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# CO<sub>2</sub>-HF: A linear molecule<sup>a)</sup>

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The results of microwave and radio frequency spectroscopy of the weakly bound complexes of hydrogen fluoride with carbon dioxide and carbonyl sulfide are presented. The following spectroscopic constants are determined:

|                 | CO <sub>2</sub> -HF | CO <sub>2</sub> -DF | SCO-HF        |
|-----------------|---------------------|---------------------|---------------|
| $B_0$ (MHz)     | 1951.1696(11)       | 1935.9959(7)        | 1307.462(4) , |
| $D_0$ (MHz)     | 0.01069(7)          | 0.01121(3)          | 0.00246(9) ,  |
| $\mu$ (D)       | 2.2465(4)           | 2.3024(1)           | 3.2085(20) ,  |
| $S_a$ (MHz)     | 0.1047(6)           | 0.01739(24)         | 0.105(5) ,    |
| $eqQ_a^D$ (MHz) | ...                 | 0.2639(5)           | ...           |

A nearly linear hydrogen bonded equilibrium structure with an O-H bond length of  $\sim 1.9$  Å is consistent with all the experimental data. The stretching force constant, estimated from the distortion constant to be  $k_s = 0.021$  mdyne/Å for CO<sub>2</sub>-HF, appears anomalously small for such a short bond.

## INTRODUCTION

The study of the interactions of CO<sub>2</sub> with other atoms and molecules is of interest for a variety of reasons. In particular, the CO<sub>2</sub>-HF system has been the subject of extensive study because of interest in CO<sub>2</sub> and HF lasers. Experimental work<sup>1</sup> has been mainly conducted on the deactivation of vibrationally excited CO<sub>2</sub> by collision with HF or DF, and vice versa. The models used to fit the experimental results employ an intermolecular potential for CO<sub>2</sub>-HF that has an energy minimum for the linear hydrogen bonded arrangement of the submolecules.<sup>1(b),1(c)</sup> The present experiment is ideally suited to test this proposed CO<sub>2</sub>-HF structure at the potential energy minimum. The complex CO<sub>2</sub>-HF has also been used as a catalyst for several organic chemical reactions. Several patents have been granted for the use of CO<sub>2</sub>-HF as a catalyst in the alkylation of phenols and alkoxybenzenes.<sup>2</sup>

Some theoretical work done by Kollmann included calculations on CO<sub>2</sub>-HF.<sup>3</sup> He considered two possible interactions. The first possibility, a hydrogen bonding interaction, arranges the submolecules in a linear manner with the hydrogen pointing towards the oxygen. The second possibility, an interaction in which HF acts as a Lewis base, gives a T-shaped structure with the fluorine pointing towards the carbon. Of the two structures considered, the hydrogen bonded structure was found to have the lower potential energy, based on electrostatic interactions between the submolecules.

The system CO<sub>2</sub>-HF was chosen with the hope that it would be representative of the entire series NH<sub>3</sub>, H<sub>2</sub>O, and HF bound to CO<sub>2</sub>. Of these three hydrides, HF is likely the poorest Lewis base. Previous work<sup>4</sup> on the complex Ar-CO<sub>2</sub> showed it to have a T-shaped struc-

ture with Ar acting as a Lewis base. Janda<sup>5</sup> has contrasted the behavior of argon and hydrogen fluoride acting as Lewis bases (see Figs. 5 and 6 of Ref. 5). If HF acts as a Lewis base in CO<sub>2</sub>-HF, the qualitative structure of CO<sub>2</sub>-NH<sub>3</sub> and CO<sub>2</sub>-H<sub>2</sub>O could be inferred.

The SCO-HF results are included in this paper because of the similarity between it and CO<sub>2</sub>-HF. SCO-HF was studied to provide a check of the CO<sub>2</sub>-HF results after work on the complex N<sub>2</sub>O-HF<sup>6</sup> showed a different structure for it compared to CO<sub>2</sub>-HF. The data on the carbonyl sulfide complex are relatively incomplete but are sufficient to establish that OCS and CO<sub>2</sub> behave similarly towards HF.

## EXPERIMENTAL

The molecular beam electric resonance technique<sup>7</sup> was used to obtain radio frequency and microwave spectra of the complexes. The only change in the apparatus from previous work was the addition of a PET-2000 microcomputer and homemade interface for the purpose of signal averaging. This low cost signal averaging system was indispensable for the SCO-HF work.

