolecules and the surface Γ varies more rapidly than $\Delta\omega$, while at a large distance the opposite assertion holds. The dependence of Γ and $\Delta\omega$ on the distance d up to the surface for the case of vibrations of the C=O bond with adsorption of CO on the Ni(111) surface is presented in Fig. 5. One can see from the figure that Γ and $|\Delta\omega|$ have a sharp maximum when the electronic level of the admolecule crosses the Fermi level.

We note that the crossing of the Fermi level by the electron resonance of the admolecule is a fundamental concept, employed for describing diverse surface phenomena, such as diffusion,[59] attachment,[60] adsorption,[61] desorption,[62] scattering of atoms by a surface,[63] restructuring in the adsorbed layer,[64] etc.

The nonadiabatic nature of the motion of the electrons leads not only to damping of the vibrations, but also adds an imaginary component to the dynamic dipole moment, i.e., $\mu = \mu_1(1 + i\omega\tau)$, where μ_1 is the real component of the dynamic dipole moment and $\omega\tau$ is the nonadiabaticity parameter.[8] The polarizability of the adatom is determined by the expression

$$\alpha(\omega) = \alpha_e(\omega) + 2\mu^2\omega_0(\omega^2 - \omega_0^2 + i\omega\gamma)^{-1}, \tag{3.42}$$

where α_e is the electronic part of the polarizability and γ is the damping parameter for the vibrations. In the Anderson-Newns model[8]

$$\alpha_e(\omega) = -\bar{\mu}^2(\rho_a(\varepsilon_F) + i\pi\omega\rho_a^2(\varepsilon_F)), \tag{3.43}$$
$$\gamma = 2\pi\omega\,(\rho_a(\varepsilon_F)\,\delta\varepsilon)^2, \tag{3.44}$$
$$\mu_1\tau = -\pi\bar{\mu}\rho_a^2(\varepsilon_F), \tag{3.45}$$

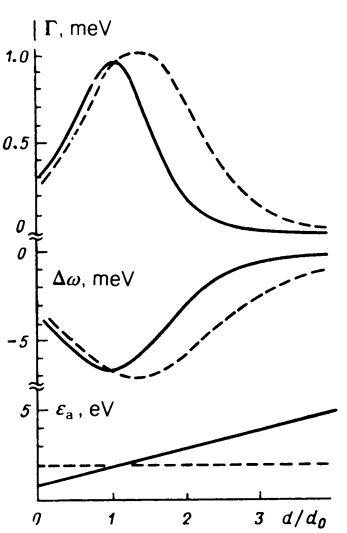

FIG. 5. The linewidth Γ, the frequency shift $\Delta\omega$, and the position of the electronic level ε_a for C=O vibrations in the case of adsorption of CO/Ni(111) as functions of the distance between the molecule and the surface.[17] For the solid lines $\varepsilon_a(d) = \text{const}$; for the broken lines $\varepsilon_a(d) = \varepsilon_A(d_0) + a(d/d_0 - 1)$; $a = 1$ eV.

where $\bar{\mu} = er_0$, r_0 is the distance between the adatom and the plane of the mirror image, $\rho_a(\varepsilon_F)$ is the electronic density of states for the adatom, and $\delta\varepsilon$ is the displacement of the electronic level of the adatom accompanying a shift in the adatom from the position of equilibrium by an amount $Q_0 = (1/2m\omega_0)^{1/2}$. The shape of the spectral line is determined by the expression[8]

$$L(\omega) = V - \operatorname{Im}\alpha(\omega) = 2\frac{\omega_0\mu_1^2(1-xy)^2}{\omega\gamma(1+x^2)}, \qquad (3.46)$$

where $x = (\omega^2 - \omega_0^2)\gamma\omega$, and $y = \omega\tau$. For vibrations of the C=O bond accompanying adsorption of CO on the Cu(100) surface the predicted line shape has an appreciable asymmetry with a low-frequency wing.[8] Experimentally, however, a weaker asymmetry in the opposite direction is observed.[54] According to Ref. 54 the main reason for the difference lies in the fact that in the theory an isolated chemisorbed molecule is studied and the lateral interactions between molecules are ignored. In the general case this interaction leads to strong transfer of intensity to high-frequency modes owing to the dipole-dipole interaction.[76] Another method for checking the electron-hole mechanism for damping is associated with the isotopic effect. According to the formula (3.38) the linewidth is inversely proportional to the reduced mass. For the $c(2\times2)$ structure the difference in the linewidth for $^{12}C^{16}O$ and $^{13}C^{18}O$ with isotopic purity exceeding 90% equals 0.3 cm^{-1}, which falls within the resolution of the experiment. At the present time, however, it is not possible to separate the dipole-dipole interaction; isotopic impurities lead to additional inhomogeneous line broadening of ~ 1 cm^{-1}, masking the isotopic effect.[54]

The strongly asymmetric line shape, described by the formula (3.46), was observed for the wagging vibrations of H on the W(100) surface with the help of IR spectroscopy with coverage $\theta = 2$.[65] For the vibrations of H on the W(100) surface three modes with the frequencies 645 cm^{-1} (wagging), 950 cm^{-1} (asymmetric), and 1060 cm^{-1} (symmetric) are observed. It follows from symmetry that of all the fundamental modes only the symmetric mode can be observed in IR spectroscopy. The first overtone at the wagging frequency $\omega = 2\omega_0$ can, however, be observed. The nature of the formation of the overtone peak was discussed in

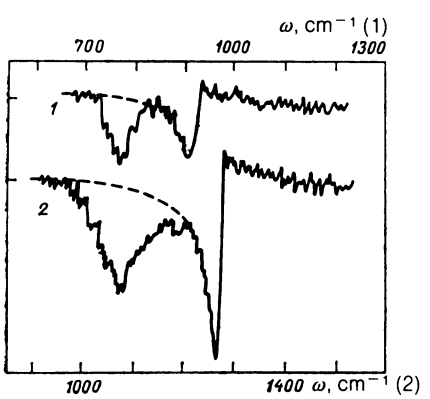

FIG. 6. The vibrational spectra of D (1) and H (2) atoms adsorbed on W(100). The solid lines show the experimental data of Ref. 65 and the broken lines are theoretical curves from Refs. 65 and 66.

TABLE III. Damping parameters for vibrations of H and D on W (100).[65]

Atom	ω, cm^{-1}	γ, cm^{-1}	$\omega\tau$
H	1270	26	0.44
D	915	22	0.46

Ref. 66. It was shown that the form of the overtone is also determined by the formula (3.46). The experimental and theoretical data are compared in Fig. 6. The parameters of the theory were determined from analysis of the experimental data (Table III). The experimental data obtained provide evidence for the fact that the damping of the wagging vibrations of H on the W(100) surface is determined by electron-hole mechanisms. The absence of an isotopic effect, which was observed in Ref. 65, could be linked, as in the case of the system CO/Cu(100), with isotopic disorder, which leads to inhomogeneous line broadening. The strong damping of the wagging vibrations of H on the W(100) surface is associated with the interaction of the hydrogen orbital with the surface states. According to calculations,[67] states with d_{xy} symmetry lie near ε_F (Fig. 7). These states do not participate in the formation of a bond ($V_{ak} = 0$), but they do make a large contribution to the relaxation rate ($V'_{ak} \neq 0$).

