

Laser diagnostics of elementary processes in molecular beam scattering on surfaces

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Abstract. We survey the main aspects of the laser techniques to study the elementary processes that take place in the scattering of molecules from crystallographic surfaces. We discuss the salient features of the accommodation of the translational, rotational and vibrational degrees of freedom of the scattered molecules and we summarize the main results of a recent comparative study of molecular beam scattering on graphite and diamond.

Keywords. Laser diagnostics; molecular beam scattering; molecular surface interaction.

1. Introduction

A tremendous experimental and theoretical effort is presently concentrated on the study of the molecule surface interaction. This concerns the understanding of the different facets of this highly complex interaction as well as its judicious control and exploitation to meet the demands of modern technology; and as the latter progresses new investigative techniques appear that throw new light on the mechanisms that underlie the different physical and chemical processes that can take place on the surface. There is no end in sight to this interplay and its impact in all areas of science and technology is expected to be immense.

The crux of the problem is to understand how the essentially localized degrees of freedom of one species, namely the single molecule, couple and interact with the more or less delocalized or collective degrees of freedom of the other species, namely the surface, and how this gives rise to the observed physical and chemical processes. We will not try to delineate here this highly complex interaction and the methods that are being devised for its study. Our aim here is to single out one approach which is both surface and single molecule specific, namely the exploitation of laser diagnostic techniques to study the molecular beam scattering from surfaces, and discuss some recent trends there.

The motivation behind this approach is two-fold: first, with the molecular beam scattering technique in ultrahigh vacuum chamber one provides the ideal conditions to study the interaction of a single molecule with an uncontaminated surface and second, with the lasers one can prepare and interrogate respectively the incident scattered molecules in a well-defined configuration or state of motion, in particular a quantum mechanical one, and study the state-to-state or configuration-to-configuration transition channels accessible through the molecule surface interaction. It is

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quite evident that this state selective approach provides an unique nondestructive way of isolating and studying any particular feature of the molecule surface interaction; its application in principle is simple and straightforward: a collimated beam of molecules in a well-defined initial state is incident on a well-characterized crystallographic surface and the residence time, angle, velocity, mass and internal state distributions of the molecular species leaving the surface are measured with laser techniques also combined with other detection and surface diagnostic techniques.

2. Experimental techniques

We cursively survey the main experimental elements of molecular beam scattering in ultrahigh vacuum chambers and the detection techniques for the scattered molecules.

2.1 Ultrahigh vacuum chamber

The necessity to perform the experiments in high vacuum is better grasped with the following order of magnitude argument. In the kinetic theory of gases one shows that the number of molecules hitting a unit area of a surface per unit time is given by

$$Z = bp(MT)^{-1/2}, \quad (1)$$

where p and T are the ambient pressure and temperature respectively, M is the mass of a gas molecule and $b = 2.63 \times 10^{26} \text{ m}^{-2} \text{ s}^{-1} \text{ K}^{1/2} \text{ mbar}^{-1}$. Assuming that all molecules that reach the surface stick on it one sees from (1) that it takes roughly 3 s at 10^{-6} torr to cover a surface of one square centimeter with an N_2 -monolayer of 10^{15} molecules/cm² and 8 h at 10^{-10} torr. Since commonly a measurement series can take several hours to be completed one sees the importance of performing the experiments in an ultrahigh vacuum chamber of less than 10^{-10} torr pressure, so that the surface sample remains uncontaminated in the course of the measurements.

The fabrication techniques of UHV chambers are now well established. To avoid corrosion and keep the rate of outgassing low the chamber with its connections are made of argon-arc welded or vacuum-braised stainless steel preferably amagnetic. The gaskets are metallic (copper or gold). The system goes through several cycles of baking up to 500°C and must be designed to be flexible and easily disassembled. Several types of pumps are used to reach the ultrahigh vacuum inside the chamber (diffusion, ionic, titanium sublimation, cryogenic, turbomolecular) and the choice depends on several factors like the gases to be pumped, the pumping rate etc. One usually connects several pumps operating at different stages of the pumping cycle which for a vacuum of 10^{-11} torr can take up to 24 h after baking. For this reason one designs the experimental set-up so that breaking of the vacuum occurs as rarely as possible. In recent experimental set-ups, like ours, the UHV-chamber is connected with a UHV-prechamber where the surface sample characterization and cleaning and other operations take place and subsequently the sample is mechanically transferred to the main UHV-chamber.

