guished by a surprisingly high efficiency for the conversion of light into chemical energy. As the triplet energy of the prophyrin is about 1.8 eV, one derives from the redox potentials of the two couples $E^\circ(\mathrm{ZnTMPyP}^{5+/4+}) = 1.2$ V[5] and $E^\circ(\mathrm{C}_n\mathrm{MV}^{2+/+}) = -0.45$ V[6] that more than 90% of the excitation energy is converted into the chemical potential of the redox products.

Conclusion

In the present study pathways were established to prevent the back-reaction of important photoredox reactions by micellar assemblies. Other types of aggregates such as vesicles and surfactant polymers are now under investigations with which the same type of inhibition is conceivable. Crucial with respect to an eventual application of these systems in light energy conversion devices is the successful coupling of the photoredox reaction with a fuel-producing step which is likely to be catalytic. Particularly encouraging in this regard is the high stability ($\tau > 10$ ms) of the intermediates achieved with our systems. The lifetimes obtained are long enough to allow for the intervention of efficient catalysts. Thus, by employing ultrafine Pt particles, we have been able to couple three relays, $C_{12}Mv^{2+}$–$C_{16}MV^{2+}$, with light-induced hydrogen production from water. This subject will be treated in a forthcoming paper.

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Laser Excitation and Emission Spectra of the Hexafluorobenzene Cation in the Gas Phase

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Abstract: Laser-induced fluorescence spectra of $C_6F_6^+$ have been recorded in the gas phase. Excitation spectra of quality far superior to previous observations have been obtained by cooling the ions to near liquid N_2 temperature. The improved S/N and resolution permit considerably more information to be obtained about both the ground $\tilde{X}\,^2E_{1g}$ and excited $\tilde{B}\,^2A_{2u}$ electronic states. Laser-excited, wavelength-resolved emission spectra have also been observed for $C_6F_6^+$. These spectra allow direct observation of the Jahn–Teller perturbed vibronic structure of the ground state. Because of their relative simplicity, assignment and interpretation are usually unambiguous. Overall, the experimental results determine rather extensively and redundantly the vibronic structure of both electronic states.

1. Introduction

The ground electronic state of a molecular cation is usually formed by the removal of one electron from the highest occupied molecular orbital of the parent neutral molecule. For benzene or any of its completely substituted derivatives, e.g., perdeuterio or perfluoro, the relevant orbital is of e_{1g} symmetry and therefore doubly degenerate. The resulting ionic state is consequently $^2E_{1g}$ and as Jahn and Teller showed[1] is subject to a distortion caused by an interaction between the electronic motion and the vibrational motion corresponding to the normal coordinates of species e_{2g}. As is well-known theoretically, Jahn–Teller distortions cause the minimum of the vibronic potential to be at other than the symmetrical D_{6h} configuration with a concurrent stabilization of the molecular bonding (lowering of the well depth).

Many theoretical papers have been written on Jahn–Teller effects and many experiments, e.g., EPR, photoelectron, visible spectroscopy, have encountered the effect. However it has proven to be nearly impossible to quantitatively measure the Jahn–Teller effect due to various experimental difficulties, averaging effects, lowered site symmetry, spectral resolution, etc. The free, gas-phase, benenoid cations represent a singularly simple and well-characterized opportunity to accomplish the elusive goal of a quantitative, experimental description of the Jahn–Teller effect.

