of the Stokes lines in the scattering spectrum will be determined by an analogous factor $\exp(-\hbar\omega_i/kT)$, which usually characterizes the temperature-dependence of the anti-Stokes lines only. Consequently, the intensity of the Stokes difference lines rises very sharply with the temperature.

The dependence on the temperature of the intensity of the anti-Stokes difference frequencies of the Raman spectrum of the second order will be somewhat stronger than that of the lines of the same frequency in the Raman spectrum of the first order.

These simple descriptive considerations are in good agreement in general with the results of theoretical calculations of the temperature-dependence of the frequencies of the second-order scattering spectra carried out for the first time by P. P. Pavinsky[1].

Thus our investigations of the scattering spectra of heated rock-salt are in good agreement with the considerations we have discussed above.

In the spectrum of scattering of heated rock-salt the strong continuous background is clearly seen, especially in the region of small frequencies (from the Rayleigh line up to 200 cm.$^{-1}$). This affords further experimental confirmation of the correctness of the fundamental concepts of the Born theory of the crystal lattice.

E. Gross
A. Stehanov

Physical Technical Institute,
Academy of Science of the U.S.S.R.,
Leningrad.
May 15.

Pavinsky, P. P., unpublished paper (1945).

Crystal Structures of para-Dinitrobenzene and para-Nitraniline

In view of the rather surprising distortions reported in the dimensions of the para-dinitrobenzene molecule[1], a redetermination of this structure was recently attempted in this laboratory. The results of our preliminary two-dimensional survey did not point to a completely symmetrical molecule, but indicated that either (a) the planes of the nitro-groups may be slightly inclined (about 5°) to the plane of the benzene ring, or (b) the nitrogen − oxygen distances within the nitro-groups may not be equal, but differ by about 0·05 A. We were unable to distinguish between these alternatives by two-dimensional X-ray methods. In the meantime, we have learned that a full three-dimensional analysis of this structure has been undertaken elsewhere, so we have not pursued the matter further. The final results will be awaited with interest.

In the course of this work a certain resemblance was noted between the crystal structures of para-dinitrobenzene and para-nitraniline. For the former structure the space-group is $P2_1/n$, with two molecules in a unit cell of dimensions

$$a = 11\cdot05 \text{ A.}, \quad b = 5\cdot47 \text{ A.}, \quad c = 5\cdot67 \text{ A.}, \quad \beta = 92° 18'.$$

The unit cell and space-group of para-nitraniline have already been determined by Prasad and Merchant[2], but if the space-group description is changed to $P2_1/n$, we obtain four molecules in a cell of dimensions

$$a = 12\cdot34 \text{ A.}, \quad b = 6\cdot02 \text{ A.}, \quad c = 8\cdot63 \text{ A.}, \quad \beta = 91° 40'.$$

The principal change is in the length of the c-axis, where the increase helps to accommodate the extra molecules. More detailed examination, however,

shows that this apparent resemblance is somewhat misleading. In the para-dinitrobenzene structure there is a considerable concentration of atoms lying close to the $(10\bar{1})$ plane, whereas in para-nitraniline the greatest concentration is in the (101) plane. The actual inclination of the molecular plane to the (010) plane increases from 48° in para-dinitrobenzene to about 64° in para-nitraniline, although there is only a small increase in the length of the b axis.

The detailed structure of para-nitraniline has been elucidated by the method of trial and error, strong reflexions from the (800), $(50\bar{7})$ and $(70\bar{5})$ planes helping to define the molecular orientation. A refinement of the structure has been made by the double Fourier series method, and the electron density map for one molecule projected on the (010) plane is shown in the accompanying figure.

SCALE
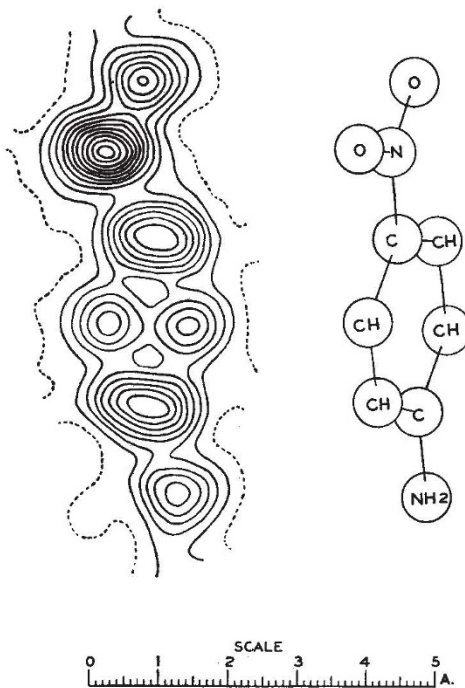
ELECTRON DENSITY MAP FOR para-NITRANILINE. CONTOURS AT UNIT ELECTRON DENSITY INTERVALS, THE ONE ELECTRON LINE BEING DOTTED

For this projection 110 terms in the $(h0l)$ series were employed, and it gives good resolution for some of the atoms. The remaining co-ordinates may be determined from other similar projections; but further refinement is necessary before discussing the molecular dimensions in detail.

The preliminary parameters show that the distance between the amino-nitrogen atom and the oxygen atoms of the nitro-group of the molecule reproduced by the diagonal glide plane is $2\cdot65 \pm 0\cdot05$ A. This close approach shows that hydrogen bonding between the reactive groups of adjacent molecules is the main factor in stabilizing the structure.

S. C. Abrahams
J. Monteath Robertson

Chemistry Department,
University of Glasgow.
July 12.

[1] James, King and Horrocks, Proc. Roy. Soc., A, 153, 225 (1935).
[2] Prasad and Merchant, J. Ind. Chem. Soc., 15, 47 (1938).