The surface sample is mounted on a manipulator of particular design to allow for control of incidence polar and azimuthal angles and determination of final scattering angles in and out of the scattering plane; in addition the manipulator serves to cool

or heat the surface sample. The actual complexity of the manipulator depends on the degree of mobility of the source and detector. As previously stated the chamber is designated to allow several *in situ* operations and measurements, some of them being relocated in the prechamber if available.

2.2 Molecular beams

Particle beams have been introduced quite early for the study of surfaces and solids; one can produce beams of ions, atoms, molecules or clusters which allow surface specific studies as these particles do not penetrate into the bulk with the possible exceptions of ions. While the diffraction of atomic beams has been extensively developed for surface structure and phonon studies, the molecular beams are not suitable for such studies. On the other hand, the energy redistribution among the internal degrees of freedom of the molecules interacting with the surface opens the possibility to observe a much richer class of physical and chemical processes (Barker and Auerbach 1985) which, in addition, are connected with important applications: thermal exchange, adsorption-desorption, heterogeneous catalysis (Ertl 1982; D'Evelyn and Madix 1984) etc.

The principle of their fabrication (Campargue 1989) is to let molecules flow through a nozzle from a high pressure chamber to a low pressure one. Depending then on whether $\lambda/D > 1$ or $\lambda/D < 1$ where λ is the mean free path in the first region and D the nozzle diameter ($K = \lambda/D$ is the Knudsen number) one distinguishes two classes of beams, the effusive and the supersonic respectively.

In the first case, $\lambda/D > 1$, the molecules flow through the orifice into a collimating aperture to produce a beam with a molecular velocity distribution very close to the thermal one prevailing in the first region mentioned above with a velocity distribution

$$I(v) = (v^3/\alpha_s^2) \exp(-v^2/\alpha_s^2), \quad (3)$$

where $\alpha = (2kT_s/M)^{1/2}$ and T_s is the source temperature. This is because the molecules do not collide while passing the orifice and therefore maintain the statistical characteristics of the first region and in particular a single temperature for all their degrees of freedom, the same as that of the source.

In the second case, $\lambda/D < 1$, the molecules flow through a nozzle followed by a skimmer that sorts out (skins off) all molecules with large transverse velocity component with respect to axis, while those directed along this axis are allowed to flow through it. Because of the large number of collisions the gas is now cooled as it expands into the vacuum and is also characterized by a narrow velocity distribution

$$I(v) \approx (v^3/\alpha_0^2) \exp[-(v - v_0)^2/\alpha_0^2], \quad (4)$$

centered around the non-zero flow velocity v_0 and $\alpha_0 = (ZkT_0/M)^{1/2}$ where $T_0 \ll T_s$. Furthermore the internal degrees of freedom can be cooled down to different temperatures as low as 1 K. By judicious expansion of dilute gas mixtures (seeded beams) besides lowering the temperature T_0 one can also vary the average velocity v_0 over a most wide range up to 3-4 Mach for NO molecules or up to 4 eV in kinetic energy. Even higher energies can be achieved first by ionizing the molecules then accelerating them to high velocities in appropriately designed electric fields before neutralizing and collimating them; the kinetic energy here can be as high as 10 keV but the molecular flux is weak and of rather poor quality.

