$H_3)_2O^-$, 62002-46-4; $CH_3(CH_2)_3CH(CH_3)O^-$, 102494-15-5; $CF_3CH_2O^-$, 24265-37-0; HCO_2^-, 71-47-6; $CH_3CO_2^-$, 71-50-1; $CH_3OCO_2^-$, 616-38-6; $C_6H_5^-$, 2396-01-2; $CH_2{=}CHCH_2^-$, 1724-46-5; $C_6H_5CH_2^-$, 18860-15-6; $C_6H_5CHCH_3^-$, 13822-53-2; HC_2^-, 29075-95-4; c-$C_6H_7^-$, 102494-16-6; $(CH_3)_2CCN^-$, 102494-17-7; CH_3CHCN^-, 42117-12-4; CH_2CN^-, 21438-99-3; F^-, 16984-48-8; $CH_3COCH_2^-$, 24262-31-5; $CH_3COCHCH_3^-$, 64723-99-5; EtS^-, 20733-13-5; HS^-, 15035-72-0; N_3^-, 14343-69-2; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5.

Vibrational Spectra of $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$ and Force Constants for This Ion System

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Abstract: Infrared and Raman spectra of the four hydrogen–deuterium isotopomers of the cyclopropenyl cation, $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$, have been recorded. A virtually complete assignment has been made of the spectroscopically active, in-plane fundamentals of the set of four ions. Assignments for the out-of-plane vibrational modes are fragmentary. For the $C_3H_3^+$ ion, the frequencies (cm^{-1}) are as follows: a_1' 3183, 1626; a_2' (1031); e' 3138, 1290, 927; a_2'' 758; e'' (990), where the values in parentheses are from normal coordinate calculations. A complete, general-valence force field of 12 constants has been fitted to the set of 31 observed frequencies. Force constants for CC stretching (7.890 mdyn Å^{-1}), CH stretching (5.284 mdyn Å^{-1}), and CH in-plane bending (0.599 mdyn Å rad^{-2}) are each larger than the corresponding force constants for benzene. The large force constant for CC stretching implies that the cyclopropenyl cation has exceptionally strong π-bonding.

Breslow and co-workers first prepared the unsubstituted cyclopropenyl cation in the late 1960s.[1] As part of the characterization of this simplest of aromatic species, they recorded infrared spectra of the $C_3H_3^+SbCl_6^-$, $C_3H_3^+AlCl_4^-$, and $C_3D_3^+SbCl_6^-$ salts and assigned the infrared-active fundamentals of the cations.[1b] To help define the bonds experimentally in this cation system, force constants for various bond motions are needed. Useful normal coordinate calculations for this purpose depend on having vibrational assignments from Raman spectra as well as from infrared spectra and on additional experimental data such as vibrational frequencies for several isotopic modifications. A previous, selective fitting of force constants of the cyclopropenyl cation was done for the fragmentary assignment of fundamentals.[2]

We now report an infrared and Raman investigation of the full set of hydrogen–deuterium isotopomers, $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$. In a preliminary account we gave the results for the in-plane vibrational fundamentals of the first three ions and reported force constants for CC stretching, CH stretching, and CH bending coordinates that were larger than the corresponding values in benzene, the standard of aromaticity.[3] The unusually large CC stretching force constant for the cyclopropenyl cation had been anticipated by the ab initio calculation of Takada and Ohno.[4] The present report, which includes the results of normal coordinate calculations for the full set of four isotopomers, confirms the preliminary findings and adds results for the out-of-plane modes. In addition, these calculations define the complete set of 12 general-valence force constants for the cyclopropenyl cation. Such a complete determination of a force field from frequencies for hydrogen–deuterium isotopomers alone is an exceptional outcome for a hexatomic species.

The role of cyclopropenyl cations in solution-phase and solid-phase chemistry is well-known. Not so well recognized is the importance of the cyclopropenyl cation in non-sooting, fuel-rich flames.[5] Because of its atomic simplicity, yet prime position as an aromatic species, the cyclopropenyl cation is of considerable interest in theoretical chemistry.

The $C_3H_3^+$ and $C_3D_3^+$ ions were prepared by reaction of 3-chlorocyclopropene and 3-chlorocyclopropene-d_3, respectively, with Lewis acids, which included BF_3, SbF_5, and BCl_3. These two chlorocyclopropenes were made by reducing tetrachlorocyclopropene with tributyltin hydride and tributyltin deuteride, respectively.[1] To obtain the isotopically mixed species, $C_3H_2D^+$ and $C_3D_2H^+$, a two-step reduction sequence was applied to tetrachlorocyclopropene. For production of the first of these ions, tetrachlorocyclopropene was reduced with the hydride to an inseparable mixture of the isomers, 1,3-dichlorocyclopropene and 3,3-dichlorocyclopropene.[1c] This mixture was then reduced with the deuteride to a mixture of 3-chlorocyclopropene-*1*-d_1 and 3-chlorocyclopropene-*3*-d_1. Reaction of this mixture of isotopomers with a Lewis acid gave the single cation $C_3H_2D^+$. Exchanging the order of reduction of tetrachlorocyclopropene with the hydride and the deuteride led to $C_3D_2H^+$.

3-Fluorocyclopropene was also prepared and evaluated as a precursor of the cyclopropenyl cation.[6] However, this halocyclopropene was uncontrollably reactive with BF_3 in sulfur dioxide solution and thus useless for Raman spectroscopy. With difficulty the low-temperature, bilayer reaction technique was used with 3-fluorocyclopropene and BF_3 to prepare samples of the cation for infrared spectroscopy.

Experimental Section

Syntheses. The synthesis of 3-chlorocyclopropene (**1**) by reduction of tetrachlorocyclopropene with tri-*n*-butyltin hydride has been described.[1,6] Typically, about one-third of the crude product, the more volatile part consisting mostly of cyclopropene, acetylene, and hydrogen chloride, was removed by bulb-to-bulb distillation before resorting to preparative GC. In the GC separation[1c] at room temperature the elution time of **1** was 5 relative to that of the cyclopropene–acetylene mixture. The principal fractions that appeared between these two peaks were 1-butene, 1-chlorocyclopropene, and propargyl chloride, $CH_2ClC{\equiv}CH$.

3-Chlorocyclopropene-d_3 (**2**) was made by the same method as was used for the d_0 isotopomer except for substitution of tributyltin deuteride (Alfa Products, Morton Thiokol, Inc.) for the hydride. Principal IR

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(1) (a) Breslow, R.; Groves, J. T.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 5048. (b) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984–987. (c) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988–993.

(2) Yoshida, Z.-I.; Hirota, S.; Ogoshi, H. *Spectrochim. Acta* **1974**, *30A*, 1105–1114.

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(6) Craig, N. C.; Sloan, K. L.; Sprague, J. R.; Stevens, P. S. *J. Org. Chem.* **1984**, *49*, 3847–3848.

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bands of **2** in the gas phase were (band center in cm^{-1}, intensity, approximate band shape) 2451 mA, 2266 mC, 2222 wA, 1527 sA (1515 cm^{-1} lit.),[1c] 1117 vsA, 929 sA, 665 vsB, 488 mC, 312 mB.

A mixture of 1,3-dichlorocyclopropene (**3**) and 3,3-dichlorocyclopropene (**4**) was prepared by reaction of Bu_3SnH with c-C_3Cl_4 at 20 °C.[1c] Separation of the crude cyclopropene mixture from the slightly cloudy, colorless product mixture and subsequent purification of the mixture of **3** and **4** was generally as described for **1**. The proton NMR spectrum of the partly purified material in CCl_4 solution confirmed the formation of **3** and **4** with a ratio (**3**:**4**) of about 1.5.[1c] The mixture of **3** and **4**, which had an elution time of 7.5 relative to that of cyclopropene at 40 °C, was inseparable due to the mobile equilibrium between these isomers.[1c] Gas-phase IR bands of the mixture of purified **3** and **4** were 3166 mB, 3138 mC, 3024 mC, 1728 sB, 1624 mB, 1475 mC, 1266 sA, 1171 vsB, 1051 mC, 1012 m, 990 sA, 888 mB, 820 m, 790 vsC, 738 sA, 679 sA, 596 m, 576 mA, 501 mA. The bands at 3024 and 1728 (1723 cm^{-1} lit.)[1c] and 1266 cm^{-1} were due to **3**, and the bands at 3166 and 1624 (1624 cm^{-1} lit.)[1c] were due to **4**.

The crude mixture of **3** and **4** was reduced with tributyltin deuteride to a mixture of 3-chlorocyclopropene-*1*-d_1 (**5**) and -*3*-d_1 (**6**) at 80 °C.[1c] The gas-phase IR spectrum confirmed the formation of the two isotopomers. Identifying bands were 3027 mC, 2396 wA, 1580 mA, and 1266 sA for **5** and 2260 m (Fermi doublet) and 1632 mA for **6**.[7] On the basis of the relative intensities of the bands due to C═C stretching, it appears that the ratio of **5** to **6** was about 2:1, the expected statistical outcome.