There are obvious attractions in the study of the benzene ion itself, but the spectroscopy of this species is hampered by its extremely low fluorescence quantum yield. However, in 1971, Daintith et al.[2] reported the emission spectra of the hexafluorobenzene radical cation and Allan and Maier later demonstrated[3] that the fluorescence in a series of fluorobenzene cations exhibits a lifetime of around 50 ns and probably occurs with near unity quantum efficiency. A Jahn–Teller distortion is predicted in the ground electronic states of the symmetrically trisubstituted benzene ions (D_{3h}) as well as in the fully fluorinated $C_6F_6^+$, and the former have been studied extensively by conventional electronic emission spectroscopy[4,5] and by a variety of laser-induced fluorescence techniques in both the low-temperature matrix[6] and gas phases.[7,8]

The hexafluorobenzene cation emission spectrum as first reported[2–4] is rather broad and unresolved, and its interpretation in terms of ground-state vibronic structure difficult. The same comments apply to the laser-induced fluorescence excitation spectrum in the gas phase[7] (this experiment yields more information on the vibrational structure in the upper $\tilde{B}\,^2A_{2u}$ electronic state involved in the transition which is not degenerate and thus will not show Jahn–Teller type perturbations) which shows extremely dense vibrational structure presumably due to sequence band congestion. The spectra taken in a low-temperature matrix environment do not suffer from this complication, and both the laser excitation and emission spectra have been recently reported in detail.[9] The spectra taken in a Ne matrix offer considerable insight into the vibrational structure of the ground state.

Information obtainable from gas-phase spectra is still desirable from several points of view. First, even though there is now considerable evidence concerning the lack of perturbation in the Ne matrix, any direct corroboration of the matrix data is always

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useful. Second, the emission spectra discussed in ref 9 all originate in the vibrationless level of the excited electronic state. The applicable selection rules allow such transitions to terminate only on certain ($j = {}^1/_2$) Jahn–Teller split levels of the ground electronic state. To analyze the Jahn–Teller effect, it is imperative to know the positions of the other ($j = {}^3/_2$, etc.) components of the Jahn–Teller levels. This paper describes the results of three gas-phase experiments: room- and low-temperature laser excitation spectra and laser-excited, wavelength-resolved emission spectra. These results together with those of the Ne matrix experiments form the data base from which we can develop a full interpretation of the Jahn–Teller effect in $C_6F_6^+$.

The early gas-phase laser-induced fluorescence work on $C_6F_6^+$ was carried out at ambient temperatures.[7] We have now modified our experimental procedure so that gas-phase spectra may be recorded with the sample molecules at close to liquid-nitrogen temperatures.[10,11] This procedure has the effect of markedly decreasing the relative population of higher vibronic levels. We have previously reported[11] gas-phase laser excitation spectra of $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$ taken under such modified experimental conditions and noted the significant increase in S/N and great improvement in resolution as compared with the cases for the earlier spectra.[7] This improved resolution is absolutely essential to the identification of hot bands in the congested region near the origin of the $C_6F_6^+$ spectrum. The intensity variation with temperature gives information about the vibrational energy of the ground-state levels and allows hot-band assignments to be made with considerable confidence. These hot bands provide a surprisingly complete picture of the low-frequency, ground-state vibrational structure.

A second type of experiment directly probes the vibronic structure in the ground electronic manifold. The laser frequency is tuned to coincide with a particular band in the excitation spectrum, and the resulting, laser-induced emission is dispersed in a monochromator. Relaxation processes are relatively slow in the gas phase, and it is possible to observe emission from the level initially excited.

All the spectra obtained give convincing evidence[12] of a Jahn–Teller distortion in the ground electronic state of the ion. Their analysis follows that previously employed[13] for $C_6F_3H_3^+$ and $C_6Cl_3H_3^+$. We defer detailed discussion[12] of these results until a later publication where the data presented here together with those obtained in the Ne matrix experiments are drawn together and the model detailed in ref 13 is used to determine the extent of Jahn–Teller stabilization and derive an approximate picture of the distorted structure in this compound.

