Microwave Spectra of Oxazole and Isoxazole

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WE have made extensive assignments of the rotation spectra of oxazole and isoxazole. They yield information about the geometry and electronic structures of the molecules, and show that more detailed knowledge will be obtainable by these methods.

Both substances show absorptions due to components of their electric dipole moments in the A- and B-axes of inertia, and rotational constants have been derived from $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions as follows (in Mc./sec. ± 0·05 Mc./sec.): Oxazole: $A = 10{,}050{\cdot}94$, $B = 9{,}645{\cdot}70$, $C = 4{,}919{\cdot}42$. Isoxazole: $A = 9{,}786{\cdot}24$, $B = 9{,}575{\cdot}07$, $C = 4{,}836{\cdot}95$. The inertial defects are small, and close to those found for furan,[1] 1,2,5-oxadiazole,[2] and several similar molecules. They indicate that both oxazole and isoxazole are planar.

Nuclear quadrupole splittings due to nitrogen-14 are readily resolved in the spectra of oxazole, the coupling constants obtained from the $0_{0,0} \rightarrow 1_{0,1}$ and six $J = 1 \rightarrow 2$ transitions being (in Mc./sec. ± 0·2 Mc./sec.):

$$\chi_{aa} = -3{\cdot}99 \quad \chi_{bb} = +1{\cdot}58 \quad \chi_{cc} = +2{\cdot}41.$$

Assignable splittings in the spectra of isoxazole, on the other hand, are difficult to resolve in instruments employing 100 kc./sec. Stark-effect modulation, with line half-widths about 0·3 Mc./sec. The corresponding coupling constants are hence smaller for this molecule and cannot greatly exceed 1 Mc./sec. numerically in the case of χ_{aa} and χ_{bb}. We expect to place more refined limits on them by means of higher resolution studies.

Electric dipole moments, and their components in the principal axes, have been determined from Stark-effect measurements on $J = 1 \rightarrow 2$ transitions as follows:

Oxazole: $\mu_a = 1{\cdot}34$ D $\mu_b = 0{\cdot}66$ D $\mu = 1{\cdot}50$ D

Isoxazole: $\mu_a = 1{\cdot}98$ D $\mu_b = 2{\cdot}12$ D $\mu = 2{\cdot}90$ D

These are preliminary values, particularly in the case of oxazole, where there is some interference from quadrupole splittings, but their uncertainties are thought to be no more than 0·1 D. The total moments agree well with results from dielectric measurements on isoxazole in solution,[3] and with the less detailed data for oxazole.[4]

The spectra show long series of Q-branch absorptions and 107 lines in eight such series have been measured for isoxazole for J-values between 3 and 22. The centrifugal corrections (average 5 Mc./sec., maximum 37 Mc./sec.) are small considering the range of J-values. They can be accounted for reasonably well by first-order theory,[5] but a more refined analysis is desirable, and is in progress.[6]

Considerable further work on other isotopic forms of these substances will be necessary for the establishment of inertial axes, dipole directions and coupling tensor axes in the molecular frameworks, as well as internuclear distances, but such information will be accessible by extensions of the measurements, now in hand. This work has been done in conjunction with theoretical computations of the structures of these substances by means of self-consistent-field methods, which will be published separately by Dr. D. W. Davies and one of us.[6] These calculations, which have to date been made in much greater detail for isoxazole, show encouraging agreement with the present findings, taken in conjunction with molecular models with the correct rotational constants and acceptable structure parameters. More critical comparisons with theory will be possible when work on other isotopic forms is complete.

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