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Molecular Scattering from Surfaces: Theoretical Methods and Results

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Contents

I. Introduction

The theory of molecular collisions with solid surfaces has gone in recent years through a remarkable period of growth. Undoubtedly, the activity in this field is motivated in part by potential applications to topics of considerable importance in chemistry, physics, and technology: catalysis, ion implantation, crystal growth, and photoconductivity are some of the diverse, frequently mentioned examples. Several other factors were, however, also important in inducing interest and activity in the subject. There has been major progress in experimental methods relevant to the study of molecule–surface interactions, e.g., developments in molecular beam scattering,[1-10] in the application of laser techniques, both to pump molecules to desired initial states and to detect the final vibrational and rotational states of scattered molecules,[11-26] and in the preparation and characterization of clean, well-defined surfaces in both chemical and crystallographic terms.[27,28] Experiments are getting closer, at least for some systems, to the ideal situation in which the initial momentum and internal state of the colliding molecules are selected, and the final momentum and internal state distributions are measured. Such experiments provide a challenge to theory since detailed quantitative tools of interpretation are required to analyze the data. Another boost of major importance to the development of molecule–surface scattering theory came from the impressive increase in recent years in computational power. If modern experiments created a need for quantitative, elaborate treatments of molecule–surface scattering, the performance of present-day computers makes it possible to meet the challenge, and carry out, for certain systems and models, the required calculations. Both the feasibility of many-particle classical simulations and of few particle quantum calculations were greatly enhanced by progress in computer power. Some of the simulations reported in this review became feasible only with

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the availability of supercomputers. Finally, the development of molecule–surface collision dynamics benefited greatly from progress in related disciplines of physics and chemistry in the last two decades. Molecular scattering from surfaces is in a sense a hybrid of gas-phase molecular collision theory with solid-state physics. Methodologies and results from these disciplines were invaluable in the development of the new field.

Several trends can be identified in the recent growth of molecule–surface scattering theory, and these will be reflected in the present review. (1) There is increased emphasis on *quantitative* comparison with experiments. Such quantitative interaction with measured data is pursued now in topics ranging from the diffraction from surfaces (where exact quantum calculations on scattering from a stationary surface model are routinely carried out) to reactive collisions with solids (where classical simulations were employed). (2) Quantum mechanical calculations are increasingly pursued for relatively simple molecule–surface collision processes that could only be treated classically until the last few years. This is the case for vibrationally and rotationally inelastic collision of diatomic molecules in which the distribution of the final quantum states of the scattered molecules is calculated. (3) Many calculations now include dynamically the role of phonons, and considerable effort is invested in the improvement of such treatments. The incorporation of phonon effects is mostly done either by classical calculations that involve the motions of many solid atoms or by stochastic force modeling of the effect of the vibrating atoms (generalized Langevin equation and related approaches). (4) Considerable attention is given to new types of surface systems and processes opened up by new experimental developments (e.g. scattering from disordered overlayers and from defects on crystalline surfaces; astrophysical applications of molecular surface collisions).

The objective of the present review is to briefly describe the main directions of progress in current work on the theory of molecular scattering from surfaces. The survey will outline developments in theoretical methods and techniques, as well as results of theoretical calculations and the insight these provide for the physical understanding of the processes studied. Comparison of theoretical results with experiment is emphasized in the review, but a discussion of the experimental aspects is outside the scope of this article. It should be of considerable benefit to the reader to consult some of the excellent surveys that deal with the experimental state of the art.[1-10] The subject matter covered is strictly confined to collision *dynamics*. Thus the topic of molecule–surface interaction potentials and their properties is not included in the review (except in the context of potentials used in specific scattering calculations). The exclusion of this topic has serious disadvantages, since a major purpose of scattering experiments is to obtain information on the underlying interaction potential. However, the author feels that the subject of molecule–surface potentials should best be treated in a review that covers also the quantum chemical methods for calculating such interactions, which could not be accommodated here. Very useful discussions of molecule–surface potentials are found in some of the previous reviews of the field.[1,8,29] Important for the scattering dynamics, but not included in the present article, are studies of vibrational properties of surfaces, which are receiving considerable theoretical as well as experimental attention at the present time.[30]

Early work on the theory of molecular collisions with surfaces has been discussed in the important textbooks by Goodman and Wachmann[31] and by Steele.[32] Several very useful review articles that describe subsequent developments were published.[2,8,33-36] In this paper we give preference to the most recent lines of developments in the theory, and those which appear at the present time to be of particular promise. The author's judgement of this is entirely subjective and arbitrary to a large extent.

The structure of the review is as follows: section II discusses light atom scattering in the regime where it is dominated by atomic scale structure and corrugation of the target surface. Section III deals with energy transfer from a colliding atom to the surface. Most of the processes dealt with involve excitations of solid vibrations, but treatments of energy transfer to the surface electrons are also discussed. Section IV reviews molecular scattering from surfaces, focussing on rotationally, vibrationally, and electronically inelastic processes at the level of state-to-state transitions. Reactions of small (nearly always diatomic) molecules upon collisions with solid surfaces are the topic of section V. Restriction is made to elementary types of processes and to the simplest, theoretically most tractable systems. Section VI reviews theories of adsorption and desorption processes. Section VII describes recent work on molecule–surface collisions that has an astrophysical context.

II. Diffractive Scattering of Atoms

A. Scattering from Stationary Crystalline Lattices

He scattering has been established as one of the most important probes of surface structure on the atomic scale. The advantages of He in this respect are many, and the recognition of their importance dates back to the earliest stages of the molecular beam scattering field: the technique is not destructive to the surface; only the outermost layer is probed, as there is no penetration into the bulk; the method is sensitive to *local* features of the structure (in principle, more so than LEED, due to the more localized scattering dynamics of massive particles); He atoms with suitable de Broglie wavelenghts (order of ~1 Å) correspond to conveniently obtainable experimental beam energies.

In contrast with these advantages in using He scattering as a probe of surface structure, the quantitative analysis of He diffraction experiments is relatively difficult, e.g., in comparison to the corresponding problem in other diffraction methods such as X-ray or neutron scattering from (bulk) crystals, or even LEED.[37] The difficulty is in determining from the measured diffraction intensities the He–surface interaction potential and the surface structure within the unit cell. Neither the extraction of the interaction potential from the data nor the separation of structural and interaction parameters is a simple task, although with certain assumptions it has been accomplished for certain systems.[6] The first requirement in this respect is to be able to calculate the diffraction intensities for given beam energy and incidence angles, when the atom–surface interaction potential is known. Fortunately, there is considerable physical relevance to solving this problem even in the framework of a static, nonvibrating crystalline lattice. The diffraction intensities from a real (vibrating) crystal are proportional to the intensities calculated from a corresponding static surface model, the proportionality factor being the Debye–Waller (D–W) coefficient.[31] The D–W relation, its limitations, and breakdown are discussed in subsection D below. However, there is substantial evidence from experiments, supported by theoretical considerations, that the D–W approximation is of sufficient accuracy for a wide range of systems and experimental conditions.

The main point of the present subsection is the following: As a result of progress in numerical algorithms and computing power, *the diffraction intensities for light atom scattering from a static, periodic surface model can be calculated essentially exactly by available procedures.* This has been an important development in the field in the last few years. A note is due on the colliders for which diffraction calculations are relevant. Although He is by far the most widely used atomic projectile in studies of diffraction from surfaces, diffraction was measured also for H and Ne atoms (as well as from H_2, HD, and D_2 molecules[38–41]). Ne atoms are relatively little in use, partly because the heavier mass leads to increased inelastic scattering which reduces the magnitude of the coherent (diffraction) scattering peaks. Also, as a larger atom the effective surface atomic scale corrugation experienced by Ne is expected to be typically lower than for He, leading to weaker diffraction. (This is, however, definitely not always true.[42] Relatively pronounced Ne diffraction was measured from metal surfaces[42–44] as well as from alkali halides[45,46].) H is a very interesting collider. The possibility of spin-polarized scattering experiments is an attractive feature, but this is outside the scope of simple diffraction processes discussed here. Experimentally, using H as a probe is complicated in some cases, since for metals and some other solids, strong chemical binding interactions between H and the surface are involved, and these result in sticking effects.

We proceed now to discuss methods for calculation of diffraction intensities in atom scattering from a rigid periodic lattice.

Close Coupling Calculations. This method, familiar from gas-phase collision theory[47] has long been in use also in the calculation of He diffraction from surfaces,[48] where it was among the very first "exact" methods.[48–51] The successful, converged calculations of recent years, even for cases where a considerable number of diffraction channels are open, are basically due to increased computing power.

Consider an atom in impact on a nonvibrating crystalline surface, taken for simplicity to have the structure of a rectangular lattice. The interaction potential V between the atom and the surface depends on z, the distance from the surface plane, as well as on x and y, the coordinates along the unit-cell vectors in the surface plane. By the periodicity of the lattice, V can be expanded in the form

$$V(x,y,z) = \sum_{p,q=-\infty}^{+\infty} V_{pq}(z)\exp(i\mathbf{G}_{pq}\cdot\mathbf{R}) \qquad \text{(II.1)}$$

where $\mathbf{R} = (x,y)$ and

$$\mathbf{G}_{pq} = \left(\frac{2\pi}{a_x}p, \frac{2\pi}{a_y}q\right) \qquad \text{(II.2)}$$

are the reciprocal space vectors corresponding to the lattice constants a_x and a_y. Calculation of the diffraction intensities requires the solution of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z) \qquad \text{(II.3)}$$

where μ is the mass and E the collision energy, with appropriate outgoing wave boundary conditions. We denote by $\mathbf{k}$ the incident wavevector of the atom, related to the collision energy by $E = \hbar^2k^2/2\mu$; $k = |\mathbf{k}|$. Further, we denote by $\mathbf{K}$, the component of $\mathbf{k}$ parallel to the surface plane, and by k_z, the component of the incident wavevector normal to the surface. The periodicity of the surface, eq II.1, suggests the following expression for the scattering wave function

$$\psi(x,y,z) = \sum_{mn}\chi_{mn}(z)\exp[i(\mathbf{K} + \mathbf{G}_{mn})\cdot\mathbf{R}] \qquad \text{(II.4)}$$

where $\chi_{mn}(z)$ is a wave function associated with the mn diffraction channel. The summation in (II.4) extends obviously over both open and closed diffraction channels. Substitution of (II.4) in the Schrödinger equation (II.2) and taking Fourier coefficients with regard to the (x,y) coordinates lead to the coupled-channel (or close-coupling) equation:[31,33,36]

$$\left[-\frac{d^2}{dz^2} + \frac{2\mu}{\hbar^2}V_{mn,mn}(z) - \{k^2 - (\mathbf{G}_{mn} + \mathbf{K})^2\}\right]\chi_{mn}(z) + \frac{2\mu}{\hbar^2}\sum_{m'n'\neq mn} V_{mn,m'n'}(z)\chi_{m'n'}(z) = 0 \qquad \text{(II.5)}$$

where the coefficients $V_{mn,m'n'}(z)$ in (II.5) are defined by

$$V_{mn,m'n'}(z) \equiv V_{(m-m'),(n-n')}(z) = \frac{1}{A}\int V(x,y,z)\exp[i\mathbf{G}_{(m-m')(n-n')}\cdot\mathbf{R}]\,d\mathbf{R} \qquad \text{(II.6)}$$

and A is the unit cell area, over which the integration in (II.6) is carried out. The boundary conditions on the channel wave function are[33]

$$\chi_{m'n'}(z) \rightarrow 0 \text{ for } z \rightarrow \infty \text{ (no penetration into the solid)} \qquad \text{(II.7a)}$$

$$\chi_{m'n'}(z) \rightarrow 0 \text{ for } z \rightarrow -\infty \text{ for closed channels } d_{m'n'}{}^2 < 0 \qquad \text{(II.7b)}$$

$$\chi_{m'n'}(z) \rightarrow (d_{mn})^{-1/2}\exp[id_{mn}z]\delta_{mm',nn'} + (d_{m'n'})^{-1/2}[\exp(id_{m'n'}z)]S_{m'n',mn},\ z \rightarrow -\infty \qquad \text{(II.7c)}$$

for open channels, $d_{m'n'}{}^2 \geq 0$. The index (mn) in (II.7c) denotes the incident diffraction channel, and

$$d_{m'n'}{}^2 = \mathbf{k}^2 - (\mathbf{K} + \mathbf{G}_{m'n'})^2 \qquad \text{(II.8)}$$

Physically, only the incident specular channel $m = n = 0$ is of interest. The complex coefficients $S_{mn,m'n'}$ defined for the asymptotic behavior of the wave functions, form the scattering $\mathbf{S}$ matrix. The probability of scattering into the (mn) diffraction peak is given by

$$P(mn) = |S_{mn,00}|^2 \tag{II.9}$$

hence only a single column of the **S** matrix is of direct physical interest.

The close-coupling equations (II.5) are solved by numerical procedures identical with those used in gas-phase calculations.[47] It should be noted that symmetry of the surface, e.g., the C_{4v} symmetry of a square-lattice array with respect to a normal incident beam, is reflected in symmetry properties of the close-coupling equations[32] via the $V_{mn,m'n'}$ and the $\mathbf{G}_{mn}$. In this way the number of coupled equations that have to be solved can sometimes be drastically reduced by simple transformations.[32] The computational effort required in solving the coupled-channel equation scales, in the more effective procedures, roughly with N^3 where N is the total number of (open and closed) diffraction channels included. The structure of the equations and of some of the algorithms used is such that one can benefit considerably from parallel computing techniques.

The close-coupling approach is undoubtedly at present the most widely used of the "numerically exact" methods for calculating diffraction intensities for an assumed potential. The method was widely applied in recent years to scattering from various types of surfaces,[33-60] ranging from smooth, low corrugation faces of metals[53] to cases of intermediate corrugation as in alkali halide and other ionic surfaces[54,60] and to high-corrugation faces of semiconductors such as GaAs(110).[55] It has proved a powerful tool in the interpretation of experimental diffraction data and the extraction of structural information from such data. One important representative example is the study of Laughlin[73] on diffraction data from GaAs(110), in which he showed the limitations of several interaction potentials based on electron-gas models and established a satisfactory empirical potential. Another example is the analysis of Hutson and Schwarz of selective adsorption resonances in He scattering from ordered Xe on graphite in which information on the interaction potential was extracted.[57] Other applications of the method are found in the studies of Engel and Weare[58] and of Drolshagen et al.,[54] which showed the need for using "soft" rather than hard wall potentials in the respective cases of He scattering from Au(110) and He scattering from LiF(001), and in the work of Ellis et al.,[59] which provided structural information on Xe monolayer and bilayer on graphite and yielded information on the interaction of H atoms (used in these diffraction experiments) with the surfaces involved. The only limitation in using the close-coupling scheme within the framework of the "static" surface treatment and for a crystalline, periodic, system is the computational effort that may be required. Computations become costly when one attempts, e.g., to adjust a multiparameter empirical potential by repeated trial and error calculations. One difficult regime is that of high-energy scattering (e.g., collision energies of the order of several tenths of an electronvolt and higher), when the number of populated diffraction channels can be very large for a strongly corrugated surface. Calculations are tedious also in cases where many (selective adsorption) scattering resonances occur, since such scattering is extremely sensitive to the potential.

Fast Fourier Transform Method for Solving the Time-Dependent Schrödinger.[61] This very recent method, introduced first by R. Kosloff and D. Kosloff in the context of gas-phase scattering problems,[62,63] provides a numerically exact solution of the equations of motion describing the scattering dynamics of quantum mechanical wavepackets. One of the recent trends in molecule–surface scattering theory has been the surge of interest in time-dependent wavepacket methods of both "numerically exact" and approximate varieties. Several methods of this kind have been proposed in the last few years and will be discussed in this review.

The fast Fourier transform (FFT) method seeks a numerically exact solution of the time-dependent Schrödinger equation which, for the atom–static surface system considered here, is

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = H\psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r},t) \tag{II.10}$$

where $\mathbf{r} = (x,y,z)$ are the coordinates, $V(\mathbf{r})$ and μ being defined as in the previous discussion. If at some $t = t_0$, $\psi(\mathbf{r},t_0)$ is known, and if $H\psi(\mathbf{r},t_0)$ is computed, then $\psi(\mathbf{r},t)$ can be obtained for $t_0 + \Delta t$, for sufficiently small Δt, by finite differencing. Using, for instance, second-order differencing (SOD)[61-63] gives, from (II.10)

$$\psi(\mathbf{r},t + \Delta t) \approx \psi(\mathbf{r},t - \Delta t) - 2i\Delta t H\psi(\mathbf{r},t)/\hbar \tag{II.11}$$

Proceeding in this way the entire time evolution of the system is obtained. The difficulty, of course, lies in the need for effectively calculating $H\psi(\mathbf{r},t)$ as a function of $\mathbf{r}$, for each time step, the main problem being with the evaluation of the second derivative $\nabla^2\psi(\mathbf{r},t)$. The FFT solves this as follows: Using the fast Fourier transform algorithm,[62] $\psi(\mathbf{r},t)$ is transformed to $\mathbf{k}$ space. The action of ∇^2 in $\mathbf{k}$ space is just the multiplication by k^2. The FFT algorithm is then used to transform back the result with $\mathbf{r}$ space, schematically

$$\psi(\mathbf{r},t) \xrightarrow{\text{FFT}} \bar{\psi}(\mathbf{k},t) \xrightarrow{k^2} k^2\bar{\psi}(\mathbf{k},t) \xrightarrow{\text{FFT}} \nabla^2\psi(\mathbf{r},t) \tag{II.12}$$

where $\bar{\psi}(\mathbf{k})$ is the Fourier transform of $\psi(\mathbf{r})$. The efficiency of the method is a result of the FFT algorithm. The computational effort scales roughly like $N_g \ln N_g$ where N_g is the number of grid points used in the FFT algorithm. An improved version of the method reduces the error in time propagation associated with second-order differencing by using a propagation scheme based on a Chebichev expansion of the evolution operator.[61,64]

The FFT-finite differencing method for solving the time-dependent Schrödinger equation was applied to He/W(110),[65] and the results obtained were in excellent agreement with close-coupling calculations.[60] The method was also applied to He scattering from the stepped surface Cu(117).[65] The selective adsorption resonances at low collision energies were obtained by the method, as were the multiple rainbow effects at higher impact energies.[65] The greatest advantage of this method probably lies in its applicability to scattering from disordered, nonperiodic surfaces and to crystalline surfaces when phonon effects are included (by a stochastic time-dependent potential, see below). Calculations with the FFT treatment of the time-dependent wavepacket dynamics were reported for both types of problems and will be discussed later on in this review. The close-coupling method, in its present form, seems inapplicable to these important problems. A major advantage of time-dependent wavepacket methods is their applicability to problems which essentially involve a continuum of channels (as is the case, for very different causes, in atom scattering from a static, noncrystalline surface as well as in atom scattering from a crystalline surface when energy transfer to phonons is included). However, the FFT time-dependent wavepacket method could also be of considerable interest in calculations involving static, periodic surface models. It appears difficult to assess its overall effectiveness compared with the close-coupling scheme for such systems, but the present author is inclined to the view that for problems where many diffraction channels are populated, the wavepacket method may prove computationally superior. The computational advantage of the wavepacket approaches lies in the fact that by beginning with an appropriate initial state and propagating it in time, up to the end of the scattering process, one calculates directly only one column of the **S** matrix, i.e., $S_{mn,00}$. In the close-coupling procedure, the entire **S** matrix is obtained, although only a single column is of physical interest, and thus implicit wasted computational effort accrues. Another major advantage, common to all wavepacket methods, is that they offer detailed physical insight into the dynamics, as is the case with classical trajectory calculations. Such physical insight is not easy to extract from close-coupling calculations.

There are other available grid methods for solving the time-dependent Schrödinger equation. One of these methods, employing a finite grid scheme to represent the kinetic energy operator,[66] was in fact applied to surface scattering before the FFT technique. This was pursued in studies by Agrawal and Raff[67] and by Smith, Agrawal and Raff[68] on H scattering from a tungsten surface. While important as pioneering calculations with wavepackets on surfaces, it appears that the method used there cannot compete in numerical efficiency and convergence properties with the FFT algorithm.

Semiclassical Gaussian Wavepacket Method and Related Schemes. This method involves a semiclassical approximation and is thus not "numerically exact", but it gives under certain conditions results of excellent accuracy. The approach is due to Heller,[69] and Heller and Drolshagen[70,71] have applied it to scattering from crystalline surfaces[70] and from disordered surface systems.[71] The main idea, elegantly formulated by Heller,[69] is the following: Heavy particle motion should usually be well described by the propagation of a highly localized wavepacket. It should thus be justified at any instant t to expand the potential in powers of $\mathbf{r} - \mathbf{r}_t$, where $\mathbf{r}_t$ is the position of the center of the wavepacket, and retain only up to quadratic terms in the expression, since the localized particle will only be sensitive to the values of $V(\mathbf{r})$ in a small vicinity of $\mathbf{r}_t$. If an initial Gaussian wavepacket is assumed at some t_0, then within the locally quadratic approximation for $V(\mathbf{r})$ in terms of $(\mathbf{r} - \mathbf{r}_t)$, the Gaussian form is preserved in the state propagation in time. With the assumption of the Gaussian form

$$\psi(\mathbf{r},t) = \exp\left[\frac{i}{\hbar}\{(\mathbf{r}-\mathbf{r}_t)\cdot\mathbf{A}_t\cdot(\mathbf{r}-\mathbf{r}_t) + \mathbf{p}_t(\mathbf{r}-\mathbf{r}_t) + \gamma_t\}\right] \quad \text{(II.13)}$$

where vector notation is used, the following equations are obtained by substitution of (II.13) in the time-dependent Schrödinger equation[69,70]

$$\dot{\mathbf{r}}_t = [\partial H/\partial\mathbf{p}_t] = \frac{1}{\mu}\mathbf{p}_t \quad \text{(II.14a)}$$

$$\dot{\mathbf{p}}_t = -[\partial V_t/\partial\mathbf{r}_t] \quad \text{(II.14b)}$$

$$\dot{\mathbf{A}} = -\frac{2}{\mu}\mathbf{A}\cdot\mathbf{A} - \tfrac{1}{2}\mathbf{V}''_t \quad \text{(II.14c)}$$

$$\dot{\gamma}_t = i\hbar\ \mathrm{trace}\left[\frac{1}{\mu}\mathbf{A}\right] + \dot{\mathbf{p}}_t\cdot\mathbf{r}_t - E \quad \text{(II.14d)}$$

where H is the classical Hamiltonian, E is the classical energy, $V_t = V(\mathbf{r}_t)$, and $\mathbf{V}''$ is the matrix of second derivatives of the potential evaluated at $\mathbf{r} = \mathbf{r}_t$. The center of the Gaussian thus follows classical equations of motion. In addition, the *widths* of the Gaussian, given by the matrix $\mathbf{A}_t$, and its phase change in time. The initial state must generally be represented as a *sum* of Gaussians, the parameters of each Gaussian satisfying equations of the type of (II.14). The solution of the equations of motion for the parameters is easy, so the method is an efficient one to use. The approximation was successfully tested against close-coupling calculations for He diffraction from LiF(001) at relatively high collision energies.[70,72,73] Application of the method to scattering from disordered surfaces, and from a model of a vibrating surface, will be discussed in the forthcoming sections. It is in applications to such problems where the main potential of the method lies. The scheme is intuitively appealing and numerically powerful. It yields good results for high-energy, direct scattering. However, it must be kept in mind that the approximation breaks down in several important cases. Thus, the method cannot describe resonance scattering (in which case the ansatz of a fixed sum of noncorrelated Gaussians does not work). The method also cannot deal with tunneling effects. (The "tails" of the Gaussians can penetrate into classically forbidden regimes, but not the center of the packet.) Difficulties may also arise for potentials for a shape such that the "local quadratic" approximation fails.

Metiu and co-workers[70] suggested that a variational principle can be used to improve upon the simple semiclassical Gaussian wavepacket approximation. In their approach, the minimum error method (MEM), it is assumed that indeed an initially Gaussian wavepacket remains Gaussian at all times, but the restriction to locally quadratic potentials is dropped. The wave function is written as a superposition of Gaussians of the form (II.13), and the parameters $\mathbf{r}_t$, $\mathbf{p}_t$, $\mathbf{A}_t$, and γ_t are determined by minimizing the error functional defined by

$$Err = \int d\mathbf{r}\left(i\hbar\frac{\partial G}{\partial t} - HG\right)^*\left(i\hbar\frac{\partial G}{\partial t} - HG\right) \quad \text{(II.15)}$$

where $G(\mathbf{r},t)$ is a Gaussian of the form of (II.13). For a locally quadratic potential the equations so obtained for the time propagation of the parameters become the same as those of the Heller method. MEM clearly improves on the simple semiclassical Gaussian approximation by removing the restriction on the potentials, but in its present form it is also not adequate in general for describing tunneling effects and resonance scattering (selective adsorption).[61]

Methods of the Distorted Wave Born Series. This numerically exact approach implements essentially a distorted-wave Born approximation[75] pursued to sufficiently high order for obtaining convergence. The method was introduced in surface scattering by Armand and Manson.[76-78] First, the atom–surface potential is decomposed in the form $V(\mathbf{r}) = V^{(0)}(z) + V^{(1)}(x,y,z)$. $V^{(0)}(z)$ is not necessarily the corrugation-averaged, flat surface part of the interaction potential $V(\mathbf{r})$: Some other choice may give improved convergence for highly corrugated surfaces.[79] The scattering states of the Hamiltonian $H^{(0)} = K + V^{(0)}(z)$ (K = the kinetic energy) are used as zero-order states, which are perturbed to arbitrary order by $V^{(1)}(x,y,z)$. An integral equation for the scattering amplitudes is written and is expanded in powers of $V^{(1)}$, which amounts to repeated iteration of the equation. Iteration of the integral equation is pursued numerically until convergence is obtained.[76-78] The method was successfully applied to several systems, including the He scattering from the (110), (113), and (115) faces of Cu.[79] Since formal conditions for convergence were not established, it is not, however, clear whether in some cases the series may not diverge or converge very slowly.

The CCGM Method.[31,36,80] Mathematically this method by Cabrera, Celli, Goodman, and Manson[80] neglects certain continuum-state contributions to Green's function of the scattering process but handles exactly the imaginary part of Green's function as well as the real-valued bound-state contributions to it. From a physical point of view, this approximation is essentially equivalent to an improved distorted-wave Born approximation constructed so as to be flux-conserving (unitary), which the distorted-wave method is not. Another method, closely related to it, is by Wolfe and Weare.[81-83] The CCGM was applied to several systems and played a major role in the early development of molecule–surface scattering theory.[31] It is used much less now, since the results it yields are not of sufficient accuracy for very corrugated surfaces and at high energies.

The Hard Corrugated Surface Model.[34] In this method the interaction potential is assumed to be an infinite hard wall of periodic shape, i.e., a corrugated boundary from which the incoming wave is reflected. The model requires numerical solution or further approximations to yield explicit diffraction probabilities. Initially due to Garibaldi et al.,[84] this method played an extremely important role in the interpretation of atom–surface scattering data.[6,31,84-95] Evidence is accumulating on the inadequacy of the hard wall model as a representation of the true potential in realistic cases.[54,58,59,79,87] The possibility of fitting data adequately with the HCS model is reasonable particularly when data are available for a small range of collision energies. Even with the increased use of more realistic "soft wall" potentials, the model should remain useful as a simple, first-estimate approach in the analysis of diffraction data. Aten and Engel[96] have, for instance, shown that results of a corrugated Morse potential system can be mapped into those of an HCS model to good approximation. They suggest that in this sense the HCS can be used in the fitting of data as a first step in determining a refined soft-wall interaction.

Semiclassical Methods. Miller[97] and Marcus[98] developed, in different versions, a semiclassical theory of striking elegance for molecular collision processes. The transition amplitudes (**S** matrix elements) in that theory are expressible in terms of specific classical trajectories, computed to satisfy certain initial and final boundary requirements (related to the initial and final quantum numbers which label the transition). This semiclassical theory includes interference effects and, in an extension that involves complex-valued trajectories, can also describe tunneling. The Miller–Marcus semiclassical theory was adapted to diffraction scattering by Doll.[99,100] Studies by Doll[99,100] Mosel et al.,[101] McCann and Celli,[102] and Hubbard and Miller[103] provided interesting insights into the scattering dynamics, e.g., on the role of interference effects in He diffraction from LiF(001).[99] Also, in comparison with close-coupling calculations, the method was found to give results of excellent accuracy.[99] Nevertheless, it appears that the method was applied only in relatively few cases, probably because of the relatively complicated computations involved.

A very different type of "semiclassical" approximation is the "Classical Path Method"[104,105] (other terminology can also be found). An essential point of this method is that some degrees of freedom are treated classically, while others are described quantum mechanically. In the context of atom diffraction from a static surface, the simplest version of the method proceeds as follows: Consider $V_{00}(z)$, the flat-surface component of the atom–solid interaction potential $V(\mathbf{r})$ in eq II.1. A classical trajectory, $z(t)$, for the motion of the atom in this potential is calculated, and the result is then substituted in the full potential to yield a time-dependent interaction $V(t) \equiv V(x,y,z(t))$ which can be used to evaluate the transitions between the discrete set of diffraction states $|mn\rangle \propto \exp[i(\mathbf{G}_{mn} + \mathbf{K})\mathbf{R}]$: For this purpose, methods of time-dependent quantum mechanics of bound states can be used.[104] In this version of the method it is assumed that the same classical trajectory can be used for all diffraction transitions. The obvious error in this assumption increases with the order of diffraction (i.e., of the energy transfer from the z to the x,y components).[104] The method does well for the weakly corrugated Ne/W system and gives less satisfactory results for He/LiF(001) where the diffraction transitions are stronger.[104] In improved versions of the method,[104,105] an attempt is made to choose the trajectory so as to be "self-consistent" with the transition, e.g., with regard to energy conservation, which does indeed lead to improved results. The classical path method is relatively economical computationally. Perhaps the most important property of the method is that it can be effectively combined with time-dependent treatments of the role of solid vibrations in the scattering. This subject will be taken up in subsequent sections.

The Sudden Approximation. An adaptation of the Sudden approximation, familiar from gas-phase collisions,[47] to atom–surface scattering was proposed by Gerber et al.[106] The method is confined to scattering conditions and systems for which the incidence momentum in the direction normal to the surface is large compared to the diffractive momentum changes, i.e.

$$k_z \gg |\mathbf{G}_{mn}| \qquad \text{(II.16)}$$

for all diffraction states m,n significantly populated in the scattering process. Several versions of the Sudden approximation, of somewhat different computational advantages, are available.[106] In one such version, the coordinate representation Sudden (CRS), the diffraction probabilities, are given by

$$S_{nm,00} = \frac{1}{A}\int\int e^{i\mathbf{G}_{mn}\mathbf{R}} e^{2i\eta(\mathbf{R})}\,\mathrm{d}\mathbf{R} \qquad \text{(II.17)}$$

where the integration is over the unit-cell area A. $\eta(\mathbf{R})$ is a phase shift for one-dimensional (z axis) scattering, calculated from the potential $V(x,y,z)$ for each fixed (x,y). The Sudden approximation was found to be of excellent numerical accuracy for weakly corrugated systems, e.g., for Ne/W(110),[53] and even for the more corrugated case of He/MgO(100).[60] It was recently used in the extraction of an interaction potential from the measured energy dependence of diffraction intensities in the case of He/MgO(100).[60] However, the approximation is not suitable for low energy-scattering, for high incidence angles (measured from the surface normal), and for systems of relatively large corrugation. The main advantage of the Sudden approximation is that it can be extended to more complicated problems: scattering from disordered surfaces; phonon participation in the scattering; rotationally inelastic molecule–surface scattering. Such applications of the Sudden will be discussed in subsequent sections.

