# Infrared Spectra of the CHFCI, CHFBr, and CHFI Free Radicals in Solid Argon

FRANK T. PROCHASKA,<sup>1</sup> BRIAN W. KEELAN,<sup>2</sup> AND LESTER ANDREWS<sup>3</sup>

Chemistry Department, McCormick Road, University of Virginia, Charlottesville, Virginia 22901

Lithium atom matrix reactions with  $CHFCl_2$ ,  $CHFBr_2$ , and  $CHFI_2$  produced new infrared absorptions due to the lithium halides LiX and the CHFX free radicals. The CHFCl assignments are supported by <sup>13</sup>C and D isotopic substitution, and the CHFBr and CHFI radical absorptions were also found in  $CH_2FBr$  and  $CH_2FI$  photolysis studies. The CHFX,  $CHF_2$ , and  $CHX_2$  radical fundamentals are compared.

#### INTRODUCTION

Infrared spectra of the dihalomethyl free radicals were reported a decade ago using matrix reactions of lithium atoms and haloform precursors (1-4). These studies were characterized by particularly large yields of the free radical product. The CHFCl free radical is of potential environmental interest as a photochemical decomposition product of Freon-21, CHFCl<sub>2</sub>, and it is the only neutral molecular fragment not identified in earlier (5-7) and recent (8-9) matrix photolysis and photoionization studies of CHFCl<sub>2</sub> and CH<sub>2</sub>FCl. The infrared spectra of CHFCl, CHFBr, and CHFI are also of interest for correlation with spectra of CHFCl<sup>+</sup>, CHFBr<sup>+</sup>, and CHFI<sup>+</sup> and possible negative molecular ions in this system (9). As supporting evidence for the infrared spectrum of CHFCl, the related CHFBr and CHFI free radicals were also produced for infrared spectroscopic studies, which will be described here.

### EXPERIMENTAL DETAILS

The cryogenic refrigeration system, vacuum vessel, alkali metal source, and experimental techniques have been described previously (1, 10). A Model 21 cryocooler (Cryogenic Technology, Inc.) operating near 12 K was used for these studies with CsI optics. Lithium metal (Fisher), sodium metal (J. T. Baker), and argon (Air Products, 99.995%) were used without purification. Dichlorofluoromethane (DuPont) and dibromofluoromethane (Peninsular Chemresearch) were distilled from glass beads prior to sample preparation. Carbon-13-enriched CHFCl<sub>2</sub> was produced from <sup>13</sup>CHCl<sub>3</sub> as described previously (11). The CDFCl<sub>2</sub> compound was

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, Western Carolina University, Cullowhee, N. C. 28723.

<sup>&</sup>lt;sup>2</sup> Undergraduate research student.

<sup>&</sup>lt;sup>3</sup> Author for correspondence.

prepared by reacting  $CDCl_3$  with  $HgF_2$  at 90°C and distilling the product from glass beads, and  $CDFBr_2$  was synthesized from the reaction of  $CDBr_3$  with  $SbF_3$  (5 g)/  $SbF_5$  (5 drops) in a glass vessel at 25°C. A sample of diiodofluoromethane containing a small amount of  $CHF_2I$  impurity was synthesized from the reaction of  $CHI_3$  with  $HgF_2$  in a Pyrex finger near room temperature (8).

Reagent samples were diluted in argon to 150/1, 300/1, or 450/1 ratios and codeposited at 2–3 mmole/hr with lithium atoms from a 420°C or sodium atoms from a 220°C Knudsen cell for periods of 18–20 hr. Infrared spectra were recorded on a Perkin–Elmer 521 spectrophotometer during and after sample deposition on expanded wavenumber scale. Wavenumber accuracy is  $\pm 1$  cm<sup>-1</sup>.

