

How Light Causes Molecules to Vibrate

Laser Optics Make Photochemical Processes Visible

Photochemical processes play an important role in basic research, not least of all in helping to understand light-induced reactions occurring in connection, for example, with questions involving environmental and chemo-atmospheric analysis. A research team in Bochum is investigating what happens when light stimulates the surface of solid bodies.

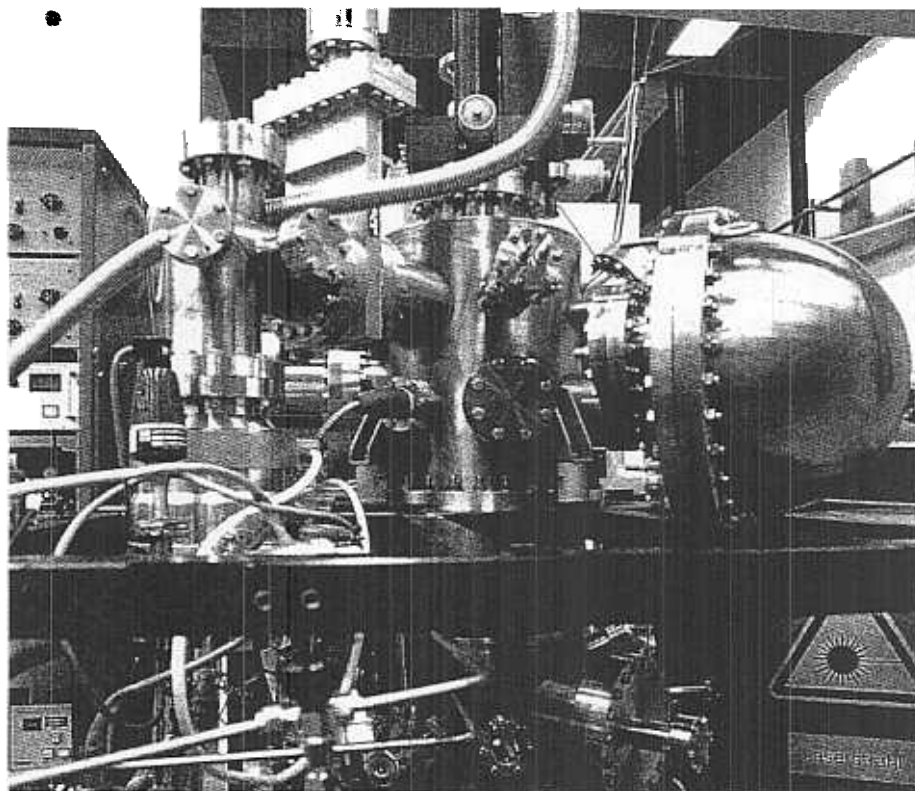
In nature, light serves as a source of energy. So, for instance, photosynthesis of green plants, in other words the formation of glucose from carbon dioxide and water, is initiated in a catalytic reaction by light, whereby the catalytic centre for the activation of the carbon dioxide molecule is localised on a metal atom in a large organic molecule. But light-induced catalytic processes occur in anorganic systems, too. Thus, the reduction of carbon dioxide to formaldehyde and methanol on semiconductor electrodes is just one concrete example of a heterogeneous catalytic reaction. In the case of these heterogeneous catalysts, the reaction occurs at the surface of the solid, i. e. at the interface between gas and solid. This particular reaction can also be intensified – photocatalysed – by light. In a similar manner, in environmental analysis and atmospheric chemistry, catalytic effects can influence light-induced reactions. Just imagine that small ice crystals or dust particles bind molecules from the gas phase to their surfaces, in other words, they adsorb them, thus altering the binding conditions in the adsorbed molecule. That such a molecule,

whose binding conditions have been altered through adsorption, produces different light-induced reactions from the molecule in the gas phase should not be surprising. However, the detailed mechanism involved in light stimulation at surfaces is still largely obscure. Only very recently have scientists begun to investigate light-induced photochemical processes on adsorbed molecules.

