Our experiments indicate, then, no basis for concluding that free electrons are produced when tungstates are excited by ultraviolet light. The 3650A-excited luminescence and the photo-conductivity of $CaWO_4$ observed by Randall and Wilkins may have been due to impurities. Also, photo-emission for the electrodes may have played a part in their photo-conductivity measurements.

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Infra-Red Absorption of Oxygen and Nitrogen Induced by Intermolecular Forces

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AN unperturbed homonuclear diatomic molecule can exhibit no rotation-vibrational absorption due to dipole transitions. However, in an attempt to detect $(O_2)_2$ complexes by infra-red absorption, we have found in liquid and compressed gaseous oxygen a marked absorption with a maximum at the vibrational frequency of the O_2 molecule, 1556 cm^{-1}. An investigation of compressed gaseous nitrogen showed a similar absorption at the N_2 vibrational frequency, 2331 cm^{-1}. The intensity-pressure relationships for both gases and for mixtures of the two gases prove conclusively that the absorption cannot be due to stable complexes or to quadrupole transitions. The effect must have its origin in dipole transitions induced by intermolecular forces during collisions.

The absorptions of the gases at pressures up to sixty atmospheres in a path length of 85 cm were measured with a Perkin-Elmer spectrometer. For pure oxygen at constant temperature, the absorption coefficient at all frequencies in the band was found to vary as the square of the pressure, as shown for two frequencies in Fig. 1. The shape of the absorption band, absorption coefficient *vs.* cm^{-1} (Fig. 2), is therefore independent of pressure. When nitrogen is added to the absorption cell and the partial pressure of oxygen is held constant, the oxygen absorption increases linearly with the partial pressure of nitrogen. The absorption observed in pure nitrogen has approximately the same intensity and shape as the oxygen band. In this case also, the absorption coefficient increases as the square of the pressure.

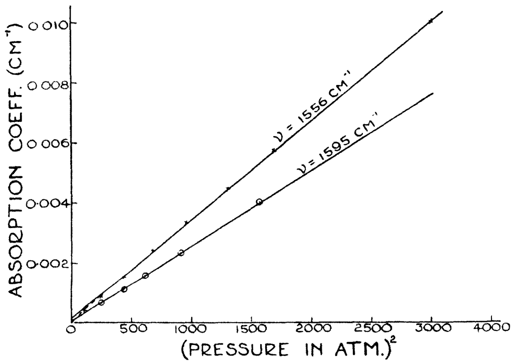

FIG. 1. Variation of the absorption coefficient with pressure at two points in the oxygen band.

These results are immediately explained on the assumption that the molecule absorbs during a collision with either a like molecule or a foreign gas molecule. The perturbation of the molecule by the strong intermolecular forces effective during the collision must produce a finite transition probability. Condon[1] has shown that the dipole induced in a molecule by a static electric field should give rise to transitions obeying the Raman rather than the infra-red selection rules. The polarization of the molecule by a colliding molecule will undoubtedly produce the same effect. Thus, the intensity distribution for the induced absorption in oxygen should be given by the Raman selection rules for rotation, $\Delta J = 0, \pm 2$. This is compared with the experimental curve in Fig. 2. The envelope of the theoretical *O*- and *S*-branches matches well the intensity contour in the wings of the band. The integrated intensity of the *O*- and *S*-branches is found to be 0.7 of the total intensity of the band. This is very close to 0.75, the value of the theoretical ratio for the anisotropic part of the Raman scattering for a diatomic molecule. There seems, therefore, to be very little intensity in the *Q*-branch corresponding to isotropic Raman scattering. The intensity contour observed for liquid oxygen is consistent with that observed for the gas when the change in the Boltzmann factor with temperature is taken into consideration.

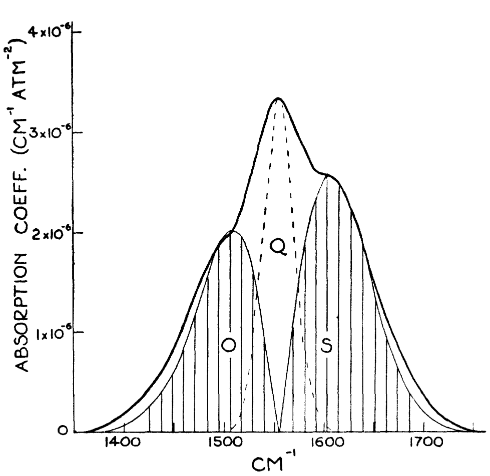

FIG. 2. The induced rotation-vibrational absorption of gaseous oxygen. The heavy curve is the experimental contour; the light curve is the theoretical envelope of the *O*- and the *S*-branch. The residual, *Q*-branch, intensity is shown as a broken line.

Discrete rotational lines were not observed. This is not unexpected, since the collisions postulated for the origin of the band should broaden the lines considerably. It is significant that the perturbation is sufficient to alter the transition probabilities but has negligible effect on the vibrational frequency.

The induced absorption established here should be a characteristic property of all molecules but is, of course, most readily detected for vibrations which are not otherwise infra-red active. It is probable that the infra-red absorption in hydrogen reported by Herzberg,[2] and attributed by him to quadrupole transitions, is due in part at least to induced transitions. The quadrupole intensity would introduce a linear term in the variation of the absorption coefficient with pressure. There seems to be an indication of this quadrupole term in oxygen at low pressures (Fig. 1).

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