Laser-Induced Fluorescence Studies of Large and Small Molecular Cations Produced by Using Electron Bombardment in a Free Jet Expansion

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Laser-induced fluorescence (LIF) excitation spectra have been obtained for a number of ions produced by electron impact in a free jet expansion. The ions observed include N_2^+, CO_2^+, $C_6F_6^+$, $C_6F_5H^+$, $C_6F_3H_3^+$, and $C_4H_2^+$. In all cases "cold" laser excitation spectra have been obtained. For the simpler ions information about rotational distributions is available, while for the larger ions the elimination of hot bands, sequence congestion, extensive rotational contours, etc., makes their spectra much easier to interpret. Under certain circumstances Penning ionization in the expansion effectively competes with direct ionization via electron impact. Some satellite structure is obtained in the $C_6F_6^+$ spectrum which may be ascribed to $C_6F_6^+\cdot Ar$.

Introduction

In the past few years supersonic free jet expansions have contributed enormously to molecular spectroscopy. The technique has been very successfully applied to the characterization of large stable molecules and weakly bound van der Waals species.[1] Extending this technique to short-lived chemical intermediates would, however, be extremely useful.

Clearly reactive species must be prepared in situ in the expansion, a task which may be of some difficulty. One group of highly reactive molecules for which considerable progress has been made in this regard are molecular ions. In some ways cations produced from neutral parents by simple electron ejection are perhaps the easiest reactive species to product "cold" in a jet. In the simplest model of this process, little or no rotational warming would be expected in the ionization step. Also since the potential surfaces for ions and their parent neutrals are in many cases similar, ionization may be accomplished with minimal vibrational excitation of ions.

Recently there have been a number of reports describing electron-excited emission spectra of both small and large ions.[2-5] These experiments have primarily exploited the fact that the jet environment gives rise to "cold" ion emission spectra. However, in some cases, more detailed investigations of how cold ions are formed have been carried out.[6-10] The disadvantage of the experiments wherein electron impact both ionizes and excites the ion is that one learns little about the ground-state population distribution of the ion. The ideal complement to the emission experiment is the laser-induced fluorescence (LIF) spectrum in which the ground state is probed directly.

Recently the first reports of laser-induced fluorescence spectra of free jet cooled ions have appeared. In one series of experiments organic ions were probed by LIF following production by multiphoton ionization.[11] In other experiments, small di- and triatomic ions have been produced by electron impact ionization.[12-14] In this paper we present our initial studies of both small, diatomic ions and large, ions produced in a free jet expansion by electron impact ionization and then probed by LIF. These studies clearly demonstrate the simplification of ionic spectra possible with the combination of jet and laser excitation techniques for both small-molecule and large-molecule spectra.

Electron impact and multiphoton ionization should play complementary roles in producing efficiently different kinds of ions in the jet. With the multiphoton ionization technique, ionic clusters have been shown to be formed in the jet and their spectra observed. The present work which utilizes electron bombardment shows the possibility of chemical reactions leading to ion production, and hence the concomitant possibility of ion–molecule reactions in the jet must also be considered.

This paper surveys a number of initial observations associated with electron impact ionization in the free jet. In many cases these observations clearly point out future directions for this type of experiment.

Experimental Section

The prsent experiments were conducted in a single-chamber vacuum apparatus. The chamber was evacuated by a 6-in. diffusion pump backed by a mechanical pump. The ultimate pressure obtained in the chamber was $\sim 2 \times 10^{-7}$ torr.

A supersonic free jet was produced by expanding a mixture of a few percent of the parent neutral species in Ar through a 75- or 150-μm nozzle. The nozzle was mounted on a length of stainless steel tubing which entered the chamber through an O-ring seal. Typical operating conditions were 1–5-atm total pressure behind the nozzle and $<5 \times 10^{-4}$ torr background pressure inside the chamber. Gas mixtures were produced by either premixing at

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high pressures or flowing the carrier gas over a volatile liquid prior to expansion.

Molecular ions are produced by crossing the supersonic free jet with an electron beam at right angles. The electron beam is generated from a home-built electron gun consisting of a heated thoria-coated iridium filament, an accelerating grid, and a collector. The components of the electron gun are positioned on a bracket so that the cathode and the collector are on opposite sides of the free jet. The nozzle–electron beam separation could be adjusted by manual positioning of the nozzle tube (±0.25 mm). The electron beam is collimated to an approximately 1-mm diameter by a permanent magnet which is located behind the collector plate. The electron energies could be coarsely varied from 0 to 160 eV by changing the cathode voltage. Using Ar as the free jet carrier gas and electron energies of approximately 100 eV, we routinely obtained collected currents in the range of 0.20–0.70 mA. For most experiments, the electron gun was operated in a pulsed mode. The electron gun, which was normally turned off by maintaining the cathode and grid at a common potential, was pulsed on for ~2-μs duration by applying an appropriate voltage pulse to the accelerating grid.

