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Studies of Hydrogen Bonding in the Vapor Phase by Measurement of Thermal Conductivity and Molecular Orbital Calculations. 2,2,2-Trifluoroethanol[†]

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Abstract: The thermal conductivity of 2,2,2-trifluoroethanol vapor was measured in a modified thick hot-wire cell between 338 and 385 K at pressures ranging from approximately 100 to 1300 Torr (13.3–173 kPa). Analysis of the data indicates that molecular association to form a dimeric species is the main source of the enhancement of the thermal conductivity of the vapor. The enthalpy of association of the trifluoroethanol dimer is -4753 cal/mol and the entropy of association is -18.73 cal/mol K. Ab initio calculations were carried out on several rotational isomers of trifluoroethanol and on four possible dimer structures. The most stable dimer is a cyclic structure involving the gauche-staggered isomer of trifluoroethanol. An extra hydrogen bond due to the presence of the fluorines enhances the stability of the dimer compared to the methanol dimer.

I. Introduction

In this paper, we report a study of the hydrogen bonding in 2,2,2-trifluoroethanol vapor by the measurement of thermal conductivity as a function of pressure^{1,2} and by use of molecular orbital calculations.

Information concerning the association of 2,2,2-trifluoroethanol (TFE) in the vapor is of interest for two reasons. First, experimental and theoretical determination of the strength of the attraction between TFE molecules can provide fundamental insights into the effect of the CF₃ substituent on the association properties of alcohols. Second, the thermal conductivity measurements can provide some important thermodynamic data on TFE which is lacking in the literature despite its potential use as a working fluid in power cycles.³

A number of studies of association in alcohols have been made using PVT, heat capacity, and thermal conductivity measurements.⁴ Although there are often large discrepancies between conclusions reached from different studies on alcohols, the majority of workers have deduced the presence of dimers and many have deduced the presence of higher polymers. The thermal conductivity technique developed in this laboratory^{1,2} has proved successful in a study of association in methanol vapor.¹ This technique uses the pressure dependence of the thermal conductivity of a gas to determine which associated species are present and their thermodynamic properties.

In thermal conductivity measurements on TFE vapor reported here, the presence of a dimeric species has been determined. The equilibrium constant and enthalpy and entropy of association for the dimer are evaluated from the data. No higher polymers are detected as in the case of methanol vapor.

There have been few ab initio molecular orbital studies of association between alcohol molecules. The only studies have been done on small clusters of methanol molecules.^{5,6} The

application of a single technique such as the thermal conductivity method to a number of alcohol vapors, TFE being the second, should provide consistent data for comparison with ab initio calculations. Hence, as a part of this study, we have carried out minimal basis set SCF calculations on hydrogen bonding between TFE molecules. Calculations were first performed on the various rotational isomers of the TFE monomer and then the lowest energy isomers were used in forming different dimer structures. The most stable dimer is found to have a cyclic hydrogen bond and has a stronger hydrogen bond than the methanol dimer. The hydrogen bond strengths are consistent with the experimental results. The structures of the monomer and dimer are used to help explain why no higher polymers are observed in TFE vapor as in the case of methanol vapor.

II. Experimental Section

A. Apparatus. The thermal conductivity of 2,2,2-trifluoroethanol was measured at five temperatures between 338 and 385 K and at pressures ranging from 100 to 1300 Torr. The apparatus employed was a modification of the thick hot-wire cell described by Kannuliuk and Carman.⁷ A platinum wire, 0.508 mm in diameter, was mounted along the axis of a precision-bore soft glass tube which was 101.6 mm long and had an internal diameter of 4.999 ± 0.005 mm. This tube was fabricated from soda lime glass whose coefficient of thermal expansion was matched to that of the platinum wire. The wire was secured at each end of the tube by directly fusing it to the soft glass while applying slight tension to maintain proper alignment. The cell was made vacuum tight by coating the glass-to-metal seals with a thin layer of low vapor pressure Torr Seal epoxy. Samples were admitted to the conductivity cell through a small hole in the tube wall near one end.

The cell assembly was submerged in a 15-gal bath filled with Dow Corning 710 silicone fluid. The temperature of the oil was maintained to within about ± 0.005 °C by a Bailey Model 124 precision temperature controller. The bath temperature was measured with a platinum resistance thermometer accurate to ± 0.001 °C.

A series of valves permitted stepwise reduction of pressure within the system. Pressures were measured with a Statham Model PA822

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temperature-compensated pressure transducer calibrated against a mercury manometer. The uncertainty of the measured pressure was less than 2 Torr over the entire range considered.

A thermal gradient between the wire and the cell wall was created by passing a well-regulated constant direct current through the platinum wire. This was provided by a Kepco Model CC7-2M power supply. The precise current was determined by monitoring the voltage drop across a thermostated Leeds and Northrup 0.1 Ω standard resistor in series with the conductivity cell. The platinum wire inside the cell was calibrated as a resistance thermometer in the usual way⁷ so that its temperature could be determined accurately. All voltages were measured directly with a Data Precision Model 3500 voltmeter.

B. Instrument Calibration. For steady-state conditions, the thermal conductivity measured in the hot-wire method is related to the heat transferred from the wire to the cell wall by the equation⁸

$$\lambda = gQ/(T_2 - T_1) \quad (1)$$

where λ is the thermal conductivity, g is a constant dependent only on the cell dimensions to a first approximation, Q is the heat flux, T_2 is the temperature of the wire, and T_1 is the temperature of the cell wall. The temperature at which the thermal conductivity of the gas is measured is taken to be the average temperature, $(T_1 + (T_2 - T_1)/2)$.

The thermal conductivity of trifluoroethanol was measured by the hot-wire method using a relative technique; no attempt at absolute measurement was made. In Appendix A, we show that, if the current input through the wire is held constant, then the thermal conductivity is a function of the voltage drop across the cell wire. All other factors are known or cancel because of the relative method used. For the cell used in these measurements, the voltage drop, V , was found empirically to vary linearly with the reciprocal of λ according to the equation

$$V = A + B/\lambda \quad (2)$$

where A and B are constants dependent only on the bath temperature. Three high-purity gases (nitrogen, argon, and krypton), whose thermal conductivities are accurately known, were used to determine A and B . Equations for the thermal conductivities of nitrogen, argon, and krypton from data in the literature were determined previously and are given in ref 1 and 2. With the sample gas in the cell, the voltage drop across the wire is measured as a function of a stepwise reduction in the total cell pressure and the thermal conductivity is determined via eq 2.