2. Experimental Section

Our experimental techniques have been described elsewhere,[8,10,11] and only a brief account of them is presented here. A mixture of a few percent of argon in 4–5 torr of helium is pumped continuously through a 2-ft coil of $^1/_8$-in. copper tubing immersed in liquid nitrogen. From this, the gas mixture flows through a dc discharge maintained at several hundred volts which is itself immersed in a liquid-nitrogen containing Dewar. The argon atom metastables created in the discharge are then reacted with the parent hexafluorobenzene which is introduced through a side arm immediately above the laser irradiation region. Under these conditions, the primary reaction product is the singly ionized parent molecule, in this case $C_6F_6^+$ formed in a Penning ionization reaction.

During their lifetimes, the ions undergo many collisions with the background helium gas atoms and the mixture equilibrates at approximately the temperature of the helium bath, which is close to liquid-nitrogen temperature, before interrogation by the laser beam some 1–2 cm downstream. The resulting laser-introduced fluoroscence is viewed at right angles to the laser beam. Two types of experiments may be performed. In the first, the laser-induced fluoroscence is viewed directly by a photomultiplier tube and monitored as a function of laser wavelength; this corresponds to taking an excitation spectrum. In the second experiment, the laser frequency is set to coincide with a particular feature in the excitation spectrum and the resulting laser-induced fluorescence dispersed by using a small monochrometer. This second experiment produces a resolved emission spectrum of the ion, and this gives information mainly on the ground electronic state vibrational level structure.

Table I. Line Positions and Assignments for the $C_6F_6^+$ Excitation Spectrum

$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	assignt[a,b]
21 047	−559	$\nu_0' \leftarrow \nu_2''$
21 106	--500	$\nu_0' \leftarrow 2\nu_{18}''$ $(^1/_2)$
21 192	−414	$\nu_0' \leftarrow \nu_{17}''$ $(^1/_2)$
21 321	−285	$\nu_0' \leftarrow \nu_{18}''$ $(^1/_2)$
21 467	−139	$\nu_{18}' \leftarrow \nu_{17}''$ $(^1/_2)$
21 545	−61	$\nu_{18}' \leftarrow \nu_{17}''$ $(^3/_2)$
21 606	0	origin
21 705	99	$\nu_{17}' \leftarrow \nu_{17}''$ $(^3/_2)$
21 728	122	$\nu_{18}' \leftarrow \nu_{18}''$ $(^3/_2)$
21 745	139	$\nu_{17}' \leftarrow \nu_{18}''$ $(^1/_2)$
21 785	179	$2\nu_{18}' \leftarrow \nu_{17}'' + \nu_{18}''$ $(^5/_2)$
21 810	204	$\nu_{17}' + \nu_{18}' \leftarrow \nu_{17}''$ $(^1/_2)$
21 874	268	ν_{18}'
21 934	328	$\nu_{17}' + \nu_{18}' \leftarrow \nu_{17}'' + \nu_{18}''$ $(^5/_2)$ (?)
21 976	370	$2\nu_{18}' \leftarrow \nu_{18}''$ $(^3/_2)$
22 031	425	ν_{17}'
22 073	467	
22 145	539	$2\nu_{18}', \nu_2'$
22 215	609	ν_a'
22 298	692	$\nu_{17}' + \nu_{18}'$
22 409	803	$3\nu_{17}', \nu_2' + \nu_{18}'$
22 416	850	$2\nu_{17}'$
22 481	875	
22 496	890	$\nu_a' + \nu_{18}'$
22 562	956	$\nu_{17}' + 2\nu_{18}', \nu_{17}' + \nu_2'$
22 638	1032	$\nu_a' + \nu_{17}'$
22 682	1075	$2\nu_2'$
22 721	1115	$2\nu_{17}' + \nu_{18}'$
22 739	1133	ν_b'
22 802	1196	ν_{16}'
22 830	1224	$\nu_2' + \nu_{17}' + \nu_{18}'$
22 876	1270	$3\nu_{17}'$
22 920	1314	$\nu_a' + \nu_{17}' + \nu_{18}'$
22 946	1340	$2\nu_2' + \nu_{18}'$
22 991	1385	$2\nu_{17}' + 2\nu_{18}', \nu_2' + 2\nu_{17}'$
23 064	1458	$\nu_{16}' + \nu_{18}'$
23 100	1494	$\nu_2' + \nu_{17}' + 2\nu_{18}'$
23 160	1554	ν_{15}'
23 223	1617	$\nu_{16}' + \nu_{17}', 3\nu_2'$
23 255	1649	$2\nu_{17}' + 3\nu_{18}', \nu_2' + 2\nu_{17}' + \nu_{18}'$
23 277	1671	
23 335	1729	$\nu_2' + \nu_{16}'$
23 362	1756	$\nu_2' + \nu_{17}' + 3\nu_{18}'$
23 407	1801	
23 425	1819	$\nu_{15}' + \nu_{18}'$

