transition of $Cr(CO)_6$ is 700, and for less symmetric derivatives of the form $LCr(CO)_5$ it is 1400.[20]

In conclusion, the description of the electronic structure of $HCo(CO)_4$ which best accounts for the photochemistry is one in which the HOMO is metal–hydrogen σ bonding in character with electron density residing mostly on the hydrogen. Excitation of an outer electron into the virtual orbitals is charge transfer in nature and results in metal–hydrogen bond weakening. This interpretation is consistent with several calculations that are published and with the calculation of Boudreaux. Of the plausible virtual orbitals that might become populated, there are those that are σ^* with respect to metal–carbon bonding, σ^* with respect to metal–hydrogen bonding, or π^* with respect to carbon–oxygen bonding. The latter orbitals are related to the 2π level of CO and are probably too high in energy to be involved in transitions in the neighborhood of 230 nm. Therefore, the band at 227 nm must be $\sigma \rightarrow \sigma^*$ in character and must be LMCT although electron density may be delocalized into the carbonyl ligands as well. This description of a LUMO may imply metal–carbon weakening as well in the excited state.

The photochemistry of other late first-row transition-metal hydridocarbonyls can be similarly explained on the basis of the work of Guest et al., and this expectation is being confirmed by this and other matrix studies. A very similar picture is presented for $CH_3Co(CO)_4$ although the photochemistry has not been studied in detail.[21] Also, these conclusions are very similar to those of many authors in studies of metal–metal bonded systems.[22]

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Registry No. $HCo(CO)_4$, 64519-62-6.

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[20] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

[21] Cser, F.; Galamb, V.; Palyi, G. *Inorg. Chim. Acta* **1979**, *37*, L517–519.

[22] See, for example, ref 20.

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Matrix Isolation Investigation of the Fluoroformate Anion

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The fluoroformate anion has been isolated for the first time in a condensed-phase synthesis, in argon matrices. The anion was formed through the gas-phase reaction of a CsF molecule with CO_2 and isolated in an ion pair with Cs^+. Two C–O stretching modes were detected at 1316 and 1749 cm^{-1}, along with a C–F stretching mode at 883 cm^{-1}. Complete isotopic labeling allowed determination of a planar C_{2v} structure for this anion, with bands quite comparable to a series of isoelectronic or isostructural species. Normal coordinate calculations determined a value of 10.2 mdyn/Å for the C–O stretching force constant, suggestive of considerable double-bond character for the carbon–oxygen bonds, while a value of 4.2 mdyn/Å was calculated for the C–F stretching force constant. CNDO/2 calculations were also performed, and these predict a geometry similar to that which was observed.

Introduction

The fluoroformate anion, CO_2F^-, has been the object of numerous synthetic attempts.[1,2] By analogy to the isoelectronic carbonate anion and the formate anion HCO_2^-, the fluoroformate anion should be quite stable. However, all synthetic attempts have failed in condensed phases, although the anion has been formed in ion cyclotron resonance studies.[3] The ICR studies determined that the fluoride ion affinity of CO_2 is 32 kcal/mol, which, while not as large as for strong Lewis acids like BF_3 and SiF_4, is still quite large. It has been postulated that the failure to form the CO_2F^- anion in condensed-phase synthesis is due to the high lattice energy of CsF, which must be overcome for products to form.[2,3]

The salt/molecule technique was developed several years ago, in conjunction with matrix isolation, for the study of halide-containing anions in ion pairs.[4-6] In this method, an alkali halide salt is vaporized and is allowed to undergo a gas-phase reaction with a suitable partner, before the product is quenched into an inert matrix. Halide ion transfer has been shown to occur in many cases such as to form HCl_2^-, SiF_5^-, and COF_3^- ions paired with alkali metal cations. The cation, while present, does not perturb the anion to a large degree. Studies have shown that the large diffuse cations, particularly Cs^+, provide the least perturbation.[7]

The salt/molecule technique appeared to be an appropriate weapon for a synthetic attempt at the fluoroformate anion; this method eliminates lattice-energy considerations as the salt is vaporized prior to reaction. The reaction, then, between gas-phase CsF and CO_2 might yield the $Cs^+CO_2F^-$ ion pair, which could be trapped for spectroscopic study. Consequently, a series of reactions of CsF with isotopically enriched samples of CO_2 in argon was conducted, and the products were analyzed.