The complexes were formed by the expansion of an appropriate gas mixture through a 25  $\mu$  nozzle into vacuum. The mixture composition and the stagnation pressure and temperature which optimized formation of the complex were determined mass spectrometrically. Due to the ease of formation of HF clusters, especially at low temperatures, all work was done at room temperature. For CO<sub>2</sub>-HF formation, a 200:5:1 mixture of Ar:CO<sub>2</sub>:HF at a pressure of approximately 2 atm gave the best results. For SCO-HF, a 200:3:2 mixture of Ar:OCS:HF was used, at a pressure of approximately 3 atm.

The species of interest were monitored mass spectrometrically. The parent ion peak at  $m/e = 64$  was observed for CO<sub>2</sub>-HF, but a much more intense peak aris-

<sup>a)</sup>This research was supported by the Air Force Office of Scientific Research.

ing from the complex was found at  $m/e=45$ , due to the HCO<sub>2</sub><sup>+</sup> ion, so all spectroscopy was done while monitoring this fragment. For SCO-HF, the parent ion peak was all but obscured by the presence of large amounts of Ar<sub>2</sub> in the beam. Hence, SCO-HF was monitored at  $m/e=61$  (HOCS<sup>+</sup>).

The transitions observed for each molecule are due to rotational energy changes, i.e.,  $\Delta J=1$ , whose frequencies are in the microwave region, or rotational orientation changes, i.e.,  $\Delta J=0$ ,  $\Delta M_J=1$ , which are observed in an applied electric field and whose frequencies are in the radio region. No radio frequency transitions were observed at zero electric field. Also, a Stark effect measurement of the  $J=3 \rightarrow 4$  transition of CO<sub>2</sub>-HF was done in which frequencies for five separate  $M_J$  components were determined at eight electric field settings. The measurements for a given  $M$  component were fit to a three parameter equation<sup>8</sup>:  $\nu_{\text{meas}} = \nu_0 + aE^2 + bE^4$ . These data were used to test for the presence of a  $b$ -type dipole moment and will be discussed later.

The quality of the spectra of SCO-HF was generally worse than that of the CO<sub>2</sub>-HF spectra. Partly, the SCO-HF work proved difficult due to the background contributed by the overlap from the OCS peak, which, unlike CO<sub>2</sub>, is focusable. An additional difficulty is a result of the much faster Stark effect in SCO-HF. For the lower rotational levels of such a molecule, the aperture of the state selecting lens is small.<sup>9</sup> The resulting low focused beam intensity leads to poor signal-to-background ratios. Consequently, the higher  $J$  rotational transitions were preferentially observed for SCO-HF.

## RESULTS

The measured frequencies of rotational transitions at zero electric field are presented in Table I for the three complexes CO<sub>2</sub>-HF, CO<sub>2</sub>-DF, and SCO-HF. Four  $\Delta J=1$  rotational transitions were observed for each of the three complexes. After removing the hyperfine structure present in some of these transitions, the frequencies fit quite well to the energy level expression for a linear molecule

$$E = B_0 J(J+1) - D_0 J^2(J+1)^2.$$

The rotational and distortion constants thus derived are listed in Table III.

Both CO<sub>2</sub> and OCS consist entirely of nuclei with spin equal to zero. Hence, the hyperfine structure patterns in the transitions of CO<sub>2</sub>-HF and SCO-HF are very similar to those of Ar-HF. The analysis of the hyperfine structure in the present species follows that in Ar-HF.<sup>10</sup> Two hyperfine parameters can be determined:  $S$ , the nuclear spin-spin coupling constant, and  $eqQ^D$ , the deuterium nuclear quadrupole coupling constant. These constants are most easily determined from the  $\Delta J=0$ ,  $\Delta M=1$  transitions in the rf region since the resolution of the apparatus is higher in this frequency range ( $\sim 1$ – $2$  kHz linewidths). These constants are then used to calculate the rotational transitions and evaluate the unsplit line positions.

