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VIBRATIONAL ANALYSIS OF 1,1-DIFLUOROETHANE

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SUMMARY

Infrared and Raman spectra have been redetermined for 1,1-difluoroethane, and the vibrational assignment has been revised slightly with the aid of normal coordinate calculations. A 30-parameter modified valence force field was used to fit the 18 frequencies with an average error of 0.66 cm^{-1}.

INTRODUCTION

Smith et al. published infrared and Raman spectra for 1,1-difluoroethane in 1952, and they proposed a partial vibrational assignment [1]. However, most of the bands were merely assigned as fundamentals or combinations, without description of the mode. Chen et al. used essentially those fundamental frequencies in their calculations of the thermodynamic properties of this compound [2]. However, there seemed to be some questions in Smith's assignment, so it was decided to redetermine the spectra and to try to make vibrational assignments with the aid of normal coordinate calculations. Calculations have been made

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for fluoroethane [3], 1-fluoropropane [3], and 2,2-difluoropropane [4], and initial force constants for 1,1-difluoroethane were taken from those molecules. Calculations had already been made for 1,1-dichloroethane [5], but it was thought that the fluorine atoms would require several force constants not used for dichloroethane. Therefore, we did not start with the dichloroethane force field, but rather transferred appropriate constants from the fluoro compounds just listed.

EXPERIMENTAL

The 1,1-difluoroethane sample was purchased from Columbia Organic Chemicals Co., and the sample was purified on a low-temperature sublimation column. The infrared spectrum was found to be consistent with the one previously reported [1].

The mid-infrared spectrum at 1 cm^{-1} resolution of the gas was recorded by using a Digilab model FTS-14C interferometer with the sample contained in a 12 cm cell equipped with CsI windows. The solution spectra were obtained in a 0.09mm thickness cell equipped with KBr windows. The solutions were prepared by bubbling the difluoroethane gas into the chloroform and carbon tetrachloride solvents. The Raman spectra were recorded from 0 to 3500 cm^{-1} with a Cary model 82 spectrophotometer equipped with a Coherent Radiation model 53A or a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The spectrum of the liquid was recorded at -10°C with the sample in a sealed glass capillary tube held in a cell similar to one previously described [6]. The cell was cooled with boiling liquid nitrogen and the temperature was monitored with an iron-constantan thermocouple. The spectrum of the vapor was obtained with a sample pressure of 500 torr using the standard Cary multipass accessory. Polarization measurements for the gas and liquid phases were made using the standard Cary accessories. The instrument was calibrated with mercury and neon emission lines. For studies in the liquid and the solid phases, the laser power at the sample was typically 0.5 W, whereas for the gas phase studies, the maximum power of nearly 3 W at the sample was used. Frequency measurements for sharp, resolvable bands are expected to be accurate to at least ±2 cm^{-1}.

CALCULATIONS

Normal coordinate calculations were done with a PDP-10 computer and utilized programs written by Schachtschneider [7,8] for calculation of the G matrix (GMAT), for solution of the vibrational secular equation (VSEC), and for the least-squares refinement of designated force constants to fit the calculated to the observed frequencies. The molecular parameters used were: C-C = 1.54 Å; C-H = 1.10 Å; C-F = 1.345 Å; all angles were taken as 109.47°. Except for minor differences in the angles, these are the parameters determined by Solimine and Dailey [9] and used by Chen et al. [2].

RESULTS AND DISCUSSION

The vapor-state IR spectrum is shown in Fig. 1. It is very similar to that of Smith et al. [1], with the difference being that the Q branches in Fig. 1 are more intense than those of Smith. In fact, Smith's spectrum in the 1360 cm^{-1} region shows the P and Q branches merely as shoulders on the more intense R branch, whereas in Fig. 1, the P, Q, and R branches of the 1362-cm^{-1} band are clearly resolved. The 1372-cm^{-1} band is assumed to be the R branch rather than a separate band because it is too broad to be a Q branch. Solution spectra were obtained in order to determine the actual number of bands observed (i.e., to distinguish between separate bands and P, Q, R branches of the same band). The spectrum of the chloroform solution, with the solvent subtracted out, is shown in Fig. 2. The solution spectra show only one band in the 1360-cm^{-1} region, as does the liquid-state spectrum of Smith et al. [1].

Another difference in interpretation of band shape concerns the vapor-state band observed at 942 cm^{-1}. We believe that the Q branch is a doublet, with the branches separated by 4 cm^{-1}. The band center is taken as the maximum between the two Q branches.

