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# Infrared and Raman spectra, vibrational assignment, and ab initio calculations of fluoromalononitrile

M. Dakkouri<sup>a</sup>, A. Grunvogel-Hurst<sup>a</sup>, Gamil A. Guirgis<sup>1,b</sup>, Zhenhong Yu<sup>2,b</sup>, Yanping Jin<sup>b</sup>, James R. Durig<sup>b,\*</sup>

<sup>a</sup> Abterlung für Physikalische Chemie, Universität Ulm, 7900 Ulm, Germany <sup>b</sup> Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499, USA

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#### Abstract

The infrared spectra  $(3500-80 \text{ cm}^{-1})$  of gaseous and solid and the Raman spectra  $(3500-30 \text{ cm}^{-1})$  of liquid with quantitative depolarization values and solid fluoromalononitrile, FHC(CN)<sub>2</sub>, have been recorded. These spectra have been interpreted in detail and a complete vibrational assignment is proposed based on infrared band contours, depolarization values, and relative infrared and Raman intensities. The assignment is supported by a normal coordinate calculation based upon force constants obtained from MP2/6-31G\* ab initio calculations. Also, from these calculations the predicted infrared and Raman spectra have been obtained. The C-H bond distance is predicted to be 1.096 Å from the isolated carbon-hydrogen stretching frequency. Optimized geometric parameters have been obtained from RHF/6-31G\*, MP2/6-31G\* and MP2/6-311 + + G\*\* ab initio calculations. These results are discussed and compared with those obtained for some similar molecules. © 1997 Elsevier Science B.V.

Keywords: Infrared and Raman spectra; Ab initio calculations; Fluoromalononitrile

# 1. Introduction

We recently carried out a Raman and infrared spectral investigation of 1,1-dicyanocyclobutane [1] and 1,1-dicyanocyclopropane [2] with particular interest in the low-frequency  $C \equiv N$  bending

modes. As a continuation of these studies, we have investigated the infrared and Raman spectra of fluoromalononitrile,  $FHC(CN)_2$ , to compare the frequencies for the CN groups relative to those in the three- and four-membered ring compounds. Further, in order to provide additional information with regard to the structural parameters of  $FHC(CN)_2$  we carried out ab initio calculations with the  $6-311 + + G^{**}$  basis set with electron correlation to the second order (MP2) [3]. Ab initio calculations with the  $6-31G^*$  basis set at the MP2 level were carried out to determine the harmonic force field in order to provide informa-

<sup>\*</sup> Corresponding author.

<sup>&</sup>lt;sup>1</sup> Permanent address: Analytical R/D Department, Organic Products Division, Bayer, Bushy Park Plant, Charleston, SC 29411, USA.

 $<sup>^{2}</sup>$  Taken in part from the dissertation of Z. Yu which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

tion about the potential energy distribution for the normal modes among a set of symmetry coordinates. We have also predicted the infrared and Raman spectra ( $RHF/6-31G^*$ ) from these calculations. The results of this spectroscopic and theoretical study are reported herein.

### 2. Experimental and theoretical methods

Many attempts have been undertaken to prepare fluoromalononitrile through halogen-halogen exchange reaction by treating monobromomalononitrile with a variety of fluorinating agents. Neither the variation of the fluorinating agent nor the alternation of the solvent, e.g. acetonitrile, diglyme, dimethylsulphoxide and Nmethylpyrrolidone have led to the target compound. We, therefore, decided to follow a modified route as first described by Bergmann et al. [4] for the preparation of the intermediate to produce diethyl fluoromalonate  $HFC(COOC_{2}H_{5})_{2}$ according to the following scheme:

 $2Na + 2CH_{3}OH \rightarrow 2NaOCH_{3} + H_{2}$   $CH_{3}O^{-} + H_{2}FC(COOC_{2}H_{5})$   $\rightarrow CH_{3}OH + \ ^{-}CHF(COOC_{2}H_{5})$   $^{-}CHF(COOC_{2}H_{5}) + ClCOOC_{2}H_{5}$   $\rightarrow HFC(COOC_{2}H_{5})_{2} + Cl^{-}$ 

Although the detailed description of the synthesis of fluoromalononitrile will be published [5] elsewhere we will summarize the preparation.