Atom scattering from nonvibrating surfaces is a highly quantitative field, where the major physical effects are well-understood, and the focus is on accurate, efficient computational algorithms. It is nevertheless useful to note, in rather simple examples, how insight into physical effects can be obtained from the available methods. First, consider the occurrence of (corrugation-induced) rainbows.[31,84,107] Rainbow phenomena in general are characterized by the fact that the classical scattering intensity distribution has a weak singularity at some point. Quantum mechanically, a strong (finite) maximum is found at the vicinity of the classical singularity, preceded typically by undulations as the (main) maximum is approached. The experimental manifestation of a rainbow in atom–surface scattering, as observed, e.g., in the case of Ne/LiF(001),[108] is strong peaking of the scattering intensity in a nonspecular maximum. The quantum theory of (corrugation-induced) rainbows in surface scattering is due to Garibaldi et al.[84] Here we consider an interpretation on the basis of the Sudden approximation. If the potential is sufficiently corrugated, the phase shift in $\eta(\mathbf{R})$ in (II.17) will have a strong $\mathbf{R}$ dependence. Also, higher order diffraction peaks can be expected. The integrand in eq II.17 should be a rapidly oscillatory function of the surface coordinates $\mathbf{R}$, which suggests a stationary phase evaluation. The stationary phase conditions for (II.17) are

$$2\frac{\partial\eta(x,y)}{\partial x} = \frac{2\pi}{a_x}m \qquad 2\frac{\partial\eta(x,y)}{\partial y} = \frac{2\pi}{a_y}n \qquad \text{(II.18)}$$

from which the stationary points x_s,y_s are found. The intensity obtained from the stationary-phase evaluation of (II.18) is

$$|S_{mn,00}|^2 \propto \left\{ \mathrm{Det} \begin{vmatrix} \partial^2/\partial x^2 & \partial^2\eta/\partial x\partial y \\ \partial^2\eta/\partial x\partial y & \partial^2\eta/\partial y^2 \end{vmatrix}^{-1/2}_{x,y=x_s,y_s} \right\} \qquad \text{(II.19)}$$

A rainbow occurs if at some m,n the determinant in (II.19) vanishes. If, approximately $\eta(x,y)$ is proportional to the potential $V(x,y,z)$, then the rainbow arises from scattering at points (x,y) on the unit cell where the force acting on the atom has a maximum: This causes both high-order diffraction and sends a high scattered flux in that direction. Hence the (classical limit) singularity. More complicated rainbows are found in high-corrugation systems, when multiple hits of the atom on two (or more) different points on the surface occur.[109] Such rainbows were observed, e.g., in scattering of K^+ ions from W(110) at 35 eV.[110] The Sudden method is not valid for collisions that involve double hits by the atom on the surface. Simple quantum models for such multiple collision rainbows are not available.

Consider now the process of selective adsorption[31] which is a Feshbach scattering resonance[75] in atom–surface collisions. Although referred to as a "quantum resonance", these processes are usually classically allowed: The atom when hitting the surface may convert some of the energy associated with the z motion into energy of motion along the surface. If the amount of z motion energy so transferred is large enough, the atom will remain with the surface. The main quantum mechanical aspect of the process is that the levels in the well are quantized. Typically, the lifetime of the selective adsorption resonances in He–surface scattering is of the order of (1–5) × 10^{-12} s, and the distances over which the trapped atom travels along the surface before regaining sufficient z motion energy and being ejected is 10–30 Å.

The detailed description of selective adsorption resonances in specific systems is computationally demanding, and the behavior of the scattering intensities can be rather complicated.[32,36,57,79,111-113] We consider here a simple model, in the framework of the close-coupling scheme. Suppose that only two diffraction states suffice to describe the scattering dynamics at low energies, the $(m,n) = (0,0)$ and $(1,0)$ states. Assume also that only the two terms $(p,q) = (0,0)$ and $(1,0)$ contribute in the Fourier expansion of the potential (eq II.1). Equation II.5 is a system of two coupled equations for $\chi_{00}(z)$ and $\chi_{10}(z)$. Using one equation to eliminate $\chi_{10}(z)$, one finds after some algebra

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}z^2} + V_{00}(z) + V_{10}\left\{ \frac{\hbar^2}{2\mu}d_{10}{}^2 - \left(\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}z^2} + V_{00} \right) \right\}^{-1} V_{10} - \frac{\hbar^2}{2\mu}d_{00}{}^2 \right] \chi_{00}(z) = 0 \qquad \text{(II.20)}$$

where the $d_{mn}{}^2$ are defined by (II.8). We consider energies low enough so that only the (0,0) channel is open. Consider the energy dependence of $\chi_{00}(z)$: When an energy value is approached such that

$$\frac{\hbar^2 d_{10}{}^2}{2\mu} \equiv E - \frac{\hbar^2}{2\mu}(\mathbf{K} + G_{10})^2 = \epsilon_n \qquad \text{(II.21)}$$

ϵ_n being a bound state of the $V_{00}(z)$ potential, the ef-

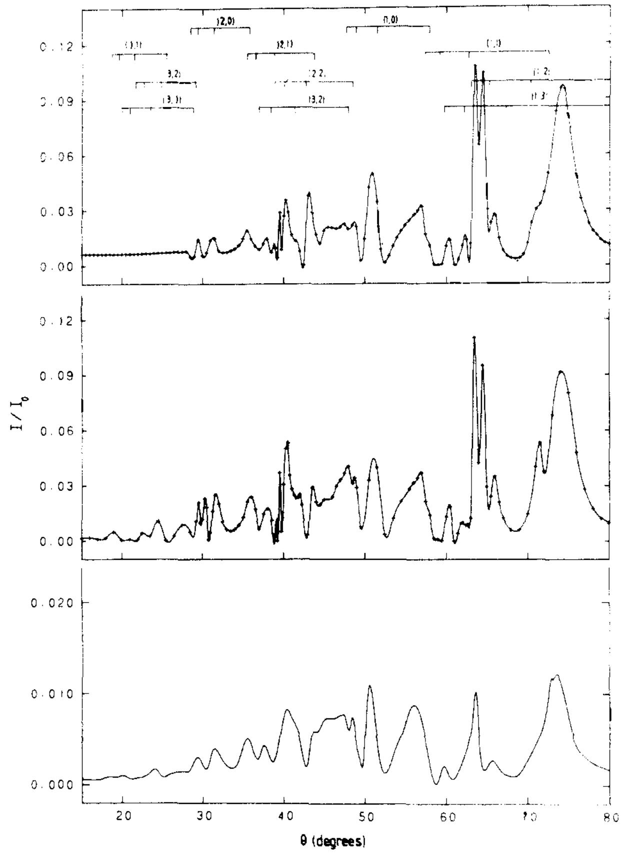

Figure 1. Selective adsorption resonances in the calculated and experimental specular intensity for He scattering from a Xe monolayer on graphite. The relative specular intensity is shown as a function of the incidence angle at azimuthal angle of $\phi = 0$. Top: results of close coupling calculations using a minimal basis of diffraction states. Middle: converged CC calculations with the same potential. Bottom: experimental data. The diffraction state levels of the resonances are shown in the top panel. (Reproduced with permission from ref 84. Copyright 1976 by Elsevier.)

fective potential term in (II.20) becomes singular. Thus at the vicinity of a collision energy that satisfies (II.21), the scattering wave function varies very rapidly with the energy. For the simple model considered here, the specular scattering intensity will not change since only the specular channel is open, and one must have $|S_{00,00}|^2 = 1$. However, there is a phase change in $S_{00,00}$ as a function of energy and it corresponds to a resonance behavior, indeed to trapping by the singular, attractive effective potential term in (II.20). Models with more than one open channel (due to additional open diffraction states or due to phonon participation) will show also a pronounced change in the specular intensity at the vicinity of a resonance, as found experimentally.[31,36] From the energy at which the resonance behavior is observed (typically by monitoring the change in the specular intensity as the incidence angle is varied),[31] the bound states of the $V_{00}(z)$ part of the atom–surface can be determined. This is in practice one of the best probes experiment can provide on atom–surface interactions. Quantitative interpretation of the scattering intensities in the resonance regime in terms of fitting an interaction potential is a far more difficult task, which has however been achieved in several cases, e.g., ref 57 and 59, through the use of the close-coupling or distorted-wave Born series methods, reviewed above. Figure 1 shows results of such intensity calculations from the work of Hutson et al.[57]

B. Interaction Potentials, Surface Structure, and Diffraction Intensities

A major objective in the study of atomic diffraction from surfaces is the determination of surface structure.[6] Since the effect of the surface on the scattered particle is contained in the interaction potential, the determination of the latter is, in principle, an essential step in the search for the structure. The problem of determining atom–surface potentials from diffraction data is also important in its own right. Although such studies can only involve a small group of atoms such as He, H, and Ne, good empirical potentials for some systems could provide very useful benchmark examples against which quantum chemical methods for calculating interactions will be tested. In any case, only in the framework of very special models or assumptions, such as the hard corrugated surface approach discussed earlier, can the issue of structure determination be approached directly, without involing first the recovery of the potential from the data.[6,93-95] There is no complete answer available as yet to the two basic questions: (a) Can a unique atom–surface potential be determined, either by fitting or by direct inversion, from diffraction data (and, perhaps some additional assumptions). (b) Can the complete surface structure be extracted once the potential is known. Partial answers to these questions are, however, available.

The question whether a unique interaction potential can be determined from a complete set of diffraction data (consisting of the intensities of all the diffraction peaks over the entire range of collision energies) was investigated and partly resolved by Gerber and Yinnon.[114] This study was restricted to the framework of the Sudden approximation,[106] and also the interaction potential was assumed to be of the type $V(\mathbf{r}) = V_0(z) + V_1(z)Q(x,y)$ although no functional form was assumed for the $V_i(z)$ and for $Q(x,y)$. The authors have shown that a unique determination of these functions from diffraction intensities only is not possible. *If, however* $V_0(z)$ *is available from some additional source, then both* $V_1(z)$ *and* $Q(x,y)$ *can be uniquely determined from the diffraction data, and an explicit inversion transform can be given to construct these potential components from the data.* Physically, the (m,n) dependence of the diffraction intensities $|S_{mn,00}|^2$ determines $Q(x,y)$, while the energy dependence of the data is used to obtain $V_1(z)$. To obtain a $V_0(z)$ which is necessary as input for this inversion, one can, e.g., determine a $V_0(z)$ from selective adsorption resonances[31] and extrapolate it to the strongly repulsive regime (small z), pertinent to the Sudden inversion. This inversion method was applied by Yinnon et al.[60] to the diffraction intensities measured by Kolodney and Amirav[115] for He/MgO(100). The $V_0(z)$ was taken from Brusdeylins et al.,[116] who obtained it by fitting the selective adsorption resonances they observed. The corrugation dependent part of the He/MgO(100) potential obtained from the inversion was tested and found to reproduce the input intensities to very high accuracy. It is important to stress, however, the implication of the "negative" part of the inversion result, namely, that the interaction potential cannot be uniquely determined even from the most complete diffraction data obtainable (if $V_0(z)$ is not known from another source) whether by fitting or by direction inversion; thus no atom–surface potential can be obtained from diffraction data alone. The problem can be overcome either by additional input of information or by making a restrictive guess on the potential function that plays a role equivalent to additional information.

Little is known in the most general case as to whether diffraction intensities suffice to determine uniquely the atomic structure of the surface. The hard corrugated surface model provides one approximate way of extracting structural information from diffraction intensities.[6,93-95] In some cases it is reasonable to write the interaction between the scattered atom and the solid as a sum of pairwise interactions with each of the surface atoms (and possibly with corrections involving three-body potentials etc.). An example is the study by Hutson and Schwartz[57] on He scattering from a Xe monolayer on the (0001) face of graphite. Whenever the assumption of a pairwise potential can be made in this problem

$$V(\mathbf{r}) = \sum_i V_i(\mathbf{r} - \mathbf{r}_i) \qquad \text{(II.22)}$$

where $\mathbf{r}_i$ is the position of the i solid atom, the extraction of structural information from diffraction data is immensely simplified, even if V_i cannot be taken as the unperturbed, known, gas-phase potential between the scattered projectile and the atom i.[29]

Another useful way by which a link can be established between diffraction intensities and surface structure is by employing a theoretically based relation between the interaction potential $V(\mathbf{r})$ and the surface electron density. The simplest relation of this kind, due to Esbjerg and Norskov,[117-119] writes for the *repulsive* part of a He/metal interaction

$$V_{\text{rep}}(x,y,z) = \alpha\rho(x,y,z) \qquad \text{(II.23)}$$

where α is a system-dependent constant and $\rho(x,y,z)$ the surface electron density. The relation to atomic structure is most easily made if ρ can be expressed as a superposition of atomic charge densities. Diffraction calculations with this approach were carried out by Garcia et al.[121,123] The results of these authors are in some conflict with calculations by Liebsch et al.,[122-124] and the quantitative accuracy of Norskov's relation (II.23) as well as that of the superposition of atomic charge densities for $\rho(r)$ is still an open question.[122-125] The approach based on these assumptions appears, however, very promising, at least as a first approximation.

Another scheme for relating the potential $V(\mathbf{r})$ to the surface electron density is based on using the method of Gordon and Kim.[126] The accuracy of the functional that relates the potential to the electron density in this approximation, very familiar from gas-phase calculations, is also the issue of controversy; Laughlin[55] tested it for He/GaAs(110) and found it unsatisfactory. However, Laughlin did not use the more refined, up-to-date versions of the Gordon–Kim method. More work will be necessary to clarify this issue.

In conclusion, while in its general form, the problem of extracting structural information from diffraction intensities presents formidable difficulties, considerable progress was made by using various assumptions and models in specific cases (e.g., the assumption of pairwise potentials). Further research on this problem, seeking to develop more such models and to refine them, seems most desirable.

C. Scattering from Disordered Surfaces and from Surface Imperfections

This subsection deals with light-atom scattering from disordered noncrystalline surfaces, as well as from crystalline surfaces that contain a significant concentration of imperfections (e.g., vacancies and other defects; adsorbed impurities). The physics of atom scattering from a (nonvibrating) perfect crystalline lattice is well-understood, and the remaining problems are mainly those of developing efficient algorithms for quantitative calculations. The situation for scattering from disordered surfaces is, at present, a very different one, and there are important open problems even at the qualitative and semiquantitative levels of understanding. Some of the main issues in the theory of scattering from disordered surfaces are as follows: (i) what are the main new effects introduced in the scattering pattern by the presence of an imperfection of a given type; (ii) at what concentration of imperfections does the coherent (diffractive) scattering from the surface disappear, and what are the main features that dominate the scattering pattern beyond that point; (iii) how can information on the quantities that characterize the disordered surface structures be extracted from the measured angular intensity distribution of the scattered atoms. In this subsection, as in the previous ones, the discussion is restricted to vibrationally frozen surfaces, although several of the experimentally studied disordered surfaces are systems for which inelastic scattering is very strong (e.g., rare gases adsorbed on a smooth metal surface).[127]

The theory of atom scattering from disordered surfaces is a very new topic, and much of the rapidly increasing activity in this field was motivated by exciting experimental progress in the last few years.[127-133] It was shown, for instance, by Comsa and his collaborators, that at low coverages of an adsorbate on a smooth metal surface, an effective cross section for He scattering can be associated with each adsorbed molecule. This cross section can be measured from the reduction of the specular intensity due to the presence of the adsorbate, and both the magnitude and the energy dependence of the cross section are rather similar to those of the He–molecule gas-phase scattering cross section.[127,128] With use of a geometric interpretation of this cross section, Comsa et al. were able to demonstrate that neither the distribution of adsorbates such as CO on Pt(111), nor that of vacancies on the same surface, is completely random: there appears to be strong repulsion between adsorbed CO molecules at neighboring sites, which excludes or reduces occupation of nearest-neighbor positions around a given CO.[127] Monovacancies on Pt(111), on the other hand, attract each other, and there is thus a propensity for clustering of such defects.[128] By a similar method, using He scattering and applying the cross section concept, it was possible to demonstrate the two-dimensional gas-to-solid phase transition for a Xe overlayer on Pt(111).[129]

The range of methods available for the calculation of atomic scattering intensities from a disordered surface is still relatively small compared with the spectrum of techniques that are used in the pure crystalline case. The difficulties are mainly as follows: (1) In the absence of periodicity, momentum transfer in the direction parallel to the surface is not restricted by Bragg's law to a discrete set of transitions. The expansion analogous to (II.4) in the noncrystalline case involves then a continuum of states. The close-coupling technique and similar methods seem then impractical. (2) A disordered surface corresponds in general to a whole statistical ensemble of microscopically different surface structures. This implies that in principle scattering calculations for many surface structures must be carried out and averaged with appropriate weights, for providing an intensity prediction for scattering from a (macroscopically single) disordered surface.

Time-dependent wavepacket methods seem very promising for calculations of scattering from disordered surfaces, since no expansion in a basis as in close-coupling techniques is involved. So far, only one method for "numerically exact" calculations is available that is applicable in principle to any type of surface disorder, namely, the solution of the time-dependent Schrödinger equation using the FFT algorithm, discussed in subsection A in the context of periodic surfaces.[134,136] The adaptation of this wavepacket method to scattering from disordered target surfaces is straightforward, as only the periodic boundary conditions in the surface (x,y) are affected. Application of the time-dependent method with the FFT algorithm was illustrated for several models representing nonperiodic and disordered surface systems.[134-136] Most of the applications involve two-dimensional scattering calculations, i.e., models in which the "surface plane" is only a line.[134,135] More recently, full three-dimensional calculations were carried out with this method, as in the pure crystalline case.[136] Calculations with the FFT "exact" wavepacket method were carried out for He scattering from (i) an isolated impurity on an underlying periodic surface,[134] (ii) a mixed disordered Xe + Ar overlayer on a smooth metal support,[135] (iii) monovacancies and vacancy clusters on Pt(111).[136]

Several other methods of scattering calculations from nonperiodic and disordered surfaces were proposed which, while approximate, should be applicable for a wide range of systems. The semiclassical wavepacket method of Heller[70] was found to give excellent results for "direct" (i.e., nonresonance) atom scattering from crystalline surfaces, as discussed in subsection A. The method should have a similar scope of applicability for nonperiodic surfaces. It was illustrated by Drolshagen and Heller[71] in calculations of He scattering from disordered stepped surfaces and from randomly arranged adsorbed atoms.

The Sudden approximation[137] is another method that was borrowed from the theory of scattering from crystalline surfaces[106] and easily adapted to disordered and nonperiodic systems. The approximation is designed for cases of high collision energies, relatively low corrugation surfaces, and incidence angles not very far from the normal direction. The method was first used by Gersten et al.[137] to analyze some qualitative aspects of the scattering intensity distribution for various models of surface disorder (e.g., lattice-constant disorder). The method was recently applied to He scattering from an isolated Ar impurity on a corrugated surface, in which case it was also tested against numerically exact wavepacket calculations.[138] At relatively high collision energies (0.0375 eV) and when the underlying surface was of moderate corrugation, the Sudden gave results of remarkable quantitative accuracy. For low-energy collisions (e.g., 0.008 eV) and an underlying surface of much larger corrugation the results were much less satisfactory. The Sudden calculations still reproduced much of the scattering pattern quite nicely but failed in predicting several humps associated with double collision events (in which the He atom strikes the Ar impurity first and then the underlying metal surface or vice versa). The Sudden results were in excellent agreement with the exact calculations also for high-energy He scattering from a mixed Xe + Ar disordered overlayer (at a 1:1 concentration ratio).[138] On the whole, this seems a method of a useful range of potential applicability, although obviously there is also a wide domain of experimental systems and conditions for which it cannot be used.

Several studies were reported of atom scattering from random, hard corrugated surfaces.[139,143] As in the pure periodic case,[84-95] this model brings out very clearly the relation between structural parameters and the scattering intensity.[139,140] Systems such as those studied experimentally in recent years by Comsa and collaborators[127-131] are out of bounds for these methods, since the large effective cross section found there for He scattering by an adsorbed molecule indicates the dominance of long-range attractive forces between the adsorbates and the scattered atom. On the other hand, the model should be very useful for, e.g., high-energy scattering of He from a randomly stepped surface, as pursued by Lapujoulade.[134] Indeed the model seems to reproduce the general behavior of the experimental results[144] (on the variation of the specular intensity with incidence angle), although there are quantitatively important deviations. Rabitz and collaborators[143-146] suggested a new approximation method for atom scattering from disordered as well as from crystalline surfaces. The approximation is referred to by the authors as the average wave function method (AWM). In this method it is assumed first that the interaction between the incoming particle and the surfaces is expressible as a sum of localized interactions with various sites on the target (e.g., the relevant potential may be a sum of interactions with each adsorbate on the surface). In the integral equation that describes the scattering process, the wave function is then replaced by its weighted average over each interaction site. The resulting approximation is valid for low collision energies. The method was applied to scattering from overlayers consisting of a random mixture of two different atoms.[146]

Work is in progress by Armand[147] on the application of a distorted-wave series type of approach to scattering from imperfect surfaces. The interaction of the incoming atom with the periodic part of the target is used as a reference potential, and the effects of the imperfections are introduced by a perturbation series which includes, in principles, all orders of multiple scattering.

We proceed to discuss several aspects of the scattering dynamics, which are predicted or reproduced by the theory for atom scattering from certain nonperiodic

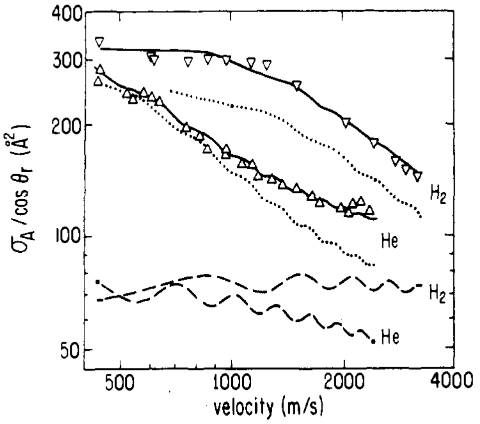

Figure 2. H_2 and He scattering by CO adsorbed on Pt(111) for varying incident velocity and at $\theta_i = 40°$. ∇ is H_2 scattering; Δ is He scattering. Dotted lines: calculated He and H_2 scattering by CO using He–CO and D_2–CO potentials determined by gas-phase scattering. Solid lines: calculated He and H_2 scattering using adjusted potentials. Dashed lines: calculated scattering from a hard hemisphere with radius equal to the classical turning point of the gas-phase D_2–CO or He–CO potentials. (Reproduced with permission from ref 149. Copyright 1984 by the American Institute of Physics.)

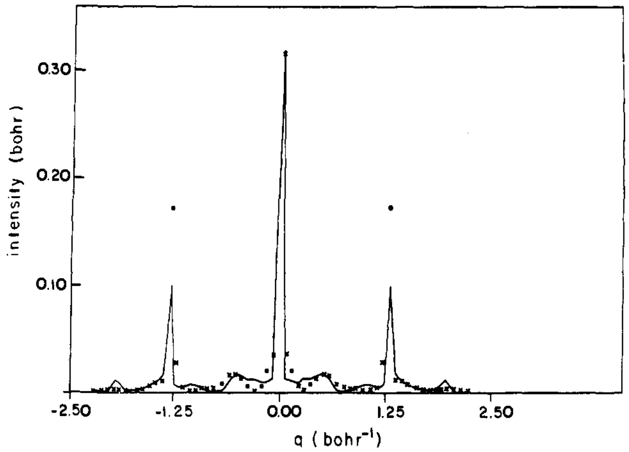

Figure 3. He scattering from a model of adsorbed Ar impurity on a corrugated crystalline Cu surface. The solid lines are results of "exact wavepacket" calculations; the x points are Sudden results. (The Sudden fails for the low energy, E = 8.57 meV, of the calculations.) The maxima not produced by the Sudden are impurity-induced double-collision rainbows. (Reproduced with permission from ref 138. Copyright by the American Institute of Physics.)

and disordered surface systems. The measurements by Comsa et al. of cross sections for the scattering of He atoms by adsorbates and other imperfections on a smooth surface,[127-131] stimulated considerable activity. Jonsson, Weare, and Levi[148,149] developed an approach in which the smooth surface (Pt(111) in the experiments) is treated as a flat, hard wall, which acts as a reflecting boundary condition only in influencing the He scattering, while all nonspecular scattering is due to the impurity. The model gave reasonable agreement with experiment for the velocity dependence of the adsorbate cross section in the cases of He and H_2 scattered from CO adsorbed on Pt(111), as shown in Figure 2.

To obtain such agreement the He/CO and H_2/CO interaction parameters had to be adjusted from the corresponding gas-phase values, presumably representing the polarization effect by the Pt surface on the He/CO and H_2/CO interactions. The effect of the surface on the van der Waals interaction potential between an incoming atom and an adsorbed one was pursued from a first-principle point of view by Gumhalter and Liu[150] and by Liu,[151] who then used the "polarized" potentials in dynamical calculations following the approach of Johnsson et al.[148,149] Bosanac and Sunjic[152] considered He scattering from CO adsorbed on Pt(111), using also the flat hard wall assumption for the underlying surface. They compared results for isotropic and anisotropic molecule adsorbate interactions and concluded that the anisotropy has important effects. All these approaches and recent exact wavepacket calculations on scattering from vacancies on Pt(111)[136] support the interpretation of Comsa et al.[137] that decrease of the specular intensity due to the presence of adsorbates, and the large cross sections associated with this decrease are due to the long-range attractive part of the interaction between the He and the adsorbate.

There is evidence for the failure of the hard flat wall model for the underlying surface for scattering at high incidence angle, where it gives poor agreement with experiment.[152] It appears likely to the author that the attractive part of the Pt surface may play a major role in this case.

A question of basic importance in the field is whether the presence of surface imperfections could give rise to pronounced nonspecular effects in the scattering. A prediction to that effect was made by Gerber et al. on the basis of wavepacket calculations.[134,138] In a model that corresponds to an isolated impurity on a corrugated underlying crystalline surface, the presence of the adsorbate was found to give rise to two major effects: (1) a broad low hump is found superimposed on each diffraction spike of the pure crystalline surface; (2) new maxima in the intensity distribution arise due to the presence of the impurity. Both effects are evident in Figure 3. Analysis has shown that the new maxima are weak rainbows.[134,135] These are in fact due to single collisions at locations having a maximal gradient of the corrugation function (as influenced by the presence of the impurity) or due to double collision events in which the atom hits both the Ar impurity and a "maximum gradient" position on the underlying surface. Similar effects were found for He scattering from vacancies on Pt(111).[138] These impurity-induced rainbow maxima are sufficiently large to allow for experimental detection. Further systematic study of the major effects of isolated imperfections on He scattering is clearly desirable and is being pursued by several groups.

The above calculations are all pertinent to scattering from an isolated adsorbate. A more complicated type of surface nonperiodicity is found in cases of random mixed overlayers.[135,146] Yinnon et al.[135] carried out calculations on a very simplified model of mixed Xe + Ar overlayers on a smooth surface, for a wide range of Xe + Ar concentration ratios. They found that as the pure Xe overlayer is increasingly "doped" with Ar, the incoherent scattering increases, but peaks at the pure-crystalline Xe Bragg positions are identifiable up to a rather high percentage of Ar. The scattering angular intensity pattern is never uniform, even when no coherent diffraction peaks can be identified. The structure still shown by the intensity distribution is due to the particular importance of small clusters of the type of Xe–Ar–Xe in the nonspecular scattering since such clusters have a high corrugation.[135]

D. Temperature Effects

The true interaction potential between an incoming atom and a surface obviously depends on the vibrations of the surface atoms. Most of the surface configurations "seen" by the atom during the collision deviate to some extent from perfect periodicity for any vibrating crystalline lattice, and only the average structure is periodic. As a result, the motions of surface atoms attenuate the coherent diffraction intensities compared with the corresponding values for a reference case of a static nonvibrating solid. This attenuation has long been recognized and studied,[31] as its experimental importance is great. The simplest treatment of the attenuation effect can be given if (1) the collision is "impulsive", to the extent that the incoming atom interacts very locally with one surface atom or with a few neighboring atoms (multiple collision effects are excluded by this assumption); (2) the scattering potential is weak enough, so that a distorted-wave Born treatment can be applied (e.g., with a flat hard wall as a zeroth-order potential); (3) inelastic scattering contributions to the scattering intensity are neglected. The derivation of the temperature effect on the diffraction intensities with these and some other more technical assumptions is then straightforward. The familiar Debye–Waller relation is obtained in similarity to the corresponding celebrated result for X-ray diffraction from crystals:[31,153]

$$I_{mn} = I_{mn}^{0} \exp(-2W) \qquad (\text{II}.24)$$

where W is given by

$$W = \langle(\mathbf{u}\cdot\Delta\mathbf{k})^2\rangle_T \qquad (\text{II}.25)$$

$\mathbf{u}$ is a displacement of a surface atom from its equilibrium position, $\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$ is the difference between the final and initial wavevectors, and the subscript T indicates thermal averaging, I_{mn}^{0} is the diffraction intensity for the (mn) peak for a static lattice obtained if the atoms of the given surface are frozen at their equilibrium positions. I_{mn}, the (approximate) intensity for the vibrating lattice is smaller than I_{mn}^{0} as a consequence of the vibrational instantaneous distortions from perfect periodicity in the real solid. Also, $I_{mn} < I_{mn}^{0}$ expresses the fact that in the vibrating solid also incoherent, nondiffractive scattering takes place and borrows part of the scattered flux. Since W is linear in the temperature, $\ln I_{mn}$ is proportional to T.

Comparison with experiment has shown, however, that the simple Debye–Waller result (II.25) may grossly overestimate the elastic scattering of atoms off surfaces.[31,154,155] This led Beeby[154,155] to suggest that in (II.25) one should not use the precollision incident wavevector for $\mathbf{k}$, but rather one should modify the value of the latter to include the effect of acceleration in the attractive well of the interaction potential.[154,155] For the attenuation of the specular beam the Beeby correction gives[154–156]

$$I_{00} = I_{00}^{0} \exp[-4k^2_{z,\text{eff}}\langle u_z^2\rangle_T] \qquad (\text{II}.26)$$

where u_z is the atom displacement from equilibrium in the direction normal to the surface and

$$\hbar^2 k^2_{z,\text{eff}} = \hbar^2 k_{zi}^2 + 2\mu D = 2\mu(E\cos^2\theta_i + D) \qquad (\text{II}.27)$$

here k_{zi} is the incident (asymptotic) wavenumber in the z direction, μ the mass of the collider, E the incident energy, θ_i the incidence angle, and D the well-depth of the atom–surface potential. Experiments by Hoinkes et al.[157] on H/LiF(100), by Lapujoulade et al. on He and Ne scatering from several single-crystal faces of Cu,[158,159] and by others[160] support the validity of Beeby's correction. At the same time, some of these experiments indicate that the form (II.26) is still not adequate and additional improvements are required.[158,159] One such further correction was proposed by Armand,[161] its physical origin being the fact that the incoming atom may strike, and interact with, not just one surface atom but several neighboring ones. This gives rise to a heavier effective mass of the surface portion that significantly interacts with the collider, and the displacement $|\mathbf{u}|$ associated with that portion is thus smaller than the single atom value previously used. Garcia et al.[162] pointed out that when several surface atoms interact with a projectile, the spatial correlation between these atoms is important, and they cannot be treated as independent. There is still a controversy as to whether the treatment of Garcia et al. fully includes Armand's effect or whether the two corrections are largely independent. A careful examination of the deviation of the Debye–Waller relation in atom–surface scattering and of the role of the various corrections proposed for the D–W factor was presented by Meyer.[163] The present reviewer is of the opinion that presently available data on the thermal attenuation factors can, at least in most cases, be fitted with one of the available "corrected" D–W factors. However, a satisfactory D–W factor form that treats all the corrections mentioned above consistently and in a unified way is still unavailable. Also, there are no general guidelines predicting in which cases will the various corrections be important (except for Beeby's effect). More work is essential before theoretical predictions on the magnitude of D–W factors can be completely freed from some "semiempirical" aspects. Part of the difficulty in developing a satisfactory Debye–Waller factor is most likely due to the fact that ultimately, the factorizable form (II.24) is itself not generally valid. A very promising approach to thermal attenuation beyond the correction factor level was recently introduced by Armand and Manson.[164,165] These authors treat thermal attenuation by a perturbation series approach, in which an expansion is carried out in terms of the part of the interaction potential that represents the coupling of the phonons. For a simple but important class of potentials (exponentially repulsive ones), Armand and Manson carried out phonon averages to all orders. The approach proved very satsifactory in calculating the temperature effect on the specular scattering of He from Cu(100), in particular it reproduces the deviation found in this case from linear behavior of $\ln I_{00}$ with the temperature T,[164,166] as shown in Figure 4. The main limitation of this approach is that simple results are obtained for certain types of potentials only (e.g., exponentially repulsive ones). Also, the final result still contains an adjustable constant.