A mixture of 3-chlorocyclopropene-*1,2*-d_2 (**9**) and 3-chlorocyclopropene-*1,3*-d_2 (**10**) isotopomers was prepared by reducing c-C_3Cl_4 first with Bu_3SnD and then with Bu_3SnH. Otherwise, procedures were the same as those used for the mixture of d_1 isotopomers. As the intermediate, a mixture of 1,3-dichlorocyclopropene-d_2 (**7**) and 3,3-dichlorocyclopropene-d_2 (**8**) was obtained. The gas-phase IR spectrum of this inseparable mixture consisted of 2450 w, 2417 mB, 2302 w, 2252 m, 1672 sB, 1520 mB, 1157 s, 984 mA, 942 vs, 780 sC, 669 s, 539 m, 480 m. The bands at 2252 and 1672 cm^{-1} (1671 cm^{-1} lit.)[1c] were due to **7**, and the bands at 2450 and 1520 cm^{-1} (1512 cm^{-1} lit.)[1c] were due to **8**. The final reduction product, a mixture of **9** and **10**, had for its gas-phase IR spectrum identifying bands at 3027 mC, 2449 mA, 1531 mA, and 1265 sA for **9** and at 3163 w, 2398 mA, and 1577 sA for **10**.[7] When the amount of impurity HCl, which was shown to promote Cl^- exchange and concomitant broadening of the proton resonances, was minimized, the NMR spectrum of the product mixture in CCl_4 at -35 °C consisted of relatively narrow singlets at 4.3 and 7.6 ppm, as expected for **9** and **10**, respectively.[1c] Relative intensities of the peaks due to the two isomers (**10**:**9**) were about 3:1, a larger ratio than expected statistically.

3-Fluorocyclopropene (**11**) was made from 3-chlorocyclopropene by reaction with a mixture of silver difluoride–potassium fluoride.[6]

For Raman and NMR spectroscopic studies, which were sometimes done with the same preparation, samples of the cations in sulfur dioxide solution were prepared in 5-mm NMR tubes by reaction of the appropriate 3-chlorocyclopropene with the Lewis acids boron trifluoride or boron trichloride.[8] Sulfur dioxide (Matheson anhydrous grade, 99.8%), boron trifluorides (Matheson C.P. grade, 99.5%), and boron trichloride (Matheson C.P. grade, 99.9%) were distilled before use. To minimize discoloration by premature reaction in the BCl_3-containing samples, the BCl_3 band was kept frozen by swabbing with liquid-nitrogen-dampened glass wool while the end of the tube containing SO_2 and the cyclopropene was dipped into a -70 °C ether bath. When melted, BCl_3 reacted with diluted cyclopropene in solution. An uncontrollable reaction of **11** with BF_3 in SO_2 gave deeply colored solutions.[6] The proton NMR spectra of $C_3H_3^+BF_3Cl^-$ and of $C_3D_2H^+BF_3Cl^-$ in SO_2 at about -30 °C were singlets at 11.1 ppm (11.0$_4$–11.2 ppm lit.).[1b] For $C_3D_2H^+$ the two ^{13}C satellites had a splitting of 264 Hz [$J(^{13}CH)$ = 265 Hz lit.].[1b] If the ring modes in the 1490–1630-cm^{-1} region are considered to have the same Raman intensities for the various isotopomers, the isotopic compositions of the Raman samples were the following: $C_3H_2D^+$ (15% $C_3H_3^+$, 76% $C_3H_2D^+$, 9% $C_3D_2H^+$); $C_3D_2H^+$ (13% $C_3H_2D^+$, 68% $C_3D_2H^+$, 19% $C_3D_3^+$); $C_3D_3^+$ (3% $C_3D_2H^+$, 97% $C_3D_3^+$).

For the IR experiments polycrystalline deposits of salts were formed by the low-temperature reaction of bilayer deposits of boron trifluoride or antimony pentafluoride and the various 3-halocyclopropenes.[8] **11** was reacted with BF_3 in this manner after some difficulty with prior reaction with surface residues from BF_3 in the vacuum system. Antimony pentafluoride (Peninsular Chem Research) was degassed before use.

Spectroscopy. IR spectra were recorded on a Perkin-Elmer 580B spectrometer in 10-cm gas cells or in a low-temperature cell of the Hornig type equipped with cesium iodide windows. All condensed-phase spectra were recorded for samples held at -196 °C. For Raman spectroscopy the instrument was a Spex Ramalog 5 spectrometer supported by a Nicolet 1180 minicomputer. Spectra were excited with 514.5-nm filtered light from a Coherent Radiation CR6 argon ion laser. Laser power at the sample was in the range of 300–500 mW. Low temperatures were maintained around the Raman samples with a Harney-Miller cold cell. Frequency accuracy for bands of prime interest was better than 2 cm^{-1} in both spectroscopies. In the presentations of the Raman spectra the solid line traces are for the polarization analyzer parallel to the polarization of the laser beam, and the dashed traces are for the polarization analyzer perpendicular. Despite careful sample preparation all Raman samples fluoresced, especially the ones prepared with BCl_3. In general, fluorescence diminished during extended exposure to laser light.

Proton NMR spectra were recorded on a Perkin-Elmer R12B cw instrument at 60 MHz with either internal Me_4Si reference (CCl_4) or external Me_4Si reference (SO_2).

Results and Discussion

Structures of the Ions. All of the spectroscopic evidence of the present and earlier studies confirms the formation of the four cationic species, $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$. This evidence comes from NMR spectra, vide supra,[1b] as well as from the vibrational spectra presented here.

The structures of the anionic counterions are, however, a more complex matter. Recently developed evidence suggested that the $B_2F_7^-$ dimer anion is a significant species in equilibrium with BF_3 and BF_4^- in sulfur dioxide solutions.[8] We have since confirmed this finding by examining Raman spectra of $Bu_4N^+BF_4^-$ and $Bu_4N^+BF_4^-$ + BF_3 dissolved in sulfur dioxide.[9]

In the present experiments in which BCl_3 was also used as a Lewis acid, the appearance of new bands that could not be associated with BCl_3 or the anion, BCl_4^-,[10] implied the formation of $B_2Cl_7^-$, a previously unrecognized species. Bands for BCl_4^- were confirmed in the Raman spectrum of $Bu_4N^+BCl_4^-$ in sulfur dioxide solution.[10] New features (cm^{-1}, intensity, polarization) in the Raman spectrum which have been tentatively assigned to $B_2Cl_7^-$ are 488 sp, 448 wdp, 348 sp, and 288 mdp.

Since both $B_2F_7^-$ and $B_2Cl_7^-$ dimer anions appear to form, we presume that mixed dimer anions also formed in the mixed halide systems that were used for most of the present experiments. For the Raman experiments the BF_3-to-Cl^- ratios were about 2:1 (F:Cl = 6:1). Thus, we represent the principal anionic species as $B_2F_6Cl^-$ in these experiments. In the infrared experiments with polycrystalline material the ultimate F:Cl ratio is likely closer to 3:1 since the single-halogen species BF_3 is quite volatile and the dimer anion species appears to break down when the temperature during the bilayer reaction technique is cycled above about -70 °C. There is certainly a marked change in the infrared spectra near this temperature.[11] We approximate the principal anionic species in these experiments as BF_3Cl^- even though some coincidences are found between "BF_3Cl^-" bands in the infrared experiments and "$B_2F_6Cl^-$" bands in the Raman experiments.

As will be seen in the subsequent sections, the $B_2F_6Cl^-$ counterion system contributes many more bands to the Raman spectrum than does the $B_2F_7^-$ ion. The problem of masking would be acute when studying cationic species having vibrational modes with frequencies below 500 cm^{-1}. In the 1100–550-cm^{-1} region the bands due to the $B_2F_6Cl^-$ system, though numerous, are sufficiently weak and polarized to be negotiable in most instances. In the infrared experiments in which excess SbF_5 was used as the Lewis acid, we assume that the chloride ion was incorporated into the dimeric antimonate ion. We approximate this dimeric species as $Sb_2F_{10}Cl^-$, even though the spectral features do not differ appreciably from those observed for $Sb_2F_{11}^-$ in systems that contain only fluorine.[8,11,12]

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[7] Full spectra will be presented in a separate paper on the vibrational spectroscopy of 3-chlorocyclopropene.

[8] Craig, N. C.; Fleming, G. F.; Pranata, J. *J. Am. Chem. Soc.* **1985**, *107*, 7324–7329.

[9] Craig, N. C.; Langon, J. L.; Reinganum, S. J., unpublished experiments.

