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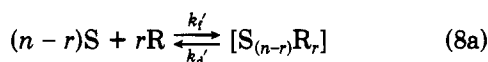
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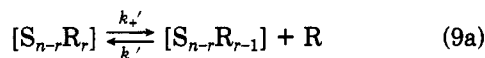
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order of microseconds.^{34,36-38}

Similar equilibria can be written by taking into account the presence of spin-probe molecule R



where $r = 1, 2, \dots$ with residence time τ_{R1}



with residence time of the probe in the micelle τ_{R2} .

The time scale of the ESR experiment allows one to follow process 9a, while process 8a does not influence the line shape. Thus, an ESR line shape analysis near the cmc allows the evaluation of τ_{R2} and these values can be compared with the exchange time $1/k_{-}$ reported for the surfactant monomers of SOS, SDS, and SHS.²⁸

The ESR line shape is determined by the relative rate of chemical exchange P_{exch} between bulk and micelle with respect to the separation between the ESR lines of the probe in both environments, $\delta\omega$ (in rad s^{-1}).³ Two extreme cases may occur:³⁹ (a) with P_{exch} very slow with respect to $\delta\omega$

$$P_{\text{exch}} \ll \delta\omega$$

two separate absorptions are observed; (b) with P_{exch} very fast with respect to $\delta\omega$

$$P_{\text{exch}} \gg \delta\omega$$

the observed spectrum is a weighted average of the signals of the probe in water and in the micelle.

In the intermediate region, the line width $1/T_2$ depends both on the relaxation time of the probe in water, $1/T_{2,0}$,

and on the exchange frequency:³⁹

$$1/T = 1/T_{2,0} + P_{\text{exch}}$$

The systems analyzed in this work are representative of the three cases: for SHS we have separate spectra, i.e., $P_{\text{exch}} \ll \delta\omega$; for SDS we do not observe separate spectra while the line width passes through a maximum near the cmc (Figure 4), i.e., $P_{\text{exch}} \cong \delta\omega$; finally, for SOS the line width increases regularly with the surfactant concentration, i.e., $P_{\text{exch}} \gg \delta\omega$. Table IV reports the $\delta\omega$ and τ_{R2} for the three systems, together with $1/k_{-}$ values reported by Aniansson et al.²⁸ and obtained from k_{-}/n and k_{-}/σ^2 measurements (σ being the distribution width of the aggregation number) in the same micellar solution without addition of spin probe.

As is seen, the monomer-micelle exchange time of the spin probe into SDS micelle equals the exchange time of SDS monomer into the same micelle. The exchange times of TM-Tempamine⁺ in SOS and SHS have the same trend as those of surfactant monomers. This fact was also observed by Nakagawa.⁴⁰

This fact, together with the finding that the same cmc values are obtained from ESR measurements as those obtained with other techniques, leads to the conclusion that very small perturbations on the properties of the micelles are introduced by the addition of small quantities of paramagnetic molecules.

Acknowledgment. We are indebted to Prof. E. Ferroni for the useful discussions during the elaboration of this paper. Thanks are also due to the Consiglio Nazionale delle Ricerche (CNR), Piani Finalizzati Chimica Fine e Secondaria, for financial support.

Registry No. SOS, 142-31-4; SDS, 142-87-0; SHA, 1120-01-0; T, 2226-96-2; TM-T⁺I⁻, 64525-01-5.

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Vapor Pressure Isotope Effects in Liquid Methyl Fluoride

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The vapor pressures of the isotopic methyl fluorides $^{12}\text{CH}_3\text{F}$, $^{12}\text{CD}_3\text{F}$, and $^{13}\text{CH}_3\text{F}$ have been measured at temperatures between 132.48 and 213.12 K by differential manometric techniques in a precision cryostat. Throughout the whole temperature range of the measurements, $P(^{12}\text{CH}_3\text{F}) > P(^{12}\text{CD}_3\text{F})$ and $P(^{12}\text{CH}_3\text{F}) < P(^{13}\text{CH}_3\text{F})$. The data are best represented by $T \ln(f_c/f_g) = (2225.2 \pm 7.4)/T - (4.444 \pm 0.046)$ for the D/H effect and by $T \ln(f_c/f_g) = (56.58 \pm 2.09)/T - (0.6383 \pm 0.0133)$ for the $^{13}\text{C}/^{12}\text{C}$ effect. A series of calculations using Wilson's GF matrix method and a modified Schachtschneider-Snyder program resulted in temperature-dependent internal-external interactions in the liquid phase: Presence of such interactions between the molecular translation in the direction of the molecular figure axis and the parallel normal modes ν_2 and ν_3 is a necessary requirement for satisfactory explanation of all isotopic vapor pressure and spectroscopic data of the liquid. The specific internal-external interactions found are consistent with the structure of CH_3F clusters obtained by ab initio molecular orbital calculations.

Introduction

The vapor pressure ratio of isotopic molecules is quite sensitive to intermolecular interactions in the condensed phases and to the perturbation of internal vibrational

motions of the molecule by these intermolecular interactions. Hence, the measurement of vapor pressure isotope effects (VPIE's) is a useful tool in obtaining information about intra- and intermolecular forces and molecular motions in condensed phases.¹⁻¹⁵ Various vapor pressure

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phenomena of isotopic molecules have been explained by the VPIE theory based on the simple cell model.^{16,17} The rather surprising success of the theory has been due to the fact that all configurational factors of the condensed-phase partition function are, within the framework of the Born–Oppenheimer approximation, invariant under isotopic substitution and thus cancel each other out^{18,19} in the isotopic reduced partition function ratio (RPFR), $(s/s')f$.

The VPIE's are measured most precisely by differential manometric techniques. In differential manometry, the ratio of the RPFR's of the two phases, f_c/f_g , f_c , and f_g being the RPFR's of the condensed and gas phases, respectively, is related to the vapor pressure ratio of isotopic species by the first-order approximation

$$\ln(f_c/f_g) = [1 + P'\{B - (V_c/RT)\}] \ln(P'/P) \quad (1)$$

where T is the absolute temperature, R is the gas constant, B is the second virial coefficient of the gas when the equation of state is written in the form

$$PV_c/RT = 1 + BP + \dots \quad (2)$$

V_c is the molar volume of the lighter isotopic species in the condensed phase, and P' and P are the vapor pressures of the lighter and heavier isotopic species, respectively. Under the approximations of Born–Oppenheimer, harmonic forces and the simple cell model description of the condensed phase, the RPFR is expressed as

$$\ln(s/s')f = \sum_i \delta \ln b(u_i) \quad (3)$$

where

$$\ln b(u) = u/2 - \ln u + \ln(1 - e^{-u}) \quad (4)$$

$$\delta \ln b(u_i) = \ln b(u_i') - \ln b(u_i) \quad (5)$$

in which $u_i = hc\omega_i/kT$, ω_i is the i th normal frequency, h is the Planck constant, c is the velocity of light, k is the Boltzmann constant, and the summation is taken over the appropriate degrees of freedom of the molecule. Normal frequencies are calculated by Wilson's GF matrix me-

thod,²⁰ using the geometry, masses of the constituent atoms, and the force field of the molecule. The internal forces of the gaseous molecule are usually well-known, which enables one to calculate the RPFR of the gas $\ln(s/s')f_g$ and, consequently, to deduce $\ln(s/s')f_c$ from the experimentally obtained $\ln(f_c/f_g)$ and, further, the force field of the molecule in the condensed phase.