Experimental Section

The matrix isolation experiments carried out in this study were conducted on a standard matrix isolation system which has been described previously.[8] CsF was the primary salt employed and was vaporized at roughly 500 °C from a resistively heated oven. Since CsF is extremely hygroscopic, the salt was dried and outgassed thoroughly at roughly 400 °C prior to the start of an experiment. CO_2 (Matheson), $^{13}CO_2$ (Merck, 99% ^{13}C), $C^{18}O_2$ (Merck 94% ^{18}O), and $C^{18}O_2$ (Isotope Labeling Corp., 50% ^{18}O) were purified by one or more freeze–thaw cycles prior to sample preparation. Argon was used as the matrix gas in most experiments, and was used without purification.

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[1] Martineau, E.; Milne, J. B. *J. Chem. Soc. D* **1971**, 1327.

[2] Lawlor, L.; Passmore, J. *Inorg. Chem.* **1979**, *18*, 2923.

[3] McMahon, T. B.; Northcott, C. J. *Can. J. Chem.* **1978**, *56*, 1069.

[4] Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1975**, *63*, 2466.

[5] Ault, B. S. *J. Phys. Chem.* **1979**, *83*, 837.

[6] Ault, B. S. *Inorg. Chem.* **1979**, *18*, 3339.

[7] Hunt, R. L.; Ault, B. S. *Spectrochim. Acta, Part A* **1981**, *37A*, 63.

[8] Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

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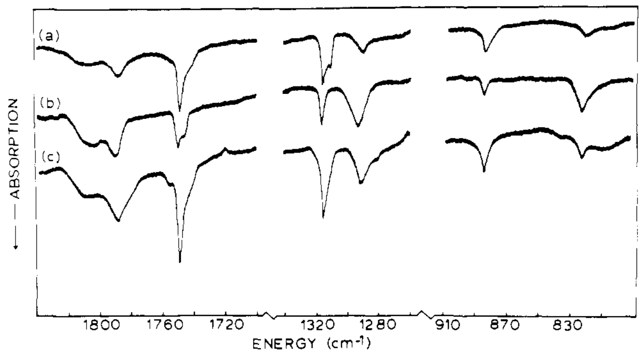

Figure 1. Infrared spectra, over selected spectral regions, of the reaction products of CsF with CO_2 in argon matrices. The top trace shows the reaction of CsF with a sample of $Ar/CO_2 = 250$, while the middle trace shows a spectrum of the same sample after annealing to 47 K. The bottom trace shows a spectrum of the reaction products of CsF with a sample of $Ar/CO_2 = 100$.

Carbon dioxide was used as matrix material in a few experiments, and was purified by passing the gas through a coil held at −77 °C.

Matrix samples were generally deposited for 20–24 h before final scans were taken on a Beckman IR-12 over the spectral region 200–4000 cm^{-1}. Survey scans and expanded-scale scans over the regions of interest were recorded at 1-cm^{-1} resolution. Normal coordinate calculations were carried out on the University of Cincinnati computer, using a program provided by the National Research Council of Canada.

Results

Before the reaction products of CsF with isotopic CO_2 molecules were investigated, blank experiments were conducted on each of the parent species. Agreement with literature gas-phase[9] spectra was quite good, as well as with matrix spectra[10] when available.

CsF + CO_2. When CsF was vaporized at roughly 500 °C and codeposited with a sample of $Ar/CO_2 = 1000$, several weak bands were observed in the spectrum. These were located at 883, 1316, and 1749 cm^{-1} and were all quite sharp. When CsF was codeposited with a similar but more concentrated sample, with $M/R = 250$, these three bands were all considerably intensified. In addition, three weak broad bands were detected near 810, 1290, and 1800 cm^{-1}, the latter appearing to have two maxima in some experiments. This experiment was repeated several times at $M/R = 250$ with slightly different CsF concentrations, and nearly identical spectra were obtained in each case. During the last of these experiments at $M/R = 250$, the sample was annealed to permit diffusion. When the sample was gently warmed to 39 K and recooled, the three initial bands grew slightly in intensity and remained quite sharp. However, when the matrix was warmed to 47 K and then recooled, these three sharp bands dramatically decreased, and the three broad bands grew in intensity.