TABLE I. Measured zero field transitions.<sup>a</sup>

| CO <sub>2</sub> -HF |                       |            |                |                         |                |
|---------------------|-----------------------|------------|----------------|-------------------------|----------------|
| <i>J</i>            | <i>F</i> <sup>b</sup> | <i>J</i> ' | <i>F</i> '     | <i>ν</i> (MHz)          |                |
| 0                   | 1                     | 1          | 2              | 3 902.308(4)            |                |
| 0                   | 1                     | 1          | 0              | 3 902.401(3)            |                |
| 1                   | 2                     | 2          | 3              | 7 804.338(3)            |                |
| 1                   | 1                     | 2          | 2              |                         |                |
| 1                   | 1                     | 2          | 1              | 7 804.440(7)            |                |
| 2                   | 3                     | 3          | 4              | 11 705.870(8)           |                |
| 2                   | 2                     | 3          | 3              |                         |                |
| 3                   | 4                     | 4          | 5              | 15 606.618(11)          |                |
| 3                   | 3                     | 4          | 4              |                         |                |
| CO <sub>2</sub> -DF |                       |            |                |                         |                |
| <i>J</i>            | <i>F</i> <sub>1</sub> | <i>J</i> ' | <i>F</i> '     | <i>F</i> ' <sub>1</sub> | <i>ν</i> (MHz) |
| 0                   |                       | 1          | 3/2            | 1                       | 3 872.003(4)   |
| 0                   |                       | 1          | 1/2            | 1                       | 3 872.030(3)   |
| 1                   | 1                     | 2          |                | 1                       | 7 743.488(17)  |
| 1                   | 1                     | 2          |                | 2                       | 7 743.623(3)   |
| 1                   | 2                     | 2          |                | 2                       | 7 743.708(8)   |
| 2                   | 2                     | 3          |                | 3                       | 11 614.765(5)  |
| 2                   | 3                     | 3          |                | 3                       | 11 614.858(10) |
| 3                   | 3                     | 4          |                | 3                       | 15 484.980(11) |
| 3                   | 3                     | 4          |                | 4                       | 15 485.098(5)  |
| SCO-HF              |                       |            |                |                         |                |
| <i>J</i>            | <i>J</i> '            |            | <i>ν</i> (MHz) |                         |                |
| 2                   | 3                     |            | 7 844.504(28)  |                         |                |
| 3                   | 4                     |            | 10 459.074(24) |                         |                |
| 4                   | 5                     |            | 13 073.393(30) |                         |                |
| 5                   | 6                     |            | 15 687.422(40) |                         |                |

<sup>a</sup>Reported uncertainties are full width at half-height divided by  $S/N$  of measured line.

<sup>b</sup>Coupling scheme,  $F_1 = J + I_H$ ;  $F = F_1 + I_F$ .

Typical radio frequency Stark spectra for CO<sub>2</sub>-HF and CO<sub>2</sub>-DF are shown in Fig. 1 for the transition  $J=1$ ,  $\Delta M_J=1$ . The rf measurements are reported in Table II. As can be seen from these numbers, the observed hyperfine splittings are essentially field independent at the voltages used.

A nonlinear weighted least squares analysis is used to fit the CO<sub>2</sub>-HF rf data to the parameters  $\mu$  and  $S$  and the CO<sub>2</sub>-DF rf data to the parameters  $\mu$ ,  $S$ , and  $eqQ^D$ . The results of this analysis are shown in Table III. All parameters showed negligible correlation (all correlation matrix elements  $< 0.3$ ).

For SCO-HF, measurements of the  $J=0 \rightarrow 1$  rotational transition at several Stark fields provide the only reliable hyperfine information. (The rf transitions were observed, but only with very low  $S/N$  ratios.) These data, and the resulting values of the dipole moment and spin-spin constant, are also listed in Tables II and III.