### RESULTS

# Dichlorofluoromethane

A sample of  $Ar/CHFCl_2 = 400/1$  was reacted with Li atoms for 20 hr. The major products in the spectrum were the strong 895.0-, 897.5-, 900.0-, 902.5-cm<sup>-1</sup> multiplet of the CHCl<sub>2</sub> radical identical to that previously reported by Carver and Andrews (2) and a 1220-, 1227-cm<sup>-1</sup> doublet due to the same species (13); a LiF doublet (12) at 837 and 842  $\text{cm}^{-1}$  was also observed, as reported by Jacox and Milligan (7) in a similar, shorter experiment. In the present, longer experiment, additional new bands were observed at 751, 754, 757, 1151, 1277, and 1283  $cm^{-1}$ and a weak LiCl band (12) was observed at 578  $cm^{-1}$ . Another experiment was done at higher concentration,  $Ar/CHFCl_2 = 150/1$ , to increase the product yield; the spectrum from this study is shown in Fig. 1a. The strong CHCl<sub>2</sub> multiplet (A = absorbance units = 0.73) and 1220-, 1227-cm<sup>-1</sup> doublet (A = 0.16, 0.27)were increased, as were the new bands at 1151 cm<sup>-1</sup> (A = 0.16), 1277 cm<sup>-1</sup> (A = 0.10), 1283 cm<sup>-1</sup> (A = 0.16), the LiF doublet at 837 and 842 cm<sup>-1</sup> (A = 0.24, 0.14) and LiCl at 578 cm<sup>-1</sup> (A = 0.05). In addition, a weak CHF absorption at 1182 cm<sup>-1</sup> (A = 0.01) (14) and the new multiplet at 751, 754, and 757 cm<sup>-1</sup> (A = 0.025, 0.08, 0.08, respectively) were observed.

One experiment was performed with a 90% carbon-13-enriched sample,  $Ar/^{13}CHFCl_2 = 450/1$ , for 22 hr; the final infrared spectrum is shown in Fig. 1b. The dominant product absorptions are the 877- to 870-cm<sup>-1</sup> multiplet (A = 0.36) and the 1213-, 1220-cm<sup>-1</sup> doublet (A = 0.06, 0.13) of  $^{13}CHCl_2$  (13), and the LiF doublet at 837 and 842 cm<sup>-1</sup> (A = 0.15, 0.04). Weak new product bands were also observed at 1121 cm<sup>-1</sup> (A = 0.02), 1269, 1274 cm<sup>-1</sup> (A = 0.02), and 578 cm<sup>-1</sup> (A = 0.02).

A final study was done with a sample of  $Ar/CDFCl_2 = 150/1$ . After matrix reaction with lithium atoms for 19 hr, the spectrum shown in Fig. 1c was recorded. The strongest CDCl<sub>2</sub> radical band at 974 cm<sup>-1</sup> was obscured by a CDFCl<sub>2</sub> absorption; however, the weaker 815-, 817-cm<sup>-1</sup> doublet (A = 0.28) of this species was observed in addition to that of LiF at 837 and 842 cm<sup>-1</sup> (A = 0.27, 0.16). New product bands were also observed at 1154 cm<sup>-1</sup> (A = 0.16) and 960 cm<sup>-1</sup> (A = 0.10), CDF was found at 1184 cm<sup>-1</sup> (A = 0.01) (14), and a weak LiCl absorption appeared at 578 cm<sup>-1</sup> (A = 0.03).

Samples of CHFCl<sub>2</sub> and CDFCl<sub>2</sub> diluted in argon were deposited for 13 and 19 hr,



F1G. 1. Infrared spectra of dichlorofluoromethane samples codeposited with lithium atoms at high dilution in argon at 12 K: (a)  $Ar/CHFCl_2 = 150/1$ , 20-hr reaction; (b)  $Ar/^{13}CHFCl_2 = 450/1$ , 90% <sup>13</sup>C, 22-hr reaction; (c)  $Ar/CDFCl_2 = 150/1$ , 19-hr reaction.

respectively, to measure all precursor and impurity absorptions in the reagent gas. These bands are labeled P and I, respectively, in the figure.