In the experimental determination of the thermal conductivity of a gas, a number of factors may introduce errors. These have been discussed in detail by a number of authors.^{7,8} Since we used a relative method, errors due to radiation, conduction through the cell ends, and eccentricity of the cell essentially cancel out and need not be considered. The two major possible sources of error in the method used in this study are convection and the temperature "jump" effect.

To test for convection, the cell was filled with argon to about 2 atm and the voltage drop across the cell wire measured after each of many stepwise reductions of the pressure down to 100 Torr. A similar series of measurements was made with nitrogen in the cell. In both cases, the voltage remained constant over the entire pressure range. This constancy of the apparent thermal conductivity of the reference gases over the pressure range of interest suggests the absence of convection.⁷ This desirable condition was achieved by making the annular gap between the wire and the cell wall small, while at the same time never allowing the temperature of the cell wire to exceed that of the oil bath by more than 7 °C.

The temperature "jump" effect arises from temperature discontinuities at the wire surface.⁷ This effect would lead to an apparent pressure dependence of thermal conductivity. The previously described test for convection indicates that there was no error introduced above 100 Torr. Below 100 Torr, the effect became noticeable as the apparent thermal conductivity for the reference gases decreased with pressure. Hence, no data for trifluoroethanol were kept below 100 Torr.

Since the magnitude of the temperature jump effect is somewhat dependent on the substance,^{8a,9} we checked the validity of the 100-Torr data cutoff for TFE by accumulating λ - P data at pressures below 100 Torr. By applying standard techniques of analysis,^{8a,8b} we showed that the temperature-jump effect introduces a negligible error at pressures over 100 Torr.

The relative method used in this study differs from the most commonly used type of relative method.^{8a,10} In the usual way of making relative measurements, only one calibrating gas is used to determine the constant g in eq 1. However, for this study where measurements at different pressures at a single temperature are necessary, this would require varying the current each time to keep $T_2 - T_1$ constant. To facilitate rapid data accumulation, we have used a method similar to Coffin and O'Neal¹¹ where the current input is kept constant for each measurement and $T_2 - T_1$ is allowed to vary. This necessitates the use of more than one reference gas to determine the parameters in eq 2 as described previously.

We have estimated the maximum error in our measured values of thermal conductivity to be less than 1%. The validity of this number can be judged by comparing λ values for water measured with our apparatus¹² with those of Vargaftik.¹³ At 100 and 110 °C and at a pressure of 750 Torr, our measured values were within 0.2% of the values in ref 13. The relative accuracy of our λ values is estimated to be less than 0.5%.

C. Application of the Technique to Trifluoroethanol Vapor. Before each run, the cell was calibrated with the reference gases nitrogen, argon, and krypton. The cell was then evacuated to a pressure less than 10^{-3} Torr while a current of approximately 0.9 A was passed through the wire. The 2,2,2-trifluoroethanol (purity, 99.87 wt % by gas chromatographic analysis as obtained from J. T. Baker Co.) was placed in a bulb connected to the cell. It was then outgassed repeatedly to remove dissolved gases before transferring a sample to the cell by vaporization through evacuated heat metal connecting tubes. The pressure in the cell was monitored continuously with the transducer to prevent condensation of the vapor during filling. When the desired starting pressure was attained, the cell was isolated from the filling bulb and sufficient time was allowed for the system to reach steady state. The voltage drop across the cell wire, the voltage drop across the standard resistor, and the cell pressure were then measured at each step in a series of reductions of the total pressure in the cell. The apparatus was pumped out through a liquid nitrogen cold trap and the above procedure repeated, starting with the reference gas calibration step.

The thermal conductivity of trifluoroethanol vapor at each pressure was obtained from the voltage drop across the cell wire by direct calculation from eq 2. The temperature of the wire at each pressure is determined from the resistance of the wire which is calculated from the current input to the cell wire and the voltage drop across its length. The current input was determined from the voltage drop across the standard resistor, which was maintained inside an auxiliary oil bath at a constant temperature.

The thermal conductivities measured as a function of pressure at five temperatures, 338.0, 347.4, 359.8, 370.8, and 385.1 K, are given in Table I.

Saturated vapor pressures of TFE have been reported for the range 273–298 K.¹⁴ Extrapolation of these results to the region 338–385 K gave vapor pressures that were incorrect. Hence, the vapor pressures at which TFE condensed in the cell were measured at 335 and 357 K (466 and 1129 Torr, respectively). The combined vapor pressure data (ref 14 and ours) were least-squares fitted to obtain a best fit to the expression $\log P = A - B/T$, where P is the vapor pressure in mmHg and T is the absolute temperature in K. The best fit gave $A = 9.320$ and $B = 2232$.

III. Data Analysis

A. Application of Theory to Data Reduction. The increase in the thermal conductivity with increasing pressure indicates the presence of associated species in the vapor. The thermal conductivities of associating vapors can be expressed as

$$\lambda = \lambda_f + \lambda_R \quad (3)$$

where λ_f is the thermal conductivity of a frozen (nonreacting) composition of all the vapor species and λ_R is the contribution to the thermal conductivity arising from the transport of association enthalpy in a thermal gradient. The λ_f is generally very weakly dependent on pressure. This dependence is due to the variation of the equilibrium composition with pressure. The λ_R is a strongly pressure-dependent term which has been calculated from gas kinetic theory by Butler and Brokaw^{15,16} to be

Table I. Experimental Thermal Conductivity (cal/cm s K) of 2,2,2-Trifluoroethanol Vapor as a Function of Pressure at Five Temperatures

