tion. Pyrene excimer emission shows a similar shift from 450 nm in crystals¹⁰ to 480 nm in solution².

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- Parker, C. A., Adv. in Photochem., 2, 305 (1964).
- ³ Birks, J. B., Moore, G. F., and Munro, I. H., Spectrochim. Acta, 22, 323 (1966).
- ^a Bowen, E. J., and Tanner, D. W., Trans. Farad. Soc., 51, 475 (1955).
- ² Chandross, E. A., J. Chem. Phys., 43, 4175 (1965).
 ⁴ Chandross, E. A., J. Chem. Phys., 43, 4175 (1965).
 ⁸ Birks, J. B., and Barnes, R. L., Proc. Roy. Soc., A (in the press).
 ⁶ Birks, J. B., Lumb, M. D., and Munro, I. H., Proc. Roy. Soc., A, 280, 289 (1964).
- ⁷ Parker, C. A., and Hatchard, C. G., Proc. Roy. Soc., A, 289, 574 (1962).
- ¹ Tanaka, J., Koda, T., Shionoya, S., and Minomura, S., Bull. Chem. Soc., Japan, 38, 1559 (1965).
 ³ Jones, P. F., and Nicol, M., J. Chem. Phys., 43, 3759 (1965).

1º Birks, J. B., and Cameron, A. J. W., Proc. Roy. Soc., A, 249, 297 (1959).

Doubly Charged Negative Ions

Stuckey and Kiser¹ recently reported an experiment in which they believed that they had produced doubly charged negative ions of oxygen and the three lighter halogens. The method used would have required the doubly charged ions to persist for 10-4 sec or more. This is unlikely on theoretical grounds-which means that the experiment will be all the more important if it is confirmed -and the absolute amount of the doubly charged ions (about 1/10 of the amount of the corresponding singly charged ions) is very surprisingly large.

It would seem sensible, therefore, to consider any possible mechanism, even if improbable, by means of which currents could be collected in the resonance mass spectrometer at twice the resonant frequency to be expected for singly charged negative ions. It is impossible to work out orbits in detail without exact information on the equipment used, but there are one or two mechanisms which should perhaps be considered.

The first of these is that whenever negative ions are accelerated in a vacuum which is less than perfect there will be a steady loss of ions by collisions in which the electron is removed with little change in the energy of the main part of the atom. This leads to a continuous supply of high energy neutral atoms which leave the orbits of the negative ions tangentially. Such neutral atoms, with energies of a few tens of electron volts or greater, may be ionized on collision with a solid surface or may cause secondary ionization. Positive ions leaving such a surface would have the same effect as would the arrival of negative ions.

If there were a mechanism by which singly charged negative ions would produce a larger number of such fast neutral particles at the double frequency resonance, a doubly charged resonant peak would appear. If the ion source region contains an adequate number of electrons and positive ions, this region ought to be at least partially conducting to the frequency concerned. Such a mechanism may exist.

Ordinarily, one would expect that at double the resonant frequency a negative ion will be accelerated away from the source if it leaves at the appropriate phase of the radiofrequency field, but before its orbit has been turned through more than a right-angle this field will reverse and it will lose energy gain. In a complete circuit it will gain energy twice and lose energy twice.

If, however, one of the parts of the orbit in which it is losing energy lies within the conducting region around the ion source, it will be partly protected from the radiofrequency field and will be slowed down less than it should be. It will therefore gain more energy than it loses in the whole cycle, and the orbit will expand until it escapes entirely from the ion source region. Although it will

precess rapidly the ion will be permanently captured into this orbit, until its discharge by collision. The neutral atom resulting will then necessarily have an energy of at least some tens of electron volts.

On the other hand, if the radio-frequency field is at not quite double the proper frequency no permanent stable orbit will be formed, and the ion will periodically be brought almost to rest. Since the cross section for neutralization varies inversely with velocity down to quite low energies, there is then a very high probability that the resulting neutral atom will have too low an energy to produce ions detectable at the target.

The second mechanism to be considered is that with certain configurations of conducting region and for particular phases of starting, it may be possible for a particle to gain energy continuously by a mechanism somewhat like that operative in a microtron, which would give rise to a directly collected negative ion current at the double resonance. Conditions for this would be rather critical, and it does not seem quite so likely as the other mechanism proposed.

A very sensitive test of the reality of the doubly charged negative ions observed would be afforded by investigating the change of relative peak heights for singly and doubly charged ions as the residual gas pressure was increased. The currents of each will fall exponentially, but the cross section for breakdown of doubly charged ions will necessarily be very much larger, with a corresponding increase in the value of the exponent.

A second method of investigation might be to use a grid over the collecting electrode with a retarding potential to a plate collector behind it. This would discriminate at once between the collection of charged and neutral particles and could be used to show whether the supposed F-- for example at 860 kc/s had correctly four times the energy of the F- at 430 kc/s.

Some information could perhaps also be obtained by pulsing the source and watching the rate at which the current died away. The acceleration of singly charged ions by a complex mechanism would take more time than would be taken by the normal acceleration of doubly charged ones. I do not fully understand the point made by Stuckey and Kiser when they say that "peaks at multiples of the resonant frequency were not observed": surely this is exactly what they are observing in the main experiment ?

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¹ Stuckey, W. K., and Kiser, R. W., Nature, 211, 963 (1966).

THE SOLID STATE

Basal Plane Contraction and Annealing of a Degraphitized Carbon

GRAPHITES damaged by radiation grow in the direction of the c-axis and shrink in the direction of the a-axis¹. Kelly² was able to account for the contraction of the basal plane by assuming that the Poisson ratio effect, the layer lattice vacancies and the layer plane buckling are caused by interstitial clusters. Similar contraction has also been observed in lamellar compounds of graphites^{3,4}. In a carbon obtained by baking graphite oxide, the regular lattice was restored at about 2,000° C as in the highly irradiated graphites.

Hofmann et al.⁵ have obtained extremely thin lamellae of graphite from graphite oxide by reduction with hydrazine. Using their method, I have obtained wide varieties of carbons for X-ray investigation. In my experiment, however, the carbon particles dispersed in the reducing liquor agglomerated slowly when maintained at 90° C for periods