To a suspension of alcohol free sodium methoxide, prepared from metallic sodium in light petroleum, ethyl fluoroacetate was added at about  $5-10^{\circ}$ C. The reaction mixture was then allowed to come to room temperature and stirred overnight. The reaction mass was cooled and ethyl chloroformate was added rapidly. After the mixture was heated to reflux for about one hour it was poured over ice. The organic layer was then treated as previously described [4] to provide diethyl fluoromalonate. A purified sample of diethyl fluoromalonate was added dropwise to a cooled 30% solution of ammonium hydroxide. The resulting diamide was dried and then dehydrated with  $P_2O_5$ . For this step in the preparation a special apparatus was designed and the particular technique as described by Bergmann et al. [4] was applied. The final product, fluoromalononitrile was purified by distillation. Fluoromalononitrile is very sensitive to moisture and air. On exposure to moisture the colorless liquid changes to a brownish color and eventually to dark brown. The purity of the sample was checked by infrared and NMR spectroscopy and mass spectrometry.

The sample was further purified with a lowpressure, low-temperature column. The Raman spectra of liquid (Fig. 1) and solid were recorded on SPEX Ramanlog spectrophotometer а equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The liquid sample was sealed in a glass capillary and the spectrum record at ambient temperature. Then the spectrum of the solid was recorded by inserting the capillary into a Miller-Harney [6] jacket cooled by N<sub>2</sub> gas obtained from liquid N<sub>2</sub>. The temperature of the solid was maintained at about  $-26^{\circ}$ C by controlling the rate of the nitrogen boil off from the liquid. The frequencies for the observed lines are listed in Table 1.

The mid-infrared spectra (Fig. 2) of the gas and the annealed solid from 3500 to 400 cm<sup>-1</sup> were recorded using a Perkin–Elmer model 2000 Fourier transform interferometer equipped with a nichrome wire source, Ge/CsI beamsplitter and DTGS detector. The spectrum of the gas was



Fig. 1. Raman spectrum of liquid (A) and theoretical (B) predicted Raman spectrum of fluoromalononitrile.

Observed infra	ared <sup>a</sup> and Ra	ıman wavenumb	ers (cm <sup>-1</sup>	) for fluorom	alononitrik	4)			- TANK TANK TANK		
Infrared					Raman					Assignment	
Gas	Rel. Int.	Calc. Int. <sup>b</sup>	Solid	Rel. Int.	Liquid	Rel. Int. and Depol.	Calc. <sup>e</sup> Int./ Depol.	Solid	Rel. Int.	y, d	Approximate description
2957 R 2953 ctr, B 2950 P	E	1.08	2973 2966	s e	2955	ш, 0.1	79.8 (0.21)	2977	SV	14	CH stretch
2631 Q 2593 Q 2478 Q	* * *		2579	M				2572	٨W		
2275 R 2272 Q	ø	42.5	2281	ш	2272	w, dp	23.8 (0.75)	2282	s	¥10	Antisymmet- ric CN stretch
2271 Q 2270 Q 2269 Q 2261 P	s	14.2	2274	ш	2268	s, 0.1	70.9 (0.14)	2275	SV	с, 1	Symmetric CN stretch
2255 R 2249 min, B 2243 P	MA				0100						
			2107 1316	W	0177	3	,				
1316 R 1312 Q 1305 P	s	12.2	1314	E E	1313	w, dp	6.24 (0.74)	1305	E	r, V	CH in-plane bend
1304 max	M	20.0	1305	ш			1.91 (0.75)			V <sub>t1</sub>	CH out-of- plane bend
1216 R 1210 ctr 1205 P	ΜΛ		1231	w							
1100 Q	s		1090 1082 1073	s ž ž	1100	wv					$2v_4$ or $v_6 + v_{13}$
1086 R 1080 ctr, B	۸S	117.1	1060	SA	1076	w, 0.40	5.06 (0.53)	1064	E	۲.4	CF stretch
1074 P			1040 1028	8 X							

