

earthquake swarms is thus strong. But there is one crucial difficulty. There are a few swarms which are apparently not related to volcanism at all—the swarm which occurred in the Santa Barbara channel of California in 1968, for example. It is possible, of course, that in such regions there is magmatic activity which fails to reach the ocean floor and which thus fails to be identified as volcanism. On the other hand, there may be ways of producing stress inhomogeneities completely unrelated to volcanism or magmatic activity of any sort. At present, this matter cannot be resolved. In the meantime, Sykes makes a strong plea for on-site investigations of ridge crests soon after swarms occur to see if associated volcanism can be detected.

SPECTROSCOPY

Excited States

from our Molecular Physics Correspondent

THANKS to recent developments in lasers and pulse circuitry, the spectroscopy of transient species with lifetimes in the so-called nanosecond region (10^{-9} to 10^{-6} s) is becoming a common, if not exactly routine, possibility. A group at Cornell University (D. S. Klinger and A. C. Albrecht, *J. Chem. Phys.*, **53**, 4059; 1970) have now taken some important steps beyond the simple demonstration that such fast-decaying spectra can actually be seen by exploiting some of the unusual diagnostic techniques which have recently come into use in the more conventional time range.

Quite the most remarkable of these is the method of "photo-selection" whereby, using intense polarized sources, an oriented subset of molecules can be excited and their absorption spectra measured in the oriented condition, that is before rotational relaxation has time to be felt. This can be achieved without too much disturbance by illuminating the system in a polymer matrix and taking advantage of the high power and polarization of laser light. With sufficient intensity it is then possible to measure the direction of polarization of the emitted light in relation to the geometry of the molecule and to study the influence of chemical substituents on the dichroism as well as the wavelength pattern of the spectrum. (Although an advantage, laser techniques are not essential to photoselection; some impressive work with conventional sources has also just appeared—see, for example, T. G. Pavlopoulos, *Ber. Bunsenges. Phys. Chem.*, **74**, 989; 1970.)

In the nanosecond region none of this is easy; Klinger and Albrecht were forced to work at the very limits of time resolution, eliminating spurious fluorescence effects and concentrating on the anthracene derivatives which are well

known candidates for long lived excited states. Supplementing their recent announcement of the first ever observed singlet dichroism, in anthracene (*J. Chem. Phys.*, **50**, 4109; 1969), they have observed the change in the short-lived spectrum on methylation and have found significant new bands which show polarization in the direction of the substituent. This is adduced as evidence that the transition involves the methyl group in an essential way and must therefore imply the reorganization of σ rather than π electrons. The existence of such a low-lying σ transition would be a surprise to theoreticians, but quantum-mechanically it is not entirely out of the question. Meanwhile, the measured wavelength for transition to a second triplet state in anthracene itself gives an energy for this (4.74 eV) which agrees almost embarrassingly well with recent theoretical predictions (4.75 eV) (M. K. Orloff, *J. Chem. Phys.*, **47**, 235; 1967).

There are other surprises as byproducts

of this work. A strong isotope effect is observed on the lifetime of the excited 9-methyl anthracene, which cannot be a matter of selection rules and must point to a radiationless component in the decay mechanism. This would be worth a whole study in itself.

Clearly these results are only a beginning and will stimulate much further effort to obtain higher resolution and push measurements into the even shorter time scale where more problematic higher excited states can be expected to show up. What makes the whole field so interesting is that, by one of those powerful coincidences which mark only a few areas of research, both theoretical and experimental work seem to be straining towards similar answers with a roughly comparable degree of success. This, at least, should ensure that the study of nanosecond spectra will not fall into the dull taxonomy which tends to be associated with molecular spectroscopy on a more leisurely time scale.

Atmospheric Temperature from Scattered Laser Light

THE temperature and the ratio of aerosols in the troposphere can be measured by observing the frequency spectrum of the light scattered from a highly monochromatic laser beam. The frequency of the light undergoing Rayleigh scattering by molecules is Doppler shifted by thermal motions to produce a gaussian spectrum, the width of which depends on the temperature. Because the aerosols have much smaller random velocities, they produce a narrow spike at the peak of the molecular spectrum which can easily be identified. Winds will produce a frequency shift relative to the transmitted light and turbulence results in a broadening of the aerosol spectrum.

Fiocco and DeWolf (*J. Atmos. Sci.*, **25**, 488; 1968) were able to distinguish between aerosol and molecular scatter in a laboratory atmosphere, and now in work reported in next Monday's *Nature Physical Science*, Fiocco and his co-workers have improved the equipment and technique sufficiently to make possible its application to the troposphere. Light from an argon laser was directed upwards into the atmosphere and the backscattered light was collected by a mirror so that its spectrum could be analysed by an interferometer and photon counter. In order to study a defined height interval, the laser light was chopped to provide pulses and the receiver gated on after the appropriate time delay. The system thus operated as an optical radar. The temperature was obtained near the ground and at 4 km altitude, and the values agreed moderately well with the results of a balloon sounding some distance away. It seems that an accuracy of a few °C

is possible with Fiocco's equipment, but further studies of systematic and random errors are necessary.

The range of the apparatus could be improved by using a high power continuous laser or else a pulsed liquid or solid laser, and with some other modifications it should be possible to measure aerosol and molecular scattering to considerable heights in the atmosphere. It will be particularly valuable to obtain the aerosol/molecule scattering ratio at 30–40 km altitude, a region often used for the calibration of other optical radar experiments with the unproven assumption that the aerosol scattering is small (Kent and Wright, *J. Atmos. Terr. Phys.*, **32**, 917; 1970). Cometary and meteoric dust in the mesosphere might eventually be distinguished from molecules; this has been a matter of some controversy among the workers with optical radars who have hitherto not analysed the spectrum of their echoes. As a ground based probe for studying temperature and density in regions above the ceiling of routine balloon soundings (about 30 km), the technique might provide an economic alternative to rockets for studying stratospheric structure. This new technique for remote measurements of temperature, winds and aerosol content in the troposphere and lower stratosphere may be convenient for the research meteorologist if time and range resolution are improved. Furthermore, with such improved resolution, it may become feasible to make a direct measurement of the location and magnitude of the "clear air turbulence" which constitutes a potential hazard to high flying aircraft.