In a previous study,¹⁵ we reported a differential manometric study on $^{13}\text{C}/^{12}\text{C}$ and deuterium/protium (D/H) VPIE's in liquid fluoroform using a precision cryostat,²¹ which incorporated several modifications over the cryostat designed and constructed by Bigeleisen, Brook, Ishida, and Ribnikar (BBIR).²² The VPIE data were consistent with the blue shift in the C–H stretching frequency of fluoroform upon condensation, which is due to a kinetic energy coupling between the C–H stretching motion and the molecular translation in the direction of the C–H bond, caused in large part by a weak but directional Coulombic interaction between hydrogen and fluorine atoms of neighboring molecules. The present work was undertaken to obtain information about intra- and intermolecular forces and intermolecular interactions in liquid methyl fluoride through $^{13}\text{C}/^{12}\text{C}$ and D/H VPIE measurements. In view of the similarity between methyl fluoride and fluoroform in the nature of the intermolecular interaction,^{23,24} it was interesting to see if some of the unique features found in fluoroform could also be found in methyl fluoride. Vapor pressure measurements were made on liquid $^{12}\text{CH}_3\text{F}$, $^{12}\text{CD}_3\text{F}$, and $^{13}\text{CH}_3\text{F}$.

Experimental Section

The cryostat, temperature and pressure measurements, and calibration and control have been described previously.^{15,21}

The sample purification procedure is a critical part of the whole experimental program in order to minimize the error in the VPIE data. For each of the isotopically labeled samples, approximately 1 dm³ of gas at 1 atm and room temperature was purchased or synthesized. The methyl fluoride sample of natural isotopic composition, denoted by $^{12}\text{CH}_3\text{F}$ and used as the reference for the differential vapor pressure measurements, was chemically 99.7% pure (500 ppm $^{12}\text{CO}_2$, 200 ppm $^{12}\text{CH}_3\text{Cl}$, 100 ppm H_2O , and about 0.2% of an unknown as the impurities) when purchased from Linde-Union Carbide Corp. (The stated levels of impurities are the ratios of the areas under the chromatographic peak.) The $^{12}\text{CD}_3\text{F}$ sample, obtained from Prochem Ltd., was 99.4% pure containing about 0.6% $^{12}\text{CO}_2$, 150 ppm $^{12}\text{CD}_3\text{Cl}$, 50 ppm H_2O , and 10 ppm of an unknown as the impurities. The sample of $^{13}\text{CH}_3\text{F}$ was prepared by a two-step synthesis starting with methanol- ^{13}C . The synthesis and purification of the $^{13}\text{CH}_3\text{F}$ sample has been described previously.²⁵ The process of purification of the $^{12}\text{CH}_3\text{F}$ and $^{12}\text{CD}_3\text{F}$ samples was identical with that of $^{13}\text{CH}_3\text{F}$, except that the use of Chromosorb was not required. The gas-chromatograph analysis of the final purified samples showed 5, 10, 10, and 10 ppm of CO_2 , CH_3Cl , H_2O , and the unknown impurity, respectively, in $^{12}\text{CH}_3\text{F}$; 5, 10, 10, and 1 ppm of CO_2 , CD_3Cl , H_2O , and the unknown impurity, respectively, in $^{12}\text{CD}_3\text{F}$; and

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TABLE I: $^{13}\text{C}/^{12}\text{C}$ Vapor Pressure Isotope Effect in Liquid Methyl Fluoride