CsF was deposited with a sample of $Ar/CO_2 = 100$ as well, and all of the bands that had been seen previously grew in intensity. However, the three broad bands grew much more than the three initial sharp bands. In a final experiment to determine concentration dependence, CsF was codeposited with pure CO_2. Here, very intense bands were observed due to the CO_2; in addition broad, intense product bands were observed near 1300 and 1850 cm^{-1}. Figure 1 shows the spectra of the reaction products of CsF with samples of Ar/CO_2.

CsF + $^{13}CO_2$. When CsF was codeposited with a sample of $Ar/^{13}CO_2$ with $M/R = 250$ and an enrichment of 99% ^{13}C, a series of shifted product bands was observed. Again, a sharp, well-defined set of bands was detected at 868, 1297, and 1702 cm^{-1}, as well as a weaker, broad set of bands near 790, 1275, and 1740 cm^{-1}. The overall features, relative intensities, and band shapes were quite similar to the normal isotope experiments, with the shifts in band positions noted above.

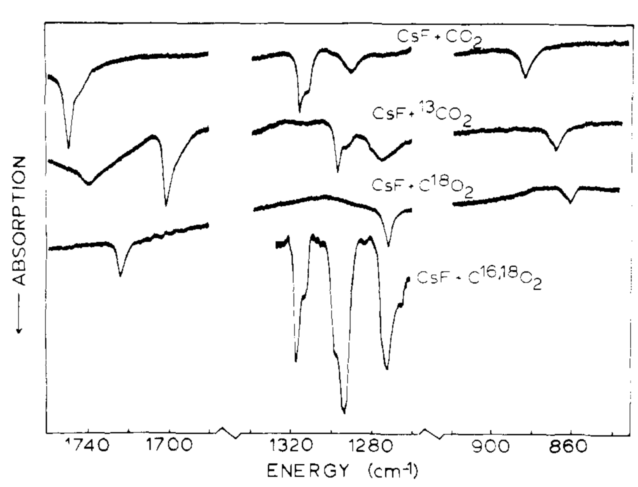

Figure 2. Infrared spectra of the reaction products of CsF with isotopic CO_2 molecules. The top trace shows the spectrum of the reaction products of CsF with a sample of $Ar/CO_2 = 250$, while the second trace shows the spectrum of the reaction product of CsF with a comparable sample employing $^{13}CO_2$. The third trace shows a spectrum of the reaction product of CsF with $C^{18}O_2$ with 94% enrichment, while the bottom trace shows the spectrum obtained when a sample of $C^{18}O_2$ with 50% enrichment was employed. In this trace, an intensity amplification of 10× was used, combined with an extremely slow scan and long time constant.

CsF + $C^{18}O_2$. CsF was codeposited in several experiments with samples of $Ar/C^{18}O_2 = 250$, with an enrichment of 94% ^{18}O. In these experiments, the yield was relatively low, but the spectra obtained were similar to those obtained with the normal isotope and with the ^{13}C-enriched sample. The same three sharp bands were again detected but were shifted in this case to 862, 1272, and 1724 cm^{-1}, with comparable relative intensities. The broad bands were only weakly detected, and only the most intense could be accurately located, at 1760 cm^{-1}.

CsF + $C^{16}O^{18}O$. CsF was also codeposited with a sample of argon and $C^{18}O_2$, with a 50% enrichment of ^{18}O, so that all three oxygen isotopic species of carbon dioxide were present. Since the product intensities would be split among three or four product species, the concentration was increased to $M/R = 200$. Even so, the product bands that were observed were quite weak. Triplet structure was observed in each of the three product regions, with the most intense bands appearing at 873, 1292, and 1738 cm^{-1}. These bands fell almost exactly halfway between the bands due to the pure oxygen-18 species and the pure oxygen-16 species. These bands, due to reaction of CsF with the $C^{16}O_2$ and $C^{18}O_2$ present, were also observed. The rough intensity ratio of each triplet was 1:2:1, but the weakness of the bands made accurate intensity measurement difficult. Figure 2 shows the infrared spectra of the reaction products of CsF with isotopically labeled CO_2.

TlF + CO_2. TlF was vaporized and codeposited with samples of $Ar/CO_2 = 250$ in several experiments. In each experiment, definite evidence of the presence of both reactants was obtained. However, only very weak product bands were detected, in the same general regions as with CsF. This supports the notion from earlier experiments that the cesium cation provides the best product yield in salt/molecule studies, as well as the least perturbation. Consequently, reactions involving other alkali fluoride salts with CO_2 were not attempted.