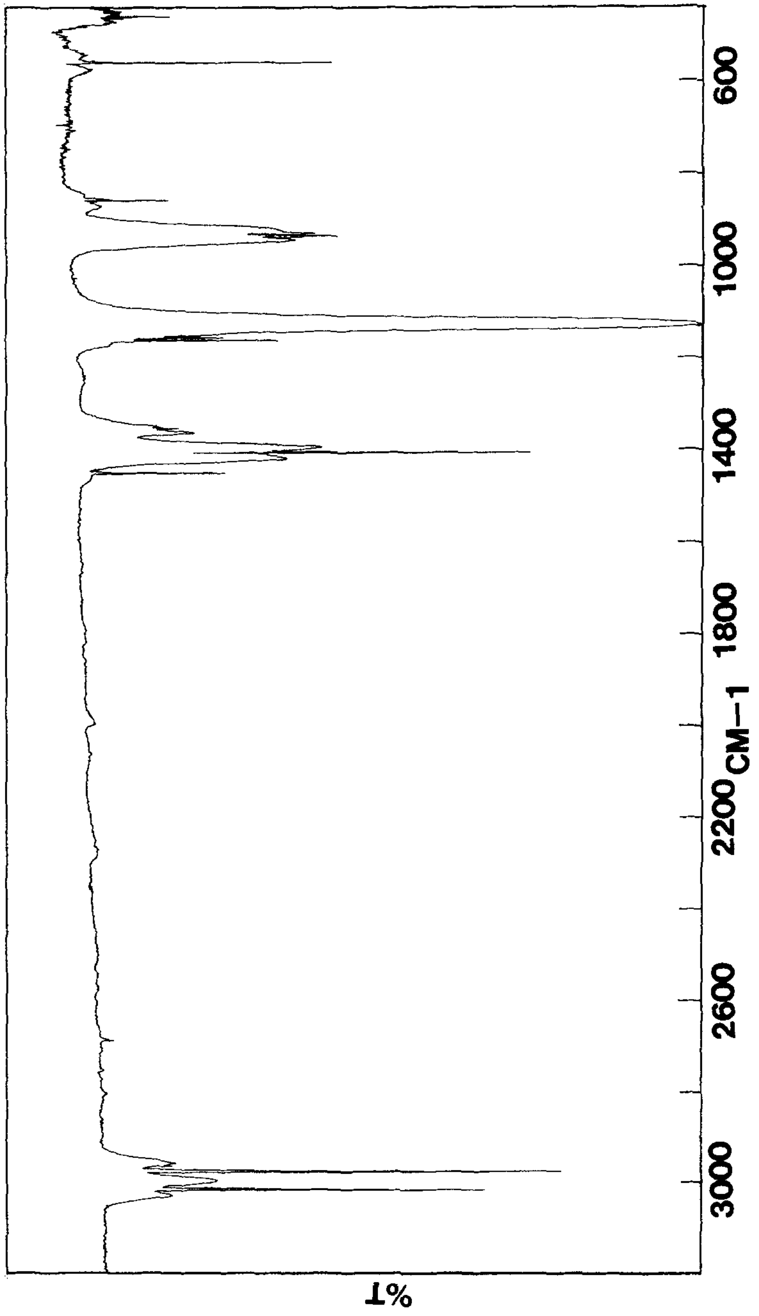

Fig. 1. Gas-phase IR spectrum of CH_3CHF_2.

