taken to be unchanged. The atmosphere is approximately a 79% N_2 and 21% O_2 mixture over the altitudes of appreciable O_4 absorption. Carrying out the same calculations as mentioned above, with the same distribution of oxygen but with this O_4 dissociation constant appropriate to air, one finds that radiation in the vicinity of 2100A will be reduced to roughly 10^{-5} of its original value. At a height of 4 km the intensity proves to be a few percent of the original, this being mentioned here because experiment has shown that no detectable radiation of these wavelengths occurs even at this height.[3] Qualitatively these calculations do not, of course, depend upon the interpretation of this absorption as being due to the molecule O_4, it being sufficient that there is this density-dependent absorption in oxygen, that is, this absorption which does not follow Beer's Law. The above is not intended to imply that O_4 is the only absorbing substance, but simply that its absorption cannot be entirely neglected. Ozone and the molecule O_2 undoubtedly also absorb weakly in this region.

At the same time this absorption accounts, at least in part, for the ozone in the lower atmosphere recently measured by Götz and Ladenburg.[4] For the absorption of this radiation leads to photochemical ozone formation as also has been shown by Warburg.[5] This ozone formation from O_4 occurs chiefly in the troposphere, because the greater part of the absorption lies in these relatively low altitudes. This ozone is in a singular position photochemically, being protected from radiation most active in its decomposition by the ozone formed at higher altitudes from O_2. In view of the observation that no detectable radiation in the region 2200–2000A reaches even a height of 4 km, the photochemical formation of this ozone of O_4 origin apparently occurs for the most part at moderate heights. No inconsistency enters here with the observations on the ozone content of the atmosphere close to the earth, however, since the troposphere is a stirred atmosphere, convection distributing the ozone more or less uniformly throughout it. The formation of ozone from O_4 depends evidently upon atmospheric density, not merely upon the total oxygen in the path, and hence will be related to latitude and weather conditions. The above considerations are obviously related to the general problem of atmospheric ozone, especially to its distribution, though further work is required to determine the quantitative importance of these relations.

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[3] Lambert, Déjardin and Chalonge, Compt. Rend. **177,** 757 (1923).

[4] Götz and Ladenburg, Die Naturwissenschaften **19,** 373 (1931); see also Fabry and Buisson, Comp. Rend. **192,** 457 (1931).

[5] Warburg, Berl. Ber. p. 746; 1911, p. 216; 1912, p. 872; 1914; Z. Elektrochem. **26,** 54 (1920); **27,** 133 (1921).

The Raman Spectra of Two Liquid Phases of Nitrobenzene

M. Wolfke and J. Mazur have found an irregularity in the heating curve[1] and also abrupt temperature variation of the dielectric constant and density[2,3] of mononitrobenzene, at a temperature of 9.5°C, i.e., slightly above the freezing point. Their results seem to imply a definite intra-molecular energy change in the liquid state at 9.5°, and, therefore, presumably the Raman spectrum should be modified at that transition temperature. An attempt was made to find such a modification, but exposures taken above and below 9.5° failed to show any evidence of one.

[1] M. Wolfke and J. Mazur, Nature **127,** 741 (1931).

[2] J. Mazur, Nature **126,** 993 (1930).

[3] J. Mazur, Nature **127,** 893 (1931).

Three types of modification of the Raman spectrum were looked for: (1) shift of one or more of the lines, (2) intensity changes, (3) disappearance of one or more of the lines in one or the other phase.

Shifts of the order of 0.2A could have been observed in the region of the Raman lines but no shift of any line was found.

At the lower temperatures, a marked increase in the intensity of all the lines in the blue end of the spectrum was observed but, by several other experiments, this was found to be due to a large but continuous change in the absorption coefficient of nitrobenzene with temperature.

Exposures up to one and a half hours were taken at 6.0°C and room temperature but

these plates show no line appearing at one temperature and not at the other. No longer comparison exposures were made since a fourteen hour exposure at room temperature brought out only one line that the one and one half hour exposure did not show.