3.4. Intermode energy transfer. An adsorbed atom has the three degrees of freedom, so that because of anharmonicity of the potential well in which the adatom moves energy transfer between different vibrational modes is possible. Taking into account the interaction between two modes A and B only the energy of mode A can be transferred to mode B, while the excess energy $\Delta\omega = (\omega_A - \omega_B)$ is transferred to phonons or electron-hole pairs of the substrate. For example, the calculation of Ref. 8 for S and O atoms adsorbed on nickel showed that the rate of energy transfer between the transverse and longitudinal modes equals at room temperature $\Gamma \approx (0.5\text{–}5)\times10^{-2}\,\omega_0$. An analogous result was also obtained for the system H/W(100).[69] In this case Γ depends strongly on the temperature.[69] Thus for $\omega_A > \omega_B$

$$\frac{\Gamma(T)}{\Gamma(0)} = 1 + n(\omega_B) + n(\omega_A),$$

while for $\omega_A < \omega_B$

$$\frac{\Gamma(T)}{\Gamma(0)} = n(\Delta\omega) - n(\omega_A).$$

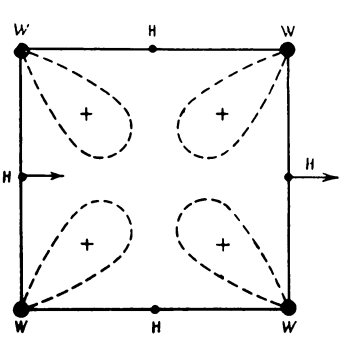

FIG. 7. A schematic diagram of the surface electronic states (broken lines) with which an H atom interacts under conditions of wagging vibrations. These states have d_{xy} symmetry (the z axis is perpendicular to the surface) and do not participate in the formation of a bond between hydrogen and tungsten.

The last process is possible only for $T>0$. In the case of a diatomic molecule the relaxation of intramolecular vibration by means of excitation of vibrations of the molecule as a whole can sometimes be significant. This relaxation mechanism was studied in Ref. 70.

If the interaction between vibrational modes is strong, then perturbation theory cannot be employed. A numerical calculation,[71] performed on the basis of classical mechanics, showed that in this case the motion of the adparticles becomes stochastic over a time $\tau \approx 10^2 \omega_0^{-1}$. In the case of strong coupling separate modes, strictly speaking, cannot be separated, and a two- or three-dimensional Schrödinger equation must be solved. This situation possibly occurs in the system H/Ni.[72] Thus the rate of energy transfer between the vibrational modes can be of the same order as the rate of energy transfer between the local mode and the substrate. It is important to note that in this process, as in the energy transfer studied below between neighboring admolecules, vibrational excitation remains within the adsorbed layer.

4. DYNAMIC INTERACTION BETWEEN ADSORBED MOLECULES

If two identical molecules are adsorbed on the surface of a crystal at the points $\mathbf{r}_1$ and $\mathbf{r}_2$, then they interact with one another with some energy $E_{\text{int}}(\mathbf{r}_1,\mathbf{r}_2)$. The main mechanisms of interaction between adsorbed molecules—direct, indirect, electrostatic (dipole-dipole), and elastic—are described in detail in Ref. 73. This interaction leads to two effects. First, the frequency of the local vibrations of the admolecule in the field of the other molecule is shifted by an amount

$$\Delta\omega \approx Q_0^2 \left(\frac{\partial^2 E_{\text{int}}}{\partial Q_1^2}\right)_{Q_1=Q_2=0}. \tag{4.1}$$

Second, the frequencies are split: $\omega_{\pm} = \omega_0 + \Delta\omega \pm \beta$, where

$$\beta = Q_0^2 \left(\frac{\partial^2 E_{\text{int}}}{\partial Q_1 \partial Q_2}\right)_{Q_1=Q_2=0}. \tag{4.2}$$

If one admolecule is excited while the other is not, then the quantity $\tau = \beta^{-1}$ determines the transfer time from the first admolecule to the second one.

The formulas (4.1) and (4.2) give the adiabatic contribution to the interaction of oscillators. In addition there exist nonadiabatic corrections, owing to the delay in the response of the substrate to the vibration of the admolecule. Such a nonadiabatic interaction in the asymptotic limit ($R \to \infty$, where R is the distance between the molecules) can be stronger than the adiabatic interaction. Nonadiabatic interaction has been studied for electrostatic[12,74] and indirect[75] interaction mechanisms.

If a film with a defective structure is adsorbed on the surface of a crystal, then the interaction between the adparticles leads to inhomogeneous broadening of the vibrational line (see Sec. 5). If, however, the film is ordered, then dispersion of the vibrations appears owing to the interaction, i.e., the component of the wave vector $\mathbf{q}_{\parallel}$ parallel to the surface depends on the frequency of the vibrations ω. For example, for a simple square lattice of adatoms

$$\omega^2(\mathbf{q}_{\parallel}) = (\omega_0+\Delta\omega)^2 + 4\beta\omega_0(\cos q_x a + \cos q_y a), \tag{4.3}$$

where a is the lattice constant. The vibrational dispersion can be measured by the method of electron energy losses (EELS) with angular resolution. The evolution of the dispersion characteristics as the degree of coverage θ of the substrate changes is especially interesting. However the restructuring of the surface often makes the main contribution to the change in the vibrational frequencies as the coverage θ changes. We note that the wave vector of infrared photons $q \ll 2\pi/a$, so that owing to the law of conservation of momentum only phonon modes with $q_{\parallel} \approx 0$ are observed in the IR spectroscopy method.

The energy of the electrostatic interaction of admolecules has the form[73]

$$E_{\text{int}} = 2\tilde{\mu}(Q_1)\,\tilde{\mu}(Q_2)\,R^{-3}, \tag{4.4}$$

where $\tilde{\mu}$ is the dipole moment formed by the charged adatom together with its image. Using the expressions (4.1) and (4.2) gives for the transverse vibrations

$$\Delta\omega_{\perp} \approx 2Q_0^2 \frac{\partial^2 \mu(Q)}{\partial Q^2} E_{\text{int}}, \tag{4.5}$$

$$\beta_{\perp} \approx \left(\frac{\mu}{\tilde{\mu}}\right)^2 E_{\text{int}}, \tag{4.6}$$

where μ is the dynamic dipole moment, while for longitudinal vibrations

$$\Delta\omega_{\parallel} \approx -\beta_{\parallel} \approx 12\left(\frac{Q_0}{R}\right)^2 E_{\text{int}}. \tag{4.7}$$

It follows from here that the electrostatic interaction is strongest for longitudinal vibrations of admolecules with a large static dipole moment $\tilde{\mu}$, as, for example, for the system Cs/W(100). We note that $\beta_{\perp} \neq 0$ even when $\tilde{\mu} = 0$. The electrostatic interaction plays the main role in adsorption of CO on Cu(100).[76,77] In calculating the susceptibility in this case the screening arising owing to the electronic polarizability of the molecules must be taken into account.

In the infrared region the susceptibility of an isolated molecule equals[76]

$$\alpha_A(\omega) = \alpha_e(\omega) + \alpha_i\omega_A^2[\omega_A^2 - \omega(\omega + i\gamma)]^{-1}, \tag{4.8}$$

where α_e and α_i are the electronic and ionic polarizabilities. Let a molecule with the dipole moment $\tilde{\mu}$ and located at the point $\mathbf{R}_1$ produce at the point $\mathbf{R}_2$ the field $E(\mathbf{R}_2) = -U(\mathbf{R}_2 - \mathbf{R}_1)\mu(\mathbf{R}_1)$, where $U(R) \sim R^{-3}$. Then a Fourier transform of the equation

$$\tilde{\mu}(\mathbf{R}_i) = \alpha_A\left[E(\mathbf{R}_i) - \sum_{i\neq j} U(\mathbf{R}_i - \mathbf{R}_j)\,\tilde{\mu}(\mathbf{R}_j)\right], \tag{4.9}$$

gives

$$\alpha(\omega, \mathbf{q}) = \tilde{\mu}E^{-1} = \alpha_A(1 + \alpha_A\tilde{U}(q))^{-1}, \tag{4.10}$$
$$\tilde{U}(\mathbf{q}) = \sum_j \exp(i\mathbf{q}\mathbf{R}_j)\,U(\mathbf{R}_j).$$

The expression[76] for the reflecting power of the surface follows from here (in the limit $\gamma \to 0$):

$$\delta R \sim \operatorname{Im}\alpha(\omega, 0) = \frac{\pi\alpha_i\omega_A^2}{2\omega_0(1+\alpha_e\tilde{U})^2}\,\delta(\omega - \omega_0), \tag{4.11}$$

where the frequency shift is determined by the formula

$$(\omega_0\omega_A^{-1})^2 = 1 + \alpha_i\tilde{U}(0)[1 + \alpha_e\tilde{U}(0)]^{-1}. \quad (4.12)$$