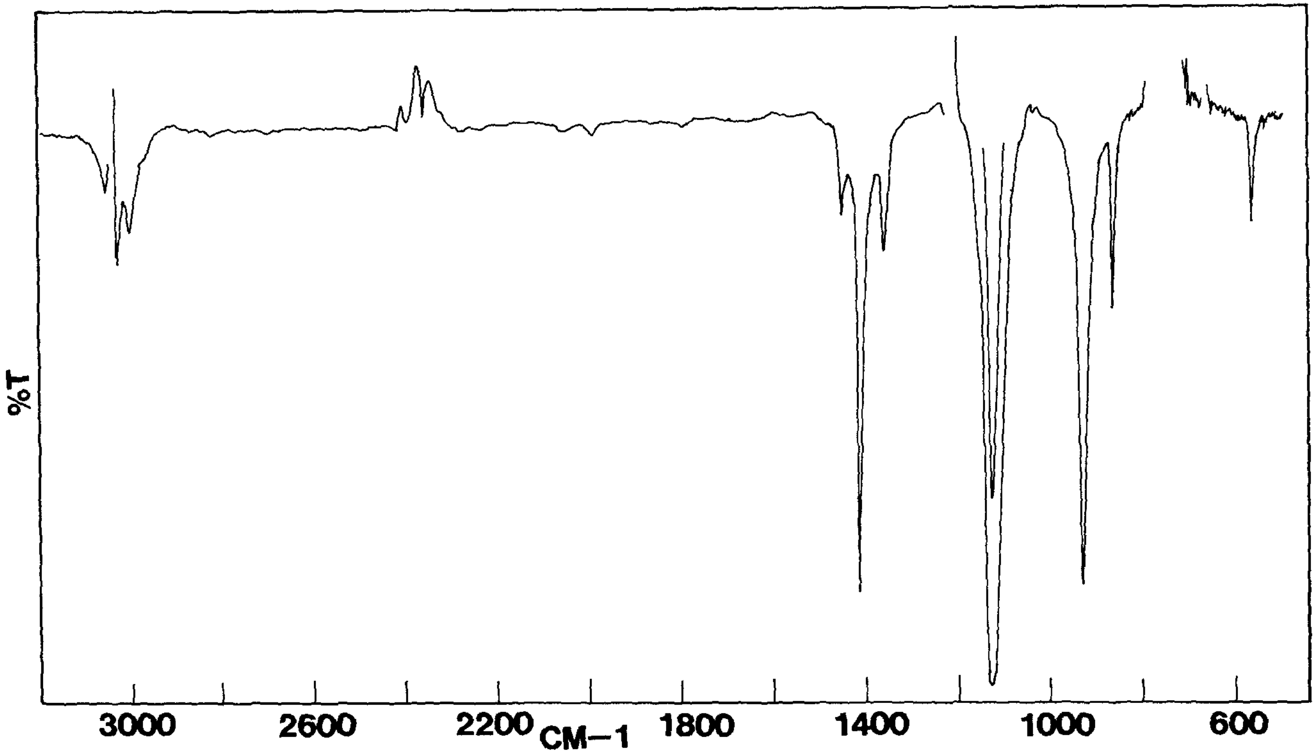

Fig. 2. IR solution spectrum of CH_3CHF_2 with solvent bands subtracted out.

The next step in the analysis of the spectra involved normal coordinate calculations. A 30-parameter modified valence force field was used, but the transferred values did not result in very good agreement between observed and calculated frequencies. Manual changes in several force constants during the next several runs resulted in a reasonably good fit with Smith's assignment, except for one a' frequency. Smith assigned liquid-state IR bands at 1118 and 1140 cm^{-1} to a' fundamentals, whereas only one frequency was calculated for this region. Both Raman bands were reported by Smith to be highly polarized, although both were weak. In all our initial calculations, the frequency just below that at 1135 cm^{-1} was calculated around 950 cm^{-1}. The force constant Jacobian matrix showed this frequency to be fairly insensitive to all force constants, and it would seem to be difficult to increase the calculated value by very much. This observation initially led to the conclusion that the 956 cm^{-1} band, assigned by Smith *et al*. as a combination band, was in fact a fundamental. If so, then one of the three bands 1118, 1140, 1166 cm^{-1} assigned by Smith as fundamentals would be a combination. The 1115 and 1139-cm^{-1} liquid-state Raman bands were reported by Smith to be polarized, and if so, neither of them could be an a" mode. Examination of Smith's IR spectra showed the 1135-cm^{-1} band to actually be a shoulder on the more intense 1118-cm^{-1} band and its intensity was difficult to judge. Smith reported Raman liquid-state (-40°C) wavenumbers, but did not show the spectra.

We therefore redetermined the liquid-state Raman spectrum, including polarization data. There is a shoulder at ca. 1122 cm^{-1} on the more intense band at 1141 cm^{-1}. Although the 1122-cm^{-1} band is a shoulder, it seems to be depolarized, whereas the 1141-cm^{-1} band is definitely polarized. The 1122-cm^{-1} band could therefore be assigned as an a" fundamental in place of the weak 1166-cm^{-1} band assigned by Smith. Normal coordinate calculations were then completed with the assignment of Smith, except for the change just mentioned. A good least-squares fit was obtained without much difficulty. Twelve force constants were refined to fit the 18 frequencies, with the average error being 1.0 cm^{-1}.