[10] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 3rd ed.; Wiley-Interscience: New York, 1978; pp 128 and 136.

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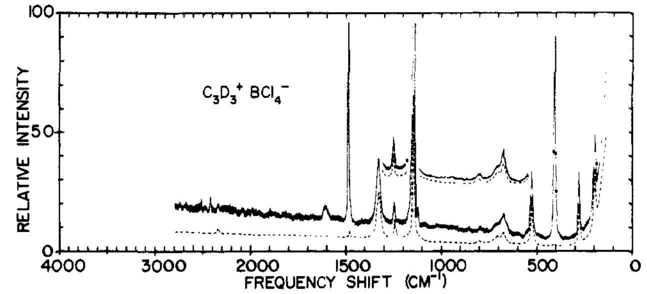

Figure 1. Raman spectrum of $C_3D_3^+BCl_4^-$ in solution in SO_2 at −50 °C. Inserts: accumulation of 6 scans, after 9-point smoothing. Composition of reaction mixture was SO_2:C_3D_3Cl:BCl_3 = 12:1:1.5.

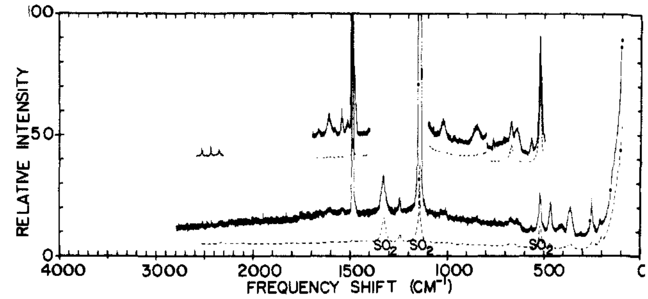

Figure 2. Raman spectrum of $C_3D_3^+B_2F_6Cl^-$ in solution in SO_2 at −50 °C. Uppermost insert: 4 scans; others, 9 scans. Uppermost and lowermost inserts: after 9-point smoothing. Composition was SO_2:C_3D_3Cl:BF_3 = 10:1:2.

Although the use of BCl_3 as the principal Lewis acid in the Raman experiments might have simplified the interpretation of spectra, most of the present work was completed before BCl_3 was tried for the first time. Furthermore, it proved to be more difficult to prepare samples with BCl_3 than with BF_3 that were adequately free of fluorescence. Since the bilayer reaction technique used for the infrared experiments depends on an appreciable difference in volatility between the halocyclopropene and Lewis acid reactivity, BCl_3 does not seem applicable in such experiments.

To save space in the tables that follow many anion bands of comparable frequency, which may be due to different species, are tabulated together.

Assignments for Cations. The $C_3H_3^+$ ion and the fully deuterated $C_3D_3^+$ ion have D_{3h} symmetry. For the normal modes of vibration, group theory predicts symmetry species and selection rules as follows (IR = infrared active; R = Raman active, p = polarized, dp = depolarized; – = inactive in IR or R): 2a₁′ (–; R, p); 1a₂′ (–; –); 3e′ (IR; R, dp); 1a₂″ (IR; –); 1e″ (–; R, dp). The modes of e symmetry are doubly degenerate. For the $C_3H_2D^+$ and $C_3D_2H^+$ ions which have C_{2v} symmetry, the group theory predictions are 5a₁ (IR; R, p), 1a₂ (–; R, dp), 4b₁ (IR; R, p), 2b₂ (IR; R, dp).

$C_3D_3^+$ Ion. We begin the discussion of assignments with the $C_3D_3^+$ ion because the spectroscopic evidence for this ion is the most compelling. The availability of good quality Raman spectra for $C_3D_3^+$ with the BCl_4^- counterion (Figure 1) as well as with the $B_2F_6Cl^-$ counterion (Figure 2) is the principal advantage. The reaction of the 3-chlorocyclopropene-d_3 precursor with the BCl_3 Lewis acid gives a counterion species which not only is simpler but also is the source of lower frequencies than the mixed-halide counterion formed by BF_3. Furthermore, under the conditions of the reported experiment only the monomeric BCl_4^- ion was formed to a significant extent. Comparison of the spectral regions between 550 and 1100 cm⁻¹ in Figures 1 and 2 shows the marked differences. Six weak bands due to the $B_2F_6Cl^-$ and BF_4^- ions are found in this region at 1026, 851, 766, 705, 644, and 570 cm⁻¹. A band at 874 cm⁻¹ due to BF_3 itself may be distinguished in some spectra. BCl_4^- has only one weak band at 703 cm⁻¹ in this region. Both counterion systems contribute numerous bands below 500 cm⁻¹, a region in which none of the isotopomers of the cyclopropenyl cation have bands.

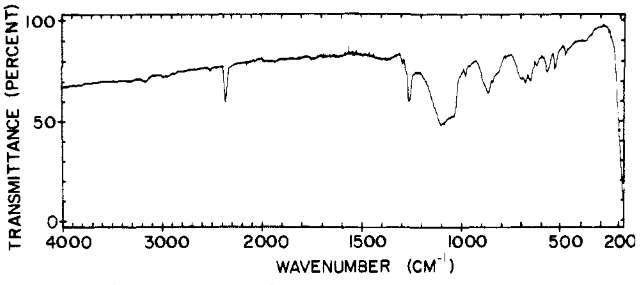

Figure 3. Infrared spectrum of polycrystalline $C_3D_3^+BF_3Cl^-$, after temperature cycling up to −70 °C.

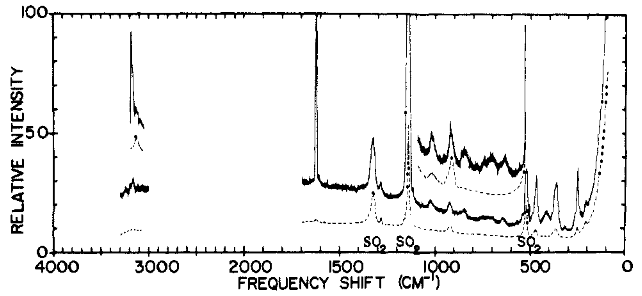

Figure 4. Raman spectrum of $C_3H_3^+B_2F_6Cl^-$ in solution in SO_2 at −65 °C. Higher frequency insert, 16 scans; lower insert, 9 scans. Composition was SO_2:C_3H_3Cl:BF_3 = 10:1:2.

Table I gives the details of the assignments for the two Raman spectra and for the infrared spectrum of the polycrystalline material formed with BF_3 as the Lewis acid. This table also has the infrared observations of Breslow and Groves made for the $SbCl_6^-$ salt in a Nujol mull.[1b] These reported values seem to be systematically low.

For the a₁′ modes, ν_1 and ν_2, the assigned bands are Raman-active only and polarized. A minor complication in the assignment of ν_1 is that two bands of comparable intensity appear as a consequence of Fermi resonance between the fundamental and the overtone of ν_5. For use in the normal coordinate calculations an unperturbed fundamental frequency of 2471 cm⁻¹ was computed by the standard method. The band for ν_2 at 1490 cm⁻¹ is the strongest feature of the spectrum.

The a₂′ mode is neither infrared nor Raman active in the isolated ion approximation, and no spectral evidence was found for it. However, a frequency has been computed in the normal coordinate calculations (vide infra).

For the e′ modes, ν_4, ν_5, and ν_6, straightforward assignments are made to the three depolarized Raman bands at 2348, 1248, and 674 cm⁻¹, which have infrared counterparts in both the BF_3Cl^- (Figure 3) and $SbCl_6^-$ systems (Table I).

The lone mode of a₂″ symmetry ν_7 is found at 560 cm⁻¹ in the infrared spectrum of $C_3D_3^+BF_3Cl^-$ with a corresponding band at a somewhat lower frequency in the spectrum of $C_3D_3^+SbCl_6^-$. That the 560-cm⁻¹ band is due to $C_3D_3^+$ and not to BF_3Cl^-, as are neighboring bands, is confirmed by comparisons with the corresponding spectra for the other cation isotopomers. The polarized band at 570 cm⁻¹ in the Raman spectrum of $C_3D_3^+B_2F_6Cl^-$ is due to the anion system rather than $C_3D_3^+$, as is shown by its absence from the spectrum with the BCl_4^- counterion.

The only somewhat tentative assignment of a fundamental for $C_3D_3^+$ is for ν_8(e″). The weak, depolarized feature at 802 cm⁻¹ in the Raman spectrum of the $C_3D_3^+BCl_4^-$ sample is selected. A corresponding band was found in the Raman spectrum of $C_3D_3^+B_2F_6Cl^-$ but was regarded as uncertain due to the plethora of $B_2F_6Cl^-$ counterion bands in this region. Additional support for this assignment may be the polarized band at 1610 cm⁻¹ that can be assigned best as the first overtone of ν_8.