CsCl + CO_2. CsCl was vaporized and codeposited with a sample of $Ar/CO_2 = 5.00$ in one experiment, and after 22 h

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(9) Herzburg, G. "Infrared and Raman Spectra"; Van Nostrand: New York, 1945.
(10) Fredin, L.; Nelander, B.; Ribbegard, G. *J. Mol. Spectrosc.* **1974**, *53*, 410.

Table I. Band Positions and Assignments for the Matrix-Isolated Fluoroformate Anion

CO_2F^-, cm^{-1}	$^{13}CO_2F^-$, cm^{-1}	$C^{18}O_2F^-$, cm^{-1}	$C^{16}O^{18}OF^-$, cm^{-1}	assignment[a]
883	868	862	873	ν_1, A_1, C-F stretch
1316	1297	1272	1292	ν_2, A_1, sym, C-O stretch
1749	1702	1724	1738	ν_4, B_2, antisym, C-O stretch

[a] C_{2v} symmetry.

of deposition, no evidence was obtained for a reaction product. The presence of CsCl was indicated by the observation of bands that have previously been assigned to the $CsCl{\cdot}H_2O$ complex,[8] through reaction of CsCl with impurity H_2O.

Discussion

The spectra obtained after the codeposition of CsF with samples of Ar/CO_2 clearly indicate that a reaction occurs and that the yield of product increases as the concentration of CO_2 increases. Moreover, the spectra collectively suggest that two products are formed, one species of which is characterized by the sharp set of bands at 883, 1316, and 1749 cm^{-1}, and the second by the broader set of bands near 810, 1290, and 1800 cm^{-1}, the latter appearing as a broad doublet in some experiments. This second set of bands was more prominent at higher CO_2 concentrations and was the only set of bands observed when CsF was deposited into a matrix of pure CO_2. These bands were, on the whole, quite close to the sharp set of bands and probably can be ascribed to a perturbed or aggregated form of the product responsible for the sharp set of absorptions. The observation of both an isolated product and an aggregated product in matrix isolation studies is a well-known phenomenon,[11] and the aggregated products generally show the concentration dependence observed here.

The isolated product, observed at dilutions as high as $Ar/CO_2 = 1000$, was characterized by three bands, at 883, 1316, and 1749 cm^{-1}. All three product bands showed distinct shifts upon substitution of either ^{13}C or ^{18}O, indicating that the product species contains these elements. The reaction of CsF with CO_2 may involve either reaction of the anion F^- or the cation Cs^+ with the CO_2. However, no reaction occurred when CsCl was codeposited with CO_2, indicating that the fluoride ion is the reactive entity and is probably contained in the product species. The product of a salt/molecule reaction under these conditions is usually that of addition of the halide portion of the salt to the Lewis acid under consideration. Moreover, the formation of the CO_2F^- anion is anticipated from the gas-phase ICR data.[3] These facts, combined with the concentration dependence and the isotopic shifts, lead to the assignment of the three sharp bands observed at 883, 1316, and 1749 cm^{-1} to the fluoroformate anion, CO_2F^-, ion paired with a Cs^+ cation. All isotopic band positions are listed in Table I.

Band Assignments. The structure of the fluoroformate anion, by analogy to the carbonate anion and to the formate anion, is expected to be planar, with C_{2v} symmetry. The experiments in which CsF was reacted with $C^{16}O^{18}O$ gave 1:2:1 triplets for each band, indicative of two equivalent oxygen atoms in the product species, as is required for C_{2v}. Upon substitution of a fluorine for an oxygen on the carbonate anion to form the fluoroformate anion, the E mode of the D_{3h} CO_3^{2-} anion splits into two C–O stretching modes, a symmetric and an antisymmetric combination of A_1 and B_2 symmetry, respectively.[12] These should be located near the E mode of the carbonate anion,[13] at 1450 cm^{-1}, and certainly the bands at 1316 and 1749 cm^{-1} are likely candidates. Being primarily carbon–oxygen stretches in nature, each should exhibit large ^{13}C and ^{18}O shifts, and both of these bands do. The symmetric mode should show a larger ^{18}O shift and lesser ^{13}C shift, while the antisymmetric mode should show the opposite behavior. On this basis, the 1749-cm^{-1} band is assigned to the antisymmetric carbon–oxygen stretching mode of the fluoroformate anion, while the 1316-cm^{-1} band is assigned to the symmetric mode. The symmetric mode, being of A_1 symmetry, can and will mix with the C–F stretching mode, which is also of A_1 symmetry, so that its designation as a symmetric C–O stretch is only an approximate description.