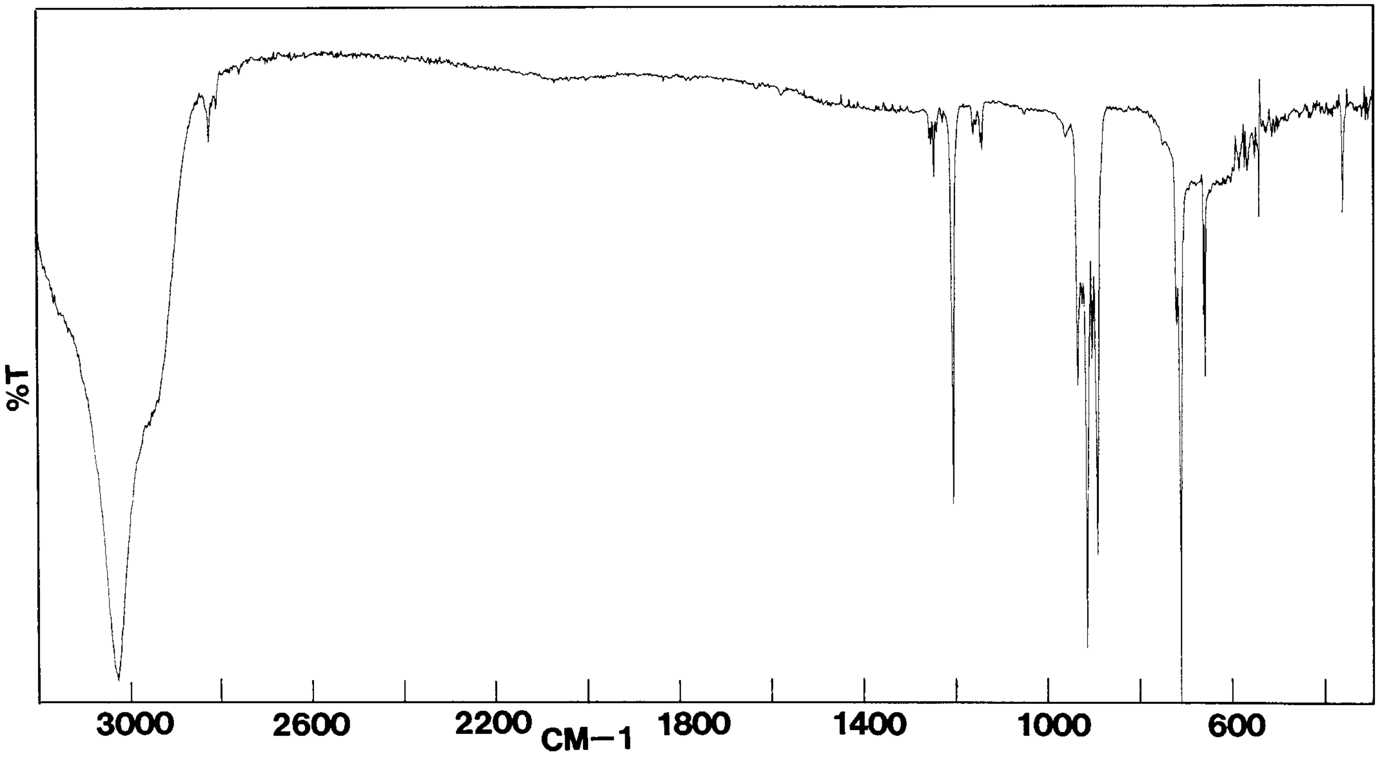

Fig. 3. Solid-state IR spectrum of CH_3CHF_2 at <u>ca.</u> 80K.

At this point in the project, it was decided to obtain the solid-state IR spectrum to see if additional information could be obtained about the assignment of the fundamentals. The spectrum (Fig. 3) shows three strong bands around 1000 cm^{-1}, rather than just one strong band as in the solution spectrum. We also decided to determine the Raman spectrum of the gas because Smith did not list very many vapor-state Raman bands. Our spectrum shows four bands in the 1100-1200 cm^{-1} region (Fig. 4), all of which seem to be too strong to be due to overtones or combination modes. The 1167 and 1173-cm^{-1} Raman bands correspond to the much weaker IR bands and 1164 and 1171 cm^{-1} (Fig. 1), and the 1142-cm^{-1} Raman band was not observed in the IR spectrum. There is apparently an appreciable shift in frequency from the condensed-phase spectra to the gas phase for three of the bands in this region.