# Dibromofluoromethane

One  $Ar/CHFBr_2 = 150/1$  sample was reacted with lithium atoms for 18 hr, and the intense new product bands are shown in Fig. 2c. Note the very intense,



FIG. 2. Infrared spectra of dibromofluoromethane samples codeposited with alkali metal atoms and bromofluoromethane after matrix photolysis: (a)  $Ar/CDFBr_2 = 300/1$ , 20-hr reaction with Li atoms; (b)  $Ar/CH_2FBr = 400/1$ , 17-hr argon resonance photolysis; (c)  $Ar/CHFBr_2 = 150/1$  18-hr reaction with Li atoms; (d)  $Ar/CHFBr_2 = 200/1$ , 20-hr reaction with Na atoms.

sharp band at 1149 cm<sup>-1</sup> (A = 1.0), the sharp doublet at 1124, 1129 cm<sup>-1</sup>, the strong 1266-cm<sup>-1</sup> band (A = 0.28), and the strong LiBr band (I2) at 504 cm<sup>-1</sup> (A = 0.26). A new absorption appeared at 650 cm<sup>-1</sup> ( $A \approx 0.3$ ) superposed on top of a weak absorption (A = 0.1) in the precursor spectrum. The deformation mode of CHBr<sub>2</sub> was observed at 1155 and 1166 cm<sup>-1</sup> (A = 0.23, 0.29), while the C-Br<sub>2</sub> stretching mode appeared at 779 and 786 cm<sup>-1</sup> (A = 0.52) (I); LiF was also produced, absorbing at 837 and 842 cm<sup>-1</sup> (A = 0.11, 0.05). An experiment was done with sodium atoms and CHFBr<sub>2</sub>; new absorptions of interest observed at 1266 cm<sup>-1</sup> (A = 0.05) and 1149 cm<sup>-1</sup> (A = 0.21) are contrasted in Fig. 2d with the spectrum from the lithium atom reaction.

Dibromofluoromethane was also subjected to argon resonance radiation during condensation at 15 K in a series of detailed studies (8). Weak new bands at 1266 cm<sup>-1</sup> (A = 0.01), 1145 cm<sup>-1</sup> (A = 0.03), and 1149 cm<sup>-1</sup> (A = 0.05) in an Ar/ CHFBr<sub>2</sub> = 400/1 experiment using a 3-mm orifice argon discharge tube are of interest here.

One experiment was performed using the lithium matrix reaction for 20 hr with an Ar/CDFBr<sub>2</sub> = 300/1 sample containing a small amount of CDF<sub>2</sub>Br impurity. Absorptions were observed for lithium fluoride at 837 and 842 cm<sup>-1</sup> (A = 0.10) with sharp bands for the CDBr<sub>2</sub> radical at 725 cm<sup>-1</sup> (A = 0.12) and CDF at 1184 cm<sup>-1</sup> (A = 0.04); the stronger CDBr<sub>2</sub> absorption at 899 cm<sup>-1</sup> was obscured by the precursor. New product features were observed at 1162 cm<sup>-1</sup> (A = 0.12) and 913 cm<sup>-1</sup> (A = 0.06) which are shown in Fig. 2a, along with a 1215-cm<sup>-1</sup> band for the CDF<sub>2</sub> radical (3) produced from the CDF<sub>2</sub>Br impurity.

Argon matrix samples of CHFBr<sub>2</sub> and CDFBr<sub>2</sub> were deposited for 20 hr, and the spectra of precursor and impurities were recorded; these features are also labeled P and I in the figure.

# **Bromofluoromethane**

The compound CH<sub>2</sub>FBr was diluted in argon to Ar/CH<sub>2</sub>FBr = 400/1 and codeposited with simultaneous argon resonance photolysis (9). Among the new bands observed were sharp features at 1266 cm<sup>-1</sup> (A = 0.05) and 1149 cm<sup>-1</sup> (A = 0.25), which are illustrated in Fig. 2b. Strong new bands were also observed at 1157 and 656 cm<sup>-1</sup> and assigned to the CFBr intermediate (9).