To gain a microscopic understanding of the underlying processes, heavily experimental methods borrowed from the field of laser optics are coupled with those employed in surface sciences. Our research team has developed an experiment in

which molecules are adsorbed on clean anorganic surfaces under ultrahigh vacuum conditions, i. e. conditions under which surfaces can be kept atomically clean, and can then be subjected to photochemical reactions.

The molecules are located on well defined “spots” on a metallic oxide surface where they are able to perform specific motions, such as, for example, nitrogen monoxide molecules on a nickel oxide catalyst. The nitrogen monoxide molecule lies, with its molecular axis inclined at an angle, on a nickel oxide surface 2.5 \AA , i. e. $2.5 \times 10^{-10} \text{ m}$, above the oxide surface and directly over a positively charged



Overall view of apparatus: The ultrahigh vacuum chamber in the upper part contains instruments for surface analysis. The lower chamber is where the laser experiments take place. The desorption laser light enters through the illuminated window.

nickel ion. From the energy point of view, this is the most favourable position on this surface, where the binding energy between molecule and solid is relatively weak, so that the molecules only remain on the surface at temperatures below room temperature ($-50\text{ }^{\circ}\text{C}$). However, this relatively weak bond between molecule and surface is sufficient to produce distinct effects when a photo-induced rupture of the bond occurs. If the bond to the substrate is ruptured through the energy introduced by the photon – as these light particles are called in the quantum theory – the molecule can separate from the surface; the energy which was introduced is divided between the molecule and the surface. The energy remaining on the molecule distributes itself between the external and internal motion of the molecule, i. e. on the energy of forward movement, the so-called centre-of-gravity motion, and on the internal rotatory and vibratory energy of the particle leaving the surface. Once the diverse energy inputs can be determined experimentally, there is a chance that both the photochemical mechanism of stimulation, and also the process whereby the energy is converted into heat, can then be elucidated.

Under the terms of this experiment, the crystal surface is illuminated by a laser beam for approximately 10^{-8} s. The intensity of the light is degraded to such a degree that no, or only very minute, heating of the crystal, which will have been cooled to $-170\text{ }^{\circ}\text{C}$, takes place. Stimulated by the laser light, a "cloud" of molecules escapes in every direction. A second laser is employed to measure the energy distribution in the escaping molecules. Once the illuminating laser has been switched off, this second laser is switched on in the form of a band of light for some few nanoseconds and is aimed parallel to the surface of the crystal in such a manner that the particles separating from the surface of the crystal have to move through it.