2.3 Detection of scattered molecules

For neutral molecules one may distinguish two main classes of detection techniques. In one the scattered molecules are first ionized and the ions detected with mass spectrometer techniques; in the other the energy content of the neutral molecules is measured. In the first class falls the most widely used quadrupole mass spectrometer (Lee *et al* 1969), where the molecules are ionized with electron bombardment, while in the second class falls the much less used bolometers (Gallinaro *et al* 1918). The main disadvantages of bolometers are the low temperatures used during operations and the difficulty in calibration in particular when internal degrees of freedom are involved. Unfortunately neither the quadrupole mass spectrometer nor the bolometer can be used for state selective studies and both have been now surpassed by techniques employing lasers which in addition allow one to prepare the incident molecules in well-defined quantum states before they interact with the surface. Owing to these and several other advantages laser diagnostic techniques are being introduced increasingly in the study of the molecule surface interaction, the only constraints right now being the access to laser sources with specific characteristics like high resolution, frequency stability and wide tunability range in the infrared and near ultraviolet. Besides their exclusive use for state to state selective studies, laser techniques provide unique information concerning velocities using Doppler measurements as well as time of flight measurements, the latter performed by chopping the beam and adjusting the delay of the laser pulse.

2.3a Laser diagnostic techniques: With these techniques the scattered molecules are allowed to resonantly interact close to the surface with tunable laser sources and then products issued from this resonant interaction are detected; here too, one either detects molecular ions produced by multiphoton ionization (Häger and Walther 1985) of the scattered molecules or photons (Frenkel *et al* 1981) produced by the resonant laser excitation of the scattered molecules. The intensity of the signal is directly related to the population distribution over the states of the scattered molecules. The techniques that have been used up till now are the multiphoton ionization (MPI) and the laser induced fluorescence (LIF) but other techniques in particular nonlinear optical ones could also be used. The MPI and LIF techniques have been extensively used to probe the rotational state population distribution in the scattered or desorbed molecules (Zacharias 1990), both are very sensitive, in particular the MPI technique, because ions can be collected with almost 100% efficiency, which is far from being the case for the fluorescence photons, but on the other hand difficulties may arise because of our limited knowledge of the ionization step. Those techniques also allow determination of the direction of the angular momentum by varying the laser polarization (Jacobs and Zare 1986) and the velocity distribution with time-of-flight measurements.

Despite their exclusive use in state selective studies these two techniques present several limitations intrinsic to the processes and in addition they require precise knowledge of the spectral characteristics in regions inaccessible with present day laser sources. Furthermore with the need to go to larger and larger polyatomic molecules the complexity of their spectra, rotational, vibrational or electronic and state selective ionization cross-section introduce unsurmountable limitations on the use of these techniques here. In this respect other laser techniques based on nonlinear coherent processes can yield very accurate results but need higher molecular beam

densities than currently accessible. Examples of such techniques are the Coherent Antistokes Raman Scattering (CARS) (Levenson 1982) and its variants, which can be used for a wide range of polyatomic molecules for the determination of the rotational or vibrational temperatures as well as the optoacoustic detection technique.

2.3b *Lasers sources:* Presently these are based on the use of pulsed high power fixed frequency lasers, frequency doubled Nd: YAG ($\lambda = 532$ nm) and excimers (XeCL, $\lambda = 308$ nm) to pump dye lasers that emit frequency tunable coherent radiation in the range from 330–1400 nm with a spectral bandwidth of 0.05 – 0.3 cm^{-1} and pulses of a few nanoseconds duration. By frequency doubling in nonlinear crystals or tripling in gases or four-wave interactions one may extend upwards their spectral range in the near UV and by frequency mixing (difference) or stimulated Raman processes downwards in the infrared or near infrared; the UV is used for the detection of the scattered molecules in the MPI and LIF techniques, while the infrared is the selective excitation of the incident molecules. Despite important progress in the exploitation of the nonlinear processes the reliability and availability of such sources are still limited and some of them may be replaced in the near future by primary tunable laser sources like titanium-doped sapphire, semiconductor lasers or even synchrotron radiation.

As previously stated, the laser sources, besides their use in state selective detection of the scattered molecules, can also be used to prepare the incident molecules in a well-defined rotational, vibrational or electronic state before they are allowed to interact with the surface (Zacharias *et al* 1982). Here direct excitation with one photon absorption or nonlinear optical techniques like coherent excitation can be used very efficiently to excite a large quantity of molecules within a pulse duration.