### Diiodofluoromethane

Three experiments were performed with  $CHFI_2$  samples. The first study employed the lithium reaction with an  $Ar/CHFI_2 \approx 150/1$  sample for 22 hr. A strong LiI absorption (15) was observed at 448 cm<sup>-1</sup> (A = 0.28) along with strong new product bands at 1256 cm<sup>-1</sup> (A = 0.59), 1153 cm<sup>-1</sup> (A = 0.41), and 1138 cm<sup>-1</sup> (A = 0.72) and new features at 1165, 1175, and 1181 cm<sup>-1</sup> which are illustrated in Fig. 3b. A weak new band appeared at 560 cm<sup>-1</sup> (A = 0.03); no LiF was observed.

Diiodofluoromethane, diluted in argon to  $Ar/CHFI_2 \approx 300/1$ , was codeposited with concurrent argon discharge photolysis from a 1-mm orifice tube for 9 hr. Weak new product absorptions were observed at 1256 cm<sup>-1</sup> (A = 0.05) and

1138 cm<sup>-1</sup> (A = 0.03). An identical sample was deposited without discharge photolysis to measure precursor and impurity absorptions, which will be given in another report (8).

### Iodofluoromethane

The CH<sub>2</sub>FI precursor was condensed with simultaneous argon resonance photolysis from a 3-mm orifice tube for 16 hr, and that portion of the infrared spectrum of interest here is shown in Fig. 3a. A sharp new product band was observed at 1256 cm<sup>-1</sup> (A = 0.10), and a new feature was found at 1133 cm<sup>-1</sup> (A = 0.42) with a resolved shoulder at 1138 cm<sup>-1</sup>. Other product features previously identified include CF at 1280 and 1276 cm<sup>-1</sup> (A = 0.07), CHF at 1182 cm<sup>-1</sup> (A = 0.02) (14), and the CH<sub>2</sub>F radical at 1162 cm<sup>-1</sup> (A = 0.60) (14, 16). The lower-wavenumber region contained a new shoulder at 560 cm<sup>-1</sup> on the very intense 565-cm<sup>-1</sup> precursor absorption and a sharp new band at 573 cm<sup>-1</sup>. The 1133- and 573-cm<sup>-1</sup> absorptions are due to the carbene CFI, as discussed in a separate paper (9).

### DISCUSSION

The new fluorohalomethyl radicals produced here will be identified, and the vibrational assignments will be characterized.

# The CHFBr Radical

Following the earlier use of the lithium atom matrix reaction technique to produce the CHBr<sub>2</sub> radical and LiBr from bromoform (1), the observation of LiF and LiBr in the CHFBr<sub>2</sub> sample codeposited with lithium atoms confirms that reaction occurs and shows that the CHBr<sub>2</sub> and CHFBr radicals are likely products according to reactions (1) and (2):

$$CHFBr_2 + Li \rightarrow LiF + CHBr_2, \tag{1}$$

$$CHFBr_2 + Li \rightarrow LiBr + CHFBr.$$
 (2)

The CHBr<sub>2</sub> radical bands observed here, 786 and 1166 cm<sup>-1</sup>, are in precise agreement with the bromoform work (l).

The strong 1149- and 1266-cm<sup>-1</sup> bands in the lithium reaction study appeared with reduced intensity at the same positions in the sodium experiment. This behavior is typical of an isolated free radical product not perturbed by the LiBr or NaBr reaction product (1). The 1129-cm<sup>-1</sup> absorption labeled C in the lithium study not found in the sodium experiment may be due to a CHFBr-LiBr complex species.

The new 1149- and 1266-cm<sup>-1</sup> absorptions were produced in moderate yield from the photolysis of  $CH_2FBr$  and as weak bands in  $CHFBr_2$  photolysis. Since the only free radical common to these two precursors is CHFBr, the 1149- and 1266-cm<sup>-1</sup> absorptions are assigned to this species. The 650-cm<sup>-1</sup> absorption in the most productive experiment is probably due to the C-Br stretching mode of the CHFBr radical.



