JoshiEffect

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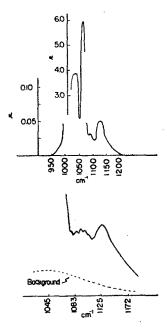**Articles you may be interested in**

FIG. 1. Ozone bands near 1100 cm⁻¹.

relative intensities of the bands. In previous estimations of relative intensity the observations of Hettner, Pohlmann and Schumacher[2] appear to have been misinterpreted. It is now evident that in this earlier investigation about 5 percent of stray light was present at 10μ and that the 1043 cm⁻¹ band is much more intense than was supposed.

The particularly new observation made in the course of this work was the discovery of a new fundamental band with center at about 1110 cm⁻¹, shown in Fig. 1. This band has nearly as great intensity as the fundamental at 705 cm⁻¹. It is suggested in several previously published tracings of the ozone spectrum but has apparently escaped special notice because of its proximity to the extremely intense band at 1043 cm⁻¹. Under conditions suitable for study of the latter band the former may easily escape detection. As shown in the lower tracing the new band shows no suggestion of a Q branch, but four lines with an average spacing of about 5 cm⁻¹ have been resolved on the long wave-length side of the minimum. Evidently the new band is similar in structure to the fundamental at 705 cm⁻¹, recently investigated by Adel and Dennison, and these two bands are to be described as ν_1, and ν_2, respectively. The extremely intense band at 1043 cm⁻¹ is then evidently the fundamental ν_3. There has been some question as to the structure of this band, and it has been suggested that the observed fine structure is due in part to CO_2 contamination. This may be possible in observations of atmospheric absorption, but our observations indicate that this is most unlikely under the laboratory conditions employed by Gerhardt.[1] The Q branch of this band is certainly not prominent, but the tracings of Gerhardt strongly suggest its presence, though somewhat displaced and "washed out" by convergence.

The new observations make possible the revised vibrational analysis presented in the table, which is in agreement with all observations on the band structures, and supports the approximate analysis of fine structure made by Miss Simpson on the basis of the obtuse angled model.[7] Some previous difficulties in the apparent divergence in band progressions and combination bands are now resolved, and the observed relative intensities of the bands support the proposed analysis.

The more accurate determination of the apex angle and internuclear distances of the ozone molecule must await better resolution of the fine structure of one or more of the B type bands which we propose to attempt in the near future.

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Joshi-Effect

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IN recent years a large number of papers have been published on the Joshi-effect.[1] The effect may be described as follows: An alternating field is applied to gases at low pressures and the gaseous current is measured. It is observed that the gaseous current diminishes when the discharge tube is exposed to light. The diminution in the gaseous current, which is an ionic current, is observed in a number of gases, and with light of different wavelengths. As the frequency of the incident light is generally not sufficient to produce photoelectrons in the gas, we shall be justified in excluding the photoelectric effect from the plausible agents which could reduce the ionic current. In addition "photo-ionization" or "resonance excitation[2] leading to ionization" may occur. Both these effects will lead to an increase in the gaseous current. Their mechanisms are well known and hence they are not considered here. But it is necessary to remember that unless the experimental conditions are isolated, both these effects are likely to occur along with the Joshi-effect and this may lead to an increase in the current occasionally observed.[3]

It is a well-known fact that the gaseous ionic current can be written as

$$Q = \Sigma nev,$$

where n is the number of charged particles carrying a charge e and moving with a velocity v. Or it can be written as

$$Q = \Sigma nekX,$$

where k is the ionic mobility and X the field strength. Joshi and others observe a diminution in Q. From the above equation it can be seen that Q can be reduced by changing n or e or k. That is, a change in the discharge current is

produced either by changing the number of charged particles or their average charge or their mobility. In the low pressure discharge as observed by Joshi and others, a large number of metastable ions will be formed.[4] It has been pointed out by the author in that paper that "the chemical effects can be produced more conveniently by means of a high frequency discharge in a gas enclosed in a chamber." This is the type of discharge used in the study of the Joshi-effect and chemical effects are very easily produced in such a discharge. As pointed out above, the frequency of the light used is inadequate to produce photoelectrons in the gas used in the discharge tube. Under the circumstances it is but natural to assume that the role of light is to modify the chemical action which takes place in such a discharge tube.