[a] In expressions of the form, ν_{17}'' $(^3/_2)$, the symbols represent the $j = {}^3/_2$ component of mode 17 ($v = 1$) in the ground electronic state.[8] [b] Where no lower state level is indicated, the vibrationless level is implied.

In the present experiments a Molectron UV24 nitrogen laser was used to pump a Molectron DLII dye laser. The monochrometer used was an ISA HR320.

3. Results

3.1. Excitation Spectrum. The observed excitation spectrum is shown in Figure 1. The difference between this spectrum, taken with the rare gas stream cooled to near liquid-nitrogen temperature, and that obtained previously (Figure 3 of ref 7) at ambient temperature is remarkable. The line width has been reduced from ~35 cm^{-1} fwhm to less than half this figure, and features due to hot bands are much reduced in intensity. Table I lists the observed line positions and gives assignments on the basis of the Jahn–Teller distortion model previously described.[13]

The spectrum shows good agreement with that taken in the Ne matrix[9] confirming the now expected absence of medium shifts in these circumstances. The major differences between the spectra

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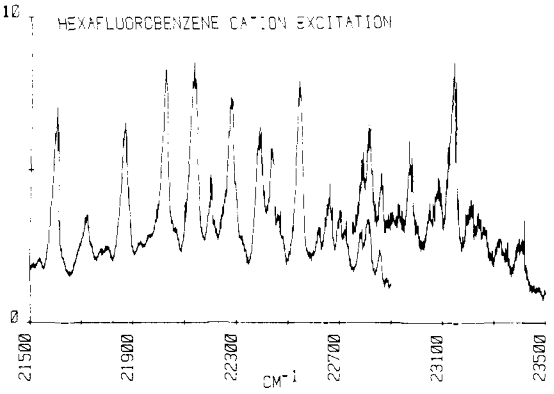

Figure 1. Gas-phase excitation spectrum of $C_6F_6^+$ taken at close to liquid-nitrogen temperature. The spectrum was obtained in two separate scans, and no correction for variation in laser power across the spectrum has been made.

occur close to the origin where a medium strength band is measured in the gas-phase spectrum at 122 cm^{-1} from the origin, and numerous weaker bands are also evident. Following our analysis of the spectra of the related trifluoro- and trichlorobenzene cations, we assign many of these features to hot bands originating in the $j = {}^3/_2$ components[13] of the Jahn–Teller active modes 17 and 18, which are expected to be among the strongest hot bands in the spectrum.

Further away from the origin, the spectrum is essentially identical with that observed in the matrix; we could, however, because of the larger line widths, not resolve the bands measured at 530 and 540 cm^{-1} in the matrix assigned to $2\nu_{18}'$ and ν_2', respectively. The two bands labeled ν_a' and ν_b' and their combinations which were also observed in the matrix spectrum probably correspond to overtones of some nontotally symmetric modes. Interestingly, ν_a' shows the greatest variation between the gas-phase and matrix frequencies, as did a similar mode in the $C_6F_3H_3^+$ excitation spectrum.

Besides the excitation spectra at low temperature, we have also taken new excitation spectra at ambient temperature with emphasis on the region below the origin. These resulted in observation of numerous hot bands. These are included, along with their assignments, in Table I.