Our plates show a number of lines which Kohlrausch does not report[4] for nitrobenzene, but, pending further study, we cannot say whether these lines belong to nitrobenzene, nitrothiophene (which may have been present at least as a trace), or some other impurity. These unidentified lines occur at wave-number separations approximately equal to: 675, 1025, 1080, 1175, 1385, 1415, 1755, 1805, 2450, 2690, and 2830 cm^{-1}.

The sample used was C. P. mono-nitrobenzene which had been washed first with dilute Na_2CO_3 and then many times with distilled water, dried a week or more over $CaCl_2$, and triply distilled under about 1 mm of Hg pressure. The original sample had shown the presence of a trace of nitrothiophene and it may be that the distillation did not completely remove this impurity.

The spectra were taken with a Hilger constant deviation spectrograph with dispersion of about 20A/mm at 4358A. The General Electric Company Raman Outfit was used for irradiating the sample, with a 220 volt hot cathode mercury arc along one focus of the elliptical reflector and the sample tube along the other focus. Highly distilled nitrobenzene has still a slight yellow color and absorbs strongly the exciting radiation we used (4358A). Therefore the sample tube was made conical, and of such a taper as to just fill the spectrograph aperture. This arrangement greatly increased the intensity of the Raman spectrum. A glass walled cooling system was placed in contact with the whole length of the sample tube. In a final 18 hour exposure at room temperature, the cooling system contained distilled water with enough potassium chromate to absorb completely the 3650, 4046 and 4078 lines. The sample itself aided in this complete absorption. All of the lines on the final plate must have been excited by the 4358 line and its two companions or have been anti-Stokes lines due to 4916 line or those of longer wave-lengths. Computations, however, proved that none of the lines was an anti-Stokes term.

Eastman 40 and Ilford Golden Iso Zenith (H and D 700 and 1400) plates were tried but the Eastman 40 plates were selected because much less trouble was had from fogging during development with this type. The slightest fog covered up many weak lines.

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[4] K. W. F. Kohlrausch, Der Smekal-Raman Effect. Julius Springer, Berlin, 1931.

A New Band System of Barium Hydride in the Infrared

With the aid of the new Eastman Infrared Sensitive plates the writer has discovered an intense band system of BaH in the infrared with principal heads at about 9020A and 10,000A, degraded to the red. The experimental conditions were identical with those used by Fredrickson and Watson[1] in photographing the $^2\Pi \rightarrow {}^2\Sigma$ BaH bands in the visible red region. The bands in the infrared are also $^2\Pi \rightarrow {}^2\Sigma$, the two systems having a common final $^2\Sigma$ state, but with considerably different spin multiplet spacing in the $^2\Pi$ states. For the spacing between the two groups of branches in the infrared band is about 1000 cm^{-1}, whereas $A = 462$ for the red system previously investigated.

The shorter wave-length group of branches from 8920A to about 9250A has been photographed at high dispersion with good intensity using the Infrared Sensitive plates A, but with the new Eastman Infrared Sensitive plates B only the strongest lines of the branches beyond 10,000A have been registered even with long exposure.

This is the first instance among the diatomic hydride molecules for the alkaline earths of a second $^2\Pi$ state, and the nearness of these two $^2\Pi$ levels in BaH is undoubtedly to be correlated with the fact that only for Ba is the ^3D level found below ^3P. But $A = 832$ for the lowest ^3P levels of the Ba atom, and so no definite assignment of either of the observed $^2\Pi$ levels of BaH to the ^3P level of Ba seems possible. Rather, as now seems even more evident,[1] these molecular levels must come from a forcing together of the ^3P and ^3D levels of the Ba atom. This point will be discussed and the data on this infrared BaH system presented in a later communication.

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[1] W. R. Fredrickson and W. W. Watson, Phys. Rev. **39**, 753 (1932).