For the system CO/Cu(100) calculations give $\alpha_e\tilde{U}(0) \approx 1$,[76] i.e., the screening owing to the polarizability of the molecules is significant. For this system the dipole-dipole interaction explains the observed dispersion ~ 40 cm^{-1},[52] while the contribution of the indirect interaction is small.[78]

The indirect interaction has the following asymptotic form[73]

$$E_{int} \sim f(Q_1)f(Q_2)\cos(2k_FR)R^{-5}, \quad (4.13)$$

where the function $f(Q)$ is determined by the interaction of the admolecule with the substrate owing to overlapping of the orbitals of the molecule and substrate atoms. If the Fermi level crosses the band of surface states, then $E_{int.} \sim \cos(k_FR)/R^2$,[79] i.e., in this case the range of the indirect interaction is greater than that of the dipole-dipole interaction. The indirect interaction is the dominant interaction for adsorption of H and O on the surface of transition metals.[73,80] Calculations[14] for the system H/W(100) give $\Delta\omega_\perp \approx \beta_\perp \approx 40$ cm^{-1} and $\Delta\omega_\parallel \approx \beta_\parallel \approx 400$ cm^{-1}. In an experiment for the system H/Pd(100) with $\theta = 1$ the shift $\Delta\Omega = 28$ cm^{-1} was observed.[81] Finally, the elastic interaction energy between the adatoms S and O on Ni(100) was calculated in Ref. 68. It gives the value $\Delta\omega_s = 8$ cm^{-1}.

The picture of dispersion described above is valid only for small displacements of adatoms from their position of equilibrium, when the finiteness of the height of the potential relief along the surface and the nonlinearity of the interaction between the molecules can be neglected. The nonlinearity of the interaction could play an important role for transverse vibrations of H on W(100) with coverage $\theta = 2$. For these vibrations the unusually large linewidth $\Gamma \approx 100$–120 cm^{-1} has been observed with the help of IR spectroscopy.[82] Such a large width cannot be associated with either inhomogeneous broadening or excitation of electron-hole pairs or phonons in the substrate. The frequency shift and spectral-line narrowing accompanying a change in the isotopic composition of the adfilm indicates that there is a strong dynamic interaction between adsorbed hydrogen atoms. While the linear interaction between oscillators leads to a frequency shift, the nonlinearity of the interaction can lead to line broadening. The nature of the dynamic interaction between hydrogen atoms is not clear at present. The dipole-dipole interaction cannot explain the change in the spectral lines accompanying isotopic substitution and is too weak to explain the observed frequency shift. The elastic interaction must be small because of the smallness of the mass of H as compared with the mass of W. Other alternatives are diffusion and indirect interaction. We note that a large width of the optical peaks $\Gamma \approx 160$–200 cm^{-1} is observed for vibrations of hydrogen in transition-metal alloys.[83] It is possible that broadening of the optical peaks for vibrations of a hydrogen atom in the bulk and at the surface is of the same nature.

For large amplitudes of longitudinal vibrations there always exist, in addition to delocalized modes with dispersion $\omega(q_\parallel)$, modes that are localized along the surface. For example, in the case of a one-dimensional chain of adatoms, which is described by the well-known sine-Gordon equation, the local modes correspond to bionic (breather) solutions of the equations.[84] As the energy of the vibrations increases further the bion breaks up into a kink-antikink pair and a defect appears in the structure of the adfilm. It would, of course, be of great interest to observe such bionic modes experimentally.

5. INHOMOGENEOUS LINE BROADENING

Inhomogeneous line broadening is caused by the difference in the local environment of absorbing adsorbed particles occupying different sites on the surface.

The case of adsorption on a uniform surface, when the change in the local environment is associated with a change in the number of neighboring adsorbed particles, has been studied in greatest detail theoretically.[76] Let the adlayer consist of particles A and B, which are distributed randomly over adsorption sites. In the case of isotopic disorder A and B represent different isotopes of the same element. If, however, A is an admolecule and B is a vacancy, then we obtain a description of structural disorder. If the adparticles do not interact with one another, then the reflecting power equals

$$\Delta(\omega) = c_A\Delta_A(\omega) + c_B\Delta_B(\omega), \quad (5.1)$$

where c_A and c_B are the concentrations of molecules of the type A and B, and $\Delta_j(\omega) \sim \mathrm{Im}\,\alpha_j(\omega)$, where j = A or B. A method for calculating the susceptibility $\alpha(\omega)$ in the coherent potential approximation (CPA) for a mixture of molecules interacting by the dipole-dipole mechanism is described in Ref. 76. In the CPA it is assumed that all adsorption sites are filled with identical particles with "average" susceptibility $\alpha_0(\omega)$, determined from the equation

$$\alpha_0 = \sum_{j=A,B} c_j\alpha_j\left[1 + (\alpha_j - \alpha_0)\int \frac{d^2q_\parallel \tilde{U}(q_\parallel)}{S(1 + \alpha_0\tilde{U}(q_\parallel))}\right]^{-1}, \quad (5.2)$$

where S is the area of the surface Brillouin zone and $\tilde{U}(q)$ is the Fourier component of the interaction potential. The line shape is proportional to the imaginary part of the susceptibility

$$L(\omega) \sim \mathrm{Im}\,\alpha(\omega) = \mathrm{Im}[\alpha_0(\omega)(1 + \alpha_0(\omega)\tilde{U}(0))^{-1}]. \quad (5.3)$$

Calculation[56] of the reflecting power of an adlayer consisting of the isotopic mixture A = $^{12}C^{16}O$ and B = $^{12}C^{18}O$ with adsorption on Cu(100) shows that as the $^{12}C^{16}O$ concentration decreases the width of the high-frequency peak increases. In particular, for a mixture with $C_A = 0.5$ the increase equals 1 cm^{-1}, which is in good agreement with experiment.[76] An interesting effect is observed in the case of isotopic disorder—the intensity of the absorption of the low-frequency peak B decreases and the intensity of the high-frequency peak A increases as the interaction between the molecules increases. This is linked with the fact that owing to the dipole-dipole interaction a large part of the intensity of the absorption is transferred from the low-frequency peak to the high-frequency peak. For $\omega \approx \omega_B$ the molecules A emit more energy than they absorb. We note that for isotopic disorder the theory predicts an asymmetric line shape with a low-frequency wing.

Experimental and theoretical[76] data on the IR spectra for the isotopic mixture $^{12}C^{16}O/^{12}C^{18}O$ with adsorption on Cu(100) and complete filling of the (2×2) structure are

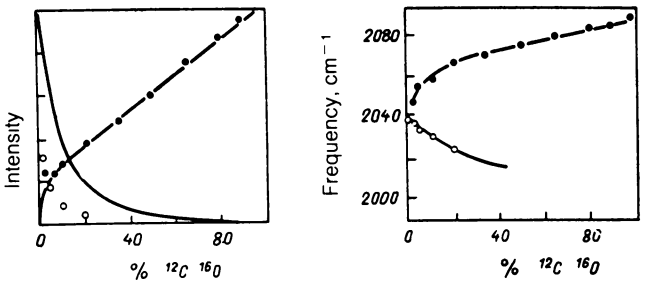

FIG. 8 The positions and intensities of the absorption peaks for $^{12}C^{16}O/^{12}C^{18}O/Cu(100)$ and coverage corresponding to a $c(2\times2)$ structure as a function of the $^{12}C^{16}O$ content.[76] The dots are the experimental points and the solid lines are the computed dependences.

presented in Fig. 8. One can see that the theory is in very good agreement with experiment.