Table 1

Table 1 (con	tinued).										
Infrared					Raman			-		Assignment	-
Gas	Rel. Int.	Calc. Int. <sup>b</sup>	Solid	Rel. Int.	Liquid	Rel. Int. and Depol.	Calc. <sup>c</sup> Int./ Depol.	Solid	Rel. Int.	V, d	Approximate description
1019 R 1013 Q, A 1007 P	SA	50.2	1016	SV	1015	vw, dp	1.56 (0.75)	1018	B	<sup>V</sup> 12	CC <sub>2</sub> antisym-
			906 206	мШ							metric stretch
800 V 872 Q, C 868 P	s B	20.5	868 865	vs w, sh	872	s, 0.1	6.13 (0.20)	873	Ś	¥5	CC <sub>2</sub> symmetric stretch
828 R 824 ctr 820 D	M/										
о20 F 604 Q, C 564 P	м	1.14	617 571	з E	611	s, 0.1	3.11 (0.24)	617	ж	\$ \$	CF in-plane bend
558 ctr, B 552 R	wv	0.49	565	ø	570	w, 0.3	3.29 (0.52)	570	w	$\nu_7$	C(CN) <sub>2</sub> bend
509 R 502 Q, A 495 P	MA	2.75	516	м	512	vw, dp	1.76 (0.75)	517	8	۲ <sub>13</sub>	CF out-of- plane bend
431 R 426 ctr 421 P	WA									$v_8 + v_{15} = 437$ or $2v_{15} = 450$	
332 Q 331 Q 323 P	ww s	0.35	344	E	344	dp .m	4.15 (0.75)	350	ш	$v_8 + v_9 = 343$ $v_{14}$	(CN), in-phase bend
225 Q 224 O	s	5.46	238	٧S	238	s, dp	4.28 (0.75)	240	VS	<sup>1</sup> ,15	(CN) <sub>2</sub> out-of- phase bend
212 Q 207 P	so	16.6	222	٧S	228	m, dp	2.72 (0.73)	234	s	1. <sup>8</sup>	(CN) <sub>2</sub> m-phase bend

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Table 1 (cont	tinued)										
Infrared					Raman					Assignment	
Gas	Rel. Int.	Calc. Int. <sup>b</sup>	Solid	Rel. Int.	Liquid	Rel. Int. and Depol.	Calc. <sup>c</sup> Int./ Depol.	Solid	Rel. Int.	V <sub>i</sub> d	Approximate description
137 R 131 min, B 127 P		7.47	162	s, bd	154	s, dp	5.10 (0.74)	166	ш	y <sub>9</sub>	(CN) <sub>2</sub> out-of- phase bend
			116	w				148	s		
			87	M				91	ΜΛ		
			81	W				80	w		Lattice modes
								57	s		
								48	s		
<sup>a</sup> s, strong, m the rotational <sup>b</sup> Calculated i <sup>c</sup> Calculated I <sup>d</sup> For vibratio	, moderate; w. 1-vibrational 1 Infrared intens Raman scatter n numbers set	, weak: v, very; branches, the pi sities in km mol ing activities in e Table 4.	bd, broad time indic $^{-1}$ . Using $\mathring{A}^{4}$ amu	I; sh, shoulder: ates <i>gauche</i> -2 ( the MP2/6-3)	; p, polariz modes, an IG* basis HF/6-31G	ced; dp, depolari d double primes set. * basis set.	zed; A, B, and indicated <i>cis</i> n	C refer to todes.	o infrared bar	nd envelopes; P,	Q, and R refer to

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Fig. 2. Infrared spectra of gas (A), solid (B) and theoretical (C) predicted spectrum of fluoromalononitrile. The low frequency spectra (400 cm<sup>-1</sup> in A and 650 cm<sup>-1</sup> in B) were recorded from different samples than those for the mid-infrared data.

obtained by using a 12 cm cell equipped with CsI windows. Atmospheric water vapor was removed from the interferometer chamber by purging with dry nitrogen. For the solid, the spectrum was recorded by depositing a solid sample film onto a CsI substrate cooled by boiling liquid nitrogen and housed in a vacuum cell filled with CsI windows. The sample was annealed until no further changes were observed in the spectrum. Interferograms obtained after 128 scans for the gaseous sample and reference and 64 scans for the solid and reference were transformed by using a boxcar truncation function with a theoretical resolution of 0.5 and 1.0 cm<sup>-1</sup> for the gas and solid samples, respectively.

