

was included with each term to represent the effect of the variation of each distance. Three distances were treated as independent variables: the two near-neighbor O-O framework distances parallel and roughly perpendicular to the triad axis and the shortest distance from the interstitial oxygen atom to the framework. All other distances in the model (out to 10 Å.) were properly related to the foregoing. These three adjustable parameters, together with associated "temperature" coefficients, were sufficient to yield a good fit to all but the low-angle region of the intensity function; ultimately this region was also fitted well through the introduction of additional "temperature" coefficients associated with longer distances and adjustment of the distance characteristic of the start of the continuum. The calculations were performed on an IBM 7090 computer with a general least-squares program prepared by Busing and Levy,¹² suitably modified for the problem. The "occupancy" of cavities by interstitial molecules was constrained to that required for proper density.

Figure 1 compares observed and calculated radial distribution functions. Significant features of the refined model are the following: (a) each framework oxygen atom has one framework neighbor at 2.77 Å. and three framework neighbors at 2.94 Å. (b) Each interstitial oxygen atom has three framework neighbors at each of the distances 2.94, 3.30, 3.40 and 3.92 Å. (c) The ratio of framework molecules to interstitial molecules is 4.0, corresponding to filling 50% of the framework "cavities."

The present model is, in a sense, a clathrate, since it consists of a framework and a guest, the interstitial molecule. The qualitative distinction between framework and interstitial molecules is supported by a distinctly larger "temperature" coefficient associated with distances involving interstitials. This model, however, is not the clathrate model suggested by Pauling,¹³ which is built of pentagonal dodecahedra and is based on the crystal structure of chlorine hydrate; its calculated radial distribution function, shown in Fig. 1, indicates the model to be inconsistent with our observations.

The observed radial distribution of Fig. 1 is in substantial agreement with that recently presented by Brady and Romanow,⁴ and that reported earlier by Morgan and Warren,³ except for greater resolution and detail present in the current results; these arise from the greater range of scattering angle in which interference was observed. The disagreement with the results of van Panthaleon van Eck and co-workers,⁵ as pointed out by Brady, is thus confirmed.

Full details of this study will be reported elsewhere.

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THE STRENGTHS OF HYDROGEN BONDS FORMED BY PROTIUM AND DEUTERIUM

Sir:

The deuterium isotope effect in hydrogen bonding has been measured for the system fluoroform, tetrahydrofuran and cyclohexane. In this system only one type of hydrogen bond interaction is present, the hydrogen bond is linear, and no interference arises from dimers and polymers. The fluorine chemical shifts of fluoroform and fluoroform-*d* reflect their hydrogen bonding propensities.

Previous investigations¹⁻¹⁰ of the isotope effect in hydrogen-bonding have involved complicating factors including competing equilibria and the formation of large aggregates, and are reviewed elsewhere.¹¹

Fluoroform was obtained from trifluoromethyl iodide and potassium hydroxide in acetone.¹² Fluoroform-*d* was prepared from potassium deuterio-oxide, trifluoromethyl iodide, and a solution of ethyl alcohol and ethyl alcohol-*d*. Fluorine n.m.r. indicated a mixture of 52% fluoroform-*d* and 48% fluoroform.

Fluorine n.m.r. spectra were observed at 56.45 Mc./sec. using 5 mm. o.d. sample tubes containing 14 cm. of solution and 2 cm. of dead space and thermostated to within $\pm 0.3^\circ$. All chemical shifts, measured by the side-band technique with a standard deviation of approximately 0.003 p.p.m., were up-field from the reference, hexafluoro-2,2,3,3-tetrachlorobutane.

In Table I are presented the chemical shifts of fluoroform in solutions containing cyclohexane, 0.0096 mole fraction (m.f.) fluoroform, 0.0104 m.f. fluoroform-*d*, 0.049 m.f. hexafluoro-2,2,3,3-tetrachlorobutane, and various mole fractions of tetrahydrofuran. The decrease of the chemical shift of the reference with increasing temperature due to different populations of rotational isomers did not affect the results since the relative shifts at each temperature were employed.

The observed chemical shift, $\delta_{\text{obsd.}}$, can be represented by the equation^{13,14}

$$\delta_{\text{obsd.}} = (C/A)(\Delta) + \delta_{\text{free}}$$

where C/A is the ratio of moles of complex to initial moles of fluoroform, Δ is the "hydrogen bond shift" ($\delta_{\text{complex}} - \delta_{\text{free}}$) of the fluorine resonance and

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TABLE I

OBSERVED FLUORINE CHEMICAL SHIFTS OF FLUOROFORM IN SOLUTIONS CONTAINING 0.0096 m.f. FLUOROFORM, 0.0104 m.f. FLUOROFORM-*d*, 0.049 m.f. HEXAFLUORO-2,2,3,3-TETRACHLOROBUTANE, TETRAHYDROFURAN AND CYCLOHEXANE