Another approach to thermal attenuation of atom diffraction beyond the D–W level was formulated by Celli and Maradudin.[166] They use an effective (optical)

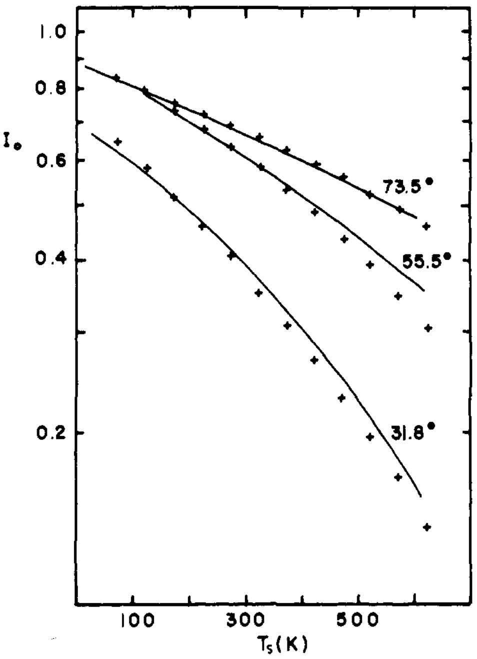

Figure 4. Specular intensity as a function of temperature for He scattering from Cu(110). The collision energy is 21 meV. The solid lines are the theoretical results of Armand and Manson.[164] The + signs show the experimental values. (Reproduced with permission from ref 164. Copyright 1984 by the American Institute of Physics.)

potential to represent phonon effects on the scattering and obtain explicit expressions for the temperature effects on low-order perturbation theory.

An approach of considerable power and flexibility to study the influence of surface vibrations on the angular distribution of atoms scattered from surfaces is based on relating the observable intensities to time-dependent correlation functions of the vibrating atoms.[167-171] Treatments of this type proved extremely useful in the theory of neutron scattering, where the problem is much simpler due to the localized, nonoverlapping force centers in this case. To relate the scattering intensities to the correlation functions in a simple way, approximations such as the classical path treatment of the collider or an impulsive-collision model are invoked. Such methods should be very useful in cases when multiphonon inelastic scattering effects are important, e.g., in high-energy collisions of Li^+ with W(110), studied by Micha.[170,171] It may also be possible to use such approaches to extract information on the vibration dynamics (as contained in the correlation function) from scattering data.

Adams and Miller[172] treated temperature effects on the angular distribution in atom–surface scattering by applying the Sudden approximation with respect to phonon excitation. Also corrugation (diffraction) effects were described in the framework of a Sudden limit (as discussed in subsection II.A). A necessary condition for treating phonon excitations in the Sudden approximation is that the collision time scale should be short compared with the time scale of surface vibrations. The advantage of the approach is that it gives relatively simple results in cases where high-order multiphonon excitations are important. Other methods for the calculation of temperature effects on atom-surface scattering will be discussed in section II, in the context of studies of energy transfer to the solid.

In conclusion of this subsection, considerable progress was made in recent years on quantitative understanding of surface-temperature effects on atom diffraction. However, a complete practical theory is still not on hand. In particular, no satisfactory treatment is available when multiple collisions occur, or in the case of (selective adsorption) resonances.

III. Energy Transfer to the Solid

A. Single Phonon Excitation in He Collisions

Excitation of a single surface vibrational mode by one quantum of energy is the simplest inelastic transition that can occur in atomic collisions with crystalline solids. The occurrence of this basic elementary process is, however, the exception rather than the rule for all but the lightest atomic projectiles and the lower range of feasible collision energies. As physical intuition suggests, the propensity for multiphonon excitation processes increases rapidly with the mass of the incoming atom, with the collision energy, and with the density of soft, low-frequency vibrations of the target system. More quantitatively, the relative importance of single vs. multiphonon excitation processes was discussed by Meyer,[163] Weare,[173] and others. Weare gave the following criterion for the predominance of one-phonon processes

$$\frac{\mu}{M}\frac{E_z T_s}{k_B \theta_D{}^2} < 0.01 \qquad \text{(III.1)}$$

where μ is the collider mass, M the mass of a surface atom, E_z the incidence energy in the direction normal to the surface, k_B the Boltzmann constant, T_s the surface temperature, and θ_D the Debye temperature. Experimental evidence for single-phonon transitions in atom scattering from surfaces dates back to over a decade ago.[174] However, the importance of the topic was enhanced when J. P. Toennies and his collaborators, using a time-of-flight (TOF) technique and high velocity resolutions ($\Delta v/v \approx 0.8\%$), showed that single-phonon transition in He scattering from surfaces could be measured with precision and be turned into a probe of surface phonon spectra.[175,176-178] In this way, phonon dispersion curves were determined experimentally for a large number of insulator crystals (mainly alkali halides),[175,178] of noble metals,[177] etc. A very interesting recent result in the field was the measurement of the phonon dispersion curves of rare-gas monolayers and multilayers (on a metal surface support) by Sibener and collaborators.[179] To determine the phonon spectrum of the surface from TOF measurements of He scattering, the expressions for energy and momentum conservation in the process are employed:[175,178]

$$\frac{\hbar^2(k')^2}{2\mu} = \frac{\hbar^2 k^2}{2\mu} \pm \hbar\omega(\mathbf{Q}) \qquad \text{(III.2a)}$$

$$\mathbf{K}' = \mathbf{K} + \mathbf{G} + \mathbf{Q} \qquad \text{(III.2b)}$$

Here $\mathbf{k}'$ and $\mathbf{k}$ are, respectively, the final and initial wavevectors of the scattered atom; $\mathbf{K}'$ and $\mathbf{K}$ are the final and initial He wavevector components parallel to the surface; $\mathbf{G}$ is a reciprocal space vector, $\omega(\mathbf{Q})$ the frequency of the phonon (created or annihilated in accordance to the ± sign), and **Q** the phonon wavevector. The experimental data, together with eq III.2, yield $\omega = \omega(\mathbf{Q})$, the phonon dispersion curve. Mostly studied in this way were low-frequency Rayleigh modes[175,178] and longitudinal modes.[177] Observation of surface optical phonons in NaF(001) by He scattering was, however, also reported recently.[180] Theoretical calculations of the surface phonon dispersion curves can be carried out from the crystal potential function by available methods of lattice dynamics.[181,182] Comparison of experimental and theoretical results on the dispersion curves has led to significant progress in the knowledge of the potential functions that govern surface atom vibrations.[181,182]

Understanding of the collision dynamics requires a quantitative calculation of the single-phonon inelastic scattering intensities. The approach taken in nearly all calculations of the process follows the suggestion by Levi[168] of using the distorted-wave Born approximation.[183,184] In this method, the "zeroth-order" wave functions correspond to *elastic* diffraction scattering, and can be obtained very accurately, e.g., by close-coupling calculations.[184] The zeroth-order wave functions contain the effects of the (static) surface corrugation, the (elastic) scattering resonances due to the attractive part of the atom–surface interaction, etc. The inelastic one-phonon transitions are then obtained by treating the "dynamical" potential (which represents the coupling of the He atom to surface vibrations) as a perturbation in the framework of first-order distorted-wave Born theory.[183,184] A description of the surface lattice dynamics is essential input in the scattering calculations. Garcia and Benedek[183] and Eichenauer and Toennies[184] reported such distorted-wave Born calculations and compared the results with experiment. As Figure 5 shows, the calculations are able to reproduce most of the structures seen in the experimental angular distributions and time-of-flight spectra. Eichenauer and Toennies examined the selective adsorption scattering regime in He collisions with LiF(001).[184] The experimental findings could be satisfactorily interpreted in terms of one-phonon-assisted adsorption into and one-phonon-assisted desorption out of bound states of the (static) atom–surface potential.

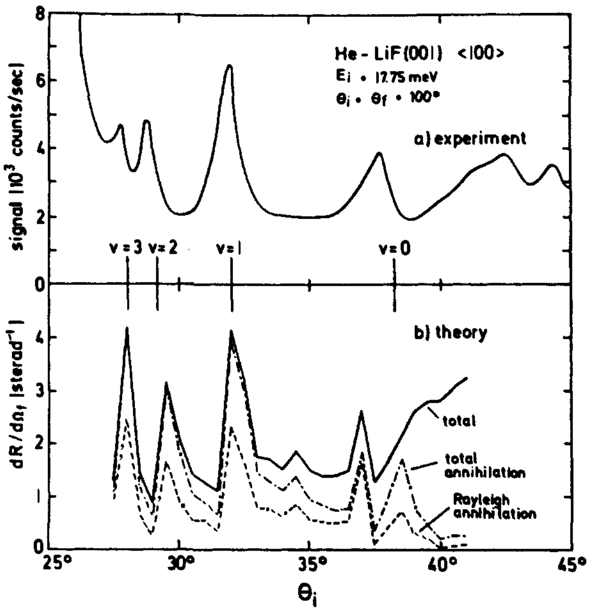

Figure 5. Angular distribution of He atoms scattered along the ⟨100⟩ direction of a LiF(001) surface as a function of the incident polar angle θ_i. The initial kinetic energy of the atom is $E_i = 17.75$ meV; the sum of initial and final scattering angles is kept constant: $\theta_i + \theta_f = 100°$. The experimental curve in (a) is to be compared with the theoretical results in (b). The calculated total one-phonon inelastically scattered intensity (—) as well as the contributions of phonon annihilation processes (-·-) and especially of Rayleigh phonon annihilation (---) are shown. The vertical bars labeled by $\upsilon = 0, ..., 3$ show the expected positions of the initial state resonances involving the surface reciprocal lattice vector and the bound states with vibrational quantum numbers υ. (Reproduced with permission from ref 184b. Copyright 1984 by D. Reidel Publishing Co.)

When the only approximation in the treatment involves the "dynamical" phonon-dependent part of the potential, quantitatively satisfactory results for one-phonon processes in He–surface collisions are evidently obtained. One may, however, choose in some cases the advantage of simplicity of treating the diffraction scattering approximately as well. This line of approach dates back to the early studies of gas–solid energy transfer by Devonshire[185] and Strachen.[186] Several authors developed further these early studies, based on treating both the phonon-dependent and the static, but corrugated part of the potential as perturbation to zeroth-order wave functions determined by the flat part of the surface potential. Contributions along this line were made by Manson and Celli,[187] by Cabrera et al.,[189] by Garcia and Solar,[189] and by several other authors.[190–192] Better than use the distorted-wave type of perturbation for the corrugated part of the potential, one can employ the CCGM approach (discussed in section I) in which framework flux conservation (unitarity) is assured. This was pursued by Manson and Celli,[187] Goodman,[193] and Lagos.[194] The accuracy one can expect from such treatments is essentially unknown, although such methods certainly provide insight into the main effects that can be expected. We note the application to the analysis of scattering data for Ne/Ni(111) which employed this approach successfully.[191]

Obviously when coupling to surface vibrations is sufficiently strong, the distorted-wave approach will fail even when applied only to the "dynamical", phonon-dependent part of the atom–surface interaction. Wolken[195] and Wolken and Lin[196] suggested that one can apply the close-coupling method to treat single phonon processes of this type. Their approach is based on numerical discretization of the coupled channel equations. It is questionable if this approach can be applied to a sufficiently realistic model.

In conclusion, the theory of single-phonon processes in atom–surface scattering is important in two respects: First, it can be compared with the well-resolved experimental data in this field and by reproduction of the measured TOF intensities provide information on the phonon-dependent part of the atom–surface potential. This adds to the basic exploitation of the experiments as a probe of the surface frequency spectrum. Second, single-phonon transitions in He–surface collisions can provide a useful reference case against which methods, designed for more complicated processes (i.e., multiphonon ones), can be tested. Single-phonon processes occur, as was argued at the outset of this subsection, only in few systems. However, in these cases a reasonably reliable working method (distorted-wave treatment with the dynamical perturbation) is available.

This provides a useful limiting case which more versatile theories should reproduce.

B. Classical Models and Simulations of Surface Vibrational Excitation

As pointed out in the foregoing subsection, with the exception of the lightest colliders and of the low-energy collision regime, typical conditions and system parameters are such as to favor multiphonon processes in atomic and molecular impact on crystalline solids. For high-order multiphonon transitions, the classical limit is expected to provide a valid description of the process. Much of the theoretical work on gas–solid energy transfer in atom collisions with surfaces employs classical dynamics, either at the level of a "realistic" elaborate simulation or in the framework of much simpler approximations and models. The following classical methods were used and received considerable attention in studies of energy tranfer between a colliding atom and surface vibrations:

Molecular Dynamics Simulations. This approach is an adaptation to the process of atom/solid energy transfer of the classical trajectory method for many particle systems, known as the "molecular dynamics method". Classical trajectory simulations have been a tool of primary importance in fields ranging from molecular reaction dynamics[47] to the statistical mechanics of gases and fluids.[197] An illuminating discussion of classical trajectory simulations of atomic collisions with surfaces is found in an article by Barker et al.[198] The method involves solution of Hamilton's equations of motion for an atom in collision with a "slab" which has an atomic structure similar to that of the solid it represents. The slab must be sufficiently large (contain a sufficient number of solid atoms), for the results not to be sensitive to the boundary conditions imposed. Periodic boundary conditions are imposed at the boundaries of the slab, in the directions parallel to the surface plane. Most simulations to-date employed harmonic interactions between the solid atoms.[198] This proved insufficient in recent studies by Kolodney et al.[199-201] of high-energy impact of heavy-mass projectiles (I_2, Hg) on solids of light atoms and high vibrational stiffness (e.g., MgO(100)): The excitation in this case involves an anharmonic shock wave component, propagating from the impact zone into the solid.[199,201] In the case of MgO(100), a potential function was constructed from ion–ion pairwise forces which include the required effect of anharmonicity. The time-of-flight experiments of Kolodney et al.[199,201] on I_2 and Hg scattered from MgO(100) in the energy range of 1–10 eV showed that the kinetic energy loss of the projectile had little or no dependence on the surface temperature, for temperature as high as 800 °C. This is also intuitively expected for very high-energy impact, in the absence of special complicating effects. In this case, the approximation can be made in the simulations that the solid atoms are all taken initially at their (classical) equilibrium positions. Simulations using this assumption gave energy transfers in excellent agreement with experiment.[199,201] The simplification gained by this assumption is very large, since then there is no need to sample over the initial positions and velocities of the solid atoms. In all cases where temperature effects are expected, such a sampling is essential. Different solid–atom configurations and velocities must be sampled, e.g., by a Monte Carlo procedure, subject to the canonical distribution function $P(\mathbf{p},\mathbf{q}) \propto \exp[-H_s(\mathbf{p},\mathbf{q})/k_BT_s]$, where H_s is the Hamiltonian of the solid (slab), $(\mathbf{p},\mathbf{q})$ the momenta and positions of the solid atoms, and T_s the solid temperature. In addition to this thermal averaging, sampling is also required with regard to the initial coordinates of the incoming atom in the surface plane, which must cover the unit cell (for a crystalline surface). Pioneering classical trajectory studies of the angular intensity distributions in Ne collisions with LiF(001), including the effects of surface vibrations, were carried out by McClure.[107] This study predicted the occurrence of surface rainbow scattering. Barker et al.[197] studied Ne scattering from Ag(111) and demonstrated the "washing out" of the rainbow structure as surface temperature is increased. The classical trajectory method is a rigorous one and provides detailed insight when atom motions are analyzed. On the other hand, it is computationally very demanding (if temperature averaging of the solid atoms initial conditions must be carried out). The computational effort is largest for collisions that involve trapping, since the long-lived trajectories that must be evaluated in such cases can be subject to an accumulation of numerical integration errors, numerical instabilities, etc. Also, the more resolved the observables one is pursuing, the harder are the demands on the trajectory statistics. To compute the joint angular and velocity distribution of the scattered atoms, for instance, requires many more trajectories than are necessary to calculate the distributions in one of the variables only. The feasibility of molecular dynamics calculations of surface scattering is likely to increase considerably in forthcoming years, partly because of expected developments in computing (i.e., "dedicated" processors for such calculations are becoming available) and partly also because of improvements in algorithms that can be anticipated, at least in the view of the present reviewer.

Method of Generalized Langevin Equation (GLE). This method has been extensively applied to energy-transfer processes in collisions of atoms and molecules with surfaces. It is clearly one of the major tools in the field at the present time. The GLE method was motivated and inspired by the Zwanzig–Mori–Kubo[202-204] formalism of nonequilibrium statistical mechanics. Adelman and Doll[205] recognized that with suitably physically based adaptations, this formalism could be turned into a powerful instrument for simulations of many particle dynamics, including molecule–surface scattering. Adelman and Doll[205] provided on this basis a very elegant and intuitively appealing approach. The application of the method to atomic and molecular collisions with surfaces is mainly due to contributions by J. C. Tully and co-workers in recent years.[34,35,206-211] Adelman and Doll[205] utilized in their approach the recognition that molecule–surface energy transfer is typically dominated by localized interaction, i.e., upon impact on a give site the molecule couples strongly to it and transfer energy directly to atoms in its vicinity. Sufficiently far away atoms are however not directly coupled to the molecule, although energy may ultimately be transferred to them via atoms near to the collision site. The solid atoms are thus divided into (i) "primary zone" atoms which are included explicitly in the calculation at the detailed level of molecular dynamics, and (ii) secondary atoms, further removed from the collision site and not directly coupled to the collider. The effect of these atoms on the collision process can be described by a stochastic model involving friction and a fluctuating force. The fundamental assumption which leads to a practically feasible, effective form of the method is that *interactions among secondary atoms are purely harmonic.* The secondary atoms can then be eliminated from the explicit equations of motion, and the following generalized Langevin equations are obtained for the primary atoms (including the collider)[205,206]

$$\dot{\mathbf{r}}_p(t) = M_p^{-1}\mathbf{p}_p(t) \qquad \text{(III.3a)}$$

$$\dot{\mathbf{p}}_p(t) = \mathbf{G}[r_p(t)] - \int_0^t \Delta(t - t')\dot{\mathbf{r}}_p(t')\,\mathrm{d}t' + \mathbf{R}(t) \qquad \text{(III.3b)}$$

where matrix notation is used, $\mathbf{r}_p(t)$ being the position of the p primary zone atom at time t, $\mathbf{p}_p(t)$ its momentum, M_p the mass of atom p, $\mathbf{G}(\mathbf{r}_p)$ the local force function acting on atom p, and $\mathbf{R}(t)$ a fluctuating "stochastic" force representing part of the effect of the secondary atoms on the primary ones. Another effect is given by the integral in (III.3b), which is a friction term representing dissipation into the secondary lattice and which includes memory effects. The friction kernel $\Delta(t - t')$ and the fluctuating force are related by the "second fluctuation–dissipation theorem",[204] familiar from nonequilibrium statistical mechanics

$$\Delta(t) = k_{\mathrm{B}}T\langle\mathbf{R}(t)\mathbf{R}(0)\rangle \qquad \text{(III.4)}$$

i.e., $\Delta(t)$ is a correlation function of the random force. Formally the GLE equations (III.3) represent an enormous simplification over Hamilton's equations of the total system, since the number of primary-zone atoms is typically of the order of 5–50, while the secondary zone is, in principle, an extended system. As pointed out by Tully,[206] the difficulty has not been eliminated but "buried" in the functions $\mathbf{R}(t)$ and $\Delta(t)$, the exact calculation of which is equivalent to solving the classical equations of motion for the full system. The real advantage of the GLE is in the fact that simple models seem to provide a sufficiently accurate description of the "stochastic" quantities, for the purpose of scattering calculations.[206–211] In such models the random force is constructed so as to satisfy the fluctuation–dissipation theorem. Thus, known vibrational properties such as the phonon frequency distribution are used in calibrating a kernel function, $\Delta(t)$, consistent with the input.

As used in practice, the GLE scheme is thus an approximation, although in principle it could be made "exact" if a true $\mathbf{R}(t)$ (hence $\Delta(t)$) could be obtained. There is ample evidence of successful applications of the GLE in the context of interpreting experimental data of molecule–surface scattering.[206–211] The present reviewer believes that it should be most desirable, however, to test the method further against "full" molecular dynamics simulations. Direct comparison with experiment is not always a sufficiently conclusive test, because the applications usually involve many unknown potential parameters: Reproduction of experimental data could perhaps be fortuitous in some cases, and a direct comparison with an "all particles" classical dynamics calculation could be a better guide for assessing the accuracy of presently accepted models of $\Delta(t)$.

Hard-Cube Model. The original version of this model is due to Goodman[212] and to Logan and Stickney.[213] Several modifications and extensions of the model have been proposed.[214–218] Basically this model in its simpler version replaces each surface atom by a flat surface segment, constrained to move in the direction normal to the surface only. Assuming the surface "segments" or "cubes" behave as independent particles when colliding with the incoming atom and taking a hard-wall interaction between the collider and the "cube", one can readily obtain from kinematics expressions for the velocity distribution, angular distribution, and mean-energy transfer of the scattered atoms.[214–218] Comparison of the model to experiment gave satisfactory results especially for averaged quantities such as the mean-energy transfer. The model is valid only when μ/M, the ratio of gas to surface atom mass, is less than unity. Grimmelmann et al.[210] extended the model by incorporating heuristically the effect of a square-well attractive potential. Also, Steinbrüchel[217,218] and Barker and Auerbach[215] proposed a version in which the "cube" or flat surface segment is replaced by a "spherical cap", also subject to a hard-wall interaction. Some of the results obtained by the "hard-cube" model in comparison with experiments are discussed below.

Soft-Cube Model. Logan[214,219] describes this model as the logical extension of the "hard-cube" approximation. In this model it is also assumed that the surface is locally flat, but a "soft" exponential function is taken to model the repulsive atom–surface interaction.[214,219,220] Surface atoms are treated in the simpler versions of this model as local Einstein oscillators. The equations of motion are solved perturbatively; i.e., first the trajectory of the incoming atom is computed, neglecting energy transfer to the solid. Then with use of this trajectory in the atom–surface interaction potential, a time-dependent force on the surface oscillators is obtained, and the energy transfer due to the latter is calculated. The "soft-cube" model was applied to calculations of angular distributions and of accommodation coefficients in atom–surface collisions. As the hard-cube model, it is inapplicable when surface corrugation is strong, and plays a major role, and when energy transfer is so large as to greatly modify the trajectory of the scattered atom. An excellent, if not recent, account of this method is given by Logan.[213]

We consider now several properties of atom/surface energy transfer, as unfolded in comparison of experimental results with theoretical calculations by the methods discussed above.

The mean final energy of an Ar scattered from a tungsten surface was found by Janda et al.[221] to be linear in the incident energy and in the surface temperature, i.e.

$$\langle E_f\rangle = a_1E_i + a_2k_{\mathrm{B}}T_{\mathrm{s}} \qquad \text{(III.5)}$$

where $\langle E_f\rangle$ is the mean final energy of the atom, E_i the initial energy, and T_{s} the surface temperature. The coefficients a_1 and a_2 are independent of E_i and T_{s} but dependent on the incidence angle of the incoming beam. Barker and Auerbach[215] and Grimmelmann et al.[216] have shown that this relation can be derived from the

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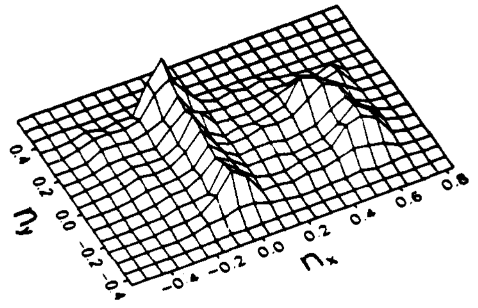

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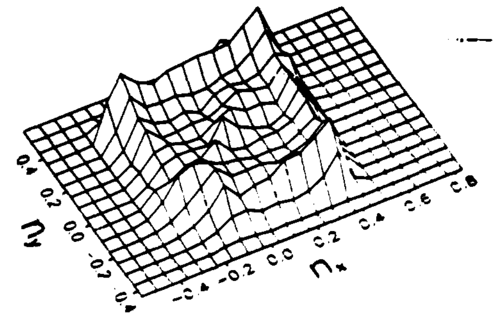

Figure 6. Differential cross sections for Ar scattered from Si(100) at a surface temperature of 300 K. Initial conditions are $\theta_i = 45°$ and $E_i = 0.65$ eV. (a) Scattering from (2 × 1) reconstructed surface. (b) Scattering from unreconstructed surface. (n_x,n_y) is a vector of unit length in the direction of the *difference* between the final and initial moments.

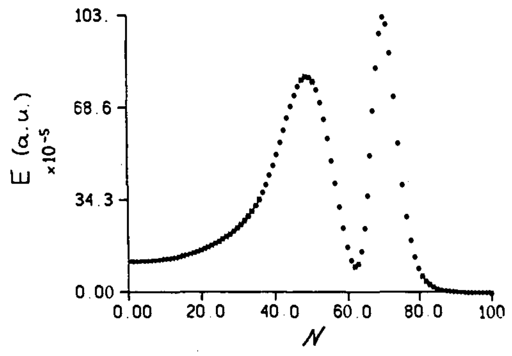

Figure 7. Shock wave produced by Hg impact at 9 eV on MgO(100). The figure shows the energy in each crystal layer N (where $N = 0$ is the surface layer). The results shown are for a "snapshot" at time t corresponding to the end of the collision (from ref 200).

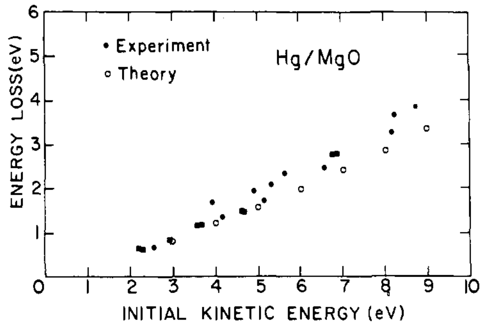

Figure 8. Hg energy loss in collision with MgO vs. the collision energy (results from ref 200).

hard cube model. Interestingly, a relation of the type of (III.5) is also obtained from information theoretic arguments (representing a statistical treatment of gas-solid energy transfer), as shown by Levine and Silbey.[222]

The angular distribution of atoms scattered from surfaces has been the pivot of considerable theoretical and experimental attention. A very interesting effect that can be manifested by the angular distribution in the case of a sufficiently corrugated surface is that of surface rainbow scattering, discussed in section I, which was studied theoretically for a vibrating surface by both the molecular dynamics method[107,198] and by the GLE approach.[211] Barker et al.[198] showed in simulations of Ne scattering from Ag(111) that at sufficiently high surface temperature, the surface rainbow intensity structure is ultimately "washed out". Lucchese and Tully explored the scattering of Ar from both unreconstructed and reconstructed Si(100). The purpose of this study was to explore whether rainbow scattering of a heavy atom could replace He diffraction as a probe of surface structure. It was found (see Figure 6) that the main rainbow feature survived thermal averaging at room temperature and that the corrugation parameters can accurately be determined from the observed (simulated) rainbows. This encourages the hope that rainbow scattering of atoms heavier than He can serve as an additional structural probe, interpretable by classical calculations rather than by quantum diffraction theory.

There seem to have been thus far few studies involving impact at high energies of a heavy atom onto a crystal of light atoms. In recent studies on I_2/MgO(100)[199,201] and Hg/MgO(100)[200,201] a rather interesting new type of solid vibrational excitation was predicted: The molecular dynamics simulations show that upon impact of the high velocity projectile on the light surface atoms, the solid atoms recoil at high velocity generating a coherent cascade of collisions in the crystal. This takes the form of a shock wave, propagating from the surface collision zone into the bulk. The shock wave is relatively narrow and travels over substantial distances (>100 Å) without changing its profile significantly. It is rather sensitive to crystal anharmonicity, and Gerber and Elber[223] found that this excitation can be described approximately and phenomenologically as a soliton. The heavy atom may not recoil from the surface after initiating the pulsed shock wave but may "press on" by inertia, over a time scale of $\sim 10^{-13}$ s to create a second pulse, more spread out hence more harmonic in nature. Figure 7 shows results obtained in classical trajectory simulations of Hg/MgO(100).[200,201] Given is the energy in the crystal as a function of the distance (measured in unit cells) from the outermost surface layer at a time corresponding to the end of the collision. The "soliton like" shock wave and the broader second pulse are clearly seen. Details of the model are discussed by Kolodney et al.[199,200] and by Gerber and Amirav[201] and Gerber and Elber.[223] The "shock-wave" excitations predicted by molecular dynamics could not be tested directly yet. However, the energy transfer calculated from the model is, over a range of collision energies, in good agreement with experiment (see Figure 8). In any case, it appears reasonable that the result of the "shock-wave" excitations in the case of Hg/MgO(100) is merely a first example of anharmonic excitation phenomena in atom impact on surfaces.

C. Semiclassical Treatments of Energy Transfer to Phonons

Between the quantum mechanical regime of single phonon excitations in He scattering and the near-classical behavior expected for high-energy, heavy-atom impact on surfaces, there is a wide intermediate range, where semiclassical methods seem a natural choice. Most of the proposed and practiced semiclassical approaches to gas–solid energy transfer treat some of the degrees of freedom classically, while other modes involved are described quantum mechanically. Mixed classical–quantal methods become especially important for phonon participation in *molecular* scattering from surfaces. There are considerable advantages in this case to a scheme that can offer a detailed quantum description of the internal states of the molecule, given that the distribution of such final states in surface collisions were measured for several systems.

