

shows that the ratio of absorptivities, $\frac{a_{0.047M}}{a_{\text{pure}}}$, is a maximum around 2000 Å.

The absorptivity of the monomeric methanol in *n*-hexane appears to reach a maximum of about 240 l./mol.-cm. at 1800 Å. This is somewhat higher than Harrison *et al.* found for methanol vapour⁴.

Results similar to this have been obtained on *n*-propanol solutions. Water exhibits an even more pronounced change in absorptivity on going from liquid to vapour phases. We have confirmed the results of Barrett and Mansell and extended the absorptivity data to 1750 Å. (ref. 5). At 1750 Å. liquid water at 30° C. has an absorptivity of 3.97 l./mol.-cm. Watanabe and Zelkoff report that water vapour at the same wave-length has an absorptivity of about 1,570 l./mol.-cm. (ref. 6). Of course, some of the variation can be caused by factors other than hydrogen bonding, but such a mechanism is probably responsible for most of the 400-fold change in absorptivity with change in state. The above explanation accounts for the strong dependence on temperature noted by Barrett and Mansell for liquids capable of hydrogen bonding.

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Propargyl Fluoride and its Microwave Spectrum

ALTHOUGH propargyl halides have long been known, there appears to be no report of propargyl fluoride (3-fluoropropyne), $\text{FCH}_2\text{C}\equiv\text{CH}$. This substance is of interest from the point of view of its chemical reactivity, and of its molecular structure, which is very suitable for spectroscopic study. We have found that propargyl fluoride can be made by the method, applied to certain other fluorides¹, of treating the *p*-toluene sulphonate of the corresponding alcohol with potassium fluoride. Specimens boiling at approximately 15° C. (760 mm.) have been characterized as essentially pure by examination of their spectra. Infra-red bands establish the presence of the $-\text{C}:\text{CH}$ residue, while the CH_2 and CF groupings give rise to bands closely resembling those which we have also found in the spectrum of fluoroacetonitrile, FCH_2CN . The CF stretching mode in propargyl fluoride yields a very strong band at 1,045 cm^{-1} , whereas the corresponding band in fluoroacetonitrile lies at 1,070 cm^{-1} . More detailed infra-red studies of these molecules are in progress in this laboratory.

Nuclear magnetic resonance spectra of pure liquid propargyl fluoride, at 33° C., are consistent with the anticipated structure. Coupling to the methylene and acetylenic protons respectively splits the fluorine-19 resonance into a triplet ($J = 47.3$ c./s.) of doublets ($J = 6.5$ c./s.), with a chemical shift, determined by substitution, of +142 p.p.m. from trifluoroacetic acid. The acetylenic proton spectrum consists of a

doublet ($J = 6.5$ c./s.) of triplets ($J = 2.5$ c./s.) at -2.8 p.p.m. from the resonance in tetramethyl silane as internal reference. The methylene proton signal is a doublet ($J = 47.3$ c./s.) of doublets ($J = 2.5$ c./s.) at -4.9 p.p.m. from the tetramethyl silane resonance. The coupling constant of 2.5 c./s. between the methylene and the acetylenic protons is close to those found² in other propargyl derivatives. The coupling between the fluorine and the acetylenic proton is believed to be the first of this type to be measured; the coupling constant of 6.5 c./s. may be compared with that of 21 c./s. for coupling between similar nuclei at closer approach in fluoroacetylene³.

The microwave spectrum of propargyl fluoride, which is intense, further confirms the identity of the molecule and shows the expected strong resemblance to the spectrum of fluoroacetonitrile⁴, with appreciable components of the molecular dipole moment in both the *A*- and *B*-rotational axes. For the principal isotopic species, transitions of the *R*-branch, arising from the *A*-component of the dipole, have been assigned for $J = 2 \rightarrow 3$ and $3 \rightarrow 4$. Lines arising from the *B*-component of the dipole, of the type $J_0, J \rightarrow J_1 (J-1)$, have been measured for *J*-values from 2 to 5. The derived constants, in Mc./s., are:

$$\begin{array}{ll} A = 35,637.79 \pm 0.15 & DJ \approx 0.003 \\ B = 4,608.79 \pm 0.03 & DJK = -0.072 \pm 0.002 \\ C = 4,183.60 \pm 0.03 & \end{array}$$

As in the case of fluoroacetonitrile⁴, a negative value is found for the centrifugal distortion constant, D_{JK} , which has similar magnitude in the two substances. A negative value of this constant was also found for the related molecule, propynal⁵.

If the structure of the $-\text{CH}_2\text{CCH}$ group is taken to be the same as in methyl acetylene⁶, the inertial constants of propargyl fluoride are consistent with an angle FCC near 111°, and a CF bond-length near the value of 1.385 Å. found in methyl fluoride⁷. Such a structure would show a parallel with the findings for propargyl chloride⁸. We expect to measure spectra of enough isotopically substituted forms of propargyl fluoride for a complete structure determination, and to evaluate the molecular dipole components from Stark effects. Full results will be given in a later detailed publication.

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