T , K	P_r , torr	$\delta P = P_r - P_i$, torr	$T \ln f_c/f_g$, K	date (1980)	T , K	P_r , torr	$\delta P = P_r - P_i$, torr	$T \ln f_c/f_g$, K	date (1980)
132.48	3.712	-0.004 72	-0.205	10/06	155.44	46.311	-0.068 54	-0.2764	10/08
133.22	4.085	-0.005 68	-0.227	10/06	156.04	48.943	-0.071 24	-0.2740	10/02
133.22	4.085	-0.006 30	-0.250	10/06	156.66	51.751	-0.079 36	-0.2931	10/08
133.60	4.314	-0.005 45	-0.204	10/13	157.25	54.512	-0.078 52	-0.2722	10/02
133.60	4.328	-0.006 19	-0.233	10/13	157.87	57.585	-0.089 58	-0.2983	10/08
133.84	4.460	-0.007 54	-0.274	10/13	158.59	61.298	-0.090 75	-0.2846	10/02
133.85	4.459	-0.006 07	-0.223	10/13	159.85	68.433	-0.101 43	-0.2850	10/02
134.00	4.529	-0.007 33	-0.263	10/06	161.17	76.595	-0.113 88	-0.2896	10/02
134.03	4.565	-0.006 78	-0.243	10/13	162.48	85.401	-0.127 47	-0.2937	10/02
134.78	4.988	-0.006 31	-0.208	10/06	163.13	90.232	-0.136 35	-0.2964	09/23
135.30	5.323	-0.006 49	-0.201	10/06	163.75	94.956	-0.142 80	-0.2972	10/02
135.59	5.572	-0.008 46	-0.252	10/14	164.64	102.09	-0.152 16	-0.2914	09/23
135.59	5.572	-0.009 16	-0.273	10/14	165.17	106.34	-0.162 78	-0.2992	09/24
135.71	5.608	-0.006 51	-0.192	10/06	165.68	110.72	-0.166 26	-0.2882	10/02
136.23	5.988	-0.007 88	-0.219	10/06	166.20	115.37	-0.170 91	-0.2946	09/23
137.03	6.605	-0.009 37	-0.238	10/07	167.16	124.28	-0.190 32	-0.3073	09/24
137.30	6.838	-0.008 68	-0.213	10/15	167.37	126.34	-0.190 89	-0.3026	10/02
137.34	6.898	-0.008 73	-0.211	10/15	168.68	139.59	-0.214 35	-0.3047	09/24
137.95	7.392	-0.010 41	-0.2364	10/07	169.47	148.29	-0.226 59	-0.3154	10/08
138.06	7.509	-0.011 37	-0.2552	10/10	170.17	156.34	-0.240 24	-0.3133	09/24
138.14	7.569	-0.011 18	-0.2489	10/10	170.98	165.92	-0.256 53	-0.3088	10/08
138.25	7.678	-0.011 54	-0.2521	10/10	171.67	174.56	-0.268 7	-0.3181	09/24
138.42	7.846	-0.009 21	-0.1977	10/14	173.17	194.55	-0.299 4	-0.3194	09/24
138.82	8.201	-0.012 17	-0.2514	10/07	174.54	214.52	-0.332 3	-0.3208	09/24
139.35	8.733	-0.012 63	-0.2448	10/07	174.88	219.72	-0.337 6	-0.3232	09/24
139.82	9.262	-0.011 82	-0.2169	10/15	176.26	241.78	-0.371 9	-0.3217	09/25
139.96	9.409	-0.011 39	-0.2065	10/15	177.95	271.48	-0.416 4	-0.3198	09/25
140.34	9.834	-0.014 86	-0.2588	10/07	179.19	294.83	-0.447 6	-0.3251	10/02
140.84	10.444	-0.012 92	-0.2134	10/15	179.65	304.05	-0.466 7	-0.3298	09/25
141.34	11.018	-0.016 67	-0.2653	10/07	181.20	336.56	-0.514 7	-0.3257	10/02
141.74	11.555	-0.013 97	-0.2090	10/15	181.37	340.24	-0.522 7	-0.3349	09/25
141.89	11.747	-0.013 57	-0.2058	10/15	183.02	378.15	-0.580 2	-0.3323	09/25
142.34	12.310	-0.011 98	-0.1689	10/07	184.16	405.98	-0.624 2	-0.3376	09/25
142.34	12.326	-0.020 16	-0.2950	10/07	184.79	422.45	-0.648 1	-0.3356	09/25
142.43	12.465	-0.017 06	-0.2363	10/10	185.89	451.84	-0.692 1	-0.3396	09/25
142.58	12.644	-0.015 55	-0.2058	10/10	187.56	500.11	-0.768 0	-0.3396	09/25
142.62	12.706	-0.013 05	-0.1776	10/07	188.54	529.77	-0.810 2	-0.3386	10/08
143.17	13.487	-0.016 78	-0.2066	10/15	189.28	553.15	-0.850 1	-0.3413	09/25
143.63	14.193	-0.017 19	-0.2092	10/07	190.24	585.37	-0.900 0	-0.3426	10/09
144.13	14.998	-0.019 92	-0.2221	10/16	190.97	610.25	-0.938 4	-0.3442	09/25
144.25	15.185	-0.018 95	-0.2195	10/16	192.75	675.46	-1.042 2	-0.3496	09/25
144.75	16.010	-0.020 81	-0.2308	10/07	194.85	759.89	-1.177 2	-0.3518	09/25
145.34	17.045	-0.023 58	-0.2485	10/16	196.17	815.85	-1.239 3	-0.3430	10/02
145.86	18.021	-0.024 58	-0.2360	10/07	196.73	841.31	-1.317 3	-0.3550	09/25
146.40	19.068	-0.027 43	-0.2612	10/16	197.97	898.83	-1.369 2	-0.3489	10/02
146.52	19.283	-0.025 93	-0.2401	10/16	198.75	936.57	-1.425 0	-0.3479	10/09
146.95	20.169	-0.028 52	-0.2568	10/07	199.95	998.08	-1.521 0	-0.3507	10/02
147.54	21.464	-0.030 75	-0.2504	10/16	200.87	1046.9	-1.606 5	-0.3528	10/03
148.04	22.618	-0.032 39	-0.2544	10/07	201.97	1106.6	-1.693 5	-0.3558	10/03
148.61	23.982	-0.031 97	-0.2408	10/01	202.66	1145.6	-1.708 8	-0.3444	10/09
149.34	25.830	-0.035 60	-0.2527	10/16	202.85	1157.8	-1.789 5	-0.3610	10/03
149.72	26.831	-0.037 81	-0.2506	10/01	204.86	1279.6	-1.953 6	-0.3466	10/03
150.82	29.926	-0.043 07	-0.2629	10/01	205.57	1324.1	-1.936 5	-0.3533	10/09
151.92	33.269	-0.047 81	-0.2602	10/01	206.85	1408.8	-2.202 0	-0.3665	10/03
153.02	36.974	-0.053 55	-0.2709	10/01	207.75	1471.4	-2.294 4	-0.3676	10/09
153.57	38.917	-0.054 77	-0.2630	10/01	208.83	1548.0	-2.455 5	-0.3656	10/03
154.15	41.081	-0.059 87	-0.2727	10/01	209.85	1622.7	-2.565 6	-0.3787	10/09
154.84	43.863	-0.064 90	-0.2779	10/02	211.13	1724.5	-2.771	-0.3847	10/03

10, 10, 5, and 15 ppm of $^{13}\text{CO}_2$, $^{13}\text{CH}_3\text{Cl}$, H_2O , and the unknown impurity, respectively, in $^{13}\text{CH}_3\text{F}$.

The isotopic composition of the purified methyl fluoride samples was determined by using a Kratos MS 30 dual-beam mass spectrometer with DS 50 data base system. The results of the mass-spectroscopic analysis were corrected for relative intensities²⁶ of peaks. The isotopic composition of the three labeled samples are as follows. The reference sample consists of 98.48% $^{12}\text{CH}_3\text{F}$ and 1.52% $^{13}\text{CH}_3\text{F}$. The carbon-13-labeled sample consists of 83.28% $^{13}\text{CH}_3\text{F}$ and 16.72% $^{12}\text{CH}_3\text{F}$. The deuterated sample consists of 97.41% $^{12}\text{CD}_3\text{F}$, 1.15% $^{12}\text{CHD}_2\text{F}$, 0.60%

$^{13}\text{CD}_3\text{F}$, 0.59% $^{12}\text{CH}_2\text{DF}$, and 0.25% $^{12}\text{CH}_3\text{F}$.