3. Theoretical description

The theoretical treatment of the molecule surface interaction is a highly complex problem because of the inherently different natures of the two interacting systems, the molecule and the surface, in regard in particular to the dynamics of their excitations. Drastic simplifications and approximation schemes are needed to reach a certain understanding of the elementary steps and obtain meaningful results. A coherent description, albeit a very approximate one, is slowly emerging that in many cases allows one to quantitatively account for the experimental behaviour of the scattering patterns from simple crystallographic surfaces of metals and insulators.

3.1 *Surface potential and elementary interaction processes*

The essence of the molecule surface interaction can be grasped in terms of some very simple models while the quantitative agreement with the experimental results needs quite involved numerical treatment of the molecular trajectory in the field of the surface potential.

The latter, in principle, can only be obtained with the help of quantum mechanics and a prerequisite is the knowledge of the electronic distribution and the atomic arrangement of the surface. Actually these cannot be simply related to those of the

underlying crystalline solid. Indeed the surface atoms, in order to counterbalance the absence of bonding forces on one side of the surface plane, undergo a rearrangement of their positions both along the surface normal and sidewise within the surface plane. The first, also termed relaxation, preserves the symmetry of the atomic arrangement but modifies the relative distances between the surface plane and the two or three planes that follow it, while the second, also termed reconstruction, leads to more profound changes and in particular imposes a symmetry within the surface plane altogether different from that of the bulk; the latter is particularly dramatic in the case of covalently bonded solids like semiconductors but also metals. The global consequence is that the electronic distribution and the spectrum of the collective motion of the surface atoms, its dynamics and thermodynamics are strikingly different from those of the bulk (volume) (Wallis 1972; Inglesfield 1982).

Thus, the Debye temperatures, θ_B and θ_S for the bulk and surface respectively are vastly different with $\theta_B < \theta_S$; we remind ourselves that the Debye temperature measures the mean-square thermal amplitude of the vibrational motion or

$$\langle u^2 \rangle \approx T/\theta^2, \quad (5)$$

and hence the previous inequality leads to $\langle u_S^2 \rangle > \langle u_B^2 \rangle$ which implies that anharmonic dynamical effects may play an important role in surfaces and quantum behavior is expected at much lower temperatures than in the bulk.

Even for diatomics, the determination of the molecule surface interaction potential is prohibitively difficult, far more so than the atom surface interaction, because of the anisotropic shape of the molecule and its internal motion. The simplest approach, in connection with scattering of diatomics, is to altogether neglect the surface periodicity and corrugation and represent the surface with a flat potential wall,

$$V(r, \theta) = V(z, \theta), \quad (6)$$

where z is the distance of the center of mass of the molecule and θ the angle between the molecular axis and the surface normal. The potential equation (6) contains a long range attractive part that roughly goes to zero as $(z - z_0)^{-3}$ and a short range repulsive core part in which one must include the rotational barrier potential as well as the bond length change of the molecule if rotational and vibrational energy transfer or dissociation processes take place; the electronic state of the molecule must also be specified.

For more detailed calculations one must also introduce the surface structure either through a rigid corrugation $z_0(x, y)$, a periodic function of x and y , or explicitly introduce the interaction potential of the molecule with the individual surface atoms and the mutual interactions of the latter.

The interplay of repulsive and attractive parts however is a quite general feature. It leads to one or more valleys in the molecule surface potential where the molecule can be accommodated for a more or less long time by physisorption, a single shallow valley without electron exchange. Eventually it can act as precursor state to the chemisorption in a deeper valley where a bonding between the molecule and the surface takes place through an electron exchange. The description of the latter is far more complex as it leads to profound electronic rearrangements in contrast to the former which is due to Van der Waals interaction. However some understanding at the fundamental level has been gained in simple metals using quantum chemical

techniques and free electron gas concepts. In the case of the physisorption the mean average stay time of the molecule upon the surface is roughly

$$\tau = \tau_0 \exp(E_A/kT_S), \quad (7)$$

where τ_0 is the vibration period of the molecule within the shallow physisorption potential well of depth E_A at surface temperature T_S .