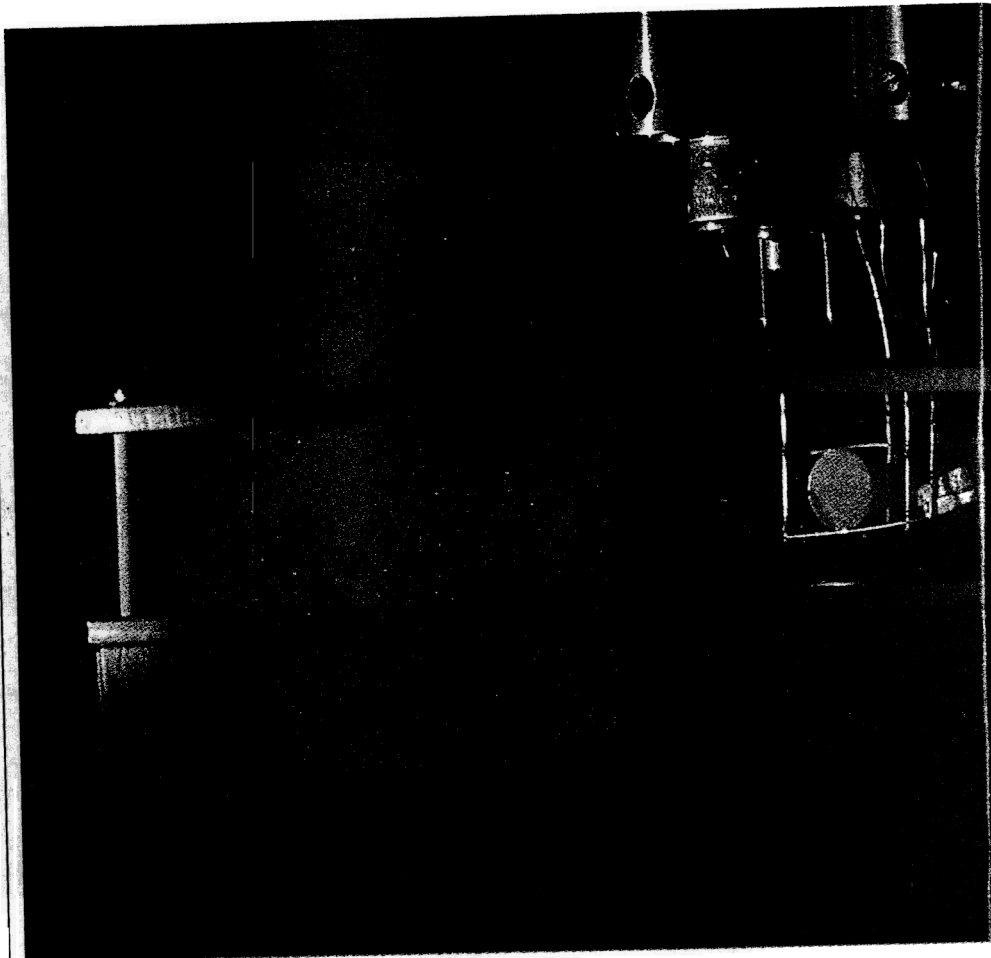
The energy of the light quanta – the energy particles –, which move at the speed of light, can be adjusted with high resolution, i. e. small energy width, by changing the wavelength of the laser light. The laser light always stimulates the molecules when its energy is precisely harmonised

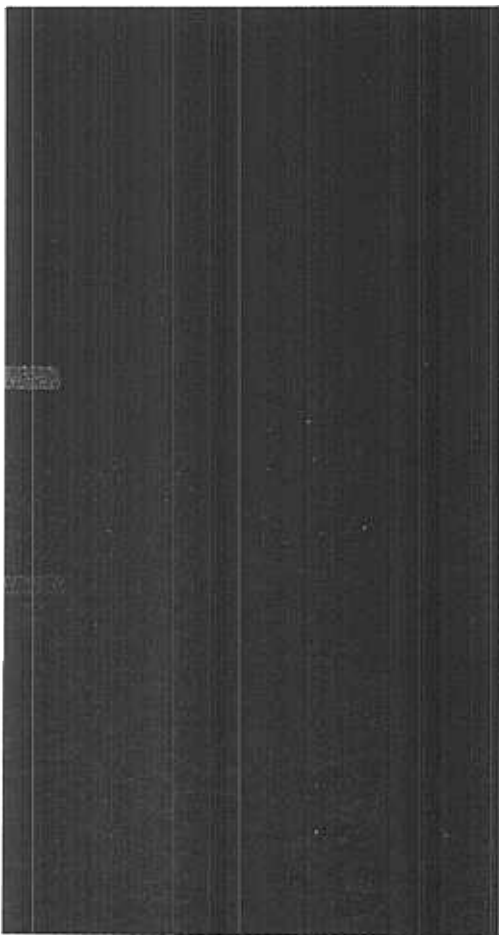
with a quantum state, i. e. a given energy state of the desorbing molecule. The particles are only stimulated if they are fast enough to reach the region of the light band in the interval between their separation and the switching on of the detection laser. Their velocity determines which area of the light band they can reach. The spatial distribution of the desorbing particles is displayed in a detector order and recorded by a computer. Once this spatial distribution has been determined, the velocity distribution can be worked out, and from that the kinetic energy. Since, on the other hand, as has already been mentioned, the identification of the particles as "clouds" occurs in individual quantum states, due to their high energy resolution, the energy distribution of the molecules can be determined in the form of centre-of-gravity energy, rotational energy and vibratory energy. In this manner it can be demonstrated that only some 15 to 20 per cent of the total light energy is transferred to the