The spectroscopic constants can now be used to de-

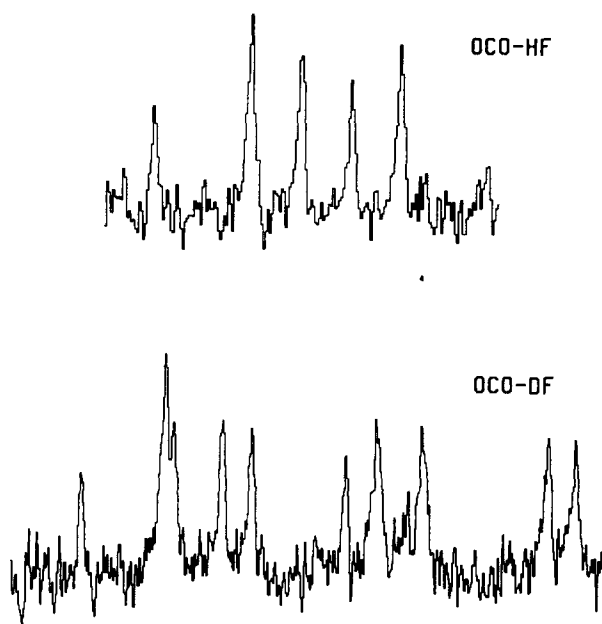


FIG. 1.  $J=1$ ,  $\Delta M_J=1$  Stark spectra. Top: Average of two scans through the region 8.70–8.95 MHz at 300 V/cm, a time constant of 3 s, and a resolution of 1.25 kHz/channel. Bottom: Eight scans through the region 3.015–3.315 MHz at 174.6 V/cm, 3 s time constant, and 0.5 kHz/channel.

rive an average structure for each molecule. We assume that the equilibrium structures are linear and that zero point vibration about this equilibrium structure gives rise to the average structure. (The validity of this assumption will be discussed later.)

The rotational constant  $B_0$  is used to calculate  $r_{c.m.}$ , the average distance between the centers of mass of the submolecules. The HF hyperfine constants can be used to establish its average orientation with respect to the principal axis of the complex. The relations are

$$S_a = \frac{1}{2}S_0(3\langle\cos^2\theta\rangle - 1) ,$$

$$eqQ_a^D = \frac{1}{2}eqQ_0^D(3\langle\cos^2\theta\rangle - 1) .$$

In these expressions,  $S_0$  and  $eqQ_0^D$  are the constants of free HF or DF, and  $\theta$  is the angle made by the HF submolecule with the  $a$  axis of the complex. This model assumes that the properties of free HF do not change significantly when bound in a complex.  $\theta$  is calculated for each molecule using<sup>11</sup>  $S_0^{\text{HF}} = 0.143\,375$  MHz,  $S_0^{\text{DF}} = 0.022\,17$  MHz, and  $eqQ_0^D = 0.354\,238$  MHz. The angle that the HF makes with the center of mass line  $\gamma$  is then estimated from this. These structural parameters are summarized in Table IV.

In CO<sub>2</sub>-DF two measurements of the angle are available.  $S_a$  gives an angle of 22.28(58)°, while  $eqQ_a^D$  gives

TABLE II. Measured transitions at nonzero static electric fields (MHz).<sup>a</sup>

| CO <sub>2</sub> -HF             |              |              |              |              |
|---------------------------------|--------------|--------------|--------------|--------------|
| $J=1, M_J=0 \rightarrow M_J'=1$ |              |              |              |              |
| $M_F$                           | $M_F'$       | 100.0 V/cm   | 200.0 V/cm   | 300.0 V/cm   |
| 1                               | 0            | 0.8925(30)   | 3.8375(45)   | 8.7390(40)   |
| 1                               | 2            | 0.9519(10)   | 3.8988(6)    | 8.8010(25)   |
| 0                               | 1            | 0.9831(20)   | 3.9294(15)   | 8.8340(25)   |
| 1                               | 0            | 1.0144(45)   | 3.9625(10)   | 8.8660(20)   |
| 0                               | 1            | 1.0481(20)   | 3.9938(10)   | 8.8960(30)   |
| CO <sub>2</sub> -DF             |              |              |              |              |
| $J=1, M_J=0 \rightarrow M_J'=1$ |              |              |              |              |
| $M_F$                           | $M_F'$       | 144.7 V/cm   | 174.6 V/cm   | 300.0 V/cm   |
| -1/2                            | 1/2          | 2.0570(10)   | 3.0505(8)    | 9.2344(10)   |
| 1/2                             | 3/2          | 2.1010(10)   | 3.0930(10)   | 9.2768(30)   |
| -1/2                            | 1/2          | 2.1045(10)   | 3.0975(10)   |              |
| 3/2                             | 1/2          | 2.1290(6)    | 3.1220(6)    | 9.3048(20)   |
| -1/2                            | 1/2          | 2.1435(7)    | 3.1368(6)    | 9.3192(25)   |
| -1/2                            | 1/2          | 2.1908(6)    | 3.1840(9)    |              |
| 3/2                             | 5/2          | 2.2070(9)    | 3.2003(11)   | 9.3828(20)   |
| 1/2                             | 3/2          | 2.2295(6)    | 3.2230(6)    | 9.4044(30)   |
| 1/2                             | 3/2          | 2.2930(7)    | 3.2863(9)    | 9.4688(40)   |
| -1/2                            | 1/2          | 2.3070(8)    | 3.3003(9)    | 9.4820(30)   |
| SCO-HF                          |              |              |              |              |
| $J=0 \rightarrow J'=1, M_J'=0$  |              |              |              |              |
| $M_F'$                          | 49.21 V/cm   | 69.98 V/cm   | 100.0 V/cm   | 150.0 V/cm   |
| 0, 1                            | 2616.193(22) | 2617.506(12) | 2620.212(12) | 2626.846(8)  |
| 0                               | 2616.252(10) | 2617.560(12) | 2620.269(23) | 2626.902(13) |