Some of the methods discussed below treat surface motions classically, while the projectile is described quantum mechanically; other methods apply quantum mechanical equations of motion to the surface oscillators and employ classical dynamics for the colliding atom. The choice depends, obviously, on the physical properties and systems for which the method is designed. In any approximation that mixes classical and quantal degrees of freedom, the question of the consistency of the treatment arises. One approach, followed in different versions by several authors, is based on using the time-dependent self-consistent field (TDSCF) approximation.[224] Let **r** be the position vector of the atom and denote by **q** the phonon coordinates. In the TDSCF approximation it is assumed that the total time-dependent wave function can be approximately factorized in the form

$$\psi(\mathbf{r},\mathbf{q},t) = \phi_1(\mathbf{r},t)\phi_2(\mathbf{q},t) \tag{III.6}$$

This is substituted in the time-dependent Schrödinger equation for $\psi(\mathbf{r},q,t)$

$$i\hbar\frac{\partial\psi}{\partial t} = \left[H_{\mathrm{ph}}(\mathbf{q}) - \frac{\hbar^2}{2\mu}\nabla_{\mathrm{r}}^2 + V(\mathbf{r},\mathbf{q})\right]\psi \tag{III.7}$$

where $H_{\mathrm{ph}}(\mathbf{q})$ is the Hamiltonian for the solid phonons and $V(\mathbf{r},\mathbf{q})$ the atom–surface interaction. From (II.6) and (II.7) one obtains the TDSCF equations for atom–surface scattering

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathrm{r}}^2 + V_{\mathrm{A}}^{\mathrm{eff}}(\mathbf{r},t)\right]\hat{\phi}_1(\mathbf{r},t) = i\hbar\frac{\partial\hat{\phi}_1(\mathbf{r},t)}{\partial t} \tag{III.8a}$$

$$[H_{\mathrm{ph}}(\mathbf{q}) + V_{\mathrm{ph}}^{\mathrm{eff}}(\mathbf{q},t)]\hat{\phi}_2(\mathbf{q},t) = i\hbar\frac{\partial\hat{\phi}_2(\mathbf{q},t)}{\partial t} \tag{III.8b}$$

where $\hat{\phi}_1(\mathbf{r},t)$ and $\hat{\phi}_1(\mathbf{q},t)$ are related to $\phi_1(\mathbf{r},t)$ and $\phi_2(\mathbf{q},t)$ of eq II.6 by physically unimportant phase factors. Phonon effects on the atom dynamics are contained in the potential

$$V^{\mathrm{eff}}{}_{\mathrm{A}}(\mathbf{r},t) = \langle\hat{\phi}_2(\mathbf{q},t)|V(\mathbf{r},\mathbf{q})|\hat{\phi}_2(\mathbf{q},t)\rangle_{\mathrm{q}} \tag{III.9a}$$

and similarly the perturbation of the phonon vibrations by the incoming atom as described by

$$V_{\mathrm{ph}}^{\mathrm{eff}}(\mathbf{q},t) = \langle\hat{\phi}_1(\mathbf{r},t)|V(\mathbf{r},\mathbf{q})|\hat{\phi}_1(\mathbf{r},t)\rangle_{\mathrm{r}} \tag{III.9b}$$

Equations III.8 and III.9 are solved self-consistently in quantum mechanical TDSCF.[224] Mixed quantum classical treatment can now be introduced without violating consistency of the treatment, conservation of energy, and other properties.[224,225] To treat for instance the phonons classically, the Hamilton equations for the surface vibrations are solved by using the effective time-dependent Hamiltonian on the left hand side of (III.8b). Also, the quantum average in (III.9a) is replaced by its classical limit obtained by using classical trajectories for the phonons: $V_{\mathrm{A}}^{\mathrm{eff}}(\mathbf{r},t) = V(\mathbf{r},\mathbf{q}(t))$. Such mixed classical–quantal TDCSF was studied in detail for several gas-phase processes by Gerber et al.[225] where they proved quantitatively in good agreement with quantum TDSCF, provided the appropriate choice is made as to which dynamical variable is treated classically. Unlike the simplest mixed classical–quantal treatments mentioned in the context of classical path methods in section II, the approach via TDSCF to "mixed" dynamics does not violate energy conservation, time-reversal symmetry, etc.[225] Several studies of gas–surface scattering processes use this method or some modification thereof and will be discussed in this and other sections. Kosloff and Cerjan[224] studied He desorption and scattering from a Pt surface at the temperature range of 100–800 K. Obviously, in this case a quantum treatment of the He and a classical description of surface vibrations are called for. This was carried out in terms of a TDSCF approximation, as discussed above. Kosloff and Cerjan solved the time-dependent Schrödinger equation for the He scattering by the fast Fourier transform algorithm, discussed in section IIA, and dealt with surface atom vibrations by the generalized Langevin equation scheme, the classical and the quantum mechanical equations being solved self-consistently. De Pristo and collaborators[227-230] studied molecular collisions with surfaces by an approach that treats surface vibrations by the GLE method, while internal degrees of freedom of the molecule and its diffractive motion are handled quantum mechanically. Also the translation normal to the surface is described by a classical trajectory. Consistency of the classical and quantum mechanical motions is obtained in this scheme by enforcing an energy conservation condition.[105] To solve the time-dependent Schrödinger equation for the quantum degrees of freedom, De Pristo et al. expand in a basis set of stationary wave functions and then calculate the time-dependent coefficients.[105,227-230]

Jackson and Metiu[231] developed a semiclassical approach for dealing with the effect of surface vibrations on diffractive scattering. Jackson and Metiu treat the scattered projectile by a semiclassical Gaussian time-dependent wavepacket method, as discussed in section II.A. The vibrations of the surface are modelled by GLE equations. While in De Pristo's theory one translational degree of freedom (the motion normal to the surface) of the incoming particle is handled classically, Metiu's approach applies semiclassical wavepackets to all the coordinates of the colliding atom, as in the Drolshagen–Heller scheme.[70] Treating also the motion normal to the surface by wavepackets is advantageous when interference effects are present in the dynamics along that coordinate.

For heavy projectiles and for surfaces at low temperatures, it can be argued that one should prefer using classical dynamics for the collider, while treating the target solid as quantum mechanical oscillators perturbed by the collision process. Such an approach benefits from the simple properties of driven quantum harmonic oscillators, which give rise to tractable equations even in the regime of wave mechanics. Such an approach was formulated by Billing,[232] who applied it to multiphonon excitation in Ar collisions with W(110). Billing also introduced a stochastic approximation for the collision dynamics and obtained an explicit expression for the effective potential that governs the collision dynamics. This potential depends on surface temperature and on the amount of energy transferred. The method described energy transfer in both direct and "sticky" collisions.[232a,232b]

Another forced-oscillator method for studying phonon excitation was employed by Park and Bowman.[233] They adopted the DECENT scheme, familiar from atom–molecule collision theory, to scattering by phonons.[233] In this approach the solid atoms are set initially at rest at their equilibrium positions. The classical equations of motion for the colliding atom and the surface oscillators are then solved numerically, and from the trajectory $\mathbf{r}_1(t)$, ..., $\mathbf{r}_N(t)$ of all the surface atoms so obtained one can readily compute the energy of each normal (phonon) mode during and after the collision. The final energy of each normal mode is then used in a quantum mechanical forced oscillator expression to obtain the transition probabilities from initial state i to final states for that mode. The method clearly neglects anharmonic coupling between difference surface modes during the collision, and the latter may in principle be important when the collisional energy transfer is large. The method is, however, simple and the record of the gas-phase DECENT approximation is encouraging as to its expected accuracy. Park and Bowman applied the method to He scattering from Si(100)–(2 × 1).[233] They found a high degree of phonon-mode specificity for the collisional energy transfer. Basically, the solid phonon modes that involve mainly displacements of the outermost surface layer atoms were those that gave rise to the largest inelastic scattering probabilities.

An interesting quantum mechanical description of the surface vibrations, coupled with a classical trajectory equation for the incoming particles, was also proposed by Newns.[234] This author first derived a rigorous, exact, path-integral expression for the probability of transferring energy E in an atom–surface collision. By approximate (stationary phase) evaluation of the path integral, a series of approximations of semiclassical nature was obtained. The crudest level involves using a trajectory for the scattered atom that does not respond to the effect of energy loss to the solid. Improved trajectory approximations obtained from the corrections mentioned include the effect of response to energy transfer in the course of the collision. Newns showed that the "improved trajectory method" becomes asymptotically correct as the mass of the collider is increased.

It can be concluded from the above survey that semiclassical methods in the treatment of gas–solid energy transfer are being intensively pursued. An impressive variety of methods and versions has been proposed, the most broadly followed line being that which combines a classical, generalized Langevin equation treatment of surface vibrations, with a quantum mechanical description of the scattered particle. Realistic calculations of, e.g., multiphonon scattering of He from surfaces should probably become a practical tool in this line of approach in the near future.

D. Electron-Hole Pair Excitations

The role of electronic excitation in molecular interactions with solid surfaces is an issue of fundamental physical importance, particularly in the case of metals and semiconductors. Thus, on this topic depends the question whether indeed one is justified in using a molecule–surface potential function (in the Born–Oppenheimer sense) as is almost universally practiced in theoretical studies of gas–solid interactions. Unfortunately, the present understanding of the topic seems far from a truly quantitative stage. Estimates by different authors of the excitation probabilities of the processes discussed here differ in many cases by several orders of magnitude. The origin of much of the difficulty is that there are almost no experimental results that bear directly on this issue and that can be used to guide the theory. Very recently, a first direct observation was made of electron-hole pair excitations in a semiconductor, due to Xe atom impact on the surface.[235] Perhaps future experimental developments will follow on this breakthrough and pave the way to quantitative theories that can be meaningfully compared with measured data.

Against the background of hardly any direct quantitative experimental data to compare with, most theoretical studies aim essentially at qualitative understanding and employ very simple, probably unrealistic, models for the electronic states and for the molecule–surface interactions. Nourtier, in an early study,[236] used an essentially phenomenological model in which the role of metal electrons in atom–surface collision processes is described by a friction force. In his estimates, Nourtier employed a contact (delta function) interaction between the colliding atom and the surface. Nourtier's conclusion is that metal electrons could be important in promoting energy transfer from the atom to the solid,[236] although the mechanism he advocates is an indirect one, involving collisional excitation of phonons and a role for electron-phonon coupling in the process. The very recent work of De Pristo et al.[237] also includes the role of metal electrons as a friction force, within the framework of the generalized Langevin equation formalism. These authors find a relatively large role for collisional energy transfer to electron-hole pairs in the case of H_2 scattering from Cu(100). To estimate the friction coefficients pertaining to the electrons in the GLE framework, they were calibrated by several criteria, one of which was that they should duplicate the calculated vibrational damping of H_2 on Jellium.[238] Although the approach is a very interesting one, it is doubtful that the results are quantitatively reliable, since the "calibration" of the dumping coefficient is of unknown accuracy. A study aiming at systematic derivation of the stochastic force induced by electron-hole pair excitations in the dynamical equation of motion of an atom colliding with a (Jellium) solid was reported by Leung et al.[239] The authors obtained a Langevin-type equation for the dynamics of the scattered atom which can be applied to both phonon and electron-hole pair excitations.[239] The scheme was, however, not yet applied computationally, and the authors do not provide estimates for the errors involved in the approximation used in the derivation. It thus remains to be established rigorously whether electron-hole pair excitations can be treated as an additional damping mechanism in an otherwise classical scattering process or could it be that breakdown of the Born–Oppenheimer approximation that occurs here cannot be adequately described in such a framework.

There is a large body of work that employs time-dependent perturbation methods. Muller-Hartman et al.,[240] who used such a weak coupling theory, introduced also a Tomonaga model (which represents electron-hole pairs as independent bosons) in describing the electronic excitations, an aspect followed by several authors since. Other time-dependent perturbation studies were pursued by Brako and Newns,[241] by Nozieres and de Dominics[242] and by Gadzuk and Metiu.[243,244] In particular, Gadzuk and Metiu considered the effect of the increasing atom perturbation in both the sudden and adiabatic switching limits. The description these authors employed for the low-lying electronic excitation was that of the Tomonaga independent-boson model. Gadzuk and Metiu estimate sizeable effects for electron-hole pair participation in molecular collisions and reactions with surfaces.[243,244] Kumamoto and Silbey[245] employed a TDSCF approximation, of the type described in section III.C, where the quantum degrees of freedom are those of the electron. As in the case of nearly all other studies in the field, the basic dynamical method is simplified by the introduction of further drastic approximations and by interaction models which are probably of semiquantitative validity only. Kumamoto and Silbey estimate large accommodation coefficients due to electron-hole pair excitation for molecular collisions with low-temperature surfaces.[245] Kirson et al.[246] studied electron-hole pair excitations in very high-energy (300-eV) collisions of Ar, He, and H with metal surfaces. With use of a Sudden approximation, the finding was that the electron-hole pair excitation efficiency is in the order H >> Ar >> He, the mean energy transfer to electrons being rather small in the case of He even at the high collision energies considered. The study of Gunnarson and Schönhammer[247] is among the most quantitative and careful ones reported so far on electron-hole pair collisional excitation processes. These authors explored the example of He scattering from a Cu surface at collision energies of the order of 0.1 eV. Gunnarson and Schönhammer employed a time-independent distorted wave approximation, using elastic scattering wave functions for the zeroth-order description, with the He coupling to the electron-hole pairs as a first order perturbation. They found negligible electron-hole pair excitation probabilities,[247] in apparent contradiction with some of the previously mentioned studies. Kirson et al.[248] solved numerically the TDSCF equations for the excitations of independent electrons in a Jellium solid due to collision of a classically described atom with the surface. The classical equation of motion for the atom was solved self-consistently with the Schrödinger equation that governs the evolution of the electron wavepacket. This demonstrates yet another example of the power of wavepacket methods in dealing with collision problems involving a continuous excitation spectrum. Unlike atomic particles, electrons in force fields are not adequately described in general by semiclassical wavepackets, such as discussed in section II.A. Kirson et al.[248,249] employed a variational principle for solving the time-dependent Schrödinger equation for the electron wavepacket, having used a variational trial form with explicit time-dependent parameters. Frenkel's variational functional is[249]

$$I\{\psi,\theta\} = \int |H\psi - \theta|^2 \, d\mathbf{r} \qquad \text{(III.10)}$$

where the integration is over the entire configuration space. I vanishes if $\theta = i\hbar\partial\psi/\partial t$. The variational property of $I\{\psi,\theta\}$ is that it is stationary to first order in $\delta\theta$, i.e., to first order one has

$$\delta I = 2Re \int \delta\theta^*(H\psi - \theta) \, d\mathbf{r} = 0 \qquad \text{(III.11)}$$

To apply the method, a time-dependent trial function involving time-dependent coefficients is chosen on physical grounds. Assume the initial state $\psi(t_0)$ is given at t_0. Then for a small time increment

$$\psi(t_0 + \Delta t) \approx \psi(t_0) - i\theta(t_0)\Delta t/\hbar \qquad \text{(III.12)}$$

Solving (III.12) for θ (at $t = t_0$), eq III.11 is used and the process repeated until the entire time evolution is obtained. Kirson et al. used the following wavepacket form (in one dimension)

$$\psi_e(z,t) = \int_{k=0}^{\infty} g_k(t - t_0) f_k(z) \exp[-iE_k(t - t_0)\hbar] \, dk \qquad \text{(III.13)}$$

where the f_k are stationary eigenstates of the electrons in the metal and $g_k(t - t_0)$ is taken to be a Gaussian in the wavevector k, the center and the width of which are employed as (time-dependent) variational parameters, and solved for. This and other possible wavepacket methods seem very promising for the dynamics of electrons in metals, especially in view of the continuous excitation spectrum which can be assumed in such approaches. However, while solving accurately for the dynamics, the approach of Kirson et al. is still very unrealistic with regard to the "particle in a box" treatment of the electrons: Band structure effects, i.e., the potential field in the crystal, must probably be included in quantitative calculations of the electron excitation dynamics. Kirson et al.[248] carried out such wavepacket calculations of electron-hole pair excitations for He, Ar, and H in collisions at energies ranging from 0 to 1 eV with a model of a Li surface. In the case of He, Kirson et al. find in essential agreement with Gunnarson and Schönhammer[247] that electron-hole excitations are virtually negligible (at a collision energy of 0.01 eV, the fraction of energy transferred to electron-hole pairs ≈ 0.2%). On the other hand for H atoms, Kirson et al.[248] find rather large energy transfers (~10% of the incidence energy at 0.01-eV collision energy), which should definitely be experimentally detectable. Also, these authors found that trapping due to transfer of energy to electron-hole pairs occurs with a high probability at sufficiently low collision energies. H trapping takes place with almost unit probability for collision energies below 20 K. Finally, Kirson et al.

applied the same method to molecular dipoles (modeling CO and HCl) in impact on surfaces of Li and Al.[250] A substantial fraction of the collision energy was found to convert to electron-hole pair excitations.

Perhaps some solid common ground of agreement can be distilled from the above, partially conflicting, studies. First, electron-hole pair excitations in He scattering from surfaces are unimportant. This is not surprising on physical grounds: The He is stopped by the repulsive part of its interaction with the solid at distances where the surface electron density is very low, corresponding to the weak, long tail part of the electron wave functions in the highly classically forbidden region outside the Jellium bulk. Obviously, the coupling between the He atom and the electron-hole pairs is therefore extremely weak. Second, heavier rare-gas colliders such as Ar will produce substantially greater electron-hole pair excitations than He, because the electron densities of such atoms will, as the estimates show, overlap more extensively with the surface electron density. Third, open-shell atoms can give rise to large, measurable effects of electron-hole pair excitations. This is due to the longer range "chemical" interaction between such atoms and the solid electrons, as a consequence of which regions high in surface electron density are probed by this interaction. H atoms appear a particularly suitable candidate for experimental examination of this conjecture, since they cause less phonon excitation than heavier colliders. (The separation of phonon and electron excitation effects and the possible risk of overshadowing dominance of phonon effects in any given situation are major difficulties that experiments in this subject must come to grips with.) By the available theoretical evidence at hand, both the heavy rare gases and H atom should give rise to very substantial effects of electron-hole pair excitations, reflected both in kinetic energy loss of the atom and, in some cases, in trapping.[248] Finally, the fact that indications exist that open-shell atoms interact rather effectively with electrons in metals suggests strongly that electron-hole pairs may play an important role in chemical processes at metal surfaces, when open-shell atoms are obtained, e.g., as dissociation products. On the other hand, fundamental questions in this subject remain widely open. As noted at the beginning of this section, the Born–Oppenheimer approximation on which rests the notion of a molecule–surface interaction potential breaks down when the probabilities of exciting surface electronic states are substantial. Can one somehow describe molecule–surface interactions by a single potential function also in cases where a continuum of surface electronic states are involved in a significant way in the scattering process? This obvious and crucial question in the case of metals has yet to be tackled.

Definitely experimental progress on the topic of collisional excitation of electron-hole pairs is crucially needed to provide a basis for better future theories. In any case, it seems that in terms of potential importance and the fundamental nature of the questions involved, the subject of energy transfer to and from electron-hole pairs in molecule–surface scattering, deserves considerably greater attention than it presently receives, especially with regard to quantitatively reliable estimates, which should focus on improved modeling of the surface electron states and on the interaction potentials between the electrons and incoming atoms.

IV. Rotational, Vibrational, and Electronic Energy Transfer

A. Rotational Transitions in Scattering from Rigid Surfaces

Rotationally inelastic scattering from surfaces is a probe of the dependence of molecule–surface interactions upon the orientation of the molecule with respect to the surface. As such it is a topic of great chemical interest. Research on the theory of such processes gained considerable impetus from the remarkable recent experimental progress in this field. Spectroscopic techniques, such as laser induced fluorescence, and molecular beam methods, in particular rotationally inelastic diffraction measurements and time-of-flight techniques, have provided in the last few years a wealth of information on the final rotational state distributions of molecules scattered from surfaces (ref 12–24, 25, 28, 38–41, 251–253, 255–260). Important theoretical insights into rotationally inelastic scattering from surfaces have been obtained in part from studies that assume a static, nonvibrating solid. Treatments confined to this simple framework will be the topic of the present subsection. While in most realistic cases phonon participation in rotationally inelastic scattering can be very useful, it is important to emphasize that there are several systems where it seems that a rigid-surface treatment can successfully account for the main experimental findings. Examples will be discussed below where a static surface model is indeed useful in semiquantitative or even qualitative interpretation of experimental data. Both in this and in the forthcoming subsection we shall discuss the physical reasons for the validity of the rigid-surface approximation in the particular cases where it works. It will be useful in this part of the review to examine the theoretical methodology in the context of specific physical regimes and phenomena, since different types of processes often require very different approximation methods.

Rotationally Mediated Selective Adsorption. These are scattering resonances, in which the molecule, upon impact on the surface is excited rotationally at the expense of its translational energy normal to the surface, to the extent that it becomes temporarily trapped in the attractive well of the molecule–surface interaction potential. The approximate condition for such a resonance in close analogy to eq II.20 for the "usual", corrugation-induced selective adsorption is

$$E_v = E - \frac{\hbar^2}{2\mu}(\mathbf{K} + \mathbf{G}_{mn})^2 - \Delta E_{\text{rot}} \qquad \text{(IV.1)}$$

where E_v is a bound state in the molecule–surface attractive potential well, **K** the incident wavevector parallel to the surface, E the incident energy, and ΔE_{rot} the (temporary) change in rotational energy. Rotationally mediated selective adsorption resonances were first seen by S. J. Sibener and co-workers for HD scattering from Pt(111)[254] in an experiment in which intensities of rotational transitions $J = 0 \rightarrow J'$ were studied as a function of incidence angle, at fixed initial energy. Dips were found to occur in the probability $P_{J\rightarrow J'}$, when condition (IV.1) is satisfied for $\Delta E_{\text{rot}} =$

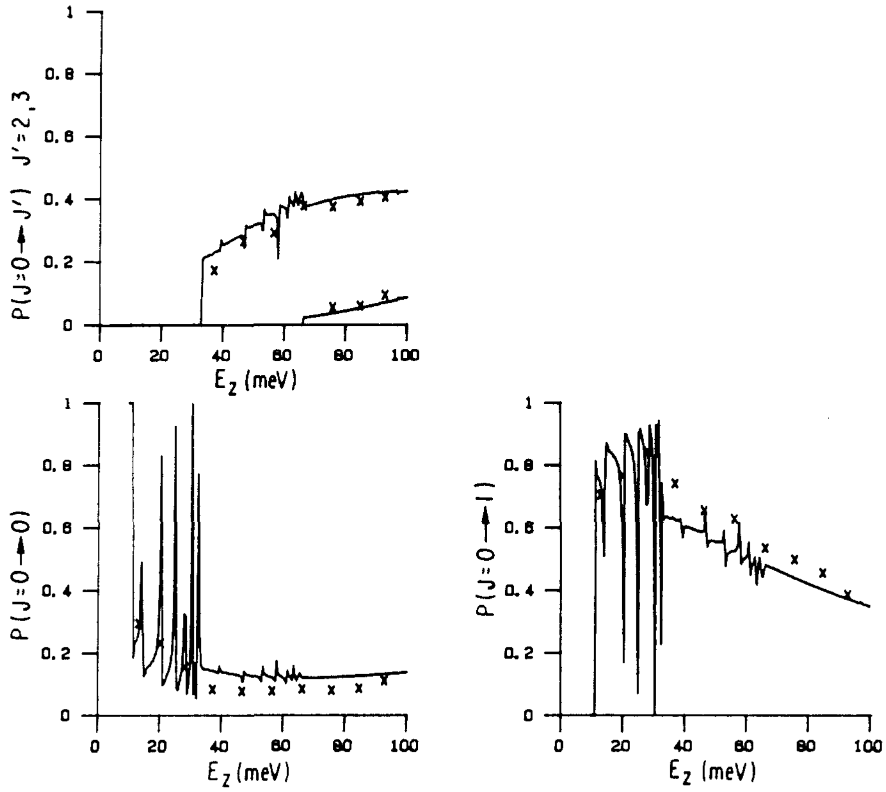

Figure 9. Rotationally inelastic transition probabilities for HD/Hg(111) vs. collision energy normal to the surface. Solid lines are the close coupling results obtained with a fitted potential. Experimental points are marked by x. (Reproduced with permission from ref 267. Copyright 1985 by the American Institute of Physics.)

$\Delta E_{J+1} - E_J$. Sibener et al. studied also such resonances in HD/Ag(111)[255] and for H_2, D_2/Ag(111).[261] To obtain theoretically the scattering intensities in the regime of these rotationally mediated selective adsorption (RMSA) resonances, the scattering equations for the coupled rotational and diffraction states involved must be solved. As pointed out, however, by Yu et al.,[253] for smooth surfaces such as Ag(111) and Pt(111), only the $m = n = 0$ diffraction channel is significantly involved, and the rotational transitions are little affected by the corrugated part of the potential. A laterally averaged molecule-surface interaction $V(z,\theta)$ (where z is the distance of the molecular center of mass (c.m.) from the surface and θ the molecular orientation angle with respect to the surface normal) can thus approximately describe the RMSA behavior. Schinke[262-264] and Whaley et al.[255,261,265-267] carried out coupled-channel scattering calculations in order to fit a potential to the RMSA resonance data (and to other experimental information).[266] Schinke[262,263] carried out close-coupled calculations for the rotational and diffraction channels involved in the RMSA regime for HD/Ag(111) and HD/Pt(111). He emphasizes that in his experience RMSA resonances are not sufficient or suitable for fitting a reliable anisotropic potential function.[263] Much of the difficulty is that for HD the "true" intrinsic anisotropy of the potential (as present in H_2) is masked by the dominant anisotropy associated with the mass asymmetry.[267] Whaley et al. thus suggested that H_2, D_2 scattering data should be a better source for determining an anisotropic potential function.[266,267] Since the RMSA effect for H_2, D_2 is weak and only few such resonances were observed, the implication is that the best source for determining a potential for hydrogen/Ag(111) should be rotationally inelastic scattering probabilities (in the direct collision regime), combined with the usual (corrugation induced) selective adsorption data. Indeed, in an impressive and exhaustive study, Whaley et al.[263,266] fitted by close-coupling calculations rotationally inelastic scattering probabilities (over a range of collision energies), selective adsorption resonances, and other data measured by Sibener and collaborators, to produce both an isotropic and anisotropic laterally averaged hydrogen/Ag(111) interaction, which is probably the most accurate experimental molecule–surface potential available at present. RMSA resonances for HD/Ag(111) play only a limited role in that determination, together with other data for the mass symmetric H_2, D_2 isotopes. Figure 9 shows the energy dependence of rotationally elastic and inelastic transition probabilities for HD/Ag(111) from Whaley et al.[267] using a laterally averaged potential fitted to the H_2, D_2, and HD scattering data. The RMSA resonance structure is clearly seen in the results.

An algorithm for solving the close-coupling equations that has particularly appealing features in the resonance scattering regime is the **R** matrix technique, used by Yu et al.[255] and Whaley et al.[266,267] The **R** matrix calculation employs a basis of direct product of free rotor states with a translational basis. An "inner region" of finite range is defined and the bound vibrational states of the molecular surface attractive potential are expanded in the translational basis over that finite region. The confined, bound state nature of the inner region is physically advantageous for describing resonances states. However, increasing the size of the inner region allows the bound vibrational states to be calculated to any specified accuracy. The product rotational–translational basis is then used to construct a matrix at the outer boundary of the inner region (**R** matrix) which contains all the scattering information and from which the observable scattering probabilities are obtained.[255]

Moiseyev et al.[268] applied to RMSA resonances the *complex rotation* approach.[268] This is a "numerically exact" method for calculating resonance positions and widths, which proved efficient and powerful in dealing with electron–molecule scattering resonances and other gas-phase resonance collision processes.[269] In this method, the scattering coordinate is scaled by a complex-valued scale factor. This "complex rotation" can be rigorously shown to transform resonances into bound (i.e., asymptotically decaying) states. The spectrum of bound states is found by matrix-diagonalization, a stability criterion being used to determine the appropriate value of the complex scale factor. The method is "specialized" to resonances only, yielding positions and widths, but no other aspects of the scattering dynamics. On the other hand, it is rather efficient in calculating the resonances.

Moiseyev et al.[269] explored the extent to which RMSA resonances can be adequately described by classical dynamics. Resonance lifetimes for HD scattering from flat Pt were calculated by classical trajectories and the result compared with exact quantum mechanical calculations (by the complex-rotation method). Also qualitative properties of the wave functions and the trajectories were compared. It was found that the classical calculations reproduced correctly the major trends (e.g., the variation of the lifetime with the vibrational level in the molecule–surface potential well) and gave the same qualitative description of the resonances as the quantum results. In particular, the trapped HD was found to be an almost free rotor in the resonance state with virtually no librational character. On the other hand, classical dynamics gave lifetimes too long by about a factor of 5. Moiseyev et al.[268] suggested that this is due to penetration of the quantum mechanical wave functions into classically forbidden strongly repulsive regions of the potential, that shortens the lifetime.

The validity of the rigid-surface model in treating RMSA resonances is widely accepted and applied, but experimental and theoretical evidence for this is insufficient. The short lifetime of such resonances (of the order of 10^{-12} s, typically) and the large mass scale separation of H_2 and Pt or Ag may provide arguments for the assumption that rotational-to-phonon energy transfer does not take place during the resonance lifetime, but this seems far from clear. Kaufhold and Toennies[270] studied RMSA resonances by an optical potential approach, in which framework the width of the resonances is related to the imaginary (absorbing) part of the potential. They fit the above potential so as to reproduce the Debye–Waller attenuation, which is tantamount to attributing that optical potential to phonon effects. Kaufhold and Toennies analyze the data of Yu et al.[255] by their theory, which produces a good fit in this case. More evidence seems necessary on this point, and theoretical simulations which explicitly include phonon participation (e.g., by the GLE scheme) seem desirable. Such simulations may provide indications on the specific rotation-to-phonon energy transfer in the trapped state, if it exists.

Diffractive Selective Adsorption of Molecules. The resonances induced by surface corrugation in the case of light molecules are very similar to the (diffractive) selective adsorption of atoms, discussed in section II.A. There are, however, some interesting differences. The laterally averaged zero-order potential in which the molecule may be considered trapped after the diffractive selective adsorption transition is, of course, anisotropic. For a potential $V(z,\theta)$, where θ is the molecular orientation angle, the matrix elements $\langle Jm_J|V(z,\theta)|Jm_J\rangle$ depend on the magnetic quantum number m_J. As a result, the resonance levels in diffractive selective adsorption are in general split into magnetic sublevels. This feature was pointed out by Chiesa et al.,[271] who in an elegant experiment observed such splittings for H_2/Ag(110). The effect was used by Schinke and coworkers[263,272] to extract the anisotropic part of the H_2/Ag potential from the data. Figure 10 from ref 263 shows the good agreement obtained between the measured magnetic splittings of the selective adsorption resonances and the calculated values from fitted potentials. Magnetic sublevel splitting data was used also by Whaley et al.,[267] together with other scattering data, in their determination of an hydrogen/Ag(111) potential.

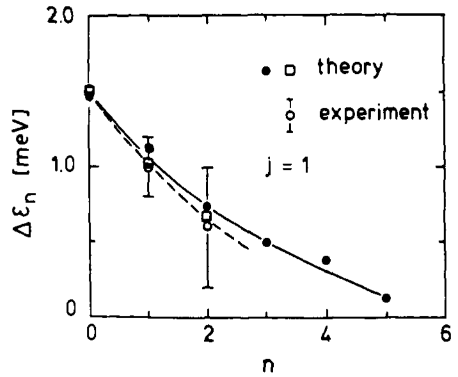

Figure 10. Magnetic sublevel splittings $\Delta\epsilon_n = \epsilon_n$ ($J = 1$, $m_J = 0$) $- \epsilon_n$ ($J = 1$, $m_J = \pm 1$) vs. vibrational quantum numbers in the attractive potential well of H_2 and Ag(110).