These elementary trapping processes or adsorption can be followed by desorption which can occur by thermal or forced energy gain provided by an external nonthermal source or by tunneling; in the meantime the molecule may also execute a more or less random walk or diffusion on the surface or undergo dissociation or other reactive processes.

Thus from the outset a molecule colliding with a surface can undergo the following elementary processes:

- specular scattering: no exchange of momentum or energy between molecule and surface;
- diffraction; momentum exchange but no energy exchange between molecule and surface;
- intramolecular energy transfer without energy contribution from the surface;
- inelastic scattering: energy exchange between molecule and surface;
- trapping and physisorption;
- sticking and chemisorption;
- diffusion upon the surface and desorption;
- formation of a more or less ordered layer;
- chemical reaction;
- diffusion into the bulk;

all these processes besides their fundamental interest are related to very important technological applications.

3.2 *Hard cube models*

The molecular motion even with the simplest possible physisorption potential is quite complex, the molecule suffering acceleration when approaching the surface and a deceleration when leaving it because of the attractive part. If we assume that the two effects globally cancel each other and altogether neglect the attractive potential while we replace the repulsive part with a hard wall one can gain some first hand insight of the scattering pattern using the so-called hard or soft cube models.

In the hard cube model the surface region around the geometrical collision site is replaced by a hard cube of mass M_c and vertical velocity V_c ; M_c and V_c are effective quantities. Straightforward application of classical mechanics allows one to derive all kinematical features of the collision. Thus if the collision occurs without friction and the molecule is represented as a hard sphere (no rotation, effective impact parameter equal to zero) only the normal momentum and energy components change with gain or loss for the molecule (Logan and Stickney 1966). Additional gross features of the scattering can be accounted for by introducing a friction and a spring force on the cube; they are the soft cube models.

In the hard cube model (Nichols and Weare 1975), if the molecule is taken to be a hard ellipsoid (ellipticity $e = b/a$, b and a semimajor and semiminor axes) one has

in general a nonzero effective impact parameter and rotation of the molecule which may couple with the translational motion; the amount of the rotational energy imparted to the molecule is easily obtained from conservation laws and can be simply expressed in terms of the effective impact parameter

$$I = \frac{b(e^2 - 1) \sin 2\theta}{2e(e^2 \cos^2 \theta + \sin^2 \theta)^{1/2}}, \quad (7)$$

which for the extreme case of a rod ($a = 0$) reduces to

$$I_\infty = b \sin \theta. \quad (8)$$

The scattering pattern can be calculated by averaging over all the incident velocity and incident angle θ distributions. Because of the periodic dependence of the impact parameter on θ one obtains two accumulation points for the scattering pattern related to $\theta = 0$ and $\theta = \pi/2$, or $I = 0$ in (9). This is the physical origin of the rotational rainbow which has been experimentally confirmed (Kleyn *et al* 1981). Actually if the imparted rotational energy is very high, the molecule may hit the surface with its other end repeatedly and this is the rotational trapping. These manifestations of the classical rotation are also recovered with quantum mechanics where in addition one gets subsidiary oscillations between the two accumulation points because of quantum interference between different rotational channels (Barker *et al* 1983) but these still escape experimental confirmation because of broadening mechanisms that wash them out. Note that in addition to rotational rainbows one may also have periodic corrugation rainbows which are due to the inherent periodic corrugation of the surface and can be accounted for in terms of a periodic effective impart parameter. Such rainbows can also appear with spherical particles and actually have been observed in scattering of atoms (Smith *et al* 1969) but in the case of molecules these are dominated by the broadening mechanisms.