C ₆ H ₆ O, m.f.	$\delta_{\text{obsd.}}$ (p.p.m.) at °C.										
	-5.7	1.2	7.5	17.1	25.6	25.8	26.4	36.2	38.0	45.8	49.5
0.000	7.480	7.524	7.604	7.655	7.754	7.729	7.742	7.825	7.850	7.901	7.926
.147	8.259	8.256	8.288	8.303	8.339	8.326	8.339	8.367	8.367	8.397	8.420
.196	8.371	8.344	8.403	8.394	8.447	8.433	8.438	8.468	8.479	8.497	8.500
.245	8.443	8.440	8.472	8.484	8.527	8.507	8.527	8.551	8.569	8.583	8.594
.882	8.780	8.796	8.849	8.886	8.939	8.924	8.943	8.982	8.994	9.023	9.040
<i>K</i> , m.f. ⁻¹	8.00	6.86	6.24	5.35	4.70	4.80	4.70	4.09	3.91	3.58	3.44

TABLE II

OBSERVED FLUORINE CHEMICAL SHIFTS OF FLUOROFORM-*d* IN SOLUTIONS CONTAINING 0.0104 m.f. FLUOROFORM-*d*, 0.0096 m.f. FLUOROFORM, 0.049 m.f. HEXAFLUORO-2,2,3,3-TETRACHLOROBUTANE, TETRAHYDROFURAN AND CYCLOHEXANE

C ₆ H ₆ O, m.f.	$\delta_{\text{obsd.}}$ (p.p.m.) at °C.										
	-5.7	1.2	17.1	25.6	25.8	26.4	36.2	38.0	45.8	49.5	
0.000	8.273	8.326	8.452	8.533	8.521	8.532	8.603	8.638	8.690	8.714	
.147	9.046	9.048	9.090	9.120	9.111	9.115	9.138	9.163	9.182	9.195	
.196	9.161	9.140	9.184	9.226	9.216	9.210	9.248	9.253	9.269	9.278	
.245	9.239	9.225	9.267	9.310	9.287	9.306	9.324	9.347	9.356	9.356	
.882	9.549	9.556	9.652	9.698	9.696	9.694	9.742	9.760	9.785	9.790	
<i>K</i> , m.f. ⁻¹	8.41	7.34	5.55	5.00	4.85	4.87	4.21	4.05	3.63	3.50	

δ_{free} and δ_{complex} are the fluorine chemical shifts of unassociated and associated fluoroform, respectively. The value 0.02 was used for *A* and will be justified below. The fraction *C/A* can be evaluated from the mole fraction equilibrium expression

$$K = \frac{C(A + B + S - C)}{(A - C)(B - C)}$$

(where *S* is the number of moles of solvent plus reference and *B* is the initial number of moles of tetrahydrofuran), for any assumed value of *K*. The plot of $\delta_{\text{obsd.}}$ as a function of *C/A* is a straight line only for the correct *K*. The best least-squares line gave the correct *K* with a probable error averaging 0.02 but not exceeding 0.05. The slope of that line gives the value for Δ . The minimization of solvent effects is discussed elsewhere.¹⁵ Values of *K* are presented in Table I.

For solutions containing 0.02 mole fraction of fluoroform, *no* fluoroform-*d*, and the same concentrations of tetrahydrofuran, cyclohexane, and reference as those listed in Table I, the fluorine shifts were exactly equal to the values in Table I. The equality, within experimental error, is consistent with the equilibrium constants obtained below. Therefore, the equilibrium constant for the association of fluoroform (or fluoroform-*d*) with tetrahydrofuran can be calculated from the data in Table I (or Table II) by using *A* equal to 0.02 for fluoroform (or fluoroform-*d*). Thus, the use of identical temperatures and concentrations of tetrahydrofuran for fluoroform and fluoroform-*d* led to high accuracy in the *relative* strengths of hydrogen bonds formed by protium and deuterium.

Equilibrium constants for the association between fluoroform and tetrahydrofuran obtained from the p.m.r. of fluoroform agree with the above results and will be reported elsewhere.

Values of $\delta_{\text{obsd.}}$ of fluoroform-*d* in the solutions which contained 0.0104 m.f. fluoroform-*d* and 0.0096 m.f. fluoroform are presented in Table II.

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The fluoroform-*d*-tetrahydrofuran association constants are listed also. The fluoroform doublet, *J* = 79.5 c./sec., occurred 0.780 p.p.m. up-field from the fluoroform-*d* triplet, *J* = 12.0 c./sec. The average values of Δ (fluorine resonance) and the probable errors of the individual observations are 1.480 ± 0.005 and 1.437 ± 0.007 p.p.m. for the fluoroform-tetrahydrofuran and the fluoroform-*d*-tetrahydrofuran associations, respectively.

In Table III are presented the thermodynamic constants.

TABLE III

THE THERMODYNAMIC CONSTANTS FOR HYDROGEN-BOND FORMATION TO TETRAHYDROFURAN

	Fluoroform	Fluoroform- <i>d</i>
K_{25° , (m.f.) ⁻¹	4.77 ± 0.02^{16}	4.95 ± 0.02^{16}
ΔH , kcal./mole	-2.593 ± 0.024^{16}	-2.727 ± 0.022^{16}
ΔG_{25} , kcal./mole	-0.926	-0.947
ΔS_{25} , cal./mole deg.	-5.59	-5.97

The enthalpy values, obtained from least-squares plots of $\log K$ versus $1/T$, differ by $134 \pm 35^{16,17}$ cal./mole. A test¹⁷ for the significance of the difference between the ΔH values led to the conclusion that at the 97% confidence level deuterium forms stronger hydrogen bonds than protium in this system.¹⁸

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