$C_3H_3^+$ Ion. Table II gives the observations and assignments for the full range of experiments done with the $C_3H_3^+$ ion. Figure 4 shows the Raman spectrum of $C_3H_3^+B_2F_6Cl^-$ in solution in sulfur dioxide. Several samples were prepared in an attempt to record

Table I. Observed Vibrational Frequencies (in cm^{-1}) and Assignments for the $C_3D_3^+$ Ion

Raman, SO_2 solution[a]		infrared, polycrystalline[a]		
with BF_3	with BCl_3	with BF_3	with $SbCl_5$[b]	assignment[c]
2528 w, p	2523 w, p			ν_1 a_1' sym CD str
2432 w, p	2428 w, p			F.R. $2\nu_5 = 2496$ A_1'
2348 vw, dp	2343 vw, dp	2348 s	2327	ν_4 e′ asym CD str
1665 vw, p				SO_2
1613 vw, p	1612 w, p			$2\nu_8 = 1604$ A_1'
1582 vw, p				$C_3H_2D^+$ impurity
1546 w, p				$C_3D_2H^+$ impurity
1516 vw, p				
1490 s, p	1490 s, p			ν_2 a_1' sym CCC str
1480 w, p	1480 w, p			ν_2 ^{13}C
1332 m, dp	1333 m, dp			SO_2
1248 w, dp	1247 w, dp	1250 s	1239	ν_5 e′ asym CCC str
1145 vs, p	1145 vs, p			SO_2
	1120 w, p			^{18}OSO
		1070 vs, br		BF_3Cl^-
1026 w, p				$B_2F_6Cl^-$
851 w, p		860 m		$B_2F_6Cl^-$, BF_3Cl^-
802 vw, dp	801 wv, dp			ν_8 e″ asym CD flap
766 vw, p				BF_4^-
~705 vw, p				$B_2F_6Cl^-$
	703 w, dp			BCl_4^-
		695 m		BF_3Cl^-
674 m, dp	674 m, dp	670 m	665	ν_6 e′ asym CD bend
644 w, p		643 m		$B_2F_6Cl^-$, BF_3Cl^-
570 w, p				$B_2F_6Cl^-$
		560 m	542	ν_7 a_2'' sym CD flap
525 m, p	524 m, p			SO_2
		521 m		BF_3Cl^-
469 m, p		470 w		$B_2F_6Cl^-$, BF_3Cl^-
415 w, p				$B_2F_6Cl^-$
	406 s, p			BCl_4^-
367 m, p				$B_2F_6Cl^-$
	350 vw, p			$B_2Cl_7^-$
318 vw, p				$B_2F_6Cl^-$
	276 m, dp			BCl_4^-
256 m, p				$B_2F_6Cl^-$
210 w, dp				$B_2F_6Cl^-$
	193 m, p?			BCl_4^-

[a] s = strong, m = medium, w = weak, v = very, br = broad; p = polarized, dp = depolarized. [b] Reference 1b. Nujol mull. Also 336 cm^{-1} due to $SbCl_6^-$. [c] F.R. = Fermi resonance; str = stretch; sym = symmetric, asym = antisymmetric.

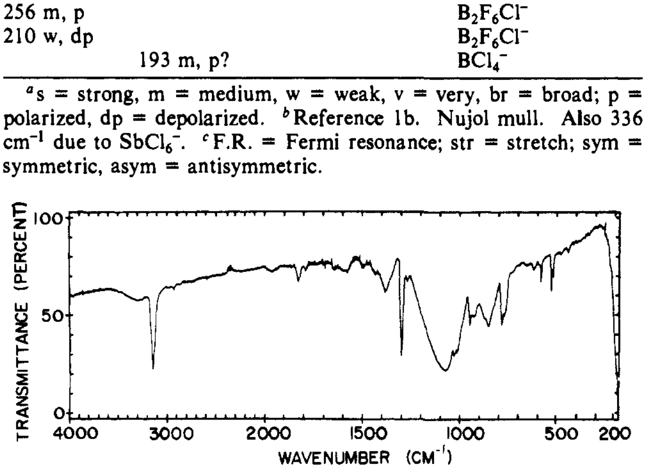

Figure 5. Infrared spectrum of polycrystalline $C_3H_3^+BF_4^-$, after temperature cycling up to −25 °C.

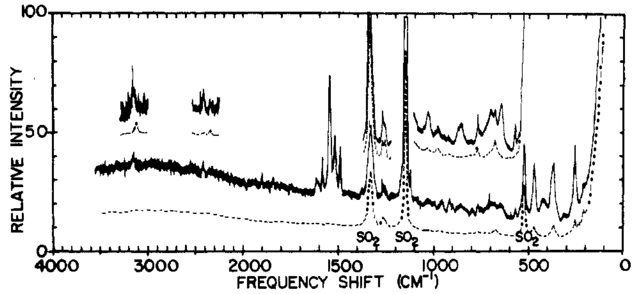

Figure 6. Raman spectrum of $C_3D_2H^+B_2F_6Cl^-$ in solution in SO_2 at −52 °C. Uppermost insert, 4 scans; next, 8 scans; next, 9 scans; lowermost, 19 scans. All after 9-point smoothing. Composition was SO_2:C_3D_2HCl:BF_3 = 9:1:2.

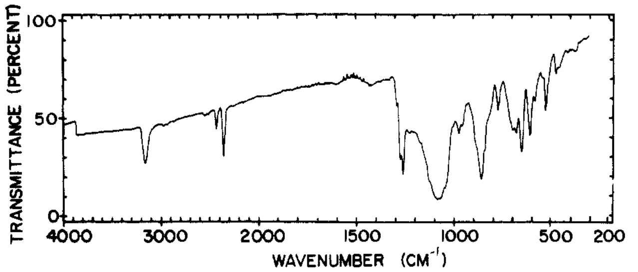

Figure 7. Infrared spectrum of polycrystalline $C_3D_2H^+BF_3Cl^-$, after temperature cycling to −50 °C.

a good spectrum of the product of reaction of 3-chlorocyclopropene with BCl_3. However, high levels of fluorescence and of concomitant noise did not justify reproducing even the best of these spectra here. Given in Table II are the results for a Raman spectrum in which the principal anion was $B_2Cl_7^-$.

For infrared spectra of the $C_3H_3^+$ ion, labile 3-fluorocyclopropene was reacted with difficulty with BF_3 by the low-temperature, bilayer reaction technique. This spectrum, which lacks some of the complexity of the mixed halogen systems, is presented in Figure 5. Features in the spectra of the product of reaction of BF_3 with 3-chlorocyclopropene and of.the product of reaction of chlorocyclopropene with SbF_5 are given in Table II. Along with the results of these various experiments Table II includes the infrared frequencies observed by Breslow and Groves for $C_3H_3^+SbCl_6^-$ and $C_3H_3^+AlCl_4^-$ in Nujol mulls.[1b] These frequencies appear to be systematically low as were the frequencies for the $C_3D_3^+$ ion.

The two a_1' modes, ν_1 and ν_2, are immediately assigned to the strongly polarized Raman features at 3183 and 1626 cm^{-1}. The three e′ modes, ν_4, ν_5, and ν_6, are represented by depolarized Raman bands at 3138, 1290, and 927 cm^{-1}. Comparable bands are found in the infrared spectra with the four different anion systems. The 1290-cm^{-1} band for ν_5 that is seen weakly in the Raman experiment has an equivalent infrared band that is quite prominent in the spectra. The one a_2'' mode ν_7, which is expected to be only infrared active, is well supported by bands in the 760-cm^{-1} region in all four infrared spectra.

No unambiguous spectral feature was found for the Raman-active-only e″ mode ν_8. Estimates from normal coordinate calculations place this fundamental in the 1000-cm^{-1} region, a location that is close to a weak, polarized Raman band due to the $B_2F_6Cl^-$ counterion system. Comparison of the intensities in this spectral region with intensities of neighboring counterion bands between Figures 2 and 4 suggests that a second, weak, depolarized feature, as expected for ν_8 in keeping with the corresponding result for the $C_3D_3^+$ ion, may contribute to the spectrum of $C_3H_3^+B_2F_6Cl^-$ in Figure 4. Although this spectral region is clear of anion bands in the purely chlorine-containing system, the noise level of our spectra of $C_3H_3^+BCl_4^-$ or $C_3H_3^+B_2Cl_7^-$ obscured any such weak feature despite accumulating many scans in the computer.