FIG. 3. Infrared spectra of diiodofluoromethane codeposited with lithium atoms and iodofluoromethane after matrix photolysis: (a)  $Ar/CH_2FI = 400/1$ , 16-hr argon resonance photolysis; (b)  $Ar/CHFI_2 \approx 150/1$ , 22-hr reaction with Li atoms.

An experiment with lithium and CDFBr<sub>2</sub> produced strong LiF and LiBr bands, again confirming reaction. The CDBr<sub>2</sub> radical was identified at 725 cm<sup>-1</sup> (l), and the observation of CDF at 1184 cm<sup>-1</sup> (l4) gives more evidence for bromine

abstraction from CDFBr<sub>2</sub> and provides a basis for the observation of CDFBr radical in the sample. The new 913- and 1162-cm<sup>-1</sup> absorptions assigned here to CDFBr show the expected deuterium isotopic shifts for a H (or D) bending mode and a C-F stretching mode.

# The CHFCl Radical

A similar case can be made for the 751-, 754-, 757-cm<sup>-1</sup> multiplet, the 1151cm<sup>-1</sup> band, and the 1277-, 1283-cm<sup>-1</sup> doublet in the CHFCl<sub>2</sub> studies, although the bands are weaker owing to a less favorable reaction. The observation of LiF and CHCl<sub>2</sub> free radical absorptions shows that reaction takes place, and the observation of LiCl makes the CHFCl free radical a likely product.

Isotopic observations verify assignment of these absorptions to the CHFCl free radical. The 1277, 1283 cm<sup>-1</sup> doublet exhibits an 8-cm<sup>-1</sup> <sup>13</sup>C shift and a large displacement to 960 cm<sup>-1</sup> upon deuteration, whereas the 1151-cm<sup>-1</sup> band shifts to 1121 cm<sup>-1</sup> on <sup>13</sup>C substitution and *up* to 1154 cm<sup>-1</sup> in the deuterium species. The latter behavior is characteristic of a C-F stretching mode in a hydrogen-containing species, as illustrated by CHF at 1182 cm<sup>-1</sup>, which shifted to 1163 cm<sup>-1</sup> for <sup>13</sup>CHF and 1184 cm<sup>-1</sup> for CDF (*14*). The relative intensities of the 757-, 754-, 751-cm<sup>-1</sup> multiplet are appropriate for two superposed 3/1 doublets characteristic of the vibration of a single chlorine atom in two different matrix sites. The sharp multiplet for CHCl<sub>2</sub> at 902 cm<sup>-1</sup> is also due to a combination of chlorine isotopic and matrix site splittings (2).

# The CHFI Radical

The lithium atom matrix reaction with  $CHFI_2$  produced a strong LiI band and no LiF absorption, which indicates that the CHFI radical is a likely product. Strong new 1256- and 1138-cm<sup>-1</sup> absorptions in the lithium experiment with  $CHFI_2$  were also observed unshifted in the  $CH_2FI$  photolysis study. These absorptions are assigned to the common free radical product CHFI; the weak 560-cm<sup>-1</sup> band in both experiments is probably due to the C-I stretching mode of the CHFI radical. The 1153-cm<sup>-1</sup> absorption in the lithium experiment could be due to a CHFI-LiI complex or a different matrix site of the CHFI species.

The 1165-, 1175-cm<sup>-1</sup> doublet in the CHFI<sub>2</sub> experiment is due to CHF<sub>2</sub> radical (3) produced by the reaction of lithium atoms with CHF<sub>2</sub>I impurity in the CHFI<sub>2</sub> sample. The 1181-cm<sup>-1</sup> absorption is probably due to the CHF<sub>2</sub>-LiI complex observed at 1190 cm<sup>-1</sup> for the LiBr complex species (3).