Table II. Comparative Band Positions for the Fluoroformate Anion and Related Species

species	symmetry	ν_3, cm^{-1}	$\nu_2 + \nu_4$, cm^{-1}	ref
CO_3^{2-}	D_{3h}	1450		13
FCO_2^-	C_{2v}		1316, 1749	*a*
HCO_2^-	C_{2v}		1351, 1585	14
$HOCO_2^-$	C_{2v}		1338, 1697	15
NO_3^-	D_3	1360		18
FNO_2	C_{2v}		1310, 1697	16
$HONO_2$	C_{2v}		1320, 1710	17

[a] This work.

Table II lists the carbon–oxygen or nitrogen–oxygen stretching modes for several species that are comparable to the CO_2F^- anion. For the formate anion, HCO_2^-, the analogous modes are observed at 1351 and 1585 cm^{-1}, with the same symmetric and antisymmetric designations.[14] Perhaps a more comparable species is the bicarbonate anion, HCO_3^-, which may be viewed as a hydroxide anion bound to a CO_2 molecule. For this anion, the symmetric and antisymmetric carbon–oxygen stretching modes[15] are observed at 1338 and 1697 cm^{-1}, in relatively good agreement with the bands observed here at 1316 and 1749 cm^{-1}. The fluoride ion is more basic than the hydroxide ion and hence should cause a larger splitting of the C–O stretches. This is observed[16,17] for the isoelectronic analogues $HO{-}NO_2$ and $F{-}NO_2$, where the symmetric and antisymmetric modes are split by 390 cm^{-1} for $HO{-}NO_2$ and by 482 cm^{-1} for $F{-}NO_2$. Also, the band positions for $F{-}NO_2$ of 1310 and 1792 cm^{-1} are just slightly higher than those observed here for the isoelectronic fluoroformate anion, as might be expected.

The symmetric stretching mode of the CO_3^{2-} anion transforms into the C–F stretching mode of the CO_2F^- anion. This mode occurs at 1080 cm^{-1} for the CO_3^{2-} anion and should occur at somewhat lower energy for the CO_2F^- anion. The band at 883 cm^{-1} is an excellent candidate for this mode and also falls in the spectral region associated with anionic C–F stretching vibrations. The symmetric C–F stretching mode of the COF_3^- anion[11] has been detected near 810 cm^{-1} and the antisymmetric mode at 960 cm^{-1}, both near the 883-cm^{-1} band observed here. Also, since this mode is derived from the symmetric stretch of the carbonate anion, which is infrared inactive, this mode should be of relatively low intensity, as was observed. Thus, the assignment of the 883-cm^{-1} band to the C–F stretching mode of the CO_2F^- anion is made. For comparison, the N–F stretch of the isoelectronic NO_2F species has been observed[16] near 822 cm^{-1}. Finally, one would certainly anticipate additional vibrational modes of this anion at lower energies due to deformations. However, these are generally

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(11) Ault, B. S. *J. Phys. Chem.* **1980**, *84*, 3448.

(12) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978.

(13) Bhagavantum, S.; Venkatarayudu, T. *Proc.—Indian Acad. Sci., Sect. A* **1939**, *9A*, 224.

(14) Bernstein, H. J.; Itoh, K. *Can. J. Chem.* **1956**, *34*, 170.

(15) Bernitt, D. L.; Hartman, K. O.; Hisatsune, I. C. *J. Chem. Phys.* **1965**, *42*, 3553.

(16) Cohn, H.; Ingold, C. K.; Poole, H. G. *J. Chem. Soc.* **1952**, *4272*.

(17) Bernitt, D. L.; Miller, R. H.; Hisatsune, I. C. *Spectrochim. Acta, Part A* **1967**, *23A*, 237.

less intense than stretching modes, and none were detected in this study.

In matrix-isolated ion pairs, the location of the alkali-metal cation is always subject to question. In many cases, the lowering of the symmetry of the anion gives some indication, as degenerate vibrations are often split.[7,18-20] In the present case, there are no degenerate vibrational modes, so no direct evidence concerning cation location is available. The equivalence of the two oxygen atoms, as noted above, rules out certain cation arrangements. The most likely possibilities are a monodentate interaction with the fluorine or a bidentate structure with the two oxygens. One might anticipate that the cation will reside near the largest concentration of negative charge, which is expected to be the fluorine atom, as was observed for the $Cs^+COF_3^-$ ion pair.[3] However, no firm conclusions can be drawn on this point.