<sup>a</sup>Reported uncertainties are full width at half-height divided by  $S/N$  of measured line.

TABLE III. Spectroscopic constants.<sup>a</sup>

|                 | CO <sub>2</sub> -HF | CO <sub>2</sub> -DF | SCO-HF      |
|-----------------|---------------------|---------------------|-------------|
| $B_0$ (MHz)     | 1951.169 6(11)      | 1935.995 9(7)       | 1307.462(4) |
| $D_0$ (MHz)     | 0.010 69(7)         | 0.011 21(3)         | 0.002 46(9) |
| $S_a$ (MHz)     | 0.104 7(6)          | 0.017 39(24)        | 0.105 (5)   |
| $eqQ_a^D$ (MHz) | ...                 | 0.263 85(46)        | ...         |
| $\mu_a$ (D)     | 2.246 5(4)          | 2.302 4(1)          | 3.208 5(20) |

<sup>a</sup>Reported uncertainties are statistical so as to give 97% confidence limits.

an angle of 24.36(17)°. Hence, the assumption made above is faulty—the hyperfine constants of HF do change slightly on binding to CO<sub>2</sub>. Of the two angles available for CO<sub>2</sub>-DF, the angle obtained from  $S$  is taken as the average angle.

There are several reasons for this choice. First, a more valid comparison between the two average structures for CO<sub>2</sub>-HF and CO<sub>2</sub>-DF will be had if the angles used are obtained from the same hyperfine parameter. Second, since  $S_0$  depends only on the average HF internuclear distance ( $S_0 \propto \langle 1/r^3 \rangle$ ), assigning the discrepancy in the measured values of  $\langle \cos^2 \theta \rangle$  to a change in  $S_0$  would imply a 1%–2% decrease in the HF bond length, rather than the increase expected for hydrogen bonded systems. Finally, the trend in the observed  $\theta$  values closely parallels that found<sup>5</sup> for  $\theta_{DCI}$  in HF-DCI. In that complex, the chlorine and deuterium quadrupole coupling constants were used to derive angular expectation values and the value obtained from  $eqQ_a^D$  was shown to be too high, which is also the behavior observed in CO<sub>2</sub>-DF.

The atomic order in CO<sub>2</sub>-HF is readily established by comparison of the rotational constants of CO<sub>2</sub>-HF and CO<sub>2</sub>-DF, which best fit a structure in which the hydrogen end of HF points towards the carbon dioxide molecule. Figure 2 illustrates the proposed equilibrium structure. The O-H equilibrium bond length can be estimated from the average separation  $r_{c.m.}$ , giving a value of 1.91 Å. The inclusion of atomic van der Waals radii on Fig. 2, while not quantitative, does serve to illustrate that significant charge cloud overlap takes place in this complex.

The broken lines drawn in Fig. 2 represent the HF average position, and they give some idea of the amplitude of the HF motion about its equilibrium position.