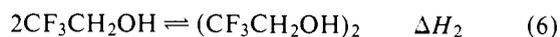
$T = 385.1$ K		$T = 370.8$ K		$T = 359.8$ K		$T = 347.4$ K		$T = 338.0$ K	
p , Torr	$10^5 \lambda$								
1274.8	4.868	1050.6	4.586	904.3	4.441	497.2	4.079	411.7	3.919
1227.0	4.841	1008.2	4.587	877.7	4.428	440.4	4.042	406.0	3.915
1198.4	4.811	936.2	4.558	833.8	4.402	390.2	4.022	363.6	3.877
1157.4	4.828	889.6	4.542	782.0	4.378	346.5	3.989	324.6	3.842
1123.2	4.803	825.4	4.519	753.8	4.367	307.1	3.970	315.7	3.839
1030.8	4.794	791.6	4.510	700.5	4.337	259.4	3.944	278.9	3.808
998.2	4.773	735.2	4.488	653.9	4.318	221.2	3.922	278.1	3.811
935.3	4.756	702.8	4.487	607.0	4.293	178.2	3.894	230.6	3.780
914.2	4.764	618.8	4.449	552.2	4.271	140.8	3.878	208.8	3.765
832.6	4.730	618.4	4.464	521.4	4.253	111.6	3.857	191.0	3.750
812.7	4.739	512.1	4.418	496.1	4.250			165.5	3.735
737.5	4.701	488.6	4.408	453.7	4.228			131.9	3.709
723.2	4.706	418.5	4.391	432.4	4.229			122.9	3.712
646.4	4.676	416.7	4.385	390.4	4.204				
641.2	4.697	347.2	4.356	346.3	4.169				
568.7	4.677	315.4	4.350	294.7	4.170				
541.3	4.672	265.7	4.327	267.5	4.132				
471.6	4.649	233.7	4.318	205.4	4.129				
453.7	4.648	203.0	4.291	147.3	4.072				
395.6	4.629	164.5	4.292	108.7	4.062				
359.8	4.608			101.7	4.063				
313.6	4.589								
284.2	4.572								
249.1	4.558								
224.1	4.537								
176.3	4.523								
110.6	4.489								
108.3	4.476								

$$\lambda_R = -\frac{1}{RT^2} \begin{vmatrix} 0 & \Delta H_2 & \cdots & \Delta H_{\nu+1} \\ \Delta H_2 & A_{11} & \cdots & A_{1\nu} \\ \vdots & \vdots & \ddots & \vdots \\ \Delta H_{\nu+1} & A_{\nu 1} & \cdots & A_{\nu\nu} \end{vmatrix} \div \begin{vmatrix} A_{11} & \cdots & A_{1\nu} \\ \vdots & \ddots & \vdots \\ A_{\nu 1} & \cdots & A_{\nu\nu} \end{vmatrix} \quad (4)$$

where ν is the number of independent chemical reactions (associations to form polymers in this case) occurring in the mixture; ΔH_i is the enthalpy change for the formation of an i -mer and the A_{ij} 's are numerical factors which depend on n , the stoichiometric coefficients; x_i , the mole fractions of the species in the gas; p , the total pressure; and D_{kl} , the binary interdiffusion coefficient for species k and l . The A_{ij} 's are defined by

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu-1} \sum_{l=k+1}^{\mu} \left(\frac{RT}{pD_{kl}} \right) \times x_k x_l \begin{bmatrix} n_{ij} & -n_{il} \\ x_k & x_l \end{bmatrix} \begin{bmatrix} n_{jk} & -n_{jl} \\ x_k & x_l \end{bmatrix} \quad (5)$$

The subscripts on the coefficients n and mole fraction x refer to the k th or l th chemical species in the i th or j th reaction. The subscripts i and j can have values between 1 and ν . The parameter μ is the number of distinct chemical species. For the present case, we will show that the only significant species are monomers and dimers. This gives $\nu = 1$, $\mu = 2$, $i = j$, $k = 1$, $l = 2$, $n_{11} = 2$, $n_{12} = -1$, and the association reaction is



The equilibrium constant K_2 for eq 6 may be expressed in terms of the partial pressures of the monomer, p_1 , and the dimer, p_2 :

$$K_2 (\text{atm}^{-1}) = p_2/p_1^2 \quad (7)$$

The mole fractions of the species, x_i , can be expressed in terms of K_2 and p_1 as follows:

$$x_1 = p_1/p = p_1/(p_1 + K_2 p_1^2) \quad (8)$$

$$x_2 = p_2/p = K_2 p_1^2/(p_1 + K_2 p_1^2) \quad (9)$$

For the case where only monomers and dimers are present, eq 4 and 5 lead to a simple form for λ_R :

$$\lambda_R = \left(\frac{pD_{12}}{RT} \right) \left(\frac{\Delta H_2^2}{RT^2} \right) \frac{K_2 p_1}{(1 + 2K_2 p_1)^2} \quad (10)$$

If D_{12} is known, then ΔH_2 and K_2 can be determined from the pressure dependence of the thermal conductivity.

The above expressions (eq 4, 5, and 10) are strictly valid only if the chemical reaction rates are sufficiently fast to guarantee that, after a short time, a steady-state condition is realized in which the pressure remains constant and the temperature and chemical composition at any point are constant.¹⁷ In other words, the system is in chemical equilibrium at the local temperature. For gas-phase association reactions, one would expect very fast reaction rates approaching the kinetic theory collision frequency. This is due to the fact that gas-phase clustering reactions should have extremely small activation energies since no monomer bonds are being broken and no extensive molecular rearrangements are taking place.

If $K_2 p_1$, the ratio of dimer to monomer, is not very large, then we can deduce from eq 10 that a plot of thermal conductivity vs. pressure should be essentially linear (the pD_{12} term is independent of pressure). The data for TFE vapor in Table I, when so plotted, do exhibit such a linearity. Since it can be shown that eq 4 is extremely sensitive to the presence of higher polymers¹ ($n > 2$), it is likely that the major associated species in TFE vapor is the dimer and that larger associated species make, at most, a very small contribution to the thermal conductivities at high pressures.