Results and Discussion

The VPIE measurements were made at temperatures between 132.48 and 213.12 K. The results for the carbon and hydrogen VPIE measurements are summarized in Tables I and II, respectively. The absolute temperature, T , and pressure, P_r , were obtained by the methods described previously.¹⁵ P_r and P_i refer to the observed vapor pressures of the reference ($^{12}\text{CH}_3\text{F}$) and isotopic ($^{12}\text{CD}_3\text{F}$ or $^{13}\text{CH}_3\text{F}$) samples, respectively, but differ from the isotopic vapor pressures, P' and P , of eq 1 in that P_r and P_i are the total observed pressures of the mixtures of isotopic species. Each $T \ln f_c/f_g$ datum was obtained by correcting for the presence of the isotopic impurities

(26) American Petroleum Institute, "Mass Spectral Data", Carnegie Institute of Technology, Pittsburgh, PA, 1953.

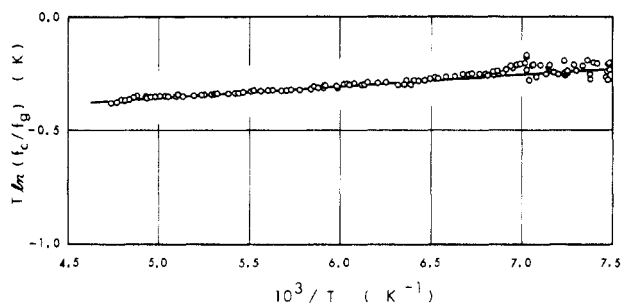


Figure 1. $T \ln f_c/f_g$ vs. $1/T$ for $^{13}\text{C}/^{12}\text{C}$ VPiE: The solid line has been computed from the F matrices on Tables IV, VII, and VIII.

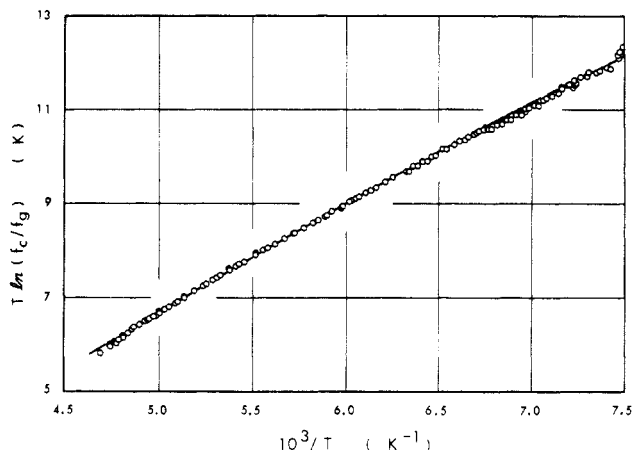


Figure 2. $T \ln f_c/f_g$ vs. $1/T$ for D/H VPiE: The solid line has been computed from the F matrices of Tables IV, VII, and VIII.

using Raoult's law and the rule of the geometric means of isotopic vapor pressures for the mixed isotopic species, gas nonideality and liquid molar volume using Zwolinski's virial coefficient data,²⁷ and the condensed-phase molar volume data of Grosse et al.²⁸

In Figures 1 and 2 are shown the plots of $T \ln f_c/f_g$ vs. $1/T$ for the carbon and the hydrogen VPiE's, respectively. Over the entire temperature range of our measurements the deuterium/protium (D/H) VPiE is normal, i.e., $P'(^{12}\text{CH}_3\text{F}) > P(^{12}\text{CD}_3\text{F})$, while the $^{13}\text{C}/^{12}\text{C}$ VPiE is inverse, i.e., $P'(^{12}\text{CH}_3\text{F}) < P(^{13}\text{CH}_3\text{F})$. The least-squares-fit coefficients for the functional form

$$T \ln(f_c/f_g) = A/T + B \quad (6)$$

are as follows: For the D/H effect, $A = 2225.2 \pm 7.4$ and $B = -4.444 \pm 0.046$ and, for the $^{13}\text{C}/^{12}\text{C}$ effect, $A = 56.58 \pm 2.09$ and $B = -0.6383 \pm 0.0133$. A fit of $T \ln f_c/f_g$ to a three-term form, $A/T + B + CT$, yielded a similar degree of goodness. Interpretation of these coefficients along the conventional lines, i.e., A being the contribution of the lattice vibrations and hindered molecular rotations via the first quantum correction, and B the isotope effect in the zero-point energy shift upon condensation, should be made carefully. In fact, as will conclude later, the observed VPiE's cannot be explained without considering temperature-dependent rotational force constants and temperature-dependent interactions between internal vibrations and the lattice vibration along the molecular figure axis of methyl fluoride. As such, the values of A and B obtained here do not have the conventional meaning.

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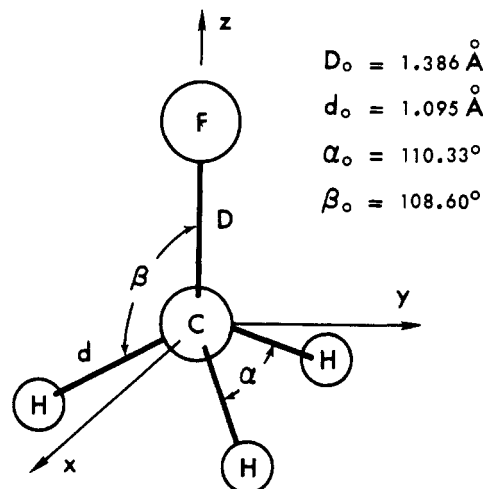


Figure 3. Equilibrium geometry and valence coordinates of methyl fluoride.

The remainder of the present discussion will be devoted to substantiating the conclusions mentioned above.

Before proceeding further we note the least-squares-fit parameters obtained for natural-abundance methyl fluoride, P_r , for the functional form

$$\log P(\text{torr}) = A - B/[C + t(^{\circ}\text{C})] \quad (7)$$

are $A = 7.09204$, $B = 741.597$, and $C = 254.381$. The average deviation is 0.07% over the entire temperature range studied. Our least-squares-fit coefficients compare reasonably well with Zwolinski's tabulation.²⁷ His values are $A = 7.11232$, $B = 745.52$, and $c = 254.51$ over the pressure range of 0.004 ~ 10 torr and $A = 7.09761$, $B = 740.218$, and $C = 253.89$ over the range of 10 ~ 1500 torr. The average absolute deviation of vapor pressure values computed from the Zwolinski equations over our temperature range are 1.40% below 10 torr and 0.58% between 10 and 1500 torr.