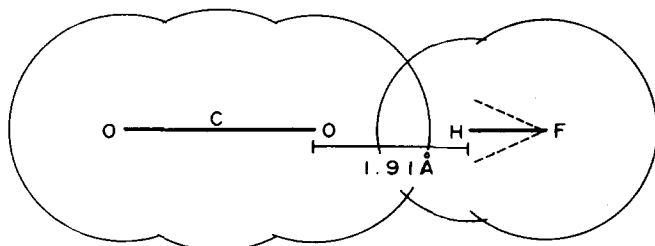


FIG. 2. Estimated equilibrium structure of CO<sub>2</sub>-HF. The broken lines represent the average HF position. The following values of van der Waals radii are used: C=1.5 Å, O=1.4 Å, H=1.2 Å, and F=1.35 Å.

If HF underwent harmonic motion about the assumed linear equilibrium structure, the following relation would hold:

$$\frac{\gamma_{CO_2-DF}}{\gamma_{CO_2-HF}} = \sqrt{\frac{M_b^{HF}}{M_b^{DF}}},$$

where the bending reduced mass  $M_b$  may be approximated by the HF moment of inertia. Given that  $\gamma_{CO_2-HF}$  is 25.1°, this predicts  $\gamma_{CO_2-DF}$  to be 21.4°, which is close to the measured value of 22.28°. This lends rough support to the assumption of a linear equilibrium structure.

The atomic order in SCO-HF can unambiguously be established despite the lack of isotopic data. Only two nearly linear atomic arrangements are consistent with the large observed dipole moment. For the O-H bonded structure, the estimated O-H bond length is about 1.94 Å, quite similar to that of CO<sub>2</sub>-HF, while the F-S bonded structure would imply a bond length of 3.41 Å, 0.2 Å longer than the sum of the van der Waals radii.

To the extent that the stretch of the weak bond can be described by a harmonic potential, the distortion constant is related to the stretching force constant as<sup>10</sup>

$$k_s = (4\pi)^4 M^2 r_{c.m.}^2 B_0^4 / 2h D_0.$$

In this expression,  $M$  is a reduced mass given by  $M_{HF}M_{CO_2}/(M_{HF} + M_{CO_2})$ . The force constant for the bend of the HF submolecule, again assuming a harmonic potential, can be approximated by

$$k_b = \hbar^2 / M_b \langle \gamma^2 \rangle^2.$$

 TABLE IV. Structural parameters.<sup>a</sup>

|                             | CO <sub>2</sub> -HF | CO <sub>2</sub> -DF | SCO-HF    |
|-----------------------------|---------------------|---------------------|-----------|
| $r_{c.m.}$ (Å)              | 3.953 87(3)         | 3.900 29(10)        | 4.4929(1) |
| $\theta^b$                  | 25.10(21)           | 22.28(58)           | 25.0(17)  |
| $\gamma^b$                  | 25.17               | 22.40               | ...       |
| $k_s$ (mdyn/Å)              | 0.021               | 0.020               | 0.028     |
| $\nu_s$ (cm <sup>-1</sup> ) | 51                  | 49                  | 56        |
| $k_b$ (mdyn/Å)              | 0.022               | 0.018               | ...       |
| $\nu_b$ (cm <sup>-1</sup> ) | 210                 | 140                 | ...       |

<sup>a</sup>Reported uncertainties are statistical so as to give 97% confidence limits.

<sup>b</sup> $\theta$  is the average angle HF makes with the principal axis of the complex.  $\gamma$  is the average angle HF makes with the line joining the centers of mass of the submolecules.

TABLE V. Estimated hydrogen bond lengths and stretching force constants<sup>a</sup> of related complexes.

|  | $r_e$ (Å) | $k_s$ (mdyn/Å) |
|--|-----------|----------------|
| OCO-HF   | 1.91      | 0.021          |
| SCO-HF   | 1.94      | 0.028          |
| OC-HF <sup>b</sup>                             | 2.12      | 0.086          |
| HCN-HF <sup>c</sup>                            | 1.87      | 0.24           |
| H <sub>2</sub> O-HF <sup>d</sup>               | 1.74      | 0.16           |
| H <sub>2</sub> O-H <sub>2</sub> O <sup>e</sup> | 2.02      | 0.11           |
| HF-HCl <sup>f</sup>                            | 2.09      | 0.056          |
| HF-HF <sup>g</sup>                             | 1.87      | 0.063          |

<sup>a</sup>All force constants were estimated using the method described in the text.

<sup>b</sup>A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.* **73**, 583 (1980).