The far-infrared spectrum (600 to  $50 \text{ cm}^{-1}$ ) of the solid was obtained by using a Perkin-Elmer model 2000 Fourier transform interferometer equipped with a far infrared grid beam splitter and a DTGS detector. The spectrum was obtained by condensing the sample on to a silicon plate held in a cell equipped with polyethylene windows and cooled with boiling liquid nitrogen.

The far infrared spectrum (Fig. 2) of the gas was recorded on a Bomem model DA 3.002 Fourier transform interferometer equipped with a vacuum bench, a Globar source and a liquid helium cooled silicon bolometer with a wedged sapphire filter and polyethylene windows. The gaseous sample was contained in a 1 m optical path cell. A 6.25 mm Mylar beamsplitter was used to record the spectra at a resolution of  $0.1 \text{ cm}^{-1}$ . Typically, 256 scans were needed for both the sample and reference to give a satisfactory signal-to-noise ratio.

The geometry optimization of fluoromalononitrile was performed by the LCAO-MO-SCF restricted Hartree–Fock calculations with the program [7] Gaussian 92 using the 6-31G\* Gaussian-type basis set. The energy minimum with respect to the nuclear coordinates was obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay. [8] Calculations were also carried out with electron correlation to second order, i.e. MP2/6-31G\* and a larger basis set, MP2/6-311 + + G\*\*. These parameters are listed in Table 2.

The intramolecular harmonic force fields were calculated with the Gaussian 92 program [7] at the RHF/6-31G\* and MP2/6-31G\* levels. Internal coordinates were defined as shown in Fig. 3. which were used to form the symmetry coordinates listed in Table 3. The Cartesian coordinates obtained for the optimized geometry were used to calculate the B-matrix elements with the G matrix program of Schachtschneider [9]. These B-matrix elements were used to convert the ab initio force fields in Cartesian coordinates to a force field in desired internal coordinates and the resulting force constants are listed in Table 4. This force field was used in a mass-weighted Cartesian coordinate calculation to reproduce the ab initio vibrational frequencies without a scaling factor which are given in Table 5. Scaling factors of 0.9 for all of the stretches, except the  $C \equiv N$  stretch, and for the C-H bends, and 1.0 for all other diagonal force constants along with the geometric average of the interaction terms were input along with the force field into the perturbation program



[9] to obtain the 'fixed scaled' force fields, vibrational frequencies, and potential energy distributions (PED). These data are listed in Table 5.

# 3. Results and discussion

The fluoromalononitrile molecule has a plane of symmetry which contains the b and c axes so the nine fundamentals of A' symmetry will give rise to infrared bands with B, C, or B/C hybrid contours and polarized Raman lines. The six A" fundamentals will give rise to pure A-type contours. The three band types are shown in Fig. 4 and there is a clear difference between the A- and C-type contours. Also, the B-type contour is quite distinct and any vibration giving rise to this band

Table 2

Structural parameters, rotational constants, dipole moments, and energy for fluoromalononitrile<sup>a</sup>

Parameter	RHF/6-31G*	MP2/6-31G*	MP2/6-311+G**
$r(C_1 - C_2)$	1.478	1.472	1.471
$r(C_1 - C_3)$	1.478	1.472	1.471
$r(C_1 - F)$	1.347	1.384	1.377
$r(C_1 - H)$	1.080	1.095 <sup>b</sup>	1.094 <sup>ь</sup>
$r(C_2 - N_4)$	1.132	1.180	1.174
$r(C_3 - N_5)$	1.132	1.180	1.174
∠FC <sub>1</sub> H	108.9	108.3	108.2
$\angle C_1C_2C_3$	110.8	110.6	110.8
$\angle N_4C_2C_1$	178.4	178.5	178.6
$\angle N_5C_3C_1$	178.4	178.5	178.6
$\angle FC_1C_2$	109.7	109.3	109.8
$\angle HC_1C_2$	108.9	109.6	109.1
A	6032	5847	5809
В	2928	2855	2881
С	2072	2022	2026
$ \mu_{a} $	0.000	0.000	0.000
$\mu_{\rm h}$	1.811	1.673	1.655
$ \mu_{i} $	2.319	2.444	2.468
$ \mu_t $	2.942	2.962	2.972
-(E	0.472618	1.353958	1.601608
+ 322)			

<sup>1</sup> Distances in Å and angles in degrees, rotational constants in MHz, dipole moments in Debyes and energy in Hartrees. <sup>b</sup> Value from isolated C-H stretching frequency is 1.096 Å.



