

20.0 Molecular Physics

20.1 Molecule Microscopy

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National Institutes of Health (Grant AM 25535)

Whitaker Foundation

We have been working on molecule microscopy (MM) ever since the first ideas were formulated two decades ago. Much has been accomplished towards defining this rich and complex field; but no single sufficiently important scientific or engineering application has emerged with which we could achieve the successful demonstration needed to guarantee adequate support and rapid progress.

MM involves the detection, with spatial and temporal resolution, of neutral molecules emitted from samples. The sample may be rough or smooth, thick or thin and may be metal, semiconductor, plastic, ceramic, natural or man-made biomaterial. Emitted molecules may diffuse through the sample or evaporate from its surface. These molecules may have been part of the sample or previously deposited from a staining molecular beam. They may evaporate spontaneously either uniformly or non uniformly spatially; in either case spatial resolution is obtained by limiting the solid angle in which molecules are detected by scanning with a small detector or aperture, at some distance from the sample or with a micropipette or field ionizing tip in contact with the sample. Molecules may also evaporate as a result of localized stimulation by focussed beams of radiation or particles, in which case spatial resolution is provided by scanning the beam. Sample temperature is usually set to hold general evaporation at the desired level or to preserve sample integrity. Finally, samples may be in UHV, gaseous atmospheres or in liquids as required provided appropriate detectors are used.

It is clear that the MM is not a single instrument but rather a collection of techniques chosen depending on the nature of the sample and the problem to be investigated. In the next paragraphs we describe some of the work that has been done to date.

Our first instrument used a small scanned aperture to provide spatial resolution. Low resolution images from a variety of samples were obtained. Another kind of MM depends on localized thermal desorption and, because we wish to study the distribution of water on biomaterials we have investigated the desorption of water from representative proteins, carbohydrates and liquids applied in monolayer amounts to a heatable platinum surface. We have also investigated by similar methods the desorption of water from cells grown in situ, cholesterol, DPPL, acrylic gels and CuSO_4 . Focussed laser light pulsed and scanned, has been used for localized sample heating so as to produce desorption. Yet another MM uses pulsed focussed electron beams to desorb molecules by ESD. We have measured the cross section for these processes under various conditions. This data along with our extensive experience with field desorption and ionization has made it possible to design an instrument capable of detecting small numbers of molecules adsorbed on sample regions of 1 nm extent or less.

This emphasis on water in biomaterials stems from our conviction that knowledge of the distribution of water on biological samples will shed light on the various mechanisms that provide specificity and selectivity in the interaction of various entities, from ions to viruses.

We have constructed two scanning micropipette MM and have used them to study transport of water in surviving tissue immersed in appropriate solutions. We found that contrary to some hypotheses there is negligible water transport through tight junctions between cells. We are currently considering applying these instruments to studies of localized gaseous transport in polymeric materials, as used in such varied applications as drug release systems and electronic device packaging.

We have designed a specialized MM for studies of hydrogen transport along grain boundaries in ferric metals. This hydrogen appears responsible for stress corrosion fracture according to several hypothetical mechanisms. We also prepared a grant proposal, but received no funding.

Lack of funding has plagued the development of these techniques and devices from the start. With hindsight it seems obvious that substantial funds would not be available to develop complex systems in which problems, solutions and applications cannot be known in advance. Nonetheless, we have accumulated a large amount of miscellaneous data, obtained preliminary results, designed apparatus and prepared grant proposals. Progress has been debilitatingly slow, however, since in a project such as this much effort necessarily is expended in developing each part of the system with many false starts and blind alleys.

20.2 Electrical Neutrality of Molecules

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The assumed equality of the electron and proton charges represents a symmetry in nature which corresponds to no known conservation law, but is based directly on a series of sensitive experimental measurements dating from 1925. These measurements have involved four different experimental techniques: 1) the gas-efflux method; 2) the isolated-body method (analogous to the Millikan oil-drop experiment); 3) the molecular-beam method; and 4) acoustical methods. During the period 1960-1965 we carried out many gas efflux experiments. In these experiments the electric charge carried by a gas can be determined by measuring the change in potential of the electrically insulated container from which it escapes. A reliable upper limit on the net charge per molecule can be inferred provided that suitable precautions are observed. Many procedures, tests and calibrations intended to prevent the appearance of spurious charge or the masking of genuine charge were carried out. The result of 1356 effluxes with seven gases (H_2 , D_2 , He, N_2 , O_2 , A, SF_6) under various experimental conditions can be summarized thus: no molecule carries a charge greater in magnitude than 10^{-20} of the magnitude of the elementary charge, e.

Further interpretations arise with various assumptions. Assuming that the sum of the proton and electron charge $Q_p + Q_e = \alpha e$ and that the charge on the neutron $Q_n = \beta e$ the A and N_2 data yield $\alpha \leq (0 \pm 0.1) \times 10^{-20}$ and $\beta \leq (\pm 0.4) \times 10^{-20}$. Assuming that $Q_p + Q_e = Q_n$ (as suggested by charge conservation, the decay of the free neutron and the neutrality of (anti) neutrinos), that the charges add up in atoms or molecules composed of Z protons and electrons and N neutrons and that matter is not a mixture of constituents with opposite charge differences, the experiments with SF_6 imply $Q_p + Q_e = Q_n \leq (0 \pm 3) \times 10^{-23} e$. Finally, assuming that the charge has a velocity dependence $q = q_0(1 + kv^2/c^2)$ and that protons and electrons in argon have mean square velocities corresponding to their binding energies gives $k \leq 5 \times 10^{-20}$. In 1973 we published results of first acoustical neutrality experiment in which an oscillating electric field drives the hypothetically charged gas to produce sound. Later attempts to refine this method ran into difficulties with large second harmonic signals which put impossibly stringent requirements on linearity and waveform purity. Now, however, we feel that the inverse experiment in which an acoustic standing wave results in detectable periodic oscillations of charge density can yield limits six to eight orders of magnitude better than any previous result. The experiment is in effect a periodic version of the gas efflux method with no average transport of gas. Design studies and pilot experiments are now being carried out in order to prepare a proposal.