If all four bands in the 1100-1200 cm^{-1} region are due to fundamentals, the most logical explanation is that one of these bands is due to a CCH bend, rather than the two CCH bends coinciding at 1362 cm^{-1}. This change in assignment was made and the normal coordinate calculations were repeated. Several computer runs were necessary to decrease the 1360-cm^{-1} a'' frequency by ca. 200 cm^{-1}. Manual changes were made in several force constants, with the force constant Jacobian matrix being used as the guide in deciding which constants to change. In the final run, FPERT was used to refine 12 force constants to fit the 18 observed frequencies, with the average error being 0.66 cm^{-1}. The observed and calculated wavenumbers and band assignments are given in Table 1, and the force constants are listed in Table 2.

The change in assignment of the one fundamental frequency will result in a change in calculated thermodynamic functions. Those functions were recalculated for the rigid rotor, harmonic oscillator model. The internal rotational contributions were taken from the tables of Pitzer and Gwinn [10], and the recalculated functions are given in Table 3.

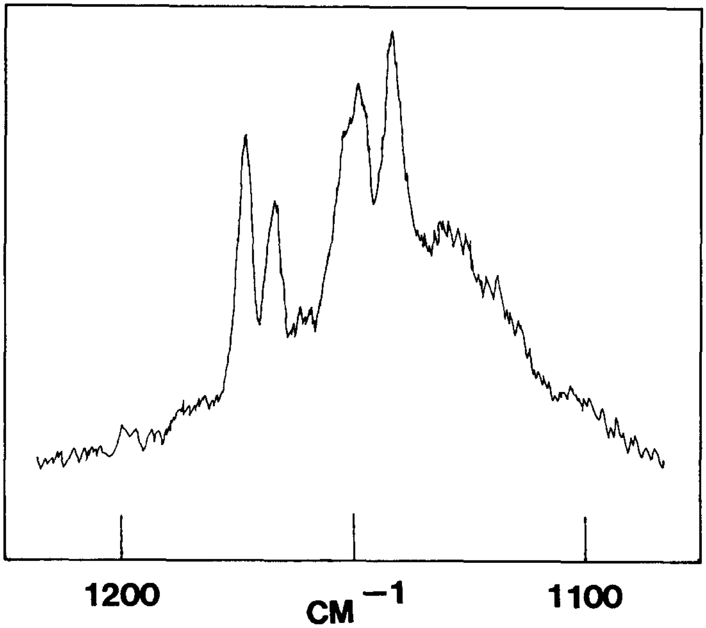

Fig. 4. Partial gas-phase Raman spectrum of CH_3CHF_2.

COMMENT

The assignment of the fundamentals listed in Table 1 is based mainly on observed intensities, and not on goodness of fit of the calculated frequencies. It is often possible to adjust force constants to fit different assignments for a compound with reasonable force constant values for the different assignments. We were also able to fit the original assignment [1] with reasonable force constant values, so the calculations cannot be used to determine the correct assignment. However, one of the purposes of doing normal coordinate calculations for simple molecules is to obtain force constants that are transferable to similar molecules. The property of transferability suggests some significance to the force field and therefore to the vibrational assignment from which the force field was obtained. Additional support for the correctness of our vibrational assignment for 1,1-difluoroethane would be obtained if our force field could be transferred successfully to similar molecules, such as 1,1-difluoroethane-d_4 or 1,1-difluoropropane. Unfortunately, these compounds are not available at the present time.

TABLE 1

Observed and calculated fundamental wavenumbers and assignment based on potential energy distributions

Obs.[a] cm^{-1}	Calc. cm^{-1}	Assignment[b]
a'		
3016	3017	CH_3as
2975	2975	CHs
2959	2959	CH_3ss
1466[c]	1467	CH_3aδ
1413	1413	CH_3sδ
1362	1363	CHδ, C-Cs, CH_3aδ, C-Fs
1171	1171	CHδ, C-Fs
1142	1143	C-Cs, CH_3r
868	865	CH_3r, CHδ, C-Cs
569	568	CF_2δ, C-Fs
469	469	CF_2w, C-Cs, CHδ
a''		
3016	3015	CH_3as
1457	1456	CH_3aδ
1164	1164	CHδ, C-Fs
1149[c]	1149	CHδ, C-Fs
942	944	CH_3r, C-Fs
383	383	CF_2t
222[d]	222	torsion

[a] Vapor-state frequencies

[b] Abbreviations: a = antisymmetric; s = stretch or symmetric; δ = bend; r = rock; w = wag; t = twist.