Fig. 3. Internal coordinates for fluoromalononitrile.

type can clearly be assigned as an A' mode. The ab initio calculations predict that three of A' fundamentals will have depolarization ratios of 0.73-0.74 so the depolarization ratios for these fundamentals can not be used to distinguish them from the A" fundamentals. However, the fundamental at  $131 \text{ cm}^{-1}$  has a 'pure' B-type contour

Table 3 Symmetry coordinates<sup>a</sup> for fluoromalononitrile

Description	Symmetry coordinate <sup>a</sup>
CH stretch	$S_1 = T$
(CN) <sub>2</sub> symmetric stretch	$S_2 = P + Q$
CH bend	$\mathbf{S}_3 = 2\varphi - \gamma_1 - \gamma_2$
CF stretch	$S_4 = S$
CC <sub>2</sub> symmetric stretch	$\mathbf{S}_5 = \mathbf{r}_1 + \mathbf{r}_2$
CF bend	$S_6 = \beta_1 + \beta_2$
CCC bend	$S_7 = \alpha$
(CN) <sub>2</sub> in-phase bend	$\mathbf{S}_8 = \varepsilon_1 - \varepsilon_2$
(CN) <sub>2</sub> out-of-phase	$\mathbf{S}_9 = \tau_1 + \tau_2$
bend	
redundancy	$\mathbf{S}_{1\mathbf{R}} = \alpha + \beta_1 + \beta_2 + \varphi$
	$+\gamma_1+\gamma_2$
$(CN)_2$ asymmetric	$\mathbf{S}_{10} = P - Q$
CH bend	$S_{11} = v_1 = v_2$
CC asymmetric stretch	$S_{11} = r_1 = r_2$
CF bend	$\mathbf{S}_{12} = \beta_1 - \beta_2$
(CN), in-phase hend	$\mathbf{S}_{13} = \mathbf{\tau}_1 + \mathbf{\tau}_2$ $\mathbf{S}_{14} = \mathbf{\tau}_1 + \mathbf{\tau}_2$
(CN), out-of-phase	$S_{14} = \epsilon_1 + \epsilon_2$
bend	$v_{15} = v_1 + v_2$
	CH stretch (CN) <sub>2</sub> symmetric stretch CH bend CF stretch CC <sub>2</sub> symmetric stretch CF bend CCC bend (CN) <sub>2</sub> in-phase bend (CN) <sub>2</sub> out-of-phase bend redundancy (CN) <sub>2</sub> asymmetric stretch CH bend CC <sub>2</sub> asymmetric stretch CF bend (CN) <sub>2</sub> in-phase bend (CN) <sub>2</sub> out-of-phase bend

<sup>a</sup> Not normalized.

Tab For	le 4 ce consta	unts (mdyn	,Å⁻¹) for f	fluoromalon	onitrile											
	r1	r <sub>2</sub>	ď	6	S	T	ð	β1	β2	γ1	$\gamma_2$	¢	12	12 2	ŝ	- 5
r_,	5.060	0.226	- 0.007	-0.100	0.503	0.129	0.178	0.146	-0.127	0.141	-0.194	-0.151	-0.002	0.026	0.000	0.000
$r_2$		5.060	-0.100	-0.007	0.503	0.129	0.178	-0.127	0.146	-0.194	0.141	-0.151	0.026	-0.002	0.000	0.000
Ь			15.818	-0.044	-0.040	-0.030	0.016	0.004	-0.020	0.001	-0.005	0.004	-0.004	0.014	0.000	0.000
ð				15.818	-0.040	-0.030	0.016	-0.020	0.004	-0.005	0.001	0.004	0.014	-0.004	0.000	0.000
S					5.773	0.165	-0.289	0.309	0.309	-0.284	-0.284	0.254	-0.008	-0.008	0.001	0.001
Т						5.149	-0.067	-0.046	0.046	0.070	0.070	0.019	-0.005	-0.005	0.000	0.000
ş							0.753	-0.147	-0.147	-0.129	-0.129	-0.221	0.058	0.059	-0.001	0.001
$\beta_1$								0.893	-0.196	-0.142	-0.220	-0.186	0.003	0.001	0.002	0.000
$\beta_2$									0.893	-0.220	-0.142	-0.186	0.001	-0.003	0.000	- 0.002
۲ı										0.653	-0.082	-0.082	-0.054	-0.001	-0.001	0.000
$\gamma_2$											0.653	-0.082	-0.001	-0.054	0.000	0.001
ø												0.778	-0.003	-0.003	0.000	0.000
ť1													0.292	0.005	0.000	0.000
$t_2$														0.292	0.000	0.000
పే															0.000	0.000
s'																0.000
-	-				and the second se											