3.3 Stochastic trajectories; accommodation

We will not dwell more on these simple hard or soft cube models as they suppress the most relevant features and information one wishes to extract from these studies: in particular the ones relevant to the residence of the molecule on the surface. Whatever elementary process may occur during this residence an important question is the determination of the so-called accommodation coefficient (Tully *et al* 1982) of the different degrees of freedom of the molecules scattered from the surface kept at temperature T which for each degree of freedom j is defined by

$$\alpha^j = \frac{E_f^j - E_i^j}{E_s^j - E_i^j},$$

where E_f and E_i are the final and initial flux-averaged energies after and before the collision respectively and E_s is the flux-averaged energy for molecules in thermal equilibrium with the surface at temperature T . Thus α^j ranges from zero to one and if each degree of freedom reaches equilibrium for the initial, final and surface states or $E_f \approx kT_f$, $E_i \approx kT_i$ and $E_s \approx kT_s$, one also has

$$\alpha^j = \frac{T_f^j - T_i^j}{T_s^j - T_i^j}.$$

The hard and soft cube models are of little or no help to account for these coefficients and the only relevant progress here was made with the classical trajectories approach in particular when this is cast in the form of generalized Langevin equations the so-called stochastic trajectories approach initially proposed for atoms and subsequently extended and substantially developed for molecules. The main assumptions here are

- the atoms within the relaxation depth are separated into primary atoms, the ones of closest geometrical approach of the incident molecule, usually no more than $3 \times 3 \times 3 = 27$ atoms, and into secondary ones which include all other atoms and are assumed to randomly interact with the primary ones with harmonic forces and constitute the so-called bath;
- the molecule interacts only with the primary atoms with atom–atom pair potentials;
- the motion of the secondary atoms is projected out and replaced by a random Langevin force;
- the equation of motions with the initial probability distributions are calculated with Monte Carlo techniques. This approach is presently the most powerful and physically most appealing as it allows the quantitative accounting of the molecular scattering behavior and thermodynamics in particular when heavy molecules are involved and specific quantum mechanical features are washed out except for very low temperatures where however the residence time (Zacharias 1990; Matsuo *et al* 1991) is expected to be so long that the scattering process becomes different. Very subtle features of the molecular motion have been studied and predicted with this technique which is expected to further improve.

Quantum mechanical calculation and models have also been proposed and developed using some highly sophisticated approximation schemes and have some success in accounting for the scattering of light molecules like H_2 , HD or D_2 . Efforts to extend them to heavier molecules have been undertaken. Besides the possibility of better accounting for the state to state transitions, quantum mechanical models also allow one to introduce tunneling processes, a specifically quantum mechanical effect which may certainly be the dominant mechanism at very low temperatures.

We wish to stress here that all these calculations are rather long and computer-time consuming; they are meaningful only if the interaction potential is known with a certain precision. Actually most theoretical effort is presently directed towards this very crucial point. With the increasing experimental precision and increasing sophistication, subtle details of the interaction potential are constantly unravelled and checked and this puts huge demands on theoretical models and calculations.

4. Survey of experimental studies with laser techniques

These mostly concern scattering of light diatomics, like H_2 , H_D or D_2 , from metal or insulator crystallographic surfaces, as well as scattering of heavier diatomics N_2 , O_2 , NO and CO and a few polyatomics CO_2 , CH_4 and NH_3 from the same surfaces. As of today the main factors that restrict the extension of the laser diagnostic techniques to other heavier molecules besides the problems related to the production of sufficiently intense and well-characterized molecular beams are their complicated spectra and the lack of widely tunable laser sources in the far infrared for the excitation of the incident molecules and more importantly in the UV for the detection of the scattered ones either with the LIF or the MPI techniques. Other nonlinear optical

techniques that have not been applied yet need intense molecular beams. We will succinctly survey the main aspects and results of experimental studies using laser techniques.

4.1 *Light molecules*

Here the phonon creation and annihilation are very unlikely and one has predominantly elastic scattering, diffractive or non-diffractive with eventually very weak one-phonon scattering. In addition one has rotational and vibrational excitations, chemisorption and reactive processes. Unfortunately laser techniques are still difficult to implement here because of the large spacing between the ground and excited electronic states and the smallness of the relevant cross sections. Some isolated studies however have been performed (Kubiak *et al* 1985). Actually, precisely because of the small size of these molecules and their low masses, the usual mass detection and time-of-flight techniques allow one to have state selection as well because of their wide rotational and vibrational state spacings which are far larger than the angular widths of the scattering lobes and give rise to easily detectable scattering peaks at angles that depend on the energy lost or gained. With the advances of tunable UV and IR sources the study of these molecules will be intensified as they allow meaningful confrontation of experiment and sophisticated quantum mechanical models and predictions.