<sup>c</sup>A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London Ser. A* **370**, 213 (1980).

<sup>d</sup>J. W. Bevan, Z. Kisiel, A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London Ser. A* **372**, 441 (1980).

<sup>e</sup>T. R. Dyke, K. R. Mack, and J. S. Meunter, *J. Chem. Phys.* **66**, 498 (1977).

<sup>f</sup>Reference 5.

<sup>g</sup>T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.* **56**, 2442 (1972).

Table IV contains calculated values of the force constants and associated vibrational frequencies for CO<sub>2</sub>-HF and SCO-HF. (Since there is a large error associated with the average angle in SCO-HF, the bending force constant is not tabulated.)

## DISCUSSION

The estimated equilibrium bond lengths and stretching force constants of both CO<sub>2</sub>-HF and SCO-HF can be compared to the similarly estimated parameters in related complexes. Table V lists the appropriate values for a few of these complexes. It is immediately apparent from the values in Table V that, compared with the other complexes, both CO<sub>2</sub>-HF and SCO-HF have surprisingly small stretching force constants given their relatively short O-H bond lengths.

This discrepancy in the stretching force constants, as well as the quite different structure obtained for the isoelectronic complex N<sub>2</sub>O-HF, brings into question the assumption made in the structural analysis—namely, that the equilibrium structures of CO<sub>2</sub>-HF and SCO-HF are linear. The measured  $\Delta J = 1$  rotational transitions would also be consistent with a slightly bent equilibrium geometry. If  $\chi$  is the angle made by the triatomic with the line joining the centers of mass, then the maximum value of  $\chi$  still consistent with the rotational transitions is  $\sim 30^\circ$  for CO<sub>2</sub>-HF and  $\sim 25^\circ$  for SCO-HF. (At these angles the change in the rigid rotor rotational frequencies due to asymmetry accounts for  $\sim 30\%$  of the observed change attributed to centrifugal distortion.) If such a structure is assumed for CO<sub>2</sub>-HF (i.e.,  $\chi = 30^\circ$ ), then both  $r_e$  and  $k_s$  for the complex would have to increase to fit the measured data, alleviating the discrepancy described above. In fact, at  $\chi = 30^\circ$ ,  $r_e$  increases

to 2.17 Å. This can be compared to N<sub>2</sub>O-HF,<sup>6</sup> which has a bond length  $r_e = 1.94$  Å and an angle  $\chi \cong 46^\circ$ . If CO<sub>2</sub>-HF is bent, its O-H bond length would seem inconsistent with that of N<sub>2</sub>O-HF.

There is other experimental evidence which shows that the upper limit for  $\chi$  established by the rotational transitions is unreasonably large. Extensive searches of the rf region at zero electric field yielded no signs of asymmetry doublet transitions for CO<sub>2</sub>-HF. Furthermore, no *b*-type rotational transitions were observed while scanning the microwave region. These would be expected if the molecule were bent and thus possessed a permanent perpendicular dipole moment. Both of these kinds of transitions were easily observed for N<sub>2</sub>O-HF under similar experimental conditions.

In another effort to determine the presence of a *b* moment, a very careful Stark effect measurement was done of five Stark components of the  $J = 3 \rightarrow 4$  transition in CO<sub>2</sub>-HF. Analysis of those data indicates the presence of a small but statistically significant perpendicular second order perturbation. In the limit of large energy separation, the value of this perturbation is  $1.56 \times 10^{-2}$  D<sup>2</sup>/cm<sup>-1</sup>. This may be interpreted as arising from a transition dipole moment, with a possible contribution from a permanent *b* moment due to a slight tilt ( $\chi \sim 5^\circ - 15^\circ$ ) in the equilibrium orientation of the triatomic. An attempted estimate of the transition moment based on the HF bending frequency and the assumption of a harmonic oscillator model only accounts for a fraction (0.3 to 0.4) of the measured perturbation, but a large error is expected due to anharmonic effects.