Craniac	Wihe	Eundomental	Ab initio <sup>a</sup>	Fivedb	11	Daman	чr	Ohe f	DEDE	
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	no.			scaled	лиг.	acı.	rauo'		THE STATE OF	
Α'	<sup>1</sup> A	CH stretch	3137	2976	1.08	79.77	0.21	2953	100S <sub>1</sub>	
	$V_2$	(CN) <sub>2</sub> symmetric stretch	2212	2199	14.17	70.88	0.14	2269	88S <sub>2</sub> , 12S <sub>5</sub>	
	1,3	CH bend	1382	1313	12.16	6.24	0.74	1312	96S <sub>3</sub>	
	v4	CF stretch	1125	1070	117.15	5.06	0.53	1080	$88S_4$	
	V5	CC <sub>2</sub> symmetric stretch	911	881	20.54	6.13	0.20	872	$41S_5, 21S_7, 17S_6$	
	۲ <sub>6</sub>	CF bend	617	604	1.14	3.11	0.24	604	50S., 19S., 19S.	
	$V_{T}$	CCC bend	567	559	0.49	3.29	0.52	558	$41S_7, 26S_9, 20S_5$	
	r,	(CN), in-phase bend	213	211	16.61	2.72	0.73	212	49S <sub>8</sub> , 25S <sub>6</sub> , 25S <sub>9</sub>	
	04	(CN) <sub>2</sub> out-of-phase bend	130	130	7.47	5.10	0.74	131	$40S_0, 37S_7, 21S_8$	
Α"	P10	(CN) <sub>2</sub> antisymmetric stretch	2218	2204	42.52	23.78	0.75	2272	87S <sub>10</sub> , 14S <sub>12</sub>	
	V11	CH bend	1374	1308	19.96	1.91	0.75	1304	88S <sub>11</sub>	
	V12	CC, antisymmetric stretch	1053	1010	50.18	1.56	0.75	1013	67S <sub>12</sub> , 11S <sub>11</sub> , 11S <sub>10</sub>	
	V13	CF bend	513	509	2.75	1.76	0.75	502	56S <sub>13</sub> , 31S <sub>15</sub> , 11S <sub>12</sub>	
	$V_{14}$	(CN) <sub>2</sub> in-phase bend	341	341	0.35	4.15	0.75	330	96S <sub>14</sub>	
	r15	(CN) <sub>2</sub> out-of-phase bend	222	222	5.46	4.28	0.75	225	65S <sub>15</sub> , 31S <sub>13</sub>	

<sup>b</sup> Scaled ab initio calculations with factor 0.9 for stretches except CN and 1.0 for bends except 0.9 for two CH bends using the MP2/6-31G\* basis set.  $^{\circ}$  Calculated infrared intensities in km mol<sup>-1</sup> at the MP2/6-31G\* level.

 $^d$  Calculated Raman activities in A<sup>4</sup> amu $^{-1}$  at the RHF/6-31G\* level.  $^e$  Calculated depolarization ratios at the RHF/6-31G\* level.

<sup>4</sup> Frequencies are taken from the infrared spectrum of the gas. <sup>g</sup> Calculated with the MP2/6-31G\* basis set. Contributions less than 10% are omitted.