3.2. Wavelength-Resolved Spectra. Wavelength-resolved emission spectra were obtained following excitation of the bands assigned to the origin, ν_{18}' (at 21 874 cm^{-1}) and ν_{17}' (at 22 031 cm^{-1}). The assignments given in Table II require some explanation. As noted earlier $C_6F_6^+$ is nominally of D_{6h} symmetry with an $\tilde{X}\ {}^2E_{1g}$ ground electronic state and there are four modes of the appropriate symmetry (e_{2g}) to show Jahn–Teller activity. These are ν_{15}–ν_{18} in our numbering system,[14] and they are all observed to a greater or lesser extent in the excitation spectrum, suggesting that all contribute to the total Jahn–Teller stabilization of the molecule. In the closely related compounds $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$ considerable mixing occurs[8,10,13] between the Jahn–Teller active modes, and it is not likely that the situation is markedly different in the present case. Indeed, a separate treatment of each mode does not adequately reproduce the observed energy level structure. We found it essential to perform a multimode analysis such as we have recently described[13] for $C_6H_3F_3^+$ and $C_6H_3Cl_3^+$. The details of this analysis and our resulting quantitative conclusions about the ion's distortion and stabilization energy will be given in a separate publication.[12]

The actual assignments of given lines in our present spectra are, however, incumbent upon this calculation. We first made tentative assignments and then checked these by trial calculations until consistency was obtained. Subsequently we traced back adiabatically the eigenstates of the calculation to the limit where the Jahn–Teller effect vanishes. The spectral assignments in both Tables I and II are then given in terms of states identified in this way. It should be emphasized that these assignments are little more than labels, although in many cases ones that can be fairly easily physically rationalized. In any case the final criterion is the agreement, or lack thereof, between the observed and calculated line positions.

Table II. Wavelength-Resolved Emission Spectra of $C_6F_6^+$ and Assignments

$\Delta\bar{\nu}$, cm^{-1}	assignt	$\Delta\bar{\nu}$, cm^{-1}	assignt
(a) Excitation of the Origin at 21 606 cm^{-1}			
281	ν_{18}'' (1/2)	490	$2\nu_{18}''$ (1/2)
405	ν_{17}'' (1/2)	556	ν_2''
(b) ν_{18}' Excitation at 21 874 cm^{-1}			
156	ν_{18}'' (3/2)	698	$\nu_0' \to \nu_{17}''$, $3\nu_{18}''$ (1/2)
284	ν_{18}'' (1/2)	835	$\nu_0' \to \nu_2''$ (relaxed)
409	ν_{17}'' (1/2)	958	
546	$\nu_0' \to \nu_{18}''$ (relaxed); $2\nu_{18}''$ (3/2)	1086	
604	$\nu_{18}'' + \nu_{17}''$ (1/2)	1247	
(c) ν_{17}' Excitation at 22 031 cm^{-1}			
153	ν_{18}'' (3/2)	546	$\nu_{18}' \to \nu_{18}''$ (1/2) (partially relaxed); $2\nu_{18}''$ (1/2)
328	ν_{17}'' (3/2)		
426	ν_{00} (relaxed)		
		695	$\nu_{18}' \to \nu_{17}'$ (1/2)

We deal first with the spectrum obtained upon excitation of the origin band at 21 606 cm^{-1} which should be directly comparable to the relaxed Ne matrix emission. The emission bands show, under our experimental conditions, fwhm of approximately 35 cm^{-1}. Their frequencies are compiled in Table II. As we have now come to expect, there is indeed exceptionally close agreement between the gas plane and matrix results with the strongest features assigned to ν_{18}'', ν_{17}'', and ν_2''. At first surprising was a seemingly "extraneous" band removed 490 cm^{-1} from the laser; however, calculations including mode-mixing effects between the strongly Jahn–Teller active vibrations ν_{17}'' and ν_{18}'' show that a level adiabatically traceable to $2\nu_{18}''$ is to be expected at this position and that it is accessible from the zero-point level of the upper electronic state.