B. Estimation of Binary Diffusion Coefficients. Values of the product pD_{kl} may be calculated from an equation derived

from the molecular theory of gases in Hirschfelder, Curtiss, and Bird¹⁸ (Chapter 8, p 539):

$$pD_{kl} = \frac{2.6280 \times 10^{-3} T^{3/2} [(M_k + M_l)/2M_k M_l]^{1/2}}{\sigma_{kl}^2 \Omega_{kl}^{(1,1)*}} \quad (11)$$

where σ_{kl} is the sum of collision radii, $\Omega_{kl}^{(1,1)*}$ is a reduced collision integral dependent on the interactions between the k and l species, and M_k and M_l are the molecular weights of the two species k and l . The pair potentials are not known so that the reduced collision integrals cannot be calculated. Since the monomer and dimer are composed of the same molecules, we may assume that the ratio of the reduced collision integrals for monomer–monomer and monomer–dimer interactions is nearly unity. Hence, from eq 11:

$$\frac{pD_{12}}{pD_{11}} = \left(\frac{3}{4}\right)^{1/2} \left(\frac{\sigma_{11}}{\sigma_{12}}\right)^2 \quad (12)$$

Setting $\sigma_{kl} = (\sigma_k + \sigma_l)/2$ and the dimer volume at twice the monomer volume so that $\sigma_2^3 = 2\sigma_1^3$, eq 12 becomes

$$pD_{12} = 0.6783 pD_{11} \quad (13)$$

Thus, the coefficient of self-diffusion, D_{11} , of TFE monomers is needed to determine D_{12} . The D_{11} is related to λ_{11} , the thermal conductivity of a polyatomic molecule without contributions from the internal degrees of freedom, by the expression¹⁸

$$pD_{11} = 8A_{11}^* T \lambda_{11} / 25 \quad (14)$$

The λ_{11} is defined in Hirschfelder, Curtiss, and Bird¹⁸ (p 534) by

$$\lambda_{11} = \lambda_1 / E \quad (15)$$

where E is the Eucken factor and λ_1 is the value of the frozen thermal conductivity, λ_f , at zero pressure. The λ_1 is obtained by extrapolating the experimental thermal conductivity data to zero pressure for each temperature. The Eucken factor, E , which takes into account internal degrees of freedom, is given by¹⁸

$$E = (1 - \delta) + 2\delta C_p / 5R \quad (16)$$

where R is the gas constant and C_p is the constant pressure heat capacity. The factor δ is a reduced, dimensionless coefficient of diffusion. Hirschfelder¹⁹ derived a value of 0.885 for δ . Values of the constant pressure heat capacity, C_p , were calculated from the expression²⁰

$$C_p(\text{cal/mol K}) = 5.391 + 7.491 \times 10^{-2} T - 5.309 \times 10^{-5} T^2 + 1.371 \times 10^{-8} T^3 \quad (17)$$

The A_{11}^* in eq 14 is a numerical constant which depends on the Lennard–Jones potential parameter, ϵ/K . The ϵ/K is not available in the literature for TFE so it was determined by a procedure described by Hirschfelder, Curtiss, and Bird (Chapter 8, p 563) which uses the gas viscosity. The viscosity of TFE was calculated from the experimentally measured thermal conductivity at the limit of zero pressure, λ_1 , from the relation (ref 18, p 534)

$$\lambda_1 \times 10^7 = 15R\eta E / 4M (\text{cal/cm s K}) \quad (18)$$

The ϵ/K obtained in this manner had a value of approximately 450 K.

Two of the parameters, δ and ϵ/K , necessary in determining pD_{11} from eq 14 have a large uncertainty due to the fact that TFE is a polar molecule. Hirschfelder¹⁹ found that δ may be as low as 0.55 for polar hydrocarbons. The ϵ/K also may have a large uncertainty (± 100 K) because of difficulties in determining it for polar molecules. Fortunately, the final thermodynamic quantities that are obtained for the association of TFE

Table II. Values of Numerical and Physical Constants of 2,2,2-Trifluoroethanol Vapor Required for Calculation of Viscosity, η , and the Pressure–Binary Diffusion Coefficient Products, pD_{12}

T , K	$10^5 \lambda_1$, ^a cal/cm s K	C_p , ^b cal/mol K	E	A_{11}^*
338.0	3.613	25.17	4.595	1.105
347.4	3.795	25.58	4.668	1.105
359.8	4.017	26.11	4.763	1.105
370.8	4.238	26.57	4.844	1.105
385.1	4.528	27.15	4.948	1.105

$\sigma_{11} = 4.95 \text{ \AA}$ $\sigma_{12} = 5.59 \text{ \AA}$ $\epsilon/k = 450 \text{ K}$

^a The value of thermal conductivity at zero pressure, λ_1 , obtained by least-squares fitting of the data points at each temperature in Table I to a linear curve. ^b From eq 17.

Table III. Values of Viscosity and Pressure–Binary Diffusion Coefficients for 2,2,2-Trifluoroethanol

T , K	$10^6 \eta$, ^a P	pD_{11} , ^b atm cm ² /s	pD_{12} , ^c atm cm ² /s
338.0	105.5	0.0388	0.0264
347.4	109.1	0.0413	0.0280
359.8	113.2	0.0444	0.0300
370.8	117.4	0.0474	0.0322
385.1	122.8	0.0515	0.0349

^a Calculated from eq 18. ^b Calculated from eq 14. ^c Calculated from eq 13.

molecules are not very sensitive to the values used for δ and ϵ/K . (The uncertainties in δ and ϵ/K will introduce an uncertainty of ± 0.4 kcal/mol in the enthalpy of dimerization and ± 1.0 cal/mol deg in the entropy of dimerization.)

The values of λ_1 , C_p , E , and A_{11}^* obtained in this procedure are given in Table II, and the viscosity and pressure-diffusion coefficients, pD_{12} , calculated from them are given in Table III. For data reduction purposes, the values of pD_{12} were least-squares fitted to obtain a best fit to the expression

$$pD_{12} \times 10^5 = aT^{3/2} + b (\text{atm cm}^2/\text{s}) \quad (19)$$

The best fit gave $a = 0.638$ and $b = -1334$.