The Propensity for Large ΔJ Transitions and the Rotational Rainbow Effect. We consider how scattering of molecules substantially heavier than H_2 (for which only a few rotational quantum levels are populated in scattering processes at chemical relevant energies). The rotational rainbow effect in surface scattering was experimentally observed by Kleyn et al.,[13] who studied the rotational state distribution of NO in collisions with Ag(111). The experimental rotational distributions, especially for the higher J values showed a strong dependence on the incidence energy normal to the surface, as the latter was varied in the range of 0.19–0.98 eV, which was indicative of direct inelastic (rather than trapping-desorption) scattering. At high values of E_n, the incidence energy normal to the surface (for $E_n > 0.3$ eV), a broad maximum appeared in the distribution of the high J values. Kleyn et al. recognized that this was analogous to the rotational rainbow effect observed a few years ago in rotationally inelastic atom–molecule scattering, e.g., for Ne–Na_2 by Bergmann and co-workers[273] and for K + CO by Beck et al.[274] A first treatment of surface rotational rainbows (SRR) was given by Schinke,[275] who used the rotational Sudden approximation. This approximation, a natural extension of the Sudden method for diffraction scattering discussed in section II.A, was proposed by Gerber et al.[276] for collisions where the incidence energies are high compared with both the rotational and diffractive energy changes, i.e.

$$k_z^2 >> |\mathbf{G}_{mn}|^2 \qquad E >> |E_J - E_{Ji}| \qquad \text{(IV.2)}$$

for all diffraction states (mn) and for all rotational states J that are significantly populated in the scattering process (J_i is the initial rotational state). In one of the versions of the Sudden approximation the rotational–diffraction transition probabilities are written in the form

$$P_{00,Jm_J \rightarrow mn,J'm'_J} = |S_{mn,J'm'_J;00,Jm_J}|^2 = \frac{1}{A^2}\left|\int_A \int_0^{2\pi} \int_0^{\pi} e^{iG_{mn}R} e^{2i\eta(\mathbf{R},\theta,\phi)} Y^*_{J'm'_J}(\theta,\phi)\, Y_{Jm_J}(\theta,\phi) \sin\theta \; d\theta\, d\phi\, d\mathbf{R}\right|^2 \quad \text{(IV.3)}$$

where the $\mathbf{R}$ integration is over the unit cell area and $Y_{Jm_J}(\theta,\phi)$ is the rigid-rotor (J,m_J) eigenstate. $\eta(R,\theta,\phi)$ is an elastic scattering phase shift calculated from the molecule surface potential $V(x,y,z,\theta,\phi)$ for each fixed value of x,y,θ,ϕ. Schinke[275] arrived at a semiclassical-limit stationary phase evaluation of (IV.3), from which the possible existence of both diffractive and rotational rainbows becomes evident. If the surface is flat, η depends only on the molecular orientation θ with respect to the surface normal. It can readily be shown that as the classical limit is approached

$$P_{J\rightarrow J'} \propto \left|\frac{d^2\eta}{d\theta^2}\right|^{-1}_{\theta=\theta_s} \qquad \text{(IV.4)}$$

(the indices mn,m_J are irrelevant for a flat surface and were dropped). The "stationary phase" value θ_s is given by the solution of[276]

$$J' - J = \Delta J = 2\frac{\partial\eta(\theta)}{\partial\theta} \qquad \text{(IV.5)}$$

Rotational rainbows, in analogy to diffraction rainbows discussed in section II.A, correspond in this case to a singularity of $P_{J\rightarrow J'}$ as $(d^2\eta/d\theta^2)_{\theta s} = 0$ for some transition ΔJ. Equation IV.4 is given for the case when a single stationary phase point exists. In general, (IV.5) may have more than one solution. It should be noted that only the primitive classical limit of $P_{J\rightarrow J'}$ diverges: Neither the exact Sudden expression nor uniform semiclassical approximations to the latter show such behavior.[275,277] Barker et al.[278] carried out close-coupling calculations for the NO/Ag(111) system and have shown that reasonable agreement with the experimental results can be obtained from a simple potential function, provided adequate averaging over the initial states corresponding to the experimental conditions (in particular with regard to the finite rotational temperature of the incident beam) is carried out. Barker et al.[278] have also carried out classical trajectory calculations, which confirm the rainbow interpretation for the model potential used. Voges and Schinke[279] carried out both Sudden and close-coupling calculations using the potential function

$$V(z,\theta) = A(z - \alpha\cos\theta - \beta\cos^2\theta)^{-8} - B(z - \delta\cos\theta)^{-3} \qquad \text{(IV.6)}$$

which differs from the one used by Barker et al.[278] in being asymmetric with regard to the N and the 0 ends of the NO molecule due to the presence of odd powers of cos θ. This modification of the potential proved important, for it leads to a second weak rainbow at low J values (in addition to the main one at high J). While this rainbow is hard to identify explicitly in the experimental data, it resulted in improved agreement with the experimental final state distributions at low J values. Results are shown in Figure 11. Similar quantitative observations on the role of odd cos θ terms in the potential were made by Tanaka and Sugano,[280] who used the Sudden approximation. While all this presents a strong case for the interpretation of the NO/Ag(111) system as one of direct inelastic scattering (at least for $E_n > 0.2$ eV) and which provides a manifestation of rotational rainbows, there are also dissenting views, e.g., Polanyi and Wolf[281] and Zamir and Levine,[282] who argue in different ways, for an interpretation that involves substantial trapping-desorption scattering. Given the many uncertainties regarding the interaction potential for this system, such an interpretation cannot be ruled out, although it seems less likely at the present time. (Treatments of rotationally inelastic scattering that involve the effects of surface vibrations will be discussed in the next subsection.) Regardless, however, of the specific interpretation adopted for the NO/Ag experiments, the theoretical evidence that rotational surface rainbows should occur in certain conditions is a very compelling one. It should be desirable to search experimentally for this effect in new systems, preferably in cases where the attractive potential is weak, and the possibility of trapping-desorption scattering can be excluded. A questionable

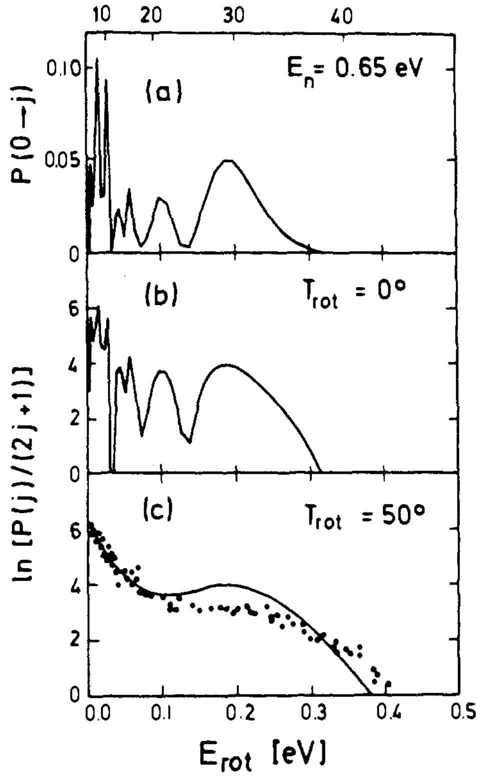

Figure 11. (a) Sudden approximation 0 → J transition probabilities vs. the rotational quantum number J (upper scale) or rotational energy transfer E_{rot} (lower scale). (b) As in (a), but shown on a Boltzmann plot. (c) Comparison of experimental and theoretical rotational state distributions. The theoretical results were averaged over the initial state distribution (T_{rot} = 50°). (Reproduced with permission from ref 263. Copyright 1984 by D. Reidel Publishing Co.)

aspect of the theoretical calculations referred to above is that they computed the *total* rotational state distribution, summed over all final angles, and compared it with an experiment[13] that probed the distribution at a fixed (specular) direction. At least in the rigid-surface calculations, molecules with high final J values are expected to be scattered into angles much nearer to the surface than the low J ones. Perhaps surface vibrations are important in "bringing back" the high J states to the near specular direction, but theoretical results for both angular and rotational state resolved distributions are needed, and the consistency with experiment of the presently available close-coupling and Sudden results for NO/Ag should be examined carefully also with regard to the question of the angular distribution. It should be noted that Kleyn et al.[283] carried out experiments on the angular distribution of NO scattered from Ag(111) and found that while the low J states ($J \leq 23.5$) were scattered near specularly (which supports the interpretation of direct rather than trapping-desorption collisions), the $J = 40.5$ was scattered at higher angles, nearer to the surface.

The range of methods employed to study rotational rainbow scattering in the rigid-surface framework is a wide one. We referred above to close-coupling calculations[278,279,284] and to the Sudden method[275-277,285] which for the regime of rainbow scattering appears to be in excellent agreement with the exact results.[263,279] Classical calculations provide very useful insight[278,281,286,287] and are helpful in identifying the rotational rainbow effect when it occurs. The quantitative reliability of classical trajectory calculations is the matter of some disagreement. Barker et al.[278] point out that they found rather large differences between the classical and quantum mechanical calculations they carried out for NO/Ag. On the other hand, Tully and co-workers[206,288] have reproduced with a classical simulation, using an empirical potential (and including surface atom motions by the GLE approach) the experimental rainbow structure of Kleyn et al.[13] almost quantitatively. It seems reasonable to suggest that the large difference found by Barker et al.[278] between their computed close-coupling and classical rainbow structures stems from the fact that they compared the rotational distributions from the two methods in calculations that included no averaging effects (corresponding to the initial conditions). Classical and quantum mechanical results for rainbow structures in scattering processes in which averaging is not involved differ considerably because of the effect of the singularity present in the classical result, because of the penetration of the quantum mechanical wave function into the classically forbidden regime, which produces a greater spreading of the quantum distribution, and because of interference effects that always occur in quantum dynamics near the rainbow regime.[289] Indeed, quantum rotational rainbows are, for instance, shifted to lower J values compared with the classical ones. However, the difference between classical and quantum rainbow patterns is drastically reduced, as experience in gas-phase calculations shows, when some averaging on initial conditions is included. Classical dynamics will do better in simulating a realistic experiment, than for idealized unaveraged conditions. Another point that should be stressed is that Tully et al., in their calculations that reproduce the NO/Ag experimental rainbow structure, employ a potential function very different from that used by Barker et al.[278] or Voges and Schinke[279] (for instance, the lowest energy configuration for the NO molecule by the potential of Tully et al. is normal to the Ag(111) surface, while the potentials of ref 278 and 279 suggest that the parallel orientation is preferable). It is unclear as yet which potential is preferable, and the results merely show that the available data for NO/Ag(111) is insufficient to determine a unique interaction potential.

In addition to coupled-channel calculations, to the Sudden approximation, and to classical trajectory simulations, also "hard-wall" potential functions can be used to model some of the characteristics of rotationally inelastic scattering in the rainbow (impulsive collision) regime.[293-298] Such models do predict the rainbow effect and show in general the propensity for large ΔJ transitions in high-energy rotationally inelastic molecule–surface scattering. Nearly all these models treat the molecule as a hard rod or a hard ellipsoid in impact on a flat surface. Garibaldi et al.[293] dealt with an ellipsoid colliding with a hard corrugated surface, in which case a Rayleigh approximation was used to obtain simplified results. Perhaps the most interesting consequence of such models is to provide a simple framework of studying the effects of surface motions on rotationally inelastic collisions. This can be done by extending for a hard ellipsoid the "hard-cube" model for atom solid energy transfer. Hurst et al.[296] and Kubiak et al.[297] in their studies of rotationally inelastic scattering of NO from surfaces have significantly improved on this treatment by using a "soft", non-hard-wall interaction between the NO and the "cube".

A new type of surface rotational rainbow structure was observed by Elber and Gerber[298] in classical trajectory studies of scattering of linear molecules from surfaces. In the framework of the Sudden interpretation of rotational rainbows,[275] one can obtain only one rainbow maximum for a symmetric linear molecule, corresponding to the single orientation at which the torque for rotational excitation is maximal. However, there are conditions in which double collisions can occur, in which the molecule after hitting the surface by one end, rotates rapidly enough to strike the surface with the second end before leaving the interaction region. For appropriate system parameters two separate rainbow maxima may then occur, corresponding respectively to single and to double collision events. Elber and Gerber[298] predicted the occurrence of such a rainbow structure in scattering of CO_2 and several other molecules from smooth surfaces and observed that the occurrence of the effect is very sensitive to the interaction parameters.

Gerber and Elber[299] examined the question of whether rotational rainbows can show up also in conditions where vibrationally inelastic transitions in the scattered molecules are substantial. They carried out classical trajectory simulations of (vibrating) I_2 scattering from flat surfaces at 2.0 eV, above the energy threshold for dissociation. About 50% of the collision energy was transferred to rotation, and a rotational rainbow structure was found.[299]

Diffraction and Rotational Transition. For detailed understanding of the molecule–surface interaction potential, information will be necessary on both the diffractive and rotational transitions in the scattering process, including also combined rotational–diffractive transitions. Thus, only data of this type can indicate how a given molecular orientation interacts with different surface sites. It is a conceptually important aim of the theory to calculate the probabilities of such processes and to clarify the relation between the corrugation-dependent and anisotropic aspects of the interaction and the rotational and angular distribution of the scattered molecules. In view of the very large number of open rotation–diffraction channels and typical experimental energies, numerically exact, quantum mechanical calculations of such processes were carried out only in very few cases. Early close-coupling calculations that treat both the rotational and the diffractive degrees of freedom were carried out by Wolken[300–302] for H_2/LiF(001). Much more extensive calculations for this system were recently reported by Drolshagen et al.,[303] who were able to compute by the close-coupling method diffractive–rotational transitions at collision energies as high as 0.7 eV. These authors found, in fact, that several of Wolken's transition probabilities were not converged. Drolshagen et al. used their exact calculations to test several approximation methods, as will be discussed below. Exact results for diffraction and rotationally inelastic scattering of H_2 from corrugated surfaces by a new method that seems very promising were recently obtained by Mowrey and Kouri.[304] These authors provided a hybrid of the close-coupling and the time-dependent wavepacket approaches (CC–WP), in which the rotational degrees of freedom are treated by close-coupling, while the translations are described by the FFT time-dependent wavepacket algorithm of Kosloff and Kosloff[62,63] discussed in section II.A. The performance of the method in handling efficiently a large body of channels, and in constructing economically results at several energies, is impressive. As pointed out in section II.A, a major advantage of the wavepacket method is that they provide a single row of the **S** matrix without involving explicitly, or investing effort in, the other transitions. The reviewer's anticipating is that this should become one of the most important methods in the field.

The Sudden approximation introduced by Gerber et al.[276] has the advantage of offering very simple expressions for the rotation–diffraction transition probabilities in the impulsive collision regime, see eq IV.2 and IV.3. In addition to numerical applications, the method was also employed to derive several scaling properties, pertinent to the dependence of the transition probabilities $P_{00,Jm_J\rightarrow mn,J'm'_J}$ on the variables (mn), $\Delta J = J' - J$, and $\Delta m = m'_J - m_J$.[277] One of the interesting predictions of the Sudden approximation for H_2–LiF(001), and other systems having potential anisotropy and corrugation parameters in roughly the same range, is that to a good approximation rotationally inelastic and diffractive scattering are decoupled in the high-energy regime; that is (i) the diffractionally summed rotational transition probabilities are independent of surface corrugation and (ii) the rotationally summed diffraction probabilities are independent of surface anisotropy. These predictions are confirmed to a good degree of approximation by the close-coupling results of Drolshagen et al.[303] The Sudden predicts also certain weak couplings as systematic deviations from the rotation–diffraction decoupling behavior; e.g., rotational inelasticity for $J = 0$ is expected to increase with increasing order of the (m,n) diffraction state. This was found to hold for high energies ($E \geq 0.5$ eV) but not at low energies (e.g., $E = 0.1$ eV), where rotational energy threshold effects become important and the Sudden condition breaks down. Detailed tests by Drolshagen et al.[303] of state-specific transition probabilities which have shown that the Sudden approximation (in the MDS version[278]) gives good quantitative results at high collision energy ($E > 0.5$ eV), but at lower energies it can only be relied on for trends and for semiquantitative properties. It should be noted that H_2 is a very unfavorable system for rotational Sudden, due to the large rotational energy spacings in this case, so the results are very encouraging for the further use of the method.

Bowman and co-workers[305,306] and Sinai et al.[307] studied rotational and diffractive scattering by the quasi-classical trajectory method (QCT). This involves classical trajectory calculations for the system with "box quantization" of the final rotational energies and momenta parallel to the surface, in order to assign each trajectory to a quantum rotational and diffraction final state. For the diffraction this means rounding the expressions on the right-hand side of (IV.7) to the nearest integers

$$m = \frac{a_x}{2\pi\hbar}\Delta P_x \qquad n = \frac{a_y}{2\pi\hbar}\Delta P_y \tag{IV.7}$$

where the ΔP_x and ΔP_y are the momentum transfer components of the scattered particle along the surface lattice vectors and a_x and a_y are the lattice constants. The QCT approach is not restricted as the Sudden is to high-energy scattering, but it ignores interference effects that may be important especially in diffractive scattering. Drolshagen et al.[303] tested the QCT results of Saini, Dows, and Taylor[307] against their exact close-coupling calculations. The QCT was found to give a semiquantitatively correct description. At low energies, it gives results somewhat better than the Sudden. On the other hand, it does rather poorly at high energies ($E = 0.7$ eV in the calculations), where the Sudden is of quantitative accuracy.

Hubbard and Miller[103] studied diffractive and rotationally inelastic scattering by a perturbation method developed in the framework of Miller's semiclassical theory of inelastic scattering. The approach is referred to by the authors as the semiclassical perturbation (SCP) approximation, and it uses, in the case of molecule–surface scattering, a trajectory obtained from a flat, isotropic zero-order potential, to calculate perturbatively the effect of the anisotropic and corrugated parts of the interaction and to provide an integral representation of the **S** matrix elements. This elegant approximation was found to give for H_2/LiF(001) results in good agreement with the close-coupling calculation of Wolken et al.[302] at low energies and with the Sudden results of Gerber et al.[276] at higher energies. The expressions obtained in the SCP approximation are conveniently analyzed and can be used to derive various properties of the transition probabilities.

Another approximation applied to rotationally inelastic diffraction scattering of molecules is the mean trajectory, Gaussian wavepacket approach of Metiu and

Jackson.[231] This method is closely related to the semiclassical trajectory approach of De Pristo et al.,[227-230] and both were briefly discussed in section III. In the application to H_2/LiF(001), Jackson and Metiu find quantitatively (but not qualitatively) significant differences between their method and De Pristo's, which they attribute to the neglect of interference (coherence) effects in the latter associated with the use of a classical trajectory. The comparisons provided so far by Jackson and Metiu[231] are only with other approximations, e.g., with a version of the Sudden approximation,[276] not with exact calculations; thus its accuracy is hard to assess. The method should in any case be confined to direct scattering, since Gaussian wavepackets are employed and thus cannot be used for RMSA or diffractive selective adsorption resonances.

Δm_J Transitions in Molecule–Surface Scattering. Such transitions probe directly the reorientation of the molecule due to its collision with the surface. Consider a molecule in normal incidence to the surface. If the surface normal is chosen as the quantization axis, then obviously no $\Delta m_J \neq 0$ transitions are possible for a flat surface. It was indeed argued by Proctor et al.[308] that Δm_J transitions if measured (with the surface normal as quantization axis) could provide a useful probe of surface corrugation. Δm_J transitions of this type in which the molecule changes its angular momentum vector in perpendicular to the surface plane can be studied only in calculations that include both rotational and diffraction channels. The first such study was by Proctor et al.,[308] who used the Sudden approximation, as given in eq IV.3, to calculate Δm_J transitions in normal incidence of H_2 upon corrugated surfaces. Extremely weak m_J changing transitions were found for realistic values of the corrugation. This is dictated in part by the geometry involved, in particular the high symmetry of the (rectangular) unit cells used, which leads to cancellation effects leaving only a very small residual torque that can provide rotational excitation about an axis normal to the surface. The relative flatness of the surface, even at the higher corrugation values used, is another reason for the near m_J conservation found.[208] Proctor et al. showed, however, formally that given sufficient corrugation, Δm_J rainbows may occur. This is an effect of propensity for high Δm_J transitions involving in the classical limit a singularity in $P_{00,J0\rightarrow mn,J'm'_J}$ as a function of m'_J. Physically, the molecule then hits a "hard cap" (a surface atom) at an orientation that gives it a maximal torque for rotating in the surface plane. Proctor and Kouri[309] then demonstrated by calculations on Cl_2 scattering from a corrugated surface that such rainbow maxima may indeed be of observable magnitudes for models of realistic parameters. The calculations of Proctor and Kouri used the Sudden approximation for the diffraction but treated the rotational channels by close coupling (DSCCR method).[309] Whaley and Light[310] took a different approach to the calculation of Δm_J transitions: They solve numerically a convenient zero-order multichannel scattering problem, say rotationally inelastic scattering from a flat surface, constructed to include the strong transitions. The weak Δm_J transitions are then obtained by a first-order distorted wave treatment of the surface corrugation effect. Whaley and Light refer to this as the multichannel distorted wave Born approximation (MDW).[310] Lill and Kouri[311] reported numerically exact, close-coupling calculations of Δm_J transitions and found that the DSCCR and MDW are typically of comparable accuracy, except for specular scattering where the DSCCR is preferable.

So far, there has been no experimental demonstration of $\Delta m_J \neq 0$ transitions. An interesting effect that is related to this question was measured by Luntz et al.[312] Studying the scattering of NO from Ag(111) these authors found that the scattered molecules are strongly rotationally polarized, that is, the scattered molecules have a nonuniform distribution of the magnetic quantum number m_J for a given J value. The degree of rotational polarization was found to depend strongly on the final J state and on the incident energy and angle.[312,313] The effect has been at least qualitatively explained by Lauderdale et al.,[314] who used quantum close-coupling calculations, and by Kleyn et al., who pursued classical trajectory simulations.[313] In their elegant interpretation, Lauderdale et al. point out that the rotational polarization observed is mostly due to the fact that m_J distribution is almost unchanged by the collision, while the incident J distribution is greatly changed due to the large rotationally inelastic scattering; the net effect is a polarized final rotational state distribution. Another effect that plays a role is of a "dynamical" nature: Molecules which initially are at, say, $m_J = 0$ undergo strong rotational excitation, since many of the orientations of the molecule are suitable for high torques upon impact. Kleyn et al.[313] found from their classical simulations that both effects are necessary to interpret the measured polarization. However, while for low J values the trajectory simulation fitted nicely the experimental results, there was a significant discrepancy for the high J. They suggest that the energy exchange with the surface may affect the polarization results of these final states.

Finally, in conclusion of this subsection, it should be useful to return to the question that was at the background of many of the discussion points raised: To what extent can rotationally inelastic scattering experiments, when quantitatively analyzed by the theoretical methods discussed here, lead to the determination of a reliable anisotropic molecule–surface interaction potential. One of the best cases, if not the best in that respect, is the hydrogen/Ag(111) system discussed earlier. Whaley et al.[267] fitted rotationally inelastic and (diffractive) selective adsorption data for the H_2, D_2, and HD isotopic species, measured by Sibener and coworkers over a range of incidence energies and angles. The potential determined was of the form

$$V(z,\theta) = V_0(z) + V_2(z)P_2(\cos\theta) \qquad \text{(IV.8a)}$$

where the isotropic part was taken in the form

$$\begin{aligned} V_0 &= V_0{}^R(z) + V_0{}^A(z) \\ &\equiv Ae^{-\alpha(z-z_0)} - Bf(z)\frac{1}{z^3} \end{aligned} \qquad \text{(IV.8b)}$$

where $f(z)$ is a cutoff function going smoothly from $f(0) = 0$ to $f(z) = 1$ for large z. The anisotropic component is given by

$$V_2(z) = \beta_R V_0{}^R(z) + \beta_A V_0{}^A(z) \qquad \text{(IV.8c)}$$

β_A, β_R, and parameters in $V_0(z)$ were varied to fit the data. The *form* of eq IV.8a is suggested by ab initio theoretical studies. Whaley et al. were able to arrive at a set of parameters that fitted to a satisfactory degree and consistently the wide range of data available. Moreover, the potential determined is in good agreement with the ab initio potential of Harris and Liebsch.[315] Thus, at least in optimal cases, the state of the art is approaching a level where an extensive set of experimental data can be used to determine an anisotropic molecule–surface interaction of quantitative accuracy.

B. Phonon Participation in Rotationally Inelastic Collisions

While evidence was presented that in some cases the rigid-surface model can be directly useful in the interpretation of experimental rotationally inelastic scattering data, a major effect of surface vibrations is the rule rather than the exception in such processes. Trapping-desorption scattering of molecules is obviously a case where typically extensive accommodation of the rotations to the surface vibrations is found, but the role of phonons can be, and generally is, very important also in direct collisions. Mechanistically, one may have direct energy exchange between the rotational mode and surface phonons, as well as important indirect effects such as the one due to competition between the rotation and the phonons for the fixed available amount of collision energy. The possible variety of phonon participation channels in rotationally inelastic scattering is very large.

In an inherently complicated topic, the simplest approach for describing the effect of surface motions on rotational energy transfer is probably the one based on combining the hard, flat surface model for rotationally inelastic treatment, mentioned in subsection A above,[295,296] with the "hard-cube" treatment of atom–surface scattering, discussed in section III.B.[213,214] What emerges is a scheme in which a rigid rod or an ellipsoid is in impact on a flat, hard cube representing a surface atom or group of atoms, the latter being described as carrying out independent, thermalized translational motion in the *z* direction before the encounter. It is interesting that heteronuclear molecules can be treated by the model by placing the molecular mass off the ellipsoidal center. This simple model is criticized by Zare and co-workers,[295,296] who point out that it cannot adequately account for the experimental findings, e.g., because with realistic mass-parameter values for the surface cube it grossly overestimates the inelasticity of the collision. To interpret their experimental findings on NO/Ag,[296] Zare and his collaborators[295,296] introduced a much improved "soft-cube" model, along the lines proposed by Logan[214] for atom–solid energy transfer. In the improved model the moving surface segment with which the molecule collides is still treated as flat. However, a realistic potential function with an exponential repulsion and a long distance attractive force replaces the "hard wall" treatment. Given its great simplicity, the model is very successful in semiquantitatively describing several experimental findings for NO/Ag: the existence of rotational rainbow scattering and the broadening of the rainbow structure by surface thermal motions; the linear dependence of the mean rotational energy transfer upon surface temperature[296]

$$\langle E_R \rangle = a(E_n + D) + bk_B T_s \qquad \text{(IV.9)}$$

where E_n is the energy normal to the surface and D is a constant interpreted as the attractive well-depth. However, Kubiak et al.[296] found that the model leads to unreasonably large trapping probabilities; hence it cannot provide a consistent description of the collision dynamics in the case of NO/Ag.

Classical dynamics has probably been the most extensively employed tool for studying rotationally inelastic scattering from vibrating surfaces. In particular, several studies were reported by Tully and co-workers using the GLE technique to describe the effect of surface vibrations: Muhlhausen and Serri et al.[316] studied the scattering of N_2 from Ag(001), focussing on the angular distributions; Muhlhausem, Williams, and Tully[206,288] studied the scattering and desorption of NO from Ag(111) and Pt(111), exploring the velocity and the rotational energy distribution of the scattered molecules.

Polanyi and Wolf[281] studied NO scattering from two classical models of a vibrating solid: One model, the single harmonic–oscillator (SHO), represents the outermost surface atom (or surface segment) as an isolated, uncoupled Einstein oscillator. The second model, referred to as the generalized Langevin oscillator (GLO), describes that atom as an oscillator affected by friction and by a stochastic force, which represents the effect of the other (implicit) atoms of the solid. The GLO system is thus a simple model in the spirit of the GLE formalism. Polanyi and Wolf[281] studied the contributions of the direct inelastic, indirect inelastic, and trapping desorption mechanisms to rotational energy transfer in the collision process.

The "molecular dynamics" method that involves a full classical trajectory simulation of the colliding molecule and of a large number of solid atoms treated explicitly (see section III.B) was applied by Elber and Gerber[312] in a study of rotationally inelastic scattering of I_2 upon high-energy impact on MgO(100). In this case, there are anharmonic shock-wave-like excitations of the solid (discussed in section III.B and ref 199 and 200) that cannot be described by the GLE method in its present form.

Recently there has been considerable interest in methods that treat the rotational degrees of freedom quantum mechanically but nevertheless allow for the effect of surface vibrations. Much work in this direction was done by De Pristo and his co-workers,[229,230,237] who employed their semiclassical stochastic trajectory method, discussed in section III, which treats surface vibrations by the GLE approach and describes the internal molecular states quantum mechanically. Lee et al.[299] used the method to study rotational and magnetic quantum number transitions in H_2 collisions with Pt(111), showing the rotational–translational energy transfer probabilities to be little affected by surface temperature. Clary and De Pristo[230] studied vibrationally and rotationally inelastic collisions of CO_2 with Pt(111), in which case they simplified the semiclassical stochastic trajectory method by applying the Sudden approximation to the large manifold of rotational states in that system. De Pristo et al.[237] explored the role of rotational energy transfer in the physisorption dynamics of H_2 on Cu(100). The Langevin force in this case was modeled to include also the effect of electron-hole pairs as mentioned in section III.

Schinke and Gerber[318] developed an approximation for high-energy scattering of light molecules from solids of heavier atoms that involves Sudden approximations for the diffraction of the rotational and the phonon degrees of freedom. The restrictions on the masses of the collider and the solid are to imply conditions where energy transfer to phonons (as well as to rotation) is small on the scale of the incident collision energy. The treatment of the phonons is similar to that proposed by Adams and Miller[17] in the case of atom–solid collisions. Schinke and Gerber applied their method to explore the effect of temperature on the rotational state distribution of NO molecules scattered from Ag. Brenig et al.[319] argued that the Sudden typically overestimates the true energy transfer and suggested a simple improvement that involves a scaling of the phase shift which appears in that approximation (see eq IV.3). In test calculations for a simple model system, this improved Sudden method gave results in excellent agreement with the exact quantum mechanical calculations. Brenig et al. used their method to discuss rotational inelastic scattering from a vibrating surface modelled by a single oscillator.[319]

All the previously discussed methods are based on solving approximately the quantum or classical equations of motion. Zamir and Levine[282] follow a different, information-theoretic, approach.[320] This method introduces an entropy function, which is maximized subject to certain constraints, taken to represent dynamical restrictions on an otherwise statistical theory. Zamir and Levine[282] showed that their scheme can fit the rotational state distribution observed for NO scattered from Ag but only provided one accepts a much higher trapping probability than is generally assumed.

Several properties and phenomena of rotationally inelastic scattering from surfaces will be discussed now in terms of methods outlined above.

Validity Conditions for the Rigid-Surface approximation. This is a fundamental question, already invoked in the previous subsection: There is evidence that in some cases calculations using a static surface model reproduce approximately the correct final rotational state distribution for the scattering process (although, of course, the absolute values of the rotational transition probabilities may be largely affected by surface vibrations). It is important to clarify the cases where this is indeed valid and to establish the physical causes of this behavior. Schinke and Gerber[318] showed that in the Sudden limit discussed above the rotational transition probabilities are to first approximation affected by phonon participation only via a Debye–Waller-type of attenuation factor. Thus, the relative probabilities for scattering into different rotational states depend only weakly on temperature in the framework of the Sudden scheme. A possible interpretation of this result is that under the conditions of the Sudden limit the time scale of the collision is short compared with that required for phonon-to-rotation energy transfer. Also, the Sudden assumes collision energies so high that indirect phonon-rotation coupling due to competition for the energy is not involved.

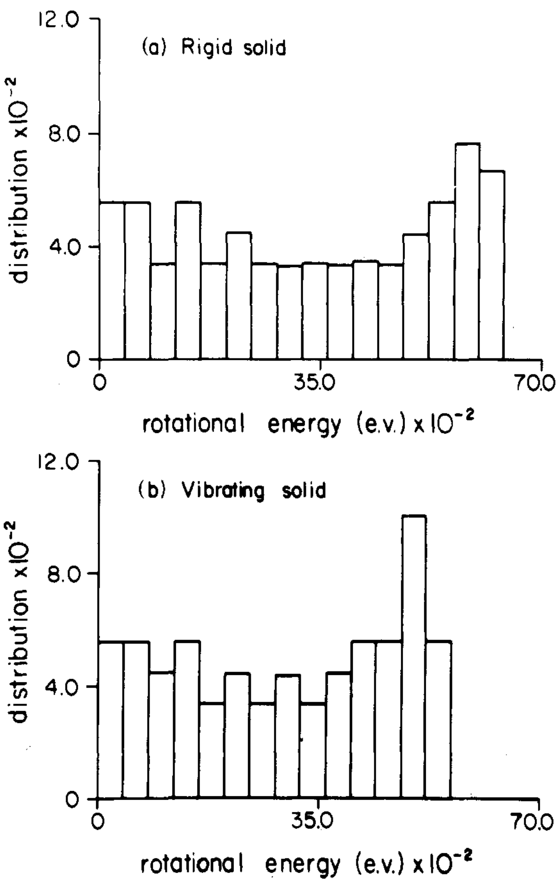

Figure 12. Histogram of the rotational energy distribution from classical trajectory simulations of I_2 collisions at 2.0 eV with MgO(100): (a) rigid solid; (b) vibrating solid. (Reproduced with permission from ref 317. Copyright 1985 by Elsevier.)

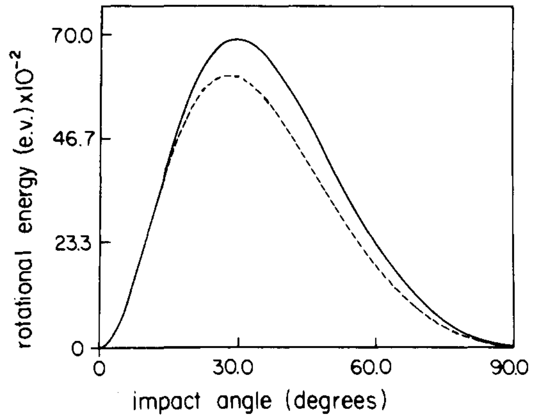

Figure 13. Final rotational energy of I_2 scattered from MgO(100) as a function of molecular orientation at impact: —, rigid solid; - - -, vibrating solid. (Reproduced with permission from ref 317. Copyright 1985 by Elsevier.)

Elber and Gerber[317] found by molecular dynamics simulations that the static surface model gives approximately the correct final rotational energy distribution for high-energy collisions (e.g., E = 2.0 eV) of I_2 with MgO(100), as shown in Figures 12 and 13. This seems very surprising since the energy transfer to the solid in this case is very high, taking up a large fraction of the collision energy (30–40%). The explanation arrived at by comparing classical trajectories for calculations with or without the participation of solid vibrations is as follows: In collisions of a heavy collider with a solid of light atoms and fairly stiff vibrational force constants, a shock-wave-like excitation of the solid typically occurs (see section III.B and ref 199–201).