It is clear from the calculations that even the three lowest frequency levels (281, 405, 490 cm^{-1}) are strongly mixed and none of them corresponds to a pure state. However it is easy to rationalize assignments of the first two lines to ν_{18}'' and ν_{17}'', respectively. These levels are also found to correlate adiabatically with those basis states.

The quantum number j is good in the absence of quadratic Jahn–Teller coupling. Preliminary calculations suggest a quadratic coupling of the same order of magnitude as that observed in $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$,[13] where the presence of a quadratic Jahn–Teller effect makes only very small changes in the observed spectra. Thus the levels can also be assigned nearly rigorously a j quantum number.

We now turn to the spectrum obtained upon excitation of ν_{18}' ($v = 1$) at 21 874 cm^{-1}; part of this spectrum is shown in Figure 2. We first assign all bands corresponding to known transitions within the $j = {}^1/_2$ manifold. In this way we can account for the lines at 284 cm^{-1} (ν_{18}'' (${}^1/_2$)) and 409 cm^{-1} (ν_{17}'' (${}^1/_2$)) as well as these features assigned, at least in part, to relaxed emission eminating from the zero point level in the upper electronic state at 546, 698, and 835 cm^{-1} removed from the excitation frequency. We are left with a strong feature at 156 cm^{-1} which we assign in our adiabatic procedure to the $j = {}^3/_2$ component of the ν_{18}'' = 1 level. This is in good agreement with the similarly assigned 157-cm^{-1} vibrational interval observed in the unrelaxed Ne matrix fluorescence. This transition is predicted to be rather strong by analogy with the corresponding transitions in $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$. A weak band at 604 cm^{-1}, which is close to the calculated position, we label as the combination, $\nu_{18}'' + \nu_{17}''$ ($j = {}^1/_2$) level. We have not assigned lines still further from the laser

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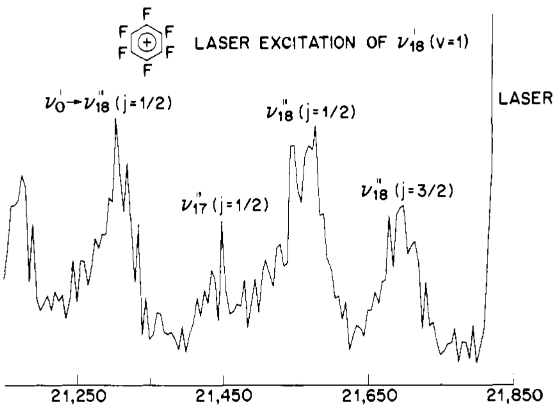

Figure 2. Wavelength-resolved spectrum obtained upon pumping the ν_{18}' band of the $C_6F_6^+$ excitation spectrum at 21 874 cm^{-1}. The assignments for the strongest bands are indicated, ν_{18}'' ($^3/_2$), for example, refers to the $j = {}^3/_2$ component[12] of the ν_{18}'' (v = 1) level (see text).

as our calculations become inaccurate higher up the ground-state vibronic level stack due to basis-set truncation effects.

The analysis of the spectrum obtained on excitation of ν_{17}' at 22 031 cm^{-1} follows in similar fashion. In this case we can distinguish emission bands corresponding to transitions to both ν_{18}'' ($v = 1, j = {}^3/_2$) and ν_{17}'' ($v = 1, j = {}^3/_2$). The latter is predicted to be weaker and partially overlapped by the strong ν_{18}'' ($j = {}^1/_2$) band in the ν_{18}' excitation experiment. Features further from the laser are all assignable to relaxed emission from either ν_{18}' or ν_0' levels.