In Ref. 76 the CPA was employed to calculate the absorption spectrum for a structurally disordered monolayer of CO with CO adsorbed on Cu(100). It was assumed that the $^{12}C^{16}O$ molecules are randomly distributed over the sites of a $c(2\times2)$ lattice. In this case the shape of the spectral line is also asymmetric and has a low-frequency wing. The width of the peak increases continuously as the coverage decreases right down to very small values. This is a consequence of the long-range nature of the dipole-dipole interaction.

With a partial monolayer of $^{12}C^{16}O$ and adsorption on Cu(100) a positive shift of the frequency of C=O vibrations from 2077 cm^{-1} with low coverage up to 2068 cm^{-1} with complete coverage of the $c(2\times2)$ structure is observed experimentally; that is, the total shift equals 9 cm^{-1}, which does not agree with the predictions of CPA,[76] according to which the shift should equal $\sim$43 cm^{-1}. This is linked with the fact that there exists a "red" shift of $\sim$30 cm^{-1} owing to the change in the chemisorption bond (chemical shift). Good agreement between theory and experiment was obtained[76] for a partial monolayer of CO with adsorption on Ru(100). This agrees with the fact that when CO is adsorbed on transition metals a large ($\sim$40 cm^{-1}) positive frequency shift, due to the dipole-dipole interaction, is observed. At the same time when CO is adsorbed on precious metals Ag, Au, and Cu a negative frequency shift is observed, i.e., in this case the chemical shift predominates.

In the case when the surface is uniform inhomogeneous broadening is also possible with almost complete coverage of the surface with adsorbed particles of the same kind, if the adsorption layer consists of ordered domains. Inhomogeneous broadening appears in this case owing to variation of the local environment of the particles located on domain walls.

Other obvious and important reasons for inhomogeneous broadening are nonuniformity of the surface itself, presence of different defects on a uniform surface, or presence of impurities on the surface. In the last case the shape of the line is sensitive to the method employed to prepare the surface.

Thus the shift, broadening, and asymmetry of the line shape are a consequence of the change in the local environment of absorbing adsorbed particles. At the present time these effects have been studied in detail only in the case of changes in the local environment owing to a change in the number of neighboring adsorbed particles.

6. DEPHASING OF VIBRATIONS

According to the experimental data the line shape of C=O vibrations with adsorption of CO on Pt(101) (Ref. 85) and Ni(111) (Ref. 86) is strongly temperature-dependent. This dependence cannot be related with multiphonon relaxation, the probability of which is negligibly small for these systems ($\omega_0/\omega_m \gg 1$). Damping owing to excitation of electron-hole pairs gives a virtually temperature-independent line shape. Thus it is natural to suppose that the temperature dependence of these vibrational lines is associated with phase relaxation. For example, in the case of anharmonic coupling of high-frequency vibrations A with low-frequency vibrations B purely phase relaxation of high-frequency vibrations is due to the random modulation of their frequency with low-frequency modes; this is the basis for the exchange model.[87-90] In the case of a diatomic molecule the mode A is related with intramolecular vibrations, while the mode B can be related with vibrations of the molecule as a whole. The Hamiltonian describing the exchange model has the form[89]

$$H = \omega_a a^+a + \omega_b b^+b + \sum_k \omega_k b_k^+ b_k + \delta\omega a^+ab^+b + \sum_k (V_k b^+ b_k + \text{h.c.}), \tag{6.1}$$

where a^+, b^+, and b_k^+ are boson operators creating a phonon of modes A and B and a substrate phonon. We note that the operator $n_a = a^+a$ commutes with the Hamiltonian, i.e., the energy of the mode A is conserved. At the same time the mode B can exchange energy with the substrate, so that the number of quanta of mode B changes with time, which leads to random modulation of the frequency of vibrations of the high-frequency mode A. The lowest order of perturbation theory gives[89]

$$\Delta\omega = \delta\omega n_b, \tag{6.2}$$

$$\Gamma = 2(\delta\omega)^2 n_b(1+n_b)\eta_B^{-1}, \tag{6.3}$$

$$\eta_B = 2\pi \sum_k |V_k|^2 \delta(\omega - \omega_k), \quad n_b = [\exp(\beta\omega_b) - 1]^{-1}. \tag{6.4}$$

It follows from these formulas that $\Delta\omega = \Gamma \sim \exp(-\beta\omega_b)$ as $T \to 0$. The formulas are valid when $\eta_B \gg \delta\omega$. A more general solution of the problem is given in Refs. 88 and 90. At high temperatures classical approaches, in particular, Langevin's equation, can be employed to describe phase relaxation processes. In this case the classical analog of the Hamiltonian (6.1) has the form[89]

$$\ddot{x}_a + \omega_a^2 x_a + \alpha x_a x_b^2 = 0, \tag{6.5}$$

$$\ddot{x}_b + \omega_b^2 x_b + \alpha \frac{m_a}{m_b} x_a^2 x_b + \eta_b \dot{x}_b = f(t), \tag{6.6}$$

where $f(t)$ is a random force with $\langle f \rangle = 0$ and the correlation function

$$\langle f(t) f(0) \rangle = 2\eta_b k_B T m_b^{-1},$$

$$\alpha = 2m_b\omega_b\omega_a\delta\omega$$

where $a = 2m_b\omega_b\omega_a\delta\omega$.

The exchange model has been used for analyzing the spectral data for vibrations of the C=O bond with adsorption of CO on Ni(111).[88-90] For adsorption of CO on

Ni(111) at sufficiently low temperatures a $c(4\times2)$ structure, corresponding to coverage $\theta = 0.5$, was observed first. All CO molecules in this case are in a bridge position. Longer exposures give a $(7/2\times7/2)R\,19°$ ($\theta = 0.57$), structure with every fourth molecule in the position on top of a surface atom, while the remaining molecules are in the bridge position. For molecules in the on top position a large part of the absorption peak is associated with radiation transfer from the molecule in the bridge position owing to the dipole-dipole interaction (see Sec. 5). Therefore the decrease in the width and position of the absorption peak of the molecule in the bridge position also affects the high-frequency peak.

The experimental and theoretical[88] temperature dependences of the width and position of the absorption peak for C=O vibrations with adsorption in the bridge position on the Ni(111) surface are compared in Fig. 9. The values $\omega_b = 220\,\text{cm}^{-1}$, $\eta_b = 37.5\,\text{cm}^{-1}$, and $\delta\omega = 34.4\,\text{cm}^{-1}$ were employed in the calculation. The agreement between theory and experiment is very good. For low temperatures the low-frequency mode is frozen, so that $\Delta\omega$ and Γ are virtually independent of T. It follows from cluster calculations[91] that the frequency of frustrated rotation $\omega_{\text{rot}} = 184\,\text{cm}^{-1}$, while the frequency of frustrated translation $\omega_{\text{tr}} = 76\,\text{cm}^{-1}$, i.e., the frequency ω_b is close to ω_{rot}. According to Ref. 88, for pure rotations $\eta_{\text{rot}} = 40\,\text{cm}^{-1}$, which also agrees with the value employed for η_b. From here it can be concluded that phase relaxation in the case under study is associated with the interaction of high-frequency vibrations with frustrated rotations. For CO molecules in the on top position the observed temperature dependence of Γ and $\Delta\omega$ was weaker; this is attributable to the lower value of $\delta\omega$ in this case.

Another example are the transverse vibrations of H with frequency $\omega_0 = 2097\,\text{cm}^{-1}$ in a hydrogen film ($\theta = 1$) adsorbed on Si(100)-(2×1).[92] The theoretical and experimental temperature dependences of the linewidth are compared in Fig. 10. The calculation was performed by the method of molecular dynamics for a cluster consisting of 44 atoms with Langevin boundary conditions. It follows from the calculation that $\tau^{-1} \lesssim 10^{-2}\,\text{cm}^{-1} \ll \Gamma$. The experimental

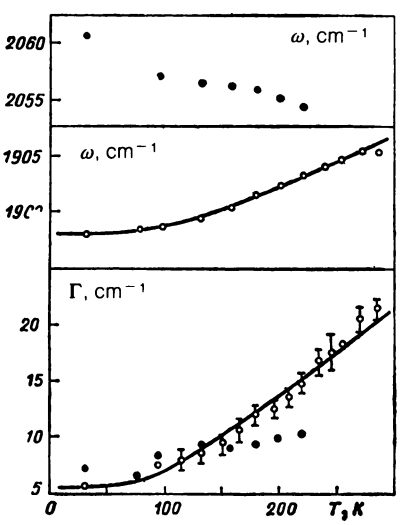

FIG. 9 The position and width of the absorption peaks of C=O vibrations for adsorption on Ni(111) [88] The dots correspond to the bridging and terminal positions of CO; the solid lines are the computed dependences.