The VPiE results obtained for liquid methyl fluoride are similar to those found in liquid fluoroform¹⁵ and just the opposite to those found in liquid methane.²⁹⁻³¹ We note that the difference in the VPiE's between fluoroform and methane was qualitatively explained on the basis of the blue and red shifts in the C-H stretching normal frequencies upon condensation,¹⁵ respectively. For methyl fluoride, the ν_4 frequency has been reported at 3006 cm^{-1} for gaseous $^{12}\text{CH}_3\text{F}$ and at 3030 cm^{-1} for liquid $^{12}\text{CH}_3\text{F}$.³² A detailed and quantitative analysis of the VPiE's in methyl fluoride, however, reveals a more complicated situation.

To quantitatively explain the present VPiE data and published spectroscopic results we used the simple cell model and Wilson's FG-matrix method. For the latter a modified version of the Schachtschneider and Snyder program was used,³³ and the G matrices (see paragraph at end of text regarding supplementary material) were calculated by using the equilibrium geometry^{34,35} and the

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TABLE II: D/H Vapor Pressure Isotope Effect in Liquid Methyl Fluoride

T, K	$P_r, \text{ torr}$	$\delta P = P_r - P_i, \text{ torr}$	$T \ln f_c/f_g, K$	date (1980)	T, K	$P_r, \text{ torr}$	$\delta P = P_r - P_i, \text{ torr}$	$T \ln f_c/f_g, K$	date (1980)
132.48	3.712	0.3255	12.41	10/06	156.04	48.943	2.970	9.899	10/02
133.22	4.085	0.3510	12.22	10/06	156.66	51.751	3.096	9.790	10/08
133.60	4.314	0.3731	12.34	10/13	157.25	54.512	3.254	9.802	10/02
133.60	4.328	0.3730	12.29	10/13	157.87	57.585	3.383	9.677	10/08
133.84	4.460	0.3805	12.18	10/13	158.59	61.298	3.585	9.673	10/02
133.85	4.459	0.3819	12.23	10/13	159.85	68.433	3.932	9.566	10/02
134.00	4.529	0.3837	12.11	10/06	161.17	76.595	4.319	9.453	10/02
134.03	4.565	0.3884	12.16	10/13	162.48	85.401	4.729	9.346	10/02
134.78	4.988	0.4126	11.88	10/06	163.13	90.232	4.943	9.276	09/23
135.30	5.323	0.4403	11.92	10/06	163.75	94.956	5.164	9.237	10/02
135.71	5.608	0.4592	11.83	10/06	164.64	102.09	5.472	9.158	09/23
136.23	5.988	0.4873	11.80	10/06	165.17	106.34	5.656	9.105	09/24
136.82	6.459	0.5248	11.83	10/14	165.68	110.72	5.865	9.093	10/02
137.03	6.605	0.5318	11.73	10/07	166.20	115.40	6.058	9.029	09/23
137.67	7.174	0.5740	11.71	10/14	167.16	124.28	6.435	8.951	09/24
137.95	7.392	0.5867	11.64	10/07	167.37	126.34	6.539	8.952	10/02
138.04	7.492	0.5955	11.66	09/29	168.68	139.59	7.081	8.839	09/24
138.06	7.509	0.5913	11.55	10/10	169.47	148.29	7.446	8.763	10/08
138.14	7.569	0.5953	11.54	10/10	170.17	156.34	7.773	8.709	09/24
138.25	7.678	0.6021	11.51	10/10	170.98	165.92	8.159	8.651	10/08
138.42	7.846	0.6181	11.58	10/14	171.67	174.56	8.509	8.593	09/24
138.42	7.851	0.6207	11.63	10/14	173.17	194.55	9.297	8.494	09/24
138.82	8.201	0.6434	11.56	10/07	174.54	214.52	10.065	8.383	09/24
139.11	8.503	0.6626	11.51	09/29	174.88	219.72	10.266	8.368	09/24
139.35	8.733	0.6792	11.50	10/07	176.26	241.78	11.091	8.262	09/25
139.73	9.159	0.7069	11.44	09/29	177.95	271.48	12.177	8.140	09/25
139.96	9.409	0.7108	11.50	10/15	179.19	294.83	13.029	8.060	10/02
140.11	9.588	0.7336	11.37	09/29	179.65	304.05	13.341	8.016	09/25
140.34	9.834	0.7510	11.36	10/07	181.20	336.56	14.487	7.917	10/02
140.72	10.294	0.7810	11.314	09/30	181.37	340.24	14.604	7.895	09/25
141.34	11.018	0.8289	11.251	10/07	183.02	378.15	15.885	7.782	09/25
141.72	11.537	0.8622	11.212	09/30	184.16	405.98	16.812	7.703	09/25
142.34	12.310	0.9078	11.111	10/07	184.79	422.45	17.349	7.659	09/25
142.34	12.326	0.9132	11.158	10/07	185.89	451.84	18.300	7.584	09/25
142.62	12.706	0.9351	11.105	10/07	187.56	500.11	19.833	7.470	09/25
142.75	12.874	0.9483	11.121	09/30	188.54	529.77	20.748	7.406	10/08
143.17	13.487	0.9843	11.058	10/15	189.28	553.15	21.480	7.361	09/25
143.63	14.193	1.0284	11.008	10/07	190.24	585.37	22.437	7.291	10/09
143.71	14.350	1.0419	11.031	09/30	190.97	610.25	23.202	7.249	09/25
144.13	14.998	1.0728	10.893	10/16	192.75	675.46	25.107	7.128	09/25
144.25	15.185	1.0848	10.888	10/16	194.85	759.89	27.490	6.985	09/25
144.75	16.010	1.1409	10.894	10/07	196.17	815.85	29.065	6.909	10/02
144.75	16.043	1.1469	10.920	09/30	196.73	841.31	29.745	6.868	09/25
145.34	17.045	1.1988	10.789	10/16	197.97	898.83	31.323	6.793	10/02
145.85	18.015	1.2684	10.841	09/30	198.75	936.57	32.299	6.738	10/09
145.86	18.021	1.2624	10.785	10/07	199.06	951.40	32.612	6.702	09/25
146.40	19.068	1.3209	10.694	10/16	199.95	998.08	33.922	6.662	10/02
146.52	19.283	1.3371	10.712	10/16	200.87	1045.7	35.093	6.597	09/25
146.93	20.163	1.3983	10.739	09/30	200.87	1046.9	35.171	6.608	10/03
146.95	20.169	1.3914	10.682	10/07	201.97	1106.6	36.698	6.537	10/03
147.54	21.464	1.4640	10.601	10/16	202.66	1145.6	37.691	6.499	10/09
148.04	22.618	1.5348	10.580	10/07	202.85	1157.8	37.944	6.466	10/03
148.04	22.633	1.5417	10.622	09/30	204.18	1236.1	39.769	6.382	09/26
148.61	23.982	1.6248	10.594	10/01	204.86	1279.6	40.940	6.362	10/03
149.15	25.304	1.6959	10.537	09/30	205.57	1324.1	42.100	6.324	10/09
149.72	26.831	1.7835	10.468	10/01	205.95	1348.3	42.415	6.259	09/26
150.24	28.226	1.8603	10.405	09/30	206.85	1408.8	43.950	6.216	10/03
150.82	29.926	1.9566	10.356	10/01	207.75	1470.3	45.239	6.144	09/26
151.37	31.510	2.0469	10.320	09/30	207.75	1471.4	45.425	6.167	10/09
151.92	33.269	2.1411	10.260	10/01	208.83	1548.0	47.092	6.095	10/03
153.02	36.974	2.3424	10.162	10/01	209.52	1602.8	48.083	6.019	09/26
153.57	38.917	2.4558	10.157	10/01	209.85	1622.7	48.723	6.025	10/09
154.15	41.081	2.5584	10.052	10/01	211.13	1724.5	50.920	5.940	10/03
154.84	43.863	2.706	9.998	10/02	211.33	1738.9	51.184	5.916	09/26
155.44	46.311	2.824	9.914	10/08	213.12	1887.1	54.255	5.812	09/26