$C_3D_2H^+$ Ion. As was true for the $C_3D_3^+$ ion in comparison with the $C_3H_3^+$ ion, the vibrational assignment for the more highly deuterated ion of C_{2v} symmetry, $C_3D_2H^+$, proceeds more directly than for the $C_3H_2D^+$ ion. Table III gives the detailed assignments for the three types of spectra recorded for the $C_3D_2H^+$ ion. Figure 6 is the Raman spectrum of $C_3D_2H^+B_2F_6Cl^-$ in solution in sulfur dioxide. Figure 7 is the infrared spectrum of a polycrystalline deposit of $C_3D_2H^+BF_3Cl^-$. Bands from the infrared spectrum of $C_3D_2H^+Sb_2F_{10}Cl^-$ are given in Table III. These samples contained about 70% $C_3D_2H^+$ with about 10% $C_3H_2D^+$ and about 20% $C_3D_3^+$ as isotopic contaminants. The two bands at 1583 and 1490 cm^{-1} in the Raman spectrum indicate the presence of the two contaminant isotopomers.

For the a_1 modes, which should be infrared and Raman active, bands for ν_1, ν_2, ν_4, and ν_5 are found in both types of spectra. In the Raman spectrum these features are at 3154, 2420, 1268, and

Table II. Observed Vibrational Frequencies (in cm^{-1}) and Assignments for the $C_3H_3^+$ Ion

Raman, SO_2 solution[a]		infrared, polycrystalline[a]				
with BF_3	with BCl_3	C_3H_3F with BF_3[b]	with BF_3	with SbF_5	with $SbCl_5$ or $AlCl_3$[c]	assignment[d]
3183 w, p	3179 w, p					ν_1 a_1' asym CH str
3138 vw, dp		3137 s	3128 s	3140 s	3105 3080	ν_4 e′ asym CH str
1626 s, p	1623 s, p					ν_2 a_1' sym CCC str
1609 w, p						ν_2 ^{13}C
~1330 m, dp	1329 m, dp					SO_2
1290 w, dp	1291 w, dp	1295 s	1289 s	1292 s	1276 1275	ν_5 e′ asym CCC str
~1145 vs, p	1144 vs, p					SO_2
		1075 vs	1080 vs			BF_4^-, BF_3Cl^-
1026 w, p						$B_2F_6Cl^-$
927 w, dp	923 w, dp	925 m	920 m	925 m	908 915	ν_6 e′ asym CH bend
874 vw, p						BF_3
859 vw, dp						$B_2F_6Cl^-$
		850 m	847 m			BF_4^-, BF_3Cl^-
752 vw, p						$B_2F_2Cl^-$
		769 m	759 m	757 m	738 742	ν_7 a_2'' sym CH flap
721 vw, p						$B_2F_6Cl^-$
				690–655 vs		$Sb_2F_{10}Cl^-$
644 vw, p			645 m			$B_2F_6Cl^-$, BF_3Cl^-
		620 w				BF_4^-
		580 w				BF_4^-
569 vw, p	568 w, p					$B_2F_6Cl^-$, $B_2Cl_7^-$
				560 m		$Sb_2F_{10}Cl^-$
525 m, p	524 m, p					SO_2
		525 m	520 m			BF_4^-, BF_3Cl^-
	488 s, p			490 m		$Sb_2F_{10}Cl^-$, $B_2Cl_7^-$
~470 m, p						$B_2F_6Cl^-$
	471 w, p					BCl_3
	448 w, dp					$B_2Cl_7^-$
~415 w, p				410 m		$B_2F_6Cl^-$, $Sb_2F_{10}Cl^-$
	406 m, p					BCl_4^-
~365 m, p						$B_2F_6Cl^-$
	348 s, p					$B_2Cl_7^-$
	288 m, dp					$B_2Cl_7^-$
	274 w, dp?					BCl_4^-
				270 s		$Sb_2F_{10}Cl^-$
~255 m, p						$B_2F_6Cl^-$
~210 vw, p?						$B_2F_6Cl^-$
	195 s, p					BCl_4^-

[a] See Table I. [b] C_3H_3F was the reactant with BF_3. [c] Reference 1b. Nujol mull. First value with $SbCl_6^-$ as counterion; second value with $AlCl_4^-$. Also, 340 cm^{-1} due to $SbSl_6^-$. [d] str = stretch; sym = symmetric; asym = antisymmetric.

675 cm^{-1}, respectively. The first three are definitely polarized, and the fourth may be near the depolarization limit. The pair of strongly polarized lines at 1546 and 1517 cm^{-1} are attributable to ν_3 in Fermi resonance with a combination tone. The unperturbed ν_3 frequency is calculated to be 1536 cm^{-1}. The implicated combination tone is 2 ν_{10}, which equals 1534 cm^{-1}. No evidence for ν_3 was found in the infrared spectra, but the assignment from the Raman spectrum is certain. For ν_5 we also considered the possibility that this fundamental contributed to the intensity of the completely polarized band at 645 cm^{-1}, which is largely due to the $B_2F_6Cl^-$ system. However, application of the Rayleigh rule eliminates an in-plane frequency in the $C_3D_2H^+$ ion less than the lowest in-plane frequency for the $C_3D_3^+$ ion, which is 674 cm^{-1}.[13]

For the four modes of b_1 symmetry, ν_7, ν_8, ν_9, and ν_{10}, bands are found in both infrared spectra at frequencies corresponding to the Raman values of 2354, 1256, 973, and 767 cm^{-1}. The Raman bands appear to be depolarized. At 767 cm^{-1} a band due to BF_4^- contributes a polarized feature that is coincident with the $C_3D_2H^+$ band.

Assignments for the three out-of-plane fundamentals are problematical. The one a_2 mode, ν_6, which is only Raman active, may be at 807 cm^{-1}. A very weak, probably depolarized feature is found in the Raman spectrum in this region. In addition, the Raman spectrum has a band at 1614 cm^{-1} which cannot be explained other than as the first overtone of ν_6. An analogous interpretation has been made of the Raman spectrum of $C_3D_3^+$ for ν_7, which is the correlate mode. Rather good evidence for one of the b_2 modes, ν_{12}, is the band at 603 cm^{-1} in the infrared spectrum of $C_3D_2H^+BF_3Cl^-$ (Figure 7). A comparable feature is found at 600 cm^{-1} in the infrared spectrum of $C_3D_2H^+Sb_2F_{10}Cl^-$ (Table III), an assignment that is made doubtful by the dominance and complexity of the $Sb_2F_{10}Cl^-$ spectrum in this region. In the Raman spectrum of $C_3D_2H^+B_2F_6Cl^-$ a very weak, probably depolarized feature is present at 604 cm^{-1}, which may be the Raman counterpart of ν_{12}. The evidence for ν_{11} is scantier. It is likely that this fundamental is nearly coincident with $\nu_9(b_1)$ in the 970-cm^{-1} region, as normal coordinate calculations (vide infra) imply. The band in this region in the infrared spectrum of $C_3D_2H^+BF_3Cl^-$ has two features, and the corresponding band for $C_3D_2H^+Sb_2F_{10}Cl^-$ has a shoulder. Only one depolarized feature is present in the Raman spectrum in this region; however, we have chosen to associate it with the in-plane fundamental.

$C_3H_2D^+$ Ion. Figure 8 is the Raman spectrum of $C_3H_2D^+B_2F_6Cl^-$ in solution in sulfur dioxide. Bands from the infrared spectrum of $C_3H_2D^+BF_3Cl^-$ are given in Table IV along

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(13) Applying the Rayleigh rule to the full set of ions of this study requires care. Not only must correlations be made within the symmetry species of the lower C_{2v} symmetry, but the implications of the double substitution must be kept in mind when comparing frequencies of $C_3H_2D^+$ with $C_3D_2H^+$. One substitution is H for D which lowers the ion's mass; the other is D_2 for H_2 which raises the ion's mass. Thus, the frequencies of a given symmetry species are not serially all lower for the $C_3D_2H^+$ than for the $C_3H_2D^+$ ion.