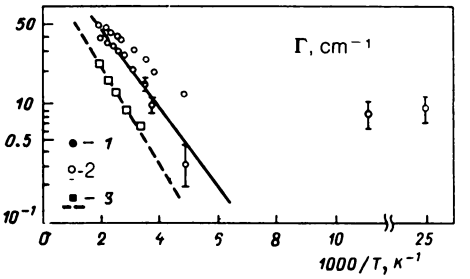

FIG. 10. The linewidth of H=Si vibrations for the system Si(100)-(2×1)H.[92] 1) Experiment; 2) experiment after the contribution of inhomogeneous broadening (9 cm^{-1}) is subtracted out; 3) calculation.

dependence is approximated well by a straight line, whose slope equals $680 \pm 50\,\text{cm}^{-1}$, which agrees well with the theoretical frequency of bending vibrations of the H=Si bond. From here it can be concluded that dephasing of vibrations of H=Si perpendicular to the surface is due to interaction of these vibrations with frustrated rotations of the H=Si bond. An analogous situation also occurs for the system Ge(100)—(2×1)—H, for which at temperatures $T > 250$ K the dependence of the logarithm of the linewidth on the inverse temperature can also be approximated well by a straight line with slope $\sim 500\,\text{cm}^{-1}$, which agrees with the frequency of frustrated rotations $\sim 550\,\text{cm}^{-1}$.[92]

Dephasing of vibrations can also occur owing to elastic "collisions" with substrate phonons. The corresponding calculation for vibrations of CO as a whole with adsorption on Ni(111) was performed in Ref. 93. In this case the interaction Hamiltonian responsible for dephasing has the form $H_{\text{int}} = cO_a^2 Q_2^s$, where c is a constant Q_a is the coordinate of the surface atom, and Q_2 is the coordinate of the vibrations of the local mode of the admolecule. It was found that dephasing makes a contribution of $\approx 1\,\text{cm}^{-1}$ to the linewidth, which is significantly less than the experimentally observed width of $\approx 15\,\text{cm}^{-1}$, associated with decay of vibrations owing to anharmonicity. Analogously for the H/W(100) system dephasing owing to elastic collisions with substrate phonons makes the contribution $\sim 10^{-6}\omega_0$ to the linewidth. It follows from the calculations performed that the dephasing of high-frequency vibrations is efficient if the local phonon density of states of the low-frequency mode has a narrow resonance.

Purely phase relaxation of vibrations of adsorbed particles could also be due to interaction with conduction electrons. This process was studied using the Anderson-Newns model in Ref. 94. It was found that in this case the linewidth $\sim T^3$. Estimates[94] give $\Gamma \approx 20\,\text{cm}^{-1}$ for CO vibrations on Ni(111); this agrees well with experiment.[95]

The dephasing studied above is related with the stochastic character of the motion in a system with many degrees of freedom. Stochastic motion can also occur in systems with a small number of degrees of freedom,[95] in particular, in a system consisting of anharmonically coupled oscillators. In this system with low energy E the vibrations are harmonic. As the energy E is increased the interaction between modes becomes stronger ($H_{\text{int}} \sim E^n$, $n \geqslant 3/2$), and this leads to "beats"—energy exchange between modes. As the energy is increased further above some critical value E_c stochastic motion appears in the system. This effect is described in greater detail in Ref. 95. Here we only note that on stochastization, first of all, the Kolmogorov-Sinaĭ entropy h,

characterizing the rate of spreading of the close-lying trajectories of the motion of the system in phase space, grows rapidly and, second, exponential decay of the time correlation function

$$\langle Q_A(t)\, Q_A(0)\rangle \sim \exp\left(-\frac{\Gamma}{2}t\right), \quad \Gamma \sim h, \tag{6.7}$$

appears, which leads to narrowing of the spectral line. This mechanism of dephasing with two-dimensional motion of the adatom (B type absorption) was studied in Ref. 71. It was shown that for the system H/W (100) $\Gamma \sim 10^{-2}\omega_0 \approx 10$ cm^{-1}. An obvious way to make the model more complex is to increase the size of a cluster, i.e., to increase the number of nonlinearly coupled modes. With the exception of exotic cases (such as the Fermi-Pasta-Ulam paradox[95]) this lowers the threshold for the appearance of chaos ($E_c > 0$).[95] In so doing taking into account the quantum character of the motion of the system does not qualitatively change the results.

7. THE ROLE OF VIBRATIONAL RELAXATION IN SURFACE DYNAMIC PROCESSES

A great deal of attention is traditionally devoted to the study of elementary dynamic processes on a surface, such as diffusion, adsorption-desorption processes, and the elementary stages of chemical reactions, since these processes play an important role in different areas of physics and chemistry, in particular, in heterogeneous catalysis. Dynamic processes on a surface are described with the help of the method of molecular dynamics or the equations of nonequilibrium thermodynamics (Langevin, Fokker-Planck, and Pauli equations). Theoretical analysis of dynamic processes is possible only if the form of the potential energy surface for the motion of adsorbed particles is known. Information about the form of potential surfaces can be obtained from calculations of the electronic structure of the system substrate + adsorbate and from experiments on scattering of molecular beams by a surface. Both these approaches are currently being intensively developed.[96]

An elementary understanding of the role of vibrational relaxation in dynamic processes can be obtained by studying the process of a particle overcoming the activation barrier. If Langevin's equation or the equivalent Fokker-Planck equation is employed to describe the motion of the particle, then the rate constant of the process, as is well-known,[97] has the form

$$k = A\exp\left(-\frac{E_a}{k_B T}\right), \tag{7.1}$$

$$A \approx \frac{\eta E_a}{k_B T}, \quad \eta < \frac{\omega_0 k_B T}{2\pi E_a}, \tag{7.2}$$

$$\approx \frac{\omega_0}{2\pi}, \quad \frac{\omega_0 k_B T}{2\pi E_a} < \eta < \omega_*, \tag{7.3}$$

$$\approx \frac{\omega_0 \omega_*}{2\pi\eta}, \quad \eta > \omega_*, \tag{7.4}$$

where E_a is the activation energy, η is the coefficient of friction, ω_0 is the frequency of oscillations near the position of equilibrium, and ω_* is the frequency corresponding to vibration in the "inverted" potential near the activation barrier. The formulas (7.1)–(7.4) were derived in describing the one-dimensional classical motion of a particle along the adiabatic potential energy surface. Analogous results are also obtained in a quantum description based on Pauli's equation.[62] The multidimensional nature of the motion can be taken into account by premultiplying (7.1) by the partition function of the activated complex and dividing by the partition functions of the starting reagents; the typical values of the preexponential factors so obtained for different processes on a surface are tabulated in Ref. 98. If the process is nonadiabatic, then the expression (7.1) must be premultiplied by a transmission coefficient (the transmission coefficient is calculated in Ref. 99).

In the case of surface processes friction is usually weak, so that the limit (7.4), as a rule, is not realized. On the other hand it is also usually difficult to satisfy the condition (7.2), since the parameter $2\pi E_a/k_B T$ is large for activated processes. Thus the condition (7.3), corresponding to applicability of the well-known[23] theory of the transient state (in the one-dimensional case this theory gives $A = \omega_0/2\pi$), is realized most often.