When the colliding species is a molecule, rotational excitation also occurs, due to the torque the molecule receives in the collision, the latter being determined essentially by the orientation of the molecule at the instant of impact. Mass ratios and other system parameters in I_2/MgO are such that the excitation of the solid lags slightly in time behind the rotational excitation: The "pressing in" of the outermost surface layer atom which causes the onset of the shock-wave occurs slightly *after* the torque that creates the rotational excitation has already been administered. In a sense, at the initial moment of impact the surface still behaves as rigid for a tiny instant of time ($\sim 10^{-14}$ s). Hence the good agreement between rigid-surface and vibrating solid calculations in this case. This, however, is a very system-dependent behavior, and in the case of, e.g., I_2/sapphire the excitation of the solid does not lag behind the rotational excitation and it does affect the rotational distribution.[201]

A very interesting example of how important features of the rotational energy distribution can be similar for collisions with rigid and with dynamical surfaces despite major differences in the scattering mechanisms in the two cases was given by Polanyi and Wolff.[281] These authors studied NO scattering from a rigid surface and from two models of vibrating surfaces that were discussed earlier in this subsection, the single harmonic oscillator (SHO) model and the generalized Langevin oscillator (GLO) model. For the rigid surface, rotational energy transfer occurred only by direct collisions. In the SHO model also *indirect* scattering (involving multiple collisions of the molecule with the surface) were found to contribute. For the GLO case, Polanyi and Wolff found also substantial contributions from the trapping-desorption mechanism. Figure 14 shows a Boltzmann plot of the final rotational state distribution for all three models. Despite the great difference in the dynamics, both the rigid and the dynamical surface results give the same essential feature of "bimodal distribution", that is, a "Boltzmann-like" behavior for the low final J states, and a different behavior for high J. As Polanyi and Wolff[281] emphasize, this shows that one can fit final rotational state distributions by both rigid-surface and vibrating surface treatments; thus such data alone cannot establish the collision dynamics.

In specific limits and cases, the relation of rigid-surface results to the "real" final rotational state distribution is established and physically understood. In general, the question is still largely open.

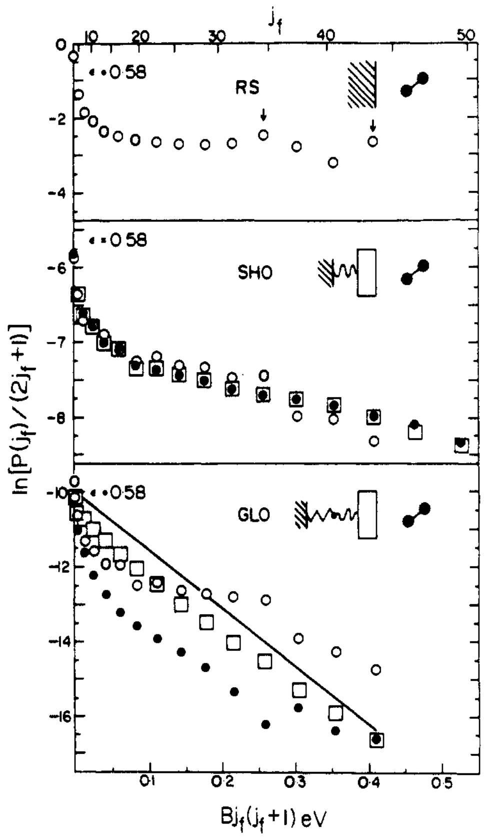

Figure 14. Boltzmann plots of the rotational state distribution for NO scattering from model surfaces. Rigid surface (RS) results are compared with those from the SHO and GLO models. Open circles denote the direct component, closed circles the indirect one, solid line the trapping-desorption contribution, and squares the composite. All results are for a collision energy of 0.7 eV and a surface temperature of 650 K. (Reproduced with permission from ref 281. Copyright 1985 by the American Institute of Physics.)

The Roles of Direct, Indirect, and Trapping Absorption Collisions: We return to the study of Polanyi and Wolff[251] for an instructive example of this question. The trajectories defined by the authors as corresponding to a direct collision are those in which the molecule reached only one classical turning point in its distance coordinate from the surface. Trajectories involving three or more such turning points were defined as "indirect". Basically indirect trajectories thus represent multiple-collision effects. Adsorption involves dissipation of a sufficient amount of energy from both the molecule and the surface oscillator into the bulk. Polanyi and Wolff found that for the rigid-surface model trajectories were direct at E = 0.7 eV, and some ($\sim$10%) indirect contribution could be found at lower collision energies. In the SHO model the situation was radically changed with almost total dominance of indirect collisions at both 0.3 and 0.7 eV (at the latter energy $\sim$10% of the trajectories were direct). In the GLO model, 80% of the collisions at 0.7 eV and $\sim$95% of the collisions(!) at 0.3 eV were of the absorption/desorption type. The model of Polanyi and Wolff may well not correspond to the realistic case of NO/Ag studied by Kleyn et al.[13] One can draw, however, the conclusion that the probabilities of multiple scattering events and of adsorption/desorption processes increase rapidly with increased phonon participation. The effect of this on the rotational distribution produced by the scattering (not including the contribution of adsorption/desorption events) is shown in Figure 15. It is interesting to note that at 0.7 eV the rainbow structure of the rigid surface is still evident also for the dynamical surface model, although to a much lesser extent. At 0.3 eV collision energy the dominance of indirect collisions is total and destroys the rainbow feature. To the extent that the rotational rainbow is present for the dynamical surface at the higher collision energy, its position is unaltered from the value in the rigid surface calculation.

Angular Intensity Distribution of Molecules Scattered from a Vibrating Surface. For molecules scattered from a rigid surface, rotationally inelastic collisions could cause a large deviation from specular scattering: A molecule undergoing rotational excitation at the expense of its z axis translational energy will emerge, for nonperpendicular incidence, at an angle

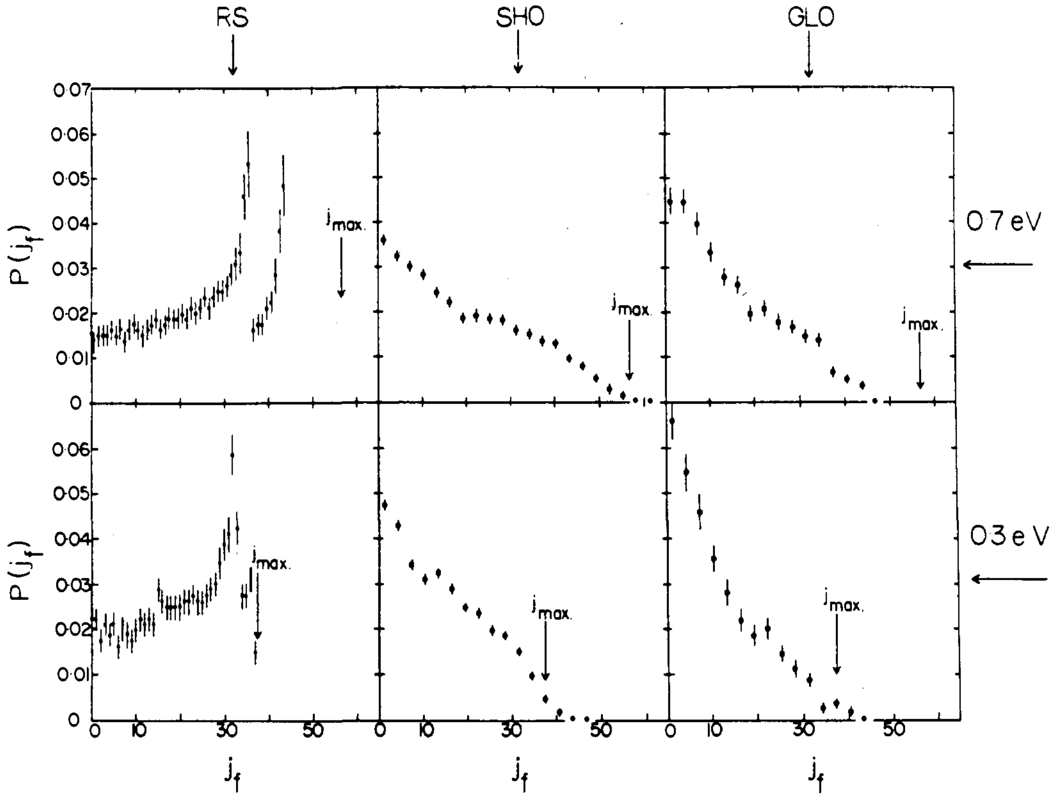

Figure 15. Rotational state distributions for scattered NO molecules for the rigid-surface and the SHO and GLO models. The position J_{max} corresponds to the energy present in the diatom before the collision.

higher than the specular one (measured from the normal to the surface). In particular for cases where a pronounced rotational rainbow occurs, the effect could be quite large. It is important to study the situation for a realistic, vibrating surface and to test the prediction against experiment. Several such studies were pursued by Tully and his collaborators,[288,316] by the GLE approach. Mulhausen et al.[316] explored N_2 scattering from Ag(001) for incidence energies between 7 and 96 kJ/mol and for surface temperatures between 205 and 600 K. Figure 16 shows the calculated angular intensity distributions of the scattered molecules in comparison with the experimental results. It is evident first that the agreement between experiment and theory is a good one and second that the scattering is centered at a near specular direction. The small shift of the intensity peak from the specular direction indicates that phonon participation essentially cancels the effect of rotational energy transfer (as in a rigid-surface case) to produce a deviation from the specular direction. The rotational inelasticity is large in this system, although N_2/Ag(001) is, in relative terms, a case of low anisotropy. It appears from the study by Muhlhausen et al.[316] that the effect of rotational energy transfer on the angular distribution is much smaller than that of the corrugation. One experimental manifestation of this is that beams of Ar and of N_2 of the same incidence velocity show remarkably similar angular intensity distributions. In a more recent study[288] Muhlhausen et al. showed that they could reproduce well the angular intensity distribution for NO scattered from NO on Ag(111), measured by Asada.[321] Also in this case the angular distribution is more sensitive to corrugation than to rotational energy transfer.

In the study of rotationally inelastic scattering from vibrating surfaces, the difficulties of fitting a reliable potential to the data are even greater than in the rigid-surface case. Tully et al.[316] used in their studies empirical potentials of the following type

$$V = \sum_i V_i(\mathbf{r}_i,\mathbf{r}_1,\mathbf{r}_2) + \frac{C}{(z - z_0)^9} - \frac{D + E\cos^2\theta}{(z - z_0)^3} \qquad \text{(IV.10)}$$

given for the homonuclear case of N_2, where $V_i(\mathbf{r}_i,\mathbf{r}_1,\mathbf{r}_2)$ are pairwise potentials between the molecule and the surface atoms, taken in the form

$$V_i(\mathbf{r}_i,\mathbf{r}_1,\mathbf{r}_2) = A[e^{-\alpha|\mathbf{r}_1-\mathbf{r}_i|} + e^{-\alpha|\mathbf{r}_2-\mathbf{r}_i|}] + Be^{-\alpha|(\mathbf{r}_1+\mathbf{r}_2)/2-\mathbf{r}_i|} \qquad \text{(IV.11)}$$

where $\mathbf{r}_i$ is the surface atom position, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the N atom positions, α, A, B, C, D, E, and z_0 are all parameters. The last term in (IV.10) is the long-range dispersion force (fluctuating image–dipole interactions between the molecule and the surface) which is taken in a form suggested by Drude's model. Otherwise the interaction is empirical and must be fitted to data. It is hard to assess the extent to which such interactions, when fitted to the limited data available, can indeed be regarded as realistic and quantitative.

Finally, it is important to bring up the question of the possible role of electron-hole pair excitations on rotational energy transfer. Nearly all studies so far assumed that phonons are the only surface modes to play an significant role in rotational transitions, which seems reasonable in view of the low frequencies of rotational motions but is by no means certain. De Pristo et al.[237] in a recent study included electron-hole pair effects in an essentially phenomenological way in the stochastic and friction GLE forces acting on the colliding molecule. When the scheme was applied to physisorption dynamics of H_2 and D_2 on Cu(100), a crucial role was suggested for electron-hole pair exci-

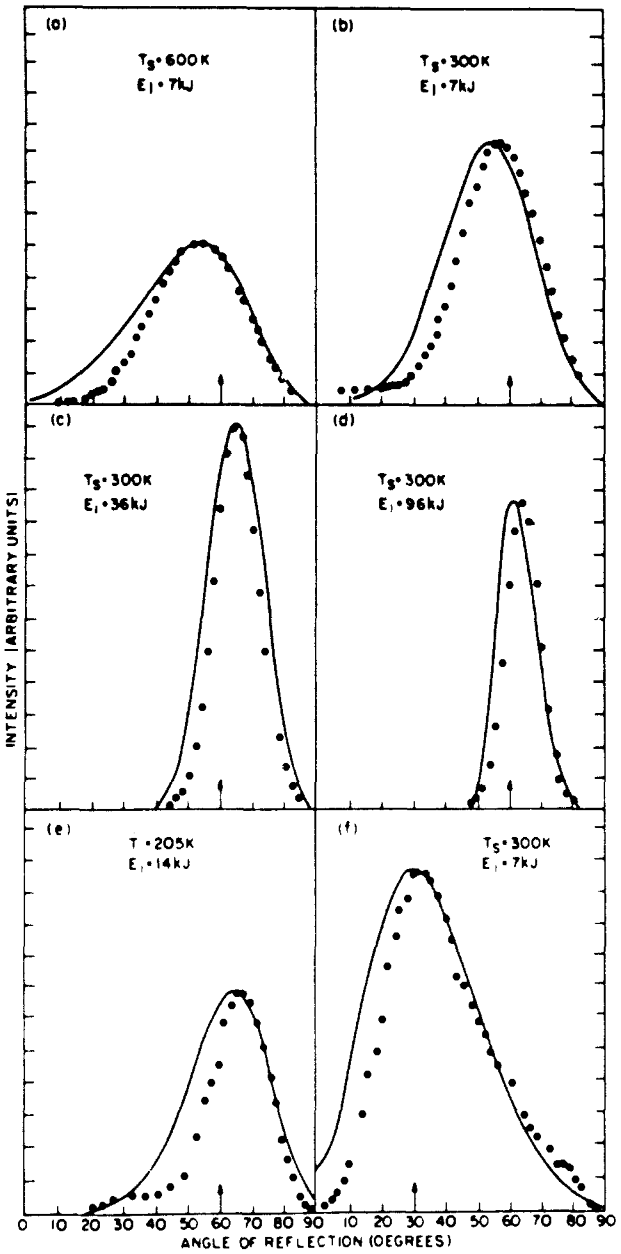

Figure 16. Angular distributions of N_2 scattered from Ag(001) for difference values of incidence energy E_i, angle, and surface temperature as indicated. Points are experimental and solid curves are theoretical results. Peak intensities are normalized. Incidence angles are indicated by solid circles. (Reproduced with permission from ref 316. Copyright 1982 by Weizmann Sci Press.)

tations in determining sticking probabilities. In fact, electron-hole pair excitations (together with phonon contributions) were found to prevail over rotational-to-translational energy transfer as a mechanism for sticking. While the quantitative reliability of the treatment of electron-hole pairs is in doubt, the suggestions of the authors are very interesting and should stimulate further work on this question.

C. Vibrational Deactivation and Excitation

Experiments for measuring vibrationally inelastic scattering from surfaces under well-defined single collision conditions are fraught with difficulties. There has been much less progress on this topic so far than in the study of rotational energy transfer. Pioneering experiments by Fenn and co-workers[322,323] involved infrared spectroscopic measurements of vibrationally excited CO and CO_2 molecules produced by molecular beam scattering from a polycrystalline surface. In this case the final vibrational populations are determined by an absorption/desorption mechanism with complete or nearly complete accommodation to the surface temperature. Asscher et al.[25] reported studies of vibrationally excited NO produced in scattering from Pt(111). The angular distribution in this case, of the cosine type, also suggests a trapping-desorption mechanism. Using a simple rate-equation scheme, Asscher et al.[323] were able to extract rates for vibrational excitation and deexcitation from the experimental data. Zacharias et al.[23] reported molecular beam experiments on the scattering of vibrationally excited NO from LiF(001). The early measurements gave very questionable results of almost 100% probability of deactivation. This, however, was withdrawn in a more recent study of the same group, which produced a much lower upper bound estimate for the deactivation probability.[324] Misewich et al.[225] measured the deactivation of the $v = 1$ vibrational level of the asymmetric stretch mode of CO_2 from Ag, Ni, and stainless-steel surfaces. In a later study, Apkarian et al.[326] continued this work so as to determine the deactivation probability of CO($v = 2$) and of CO_2(101) on polycrystalline silver surfaces, and Misewich, Houston, and Merrill[227] reported their results on vibrationally inelastic surface scattering of CO and CO_2. The above studies by the Cornell group of Houston, Merrill, and their co-workers were interpreted by a trapping mechanism, followed by transfer of the vibrational energy into electron-hole pairs.[326] Two recent experimental studies of vibrationally inelastic scattering of NO from single-crystal silver surfaces are by Misewich and Loy[328] and by Rettner et al.[329] In the experiments of Rettner et al.,[329] direct vibrational excitation of NO from Ag(111) was measured as a function of incident kinetic energy and of surface temperature. A strong dependence on T_s was found, which led the authors to propose an electronic mechanism for the excitation.[329] The above survey of experimental results indicates that progress in the field is very recent and that the first successful quantitative measurements of vibrationally inelastic scattering data date from the last 2 years or so. The unavailability of such data until just recently limited greatly theoretical progress in the field. Furthermore, even for gas-phase molecule–atom collisions reliable calculations of vibrational deactivation rates are extremely difficult.[330] Vibrational transitions are much weaker than rotational ones and are therefore much more sensitive to details of the potential energy surface. Sufficiently accurate potential surfaces are only rarely available.

One of the earliest models for vibrational deactivation in molecular scattering from surfaces was proposed by Gerber, Beard, and Kouri.[331] The model is restricted to high-energy impulsive collisions and makes the drastic simplification of a static-surface assumption. On the short time scale of fast collisions, energy transfer from the high-frequency vibration of the molecule to the soft phonons of the crystals seems unlikely, since a very high-order multiphonon process is required. Multiphonon excitation at the expense of some of the high translational energy of the collision should definitely occur but will probably not affect the relative importance of the vibration-to-translation (V-T) and vibration-to-rotation (V-R) mechanism, which is the focal point in the study of Gerber et al.[331] Following a similar method that proved successful in treating vibrational deactivation in gas-phase atom–molecule collisions,[332] the authors used a Sudden approximation for the rotational states in the process, and assuming weak vibrational inelasticity, the latter was treated by a distorted-wave Born approximation. In the final expression obtained for the vibrational deactivation probability, a major role is played by "energy gap factors" of the form $g_{n,J;n-1,J'} \equiv \exp|-a(E_n + E_J - (E_{n-1} + E_{J'})/\hbar v|$. Here a is a range parameter of the interaction potential, v denotes the collision velocity, E_n and E_J are respectively the initial vibrational and rotational energy, and J' is a given final rotational state. The approximation was applied to several model systems of molecular collisions with surfaces at collision energies in the electronvolt range.[331,333] The model predicts in these cases a strong propensity for a V-R over a V-T deactivation mechanism. Experiments reported thus far do not correspond to the conditions assumed in the model (very high collision energies, non-metal surfaces, etc.), so it is unclear as yet whether the V-R mechanism is indeed correct.

Lucchese and Tully[334] explored the vibrational deactivation of NO in collision with LiF(001), for conditions corresponding to the experimental study of Zacharias et al.[23] The authors used classical dynamics with a GLE representation of the role of surface phonons. They report very low vibrational accommodation coefficients, of the order of 2×10^{-3}, much smaller than the current upper bound estimate from the revised experiments.[224] Lucchese and Tully found that the main receiving mode for the released vibrational energy in their study were the surface phonons, the role of rotational and translational modes being much weaker. It should be noted that classical calculations of vibrational deactivation could be in substantial error in cases where the deactivation probability is extremely low, since for very weak processes quantum corrections are typically nonnegligible. A very extensive study of vibrational deactivation of CO_2 by Pt(111) was made by Clary and De Pristo,[230] using the semiclassical stochastic trajectory method reviewed in previous sections, with a full quantum treatment of the vibrational modes and a Sudden approximation for the rotational motion. Clary and De Pristo[230] carried out calculations for several initial vibrational states of the CO_2 molecule. They found the vibrational deactivation probabilities to be sensitive to surface temperature in the cases where the probabilities are small and to be rather independent of T_s when the probabilities are relatively large. In all the processes studied, trapping probabilities were quite large, even at high surface temperatures. The authors thus find that a trapping-desorption mechanism for deactivation seems most likely for systems of the type explored. In comparing their results with experiments by Houston, Merrill, and co-workers[325] (for surfaces other than Pt(111)) Clary and De Pristo find that the theoretical deactivation probabilities are smaller by orders of magnitude than the experimental one. The authors finally suggest that deactivation in the experiments of Misewich et al.[325] on CO_2/Ag, CO_2/Ni, etc. is probably due to a trapping-desorption energy in which the deactivation occurs in the trapped state via near resonant energy transfer to either electron-hole pairs (not included in the model) or to molecular rotations, an interpretation indeed offered by Misewich et al.[325,326]

There are thus indications that electron-hole pairs may provide the dominant mechanism for vibrational deactivation of molecules by metal surfaces, at least in the case of trapping-desorption scattering. A full treatment of the collision process that includes the effect of electron-hole pairs in the deactivation was not given as yet. However, insofar as one is dealing with trapping-desorption scattering with sufficiently long residence times of the molecule on the surface, estimates of the electron-hole pair mechanism for vibrational deactivation of bound adsorbed molecules become relevant. This clearly emerges from the studies by Asscher et al. of NO on Pt, in which case the molecule is essentially temporarily chemisorbed on the surface.[25,323] Estimates of the lifetimes of vibrationally excited molecules, fixed at some distance from the surface or adsorbed on it,[334,336] give typically values in the range of 10^{-3}–10^{-12} s. Such values are definitely consistent with the interpretation of deactivation as occurring by trapping followed by energy transfer into electron-hole pair excitations. A positive, direct proof of the mechanism is, however, not available as yet.

A mechanism distinct from, yet related to, that of electron-hole pair excitation is one based on long-distance dipole–dipole near resonant energy transfer from the molecular vibration to surface plasmons. The feasibility of this mechanism depends on the availability of a surface plasmon mode at the appropriate frequency. A treatment of vibrational energy transfer by this mechanism, based on the classical electromagnetic theory of an oscillating dipole coupled to a metal, was worked out by Brus.[338] It is closely related to the theory proposed by Chance, Prock, and Silbey for the transfer of electronic energy from an excited molecule to a metal.[339] This mechanism can be effective over very long distances (order of 10^2 or 10^3 Å), thus being quite related to trapping effects. An experimental search for demonstrating this mechanism should be of interest.

Finally, an interesting and potentially important mechanism for vibrational excitation of molecules in collision with surfaces, based on temporary transfer of a surface electron to the molecule, was put forward by J. W. Gadzuk. This so-called "surface harpooning" model[340] will be discussed in the next subsection dealing with nonadiabatic processes.

The theory of vibrational energy transfer in molecule–surface collisions is at an early formative stage. As stressed at the beginning of this subsection, reliable, quantitative experimental data on such processes has become available only in about the last 2 years, and certainly the experimental studies on this topic are rapidly gathering momentum. It seems reasonable to anticipate a period of quite exciting activity for theory in this field in the immediate future as much stronger, quantitative interaction with experiments is established.

D. Nonadiabatic Energy-Transfer Processes

The electron-hole pair excitations in atom and molecule–surface scattering, discussed in sections III.D and IV.C, respectively, are nonadiabatic processes, since a change of electronic state due to coupling with nuclear motion is involved. In the present subsection we focus, however, on nonadiabatic processes in which the electronic transition that occurs is associated with states of the colliding molecule or atom.

A nonadiabatic mechanism that can result in vibrational excitation, even dissociation, of molecules colliding with a surface, was proposed and extensively pursued by Gadzuk and Holloway.[339-344] The mechanism may qualitatively be described as follows: Suppose that the electron affinity of the molecule and the work function of the surface are such that as the molecule approaches the solid, a surface electron can hop to the molecule, to form a transient molecular ion. Due to the change in the electronic potential energy curve, vibrational transitions will occur, described by Franck–Condon overlaps. On the way out from the surface, the electron can hop back from the transient negative ion to the solid. Again, vibrational transitions are induced. In the process as described, the scattered molecule is the same neutral species as that which encountered the surface. Due to the intermediate charge-transfer processes, vibrationally inelastic transitions will typically have taken place, however, at the expense of the collision energy (and possibly also the energy of the surface electron). The energy level structure assumed in Gadzuk's scheme is shown in Figure 17. This electron-transfer mechanism is related to that of the so-called harpooning reactions (between alkali atoms and halide molecules)[289] and to the Bauer–Fisher–Gilmore mechanism[345] for electronic-to-vibrational energy transfer in the gas-phase, hence the term "surface harpooning" used by Gadzuk for its description. As for the quantitative formulation of the model, several levels of approximation were presented. One version[342] follows essentially the Tully–Preston scheme[346] for quasi-classical calculations of nonadiabatic transitions. Classical trajectories are pursued on the pertinent diabatic potential energy curves of the system (see the schematic Figure 17), until a crossing with another potential energy surfaces is reached. At this point, hopping to the second surface is allowed, the weight for such an event being taken from the familiar Landau–Zener expression for transition probabilities in electronic curve crossings. By continuity conditions, initial values are obtained for continuing the trajectory on the new surface.[342] Such a calculation is carried out to the completion of the collision process, trajectories being calculated for a sufficient number of initial conditions. Other versions involve different, often more drastic approximations, which thus result in simpler expressions; e.g., harmonic approximations were used by Gadzuk and Holloway[344] for the potential energy curves in the crossing region; effects of molecular orientation with respect to the surface were ignored; a mixed classical/quantum mechanical treatment was pursued in which the incoming molecule is described by a single classical trajectory and the crossing harmonic oscillators by quantum mechanics.[344] Physically, the crucial parameters which determine the importance of vibrational excitation and related processes by the surface harpooning mechanism are (1) the magnitude of the Landau–Zener surface-hopping probabilities at the potential surface crossings; (2) the location of the surface crossings, in particular whether these are at configurations that are classically accessible at the given collision energy, and (3) the magnitude and structure of the Franck–Condon overlaps between vibrational states in the two different potential energy surfaces. Unfortunately, these parameters are typically rather sensitive to the potentials and accurate potential energy surfaces for the pertinent systems are unavailable. Holloway and Gadzuk[342] reported calculations on vibrational excitation and dissociation of N_2 and of Cl_2 in collision with a model surface parametrized to represent a "typical" metal surface. Very recently, Gadzuk and Holloway[343] applied the harpooning model to NO scattering from Ag(111), a system studied experimentally by Rettner et al.[329] The authors report that they can qualitatively explain the experimental results, in particular the strong increase of the vibrational excitation probability with surface temperature.[343] Applications of the surface harpooning model to molecular dissociation and to charge-transfer reactions are discussed in section V.

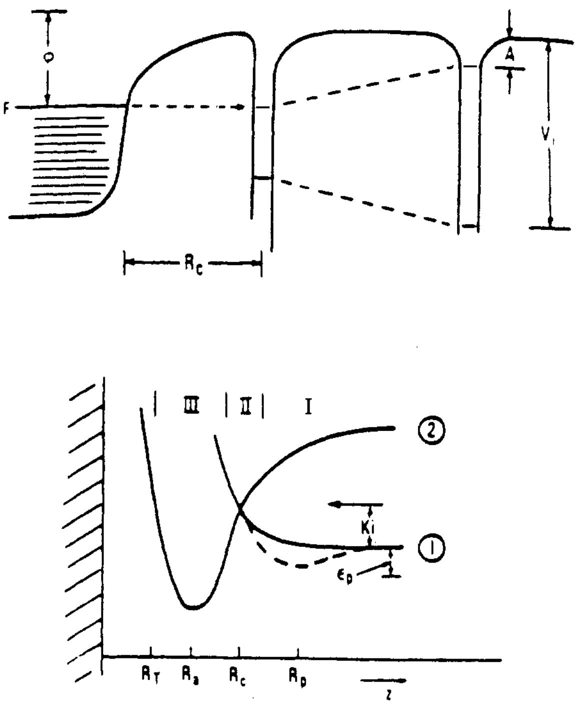

Figure 17. (a) Single electron energy levels of atom or molecule approaching a surface. The lowering of the affinity level allows a Fermi level electron from the substrate to tunnel into the molecule, thus creating a negative molecular ion. This possibility is suddenly turned on at a separation R_c where the shifted affinity level coincides with the Fermi level, and this corresponds exactly to R_c in (b), if curve 1 is regarded as a molecule curve and curve 2 as a negative molecular ion curve. (b) Diabatic potential energy curves as a function of z, the normal distance from the surface, of an incident particle initially in some electronic state 1 and with kinetic energy K_1. The full curve 1 corresponds to an electronic state giving rise to a strictly repulsive surface interaction, whereas the dashed curve represents a state which allows for a weakly physisorbed precursor state with desorption energy ϵ and equilibrium separation R_p. Curve 2 corresponds to an electronic state which strongly adsorbs at an equilibrium separation R_3. Within region II, a diabatic electronic transition from curve 1 to curve 2 can occur, with the probability peaked at $z = R_c$, the curve crossing point. Nuclear motion in region III proceeds on curve 2 up to the classical turning point R_T. (Reproduced with permission from ref 339. Copyright 1985 by Gordon and Breech.)

The electron-transfer mechanism of Gadzuk and Holloway is certainly an interesting and potentially useful one. For metal surfaces and for halogen molecules (or other, chemically similar systems) it has a strong intuitive appeal. In the case of insulator surfaces and molecules of low-electron affinity, the arguments for it are questionable. (Indeed, the Bauer–Fisher–Gilmore model for gas-phase $E - V$ energy transfer, based on the harpooning idea, appears to fail for molecules such as H_2.) For the various systems for which it appears suitable, quantitative calculations with the surface harpooning model should be most desirable. This is an admittedly difficult task, requiring improved calculations of potential energy surfaces, their crossings, and nonadiabatic coupling parameters.

A quantitative approach to the calculation of nonadiabatic transition probabilities in molecule–surface collisions was proposed by Sawada et al.[347] The scheme is an adaptation of the mean-trajectory approximation developed by Metiu and Jackson,[231] which was discussed in sections III and IV. Sawada et al. derive the approximation from a path integral method, or alternatively, from an Eikonal approximation. The formalism is built to include electronic energy transfer, charge transfer, and phonon as well as hole pair excitations. So far, numerical applications of the equations derived were not given.

V. Reactive Molecule–Surface Collisions

A. Collision-Induced Dissociation on Surfaces

We consider now dissociation processes which involve impact at high energies of diatomic molecules on chemically inert surfaces. The notion of a chemically inert surface is meant here to imply that no strong binding forces exist between the surface and the molecule, or its constituent atoms. Dissociation is then due to the steep, repulsive part of the molecule–surface interaction potential that converts the collision energy into internal energy of the molecule to an extent sufficient for overcoming the binding forces. Such processes of collision-induced dissociation are of considerable chemical importance and are pertinent to many reactions on vessel walls. We shall be interested here in their fundamental significance as perhaps the simplest type of chemical reaction at the gas–surface interface. One of the major advantages in pursuing such processes is that they can be studied and understood in the simple framework of well-defined single collision events. This is not the case for reactions having products that stick to the surface.