valence coordinate system shown in Figure 3. The F matrices were fitted by the method of partial derivatives described in a previous paper.¹⁵

The F matrix for the gas phase tabulated in Table III was obtained by a modification of Aldous and Mills' F

matrix.³⁶ The matrix of Table III accounts for Duncan's Fermi resonance correction³⁷ on ν_1 of $^{12}\text{CH}_3\text{F}$ and $^{13}\text{CH}_3\text{F}$ due to the triad of ν_1° , $2\nu_2^\circ$, and $2\nu_5^\circ$ and the similar Fermi resonance correction on ν_1 of $^{12}\text{CD}_3\text{F}$ between ν_1° and $2\nu_5^\circ$.

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TABLE III: F Matrix of Gaseous Methyl Fluoride^a

diagonals			off-diagonals	
description	notation	value, mdyn Å ⁻¹	notation	value, mdyn Å ⁻¹
C-H stretch	f_d	4.686	f_{dd}	-0.036
C-F stretch	f_D	5.662	f_{dD}	0.502
HCH bend	f_α	0.408	$f'_{d\alpha}$	-0.125
HCF bend	f_β	0.617	$f_{d\alpha}$	-0.225
			$f_{D\alpha}$	-0.258
			$f_{\alpha\alpha}$	-0.054
			$f'_{d\beta}$	0.118
			$f_{d\beta}$	0.015
			$f_{D\beta}$	0.258
			$f'_{\alpha\beta}$	-0.143
			$f_{\alpha\beta}$	-0.119
			$f_{\beta\beta}$	-0.144

^a All bending coordinates are weighted by the equilibrium C-H bond length. An F-matrix element with one subscript is a diagonal element. When two off-diagonal elements are listed to a similar interaction, e.g., $f_{d\alpha}$ and $f'_{d\alpha}$, the one without a prime refers to the interaction between two coordinates which share a common C-H bond, while the one with a prime refers to the interaction between two coordinates which do not share a common C-H bond.

TABLE IV: Observed and Calculated Frequencies of Gaseous Methyl Fluoride

mode	exptl, ^a cm ⁻¹	calcd, cm ⁻¹	
		Aldous and Mills ^b	this work

¹² CH ₃ F			
$\nu_1(A_1)^c$	2910	2924.7	2909.790
$\nu_2(A_1)$	1460	1469.4	1462.627
$\nu_3(A_1)$	1049	1059.6	1056.809
$\nu_4(E)$	3006	3028.4	3006.715
$\nu_5(E)$	1467	1468.7	1479.265
$\nu_6(E)$	1182	1178.7	1183.019

¹² CD ₃ F			
$\nu_1(A_1)^c$	2110	2112.8	2112.031
$\nu_2(A_1)$	1135	1131.5	1131.511
$\nu_3(A_1)$	992	994.5	982.646
$\nu_4(E)$	2259	2243.9	2258.930
$\nu_5(E)$	1071	1069.9	1057.561
$\nu_6(E)$	911	901.8	909.564

¹³ CH ₃ F			
$\nu_1(A_1)^c$	2906	2920.4	2904.568
$\nu_2(A_1)$	1455	1463.9	1456.819
$\nu_3(A_1)$	1027	1038.2	1036.048
$\nu_4(E)$	2995	3017.5	2992.344
$\nu_5(E)$	1465	1465.7	1478.275
$\nu_6(E)$	1174	1171.0	1175.123

^a Consensus of best values of fundamental frequencies from several authors.^{34,37-44} ^b Reference 36. ^c Corrected for Fermi resonance.

No evidence was found linking the third transition $2\nu_2^\circ$ with the resonance; $2\nu_2$ was observed in the solid phase only.³⁷ The resonance interaction parameter, $W_{155} = 27.5$ cm⁻¹, for the gaseous ¹²CD₃F yields the calculated frequencies within ± 0.5 cm⁻¹ of the experimental data. In Table IV the observed frequencies of gaseous methyl fluoride^{34,37-44} are compared with the frequencies calculated

TABLE V: Fermi Resonance Correction of Liquid ¹²CH₃F and ¹²CD₃F Frequencies

mode	$\nu_{\text{obsd}},^a$ cm ⁻¹	$\nu_{\text{unperturbed}},^b$ cm ⁻¹	$\nu_{\text{calcd}},^b$ cm ⁻¹
¹² CH ₃ F			
ν_1	2971	2915.0	2971.1
$2\nu_5$	2864	2920.0	2863.9
¹² CD ₃ F			
ν_1	2145	2107.0	2145.0
$2\nu_5$	2088	2126.5	2088.5

^a Reference 32. ^b This work.

TABLE VI: Internal Elements of F Matrix for Liquid Methyl Fluoride^a

diagonals		off-diagonals	
notation	value, mdyn Å ⁻¹	notation	value, mdyn Å ⁻¹
f_d	4.791	f_{dd}	-0.035
f_D	5.098	f_{Dd}	0.515
f_α	0.407	$f'_{d\alpha}$	-0.185
f_β	0.602	$f_{d\alpha}$	-0.125
		$f_{D\alpha}$	-0.260
		$f_{\alpha\alpha}$	-0.056
		$f'_{d\beta}$	0.094
		$f_{d\beta}$	0.021
		$f_{D\beta}$	0.260
		$f'_{\alpha\beta}$	-0.138
		$f_{\alpha\beta}$	-0.112
		$f_{\beta\beta}$	-0.149

^a See the footnote of Table III for the explanation of the internal coordinates.

