

nesium nitrates (1071, 1070, and 1060 wave numbers respectively). The values obtained with calcium, barium, and lead nitrates were not much different from the value for nitric acid (1045), while mercuric and bismuth nitrates showed smaller frequency shifts (1037 and 1040 wave numbers respectively). In some cases, for example, lithium, aluminium, and mercuric nitrates, the line was accompanied by a fainter component.

It is interesting to note that in nitrate crystals belonging to the cubic system the frequency shift is almost the same as for nitric acid in spite of the varying size of the metal atom (for example, calcium, barium, and lead nitrates). Of the other two frequencies, the  $7\mu$  line appeared only in the case of lithium and sodium nitrates. The  $13\mu$  line, however, was more persistent and appeared in the case of lithium, sodium, ammonium, potassium, barium, and lead nitrates. The Raman line corresponding to a remote infra-red frequency appeared prominently in lithium and mercurous nitrates ( $42.9\mu$  and  $57.2\mu$  respectively), and was also noticeable with sodium, calcium, barium, zinc, silver, and mercuric nitrates.

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#### Raman Effect in Liquefied Gases.

IN a recent investigation by Daure (*Trans. Faraday Soc.*, **25**, 825; 1929) on the Raman effect in liquefied gases, it was found that the spectrum of liquid ammonia includes three strong lines the displacements of which are 321, 330, and  $338\text{ mm.}^{-1}$ . Two of these lines ( $321$  and  $330\text{ mm.}^{-1}$ ) have already been observed by Dickinson, Dillon, and Rasetti (*Phys. Rev.*, **34**, 582; 1929), who found the line  $330$  to be very strong and the other slightly weaker. Now the Raman spectrum of ammonia vapour as reported by Wood (*Phil. Mag.*, **7**, 744; 1929) shows only the line  $330\text{ mm.}^{-1}$ , hence Daure ascribes the two new lines to some complex such as  $\text{H}_3\text{N}=\text{NH}_3$ . It seems to me that this observation is significant and worthy of more consideration.

To begin with, it will be noted that the two new lines may be accounted for, within the limit of accuracy of Daure's measurements, by the expression  $330 \pm 8\text{ mm.}^{-1}$ . This is precisely the sort of expression which gives the displacements of the Raman effect in general, and it suggests that the outer lines represent a scattering of the light which gives the central line by complex or associated molecules. In other words, these lines may arise from a secondary Raman effect in the liquid. Unfortunately, Daure reports only the 'negative' lines (displaced towards the red), so that no check can be made on the structure of these lines on the 'positive' side.

The chance that this relation is mere coincidence is reduced by the data of Daure for liquid ethane, which exhibits in this region a similar triplet structure which may be represented by the expression  $291 \pm 4\text{ mm.}^{-1}$ . So far as I am aware, the Raman effect in ethane vapour has not been reported, but if the viewpoint outlined above is correct, it should contain only the line displaced  $291\text{ mm.}^{-1}$ .

One experiment which suggests itself as a confirmation of this interpretation is a determination of the polarisation of these lines. If the two liquid lines have the same polarisation, it would be strong evidence that they are related in the manner suggested.

If such an effect could be established, it would provide a valuable tool for investigating molecular complexes and associated liquids. A few inferences on this basis will serve to indicate its power. The frequency displacements of the liquid lines,  $\pm 8\text{ mm.}^{-1}$  and  $\pm 4\text{ mm.}^{-1}$  would indicate that the vibrations of the components of the complex are much smaller than

those of the atoms in the molecules, which is to be expected. Moreover, the fact that both positive and negative lines are quite intense would point to the existence of a considerable portion of the complexes in an excited state, probably closely akin to Henri's conception of 'predissociation'. It is hoped that more data will shortly be available so that some of these questions may be settled. J. B. AUSTIN.

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#### Raman Lines of Mercury in Arc improbable.

A COMMUNICATION by Venkatesachar and Sibaiya appeared in NATURE for Nov. 30, 1929, in which the opinion was expressed that some of the faint nebulous lines of the mercury arc were in reality Raman lines of mercury excited by the more powerful radiations.

This did not seem to me very probable, and I have investigated the matter with a new 220-volt quartz arc provided with a window of polished optical quartz which permits end-on observation of the long narrow cylinder to which the discharge contracts when the arc operates on full load. The region surrounding this highly luminous cylinder is comparatively dark, and would seem to be the most promising field in which to search for Raman lines.

An end-on image of the discharge was focused on the slit of a large quartz spectrograph by means of a quartz fluorite objective. The image, a small circular disc of intense brilliancy, was blocked off with a strip of black paper, which was removed for half a second, at the end of the exposure. The spectrum of the irradiated vapour above and below that of the disc was comparable in density with that of the discharge. There was no relative enhancement of the lines indicated by Venkatesachar; if anything, they were a little stronger in the spectrum of the discharge than in the spectrum of the irradiated vapour.

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#### Raman Effect for Solutions of Sulphur Dioxide.

STUDIES of the Raman effect for hydrogen chloride and for ammonia as gases, as liquids, and in aqueous solution have been made by various investigators. With ammonia, the same modified line appears in all three cases. Hydrogen chloride reveals the same scattered line in the liquid and gaseous states, but, as is to be expected, not in aqueous solution.

We have investigated the scattering of sulphur dioxide in various solvents, such as water, benzene, and carbon tetrachloride, and intend to work with the pure liquid and the gas. In addition to the modified lines arising from the solvent, there occur, in each instance, lines characteristic of the sulphur dioxide molecule. The most prominent of these lines appear in all of the solvents at  $\lambda 4588$  and  $\lambda 4238$ , excited, respectively, by  $\lambda 4358$  and  $\lambda 4047$  of the mercury arc. The shift indicates an infra-red wave-length of  $8.8\mu$ . This is very close to the mean value of about  $8.7\mu$  for the band from  $8.4\mu$  to  $9.0\mu$ , which is one of the most intense two of the six infra-red absorption bands found by Coblenz for this gas.

The replacement of the broad infra-red band by a Raman line may be due to the faintness of the *P* and *R* branches in the spectrum adjacent to this line, and the appearance of a *Q* branch in the Raman spectrum, as was found by Wood for hydrogen chloride.

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