Table III. Observed Vibrational Frequencies (in cm^{-1}) and Assignments for the $C_3D_2H^+$ Ion

Raman, SO_2 solution[a] with BF_3	infrared, polycrystalline[a]		assignment[b]
	with BF_3	with SbF_5	
3154 w, p	3146 s	3148 s	ν_1 a_1 CH str
2420 w, p	2418 m	2418 m	ν_2 a_1 sym CD str
2354 vw, dp	2347 s	2347 s	ν_7 b_1 asym CD str
1614 w, p			$2\nu_{12} = 1608$ A_1
1583 m, p			$C_2H_2D^+$ impurity
1546 s, p			ν_3 a_1 sym CCC str
1517 m, p			F.R. $2\nu_{10} = 1534$ A_1
1490 m, p			$C_3D_3^+$ impurity
1332 m, dp			SO_2
	1288 w	1286 w	$C_3H_2D^+$ impurity
1268 w, p	1268 s	1270 s	ν_4 a_1 sym CC str
1256 w, dp	1256 s	1256 s	ν_8 b_1 asym CC str
1145 vs, p			SO_2
1120 w, p			^{18}OSO
	1110–1040 vs		BF_3Cl^-
1026 w, p			$B_2F_6Cl^-$
973 vw, dp		970 m, sh	ν_9 b_1 CH bd
965 vw, dp	698 m	959 m	?ν_{11} b_2 CH flap
922 vw, dp			$C_3H_2D^+$ impurity
		899 m	$Sb_2F_{10}Cl^-$
855 w, p	853 s		$B_2F_6Cl^-$
		827 w	$Sb_2F_{10}Cl^-$
807			ν_6 a_2 DCCD torsion
767 w, p			BF_4^-
767 w, dp	766 w	767 w	ν_{10} b_1 asym CD bend
		720–659 vs	$Sb_2F_{10}Cl^-$
696 w, p	692 m		$B_2F_6Cl^-$
675 w, dp?	673 m		ν_5 a_1 sym CD bend
645 w, p	645 s		$B_2F_6Cl^-$, BF_3Cl^-
604 vw, dp	603 m	600 m	?ν_{12} b_2 sym CD flap
570 vw, p	579 w		$B_2F_6Cl^-$, BF_3Cl^-
		573 w	$Sb_2F_{10}Cl^-$
525 m, p			SO_2
	522 m	523, 494 vs	$B_2F_6Cl^-$, $Sb_2F_{10}Cl^-$
472 m, p	470 w		$B_2F_6Cl^-$
		450 m	$Sb_2F_{10}Cl^-$
423 w, p			$B_2F_6Cl^-$
379 m, p		386 w	$B_2F_6Cl^-$, $Sb_2F_{10}Cl^-$
370 vw, p			$B_2F_6Cl^-$
		331 m	$Sb_2F_{10}Cl^-$
		272 vs	$Sb_2F_{10}Cl^-$
257 m, p			$B_2F_6Cl^-$
		236 vs	$Sb_2F_{10}Cl$
212 vw, dp			$B_2F_6Cl^-$

[a] See Table I. [b] F.R. = Fermi resonance; str = stretch; sym = symmetric, asym = antisymmetric.

with the corresponding assignments of both spectra. In the Raman spectrum in the ring-breathing region a band due to impurity $C_3H_3^+$ at 1627 cm^{-1} and a pair of bands due to $C_3H_2D^+$ at 1546 and 1518 cm^{-1} are apparent. The sample used in these experiments was about 75% $C_3H_2D^+$, about 15% $C_3H_3^+$, and about 10% $C_3D_2H^+$.

In close parallel with the assignments of the $C_3D_2H^+$ ion the five a_1 modes of the $C_3H_2D^+$ ion are readily associated with the Raman bands at 3179 + 3153, 2389, 1583 1267, and 924 cm^{-1}. The Fermi resonance doublet for ν_1 collapses into a frequency of 3166 cm^{-1} for this fundamental. For the four modes of b_1 symmetry satisfactory spectral evidence exists for three of them and doubtful spectral evidence for the fourth. Bands at 3134, 1284, and 718 cm^{-1} in the Raman spectrum are assigned to ν_7, ν_8, and ν_{10}, respectively. The first two have well-defined equivalents in the infrared spectrum. However, only a shoulder is found in the 720-cm^{-1} region. Normal coordinate calculations (vide infra) indicate that ν_9 cm^{-1} for the $C_3H_2D^+$ ion is about 1000 cm^{-1}, which is a region obscured by counterion bands in both the infrared and Raman spectra. We leave ν_9 unassigned.

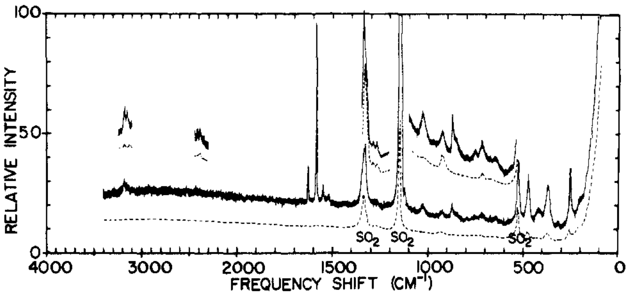

Figure 8. Raman spectrum of $C_3H_2D^+B_2F_6Cl^-$ in solution in SO_2 at −50 °C. Uppermost insert, 25 scans; next two, 66 scans; lowermost, 23 scans. All after 9-point smoothing. Composition was SO_2:C_3H_2DCl:BF_3 = 10:1:2.

Table IV. Observed Vibrational Frequencies (in cm^{-1}) and Assignments for the $C_3H_2D^+$ Ion

Raman SO_2 solution[a] with BF_3	infrared, polycrystalline[a] with BF_3	assignment[b]
3179 w, p		ν_1 a_1 sym CH str
3153 w, p		F.R. $2\nu_3 = 3166$ A_1
3134 vw, dp	3132 s	ν_7 b_1 asym CH str
2389 vw, p	2387 m	ν_2 a_1 CD str
	2348 w	$C_3D_2H^+$ impurity
1627 w, p		$C_3H_3^+$ impurity
1583 s, p		ν_3, a_1 sym CCC str
1546 w, p		$C_3D_2H^+$ impurity
1518 vw, p		
1331 m, dp		SO_2
1286 vw, dp	1288 m	ν_8 b_1 asym CCC str
1267 vw, p	1266 s	ν_4 a_1 sym CCC str
1145 vs, p		SO_2
1120 w, p		^{18}OSO
1025 w, p	1092–1034 vs	$B_2F_6Cl^-$, BF_3Cl^-
924 w, p	~920 m	ν_5 a_1 sym CH bend
870 w, p		BF_3
855 w, p	825 s	$B_2F_6Cl^-$, BF_3Cl^-
751 w, p		BF_4^-
718 w, dp?		ν_{10} b_1 CD bend
	691 s	$B_2F_6Cl^-$
674 vw, dp?		$C_3D_2H^+$ impurity
647 w, p	650 s	BF_3Cl^-, $B_2F_6Cl^-$
	577 m	BF_3Cl^-
524 m, p		SO_2
	521 m	BF_3Cl^-
473 m, p		$B_2F_6Cl^-$
	455 m	BF_3Cl^-
415 w, p		$B_2F_6Cl^-$
368 m, p		$B_2F_6Cl^-$
253 m, p		$B_2F_6Cl^-$

[a] See Table I. [b] See Table III.

Assignments for the out-of-plane modes are difficult. For the one a_2 mode, for which direct spectral evidence was marginal for the $C_3D_2H^+$ ion, the prediction from normal coordinates is about 1000 cm^{-1}. This frequency is close to the frequency predicted for $\nu_9(b_1)$, for which spectral evidence has already been seen to be weak. Consequently, no assignment is made for ν_6.

Of the two b_2 modes it is likely that the Raman band for one, ν_{11}, coincides with the seemingly depolarized band at 924 cm^{-1}. This band has already been assigned to $\nu_5(a_1)$, a totally symmetric mode for which a reasonable intensity is expected. One of the impurity isotopomers may also contribute intensity in this region. Tentatively, we assign ν_{11} at about 920 cm^{-1}, largely on the grounds of consistency with the predictions of normal mode calculations. Experimental evidence for ν_{12} is scantier. The Raman spectrum contains a very weak, possibly depolarized feature at about 674 cm^{-1}. However, this band could be due to impurity $C_3D_2H^+$. The infrared spectrum in this region is too crowded with BF_3Cl^- bands to be useful. We leave the ν_{12} fundamental unassigned from experimental data.

Table V. Fundamental Frequencies and Potential Energy Distributions (PED) of the $C_3H_3^+$ and $C_3D_3^+$ Ions

		$C_3H_3^+$			$C_3D_3^+$		
		freq, cm^{-1}			freq, cm^{-1}		
		obsd	calcd	PED[a]	obsd	calcd	PED[a]
a_1'	ν_1	3183	3183	95 a CH str, 5 s CCC str	2471	2464	79 s CD str, 21 s CCC str
	ν_2	1626	1628	95 s CCC str, 5 s CH str	1490	1488	79 s CCC str, 21 s CD str
a_2'	ν_3		1030	100 s CH bd		837	100 s CD bd
e'	ν_4	3138	3138	97 a CH str (b), 2 a CH str (a)	2348	2347	90 a CD str (a), 4 a CD str (b), 6 a CCC str (b)
	ν_5	1290	1292	72 a CCC str (a), 17 a CCC str (b), 3 a CH bd (a), 7 a CH bd (b)	1248	1246	82 a CCC str (a), 6 a CCC str (b), 5 a CD str (b), 7 a CD bd (a)
	ν_6	927	931	89 a CH bd (b), 3 a CCC str (a), 6 a CCC str (b)	674	671	88 a CD bd (b), 5 a CD bd (a), 5 a CCC str (b), 2 a CD str (a)
a_2''	ν_7	758	760	100 s CH flap	560	558	100 s CD flap
e''	ν_8		990	100 a CH flap (a)	802	804	64 a CD flap (a), 36 a CD flap (b)
av.	diff		1.7			2.8	

[a] Summed PEDs in percent; s = symmetric, a = antisymmetric, str = stretch, bd = bend. For the doubly degenerate modes the other mode of each pair is obtained by exchanging a and b designations. See ref 8.