We are therefore led to believe that the Joshi-effect is probably due to the change in the number of particles as a result of complex molecular formation or change in the ionic mobility or both. If this assumption is correct, a systematic study of the Joshi-effect may enable us to understand the mechanism of low pressure discharge. All experimental papers about the Joshi-effect published so far refer to number of gases studied at different pressures and exposed to light of different frequencies. In all these experiments the change in gaseous current is measured. But it will be clear from the above hypothesis that, to understand clearly the mechanism of the Joshi-effect, experimental data are required about the following points and workers in this branch would do well to study these points first.

1. Accurate determination, to the order of at least a microsecond, of the time lag between the switching on or off of the radiation and the reduction or restoration of the ionic current.

2. Accurate measurement in the change of the number of particles after exposure to light. (The change may be measured by a relative change of pressure by a method like that of Hutchinson and Hinshelwood;[5] or it may be determined spectroscopically by the study of the formation of quasi-molecules.)

3. Determination of the changes in the values of e/m and the ionic mobility under the conditions of the experiment. (These quantities should be measured before and after exposing the discharge tube to light. The determination could be made if necessary, by taking a portion of the gas in another discharge tube. This method of isolating a beam is commonly used in all molecular ray work.)

In the end it may be pointed out that unless these experiments are performed, it will not be possible to understand the mechanism of the Joshi-effect. All experiments other than the crucial experiments given above and all experiments in which conditions are not isolated will only add to the available experimental data and in no way clarify the obscure problem of the chemical effects of electrical discharge.

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Resistivity in the Systems Sodium-Ammonia and Lithium-Ammonia

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IN a recent paper, Birch and MacDonald[1] report measurements of the resistance of solutions of sodium in ammonia frozen in a short glass tube either by slow or by rapid cooling. These resistance measurements, as well as time-temperature curves on the slowly frozen system, confirm the solidification point near −110°C discovered by Ruff and Zedner.[2] To explain the low resistances, down to the order of one-tenth ohm, found in the range from −110 to −185°C, Birch and MacDonald assume (p. 795) "the persistence of a liquid phase due to supercooling of the eutectic" of sodium metal and ammonia.

The existence of a supercooled phase in contact with one solid component (ammonia) over a range of 70°C appears highly improbable. A more natural explanation of the observed phenomena can be based on the assumption that the solidification point of the concentrated solution is due to the formation of a solid sodium-ammonia compound, containing about 1 mole Na to 5 mole NH_3, a possibility already considered by Ruff and Zedner.[2] This compound may not have a simple stoichiometric composition. The very low and reproducible resistivity of the frozen concentrated solutions and the slight positive temperature coefficient of this resistivity then appears as a property of the solid compound; the fairly low resistance observed in quick-frozen solutions of about one mole Na in 50 moles NH_3 is due to a continuous network of the solid compound in solid ammonia; and the gradual increase of resistance of such systems kept below the solidification point is caused by recrystallization of this network tending to make it discontinuous.

The existence of a solid compound of sodium and ammonia here proposed provides an analogy to the case of lithium whose saturated solution in ammonia was found[3] to have a sharp and reversible melting point at −181°C, with a small but definite heat of fusion. The solid formed was proved not to be a eutectic of lithium and ammonia but a true compound. Among the points of evidence were the persistence of the characteristic bronze color and the extraordinarily low resistivity of $15 \cdot 10^{-6}$ ohms·cm, which is one-fourth of the resistivity of the saturated liquid phase. The equivalent conductivity per atom of Li in the solid compound was shown to be about the same as in compact lithium metal at the same temperature. Such a relationship would be impossible in an eutectic of lithium metal and solid ammonia.

X-ray diffraction studies would furnish the conclusive proof of the existence of a sodium-ammonia compound and would illuminate its structure.

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[3] Hans Jaffe, Zeits. f. Physik 93, 741 (1935).