Fig. 4. Calculated pure (A) A-type; (B) B-type, and (C) C-type infrared contours.

and the 212 cm<sup>-1</sup> band has a B/C hybrid contour. Therefore, these two bands are A' fundamentals even though the Raman lines are depolarized. The other A' fundamental with the predicted depolarized Raman line is the C-H in-plane bend but it is so close to the C-H out-of-plane bend that it is quite difficult to decide which of these modes has the higher frequency. Nevertheless, we have assigned the higher frequency band at 1312 cm<sup>--1</sup> as the A' based on the ab initio predictions that this mode has a higher frequency than the corresponding A" mode. The assignment of the remaining six A' modes can be readily accomplished based on their polarized Raman lines at 2955 (CH stretch), 2268 (CN stretch), 1076 (CF stretch), 872 (CC<sub>2</sub> stretch), 611 (CF bend) and 570 cm<sup>-1</sup> (C(CN)<sub>2</sub> deformation). The assignment of the six A" modes is straight forward using the depolarized Raman lines at 2272, 1015, 512 and 344 cm<sup>-1</sup> along with the two lines previously discussed. The assignment is summarized in Table 5.

There is significant mixing of the  $v_5$  through  $v_9$ in the A' symmetry with most of these fundamentals composed of approximately 50% of the described motion along with 20–25% of two other bending motions. In the A" symmetry block the CF bend and (CN)<sub>2</sub> out-of-phase bend have significant mixing but the other modes are relatively pure motions. Therefore, the descriptions given to the fundamentals provide a reasonable approximation of the molecular motions involved.

The force constants listed in Table 4 have values for the diagonal ones similar to those that are usually transferred for the  $C \equiv N$ , C-C, C-H, and C-F stretching force constants. The interaction constants for the C-C stretch with the C-F stretch or the other C-C stretch are relatively large. Also, the interaction constants of the C-F stretch with all of the bending coordinates around  $C_2$  atom are quite large. These constants have about twice the values of the corresponding interaction constants found between the C-C stretching force constants and the similar angles. The remaining interaction constants are relatively small. It is expected that these force constants could be transferred to the corresponding bonds in similar molecules.

The Raman spectrum for FHC(CN)<sub>2</sub> was calculated using frequencies and scattering activities determined from the Gaussian-92 program [7] using the 6-31G\* basis set at the RHF level. Calculation of the Raman activity using an analytical gradient method has been developed and this activity,  $S_i$ , can be expressed as [10]:

Table 6					
The C≡N	distances	for	some	organonitrile	molecules

Molecule	Formula	C=N distance	Technique	Reference
1,3-dicyanopropane	NCCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN	$1.161 \pm 0.003$	ED data <sup>a</sup>	[11]
1,1-dicyanocyclobutane	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(CN) <sub>2</sub>	$1.162 \pm 0.001$	ED data	[12]
Cyanocyclobutane	c-C <sub>4</sub> H <sub>7</sub> CN	$1.156 \pm 0.003$	ED data	[13]
Cyanocyclopentane	c-C <sub>5</sub> H <sub>9</sub> CN	$1.160 \pm 0.002$	ED data	[14]

<sup>a</sup> The C=N distance was assumed to be the same for the *anti/gauche* and *gauche/gauche* conformers.

$$S_j = g_j (45\alpha_j^2 + 7\beta_j^2)$$

where  $g_j$  is the degeneracy of the vibrational mode j,  $\alpha_j$  is the derivative of the isotropic polarizability and  $\beta_j$  is that of the anisotropic polarizability. The absolute differential Raman cross section can be obtained using the following equation:

$$\frac{\partial \sigma_j}{\partial \Omega} = (2^4 \pi^4/45) \left( \frac{(v_0 - v_j)^4}{1 - \exp(-hcv_j/kT)} \right) (h/8\pi^2 cv_j) S_j$$

where  $v_0$  is the exciting frequency, and *h*, *c* and *k* are universal constants. The relative differential Raman cross scattering section is  $(d\sigma_j/d\Omega)/(d\sigma_i/d\Omega)$ , where  $d\sigma/d\Omega$  refers to a chosen reference band. The calculated spectrum (Fig. 1(B)) is in reasonable agreement with the experimental one except for four lines. The CF bend at 604 cm<sup>-1</sup> is nearly four times more intense than the predicted value and the CC<sub>2</sub> symmetric stretch at 872 cm<sup>-1</sup> is about twice the predicted intensity. Also, the (CN)<sub>2</sub> bends are predicted to be too intense. Nevertheless, it is clear from these data that the Raman intensities obtained from the ab initio calculations can be very useful for assigning the vibrational spectrum.