In the last few years considerable progress was made in the study, and understanding from a first-principle point of view, of dissociation induced by collisions with surfaces. This has been a consequence of combined molecular beam scattering experiments and theoretical models and calculations.[199-201] The studies reviewed here, by Amirav, Gerber, and their repulsive collaborators, deal with molecules such as I_2 and ICl in collision with single-crystal surfaces of chemically inert insulators, e.g., MgO(100), sapphire, and diamond. An extensive recent review of the subject is available.[201]

Given the high collision energies and the heavy colliders employed, the framework of classical dynamics was used in nearly all the treatments. Some of the calculations were extensive "molecular dynamics" simulations,[199-201] such as described in sections III.B and IV.B. That is, the classical equations of motion were solved for both the colliding molecule and for many solid atoms (order of 10^2–10^3 atoms). Convergence of the results was tested with respect to the number of solid atoms used in the calculations. All the calculations of this type treated the solid atoms as being initially at their equilibrium positions (the classical $T = 0$ K limit of the solid) to avoid sampling over initial configurations of the particles. At least for relatively low surface temperatures ($T_s \leq 280$ °C) this is not expected to affect the results for any of the surfaces studied. In the cases of diamond (100) and sapphire (0001) which have an extremely high Debye temperature, the approximation should be valid even at higher T_s values. Molecular dynamics simulations are, of course, rather costly in computing time. To provide an additional quantitative tool of interpretation which is computationally much less demanding, Elber and Gerber[348] and Elber et al.[349] developed an impulse-type of approximation. This approximation assumes collision energies very high compared with the binding energy of the molecule. Also, it is assumed that the dissociation dynamics is governed by very short-range repulsive interaction; hence the (repulsive) potentials between the surface and each of the two atoms do not significantly overlap. Finally, Elber and Gerber[348] employ a truncation of a certain multiple collision expansion, the physical content of which is that dissociation always involves the following sequence of events: (1) one end of the molecule strikes the surface; (2) then a "hard collision" between the two atoms of the molecule occurs and afterwards the fragments fly away. The main basis of this assumption are the "exact" classical trajectories, from the analysis of which this behavior was observed. The approximation so derived is related to the "sequential impulse" model for collision-induced dissociation in atom–molecule collisions.[350] Effects of surface corrugation and of phonon excitation can be introduced in this model, although rather crudely, by employing a Sudden approximation with regard to the pertinent degrees of freedom.[349] It appears that the main features of the results obtained are, at the high energy of the collisions, not very sensitive to the potential used—again a consequence of the dominance of the steep repulsive core of the interactions at high energies.[201] The potentials used were sums of pairwise interactions between each atom of the molecule and every crystal atom. Also within the crystal, a sum of pairwise atom–atom (or rather ion–ion, as in MgO) potentials was employed. Of the systems studied, I_2/MgO(100) is probably the one for which the potential function developed is most reliable.[199]

We proceed now to discuss some of the main results obtained on this topic.

The Centrifugal Dissociation Mechanism. It was found by Gerber and Elber[351] from classical trajectory simulations of I_2 scattering from a rigid surface that dissociation occurs by a centrifugal mechanism; i.e., it follows high rotational excitation upon impact such that the resulting centrifugal repulsion overcomes the binding between the atoms. Collisions at orientations optimal for direct excitation of the vibrational mode (those in which the molecular axis is perpendicular or nearly perpendicular to the surface) were found to be completely ineffective for dissociation. The effectiveness of the rotational mechanism stems from the rotational rainbow effect and from the general propensity of impulsive collisions with surfaces to high ΔJ tran-

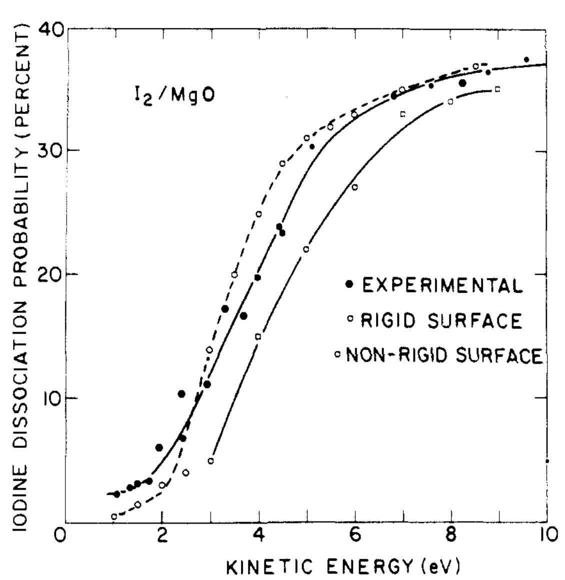

Figure 18. Dissociation probability vs. energy for I_2 in collision with MgO(100). Calculations for a rigid surface model and for a vibrating solid are compared with experiment. The experimental surface temperature was 275 °C. (Reproduced with permission from ref 199. Copyright 1984 by Elsevier.)

sitions as discussed in section IV. The centrifugal mechanism, first observed in the case of a rigid surface, was supported later by calculations which include solid vibrations. The mechanism was tested and upheld also in calculations on Li_2 dissociation, and on several mass symmetric colliders (IBr, ICl).[352]

Effect of Energy Transfer to the Solid on Dissociation. One of the most surprising findings in comparing theoretical and experimental results for I_2 dissociation in collisions with MgO(100) was that the calculations using a rigid surface model gave dissociation probabilities in excellent agreement with the molecular beam data (over the entire energy range of up to 10 eV, over which the process was measured), as seen from Figure 18.

The finding seems strange at first since time-of-flight measurements on nondissociated I_2 in the same collision process showed a kinetic energy loss of the order of ~40% which implies a massive transfer of collision energy to the solid.[199] Indeed, as discussed in sections III.B and IV.B, heavy molecule impact at high energies on a crystal such as MgO results in a shock wave excitation that takes up a substantial fraction of the collision energy. Classical trajectory simulations that included the motions of many solid atoms provided the following explanation for the success of the rigid-surface model in predicting the dissociation probabilities. As a consequence of mass ratios and other parameters, the torque for rotational excitation (the magnitude of which determines whether dissociaiton will occur) is administered to the molecule slightly before the onset of the shock-wave excitation of the solid; i.e., for a very brief time interval ($\sim 10^{-14}$ s) following impact, the solid still behaves as rigid. This is the same explanation that accounts for success of the rigid-surface model in predicting the rotational state distribution of nondissociated I_2 scattered from MgO(100). The same is not true for the sapphire (0001) surface, where the combined mass of the surface atoms in interaction with I_2 is nearer to that of the collider. Classical trajectory simulations show that in this case the onset of the solid shock-wave excitation does not lag behing the torque on the I_2 rotation. Indeed, in this case the rigid-surface model does not produce the correct dissociation probabilities, as shown in Figure 19.[201] It should be stressed that the "molecular dynamics" simulations which include surface vibrations yield results in good agreement with both the experimental dissociation probabilities (Figures 18 and 19) and the TOF data on the kinetic energy loss, not shown here. In conclusion, whether or not energy transfer to the solid affects the dissociation probability depends strongly on system parameters, both limits being manifested in real systems.

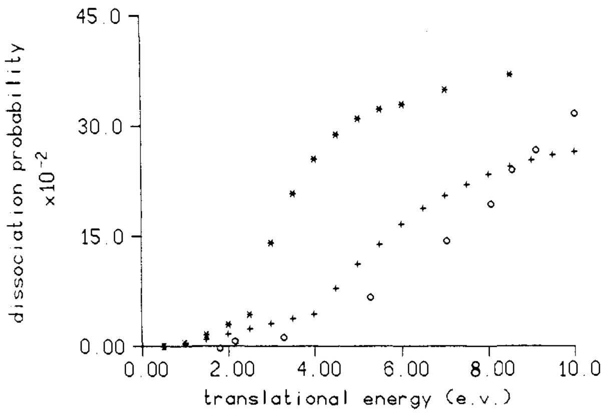

Figure 19. Dissociation probability vs. collision energy for I_2/sapphire(0001). +++, vibrating solid simulation; 000, experiment; ***, rigid surface model. (Reproduced with permission from ref 201. Copyright by the American Chemical Society.)

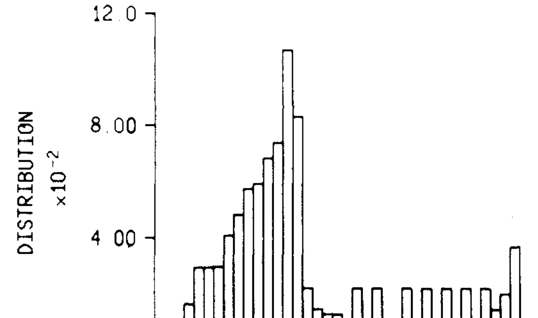

Figure 20. Angular intensity distribution of I atom fragments obtained from I_2 collisions with a rigid-surface model of MgO(100). The collision energy is 9 eV; normal incidence is used. (Reproduced with permission from ref 253. Copyright 1984 by the American Institute of Physics.)

Angular and Velocity Distributions of Dissociation Products. Elber and Gerber[253] found in simulations of I_2 scattering from a rigid surface that both the angular and the velocity distributions of the reaction fragments showed interesting pronounced structures, as in Figures 20 and 21. The angular intensity distribution shows a dip in the specular direction (here normal to the surface) and a pronounced rainbow structure in a strongly off-specular direction. That the peak is indeed a rainbow was supported by the explicit expressions of the impulsive model[348] which nicely produces this effect. The rainbow was found to be due to the "hard collision" between the two atoms of the molecule that follow the initial impact on the surface. Figure 21 shows that the energy distribution of the fragments has a double-peak structure. Also this fea-

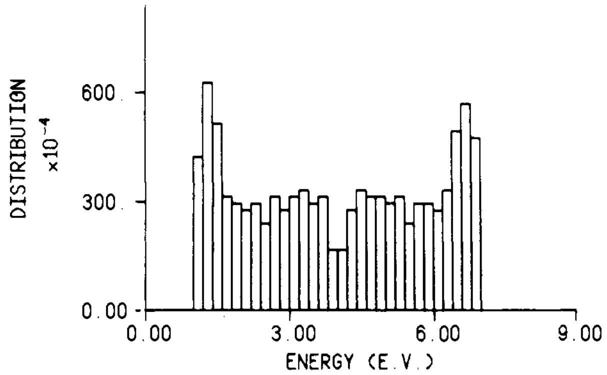

Figure 21. Calculated energy distribution for I atom dissociation products in I_2 scattering from a rigid-surface model of MgO.

ture is due to the collision between the two atoms that follows the initial impact on the surface: The atom which was stopped at the surface wall acquired energy in the collision with the second atom and emerged as the faster of the two. Dissociation dynamics is then such that the collision energy is unequally divided between the fragments.

Mass Asymmetric Molecules. Bacic and Gerber[352] found in classical trajectory simulations in a rigid-surface framework that molecules of high mass asymmetry gave rise to new qualitative features in observable properties of the dissociation process that do not exist in homonuclear systems. For instance, in the case of ICl/MgO(100) two separate regimes can be identified in the energy dependence of the dissociation probabilities. The lower energy regime corresponds only to collisions where the Cl atom strikes the surface first. Only at much higher energies can there be a contribution to dissociation from "I-first" collisions, which is the origin of the second regime.

It has recently been proposed by Gadzuk and Holloway that their electron-transfer mechanism discussed in section IV.B may contribute to dissociation also in molecule–insulator collisions, such as in the case of I_2/MgO(100). The authors do not calculate an absolute magnitude for the contribution of the harpooning effect and do not suggest which fraction of the total dissociation may be cause by it. Studies based on the harpooning model of dissociation and of charge-transfer reactions at surfaces will be discussed in subsection V.C. It should be noted that if the transient molecular anion which appears in the harpoon model is a relatively long-lived one, the angular distributions of both the dissociation fragments and of nondissociated I_2 cannot be in accord with the experiments of Amirav and Kolodney.[201,334] It is very questionable if any significant contribution of the harpooning mechanism in the cases of I_2/MgO(100) and I_2/sapphire can be expected.

B. Dissociative Chemisorption and Related Processes

A basic feature of the reactions examined in this subsection is the central role played by strong chemical binding interactions between the surface and the reagents or the products in the process. In heterogeneous catalysis this is invariably the case; hence the great importance attributed to this class of reactions. Most of the processes that will be considered are dissociative chemisorption reactions and the reversed reactions, associative desorption. However, in principle, we define the class of reactions with which this subsection deals as all processes in which at least one of the initial, final, or intermediate species involved is greatly affected by chemisorptive interactions. The topic was very actively pursured experimentally, and the pertinent literature is extensive. In particular, molecular beam studies of dissociation,[10] and permeation experiments of desorption following recombination on the surface[355] were extremely important in exploring some of the reactions discussed here. Excellent review and overview articles are available on the experimental state-of-the-art and on the basic problems in the field, e.g., D'Evelyn and Madix,[9] Asscher and Somorjai,[10] Cardillo,[5] Ceyer and Somorjai,[3] Bernasek,[356,357] and Comsa and David.[355]

There has been also a large number of theoretical studies of the reaction dynamics. Nearly all the calculations have used classical trajectory methods. Some simple methods within the classical framework have been proposed, e.g., for interpreting the $\cos^n \theta$ angular distributions (θ angle from the surface normal) with $n > 1$, found for molecules desorbing from surfaces following recombination of atom.[358,359] Of the few studies that offer a description which includes at least some quantum aspects we mention the work of Billing[360] on inelastic scattering and chemisorption in impact of CO on Pt(111). Billing used his method, discussed in section III.C, that combines a classical description of the incoming molecule with a quantum model for the surface phonons. Although it seems reasonable to suppose that quantum effects should be negligible for reactive scattering for surfaces at room temperatures and above and for typical molecular beam energies, this is not necessarily always the case. In a recent, very interesting, study by Rettner et al.[361] on the dissociation of CH_4 on W(110), evidence of a tunneling mechanism for the reaction process was found.

The largest obstacle to quantiatively reliable theoretical calculations of reactions at surfaces is the unavailability of accurate potential energy surfaces. The potential functions used are virtually all semiempirical, mostly of the LEPS type,[362-371] although also other models for the potential surface such as DIM (diatomics in molecules)[372] were employed. The LEPS models for potential surfaces describing the interactions of a diatomic and of a triatomic system with a metal face were introduced by Wolken and McCreery in their studies of H_2 + W(001) and H_2 + H/W(001)[362-365] The approach is based on a valence bond treatment of four electrons for the H_2–metal system (and of six electrons in the case of H_2 + H/metal). In this LEPS model the metal is represented as an extended source of electrons available for bonding with the atoms of the molecular systems. An illuminating analysis of the considerations used in the construction of a LEPS model potential for a diatomic and a triatomic system in interaction with a metal is given by Lin and Garrison, who employed it to develop a potential surface for O_2 + Ag(110) and O_2 + O/Ag(110).[370] Carefully constructed, supposedly realistic LEPS-type potential energy surfaces for H_2 interactions with Ni(100), Ni(110), and Ni(111) (the analytic form being the same in all cases) was recently provided by Lee and De Pristo.[373] An important tool used by the authors in fitting an interaction is a

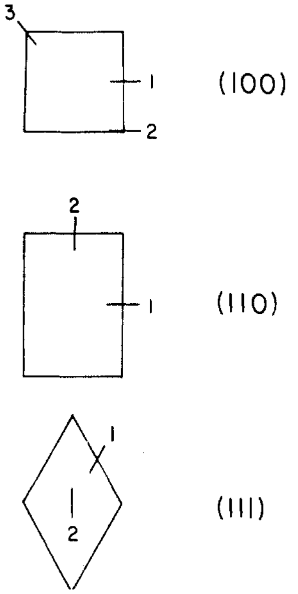

Figure 22. Definition of the dissociation sites of the H_2 molecule on Ni surfaces. (100): 1, bridge; 2, atop to bridge; 3, atop to fourfold. (110): 1, long bridge; 2, short bridge. (111): 1, bridge; 2, center. (Reproduced with permission from ref 373. Copyright 1986 by the American Institute of Physics.)

many-body expansion of the potential energy surface, in which the various terms correspond to two-body, three-body, four-body, etc. contributions.[374] A potential surface provides immediate insight into the relative importance of different dissociation sites; Figure 24 defines dissociation sites of H_2 molecules on Ni surfaces. Figure 23 shows the potential energy surface for H_2 dissociation above the short-bridge site in Ni(110). The potential is very favorable for dissociation since there is no activation barrier, and the curvature at small z (distance from surface) transforms translational into stretching motion. Figure 24 shows the potential surface for H_2 over the long-bridge site in Ni(110), and the situation is very different, since the curvatures does not favor dissociation. A molecularly adsorbed species appears to be favored in the latter site.

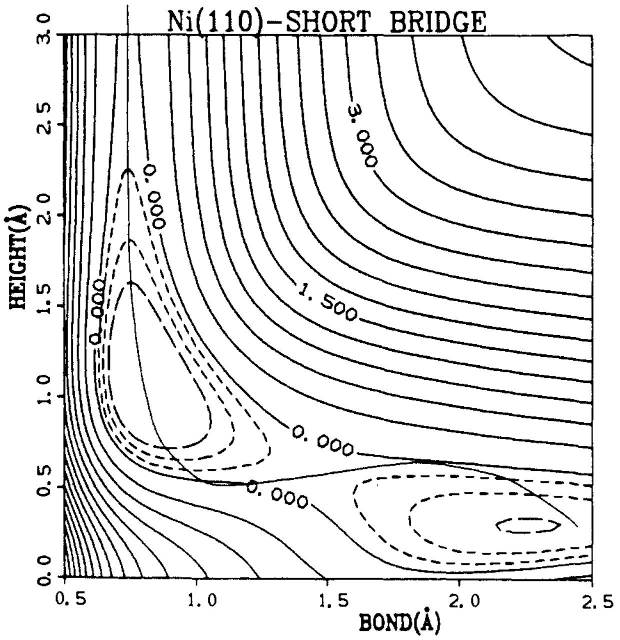

Figure 23. Potential energy contours for the dissociation of H_2 on the short bridge to center site of Ni(110). The coordinates are the H-H bond distance and the height of the molecular center of mass from the surface. Energies are relative to free H_2. A trajectory at 0.1 eV initial energy is shown. (Reproduced with permission from ref 373. Copyright 1986 by the American Institute of Physics.)

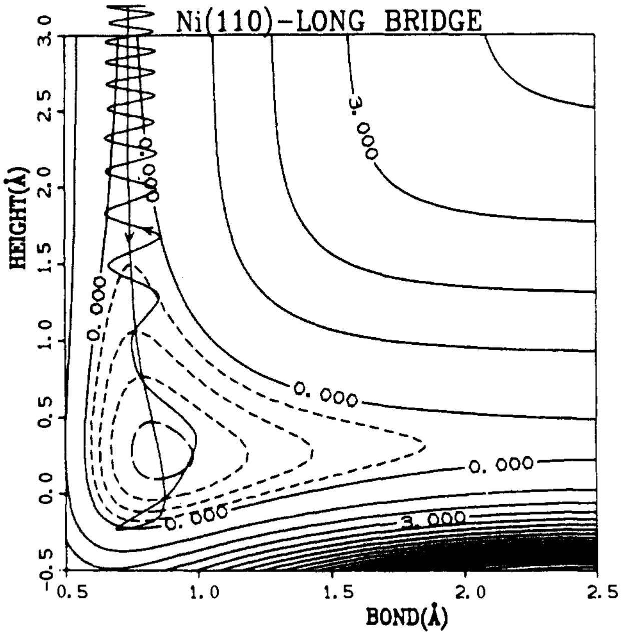

Figure 24. As in Figure 23, except that H_2 is on the long bridge to center side. The short dashed lines are at −0.25, −0.50, and −0.75 eV. The initial translational energy of the trajectory is at 0.15 eV.

Many of the reported classical trajectory calculations on reaction dynamics at surfaces are within the rigid surface model, e.g., ref 362–365,367,370,373, and 376–379. Tandardini and Simonetta[380] tested the rigid-surface result for H_2 dissociation on Pt(111)[377] by using a model that described surface atoms as Einstein oscillators. The calculations for the vibrating surface model confirmed the validity of the rigid-surface treatment for the system studied. This can probably be attributed to the very small H_2/Pt mass ratio, which is unfavorable for energy transfer between the molecule and the solid atoms. In general, however, rigid-surface results must be held suspect, especially when dissociation is not instantaneous on the time scale of surface atom vibrations. Except for the lightest reagent molecules, the strong coupling characteristic of chemisorption suggests substantial molecule–surface energy exchange. Even for H_2 the rigid-surface model may not work in various cases. For instance, Lee and De Pristo noted that the potential energy surface, in particular the curvature that couples the molecular translation to the dissociation mode, can be very sensitive to small displacements of the solid atoms.[373] This could give rise to a large effect of surface vibrations on the dissociation dynamics that does not depend on actual energy transfer to phonons.

Diebold and Wolken[381] and Tully[372] included the effects of solid vibrations on reaction dynamics at surfaces by the GLE approach. Fundamentally, validity of the GLE could be in doubt only if the energy released, e.g., upon chemisorption, were so large as to affect the *secondary* atoms of the GLE treatment to the point where the harmonic treatment is no longer valid. This seems most unlikely. The true difficulty in applying the GLE, and indeed even the simpler rigid-surface scheme, to real cases is that one is dealing with largely unknown and very complex interaction potentials, and hence a limited set of experimental data can be interpreted by fitting many free parameters. It detracts nothing from the important progress in the field to caution that a numerically very elaborate calculation which fits (limited) available data may in some cases be misleading with regard to the true mechanism of the process studied.

We proceed now to briefly discuss several results of classical trajectory calculations in this field, to illustrate the very useful insight that can be obtained.

Gelb and Cardillo[376] studied the dissociation of hydrogen on copper, using a rigid-surface model, and a LEPS-type interaction potential obtained by fitting experimental data. With the best potential function they could fit, which suggests a substantial barrier (≥ 10 kcal mol^{-1}) to lateral diffusion on the surface, good agreement was obtained with the molecular beam experiments of Balooch et al.[381] Gelb and Cardillo found that the measured dissociation probabilities were sensitive to details of the potential surface, to the point that agreement with the data could only be obtained with a sufficiently corrugated surface. It was found that the dissociation probabilities did not scale with the incidence energy in the normal direction E_n as the only variable. When calculations were carried out for fixed E_n but with different incidence angles, significantly different dissociation probabilities were obtained. This obviously stresses the importance of pursuing experimental arrangements where the incidence angle and kinetic energy parameters can be independently varied. Gelb and Cardillo could not, however, explain from their model the greater dissociation probabilities found in the experiments for D_2 than for H_2. Diebold and Wolken[381] argued from trajectory calculations on H_2/Cu, with a GLE model for the effect of surface vibrations, that an isotope effect in line with the experiment could be obtained and is due to energy transfer. It appears, however, difficult to assess if the calculations of Diebold and Wolken represent the realistic situation, or whether there could be artifacts associated with inadequate modeling of the GLE friction term that produce the large isotopic effect of the calculations.

Lee and De Pristo[373] carried out classical trajectory calculations in the rigid-surface framework for dissociation of H_2 on Ni(100), Ni(110), and Ni(111) surfaces. The authors based their justification for using the rigid-surface approximation on experimental data which indicated absence of surface-temperature effects on the dissociation.[383] The potential surface developed by these authors is, as noted earlier, one of the most carefully constructed examples for reactions of this type. Many (though not all features) of the empirical potential surface are in fairly good accord with those obtained from quantum chemical calculations.[384,385] An important aspect of the comparison with experimental dissociation data[383] is with regard to the dependence of the dissociative sticking probability on the incident kinetic energy. Lee and De Pristo find that for Ni(110) the sticking probability is independent of initial energy, while for Ni(111) it increases with incident energy, both results being in accord with experiment. On the other hand, the corresponding results for H_2 + Ni(100) are not in agreement with experiment, which may indicate inadequacy of the potential energy surface in this case.

Lin and Garrison constructed LEPS potential energy surfaces for O_2 + Ag(110), O_2 + O/Ag(110).[370] The oxygen/Ag(110) system is an example where, under the conditions employed in the experiments, adsorbate–adsorbate interactions are important, and indeed the adatoms form ordered overlayer structures on the metal surface. The authors found that the oxygen–oxygen antibonding potential had to include electrostatic and anisotropic components to account for the observed overlayer structures of oxygen atoms in this system. Trajectory calculations in the rigid-surface framework predicted both dissociative and molecular adsorption states, in accord with experiment.

C. Charge-Transfer and Nonadiabatic Reactions

This subsection deals with reactions at surfaces in which transitions between different electronic states occur in the course of the process. The simplest reactions of this kind are those in which an atomic ion undergoes neutralization in collision with a surface. Note, however, that not all charge neutralization reactions are nonadiabatic: Resonance charge transfer is an example of an adiabatic process of this type.

Early studies of the dynamics of ion neutralization in collisions with surfaces were pursued by Tully[386,387] for the case of He^+ in collisions with surfaces of Cd, Sb, Ga, Pb, etc. at energies typically in the kiloelectronvolt range. Tully developed an approach based on a classical-path treatment of the projectile combined with a time-dependent quantum mechanical description of the electronic states. Since the electron transferred to the ion comes from a band, the expansion of the electron wave function in a stationary basis involves continuum contributions. The effect of the latter is given in Tully's formulation by an approximately derived complex-valued effective potential. Tully was successful in predicting at least semiquantitatively the oscillations in the observed angular intensity distribution for the neutralization process.

Newns et al.[388] develop simple models for charge transfer in inelastic ion atom scattering from surfaces that offer penetrating physical insights into the mechanisms involved. Also Newns et al. discuss the motion of the projectile classically and the electronic states in a quantum mechanical framework. They introduce a simple model for the interaction and use physical considerations (e.g., with regard to the overlap of Jellium orbitals with atomic ones) to obtain convenient expressions in limiting cases. Auger and resonance neutralization give particularly simple results. Newns et al. obtain results in good agreement for experiment also for the neutral fraction produced in Li^+ scattering from W(110), a system where a more complicated, nonadiabatic charge-transfer mechanism is involved. Finally, the theory was successfully applied also to H^- formation in H^+ scattering from associated W(110), a process which shows strong dependence on the velocity parallel to the surface.[388]

Greelings and Los[389] reported measurements of neutral Li formation in scattering of Li^+ ions from a cesiated W(110) surface at energy of 400 eV. They determined the charged fraction as a function of the work function of the surface. The authors interpreted their experimental results by a semiclassical model, based on assuming a local electrostatic potential.

A recent theoretical investigation of ion neutralization in scattering from metals was carried out by Battaglia and George.[390] The authors used a diagrammatic time-dependent perturbation expansion and established conditions for the validity of first-order perturbation theory. Mainly the conditions require a short collision time and nonoverlap of the discrete energy level of the projectile with the continuous valence band of the solid.

George and co-workers[391,392] studied the probability of negative ion formation in positive ion scattering from surfaces. The authors went beyond previous approaches in including the effects of the correlation energy arising from the Coulombic repulsions between the two transferred electrons. Results were given for finite temperature T of the metal electrons. Good agreement was found with molecular beam experiments on the production of $H^-(D^-)$ in scattering of $H^+(D^+)$ from a cesiated surface.

Holloway and Gadzuk[341,342,390] studied the dissociation of molecules such as N_2 and Cl_2 on metal surfaces. They proposed an adiabatic model, in which the process involves crossing to a potential surface that represents formation of an intermediate negative ion A_2^-, which then undergoes dissociation when the system recrosses again to the neutral potential energy surface. (See the discussion of the Gadzuk–Holloway model in section IV.) To obtain dissociation probabilities, Gadzuk and Holloway first determine the crossing seams between the potential energy surfaces involved.[341,342] Next, they use classical trajectories, transitions between the potential surfaces being calculated when a crossing between the surfaces is reached, as discussed in section IV.D. The authors applied their model to the calculation of dissociative sticking probabilities in Cl_2 collisions with a model metal surface. Intuitively, the model appears justified for halogen molecule dissociation on metals, although the model potential functions used in illustrating the calculations are rather simplistic.[342]

VI. Dynamics of Trapping and Desorption

A. Mechanisms of Trapping

The definition of trapping adopted here is that of a process in which an atom or molecule incoming toward a surface loses an amount of kinetic energy in the direction normal to the surface so as to remain bound in the attractive well of the interaction with the solid for a time scale longer than that of a direct collision. There is considerable merit in the convention advocated by Barker and Auerbach[8] for using the term "sticking" in cases where the attraction to the surface has the strength of chemical binding forces (say 10 kcal mol^{-1} or more) and to reserve the term "trapping" to systems where the interactions correspond only to physisorption. However, such a distinction is not always made in the literature. As defined above, trapping includes as very special cases also selective adsorption or rotationally mediated adsorption of molecules, discussed in sections II and IV, respectively. These effects exist also for a rigid surface and are merely scattering resonances (quantum mechanically) or short-lived collision complexes (classically) which do not involve directly any accommodation to the solid degrees of freedom. The lifetimes associated with such resonances are typically of the order of 10^{-12} s. It is important to note that while selective adsorption or RMSA resonances do not involve energy transfer to the solid, such processes may well play the role of "doorway states", during the lifetimes of which coupling of and energy loss of the molecule to phonons or electron-hole pairs will ultimately become operative. Such a role for these resonances was for instance recently suggested by Stiles and Wilkins.[394] Another trapping, or rather sticking, mechanism which does not necessarily involve direct transfer of energy to surface modes is dissociative chemisorption. Such processes were discussed in section V and will therefore not be dealt with here. With the exclusion of the few exceptions mentioned above, trapping can occur only when the atom or the molecular projectile loses energy to phonons or to electron-hole pairs. The issue of the relative roles of the two mechanisms is a basic one and is still not fully resolved. As concluded in section III.D, there is considerable evidence that electron-hole pairs cannot play a significant role in the case of He, and probably also of the other rare gases, e.g., Gunnarson and Schönhammer[247] and Kirson et al.[248] On the other hand, calculations suggest that energy transfer to electron-hole pair excitation may be the cause of trapping in low-energy collisions of H atoms with metal surfaces at low temperature.[248] The calculations of De Pristo et al.[237] on the physisorption of H_2 on Cu(100) show that models which comprise a large role for electron-hole pairs in the trapping process give very reasonable results. On the basis of the few indications available, a significant role for electron-hole pairs compared with the phonon mechanism seems most likely for light colliders in chemisorptive interaction with a metal surface.[248] The interactions between the incoming projectile and the metal electrons must in any case be such that the coupling potential can penetrate regions where the surface electron density is relatively high, for the electron-hole pair mechanism to operate.

While energy exchange between the molecule and the solid drives the system toward accommodation, the latter may not be complete on the time scale of residence at the surface. The balance between the residence time and the energy relaxation time of the molecule in the trapped state is an important parameter in determining the properties of that state. A possible limiting behavior in trapping is that of full equilibration. The main manifestations of this will be a cos θ angular intensity distribution and a Maxwellian velocity distribution (at the solid temperature) for the desorbing molecules.[31] However, even after long residence times and complete accommodation to the surface, large deviations from the above patterns may appear due to interactions that affect the outgoing particles in the desorption process. An example of such "final state interactions" is in associative desorption, when molecules that emanate from the surface upon exoergic recombination of adsorbed atoms give rise to angular distributions of the type of $\cos^n \theta$, $n > 1$.[31] In a trapping process the time scales for equilibration of different degrees of freedom are not in general similar: Tully[201] studied trapping (and desorption) of Ar and Xe on Pt(111) and found that the atoms may continue to glide in parallel to the surface plane for distances of the order of 100 Å or more, long after equilibration has set in for the motion normal to the surface. Effects of this type, of disequilibrium in at least one of the coordinates, may be the cause of significant deviations from the cos θ distribution, e.g., in trapping-desorption scattering of Ar from Pt(111), as found by Hirst et al.[395] These authors also found that the mean kinetic energy of atoms emerging normal to the surface, presumably after having been trapped, was considerably lower than the value implied by equilibrium with the surface. Such an effect of "translational cooling" was noted by J. C. Tully in trajectory simulations for equilibrated adsorbed atoms.[209] The origin of the effect is in insufficient energy transfer upon desorption between the molecule and the surface.

The fact that trapping does not imply instantaneous equilibration renders it difficult to provide a general, unambiguous definition of a trapping event in calculations. Tully[209] defined an atom to be trapped if its total energy in the trajectory calculation fell to $-3k_BT$ or lower below the atom–surface dissociation asymptot. A similar definition was used by Polanyi and Wolf[281] in calculations on NO scattering from metal surfaces. While these definitions were operationally useful, they are neither general nor rigorously based. For instance, in calculations on models with relatively *shallow* interaction potentials, Polanyi and Wolf suggested that a drop to below $-1.5k_BT$ (from the zero defined by the dissociation asymptot) is an adequate criterion for terminating the trajectory and assigning the latter as a trapping event. Theoretically based criteria are, however, not available as yet for defining when a trajectory is "sufficiently equilibrated" to be counted as a trapping contribution.

In conclusion, trapping processes have experimental manifestations sufficiently well-defined for measurements of their properties (cos θ-like angular distribution, time delay of the molecules leaving the surface compared with those which are scattered directly, etc.). At the same time, it is hard to give a precise (and practical) definition for a trapping state. Further studies for characterizing the disequilibrium properties of such states in the transient lapse of time before they become fully accommodated (or desorbed) are clearly required.