Table VI. Fundamental Frequencies and Potential Energy Distributions (PED) of the $C_3H_2D^+$ and $C_3D_2H^+$ Ions

		$C_3H_2D^+$			$C_3D_2H^+$		
		freq, cm^{-1}			freq, cm^{-1}		
		obsd	calcd	PED[a]	obsd	calcd	PED[a]
a_1	ν_1	3166	3169	96 s CH str, 3 uni CC str	3154	3152	97 CH str, 3 s CC str
	ν_2	2389	2391	87 CD str, 12 s CC str	2420	2426	83 s CD str, 12 uni CC str, 5 s CC str
	ν_3	1583	1582	47 s CC str, 42 uni CC str, 7 CD str, 3 s CH str	1536	1536	69 s CC str, 16 uni CC str, 13 s CD str, 2 CH str
	ν_4	1267	1267	48 uni CC str, 35 s CC str, 14 s CH bd, 3 CD str	1268	1267	69 uni CC str, 21 s CC str, 6 s CD bd, 3 s CD str
	ν_5	924	923	86 s CH bd, 7 uni CC str, 5 s CC str, 2 CD str	675	674	94 s CD bd, 3 uni CC str
a_2	ν_6		990	100 HCCH torsion	807	804	100 DCCD torsion
b_1	ν_7	3134	3135	98 a CH str, 2 a CC str	2354	2350	93 a CD str, 7 a CC str
	ν_8	1286	1287	92 a CC str, 4 a CH bd, 3 CD bd	1256	1255	83 a CC str, 11 CH bd, 4 a CD str, 2 a CD bd
	ν_9		1008	93 a CH bd, 5 CD bd, 2 a CC str	973	974	81 CH bd, 11 a CD bd, 6 a CC str, 2 a CD str
	ν_{10}	718	719	92 CD bd, 4 a CC str, 3 a CH bd	767	763	87 s CD bd, 7 CH bd, 4 a CC str
b_2	ν_{11}	~920	904	73 s CH flap, 27 CD flap	~960	952	89 CH flap, 11 s CD flap
	ν_{12}		655	73 CD flap, 27 s CH flap	~603	601	89 s CD flap, 11 CH flap
av	diff		1.4			2.3	

[a] uni = unique. See Table V for definitions.

Table VII. Force Constants Fitted to the Vibrational Fundamentals of $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$ Ions

description	force constant (statistical dispersion)[b]
In-Plane Mode	
C–C stretch	7.890 (75)
C–H stretch	5.284 (2)
C–H bend	0.599 (11)
CC str/CC str	−0.428 (40)
CH str/CH str	0.031 (09)
CH bd/CH bd	−0.044 (05)
CC str/CH str (local)	−0.239 (22)
CC str/CH str (distant)	0.374 (45)
CC str/CH bd (local)	0.216 (31)
CH str/CH bd (distant)	0.234 (54)
Out-of-Plane Mode	
C–H flap	0.439 (02)
CH flap/CH flap	−0.032 (01)

[a] str = stretch, bd = bend. [b] Units of mdyn/Å for str/str; mdyn Å/rad^2 for bd/bd; mdyn/rad for str/bd. Statistical dispersions in thousandths.

Table VIII. Force Constants for CC and CH Bonds in Benzene in Cyclopropenyl Cations[a]

	C_6H_6[b]	$C_3H_3^+$	$C_3FH_2^+$[c]	$C_3F_2H^+$[d]	$C_3F_3^+$[e]
all CC stretch	6.578	7.89 (08)			7.71 (22)
two CC stretch			8.28 (14)	6.98 (35)	
unique CC stretch			6.84 (21)	8.64 (38)	
CH stretch	5.176	5.28 (01)	5.33 (03)	5.29 (04)	
CH bend (in-plane)	0.514	0.60 (01)	0.54 (12)	0.52 (19)	
CH flap (out-of-plane)	0.439	0.44 (00)	0.42 (01)	0.44 (01)	

[a] Units mdyn/Å for stretching and mdyn Å/rad^2 for bending. Values in parentheses are statistical dispersions in thousandths. [b] Reference 20. [c] Reference 11 with unequal CC bond lengths assumed. [d] Reference 12 with unequal CC bond lengths assumed. [e] Reference 8.

Normal Coordinate Calculations. Normal coordinate calculations were carried out in the harmonic approximation in internal coordinate space by means of well-known matrix formalisms and standard computer programs.[14,15] A nonredundant set of internal coordinates [three CC stretching, three CH(D) stretching, three CH(D) in-plane wagging, and three CH(D) out-of-plane flapping] was used. Bond lengths of 1.398 Å for CC bonds and 1.09 Å for the CH bonds were assumed.[4] Symmetry coordinates were defined appropriate to D_{3h} symmetry for $C_3H_3^+$ and $C_3D_3^+$ [8] and appropriate to C_{2v} symmetry for $C_3H_2D^+$ and $C_3D_2H^+$.[12] The general valence force field (GVFF) consisted of ten constants for in-plane bond motion and two for out-of-plane bond motion. As shown in detail in Table VII, the in-plane force constants consisted of constants for three valence coordinates and of seven corresponding interaction constants. For the out-of-plane motion one is the force constant for bond flapping and the other is the interaction constant. As the starting point for the refinement, zero-order diagonal force constants were those refined for $C_3FH_2^+$ on the assumption of equal CC bond lengths.[11] Zero-order off-diagonal force constants were given values of zero.

Table V gives the results of the refinement calculation of frequencies for $C_3H_3^+$ and $C_3D_3^+$ in comparison with the observed fundamental frequencies. This table includes a description of the normal-modes in terms of the potential energy distribution in symmetry coordinate space. For this purpose we have used the *summed* potential energy distribution (PED), the elements of which are the same as the "M matrix" of Pulay and co-workers

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and add to 100%.[8,16] Table VI contains the corresponding information for the two ions of lower symmetry, $C_3H_2D^+$ and $C_3D_2H^+$. The force constants for a GVFF which were fitted simultaneously to the frequencies of the four isotopomers are given in Table VIII. Where available, the experimental frequencies that were used in the calculations were the ones observed for sulfur dioxide solutions.

The spectroscopic observations for the full set of in-plane modes of the four isotopomers are sufficiently complete—27 of 28 spectroscopically active frequencies—and sufficiently well reproduced by the normal coordinate calculations that we have confidence in the fit of all 10 force constants for these modes. In our earlier communication only seven of these force constants were fitted to the assignments for three isotopomers. Differences between the previous force constants and the corresponding ones in the complete set are within statistical dispersions with one exception, CC stretch/CH stretch(distant), which differs by a factor of 2. Two of the previously neglected interaction force constants, CH stretch/CH stretch and CH bend/CH bend, are quite small. The remaining one, CH stretch/CH bend (distant), is of significant size. Small changes in some of the assigned frequencies in our further work with the spectra introduce small changes in the calculations.

The situation with respect to the out-of-plane modes is less certain. Of the 10 out-of-plane fundamentals the only settled assignments are for two modes, the $\nu_7(a_2'')$ fundamentals for the $C_3H_3^+$ and $C_3D_3^+$ ions. Fair evidence points to a third mode, $\nu_8(e'')$ of the $C_3D_3^+$ ion, and weaker evidence suggests a fourth, $\nu_6(a_2)$ of the $C_2D_2H^+$ ion. Some of the missing bands may be overlapped by stronger bands due to in-plane modes. The unobservability of most of the torsional modes for these ions is a familiar problem in similar species.[11]

In principle, only two unconnected frequencies are needed to define the two force constants for the out-of-plane modes. Since the two ν_7 frequencies of $C_3H_3^+$ and $C_3D_3^+$ are linked by the product rule, at least one more secure frequency is needed. To give greater certainty to the assignment and to the adjusted force constants yet another frequency is desirable. In the absence of a good frequency check, we used normal coordinate calculations to explore the consequences of "low frequency" alternatives for the $\nu_8(e'')$ frequencies of $C_3H_3^+$ and $C_3D_3^+$. These frequencies were considered to be ~925 and ~675 cm^{-1}, respectively, bands which could have been overshadowed by bands due to in-plane modes. However, the set of out-of-plane frequencies found with this calculation was harder to reconcile with the experimental data than the ones reported here. Furthermore, the force constant for CH flapping was 0.39 mdyn/Å, which was lower than the value of 0.43 mdyn/Å^2 that was found for the $C_3FH_2^+$ and $C_3F_2H^+$ ions.[11,12] For the refinement calculations reported here the frequencies for ν_7 of the $C_3H_3^+$ ion, and ν_7 and ν_8 of the $C_3D_3^+$ ion, were given weight 1.0, whereas the frequency for ν_6 of the $C_3D_2H^+$ was given weight 0.5. All other out-of-plane frequencies in Tables VI and VII are values calculated without reference to observed frequencies.