A second geometry that incorporates two equivalent oxygen atoms is a pyramidal C_s structure. On the basis of the three observed infrared bands and their isotopic shifts, this structure cannot be excluded. However, the analogies presented above to a number of similar structures, all of which are planar, support the planar C_{2v} structure. In addition, the semiempirical CNDO/2 calculations discussed below favor the planar structure, so that while the C_s structure cannot be ruled out the C_{2v} structure is preferred.

Force-Field Calculations. Normal coordinate calculations were performed to assist in band assignments and to derive a force field for the fluoroformate anion. Since no bending modes were observed, only stretching force constants and stretch–stretch interaction constants were employed. A geometry was assumed for the anion by comparison to the isoelectronic[21,22] CO_3^{2-} and NO_2F species as well as by considering the calculated geometry discussed below. Since the two oxygen atoms were known to be equivalent, four force constants were required, primary C–O and C–F stretching force constants as well as C–O, C–O and C–O, C–F interaction constants. These four force constants were refined to nine experimental frequencies for the three different isotopic species CO_2F^-, $^{13}CO_2F^-$, and $C^{18}O_2F^-$. A relatively good fit was obtained, with an average error of less than 2 cm^{-1} for each band, which is comparable to the spectral bandwidths in these studies. In addition, neglect of bending modes and stretch–bend interactions introduces additional error, so that a fit to within 2 cm^{-1} is quite acceptable. The calculations confirmed the nature of the vibrations and band assignments made above, and the principal force constants were found to be $K_1 = 10.2$ mdyn/Å and $K_2 = 4.2$ mdyn/Å for the C–O and C–F stretches, respectively. These values indicate a considerable amount of double-bond character to the carbon–oxygen bonds and a relatively weak carbon–fluorine bond, as might be anticipated. While a slight error is introduced into these force constants by the approximations employed, these calculations do support the qualitative band assignments and give some indication as to the bonding in the anion. However, these calculations are not sufficiently accurate to allow a conclusive determination of a C_{2v} or C_s structure.

Semiempirical Geometry Calculations. Standard CNDO/2 calculations were conducted on the CO_2F^- anion, to provide some indication as to the geometry and bonding in the anion. The energy minimization program that was employed has been shown to provide quite a good estimate of the ground-state energy and geometry for a variety of systems.[23,24] The optimized geometry did converge to a planar, C_{2v} structure, with C–O bond lengths similar to those found for the carbonate anion, 1.29 Å. The C–F bond length was calculated to be somewhat longer, 1.35 Å, while the O–C–O bond angle was calculated to be 133°. No accurate calculations of binding energies were attempted here, although previous calculations placed the fluoride affinity of CO_2 at 7.1 kcal/mol,[25] which is well below the experimental value of 32 kcal/mol.

Conclusions

The synthesis of the fluoroformate anion, CO_2F^-, has been achieved for the first time other than in an ion cyclotron resonance spectrometer, and its vibrational spectrum has been obtained. These results support the earlier suggestion that lattice-energy considerations were the primary factor in the previously unsuccessful attempts to make this anion. The infrared spectra suggest a planar, C_{2v} structure for the anion, with considerable double-bond character to the carbon–oxygen bonds and a relatively weak carbon–fluorine bond.

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Registry No. CO_2F^-, 67228-77-7; CsF, 13400-13-0; CO_2, 124-38-9.

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(18) Smith, D.; James, D. W.; Devlin, J. P. *J. Chem. Phys.* **1971**, *54*, 4437.

(19) Ritzhaupt, G.; Devlin, J. P. *J. Chem. Phys.* **1975**, *62*, 1982.

(20) Smyrl, N.; Devlin, J. P. *J. Chem. Phys.* **1974**, *60*, 2540.

(21) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell Press: Ithaca, NY, 1960; p 282.

(22) Legon, A. C.; Millen, D. J. *J. Chem. Soc. A* **1968**, 1736.

(23) Jaffe, H. H. *QCPE* **1976**, *11*, 315.

(24) Kondo, H.; Ph.D. Thesis, University of Cincinnati, 1979.

(25) Spears, K. G. *J. Chem. Phys.* **1972**, *57*, 1850.