4. Conclusions

The vibronic structure of a Jahn–Teller distorted state such as the $^2E_{1g}$ state of $C_6F_6^+$ is clearly quite complicated. It is therefore very desirable to have complete and redundant determinations of level positions. Because of the operative selection rules, the lines observed in the wavelength-resolved spectrum obtained by laser pumping the electronic origin and transitions from excited levels of the $j = {}^1/_2$ manifold appearing as hot bands in the excitation spectrum independently determine the positions of the ν_i'' ($j = {}^1/_2$) levels. Comparison of Tables I and II indicates very good agreement between the positions determined in these two experiments. These same level positions are also determined by the emission spectrum obtained in solid Ne as described in ref 9. Comparison of the present results with those in this reference again indicates very good agreement for the levels mutually observed.

The $j = {}^3/_2$ stack is likewise redundantly determined. In this case the direct determination comes from the wavelength-resolved emission spectra obtained via pumping ν_{17}' or ν_{18}'. From these levels emission is allowed into both the $j = {}^1/_2$ and $^3/_2$ stacks, although the latter is usually stronger. No discrepancies are observed with the previous $j = {}^1/_2$ positions, and new values are obtained for the $j = {}^3/_2$ levels. These $j = {}^3/_2$ level positions can now be used to interpret the hot-band structure to the high frequency side of the origin in the excitation spectrum. As seen from Table I, these hot-band transitions confirm the $j = {}^3/_2$ assignments. The $j = {}^3/_2$ lines observed are, where overlap exists, also in good agreement with the unrelaxed matrix spectra. Finally one or two lines in the $j = {}^5/_2$ stack have been observed, both in the gas phase and in the matrix, due to mixing of the $j = \pm{}^1/_2$ and $j = \pm{}^5/_2$ stacks by quadratic effects.

Taken together the experimental data fairly extensively and redundantly establish the positions of a number of the Jahn–Teller perturbed vibronic levels of the ground state. This information along with the observed line intensities forms a good data base for understanding the Jahn–Teller effect in $C_6F_6^+$. In a future manuscript[12] we will describe extensive calculations which have been carried out to determine Jahn–Teller parameters for the active modes. The agreement of these calculations with experiment and the resulting information on the Jahn–Teller stabilization energies and distorted geometries will also be reported.[12]

Charge Distribution and Bonding in the Series $(CF_3)_2O_n$ (n = 0–3) and in CF_3SCF_3 Deduced from Gas-Phase X-ray Photoelectron Spectroscopy. Evidence for Double Bonding in Saturated Compounds

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Abstract: Core-level binding energies for the gases hexafluoroethane, bis(trifluoromethyl) oxide, bis(trifluoromethyl) peroxide, bis(trifluoromethyl) trioxide, and bis(trifluoromethyl) sulfide have been measured. Unusual binding energy shifts were observed in the series $(CF_3)_2O_n$ (n = 0–3). Semiempirical minimum neglect of differential overlap (MNDO) molecular orbital calculations were performed on all of the molecules examined. Excellent correlations between the observed core-level binding energies (corrected for the site potentials) and calculated atomic charges are found. The X-ray photoelectron spectra and MNDO calculations reveal the π-type oxygen lone-pair interactions with σ^* orbitals of the $-CF_3$ groups are important in the $(CF_3)_2O_n$ (n = 1–3) compounds. A similar interaction is also present in $(CF_3)_2S$ but is only half as strong due to the poorer sulfur lone-pair $-CF_3$ σ^* overlap.

Introduction

Catenation is not a common phenomenon in oxygen chemistry and chains are generally limited to two oxygen atoms. The only well-documented, stable, three oxygen atom species are ozone and the bis(perfluoroalkyl) trioxides.[2] With the tetrad of stable compounds CF_3CF_3, CF_3OCF_3, CF_3OOCF_3, and CF_3OOOCF_3, we are afforded the opportunity to examine the effects arising from successive oxygen atom insertions on core-level binding energies

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