C. Dependence of λ_f on Pressure. The frozen thermal conductivity, λ_f , is somewhat pressure dependent. It may be calculated from the Wassiljewa equation for the thermal conductivity of a binary mixture²¹

$$\lambda_f = \lambda_1 / (1 + A_{12}' x_2 / x_1) + \lambda_2 / (1 + A_{21}' x_1 / x_2) \quad (20)$$

where λ_1 and λ_2 are the thermal conductivities of monomers and dimers, and A_{12}' and A_{21}' are constants which can be calculated from a relationship derived by Mason and Saxena.²² The calculation of these constants has been described in detail in ref 2 for acetonitrile. For TFE, the values are

$$A_{12}' = 1.5702 \quad (21)$$

$$A_{21}' = 0.6994 \quad (22)$$

The ratio λ_2/λ_1 was calculated using equations given in Hirschfelder, Curtiss, and Bird¹⁸ by a procedure described in ref 2. The ratio has a value of

$$\lambda_2/\lambda_1 \approx 0.94 \quad (23)$$

using the Eucken factor defined by eq 16 and $\delta = 0.885$. Substituting eq 8, 9, 21, 22, and 23 into eq 20 leads to the relationship

Table IV. Thermal Conductivity at Zero Pressure, λ_1 ; Dimerization Constants, K_2 ; Partial Pressure and Mole Fraction of Dimer, in Trifluoroethanol from Simultaneous Fit of Thermal Conductivity Data^a

T , K	$10^5 \lambda_1$, cal cm ⁻¹ s ⁻¹ K ⁻¹	K_2 , atm ⁻¹	p_{sat} , ^b Torr	p_2 , ^c Torr	x_2 ^c
338.0	3.562	0.0952	537	31.9	0.059
347.4	3.748	0.0785	812	58.6	0.072
359.8	3.989	0.0622	1318	118.1	0.090
370.8	4.200	0.0510	2018	217.5	0.108
385.1	4.470	0.0402	3162	402.7	0.127

^a From this fit, $\Delta H_2 = -4753$ cal/mol and $\Delta S_2 = -18.73$ cal deg⁻¹ mol⁻¹. ^b The p_{sat} was determined from the equation in the text. ^c At the saturation vapor pressure.

$$\lambda_f = \lambda_1 \left(\frac{1}{1 + 1.5702K_2p_1} + \frac{0.94K_2p_1}{0.6994 + K_2p_1} \right) \quad (24)$$

In the range of temperatures from 338 to 385 K, the pressure dependence of λ_f is small (less than 2% at pressures up to saturation in these measurements) but needs to be taken into account in order to obtain reliable values of the association constants.

D. Determination of ΔH_2 , ΔS_2 , and K_2 . Correlation of the experimental thermal conductivity data of TFE vapor with eq 3 was carried out with a minimization procedure described in detail in ref 2. This procedure utilizes the SIMPLEX version of the FORTRAN subroutine STEFIT.²³ The thermal conductivity data at all five temperatures were fit simultaneously to eq 3 with λ_R defined by eq 10 and λ_f being defined by eq 24. The variables in the fitting procedures were λ_1 , ΔH_2 , and K_2 .

The standard enthalpy and entropy of association of the TFE dimer from the five temperatures are -4753 cal mol⁻¹ and -18.73 cal mol⁻¹ K⁻¹, respectively. The equilibrium constants for dimer formation are given in Table IV. The partial pressure of the dimer present at each temperature at saturation was calculated from eq 7. These numbers are presented in Table IV, along with the mole fraction present at saturation.

The new λ_1 values, given in Table IV, were used to recalculate pD_{12} by the method described in section IIIB. The fitting procedure was repeated using a new equation for pD_{12} . The resulting ΔH_2 was within 0.5% of the original value and the new K_2 's were within 1% of the original K_2 's. Hence, the original λ_1 values obtained by a simple extrapolation of the thermal conductivity to zero pressure (Table II) were sufficiently accurate for use in calculating pD_{12} .

The assumption that only monomers and dimers are present in the vapor was tested by fitting the data with terms through pentamer in eq 4. The K_3 , K_4 , and K_5 values obtained from such a fit tended to be much smaller than the accuracy of the method can determine. Also, if the dimer is the only important associated species in TFE vapor, then a plot of the measured thermal conductivities vs. $K_2p_1/(1 + 2K_2p_1)^2$ should be linear. Such plots in Figure 1 are very close to linear with deviations from linearity being less than the experimental uncertainty. Hence, based on these tests, it is concluded that dimers are the only detectable associated species in the vapor.

Several other studies of the association of TFE molecules have been reported. A vapor density study²⁴ of TFE vapor led to the conclusion that trimers and octamers are the major species present. Our results do not lend support to this conclusion. Kivinen, Murto, and Kilpi²⁵ reported an infrared study of TFE in carbon tetrachloride where they find the enthalpy of association of the dimer to be -5.3 kcal mol⁻¹. The effect of the solvent on the dimerization energy is difficult to assess, so this value cannot be compared directly to the results presented here.

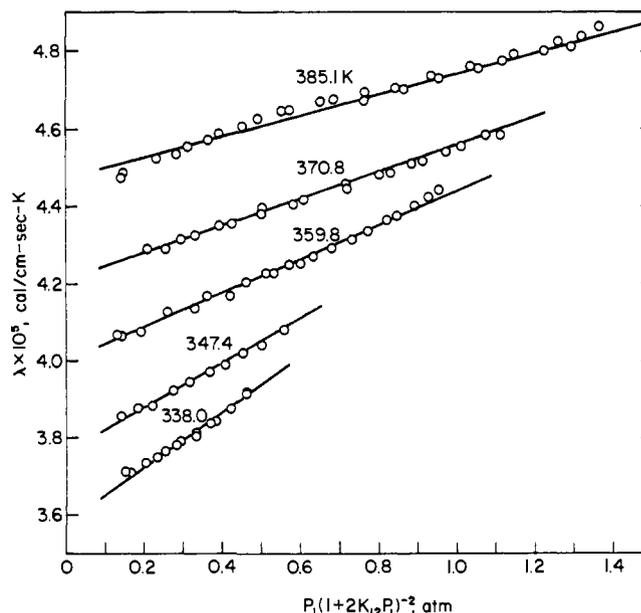


Figure 1. Thermal conductivity of 2,2,2-trifluoroethanol vapor vs. $p_1(1 + 2K_2p_1)^{-2}$ at five temperatures: p_1 is the monomer partial pressure; circles represent experimental values; the five solid straight lines were calculated from eq 3, 10, and 24.