TABLE VII: External and Internal-External Interaction Elements of F Matrix for Liquid Methyl Fluoride

element	value, ^a mdyn Å ⁻¹ or mdyn Å
f_{T_x}, f_{T_y}	0.120
f_{T_z}	0.300
f_{R_x}, f_{R_y}	$8.1527 \times 10^{-2} - (6.3040 \times 10^{-4})\Delta + (3.6677 \times 10^{-6})\Delta^2$
f_{R_z}	$f_{R_x}/8$
f_{DT_z}	$9.4169 \times 10^{-2} + (1.0788 \times 10^{-3})\Delta + (1.6879 \times 10^{-5})\Delta^2$
$f_{\beta T_z}$	$1.2045 \times 10^{-1} + (7.1425 \times 10^{-4})\Delta + (1.4527 \times 10^{-6})\Delta^2$
$f_{\alpha T_z}$	$-f_{\beta T_z}$

^a All elements are in units of mdyn Å⁻¹ except f_R 's, which are in units of mdyn Å. $\Delta \equiv T - 153$.

from the F matrix of Table III and the frequencies computed by Aldous and Mills. It is noted that our gaseous F matrix is generally in better agreement with experimental values. The calculated frequencies are listed to three decimal places in order to provide reproducibility in isotope-effect calculations to the appropriate precision.

The F matrix for the liquid phase was formulated to reproduce not only the available spectroscopic data for liquid methyl fluoride^{32,45,46} but also the present VPIE data. The observed ν_1 for the liquid ¹²CH₃F and ¹²CD₃F were corrected for the ($\nu_1^\circ, 2\nu_5^\circ$) Fermi resonance based on the data of Chao and Eggers.³² The resonance parameter obtained, $W_{155} = 43.5$ cm⁻¹, yielded the results tabulated in Table V. The construction of the liquid F matrix was started by first adding on the external force constants to

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TABLE VIII: Internal and External Frequencies (cm^{-1}) for Liquid Methyl Fluoride

mode	$^{12}\text{CH}_3\text{F}$				$^{12}\text{CD}_3\text{F}$		$^{13}\text{CH}_3\text{F}$, calcd ^d
	Chao ^a	Griffiths ^b	Gerschel ^c	calcd ^d	exptl ^a	calcd ^d	
ν_1 (A_1) ^e	2915	2912		2915.048	2107	2108.581	2910.584
ν_2 (A_1)		1456		1456.997	1112	1112.672	1450.702
ν_3 (A_1)	990	993.1		995.121	959	953.739	974.554
ν_4 (E)	3030	3021.3		3030.290	2272	2271.773	3016.366
ν_5 (E)	1468	1491 (?)		1480.227	1073	1060.658	1478.980
ν_6 (E)	1180	1179		1181.726	909	908.672	1173.827
T_x				77.382		70.582	76.099
T_y				77.382		70.582	76.099
T_z				86.608		81.857	85.455
R_x			83	83.788		78.717	82.848
R_y			83	83.788		78.717	82.848
R_z				72.890		51.561	72.890

^a Reference 32. ^b Reference 45. ^c Reference 46. ^d Calculated by using the liquid F matrix at $T = 153$ K. ^e Corrected for the Fermi resonance.

the F matrix of the gas phase and then introducing internal-external interaction elements and modification of internal force constants as required. The final F matrix for the liquid is given in Tables VI and VII. This F matrix best reproduces the observed frequencies of liquid methyl fluorides and the VPIE data among all the F matrices that were tested. Although the final F matrix is not unique, we believe there is little, if any, room for improvement.

The temperature-dependent force constants shown in Table VII were formulated to reproduce a set of rotational frequencies, $\nu_{R_i} = \nu_{R_i}$ observed in the far-IR region⁴⁶ at six temperatures, determining f_{R_i} ($=f_{R_i}$), and to yield acceptable agreement between the observed VPIE data and those calculated from the resulting F matrix. The rotational force constants determined in order to reproduce the experimental frequencies⁴⁶ at $T = 210, 200, 180, 165, 153$, and 140 K were fitted by least-squares to the functional form

$$f_{ij} = A(T - 153)^2 + B(T - 153) + C \quad (8)$$

where A, B, and C are adjustable parameters. The temperature of 153 K was chosen as the reference temperature for this purpose because the liquid frequency data of Chao and Eggers³² were obtained at this temperature. The value of f_{R_i} was somewhat arbitrarily set equal to one-eighth of those of f_{R_i} and f_{R_i} .

The most difficult problem we encountered was that of reproduction of the VPIE data and, in particular, the steep slope of the D/H effect (cf. Figure 2). As Figures 4 and 5 illustrate, any temperature-independent liquid F matrix we tried yielded a plot which is too flat for the D/H effect while producing a plot which is too steep for the $^{13}\text{C}/^{12}\text{C}$ effect. Variations of the translational force constants which yield the lattice frequencies within reason, e.g., $\leq 100 \text{ cm}^{-1}$, did not significantly change the slope of the D/H VPIE plot. In the absence of experimental data, the large values of f_T of Table VII were chosen arbitrarily, but they yield frequencies of reasonable value. The magnitude of f_T will be later justified in terms of an intermolecular interaction of a quasi-hydrogen-bond type. The value of f_T obtained here for the condensed phase at these cryogenic temperatures is not unreasonable in comparison with the magnitude for the force constant obtained from the second virial coefficient⁴⁷ for the gas phase at temperatures between 298 and 423 K. The latter is about one-tenth the magnitude of our f_T and corresponds to an interaction of a pair of molecules at elevated temperatures. Thus, in order to reproduce the VPIE data, the introduction of the

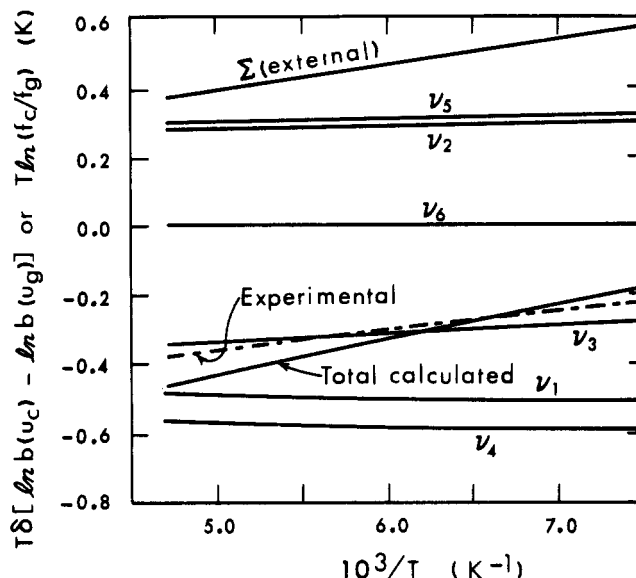


Figure 4. Contributions of individual normal modes and external motions to $T \ln f_c/f_g$ for $^{13}\text{C}/^{12}\text{C}$ VPIE: All calculated contributions were obtained by using the liquid F matrix at 153 K.

temperature dependence in the rotational force constants, and some internal-external interaction constants, was found essential.