As can be seen in Table VII, with few exceptions the normal modes are dominated by single symmetry coordinates. Thus, the common practice of describing normal modes with single symmetry coordinates is justified for the cyclopropenyl cation system. Useful group frequencies for the cyclopropenyl cation are the CH stretching frequency in the 3135–3185-cm^{-1} region and the ring-breathing frequency somewhat above 1600 cm^{-1}. This latter mode gives the dominant band in the Raman spectrum. Substituting fluorine atoms on the ring raises this frequency to a value as high as 2014 cm^{-1} in $C_3F_3^+$.[8] Substituting chlorine atoms has a smaller effect in the same sense.[8,17]

Comparative Force Constants. A comparison of the force constants of the cyclopropenyl cation with those of benzene points to some important conclusions. Table VIII provides this comparison. The values for benzene are the preferred ones from the work of Pulay, Fogarasi, and Boggs.[18] These workers have used the scaled ab initio method to resolve discrepancies between various sets of empirical force constants and to compute a best set. Each of the force constants for in-plane bond deformations of the cyclopropenyl cation is appreciably larger than the corresponding one for benzene. On the basis of the customary correlation between a bond strength and the magnitude of a force constant (e.g., CC stretching constants: saturated, acyclic hydrocarbons 4.70;[19] cyclopropane 4.29[20]), we conclude that both the CC and CH bonds are stronger in the cyclopropenyl cation than in benzene. A stronger CC bond in $C_3H_3^+$ also correlates with a shorter CC bond in the cyclopropenyl cation than in benzene. For $C_3Ph_3^+$, r_{CC} = 1.373 Å, for $C_3[N(CH_3)_2]_3^+$, r_{CC} = 1.363 Å,[21] and for benzene, r_{CC} = 1.397 Å.[18] One ab initio calculation for the $C_3H_3^+$ ion predicts a CC bond length shorter than that for benzene.[22] (The normal coordinate calculations are insensitive to the bond lengths and, in particular, to what may have been a somewhat long CC bond length in our calculations.)

From an ab initio calculation (minimal basic set + C3d + CI) for the cyclopropenyl cation Takada and Ohno found a value of 7.92 for the CC stretching force constant.[4] This surprisingly large value is now supported by our experiments.

The apparently greater CC bond strength in the cyclopropenyl cation than in benzene is remarkable in view of the lower bond order and of the strained "σ" bonds in this ion. The delocalized π-bonding under the control of the positive charge must make an exceptional contribution to the strength of these bonds. Thus, the cyclopropenyl cation may be regarded as "superaromatic".

Force constants for stretching of CH bonds are known to increase as the amount of s character ascribed to a bond increases. This pattern is seen in going from sp^3 in alkanes (4.9) to sp^2 in alkenes (5.12) to sp in acetylenes (5.9).[23] The dissociation energy of CH bonds also increases in this way but not as dramatically.[24] Thus, the CH bond in the cyclopropenyl cation with a force constant of about 5.3 is a strong bond with considerable sp character. A similar conclusion about the extent of sp character of the CH bond in this ion was drawn from the large value of the ^{13}CH coupling constant in the ion,[1c] an observation we have confirmed, and from the ab initio calculations.[4] To the contrary, the larger in-plane bending constant for the CH bond in the cation than in benzene is inconsistent with the enhanced sp character.[25]

For out-of-plane bending the force constant of the cyclopropenyl cation is essentially the same as that for benzene. Furthermore, as shown in Table VIII, this force constant is not changed significantly by substituting one or two fluorine atoms on the ring.

Fluorine substitution has a large effect on the CC stretching force constants as can be seen in Table VIII. In a recent paper on the $C_3F_3^+$ ion we have considered this effect in some detail.[8] Briefly, introducing a fluorine substituent into a cyclopropenyl cation increases the magnitude of the force constant for the stretching of adjacent CC bonds and decreases the magnitude of the force constant for a cross-ring bond. Similar effects are found in cyclopropane and cyclopropene ring systems.[8] When the ring

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is completely substituted with fluorine, the CC force constant returns to the value in the $C_3H_3^+$ ion.

Fluorine substitution also appears to affect the force constant for in-plane bending of the CH bond. Substituting one fluorine atom lowers the value of this constant to a value closer to the one in benzene. The substitution of the second fluorine atom brings the value to essentially that of benzene.

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Registry No. $C_3H_3^+$, 26810-74-2; $C_3D_3^+$, 59192-32-4; $C_3D_2H^+$, 102682-80-4; $C_3H_2D^+$, 93255-76-6.

Ionic Charge-Transfer Complexes. 1. Cationic Complexes with Delocalized and Partially Localized π Systems

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Abstract: The partially charge localized radical ion $C_6H_5NH_2^+$ and its *N*-methyl derivatives form stable complexes with the π-donor neutral $C_6H_5NH_2$ and its derivatives. The dissociation energies (ΔH°_D, kcal/mol) of the complexes are determined by pulsed high pressure mass spectrometric equilibrium measurements as follows: $(An)_2^+$, 17.5; $(MA)_2^+$, 16.4; $(DMA)_2^+$, 15.9; $(DMA^+{\cdot}An)$, 14.2 kcal/mol (An = aniline; MA = *N*-methylaniline; DMA = *N,N*-dimethylaniline). In $(An)_2^+$, charge-transfer resonance $A^+{\cdot}A \leftrightarrow A{\cdot}A^+$ should be favorable, while in $(An^+{\cdot}Bz)$ [Bz = benzene] the large difference between the ionization energies of the components (ΔIP) rules out charge transfer. The differences between ΔH°_D of $(An)_2^+$ and $(An^+{\cdot}Bz)$ suggest that the contribution of the resonance energy ΔH°_{res} to the stability of $(An)_2^+$ is ≈5 kcal/mol. In another series of complexes, where the electron donors are delocalized aromatic hydrocarbons, ΔH°_D again decreases with increasing differences between the ionization potentials of the components (ΔIP), from 18.3 kcal/mol for $An^+{\cdot}AN$ (AN = acenaphthene) (ΔIP = 1.4 kcal/mol) to 13.2 kcal/mol for $An^+{\cdot}Bz$ (ΔIP = 35.1 kcal/mol). This trend is attributed to a decrease in intermolecular charge-transfer resonance as ΔIP increases. Again, the maximum contribution of ΔH°_{res} is about 5–6 kcal/mol. In contrast with the sandwich-type structures of the above complexes, complexes with highly polar cyano and nitro ligands seem to reorient to a linear structure which optimizes ion–dipole interactions. These complexes yield bonding energies of 16–20 kcal/mol, despite the large ΔIP of the components.

Charge-transfer complexes between molecular electron acceptors and donors have been investigated extensively.[1-5] In these systems the donor is often a π system with a partial deficiency of electrons. An extreme case of electron deficiency can be produced if an electron is removed from the π system, i.e., if the acceptor is an ionized unsaturated molecule. These complexes, which contain an extremely electron deficient acceptor and a net unit positive charge, are ionic charge-transfer complexes. Since they involve an extremely efficient cationic acceptor, the study of such complexes should help the understanding of charge-transfer complexes in general. The interactions between donor and acceptor π systems in ionic complexes are also relevant to the energy of charge holes in organic conductors[6] and to the behavior of ionized states of porphyrins in photosynthesis.[7] For a basic understanding of these interactions, it is especially important to investigate the energetics of the complexes in the gas phase, in the absence of complicating solvent effects.

While there are extensive data on gas-phase ion–molecule complexes, the large majority of such data pertain to closed-shell, hydrogen-bonded systems.[8] On radical ion–molecule complexes, the data pertain mostly to rare gases and diatomic and triatomic species of atmospheric interest, such as $N_2^+{\cdot}N_2$, $O_2^+{\cdot}O_2$, $O_2^+{\cdot}N_2$, etc. Some of these, such as $N_2^+{\cdot}N_2$, were subject to theoretical study, which showed that charge-transfer, i.e., covalent bonding makes an important contribution to the total dissociation energy (ΔH°_D) of 23 kcal/mol.

In organic systems involving π acceptors and donors, photoionization data are available on the ethylene dimer ion $C_2H_4^+{\cdot}C_2H_4$, where $\Delta H^\circ_D = 17 \pm 1$ kcal/mol.[10] For larger π systems, spectroscopic observations were made on $(NP)_2^+$ (NP = naphthalene) and related systems.[11] In the case of these aromatic hydrocarbons spectral studies[12] revealed that the dimer cations have symmetric sandwich structures. The complex-for-

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