Infrared intensities were calculated using the MP2/6-31G\* basis set and are based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were taken from the ab initio calculations and transformed to normal coordinates by

$$\left(\frac{\mathrm{d}\mu_u}{\partial Q_i}\right) = \sum_j \left(\frac{\mathrm{d}\mu_u}{\partial X_i}\right) L_{ji}$$

where the  $Q_i$  is the *i*th normal coordinate,  $X_j$  is the *j*th Cartesian displacement coordinate, and  $L_{ji}$ is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by

$$I_{i} = \frac{N\pi}{3C^{2}} \left[ \left( \frac{\partial \mu_{x}}{\partial Q_{i}} \right)^{2} + \left( \frac{\partial \mu_{y}}{\partial Q_{i}} \right)^{2} + \left( \frac{\partial \mu_{z}}{\partial Q_{i}} \right)^{2} \right]$$

The experimental infrared spectra (gas and solid) for FHC(CN)<sub>2</sub> are included with the calculated spectra in Fig. 2 for comparative purposes. As expected, the agreement between the calculated and experimental infrared spectra is very good particularly for the spectrum of the gas. Therefore, these spectra clearly show that calculated infrared spectra can be useful for analytical purposes and can contribute significantly to spectral interpretation and assignments.

The calculated structural parameters are listed in Table 2 from the RHF/6-31G\*, MP2/6-31G\*, and MP2/6-311 + +  $G^{**}$  calculations. At the RHF level the  $C \equiv N$  bond lengths and the C-F distance are guite short where as these bonds from the MP2/6-31G\* calculation are too long. With the larger basis set,  $MP2/6-311 + + G^{**}$ , the  $C \equiv N$  distance also appears to still be too long. In Table 6 the  $C \equiv N$  distances (11–14) are listed for four organonitrile molecules and the values of the distances for the  $C \equiv N$  bond including the uncertainties range from 1.153 to 1.164 A with the mean value of 1.160 Å. Therefore, the predicted value of 1.174 Å is probably too long by at least 0.013 Å. The difference in the predicted angles from the MP2/6-31G\* calculations compared to those from the MP2/6-311 +  $+ G^{**}$  calculations are relatively small except for the  $\leq FC_1C_2$  and  $\leq HC_1C_2$  which differ by 0.5 degrees. Also, the slight deviation from linearity of the NCC angle is predicted to be nearly the same from all three calculations differing by 0.2 from 178.4° from the RHF calculation to 178.6° with the large basis set at the MP2 level. Therefore, it should be possible to obtain excellent structural parameters from an electron diffraction study of this molecule using a very small constraint on these CCN parameters as well as most of the other angles and carbon-carbon distances.

We have utilized the isolated C-H frequency [15] of 2953 cm<sup>-1</sup> to obtain the C-H distance of 1.096 Å. This value is in excellent agreement with the values of 1.095 Å obtained from the MP2/ 6-31G\* calculation and 1.094 Å from the MP2/  $6-311 + + G^{**}$ calculation. Therefore, this parameter could also be given a very small uncertainty in an electron diffraction determination of the structural parameters of fluoromalononitrile. Such a study would be of particular interest to obtain more exact values of the  $C \equiv N$  and C-Fdistances as well as obtaining bond angles for comparison to the predicted values.

There is little difference in the frequencies for the in-phase and out-of-phase motions of the  $C \equiv N$  stretching modes. Also, these modes do not seem to be very dependent upon the other substituents on the carbon atom. For example, in 1,1-dicyanocyclobutane the observed [1] frequency for both the in-phase and out-of-phase motion is 2250 cm<sup>-1</sup>. For the corresponding five-membered ring [2] the frequency moves up to 2263 cm<sup>-1</sup> and again, there are no differences in frequency of the in-phase and out-of-phase motions. For fluoromalononitrile the in-phase CN stretch is observed at 2269  $cm^{-1}$  and the out-of-phase motion at 2272 cm<sup>-1</sup> in the infrared spectrum of the vapor. Similar frequencies are observed in the Raman spectrum of the liquid. Therefore, the two motions are only slightly split, i.e. three wavenumbers, and shifted by approximately 7 cm<sup>-1</sup> from those observed for the corresponding modes for the three-membered ring. Therefore, the fluorine atom has not significantly changed the frequency

of the CN stretches, which is a strong indication that the CN bond distances are not drastically different in these three different molecules.

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