Above: The laser band runs parallel to the round single-crystal surface in the ultrahigh vacuum chamber. Far right: The spatial distribution of the separated nitrogen oxide molecules ten microseconds after switching off the desorption laser; red indicates high, and blue low, frequency. The diagram shows the laser beam separating the molecules as a round arrow and the laser band for detecting the desorbing molecules as a broad arrow.

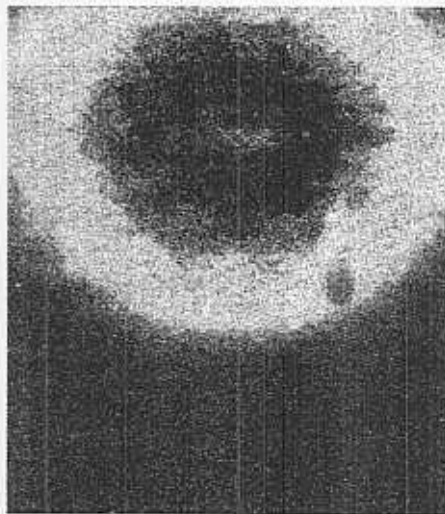
desorbing molecules, with 80 to 85 per cent remaining in the substrate, i. e. the surface.

There is a direct link between the motion of molecules and their temperature. If the temperature rises, the motion of the molecules becomes more vigorous. Hence the various movement processes can be classified in terms of "temperatures". In the example of nitrogen monoxide on nickel oxide mentioned above, oscillatory states of the desorbing particles reveal that the temperature of vibration is $1,600\text{ }^{\circ}\text{C}$, a temperature which lies $1,800\text{ }^{\circ}\text{C}$ above





the surface temperature. This shows that the stimulatory mechanism cannot work through any heating of the surface. It would be better to picture this stimulation as being something along the following lines. The light is essentially absorbed into the substrate, and not into the adsorbing molecules. Electrons are stimulated in the substrate, which can, so to speak, be "captured" by the adsorbed molecules. This creates an ephemeral negative nitrogen monoxide ion. Such an ion "lives" for some 10^{-14} s before its excitation subsides again, and the energy is redistrib-



uted between the molecule and the substrate. However, since the electrons are able to adapt to changes in charge distribution much more quickly than the atomic masses, the temporarily formed negative ion "senses" the change in the interaction with the substrate: first, it is attracted to the positive nickel ion, then the bond-distance of nitrogen to oxygen in the negative ion is greater than it had been in the neutral basic state prior to stimulation. The attraction at the surface causes a shift in the centre of gravity of the molecule and determines the velocity distributions observed. The change in the bond-distance of the nitrogen monoxide leads to the high temperature of vibration.

From the Nano- into the Femtosecond Range

The information contained in such experiments is not exhausted with what has been learnt so far about the desorbing particles. Of course, the material properties of the solid surface must also be included in these manifestations. For example, the number of particles desorbed by a stimulating flash of light is some ten thousand or hundred thousand times greater on a semi-conductor or non-conducting substrate than it is on a metallic conductor. This is of course linked to the much more efficient post-stimulatory energy distribution processes in metals. Due to their high conductivity, the energy is distributed so rapidly (at around 10^{-15} s) through the electrons in the system that the comparatively inert masses of the molecule are unable to follow or to absorb the kinetic energy required for desorption. Future experiments will aim to bring the time scale in which the stimulation and detection occur – hitherto in the nanosecond range – into the femtosecond range (some 10^{-15} s) in order to elucidate the effective mechanisms involved in the transformation of energy into heat in the substrate. Laser optics can help in the conduct of investigations into complex photochemical processes with femtosecond time resolution.

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