# Vibrational Assignments

The vibrational assignments for CHFX radicals are contrasted in Table I with vibrational data for the CHF<sub>2</sub> and CHX<sub>2</sub> free radicals. The trend in hydrogen deformation modes is straightforward, showing a decreasing frequency for increasing halogen atomic mass from 1283 to 1256 cm<sup>-1</sup> for CHFCl to CHFI. The unusual displacement of the C-F stretching modes for CHFCl and CHFBr to higher wavenumbers upon deuteration is characteristic of several fluorine

#### TABLE I

H (or D) deformation	<u>CHF</u> 2 1317	<u>CDF</u> 2 934			
C-F <sub>2</sub> antisym	1175	1217			
	CHFC1	CDFC1	CHFBr	CDFBr	CHFI
H (or D) deformation	1283	960	1266	913	1256
	1205	500	1200	520	2000
C-F stretch	1151	1154	1149	1162	1138
C-X stretch <sup>b</sup>	757	_	650	_	560
	CHC12	CDC12	CHBr <sub>2</sub>	CDBr <sub>2</sub>	<u>CHI</u> 2
H (or D) deformation	1226	974	1166	898	1107
C-X <sub>2</sub> antisym	902	816	786	725	717

### Vibrational Fundamentals (in cm<sup>-1</sup>) for Dihalomethyl Free Radicals<sup>a</sup> and Fluorohalomethyl Radicals

<sup>a</sup>References (1-4).

<sup>b</sup>Tentative assignments.

species (3) and is a consequence of interaction between the hydrogen and deuterium deformation modes and the C-F stretching mode.

The carbon-fluorine stretching modes for the CHFX radicals appear near the  $CH_2F$  radical value at 1162 cm<sup>-1</sup> (14, 16). The carbones CFX provide good models for the C-F and C-X stretching modes of the CHFX radicals. The C-F stretching mode of CHFCl at 1151 cm<sup>-1</sup> is quite close to the CFCl mode at 1146 cm<sup>-1</sup>; the latter absorption is very strong in the CH<sub>2</sub>FCl photolysis experiments (6, 9), and it possibly masks some 1151-cm<sup>-1</sup> CHFCl absorption. In the CHFBr and CFBr species, the C-F stretching modes are at 1149 and 1157 cm<sup>-1</sup>, respectively. Similar absorptions at 1138 and 1133 cm<sup>-1</sup> are assigned to CHFI and CFI.

The 757-cm<sup>-1</sup> multiplet in the CHFCl<sub>2</sub> studies, tentatively assigned to the C-Cl stretching mode of the CHFCl free radical, is slightly higher than the 742-cm<sup>-1</sup> position of this mode in CFCl. Weak bands at 650 and 560 cm<sup>-1</sup> in the CHFBr<sub>2</sub> and CHFI<sub>2</sub> experiments are tentatively assigned to the C-Br and C-I stretching modes of CHFBr and CHFI, which are near the analogous modes of CFBr and CFI at 657 and 573 cm<sup>-1</sup>, respectively (9).

### **Precursor Reactivity**

It is interesting to contrast the precursor reactivity toward lithium atoms for a series of experiments with CHFCl<sub>2</sub>, CHFBr<sub>2</sub>, and CHFI<sub>2</sub> conducted under com-

parable conditions. For the dichloro precursor, the LiF absorption yield was a factor of 10 greater than LiCl, and the  $CHCl_2$  product was likewise considerably more intense than CHFCl. However, the LiF absorbance was only half of the LiBr absorbance using the CHFBr<sub>2</sub> reagent, and the CHFI<sub>2</sub> precursor gave a large yield of LiI and no LiF.

The strong preference of fluorine abstraction over chlorine in the CHFCl<sub>2</sub> reaction in spite of the stronger C-F bond and the larger target presented by two chlorine atoms suggests greater electronic stability for the CHCl<sub>2</sub> radical relative to the CHFCl radical. Although the structures of neither of these radicals have been determined, the CHCl<sub>2</sub> radical is probably planar, and CHFCl likely departs slightly from planarity using CH<sub>2</sub>F as a model (17). The electronic stabilization of chloromethyl radicals owing to pi bonding has been discussed previously (18). A similar preference for fluorine abstraction over chlorine has been found for CH<sub>2</sub>FCl and attributed to greater electronic stability for CH<sub>2</sub>Cl as compared to CH<sub>2</sub>F (16).