4.2 *Heavy molecules*

Because of the difficulties previously evoked the studies have been restricted to N_2 , O_2 , NO, CO, CO_2 and CH_4 because of the convenience of their production in molecular beams, the availability of well-documented spectra and the access to tunable laser sources in the relevant spectral regions. Thus the scattering from metal surfaces [mostly Ag(111); Ag(110), Pt(111) (Tully *et al* 1982), Pt(110) and some extent W, Cu and Ru] or from insulator surfaces (LiF, MgO, graphite and recently diamond), was studied using the LIF and MPI techniques; the incident molecules were rotationally cool (≤ 30 K) with very narrow incident velocity distributions from thermal to supersonic average velocities and in certain cases they were vibrationally excited with infrared laser radiation.

These studies concerned the determination of the angular and velocity distributions mostly for state selective inelastic scattering. A particularly well-studied system is the NO-Ag(111) (Tully and Cardillo 1984) where it was possible to unambiguously separate the inelastic scattering from trapping and desorption and similarly the NO-graphite system.

In all the systems studied one observes Boltzmann distributions irrespective of whether the molecule was simply scattered or trapped and then desorbed. This implies that the degrees of freedom of the molecule reach thermal equilibrium but in general with temperatures that are different from the surface temperature T_s , or in terms of the accommodation coefficient (Houston and Merrill 1988), in general $\alpha \neq 1$. In the case of rotational level distributions for the scattering of NO from Ag(111) marked deviations from a Boltzmann distribution were observed at high J which these deviations become markedly so with increasing incident kinetic energy; this was tentatively attributed to rotational rainbows (Kleyn *et al* 1981).

An interesting application of the LIF technique was the determination of the

alignment distribution of the angular momentum vector \mathbf{J} in the NO scattering from Ag(111); this can be written

$$n(\theta) = \sum_l b_l P_l(\cos \theta)$$

and the experimental data were fitted with $b_2/b_0 \approx -1.44$. Similar studies but with the MPI technique were conducted for the H_2 scattering from Ag(111).

The rotational energy transfer and temperature (T_R) were determined in many of these scattering experiments. It was found that T_R in general is not equal to T_S ; in general $T_R \approx T_S$ for T_S roughly below the Debye temperature θ_S which for most crystals is close to room temperature. As T_R is higher than θ_S one always gets $T_R < T_S$ more markedly for metals than for insulators: in the latter case T_R eventually levels off for large T_S and presumably saturates as T_S is increased. In addition, most cases indicate no coupling between translation, rotation and vibration of the molecule during its collision with the surface; in particular the rotational temperatures change by very small amounts, less than a few percent, when the translation (kinetic) energy of the incident molecules is changed by an order of magnitude.

The scattering of vibrationally excited molecules has also been investigated to some extent. The survival probability of the vibration was measured for NO scattered from LiF, Ag and graphite and was found to be large, > 0.9 (Misewich *et al* 1985), in agreement with previously performed stochastic trajectory calculations. In another series of experiments vibrationally excited molecules were produced during the scattering process and in certain cases this has been shown to be effective in causing dissociative adsorption.

A lot of interest is presently being directed to the desorption process both thermal and nonthermal laser induced (Prybyla *et al* 1990), although there is no conclusive evidence for the latter. Here the laser techniques with ultrashort pulses have proven to be essential. Time resolved studies of molecular processes on surfaces will be increasingly available although their combination with molecular beams is not evident.

These and other experimental investigations are only at their initial stages but are already providing some very interesting glimpses into the molecule surface interaction processes and some exciting and unique perspectives for future work.