One would expect, however, that the limit of weak friction (7.2) is realized in the case of adsorption of light particles on the surface of metals, when excitation of electron-whole pairs makes the dominant contribution to friction. In this case any change in the electronic structure of the adsystem, for example, accompanying phase transformations[59,100] or the Kondo effect owing to electronic correlations on the adatom,[49] will change η and therefore A also. Since for the electron-hole mechanism of friction $\eta \sim \rho_a^2(\varepsilon_F)$, where $\rho_a(\varepsilon_F)$ is the electronic density of states for the adatom, any change in the electronic density of states $\rho_a(\varepsilon_F)$ will also give rise to a change in A.[59] For example, for a Peierls transition on the surface of a crystal, which apparently occurs when the (100) face of tungsten and molybdenum[101] is restructed, a gap appears in the vicinity of the Fermi level of the substrate and $\rho_a(\varepsilon_F)$ vanishes, so that friction will be determined primarily by the phonon mechanism. As the temperature of the substrate or the density of adatoms at the point when restructuring vanishes increases, the coefficient of friction should increase sharply; this can be observed by measuring experimentally[2)] the temperature or concentration dependence of the coefficient of diffusion of light atoms (H, D, Li). The rate of energy transfer owing to the electron-hole mechanism depends on the position of the electronic resonance of the adsorbage relative to the Fermi level; it is maximum when the electronic resonance crosses the Fermi level. Thus by changing the position of the electronic resonance it is possible to control the rate of dynamic processes on a surface. The position of the electronic resonance can be changed by applying an external field, by interaction between adsorbed particles, or if the adparticle moves parallel to the surface with a sufficiently high velocity.[63]

The electron-hole mechanism of energy transfer can play an important role in adsorption[41,60] and desorption[62] of light particles. For example, according to Ref. 41 a hydrogen atom incident on the surface of *Ag* with thermal energy ~25 meV completely loses its energy owing to excitation of electron-hole pairs at a distance ~1–2 Å.

For low-frequency vibrations with $\omega_0 < \omega_m$ the coefficient of friction is determined by single-phonon processes[88,102]

$$\eta_{ph} \approx \xi \frac{m_a}{m_s}\left(\frac{\omega_0}{\omega_M}\right)^3 \omega_0, \tag{7.5}$$

where $\xi \approx 1$ is a numerical coefficient (in particular, for De-

bye's model $\xi = 3\pi/2$). Calculations show that for low-frequency vibrations with $\omega_0 \ll \omega_m$ the coefficient of friction owing to the electron-hole mechanism can be of the same order as the phonon coefficient of friction.

Under conditions of weak energy transfer between the adfilm and the substrate the adfilm is very sensitive to external perturbations. External excitation of the adfilm, for example, with laser radiation, an electron beam, or accompanying the emission of field-emission current, can transfer the system into a nonequilibrium state. In this case stimulated surface processes—diffusion, desorption, disordering, attachment, etc., whose rate will be appreciably higher than the thermodynamic equilibrium rate—are possible.[103]

In the case of chemical reactions on a surface the energy of the reaction products immediately after the activation barrier is overcome is usually significantly higher than the thermal energy. If the reaction products then leave the surface, this excess energy can be observed experimentally if the evaporation process is much faster than the relaxation processes in the adsorbed layer. The superthermal energy excess has been observed for a number of dynamic processes.[104] It is interesting that the excess energy is often concentrated in the vibrational degrees of freedom.

The examples studied above show that the information about energy exchange between adsorbed particles and the substrate (in particular, the data obtained based on analysis of the vibrational spectra) has a direct bearing on the dynamic processes at the next level of complexity, such as, diffusion, adsorption, desorption, etc.

8. CONCLUSION

Over the last ten years significant progress has been achieved in developing experimental measuring methods and in the theoretical interpretation of the shape of vibrational spectra of adsorbed particles. It has been established that on a surface, just like in other media, aside from the lifetime purely phase relaxation processes as well as inhomogeneous broadening make a significant contribution to the linewidth. This fact shows, on the one hand, the limitations of the method of IR spectroscopy for determining the lifetime and, on the other, that the method is sensitive to structural, chemical, and dynamic properties of the surface. It should be emphasized that the information content of the method of IR spectroscopy is strongly predicated on the development of theoretical models of the shape of vibrational lines. Numerous examples of the theoretical interpretation of experimental results have been presented in this review.

Further progress in experimentation in the field of vibrational spectroscopy is predicated on more detailed and systematic study of line shapes as a function of the temperature, coverage, isotopic composition of the adlayer, and surface defects. Inhomogeneous broadening owing to the defective nature of the surface, the presence of domains on the surface, etc. and being responsible for the often observed nonreproducibility of results even for systems that are ordered from the viewpoint of LEED, must be studied in greater detail experimentally. Inhomogeneous broadening must also be studied theoretically in greater detail.

Natural broadening, owing to relaxation of the populations and purely phase relaxation, is understood qualitatively quite well. In this area of the theory detailed numerical calculations, whose accuracy is comparable to the experimental resolution, must now be performed. At the present few such calculations have been performed, and they are being held back by the lack of reliable data on the potential energy surface for the motion of adsorbed particles.

From the general physical viewpoint it is of interest to study vibrational spectra experimentally and theoretically under conditions of phase transitions in the adlayer, when a strong change in the line shape can be expected. Such studies are only now beginning to appear.

Progress achieved in the measurement and interpretation of vibrational spectra shows that at the present time vibrational spectroscopy is a powerful method for studying surface processes.

We thank A. G. Naumov for useful discussions.

[1)] In what follows the atomic system of units $\hbar = m_e = e^2 = 1$ is employed everywhere.

[2)] It should be noted that when the preexponential factor changes the activation energy of the process changes at the same time, so that it is a quite difficult problem to establish experimentally the change in the rate of the process owing to a change in the coefficient of friction.

[1]*Surface Physics: Vibrational Spectroscopy* (Russ. transl.), Mir, M., 1984.
[2]Y. J. Chabal, Phys. Rev. B **29**, 3677, 6974 (1984).
[3]W. Ho, R. F. Willis, and E. W. Plummer, *ibid.* **21**, 4202 (1980).
[4]H. Conrad, R. Scala, W. Stenzel, and R. Unwin, J. Chem. Phys. **81**, 6371 (1984).
[5]J. W. Gadzuk and A. C. Luntz, Surf. Sci. **144**, 429 (1984); P. Avouris, and B. N. J. Persson, J. Phys. Chem. **88**, 837 (1984); D. C. Langreth, Phys.Scripta **35**, 185 (1987); R. G. Tobin, Surf. Sci. **183**, 226 (1987).
[6]B. N. J. Persson, Solid State Commun. **30**, 163 (1979).
[7]L. D. landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, London, 1980 [Russ. original, Nauka, M., 1976].
[8]D. C. Langreth, Phys. Rev. Lett. **54**, 126 (1985).
[9]A. A. Abrokosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963 [Russ. original, Fizmatgiz, M., 1962].
[10]M. P. Casassa, E. J. Heilweil, J. C. Stephenson, and R. R. Cavanagh, J. Vac. Sci. Technol. A **3**, 1655 (1985); E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, J. Chem. Phys. **82**, 5216 (1985); Chem. Phys. Lett. **117**, 185 (1985).
[11]H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, N.Y. 1982, p. 188.
[12]O. M. Braun and E. A. Pashitskiĭ, Ukr. Fiz. Zh. **31**, 1839 (1986).
[13]H. Metiu, J. Chem. Phys. **68**, 1453 (1978).
[14]O. M. Braun and E. A. Pashitskiĭ, Fiz. Tverd. Tela **24**, 1973 (1982) [Sov. Phys. Solid State **24**, 1127 (1982)]; Poverkhnost', No. 6, 5 (1984). [Phys. Chem. Mech. Surf. (1984)].
[15]B. E. Stepanov and V. M. Tapilin, Kinet. Katal.**22**, 1376 (1981) [Kinet. Catal. **22**, 1085 (1981)].
[16]S. Efrima, C. Jedrzejek, K. F. Freed, E. Hood, and H. Metui, J. Chem. Phys. **79**, 2436 (1983).
[17]A. I. Volokitin, O. M. Braun, and V. M. Yakovlev, Surf. Sci. **172**, 31 (1986); A. I. Volokitin and O. M. Braun, Poverkhnost', No. 2, 11 (1987). [Phys. Chem. Mech. Surf. (1987)].
[18]A. I. Volokitin, *ibid.*, No. 2, 41 (1988). [*ibid.*, (1988)].
[19]E. S. Medvedev and V. I. Osherov, *Theory of Nonradiative Transitions in Polyatomic Molecules* (in Russian), Nauka, M., 1983.
[20]V. P. Zhdanov and K. I. Zamaraev, Catal. Rev.-Sci. Eng. **24**, 373 (1982); Zh. Fiz. Khim. **59**, 1112 (1985) [Russ. J. Phys. Chem. **59**, 648 (1985)].
[21]S. Andersson, P. A. Karlsson, and M. Persson, Phys. Rev. Lett. **51**, 2378 (1983).
[22]S. Chiang, R. G. Tobin, P. L. Richards, and P. A. Thiel, *ibid.* **52**, 648 (1984).
[23]H. Eyring, S. G. Lin, and S. M. Lin, *Basis of Chemical Kinetics*, Wiley, N.Y., 1980 [Russ. transl. Mir, M., 1983].
[24]V. P. Zhdanov, Teor. Eksp. Khim. **20**, 244 (1984) [Theor. Exp. Chem. (USSR) **20**, 231 (1984)].