Since the triatomic is undergoing wide amplitude vibrations, on the average it will make some nonzero angle with the principal axis. There is no experimental probe of this angle as there is for the similar HF angle, but a rough estimate can be had from results<sup>4</sup> for Ar-CO<sub>2</sub>. In that complex, the average tilt of the CO<sub>2</sub> submolecule away from its equilibrium position is approximately  $8^\circ$ . Hence, the CO<sub>2</sub> average angle in CO<sub>2</sub>-HF is expected to be somewhere between  $5^\circ$  and  $10^\circ$ . A similar range is expected for SCO-HF. A comparison of the bending force constant<sup>4</sup> of Ar-CO<sub>2</sub> ( $k_b = 0.008$  mdyn/Å) with the HF bending force constant of HF-CO<sub>2</sub> ( $k_b = 0.022$  mdyn/Å) shows a more anisotropic interaction for HF-CO<sub>2</sub>. Based on this comparison, the average CO<sub>2</sub> angle in the HF complex should be closer to the low end of the  $5^\circ - 10^\circ$  range.

The O-H bond length and the stretching force constant were recalculated for CO<sub>2</sub>-HF assuming an equilibrium structure having  $\chi = 15^\circ$  to see if any drastic changes would occur. It was found that an increase of approximately 6% in both parameters was required to fit the experimental data. In recalculating the stretching force constant, a term involving the CO<sub>2</sub> bending force constant was included in the analysis, and this accounted for most of the increase ( $k_b^{\text{CO}_2} \sim \frac{1}{2} k_b^{\text{HF}}$  was used as a rough estimate). Hence, the parameters as reported in the previous section are good to approximately 10%, and the surprisingly low force constant cannot be accounted for by either a slightly bent equilibrium structure or the effect of the triatomic's vibrational motion.

On the other hand, two properties related to the charge distribution within the complex are indicative of a relatively strong interaction between HF and the triatomic. A considerable rearrangement of the charge distribution upon weak bond formation is observed both from the standpoint of the dipole moment and the electric field gradient at the deuterium nucleus. If the dipole moment projections of the submolecules onto the principal axis are subtracted from the measured dipole moment, a dipole moment enhancement of about 0.60 and 0.84 D is exhibited by CO<sub>2</sub>-HF and SCO-HF, respectively. The similar quantity in HF-HCl is only 0.21 D. An attempt was made to calculate the dipole moment of CO<sub>2</sub>-HF using the known multipole moments and polarizabilities of the submolecules, but this calculation was unsuccessful in accounting for the large value of the dipole moment enhancement. The electric field gradient at the deuterium nucleus is decreased by 5%-10% in CO<sub>2</sub>-DF. This agrees with the effect observed in HF-DCl,<sup>5</sup> in which the decrease is also 5%-10%. In Ar-DF,<sup>10</sup> however, there is virtually no observable effect on the field gradient by the Ar atom.

In conclusion, although the experimental data do not pin down the average triatomic position, it clearly shows that the complexes CO<sub>2</sub>-HF and SCO-HF are nearly linear. This is surprising in terms of a donor-acceptor model and the conventional picture of the lone pair electrons of CO<sub>2</sub>, which would predict a bent hydrogen-bonded structure. The similarity of SCO-HF to CO<sub>2</sub>-HF as well as available results<sup>12</sup> on the nearly linear species CO<sub>2</sub>-HCl do establish some generality for the stereochemistry of the interaction. Since CO<sub>2</sub>-HF is a hydrogen-bonded species, nothing can be inferred about the structure of the water and carbon dioxide com-

plex as was hoped at the start of this work. Future structural studies of this complex, as well as the CO<sub>2</sub> complex with ammonia, will provide interesting comparisons with the present species.

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- <sup>8</sup> $M_J=2 \rightarrow 1$ :  $\nu_0=15\,606.633$  MHz,  $a=3.6242$  MHz cm<sup>2</sup>/kV<sup>2</sup>,  $b=0.00818$  MHz cm<sup>4</sup>/kV<sup>4</sup>;  $M_J=2 \rightarrow 2$ :  $\nu_0=15\,606.619$ ,  $a=1.7099$ ,  $b=0.00606$ ;  $M_J=1 \rightarrow 1$ :  $\nu_0=15\,606.624$ ,  $a=-1.8437$ ,  $b=0.00161$ ;  $M_J=0 \rightarrow 1$ :  $\nu_0=15\,606.615$ ,  $a=-3.6629$ ,  $b=-0.00314$ ;  $M_J=1 \rightarrow 2$ :  $\nu_0=15\,606.621$ ,  $a=-3.7675$ ,  $b=0.00159$ .
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