from metallic vapours in the arc or spark, illuminated by their own monochromatic radiations of very short wave-length. The conclusion was that such lines have not been observed in the spectra of the alkaline earths. An extension of this line of investigation, using very long exposures, is much to be desired.

In the spectra obtained by Raman and Krishnan with water and methyl alcohol, the modified radiation consists of broad bands. Such is not the case with benzene, toluene, pentane, and ethyl ether. It may be that the breadth of the band in the case of methyl alcohol and water is due to some specific property of the OH group, but I believe it more probable that the breadth is due to the associated character of these two liquids. It is natural to expect that the vibration frequencies of molecules would be altered by association.

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The Nierenstein Reaction.

IN their test experiment with benzoyl chloride, Bradley and Robinson (*Jour. Chem. Soc.*, p. 1316; 1928) have modified the original method described by Clibbens and Nierenstein (*Jour. Chem. Soc.*, **107**, 1491; 1915) as follows :

(1) They added the benzoyl chloride to the diazomethane instead of using the reverse procedure prescribed by us.

(2) They carried out the reaction at a temperature "maintained at $-5°$ to $0°$," whereas this is not stated by us, since we work at laboratory temperature.

(3) They attempted the separation of the ω-chloroacetophenone with light petroleum, and not by means of vacuum distillation as stated by us.

The effect of (1) was emphasised in my previous letter (NATURE, June 16, p. 940), and furthermore, by reversing their method of mixing the reactants, Bradley and Robinson (NATURE, July 28, p. 130) are now able to record a yield of 9 per cent of ω-chloroacetophenone instead of a trace, detectable "by the powerful lachrymatory properties and characteristic odour of the compound." This yield is still much lower than that recorded by Clibbens and Nierenstein, and since this can be attributed only to difference in technique, points (2) and (3) have been investigated by me, in collaboration with Dr. T. Malkin, with the result that it is found :

(a) That by working at a low temperature very little ω-chloroacetophenone is produced.

(b) That by fractional crystallisation from light petroleum, which is a most unsatisfactory procedure, the yield is reduced to 50 per cent of pure ω-chloroacetophenone.

In view of these results I briefly repeat the general technique of the reaction :—Diazomethane prepared in form of a gas according to Staudinger, or in ethereal solution according to Pechmann, is slowly passed or distilled into an ethereal solution of the acyl chloride at room temperature ; for example, in the experiment under discussion, diazomethane from 17 c.c. nitrosomethylurethane is distilled with ether over a period of 1 hour into a solution of 10 gm. benzoyl chloride, dissolved in 75 c.c. dry ether (Grignard), the temperature being 19°. To the ethereal solution (350 c.c. in the case of the experiment with benzoyl chloride) is added about 1–1·5 c.c. glacial acetic acid, and the ether evaporated off, during which process any excess of diazomethane and ω-diazoketone is destroyed. The

residues left are worked up according to the details given in each case (in the experiment with benzoyl chloride the residue is distilled *in vacuo*).

I hope that by keeping to these conditions Dr. Bradley and Prof. Robinson will now be able to corroborate our results. Failing this, Dr. Malkin or I will be glad to demonstrate the reaction to them or any other of their colleagues they should choose to send down to Bristol. The experiment with benzoyl chloride can be carried out in one afternoon.

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The NH Band and the Dissociation Energy of Nitrogen.

THE so-called ammonia band at 3360-70 A., photographed first by Eder in 1892, has since been studied and measured by many authors. Fowler and Gregory (*Phil. Trans. Roy. Soc.*, **218**, 351 ; 1919) have published beautiful photographs of it. Lately this band has been attributed by Barrat (*Proc. Roy. Soc.*, A, **98**, 40 ; 1920), Hulthen and Nakamura (NATURE, **119**, 235 ; 1927), and others to the NH molecule. Using R. W. Wood's arrangement for the optical excitation of mercury vapour (*Phil. Mag.*, Oct. 1925, Sept. 1927), I have observed the appearance of it when about 4 mm. nitrogen and very little hydrogen—perhaps a few thousands of mm.—are admitted to the quartz tube containing the mercury vapour which is being excited by the light of a water-cooled, magnetically deflected mercury arc.

The NH band appears as a result of photosensitised fluorescence ; then it disappears as soon as the line 2537 of the arc is absorbed or self-reversed. With the help of the wire-gauze method (see R. W. Wood, NATURE, **120**, 725 ; 1927) it has been determined that the intensity of the band in our case is proportional to the square of the intensity of the exciting light. The problem is to find an explanation for the appearance of the band with this intensity relation. Now, the little hydrogen present in the tube is probably completely dissociated by the excited mercury, so that we have practically a constant density of atomic hydrogen. The combination of nitrogen and hydrogen as a gas reaction will furnish sufficient energy for the emission of the band 3360-70. Its intensity will be then proportional to the product of the concentrations of atomic hydrogen and nitrogen, and since the first is practically constant, the concentration of atomic nitrogen must be proportional to the square of the intensity of the arc or, what amounts to the same thing, to the square of the number of excited mercury atoms. This relation can be interpreted if we assume that the atomic nitrogen is formed by three-body collisions of N_2 molecules with two excited mercury atoms :

$$N_2 + 2\,Hg' \longrightarrow 2\,N + 2\,Hg.$$
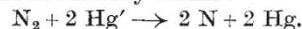
The only excited atoms which come into consideration are the 2^3P_1 atoms with 4·9 volts and the metastable atoms with 4·68 volts energy. The maximum of energy available in the best case for the dissociation of N_2 is then 9·8 volts ; two metastable atoms would give only 9·36 volts, which is 1·5 to 2 volts less than the assumed value of 11·4 volts. We could have some more energy available if we suppose that the reaction $N_2 + 2\,Hg' \longrightarrow N + HgN + Hg$ takes place. The combination energy of HgN would then help to dissociate the N_2 molecule. An explosive black deposit of HgN should then be expected, but has never been observed in the tube in spite of running it uninterrupted for several days. This reaction seems, then, not to take place in our case.

It thus appears probable that the dissociation