IV. Quantum Mechanical Calculations on Hydrogen Bonding of Trifluoroethanol

In order to understand the differences in hydrogen bonding in methanol and trifluoroethanol vapors, we have carried out ab initio calculations on isomers of TFE and on four possible dimer structures. Standard LCAO-SCF methods are employed in this study and the basis set used is the minimal STO-3G.²⁶ This basis set has been found to give reasonable results for hydrogen bonded complexes.²⁷ An extended basis set 4-31G²⁸ has also been used in calculations on the various rotational isomers of TFE. A standard experimental model²⁹ was used for the geometry of the TFE molecule. In calculations on the dimers, the intermolecular angles were optimized to $\pm 2^\circ$ and the hydrogen bond length to ± 0.01 Å.

The $\text{CF}_3\text{CH}_2\text{OH}$ molecule has a number of possible rotational isomers. Rotation of the CF_3 group about the C-C bond leads to staggered and eclipsed forms, while rotation about the C-O bond generates configurations which are described by the CCOH dihedral angle. Calculations with the STO-3G and 4-31G basis set were carried out on the five most likely configurations illustrated in Figure 2 to determine the most stable isomers for consideration in forming the dimer structures. Three staggered forms were considered with CCOH dihedral angles of 0° (structure V in Figure 2), 60° (designated as *g* for gauche), and 180° (designated as *t* for trans). Two eclipsed forms were considered with CCOH dihedral angles of 60° (*g*) and 180° (*t*). The relative energies of these structures are given in Table V.

The two lowest energy structures are the gauche-staggered and trans-staggered isomers. The theoretical prediction that the gauche form is the most stable isomer is in agreement with an infrared study³⁰ in which it was found that the gauche form was predominant. In the same study, the gauche-trans energy difference was estimated to be 3.3 kcal/mol. The STO-3G basis predicts a gauche-trans energy difference of 0.70 kcal/mol, while the larger 4-31G basis predicts an energy difference of 2.34 kcal/mol. Stabilization of the gauche isomer is apparently due to an internal hydrogen bond of the type $\text{H}\cdots\text{F}$.

The larger stabilization obtained with the 4-31G basis set is also found in calculations on hydrogen bonded complexes

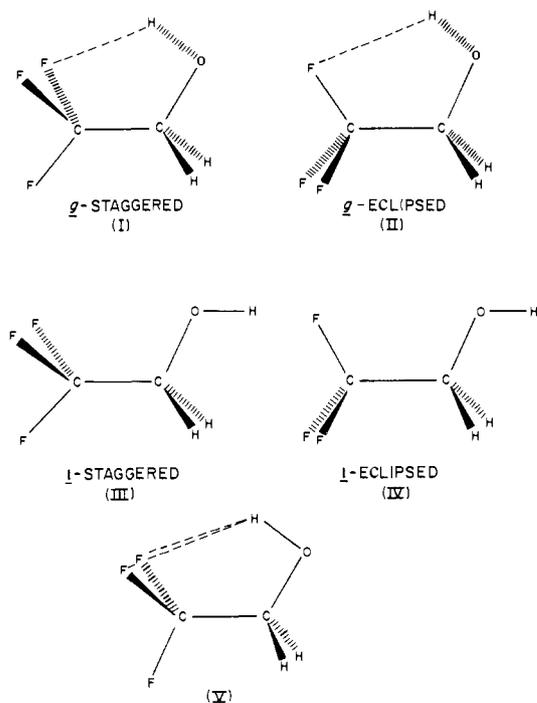


Figure 2. Various rotational isomers of 2,2,2-trifluoroethanol.

Table V. Total Energies (au) and Relative Energies (kcal/mol) of Various Rotational Isomers of 2,2,2-Trifluoroethanol

Isomer ^a	STO-3G		4-31G	
	Energy	Rel energy	Energy	Rel energy
<i>g</i> -staggered (I)	-444.508 84	0	-450.061 35	0
<i>t</i> -staggered (III)	-444.507 73	0.70	-450.057 59	2.36
<i>g</i> -eclipsed (II)	-444.505 75	1.94	-450.052 94	5.28
(V)	-444.505 49	2.10	-450.056 25	3.20
<i>t</i> -eclipsed (IV)	-444.505 24	2.26	-450.050 15	7.03

^a Structures illustrated in Figure 2.

involving H-F...H bonds.³¹ If the experimental value is correct, then these results would indicate that the minimal basis set probably underestimates the stabilization due to the H...F intramolecular bond while the 4-31G basis set gives a reasonable account of the interaction. Also, it should be noted that geometry optimization at either level of calculation could change the theoretical prediction.

We first considered complexes involving the trans isomer. Hydrogen bonding is possible at the lone pairs of either the oxygen or fluorine and is illustrated in Figure 3. For both dimers, the R and θ parameters shown in Figure 3 were optimized. The results are given in the figure. The angle, ϕ , describing the relative orientations of the two molecules was also tested and found to be nearly 180° in both cases. Structure II having the O-H...O hydrogen bond was found to be more stable with a binding energy of -5.84 kcal/mol as compared to -2.55 kcal/mol for the dimer with the O-H...F bond (I).

Two structures were then considered for dimers involving the gauche form of trifluoroethanol which has an intramolecular hydrogen bond. The structures were initially constructed with O-H...F and O-H...O hydrogen bonds similar to the dimers involving the trans isomer and are illustrated in Figure 4. In the case of the dimer with the OH...F bond (structure III), the fluorine (F') involved in the intramolecular hydrogen bond was chosen to be the lone pair donor so as to allow for interaction between the fluorines (of the proton donor) and the hydroxyl hydrogen (of the proton acceptor).