[25]V. P. Zhdanov, Surf. Sci. **197**, 35 (1988).
[26]J. E. Black, *ibid.* **105**,59 (1981).
[27]H. Morawitz, Phys. Rev. **187**, 1792 (1969); R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).
[28]B. N. J. Persson, J. Phys. C **11**, 4251 (1978).
[29]P. J. Feibelman, Phys. Rev. B **14**, 762 (1976); **22** 3654 (1980); Prog. Surf. Sci. **12**, 287 (1982).
[30]B. N. J. Persson, Phys. Rev. Lett. **50**, 1089 (1983); B. N. J. Persson and S. Andersson, *ibid.*, 2028; Phys. Rev. B. **50**, 4382 (1984).
[31]V. M. Agranovich, A. G. Mal'shukov, and M. A. Mekhtiev, Zh. Eksp. Teor. Fiz. **63**, 2274 (1972) [Sov. Phys. JETP **36**, 1203 (1973)].
[32]B. N. J. Persson and M. Persson, Surf. Sci. **97**, 609 (1980).
[33]B. N. J. Persson and N. D. Lang, Phys. Rev. B **26**, 5409 (1983). B. N. J. Persson and E. Zaremba, *ibid.* **31**, 1863 (1985).
[34]M. A. Kozhushner, V. G. Kustarev, and B. R. Shub, Surf. Sci. **81**, 261 (1979).
[35]P. Apell, Solid State Commun. **47**, 615 (1983).
[36]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon Press, London, 1984 [Russ. original, Nauka, M., 1982].
[37]A. Campion, A. R. Gallo, C. B. Harris, H. J. Robota, and P. M. Whitmore, Chem. Phys. Lett. **73**, 447 (1980).
[38]A. G. Equiluz, Phys. Rev. Lett. **51**, 1907 (1983).
[39]G. Baym, Ann. Phys. (N.Y.) **14**, 1 (1961).
[40]M. Persson and B. Hellsing, Phys. Rev. Lett. **49**, 662 (1982).
[41]B. Hellsing, M Persson, and B. I. Lundquist, Surf. Sci. **126**, 147 (1983).
[42]B. Hellsing and M. Persson, Phys. Scripta **29**, 360 (1984); B. Hellsing, Surf. Sci. **152/153**, 826 (1985).
[43]E. G. Agliano, P. Kumar, W. Schaich, and H. Suhl, Phys. Rev. B. **11**, 2122 (1975).
[44]G. P. Brivio and T. B. Grimley, Surf. Sci. **89**, 475 (1979); **131**, 475 (1983). T. T. Rantala and A. Rosen, Phys. Rev. B. **34**, 837 (1986).
[45]A. G. Mal'shukov, Fiz. Tverd. Tela **16**, 2274 (1974) [Sov. Phys. Solid State **16**, 1484 (1974)].
[46]B. N. J. Persson and M. Persson, Solid State Commun. **36**, 175 (1980).
[47]H. Ueba, J. Chem. Phys. **77**, 3759 (1982); J. Electron. Spectr. Rel. Phen. **29**, 157 (1983). V. P. Zhdanov, Chem. Phys. Lett. **119**, 550 (1985).
[48]A. I. Volokitin, Fiz. Tverd. Tela **26**, 155 (1984) [Sov. Phys. Solid State **26**, 91 (1984)].
[49]P. W. Anderson, Phys. Rev. **124**, 41 (1961). D. M. Newns, *ibid.* **178**, 1123 (1969).
[50]A. Nourtier, J. Phys. (Paris) **38**, 479 (1977). A. Yoshimori and J. Motchane, J. Phys. Soc. Jpn. **51**, 1826 (1982).
[51]D. C. Langreth, Phys. Rev. **150**, 516 (1966).
[52]W. L. Schaich, Phys. Lett. A **50**, 155 (1974).
[53]J. W. Davenport, Chem. Phys. Lett. **77**, 45 (1981).
[54]R. Ryberg, Phys. Rev. B **32**, 2671 (1985).
[55]A. I. Volokitin, Poverkhnost', No. 5, 36 (1986). [Phys. Chem. Mech. Surf. (1986)].
[56]G. W. Ford and W. H. Weber, Surf. Sci. **129**, 123 (1983).
[57]P. Hollins and J. Pritchard, Surf. Sci. **89**, 486 (1979); R. Ryberg, Surf. Sci. **114**, 627 (1982).
[58]O. M. Braun and A. I. Volokitin, Fiz., Tverd. Tela **23**, 3530 (1981); **25**, 309 (1983) [Sov. Phys. Solid State **23**, 2052 (1981); **25**, 177 (1983)]; Surf. Sci. **131**, 148 (1983).
[59]O. M. Braun and A. I. Volokitin, Fiz. Tverd. Tela **28**, 1008 (1986) [Sov. Phys. Solid State **28**, 564 (1986)].
[60]K. Schonhammer and O. Gunnarsson, *Many-Body Phenomena at Surface*, Academic Press, N.Y. 1984, p. 421.
[61]T. Einstein, J. Hertz, and J. Schrieffer, in *Theory of Chemisorption*, (Ed.) J. R. Smith, Springer-Verlag, N.Y., 1980 [Russ. transl., Mir, M., 1983, p. 256].
[62]B. Hellsing, J. Chem. Phys. **83**, 1371 (1985).
[63]A. I. Volokitin, Poverkhnost', No. 7, (1987).
[64]L. A. Bol'shov and A. P. Napartovich, Zh. Eksp. Teor. Fiz. **64**, 1404 (1973) [Sov. Phys. JETP **37**, 713 (1973)]; V. E. Kravtsov and A. G. Mal'shukov, Zh. Eksp. Teor. Fiz. **75**, 691 (1978) [Sov. Phys. JETP **48**, 348 (1978)]; A. I. Volokitin and A. A. Karpushin, Fiz. Tverd. Tela **22** 2319 (1980) [Sov. Phys. Solid State **22**, 1350 (1980)].
[65]Y. J. Chabal, Phys. Rev. Lett. **55**, 845 (1985); J. Electron.Spectr. Rel. Phenom. **36**, 159 (1986); J. Vac. Sci. Technol. A **4**, 1324 (1986).
[66]A. I. Volokitin, Opt. Spektrosk. **65**, 75 (1988) [Opt. Spectrosc. (USSR)] **65**, 46 (1988).
[67]R. Richter and J. W. Wilkins, Surf. Sci. **128**, 4190 (1983).
[68]J. C. Ariyasu, D. L. Mills, K. G. Lloyd, and J. C. Hemminger, Phys. Rev. B **30**, 507 (1984).
[69]O. M. Braun, Poverkhnost', No. 11, 5 (1987). [Phys. Chem. Mech. Surf. (1987)].
[70]V. P. Zhdanov, Teor. Eksp. Khim. **16**, 229 (1980) [Theor. Exp. Chem. **16**, (USSR) 188 (1980)]; A. Miclavc, Mol. Phys. **54**, 525 (1985).
[71]O. M. Braun, Radiofizika **30**, 788 (1987).
[72]M. J. Puska, R. M. Nieminen, M. Manninen *et al.*, Phys. Rev. Lett. **51**, 1081 (1983).