B. Trapping and Desorption of Atoms

The method used to obtain rates of adsorption and desorption can be divided into several groups. Classical trajectory calculations, allowing by various approximations for phonon participation in the collision process, are one such group and have provided much of the present understanding of trapping and desorption dynamics. "Molecular dynamics" simulations of trapping using a large slab of many atoms to represent the solid are probably the most rigorous of this variety. Calculations of this type were carried out by Barker et al.[398] for a model of Ne colliding with Ag(111). Molecular dynamics calculations of trapping are feasible when the total (adsorption + desorption) rate is large. If the adsorption lifetime (inverse of the desorption rate) is long, e.g., $>10^{-6}$ s, the method becomes impractical due to the long integration times required. An alternative to "molecular dynamics" simulations with a large slab target are classical trajectory simulations with a GLE representation of the role of phonons. As stressed in section III.B, the GLE scheme can in principle be made exact. For instance, Riley and Diestler[396] gave a numerically exact solution for energy transfer and capture when an atom collides with an initially cold, collinear harmonic lattice using equations of motion derived by Zwanzig for this system[397] that are closely related to the Adelman–Doll GLE. Riley and Diestler used their exact benchmark results to test several approximations to the memory kernel, of the types employed in realistic applications of the GLE approach. When the results for a wide range of the gas-to-solid atom mass ratios and of the force constant parameter value were examined, the friction "kernel" approximation as used by Shugard et al.[207] was found in serious error in some cases in predicting the critical energy below which trapping occurs. This may not be relevant to most uses of the GLE, but systematic tests of this method in the trapping regime (examining the friction kernels employed in realistic cases) are clearly desirable. Penetrating and realistic (within the GLE scheme) studies of trapping and desorption were carried out by Tully[209] for Ar and Xe scattering from Pt(111) and by Muhlhausen et al. for scattering of NO from Ag(111) and Pt(111).[288] When the adsorption–desorption process is very slow, of the time scale of 10^{-6} or more, direct GLE simulations, as those of "exact" molecular dynamics become rather difficult. To deal with such cases, in which e.g., the desorption of a molecule from a surface is a very infrequent event, Grimmelman, Tully, and Helfand[398] introduced a most elegant device: Following an idea by Keck,[399] they wrote the desorption rate as a product of a factor that is the prediction of transition-state theory for the rate times a "dynamicsl factor". It an be shown that in conditions of "infrequent dynamical events", the dynamical factor can be obtained from calculations of a limited set of relatively short-time trajectories. The transition-state value of the rate constant can be obtained without trajectory computations, e.g., by Monte Carlo method.

Among the simplest classical trajectory methods used to calculate trapping rates are the "hard" and "soft cube" models, as discussed in sections III and IV. On the whole, it appears that when used with the most realistic, physically justifiable parameters such models, including the much more refined "soft cube" schemes, considerably overestimate the true trapping probabilities, e.g., Kubiak et al.[297]

A very important class of methods for obtaining thermal desorption and trapping rates is based on using transition-state theory (in some version, with dynamical corrections).[400–410] The expression of transition-state theory (TST) for the desorption rate R is given by

$$R = \frac{k_BT_s}{h}\frac{Q^\dagger}{Q}\exp(-E_a/k_BT_s) \qquad \text{(VI.1)}$$

where E_a is the activation energy, T_s the surface temperature, $Q^\dagger$ the partition function for the activated complex (not including the reaction coordinate), and Q the partition function for the (adsorbate + surface) system. The main difficulty with the theory is in defining the transition state for the desorption process. One possible choice is to assume that the transition state is located at infinite distance between the adsorbate and the surface. This definition was employed, for instance, by Garrison and Adelmann,[403] who derived on this basis an expression for the rate of a one-dimensional desorption of an atom from a solid. The simplicity of the TST theory make it possible to derive very convenient explicit forms for both the temperature–dependence and average dependence of the desorption rates. Applications to both diatomic and polyatomic desorbing species were given, and results are generally in good accord with experiment, e.g., the study by Pfnür et al.[404] on CO desorption from metal surfaces, and the treatment of Redondo et al.[405] on NH_3 desorption from Ni(111). Important contributions to the theory of trapping on surfaces and of desorption based on the transition-state method and its extensions were made by Doll and Adams.[405-410] Thus, these authors[405] treated atom desorption from solids by a generalized version of Slater's theory for unimolecular reactions, which was shown to be equivalent to a transition-state treatment. The same authors developed a Monte Carlo scheme for the evaluation of the TST thermal desorption rates[406] in which the evaluation of averages over an ensemble representing the adsorbed system is required. They gave applications to desorption of Ar and Ne from solid Xe.[407] Adams and Doll[408] showed that dynamical corrections to TST can be introduced, involving trajectory calculations, such that in principle the corrected theory could be made exact. However, as in the closely related study by Grimmellmann et al.,[398] such a scheme could be practically applied also in cases of long adsorption lifetimes, where direect trajectory simulations are no longer feasible.[410]

A method for calculating thermal desorption rates, based on a classical stochastic diffusion theory (CSDT), was put forward by Redondo et al.[411] When applied to give simple expressions for the desorption rate, the CSDT approach assumes that the desorption occurs along a path normal to the surface. At least in this version the CSDT approach appears equivalent or very similar to the TST result (without dynamical corrections).

It should be noted that while TST is very successful in interpreting thermal desorption rates, it is not built, in its present form, to describe velocity or angular intensity distributions of particles desorbed from a surface.

Another important group of methods in the study of adsorption and desorption processes corresponds to approaches that treat certain degrees of freedom classically and others quantum mechanically. Such are the force oscillator methods discussed in section III.B that apply quantum mechanics to surface harmonic vibrations, coupling these motions to a classical treatment of the colliding atom.[232-234] Billing[232] used the method of this type which he developed to study the trapping of Ar by a W(100) surface at $T_s = 0$ K. Several methods used in the study of the possible role of electron-hole pairs in trapping, discussed in section III.D, also treat the motion of the atom undergoing trapping by classical dynamics, and the electronic degrees of freedom quantum mechanically, e.g., ref 243–245,248. One of the more realistic approaches in this respect is the study by Kirson et al.[246] where the time-dependent wavepacket describes an independent surface electron during the collision of the atom with the solid. Probabilities of Ar trapping and of H sticking on a metal surface were computed via this approach.[246]

Kosloff and Cerjan[224] treated desorption and low-energy scattering of He from W by a method that involves time-dependent wavepacket calculations for the He and a GLE model for including the role of phonons. Related to this is the approach of De Pristo et al. discussed in sections III and IV, which treats the role of surface phonons by the GLE scheme, applies time-dependent quantum dynamics to the diffractive, rotational and vibrational degrees of freedom of the incoming molecules and uses a classical trajectory to describe the motion along the distance coordinate between the molecule and the surface.[236,237] In a study using this method for the physisorption dynamics of H_2 on copper, De Pristo et al.[237] modeled the GLE friction and random forces so as to allow for the role of electron-hole pair excitations as well as of phonons in the process (see section III).

There is a very different group of methods that treat desorption not from the single-molecule point of view but in terms of kinetic equations (of the Master or of the Fokker–Planck type) for the ensemble of trapped particles.[412-419] The quantum version of this approach, as studied extensively by Freed, Metiu and their collaborators,[414-418] is formulated in terms of Master equations for the time dependence of the populations of the various vibrational states of the trapped atoms in the attractive well of the interaction with the surface. Terms representing transitions into the continuum (desorption) states of the adatom vibrational mode are included in these kinetic equations. The rate constants for transitions between a vibrational state, m, and a state, n (which may be bound, or part of the desorptive continuum), are obtainable from models of vibrational relaxation and excitation based on either a multiphonon mechanism[414] or on one involving energy transfer to electron-hole pairs.[418] The complexity of obtaining from a first-principle basis rate constants for the $m \rightarrow n$ transitions is very considerable. The authors overcome this by using very simple models of multiphonon processes. Consequently, such treatments were so far confined essentially to one-dimensional models of desorption, and the value of this approach has mainly been on providing physical insight rather than a realistic quantitative description for specific systems. These methods obviously involve the assumption of sufficient "loss of memory" of the atom in the trapped state for the derivation of the kinetic equations from the dynamics. On the other hand, quantum effects can be treated quite rigorously. If simplified versions of this scheme could be worked out for desorption in the full three-dimensional framework, such methods could perhaps also become a practical tool for quantitative simulations of realistic systems. These methods can probably be also usefully developed in "semiempirical" directions by suitable parameterized guesses on the rate constants for transitions between vibrational states. In addition to thermal desorption, the Master equation approaches were also applied to laser-induced desorption, e.g., in the study by Lin and George on multiphoton desorption upon laser irradiation.[419]

We now consider briefly several properties of trapping and desorption processes, obtained from some of the theoretical methods.

Low-Energy, Low Surface Temperature Limit of Trapping Probability. Although this question is not pertinent to the regime considered to be of chemical relevance, its fundamental theoretical significance is obvious. Classical dynamics predicts that as both the incidence energy of the incoming atom and the surface temperature approach zero, the trapping probability tends to unity. It appears very difficult to derive this intuitive result in a rigorous quantum mechanical framework. Early approaches, directed mostly at the interpretation of data on low-temperature He accommodation on W, used the distorted-wave Born approximation and included only single phonon transitions.[31] The zero-order wave functions in the distorted wave treatment were taken from a flat, static surface treatment.[31] This approach gave a *vanishing* trapping probability as $T_s \rightarrow 0$, E (collision energy) $\rightarrow 0$. There has been an ongoing debate in the literature, whether this approximate quantum mechanical result is correct or whether it is an artifact due to the assumptions made.[31,420,423]

The result was considered by several authors an artifact of the relatively short-range (exponential) attractive potential used in the old derivations, but Brening and Boheim[424] have shown that even with a long-range, realistic $-C/z^3$ attraction the trapping probability does go to zero in the low-energy, low T_s limit. (Although for such a potential the fall-off of the trapping occurs at much lower energies than those predicted by the Morse models.) It appears that any model which involves either the single phonon assumption or the distorted wave approximation will inherently predict a vanishing trapping probability at very low T_s and E, because the density of phonon states pertinent to the transition becomes negligibly small. Quantum treatments of the He dynamics mixed with classical (e.g., GLE) description of the phonons should, probably, give the classical result of a sticking coefficient that approaches unit for $T_s \rightarrow 0$, $E \rightarrow 0$. In any case, there appears to be no demonstration of what the true result is. Recent experiments[425] on low-energy (≥ 2 meV) He scattering from a low-temperature (T_s = 3.6 K) surface yield large sticking probabilities (≥ 0.77) which vary as a function of incidence angle, but the results may still be far from the true asymptotic limit. Further theoretical efforts to establish the limiting behavior seem desirable, as this should clarify limitations of presently used scattering methods in the highly quantum mechanical regime of low-energy and surface temperature.

Nonequilibrium Effects in Atom Desorption. Very interesting insights into this question were obtained by Tully in his GLE simulations of Ar and Xe atoms desorbing from Pt(111).[209] Figure 25 shows the results of these calculations for the mean final translational energies of atoms desorbing from the surface, as a function of surface temperature. It is evident that the emerging atoms are "colder" than expected on the basis of equilibrium with the surface, i.e., $\langle E \rangle$, the mean final kinetic energy is smaller than $2k_BT_s$, although $\langle E \rangle \rightarrow 2k_BT_s$ for very low surface temperatures. Note that $\langle E \rangle = 2k_BT_s$ is the value predicted by transition-state theory, which fails for the kinetic energy release distribution although it does work quite well for the (desorption) rate constant. Tully notes that the mean energy transfer between the solid and the adatom, over a vibrational period of the latter, is substantially lower than the value corresponding to the statistical, strong coupling result.[209] Thus, when by fluctuation the adatom acquires sufficient energy to escape, its excess energy will be relatively low. Interactions at the final stage of desorption are therefore extremely important for affecting the distribution of desorbed atoms, even if prior to that final state the adsorbates were completely equilibrated with the surface.

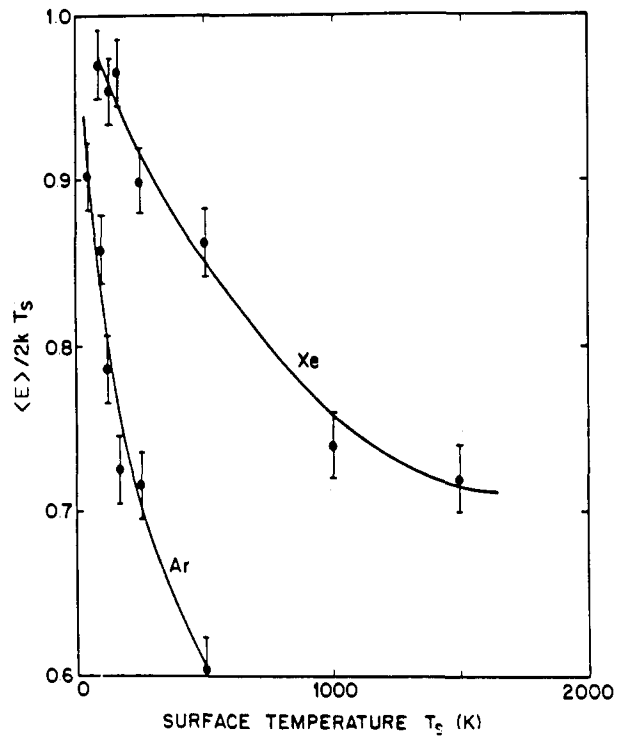

Figure 25. Mean translational energies of Ar and Xe atoms desorbing from Pt(111) in units of $2k_BT_s$. (Reproduced with permission from ref 209. Copyright 1981 by Elsevier.)

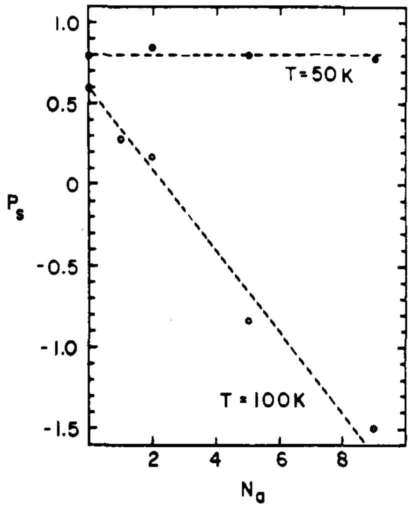

Figure 26. Coverage dependence of the Ne-Xe(111) sticking probability at two different temperatures. N_a is the number of adsorbed adatoms present on the surface slab prior to particle 1 striking the surface. (Reproduced with permission from ref 410. Copyright 1984 by the Americn Institute of Physics.)

Coverage Dependence of Trapping Probabilities. Adams and Doll[410] studied the trapping of Ne and Ar atoms on a Xe crystal, which was already partially covered with adsorbates. The method used by the authors in this case is a numerically exact calculation of the trapping probabilities in the classical framework. The computed trapping probability of a Ne atom as a function of the number of such atoms already adsorbed on a slab representing a Xe solid is shown in Figure 26.

At 50 K, the trapping probability is essentially coverage independent. At 100 K a strong decrease of the trapping probability with the number of adsorbed Ne atoms is found. The interpretation is based on the fact that at 50 K the adsorbed Ne atoms have nearly all energies below the diffusion barrier on the Xe surface. If the incoming atom does not strike directly an occupied site on the Xe surface, the existence of other adsorbates will hardly affect it. At 100 K, the adsorbed Ne atoms translate almost freely across the surface, and the notion of a trapping site becomes irrelevant. The incoming Ne may collide with one of the adsorbates and be desorbed. Hence the fall off of the trapping probability with coverage in this case.

Collision-Induced Desorption. An adsorbed atom or molecule may be knocked out from the surface into the gas phase by impact of a sufficiently energetic projectile. For a physisorbed species, such desorption induced by direct impact requires only moderate collision energies. Recently, Zeiri et al.[426] carried out classical trajectory simulations of such processes, to which they refer as collision-induced desorption (CID). Such desorption processes differ completely in their dynamics from sputtering, in which case a high-energy (order of a kiloelectronvolt, say) ion penetrates into a solid, and induces essentially by local heating effects a "boiling-off" of surface-layer atoms. Zeiri et al. found from their study that angular and velocity distributions from CID processes should provide information on interaction and dynamical parameters of the adsorbed species (e.g., the binding energy to the surface). The theoretical simulations therefore suggest that experiments to measure the CID process should provide a new probe of adsorbed overlayers.

C. Role of Molecular Degrees of Freedom

The present subsection deals with the role of internal molecular degrees of freedom in adsorption and desorption. Apart from this aspect, and when it is unimportant, the dynamics of molecular trapping/desorption processes is similar to that in the case of atoms. Also, we do not include here the topic of dissociative adsorption which was discussed in section V. The theoretical methods used to study molecular adsorption or desorption dynamics are mostly the same as those employed for atoms. Thus, we proceed to discuss the physical mechanisms and effects associated with the molecular degrees of freedom and will combine this with brief comments on models and methods when different from those already mentioned.

Rotational Distribution of Molecules Desorbed from a Surface. The rotational temperature T_R found for molecules desorbed from a surface differs in general from the surface temperature. In most experimental systems $T_R \leq T_s$, e.g., for NO desorbing from graphite and from Ru(001).[15,427,428] Exceptions with $T_R > T_s$ exist,[429,430] as in the case of NO desorbing from Ir(111), but at least in the latter case the mechanism involved appears to be of NO dissociation on the surface with desorption taking place upon recombination. It is possible that when such "chemical" mechanisms are not operative, the "rule" $T_R \leq T_s$ applies in all presently studied cases.

A simple statistical interpretation of this behavior was proposed by Bialkowski.[431] He suggests that the adsorbed NO can rotate only in parallel to the surface plane as a two-dimensional oscillator. With the assumption of weak coupling of the rotational and surface degrees of freedom, the mean rotational energy of the desorbed molecules will be $k_B T_s/2$, as implied by the classical equipartition principle. Since the rotational heat capacity increases by a factor of 2 on going from the adsorbed state to the three-dimensional gas-phase rotor, the apparent rotational temperature of the desorbed species is expected to be $T_s/2$, which is roughly in agreement with the experimental results of Cavanagh and King.[15] Qualitatively, the mechanism assumed by this simple interpretation probably plays an important role, but the description is much too simplisitc, and the relation $T_R \approx T_s/2$ is not valid in most experimental systems and conditions. A more quantitative model for the rotational cooling of desorbed molecules was given by Bowmann and Gossage.[432] This treatment assumes that the energy required for desorption, in the translational mode normal to the surface, comes at the expense of the rotational energy. The molecule is described as a nearly free rotor, with only weak coupling between the rotational and translational modes of the adsorbed species. The model of Bowmann and Gossage gave results in good accord with experiments on the rotational cooling effect. A dynamical model for the rotational state distribution of the desorbed molecules based on rather different physical assumptions than those of the "statistical" approaches discussed earlier was proposed by Gadzuk et al.[433] and by Landmann.[434] These authors considered the adsorbed molecule to be a strongly hindered rotor. An "infinite conical well" potential, defined by

$$V(\theta,\phi) = \begin{cases} 0, & \theta \leq \beta \\ \infty, & \theta > \beta \end{cases}$$

was assumed to confine the rotational motion in the trapped state (θ is the angle between the surface normal and the molecular axis, ϕ the azimutal angle, and β a parameter determining the amplitude of the angular motion). It is then assumed that the hindered rotor becomes "suddenly" unhindered when desorption occurs. The model thus implicitly postulates a desorption time scale very short compared with the rotational period of the molecule and is in the spirit of the Sudden approximation for translational–rotational energy transfer discussed in section IV. Within this scheme, the final rotational population is determined by overlaps between hindered rotor and free-rotor wave functions. The model does predict the rotational cooling effect. Also it suggests that the more confined the adsorbed rotor is, the "hotter" will be the final rotational states produced in desorption. The model does not allow for exchange of energy between the rotor and the surface upon desorption, and evidence from more detailed simulations is desirable on the validity of this assumption. Muhlhausen et al.[288] carried out classical trajectory simulations within the GLE framework of thermal desorption of NO from Ag(111). They obtain a rotational cooling behavior and state that their classical trajectory calculations support the interpretation of Gossage and Bowmann[332] for this effect, rather than the hindered rotor model of Gadzuk et al.[333] Muhlhausen et al.[288] examined the results of the two components of the rotational energy, one corresponding to

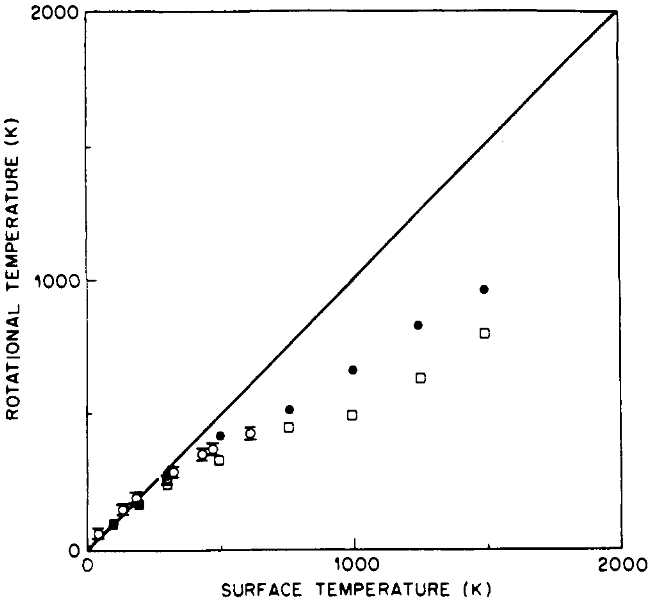

Figure 27. Mean rotational energy (in degrees K) of NO molecules thermally desorbed from Ag(111). Solid circles: calculated mean rotational energy ($\times\ 3/k_B$) associated with angular momentum along the surface normal. Open squares: calculated mean rotational energy ($\times\ 3/2k_B$) associated with angular momentum parallel to the surface. Open circles with error bars: experimental mean rotational energy. (Reproduced with permission from ref 285. Copyright 1980 by Elsevier.)

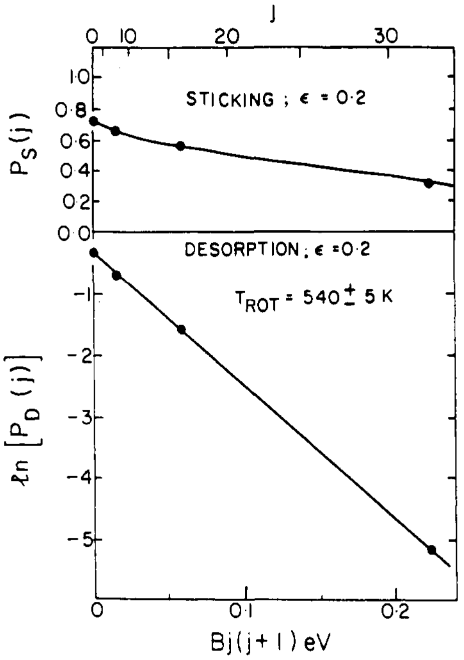

Figure 28. Sticking and desorption probabilities vs. rotational energy for NO desorbing from a model surface. The attractive well depth is 0.2 eV and the surface temperature 650 K. (Reproduced with permission from ref 281. Copyright 1985 by the American Institute of Physics.)

rotation with angular momentum rotor perpendicular to the surface normal and the other to angular momentum parallel to the surface normal. Both components show the rotational cooling effect: $\langle E_R^+ \rangle < {}^2/_3 k_B T_s$, $\langle E_R \rangle < {}^1/_3 k_B T_s$. As seen in Figure 27 VI.3, the "reductions" in rotational energy from the equilibrium values are not quite the same for the two components. The authors attribute this to the stronger coupling of the rotation with angular momentum parallel to the surface to the translational motion of the desorbing molecule. It is thus this component of the rotations which undergoes a stronger depletion of energy. Orientation of the molecule when adsorbed was found to be of no importance with regard to the role of the two rotation components. Simulations in the GLE framework were carried out also for NO desorbing from LiF(001).[335] In this case, no rotational cooling was found, and the authors argue that this is due to the weak anisotropic potential which they employed for this system. In conclusion, it appears that the rotational cooling effect in desorption is basically understood and is due to energy transfer from the rotational mode to the desorption coordinate, a mechanism that can indeed provide a significant fraction of the energy necessary for escape from the attractive potential well. The quantitative dependence of the effect on the strength of the anisotropy of the molecule–surface potential and on the possible occurrence of energy transfer to surface atoms are two of the questions yet to be elucidated.

Dependence of Trapping Probability upon Rotational Energy. This topic was pursued mainly by classical trajectory calculations, e.g., by Adams,[436] by Polanyi and Wolf,[281] and by Muhlhausen et al.[288] For the systems studied, modeling NO[281,288] and CO[436] on metals, the behavior observed can be summarized as follows:[281] For systems of sufficiently deep attractive wells in the molecule–surface interaction, the sticking coefficient is virtually independent of the rotational energy of the incoming molecule for low rotational states and shows a very mild decrease with increasing J for highly rotationally excited states. If indeed the sticking coefficient is unity for all J, then by detailed balance the desorbed molecules are expected to show a Boltzmann rotational distribution with a rotational temperature that equals T_s. In the simulations of Polanyi and Wolf[281] this is the case for a NO interacting with a model surface, when the attractive well depth is 0.58 eV. A more significant J dependence for the sticking coefficient is found for a similar model but with a much shallower attractive well (well-depth of 0.2 eV in the calculations). The sticking probability falls off as rotational energy increases in all the J ranges (see Figure 28), although the fall is a moderate one. The desorbing molecules have also in this case an (approximately) Boltzmann rotational distribution but with $T_{rot} < T_s$ (rotational cooling). For higher rotational energies, $R - T$ energy transfer becomes increasingly larger and obviously has the effect of reducing trapping probabilities. This may not be the only reason for the fall-off of the sticking coefficient with increasing J. For instance, at very high J values, the fast rotation of the incoming particle may largely average out the anisotropic component of the molecule–surface attraction and hence reduce the attractive well-depth of the effective interaction by a fraction corresponding to the anisotropic component, which also results in reduced trapping probability. The relative importance of these two effects in reducing the sticking for high J was not studied systematically yet. Related to the above topic is the dependence of the sticking probability on the molecular orientation at the instant of impact on the surface. Muhlhausen et al.[288] studied this probability for NO/Ag(111) finding that for a collision energy of 8 kJ/mol normal to the surface, "N-first" collisions gave sticking probabilities by about 75% higher than "O-first" collisions. It appears, however, that there is in none of the systems studied so far a very strong orientation dependence of the sticking probability. Keeping in mind the large steric effects frequently found for gas-phase molecular interactions, one might guess that systems with a large orientation effect on sticking are most likely to be found. This merits future exploration.

Effects of Trapping on Vibrational Energy Transfer. Relatively little is known at present on the dynamics of vibrational excitation and deactivation in collisions with surfaces. There is, however, considerable evidence that vibrational energy transfer from diatomic and triatomic molecules is typically very inefficient for direct collisions with the surface (except when the impact energies are high, in the electronvolt range[329]) as discussed in section IV.C. On the other hand, there are strong indications that collisions in which trapping occurs can result in large probabilities for vibrational energy transfer. Asscher et al.[323] have indeed assumed a trapping mechanism for a consistent interpretation of the experimental results on vibrationally excited NO molecules produced in collisions with Pt(111), and Houston, Merrill, and their co-workers[325-327] concluded that only a trapping/desorption mechanism seems to account for their results on the deactivation of CO_2 and CO by several metal surfaces. Important theoretical support for this mechanism comes from the semiclassical stochastic trajectory calculations of Clary and De Pristo[230] on CO_2 collisions with Pt(111). They found that at low collision energies ($E \leq 0.1$ eV) trapping probabilities can be large (>10%) even at high surface temperatures ($T = 1000$ K). Clary and De Pristo also reported that direct collisions produced vibrational transition probabilities that are by many orders of magnitude smaller than the values experimentally observed. To provide a direct proof of the mechanism, calculations on the desorption dynamics are, however, necessary. It is very possible that electron-hole pair oscillations are the main mechanism whereby vibrational energy transfer in the trapped state occurs as argued by both Asscher et al.[232] and Misewich et al.[325,327] Another possibility is that vibrational transitions in the trapped state or upon desorption involve a vibration-to-rotation (VR) mechanism, also mentioned by Misewich et al.[325] The study by Clary and De Pristo does not examine the relative importance of the two mechanisms (and indeed does not include coupling to electron-hole pairs in the model), and this must be regarded as an important open question at the present time. It appears that calculations on vibrationally excited molecules bound to the surface (or fixed at some distance therefrom)[334] suggest that the electron-hole pair mechanism yields reasonable magnitudes for the energy transfer rates. However, quantitative calculations of trapping/desorption dynamics which include the effect of electron-hole pairs are necessary before this mechanism for vibrational transitions can indeed be confirmed.

VII. Astrophysical Applications

Collisions between molecules or atoms have been recognized for a long time as pivotal processes for the understanding of a wide range of astrophysical phenomena. In recent years, stimulating suggestions were put forward on possible important roles of molecule–surface collisions in the chemical evolution of interstellar clouds and in several other topics of fundamental interest in astrophysics. The surfaces involved in such processes do not, of course, correspond to the well-defined crystalline species which are at the focus of many laboratory experiments and theories discussed in this review. However, surface processes in astrophysics merit the attention of the molecule–surface scattering community because the problems are challenging and because any input data on the elementary rate constants involved should be very useful. Much of the pioneering work on this topic is due to D. A. Williams and his co-workers.[437-441] They drew attention to two roles that interstellar grains may play which could influence the chemical evolution of interstellar clouds. Firstly, grains may act as sinks for gas-phase molecules by adsorbing them on their surfaces. Secondly, grains may be the sites of surface chemical reactions between species adsorbed from the gas phase. Thus, estimates of sticking probabilities on surfaces (that can model those of interstellar grains) and of reactions on and desorption from surfaces are very pertinent to the understanding of interstellar cloud dynamics. Evidence for chemical activity on interstellar oxide grains is reviewed by Jones et al.[439] The authors discuss the possible importance of steps, corners, and other defects on the irregular grains in adsorption and catalytic behavior and estimate the existence of binding energies of H atoms and protons at such sites. MgO and silicates are two of the candidates for instellar grains that may give rise to processes of H atoms and protons and which were used as models for the binding energy estimates.

A particularly strong case for a surface reaction on interstellar grain can be made in the case of H_2 formation by recombination, and of H_2CO for motion in diffuse interstellar clouds. Recently, Buch and Dalgarno[442] proposed a quantum mechanical model for the sticking of low-energy atoms to a surface and applied it to estimate the trapping probabilities of H atoms on models of interstellar grain surfaces and the resulting formation of H_2 molecules. A somewhat earlier and cruder model, by Leitch-Devlin and Williams[441] uses first-order time-dependent perturbation theory (with the free particle as zero-order initial state and the trapped particle in the attractive well as the final state). They applied this very simple model to the calculation of physisorption probabilities on several lattices modeling interstellar grains (graphite, graphite + H_2 monolayers; silicate; MgO). The perturbation treatment yields a result very sensitive to the phonon spectrum, and the latter is unlikely to be the same for a crystalline model as for the true, irregular grain. Leitch-Devlin and Williams found that vibrationally soft lattices yield high sticking probabilities for the gas and surface temperatures pertinent to interstellar grains. The same is not true for stiff lattices (MgO), and the authors argue that it is important therefore to explore the role of various chemisorption sites (corners, edges, steps, etc.) on such grains. Finally, Leitch-Devlin and Williams find that their results agree with the "canonical" requirement of a 0.3 sticking coefficient for H atoms. (This value is derived from the required interstellar cloud formation rate, and the constraints of observations are such that it cannot deviate greatly from this value.) However, the requirement of a reasonable value for the trapping probability is met only for physisorption on soft grains, not for the stiff ones such as MgO.

The results of the present models of sticking on interstellar grains are already very useful in testing the feasibility of various mechanisms for the formation of H_2 and other molecules in space. The topic of surface processes in astrophysics is, however, still in early infancy. The theoretical techniques used in the context of molecular beam scattering from surfaces are considerably more quantitative and have the advantage of direct support of detailed experiments. Applications of these theoretical methods to simulations of molecular collisions with grains should be able to provide very useful information.

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