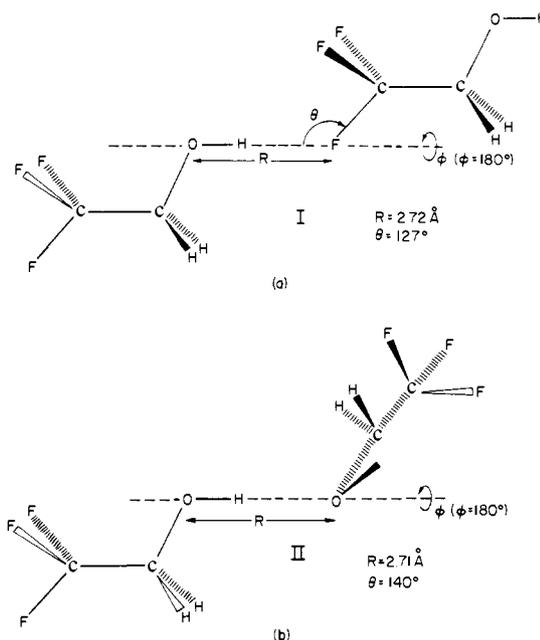


Figure 3. Dimers between trans-staggered isomers of 2,2,2-trifluoroethanol. (The values of the parameters in parentheses correspond to relative positions in the diagram.)

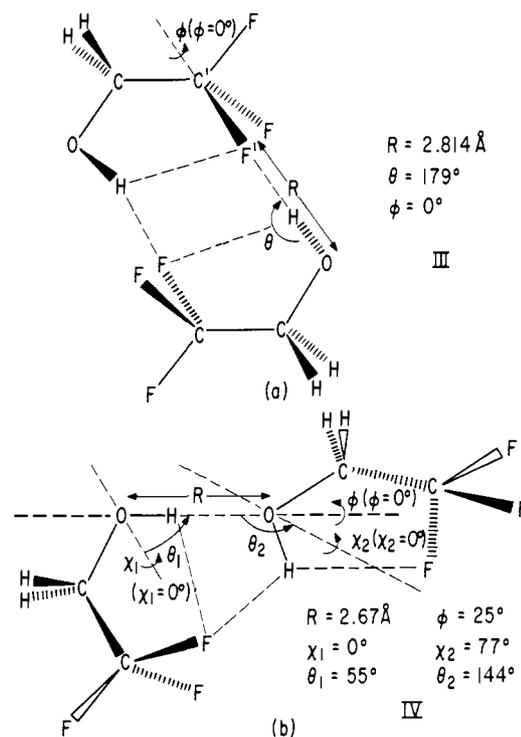


Figure 4. Dimers between gauche-staggered isomers of 2,2,2-trifluoroethanol. (The values of the parameters in parentheses correspond to relative positions in the diagram.)

The parameters (see Figure 4a) which were allowed to vary were R , the hydrogen bond length; θ , the angle OHF'; and ϕ , rotation of the proton acceptor molecule about the C'F' axis ($\phi = 0^\circ$ corresponds to the CCO and C'CO planes being parallel). The results of optimization of these parameters are shown in Figure 4a. The binding energy of this dimer is -3.15 kcal/mol.

For the dimer (structure IV) involving the O-H...O bond, a similar type of initial structure allowing for the additional H...F interaction was set up with the six intermolecular parameters indicated in Figure 4b. These are R , the hydrogen

bond distance; θ_1 and θ_2 , the hydrogen bond angles; χ_1 and χ_2 , the rotation of each molecule about an axis bisecting the COH angle; and ϕ , the orientation of each molecule with respect to each other. The results shown in Figure 4b indicate that a cyclic hydrogen bond is formed with values of ϕ and χ_2 such that the hydroxyl hydrogen of the proton acceptor interacts with an F of the proton donor. The resulting structure has two F...H internal hydrogen bonds having distances of 2.46 Å, an O-H...O bond with an H...O distance of 1.71 Å, and an external hydrogen bond F...H having a distance of 2.21 Å involving the same F that is taking part in the intramolecular bond. This structure is the most stable of the four structures investigated with a binding energy of -6.46 kcal/mol. The energies of all the structures are summarized in Table VI.

The various contributions to the hydrogen bond energy of the lowest energy cyclic structure (IV) can be approximated as follows. The O-H...O bond contributes about 5.8 kcal/mol based on the binding energy of the trans dimer (II) with the same type of bond. The external F...H interaction probably contributes about 0.7 kcal/mol on the basis of the STO-3G energy of the intramolecular F...H bond in the gauche isomer. Hence, these two bonds add up to 6.5 kcal/mol, which is close to the hydrogen bond energy of 6.46 kcal/mol of the cyclic structure. The underestimation of the F...H interaction energy by STO-3G probably indicates that the hydrogen bond energy of this structure is actually larger.

V. Comparison of Theoretical and Experimental Results

Trifluoroethanol is formed by replacing one of the methyl hydrogens in methanol by a -CF₃ group. It is of interest to investigate the effect of the -CF₃ group on the energetics and structure of the methanol and TFE dimers, as well as the higher polymers of these molecules. Thermal conductivity measurements have now been carried out on methanol¹ and TFE vapors. In this section we compare the experimental results with the theoretical calculations on the TFE dimer and previous calculations on methanol polymers.

The theoretical binding energies do not include differences in vibrational, rotational, and translational energies between the monomers and dimers which are included in the experimental enthalpies. However, the differences in the theoretical binding energies of the two dimers can be compared to the differences in the experimental enthalpies since the vibrational, rotational, and translational corrections should be about the same.

The structure of the methanol dimer has been previously optimized with the STO-3G basis set. It is predicted to have a linear hydrogen bond similar to the dimer between the trans TFE isomers with an OH...O hydrogen bond (structure II, Figure 3). The STO-3G binding energy of the methanol dimer is -6.15 kcal/mol³² using a standard experimental geometry²⁹ for the methanol monomer as was used in the case of the trifluoroethanol dimer. Del Bene⁶ has reported a binding energy of -5.57 kcal/mol using optimized geometries for the monomer. Both values are given to illustrate the dependence of the results on the monomer geometry that is used.

