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Note

THERMODYNAMIC PROPERTIES OF NORMAL AND DEUTERATED 3,3-DIFLUOROCYCLOPROPENES

PABLO A. VICHARELLI

Center for Quantum Electronics, The University of Texas at Dallas, Box 688, Richardson, TX 75080 (U.S.A.)

I. ERNESTO ADAME

Mobil Research and Development Corporation, Dallas, TX 75221 (U.S.A.)

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Three-membered ring compounds are of considerable interest because of their highly strained nature. In recent years, an increasing amount of attention has been focused on the spectroscopic [1—7] and thermodynamic [7—

TABLE 1

Structural and vibrational data of normal and deuterated 3,3-difluorocyclopropenes

	$-d_0$	$-d_1$	$-d_2$
Molecular weight (g mole^{-1})	76.0456	77.0518	78.0580
Symmetry number	2	1	2
Moments of inertia (amu Å^2) *			
I_a	60.31454	62.6579 **	65.3112
I_b	87.33886	93.0964 **	98.7190
I_c	116.7308	120.1310 **	123.1006
Vibrational frequencies (cm^{-1}) ***	3150	3148	2429
	3128	2371	2322
	1598	1557	1509
	1343	1341	1339
	1131	1121	1093
	1094	1095	1081
	968	953	833
	946	827	820
	883	823	732
	769	718	657
	680	613	587
	522	505	487
	500	478	470
	416	403	356
	393	351	352

* Taken from ref. 5, unless otherwise indicated.
** Calculated, this work.
*** Taken from ref. 1.

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TABLE 2

Thermodynamic properties of normal and deuterated 3,3-difluorocyclopropenes

Temp. (K)	C_p^0 (cal deg^{-1} mole^{-1})	S^0 (cal deg^{-1} mole^{-1})	$-(G^0 - H_0^0)/T$ (cal deg^{-1} mole^{-1})	$H^0 - H_0^0$ (kcal mole^{-1})
3,3-Difluorocyclopropene-d_0				
100.0	8.51	53.79	45.75	0.804
200.0	12.47	60.78	51.60	1.835
273.15	15.88	65.17	54.66	2.873
298.15	16.99	66.61	55.60	3.284
300.0	17.07	66.72	55.66	3.315
400.0	20.96	72.18	59.12	5.224
500.0	23.94	77.19	62.24	7.476
600.0	26.18	81.76	65.12	9.987
700.0	27.91	85.94	67.80	12.695
800.0	29.27	89.76	70.31	15.556
900.0	30.38	93.27	72.67	18.541
1000.0	31.29	96.52	74.89	21.625
1100.0	32.05	99.54	77.00	24.793
1200.0	32.70	102.35	79.00	28.032
1300.0	33.24	104.99	80.89	31.329
1400.0	33.72	107.48	82.71	34.678
1500.0	34.12	109.82	84.44	38.070
3,3-Difluorocyclopropene-d_1				
100.0	8.69	55.38	47.30	0.808
200.0	13.08	62.64	53.24	1.880
273.15	16.60	67.24	56.38	2.967
298.15	17.72	68.74	57.35	3.396
300.0	17.80	68.85	57.42	3.429
400.0	21.64	74.52	61.00	5.409
500.0	24.56	79.68	64.23	7.725
600.0	26.78	84.36	67.20	10.298
700.0	28.51	88.63	69.96	13.066
800.0	29.87	92.52	72.54	15.987
900.0	30.96	96.11	74.96	19.030
1000.0	31.86	99.42	77.25	22.173
1100.0	32.60	102.49	79.40	25.397
1200.0	33.22	105.36	81.45	28.688
1300.0	33.74	108.04	83.39	32.037
1400.0	34.18	110.55	85.24	35.433
1500.0	34.55	112.92	87.01	38.870
3,3-Difluorocyclopropene-d_2				
100.0	8.84	54.20	46.10	0.811
200.0	13.64	61.70	52.10	1.920
273.15	17.30	66.50	55.32	3.055
298.15	18.43	68.07	56.32	3.501
300.0	18.51	68.18	56.40	3.536
400.0	22.32	74.06	60.09	5.586
500.0	25.20	79.36	63.42	7.968
600.0	27.40	84.16	66.48	10.603
700.0	29.12	88.52	69.33	13.433
800.0	30.48	92.50	71.98	16.416
900.0	31.56	96.15	74.46	19.520
1000.0	32.44	99.52	76.80	22.722
1100.0	33.16	102.65	79.01	26.003
1200.0	33.75	105.56	81.105	29.350
1300.0	34.24	108.28	83.09	32.750
1400.0	34.65	110.84	84.98	36.195
1500.0	34.994	113.24	86.79	39.678

TABLE 3

Estimated uncertainties in the thermodynamic properties of 3,3-difluorocyclopropene-d_0

Temp. (K)	C_p^0 (cal deg^{-1} mole^{-1})	S^0 (cal deg^{-1} mole^{-1})	$-(G^0 - H_0^0)/T$ (cal deg^{-1} mole^{-1})	$H^0 - H_0^0$ (kcal mole^{-1})
100.0	0.04	0.01	0.002	0.001
298.15	0.15	0.13	0.05	0.024
500.0	0.12	0.19	0.09	0.042
1000.0	0.06	0.25	0.16	0.093
1500.0	0.03	0.28	0.21	0.114

10] properties of these compounds. The purpose of the present note is to extend the thermodynamic studies to include some members of the family of halogen-substituted cyclopropenes. The recent availability of the structural parameters and vibrational frequencies of normal and deuterated 3,3-difluorocyclopropenes (3,3-DFCP) has made it possible to calculate their statistical thermodynamic properties.

The microwave spectrum of 3,3-DFCP has been investigated by Ramaprasad et al. [5]. These workers have reported the principal moments of inertia of 3,3-DFCP-d_0 and 3,3-DFCP-d_2. In addition, they have reported the molecular structural parameters r(C=C) = 1.321 ± 0.001 Å, r(C—C) = 1.438 ± 0.007 Å, r(C—H) = 1.075 ± 0.001 Å, r(C—F) = 1.365 ± 0.005 Å, <(C—C—C) = 54.6 ± 0.4°, <(F—C—F) = 105.5 ± 0.5°, and <(H—C=C) = 148.4 ± 1°, which have been used here to calculate the principal moments of inertia of 3,3-DFCP-d_1.

Complete assignments of the vibrational fundamentals of 3,3-DFCP and its deuterated derivatives have been made by Craig et al. [1], who have recorded the IR and Raman spectra of these compounds. Their assignments have been verified by an extensive normal coordinate analysis [1]. These vibrational fundamentals, along with the principal moments of inertia, are listed in Table 1.

The thermodynamic functions C_p^0, S^0, $-(G^0 - H_0^0)/T$, and $H^0 - H_0^0$ have been evaluated for the temperature range 100—1500 K. An ideal gas, rigid rotor, harmonic oscillator at 1 atm pressure has been used as the model for these calculations, which have been performed using the well-known methods of statistical mechanics. The contribution due to nuclear spin has been neglected. The atomic masses [11] C = 12.011, H = 1.0079, D = 2.0141, and F = 18.9984, and the most recent fundamental constants [12] have been employed throughout this work. The results are given in Table 2.

In order to assess the uncertainties in these thermodynamic properties, the effects of varying the structural and vibrational data by amounts corresponding to their estimated uncertainties were observed. The results for 3,3-DFCP-d_0 are summarized in Table 3. The estimated uncertainties for the deuterated derivatives are essentially the same as those shown in this Table.

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