It can be shown for the D/H VPIE plot that (i) the most significant contribution to the steep slope is provided by the temperature dependencies of $f_{\alpha T_i}$ and $f_{\beta T_i}$ through their effects on the CH_3 symmetric deformation (ν_2) mode, and (ii) the temperature dependence of f_{DT_i} has a significant effect on the C-F stretching (ν_3) mode but which is counteracted by the effect on ν_2 . For the $^{13}\text{C}/^{12}\text{C}$ VPIE the change comes from the temperature dependence of f_{DT_i} , through its effect on ν_3 , and those of $f_{\alpha T_i}$ and $f_{\beta T_i}$ through their effects on ν_2 . The temperature-dependent interaction force constants listed in Table VII were obtained by using the procedures similar to that used for obtaining the rotational force constants. The only difference in the procedure is the type of experimental, temperature-dependent, data fitted to: Here, the data are those of the VPIE.

The choice of f_T has profound effects on the optimum magnitudes of f_{DT_i} , $f_{\alpha T_i}$, and $f_{\beta T_i}$. For instance, a change in f_T from 0.3 to $0.2 \text{ mdyne } \text{\AA}^{-1}$ makes a 40% change in f_{DT_i} , and a few percent change in $f_{\alpha T_i}$ ($=-f_{\beta T_i}$) necessary to reproduce all experimental data. However, the conclusions of the preceding paragraph are generally valid at all values of f_T , tested in the range $0.1 \leq f_T \leq 0.5 \text{ mdyne } \text{\AA}^{-1}$.

(47) R. J. Lunbeck and C. A. Ten Seldam, *Physica*, 17, 788 (1951).

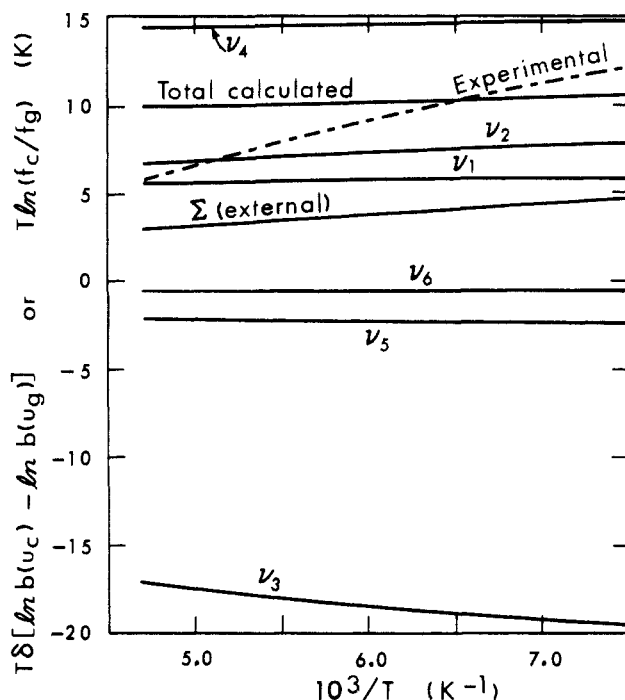


Figure 5. Contributions of individual normal modes and external motions to $T \ln f_c/f_g$ for D/H VPIE: All calculated contributions were obtained by using the liquid F matrix at 153 K.

The solid lines in Figures 1 and 2 have been computed by using the F matrices of Tables III, VI, and VII. The agreement between experimental and calculated results is excellent. In Table VIII the observed internal and external frequencies of liquid molecules are compared with the frequencies calculated by using the F matrix of Tables VI and VII at $T = 153$ K, the temperature at which Chao and Eggers' data were obtained.

The effect of f_{DT_z} on the carbon isotope effect is most significant simply because this interaction directly influences the motion of the isotopically substituted (carbon) atoms. In the ν_2 vibration the carbon and three hydrogen atoms move symmetrically, which in fact explains the dominance of the temperature dependence of this mode in both isotope effects. In contrast, all internal-external interactions involving the external modes other than T_z , i.e., T_x , T_y , R_x , R_y , and R_z , and perpendicular internal modes were found ineffective. We have been convinced

that the interactions involving T_z are the only ones with which the present VPIE data can be reproduced throughout our experimental temperature range. This implies that there is a definite directional intermolecular interaction in liquid methyl fluoride.

The existence of a directional intermolecular interaction among methyl fluoride molecules is supported by recent ab initio MO calculations on methyl fluoride clusters²⁴ using the Gaussian-70 algorithm with the STO-3G minimal basis set. It has been found from the calculations that the major cause of stability of methyl fluoride clusters is the Coulombic attraction between hydrogen and fluorine atoms belonging to separate molecules, which is best characterized as a weak or quasi-hydrogen bond: The most stable intermolecular geometry is practically independent of cluster sizes, i.e., the C-H...F angle of 180° , the H...F distance of 2.1 Å, and the H...F-C angle slightly greater than 120° . In addition, the stabilization energy obtained by such an interaction is small and practically independent of cluster sizes, i.e., about 0.83 kcal per mole of H...F interaction, as long as the geometric restrictions stated above are observed. If one regards liquid methyl fluoride as a huge cluster of molecules and if one assumes that every CH_3F is coordinated by six nearest neighbors as in crystalline methyl chloride,⁴⁸ then the representative molecule and its external force field for the purpose of the simple cell model would still maintain the C_{3v} symmetry.²⁴ This picture is consistent with the present result that the interactions of the translation in the direction of the symmetry axis with the internal coordinates, D , α , and β , satisfy the same symmetry.

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Registry No. ^{13}C , 14762-74-4; D_2 , 7782-39-0; methyl fluoride, 593-53-3.

Supplementary Material Available: G matrices for gaseous and liquid $^{12}\text{CH}_3\text{F}$, $^{13}\text{CD}_3\text{F}$, and $^{13}\text{CH}_3\text{F}$ (7 pages). Ordering information is given on any current masthead page.

(48) R. D. Burbank, *J. Am. Chem. Soc.*, **75**, 1211 (1953).