The most stable TFE dimer (structure IV, Figure 4) has a binding energy that is approximately 0.3-0.9 kcal/mol more negative (depending on the structure of the monomer in the methanol dimer) than that of the methanol dimer. The actual size of the increase in stability of the TFE dimer over that of the methanol dimer could be affected by several factors including (1) use of an experimental model geometry for TFE and (2) use of the minimal STO-3G basis set which tends to underestimate the H...F interaction energy.

Experimentally, the trifluoroethanol dimer has a larger negative enthalpy of association than the methanol dimer. Thermal conductivity measurements indicate that the $|\Delta H_2|$ for the methanol dimer is less than 4 kcal/mol.¹ Hence, the

Table VI. Energies of Dimers of 2,2,2-Trifluoroethanol (STO-3G)

Structure ^a	Energy, au	Binding energy kcal/mol
I	-889.019 63	-2.55
II	-889.024 76	-5.84
III	-889.022 70	-3.15
IV	-889.027 98	-6.46

^a Structures illustrated in Figures 3 and 4.

TFE dimer with a $|\Delta H_2|$ of 4.8 kcal/mol is more stable by at least 0.8 kcal/mol. The theoretical prediction that the TFE dimer is more stable by 0.3-0.9 kcal/mol is in reasonable agreement with the experimental results.

On the basis of the theoretical investigation of the structures of the methanol and TFE dimers, it can be concluded that the increase in stability of the TFE dimer is due to the presence of an extra H...F hydrogen bond which is formed in addition to the OH...O bond (structure IV, Figure 4). In the case of methanol, there is no possibility of an increase in stability due to formation of an extra hydrogen bond.

The theoretical binding energy of the TFE dimer is related to the experimental enthalpy of association by⁵

$$\Delta H_2 = \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot} + \Delta E_{tr} + \Delta(PV) \quad (25)$$

Assuming that each rotational and translational degree of freedom contributes $RT/2$ to the energy, eq 25 becomes

$$\Delta H_2 = \Delta E_{el} + \Delta E_{vib} - 4RT \quad (26)$$

where R is the gas constant. Since the vibrational frequencies of TFE and (TFE)₂ are not known, we have used the theoretical vibrational frequencies of the water dimer to obtain an approximate value of ΔE_{vib} as was done in ref 5 for the methanol dimer. This gives a value of 4.8 kcal/mol for ΔE_{vib} at 373 K. Hence, substituting this value of ΔE_{vib} and $\Delta E_{el} = -6.46$ kcal/mol into eq 26 gives a theoretical ΔH_2 of -4.6 kcal/mol for the most stable TFE dimer. This is in agreement with the experimental value of -4.75 kcal/mol.

The internal hydrogen bond in the TFE monomer and the cyclic structure determined for the dimer provide a possible explanation for the fact that only dimers are detected in TFE vapor as opposed to methanol and ethanol vapors where higher polymers such as tetramers are detected.^{1,33} The formation of higher polymers in the case of methanol is apparently facilitated by linear hydrogen bonds.⁵ However, in the case of TFE, the gauche isomer with an internal hydrogen bond forms a cyclic hydrogen bond in the dimer. Conversion of the gauche isomer to the trans isomer which forms a linear hydrogen bond in the dimer requires energy to break the internal hydrogen bond. If the higher polymers of TFE have linear hydrogen bonds, as in the case of methanol, the extra energy required to break the internal bonds would reduce the stability of the higher polymers. The other possibility is that higher polymers with cyclic dimerlike bonds could be formed, but it seems probable that formation of such structures would not be very favorable for steric reasons (see Figure 4b). Thus the intramolecular hydrogen bond in monomeric TFE and the cyclic structure it helps to stabilize in the dimer are possible explanations for only dimers being detected in thermal conductivity measurements of the vapor.

VI. Conclusions

The following conclusions concerning the polymers of 2,2,2-trifluoroethanol in the vapor phase can be made on the basis of these experimental and theoretical results:

(1) Dimers are the only associated species in TFE vapor between 338 and 385 K detectable by thermal conductivity measurements. The dimer is found to have an enthalpy of as-

sociation of -4753 cal/mol and an entropy of association of -18.73 cal/deg mol.

(2) Thermal conductivity measurements indicate that the trifluoroethanol dimer is more stable than the methanol dimer. Also, no higher polymers such as those found in the case of methanol and ethanol are found in trifluoroethanol vapor.

(3) The most stable dimer is predicted by ab initio calculations to be a cyclic structure involving the gauche-staggered isomer of trifluoroethanol. The increased stability over the methanol dimer is due to an extra hydrogen bond, $F\cdots H$, caused by the presence of the CF_3 group. This increase in stability is consistent with the experimental results.

(4) The presence of an intramolecular bond in the trifluoroethanol monomer could be the reason that higher polymers are not observed in trifluoroethanol vapor as they are in methanol and ethanol vapors.

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Appendix A

Heat transfer in a hot-wire cell is governed by the Fourier heat law given by eq 1, $\lambda = gQ/(T_2 - T_1)$. In this Appendix, it is shown that the thermal conductivity, λ , is a function of the voltage drop, V , across the cell wire when there is a constant current input, I .

In eq 1, there are three variables: g , Q , and T_2 , at any temperature, T_1 . The heat flux, Q , dissipated by the cell wire is given by

$$Q = IV \quad (27)$$

The wire temperature, T_2 , is given by

$$T_2 = aV/I + b \quad (28)$$

where a and b are constants determined experimentally. To a first approximation, g is dependent on the cell dimensions. However, owing to heat conduction through the cell ends and radiation loss, g is also a function of the wire temperature.

Substituting these expressions for g , Q , and T_2 into eq 1, one obtains

$$\lambda = \frac{g(T_2)IV}{aV/I + (b - T_1)} \quad (29)$$

Hence, since T_2 is determined from I and V , we see that λ is a function of V at constant I :

$$\lambda = f(V) \quad (30)$$

The functional form of eq 30 is determined experimentally. For the cell used in this study, λ in the range of interest was related to V by the equation

$$\lambda = \frac{B}{(V - A)} \quad (31)$$

where A and B are constants determined from calibration by the reference gases.

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