4.3 NO scattering from graphite and diamond. A comparative study

We summarize here the molecular beam scattering investigations with NO molecules on graphite and diamond allotrope (Flytzanis 1988; Vach *et al* 1989; Matsuo *et al* 1991) carbon partners. In order to appreciate the distinctly different scattering patterns we expect that it suffices here to state that the unreconstructed diamond (111) surface possesses noninversion symmetry while the graphite surface has inversion symmetry. Furthermore, the Debye temperature of diamond is exceptionally high, $\theta_D \approx 2200$ K for the bulk and $\theta_D \approx 1800$ K for the surface, a unique case in solid state physics while that of graphite is ≈ 700 K. Accordingly the amplitude of the mean thermal motion of the surface carbon atoms is almost 1 order of magnitude smaller in diamond than in any other crystal and does not smear out the surface features.

The graphite surface is a regular planar array of strictly planar carbon hexagons with all six carbon atoms equivalent and possesses inversion symmetry, while the diamond (111) surface does not; here too the surface consists of hexagons but these are tilted and not planar and actually consists of two groups of three equivalent

atoms each. The three atoms of one group have their dangling bonds with hydrogen atoms which start evaporating when the surface is raised above 1000 K. Up to this temperature diamond shows neither reconstruction nor relaxation as also does graphite where however no hydrogen terminated dangling bonds exist because of the planar sp^2 hybridization.

The scattering of NO from both surfaces was studied with a quadrupole mass spectrometer as well as with the MPI technique, also combined with time-of-flight measurements. The incident molecules were rotationally cool ($T_r \approx 20$ K) and their average translational energy was varied in the range of 700–2800 cm^{-1} by seeding with He atoms. The background gas pressure was kept below 10^{-10} mbar and the surface temperature was never raised above 1000 K.

In the case of graphite as previously stated we obtained two components in the scattering pattern, one consisting of molecules which underwent single scattering and the other of molecules that were trapped and desorbed and indeed shows the expected $\cos \theta$ pattern. No coupling of translation and rotation was evidenced and similarly for vibration–translation and vibration–rotation.

In the case of diamond the situation is drastically different. To begin with, the scattering pattern shows a marked left–right asymmetry when the sample is rotated by 180°; which can be traced back to the topography of the diamond (111) surface and in particular its asymmetry. Here too one has two components, a sharp and a broad one, and their relative importance differs for left and right incoming molecules and in addition on the surface temperature the rotational state and the exit angle θ_s . The sharp component originates from molecules that are specularly scattered after they suffer a hard collision with the surface and as expected a very efficient energy transfer from translation to rotation was clearly evidenced; the scattered molecules of the sharp component show a Boltzmann distribution for the rotational state distribution with a temperature T_r which is totally independent of T_s but depends on the incident angle. The broad component apparently consists of molecules that remain on the surface for a very long time, approximately 0.1 ms, but the scattering pattern does not show any $\cos \theta$ -distribution law; indeed this component shows a marked left–right asymmetry. Its rotational temperature is also independent of T_s and also of the incident and exit angles θ_i and θ_s , respectively and no correlation is apparent between the translation and rotation. The long residence time of the molecules of this component was attributed to geometrical trapping of the NO molecules inside the craterlike corrugations of the diamond (111) surface, where they undergo a complex motion before they tunnel out in the directions of easiest escape as imposed by the geometry of the traps.

These features are not restricted to the graphite and diamond cases; they may well show up in other surfaces such as unreconstructed covalent ones like in semiconductors and elsewhere.

5. Conclusion

Laser techniques were introduced only recently but their relevance is timely and their impact irreversible. They provide the most state selective techniques to prepare the molecules before they interact with a surface and to interrogate their state after the interaction. They provide many advantages that are only now being appreciated

and exploited like the use of nonlinear optical processes and time resolved techniques with ultrashort light pulses. Besides laser techniques are nondestructive. The introduction of the lasers already at this preliminary stage has enriched the surface physics and chemistry field with very promising techniques and greatly increased the interest to new directions. This trend will substantially increase as the elementary molecule surface interaction processes are the heart of several far reaching technological applications.

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