

igneous rocks. The abundance of oxygen-18 seems to decrease with increasing depth, as shown by the sequence: gneissic granite, 0.0; lavas, -1; Greenland basalt, -4.5. The tektites, which are supposed to be of meteoric origin, have varying isotopic composition, all, however, falling into the range of the terrestrial abundances.

One of the most important applications of the accurate oxygen isotope ratio determinations in silicate rocks would be the possibility of distinguishing between real igneous rocks and meta-sedimentary rocks.

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<sup>1</sup> Dole, M., *J. Amer. Chem. Soc.*, **58**, 693 (1936); *ibid.*, **62**, 471 (1940); *Science*, **109**, 77 (1949).

<sup>2</sup> Urey, H. C., *J. Amer. Chem. Soc.*, **56**, 2601 (1934); *Science*, **108**, 489 (1948).

<sup>3</sup> Reviewed by M. D. Kamen, *Bull. Amer. Mus. Nat. Hist.*, **87**, 103 (1946).

<sup>4</sup> Pettijohn, F. J., "Sedimentary Rocks" (Harper and Bros., 1949).

### Applications of Polarimetry to Infra-Red and Micro-Wave Spectroscopy

G. HERZBERG and other investigators<sup>1</sup> have recently shown that vibrational motions of homopolar molecules which should not appear in infra-red absorption give rise to absorption lines when the substance is in a condensed state (compressed gas or liquid) and when the absorption path is long enough. As the selection rules are the same as for Raman spectra, and as this absorption seems to be dependent on intermolecular forces, it seems natural to attribute it to electric moments induced in the molecules by intermolecular electric fields. The theory of electric moments induced in molecules by a macroscopic electric field can easily be derived from the classical theory of the Raman effect by substituting a constant field vector  $\mathbf{E}$  for the vibrational field  $\mathbf{E} = E_0 \sin 2\pi\nu t$  of the incident light wave, and this shows immediately that the induced absorption is governed by the same polarizability-tensor as the Raman effect. While I was developing this theory in a recent note<sup>2</sup>, my attention was directed to two papers dealing with the same subject: already in 1932 E. U. Condon<sup>3</sup> had developed the theory of this induced absorption by electric fields on a quantum-mechanical basis, and in a recent letter in *Nature*, L. A. Woodward<sup>4</sup> has pointed out that the powerful and precise methods of micro-wave spectroscopy could be extended to the study of pure rotational absorption of non-polar molecules.

I would like to emphasize that, as opposed to the absorption caused by molecular fields of random orientation, the absorption induced by macroscopic fields of fixed direction will be anisotropic, the vibration parallel to the field being always more

strongly absorbed than the vibration perpendicular to it. The ratio of the absorption coefficients perpendicular and parallel to the electric field, which we may call the 'dichroism' factor  $f$ , is given by the same expression as the 'depolarization factor'  $\rho$  of the corresponding Raman lines excited by polarized light. As the numerical value of  $\rho$  may depend on the frequency of the incident light,  $f$  represents the limiting value of  $\rho$  for zero frequency, and so its value will give information on the dispersion of  $\rho$ . For totally symmetric vibrations such as the 991  $\text{cm}^{-1}$  frequency of the benzene molecule, the anisotropy of absorption will be very marked, and for the totally symmetric vibrations of spherically symmetrical molecules ( $\text{CH}_4$ ,  $\text{CCl}_4$ ) only the vibration parallel to the field will be absorbed. For non-totally symmetric vibrations, vibration-rotation and pure rotation lines the dichroism factor will have the constant maximum value 0.75, so that the anisotropy of absorption will still be appreciable. Now it is a well-known fact, illustrated by crystal optics, that dichroism is connected with double refraction. So the induced absorption lines will give rise to a Kerr effect which will show resonance (enhancement and anomalous dispersion) in the neighbourhood of the critical frequencies. An incident wave polarized at  $45^\circ$  to the direction of the constant field will emerge as elliptically polarized, and as this is an interference effect, I believe that the use of a polarimetric device adapted to the infra-red and microwave region will be a very sensitive method for detecting resonance frequencies of molecules. In the neighbourhood of a critical frequency, the birefringence (difference of refractive index parallel and perpendicular to the field) will be of the order of

$$\Delta n \sim 2\pi N^2 \cdot \frac{g'}{g''} \frac{\mu_{\parallel}^2 - \mu_{\perp}^2}{h\Delta\nu},$$

where  $\mu_{\parallel}$  and  $\mu_{\perp}$  are the induced moments attached to the quantum transitions and  $\Delta\nu$  the distance of the frequency under investigation from the resonance frequency; the maximum desirable effect will be obtained when  $\Delta\nu$  is of the order of the line breadth. This gives for pure rotational transitions very small angles of ellipticity (of the order of  $10^{-6}$  radian for fields of 30,000 volts/cm. and for 1 metre path in gases at atmospheric pressure, if  $\Delta\nu \sim 0.01 \text{ cm}^{-1}$ ). But in a resonant cavity when the wave is going many times to and fro, the effects will add up and marked depolarization of the wave near the resonance frequency will occur and might be detected.

Another phenomenon, paramagnetic resonance, is connected with the Faraday effect near the resonance frequencies<sup>5</sup> and could also be studied by polarimetric methods in the radio-frequency range.

Polarimetric measurements can be easily adapted to radio-frequency techniques in cylindrical wave guides or resonant cavities, and have already been so applied<sup>6</sup>. They will open up new fields of research in atomic and molecular spectroscopy.

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<sup>2</sup> Kastler, A., *C.R. Acad. Sci., Paris*, **230**, 1596 (1950).

<sup>3</sup> Condon, E. U., *Phys. Rev.*, **41**, 759 (1932).

<sup>4</sup> Woodward, L. A., *Nature*, **165**, 198 (1950).

<sup>5</sup> Kastler, A., *C.R. Acad. Sci., Paris*, **228**, 1640 (1949).

<sup>6</sup> Wilson and Hull, *Phys. Rev.*, **74**, 711 (1948).