[c] Raman values

[d] From ref. 11

In order to conserve space, complete spectra are not given in this paper, but copies are available from the authors.

TABLE 2

Force constants for 1,1-difluoroethane

Force constant	Group	Coordinate(s) involved	Atom(s) common	Value[a]
Stretch				
K_r	CH_3	C-H	-	4.900[b]
K_s	CHF_2	C-H	-	4.800[b]
K_R	C-C	C-C	-	4.189
K_X	CF_2	C-F	-	5.150
Bend				
H_α	CH_3	H-C-H	-	0.540[b]
H_β	$C\text{-}CH_3$	C-C-H	-	0.673[b]
H_ξ	$C\text{-}CHF_2$	C-C-H	-	0.645
H_θ	CHF_2	F-C-H	-	0.766[b]
H_δ	CHF_2	F-C-F	-	2.256
H_γ	$C\text{-}CF_2$	C-C-F	-	1.103
Stretch-stretch				
F_r	CH_3	CH,CH	C	0.070[b]
F_X	CHF_2	CF,CF	C	0.670
F_{RX}	$C\text{-}CF_2$	CC,CF	C	0.492
Stretch-bend				
$F_{R\beta}$	$C\text{-}CH_3$	CC,CCH	C-C	0.200
$F_{R\gamma}$	$C\text{-}CF_2$	CC,CCF	C-C	-0.129
$F_{X\gamma}$	$C\text{-}CF_2$	CF,CCF	C-F	0.200
$F_{X\delta}$	CHF_2	CF,FCF	C-F	-0.100
$F_{X\theta}$	CHF_2	CF,FCH	C-F	0.420

(continued overleaf)

TABLE 2 (Cont.)

Force constant	Group	Coordinate(s) involved	Atom(s) common	Value[a]
Bend-bend				
F_{β}	$C-CH_3$	CCH,CCH	C-C	-0.012[b]
F_{γ}	$C-CHF_2$	CCF,CCF	C-F	0.119
F_{θ}	CHF_2	FCH,FCH	C-H	-0.168[b]
$F_{\gamma\theta}$	$C-CHF_2$	CCF,FCH	C-F	-0.100
$F_{\xi\theta}$	$C-CHF_2$	CCH,FCH	C-H	0.097[b]
$f^{t}_{\beta\xi}$	CH_3-CH	HCC,CCH trans	C-C	0.140
$f^{g}_{\beta\xi}$	CH_3-CH	HCC,CCH gauche	C-C	-0.069
$f'^{t}_{\beta\theta}$	CH_3-CHF_2	HCC,FCH trans	C	0[c]
$f'^{g}_{\beta\theta}$	CH_3-CHF_2	HCC,FCH gauche	C	0.030[b]
$f^{t}_{\beta\gamma}$	CH_3-CF_2	HCC,CCF trans	C-C	-0.050
$f^{g}_{\beta\gamma}$	CH_3-CF_2	HCC,CCF gauche	C-C	-0.015[b]
Torsion				
H_{τ}	CH_3-CHF_2	C-C	-	0.0100[b]

[a] Stretching constants are in units of mdyn A^{-1}; stretch-bend constants are in units of mdyn rad^{-1}; bending constants are in units of mdyn A $(rad)^{-2}$;

[b] These constants were adjusted in the final refinement process.

[c] Adjusted to 0.0002 in a previous run, so set equal to zero.

TABLE 3

Ideal gas thermodynamic functions[a] of CH_3CHF_2

T(K)	$-(G^o-H^o_o)/T$	$(H^o-H^o_o)/T$	S^o	C^o_p
273.15	55.33	10.80	66.13	15.38
298.15	56.31	11.22	67.53	16.33
300	56.39	11.25	67.64	16.39
400	59.85	13.01	72.86	20.08
500	62.92	14.77	77.69	23.26
600	65.78	16.39	82.17	25.88
700	68.43	17.90	86.33	28.04
800	70.90	19.28	90.18	29.84
900	73.26	20.54	93.80	31.37
1000	75.47	21.69	97.16	32.68

[a] All values are in units of cal/deg/mole

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