In the case of CHFBr<sub>2</sub>, lithium bromide abstraction dominates but lithium fluoride production is competitive. The earlier lithium reactions with CH<sub>2</sub>FBr produced comparable yields of LiF and LiBr (16). These observations suggest less electronic stabilization of the free radical by fluorine than chlorine or bromine, although kinetic factors probably also influence the product yield with the heavier halogen precursors. This trend is continued with the CHFI<sub>2</sub> species which gave iodide abstraction exclusively, the same behavior found for CH<sub>2</sub>FI (16).

### CONCLUSION

The lithium atom matrix reaction with CHFCl<sub>2</sub> produced LiCl and new absorptions at 1283 and 1151 cm<sup>-1</sup> appropriate for hydrogen deformation and C-F stretching modes of the CHFCl free radical; these assignments were supported by <sup>13</sup>C and D isotopic substitution. Lithium and sodium reactions with CHFBr<sub>2</sub> and matrix photolysis of CH<sub>2</sub>FBr produced identical absorptions at 1266 and 1149 cm<sup>-1</sup> for the CHFBr free radical, and a like series of studies with CHFI<sub>2</sub> and CH<sub>2</sub>FI yielded new bands at 1256 and 1138 cm<sup>-1</sup> for the CHFI free radical. The greater reactivity of lithium for fluorine abstraction from CHFCl<sub>2</sub>, as compared to chlorine removal, suggests that chlorine provides more electronic stabilization for halomethyl radicals than fluorine.

#### ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, for support of this research.

**RECEIVED:** September 19, 1978

#### REFERENCES

1. T. G. CARVER AND L. ANDREWS, J. Chem. Phys. 50, 4223-4234 (1969).

2. T. G. CARVER AND L. ANDREWS, J. Chem. Phys. 50, 4235-4245 (1969).

3. T. G. CARVER AND L. ANDREWS, J. Chem. Phys. 50, 5100-5107 (1969).

- 4. D. W. SMITH AND L. ANDREWS, J. Phys. Chem. 76, 2718-2722 (1972).
- 5. D. E. MILLIGAN, M. E. JACOX, J. H. MCAULEY, AND C. E. SMITH, J. Mol. Spectrosc. 45, 377-403 1973).
- 6. C. E. SMITH, D. E. MILLIGAN, AND M. E. JACOX, J. Chem. Phys. 54, 2780 (1971).
- 7. M. E. JACOX AND D. E. MILLIGAN, Chem. Phys. 16, 195-208 (1976).
- 8. B. W. KEELAN AND L. ANDREWS, to be published.
- 9. F. T. PROCHASKA AND L. ANDREWS, to be published.
- 10. L. ANDREWS, J. Chem. Phys. 63, 4465-4469 (1975).
- 11. L. ANDREWS, H. WILLNER, AND F. T. PROCHASKA, J. Fluorine Chem. 13, 273-278 (1979).
- 12. S. SCHLICK AND O. SCHNEPP, J. Chem. Phys. 41, 463-472 (1964).
- 13. L. ANDREWS, F. T. PROCHASKA, AND B. S. AULT, J. Amer. Chem. Soc. 101, 9-15 (1979).
- 14. M. E. JACOX AND D. E. MILLIGAN, J. Chem. Phys. 50, 3252-3262 (1969).
- 15. L. ANDREWS AND G. C. PIMENTEL, J. Chem. Phys. 47, 3637-3644 (1967).
- 16. J. I. RAYMOND AND L. ANDREWS, J. Phys. Chem. 75, 3235-3242 (1971).
- 17. R. W. FESSENDEN AND R. H. SCHULER, J. Chem. Phys. 43, 2704-2712 (1965).
- 18. L. ANDREWS AND D. W. SMITH, J. Chem. Phys. 53, 2956-2966 (1970).