[73]T. L. Einstein, Crit. Rev. Sol. State Mater. Sci. **7**, 261 (1978); O. M. Braun and V. K. Medvedev, Usp. Fiz. Nauk **157**, 631 (1989) [Sov. Phys. Usp. **32**, 328 (1989)].
[74]O. M. Braun and E. A. Pashitskii, Poverkhnost', No. 6, 5 (1986). [Phys. Chem. Mech. Surf. (1985)].
[75]A. I. Volokitin, Poverkhnost', No. 12, 127 (1985). [Phys. Chem. Mech. Surf. (1985)].
[76]B. N. J. Persson and R. Ryberg, Phys. Rev. B **24**, 6954 (1981); B. N. J. Persson, J. Electron. Spectr. Rel. Phen. **29**, 43 (1983).
[77]M. Schefter, Surf. Sci. **81**, 562 (1979); B. N. J. Persson and R. Ryberg, Solid State Commun. **36**, 613 (1980).
[78]B. N. J. Persson, Surf. Sci. **116**, 585 (1982).
[79]A. I. Volokitin, Fiz. Tekh. Poluprovodn. **13**, 1648 (1979) [Sov. Phys. Semicond. **13**, 960 (1979)].
[80]O. M. Braun, Fiz. Tverd. Tela **22**, 2079 (1980) [Sov. Phys. Solid State **22**, 1212 (1980)].
[81]C. Nyberg and C. G. Tengstal, Phys. Rev. Lett. **39**, 209 (1977).
[82]A. Adnot and J. D. Carette, *ibid.*, 209; D. M. Riffe, L. M. Hanssen, A. J. Sievers, Y. J. Chabal, and S. B. Christmann, Surf. Sci. **161**, L559 (1985).
[83]P. V. Gel'd, R. A. Ryabov, and L. P. Makhracheva, *Hydrogen and the Physical Properties of Metals and Alloys* ([in Russian], Nauka, M., 1985.
[84]K. Lonngren and A. Scott, (Eds.) *Solitons in Action*, Academic Press, N.Y., 1978. [Russ. Transl. Mir, M., 1981].
[85]B. E. Hayden and A. M Brandshaw, Surf. Sci. **125**, 787 (1983).
[86]M. Trenary, K. J. Vram, F. Bozso, and J. T. Yates, *ibid.* **146**, 269 (1984).
[87]C. B. Harris, R. M. Shelby, and P. A. Cornelius, Phys. Rev., Lett. **38**, 1415 (1977); R. M. Shelby, C. B. Harris, and P. A. Cornelius, J. Chem. Phys. **70**, 34 (1979).
[88]B. N. J. Persson and R. Ryberg, Phys. Rev. B. **32**, 3586 (1985).
[89]A. Nitzan and B. N. J. Persson, J. Chem. Phys. **83**, 5610 (1985)
[90]B. N. J. Persson, F. M. Hoffmann, and R. Ryberg, Phys. Rev. B. **34**, 2266 (1986).
[91]N. V. Richardson and A. M. Brandshaw, Surf. Sci. **88**, 255 (1979).
[92]J. C. Tully, Y. J. Chabal, K. Rayhavahari, J. M. Browman, and R. R. Hucchese, Phys. Rev. B. **31**, 1184 (1985).
[93]B. N. J. Persson, J. Phys. C **17**, 4741 (1984).
[94]H. Morawits, Phys. Rev. Lett. **58**, 2778 (1987).
[95]A. J. Lichtenberg and M. Lieberman, *Regular and Stochastic Motion*, Springer-Verlag, N.Y., 1983. [Russ. transl., Mir, M., 1984].
[96]B. I. Lundqvist, *Vibrations at Surface*, Plenum Press, N.Y., 1982, p. 541; *Many-Body Phenomena at Surface*, Academic Press, Orlando, 1984, pp. 93, 453. J. C. Tully, *ibid.*, p. 377.
[97]H. A. Kramers, Physica **7**, 284 (1940).
[98]V. P. Zhdanov, Ya. Pavlichek, and Z. Knor, Poverkhnost', No. 10, 41 (1986). [Phys. Chem. Mech. Surf. (1986)].
[99]V. P. Zhdanov, *ibid.*, No. 12, 5. [*ibid.*, (1986)].
[100]V. D. Borman, A. N. Pivovarov, and V. I. Troyan, Pis'ma Zh. Eksp. Teor. Fiz **39**, 458 (1984) [JETP Lett. **39**, 556 (1984)].
[101]P. J. Estrup, J. Vac. Sci. Technol. **16**, 635 (1979); E. Tosatti, Solid State Commun. **25**, 637 (1978).
[102]V. P. Zhdanov, Poverkhnost', No. 4, 32 (1986); Kinet. Kataliz., **28**, 247 (1987). [Phys. Chem. Mech. Surf. (1987)].
[103]O. M. Braun and E. A. Plashitskii, Poverkhnost', No. 7, 49 (1984). [Phys. Chem. Mech. Surf. (1984)].
[104]V. P. Zhdanov, *ibid.*, No. 2, 14 (1987). [*ibid.*, (1987)].
[105]W. Ho, N. J. DiNardo, and E. W. Plummer, J., Vac. Sci. Technol. **17**, 134 (1980).
[106]N. J. DiNardo and E. W. Plummer, *ibid.* **20**, 890 (1982).
[107]S. Andersson, Chem. Phys. Lett. **55**, 185 (1978).
[108]H. Conrad, R. Scala, W. Stenzel, and R. Unvin, J. Chem. Phys. **81**, 6371 (1984).
[109]C. Nyberg and C. G. Tengstal, Solid State Commun. **44**, 251 (1982).
[110]C. Backx, B. Feurbacher, B. Fitton, and R. F. Willis, Phys. Lett. A **60**, 145 (1977).
[111]A. M. Baro, H. Ibach, and H. D. Bruchmann, Surf Sci. **88**, 384 (1979).
[112]Y. J. Chabal, G. S. Higashi, and S. B. Christmann, Phys. Rev B **28**, 4472 (1983).
[113]M. Trenary, K. J. Uram, and J. T. Yates, Surf. Sci **157**, 512 (1985).
[114]R. G. Tobin, S. Chiang, P. A. Thiel, and R. L. Richards, *ibid.* **140**, 393 (1984).
[115]B. E. Hayden, K. Kretzschmar, and A. M. Bradshaw, *ibid.* **155**, 553 (1985).
[116]D. P. Woodruff, B. E. Hayden, K. Prince, and A. M. Bradshaw, *ibid.* **123**, 397 (1982).
[117]R. Ryberg, *ibid.* **114**, 627.
[118]H. Pfnur, D.Menzel, F. M. Hoffman, A. Ortega, and A. M. Bradshaw,

ibid. **93**, 431 (1980).
[119]A. Ortega, F. M. Hoffmann, and A. M. Bradshaw, *ibid.* **119**, 79 (1982).
[120]B. E. Hayden and A. M. Bradshaw, *ibid.* **125**, 787 (1983).
[121]S. R. Bare, P. Hoffmann, and D. A. King, *ibid.* **144**, 347 (1984).
[122]W. F. Banholzer and R. I. Masel, *ibid.* **127**, 339.

Translated by M E. Alferieff