Laser-excited fluorescence of the molecular cations was induced by irradiating the free jet downstream of the electron beam with the output of a Molectron DLII dye laser pumped by a Molectron UV 24 nitrogen laser. The lasre beam had a ~0.5 mm diameter waist in the jet interaction region. The dye laser was temporally delayed with respect to the electron gun pulse by 2 → 9 μs, corresponding to a spatial separation between the electron and laser beams of 0 → 5 mm. The time delay between the dye laser and electron gun pulses permitted discrimination of the laser-induced fluorescence signal from the emission that is associated with the electron-bombardment process. The laser-induced fluorescence was imaged onto a blue-sensitive photomultiplier tube (EMI 9789QA) using a quartz lens inside the vacuum chamber. A movable slit was positioned along the imaging plane of the lens to spacially discriminate against laser scatter, emission directly due to electron impact, and the continuous white light emanating from the hot filament of the electron gun. Further reduction in laser scatter and other background light was obtained by isolating the spectral range of interest with appropriate long-pass cutoff filters. The undispersed fluorescence signal was collected with a gated integrator (gate width 200 ns) as a function of laser excitation wavelength. The signals were digitized and averaged by using an HP calculator system.[15]

Results and Discussion

Laser-induced fluorescence has been observed from cold molecular ions which have been produced by electron impact in a seeded supersonic free jet expansion. To date, fluorescence excitation spectra of several molecular cations including those of nitrogen, carbon dioxide, hexafluorobenzene, pentafluorobenzene, trifluorobenzene, and diacetylene have been obtained. In all cases, a dramatic simplification of the molecular spectra can be seen. Compared to the previously observed room-temperature and even liquid-N_2-temperature laser excitation spectra of the organic cations,[16-18] the free jet spectra exhibit very narrow vibronic line widths and are nearly devoid of rotational contours and vibrational sequence congestion.

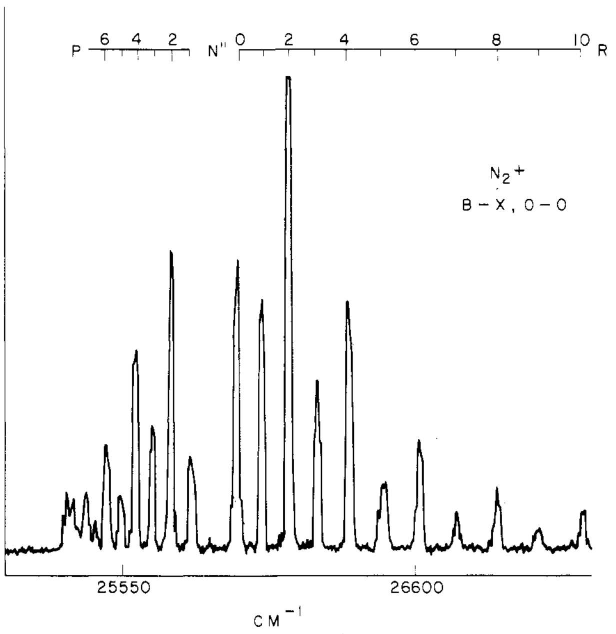

Figure 1. Laser-induced fluorescence spectrum of 0–0, B–X transition of N_2^+. The rotational assignments are as indicated.

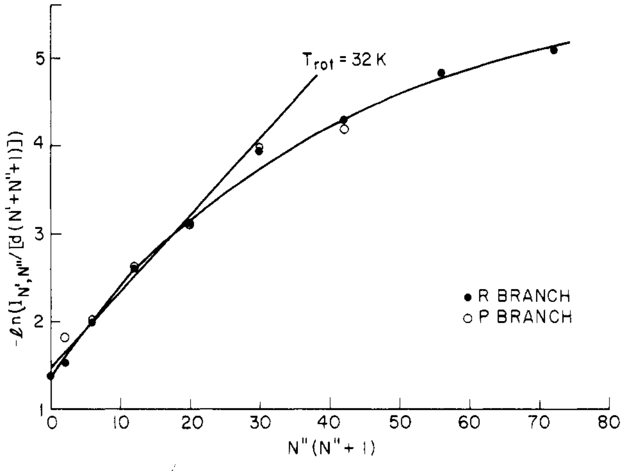

Figure 2. Plot of rotational population vs. rotational quantum number N''. The intensities, $I_{N',N''}$, are obtained from the laser-induced fluorescence spectrum.

Small Cations. Laser-Induced Fluorescence Spectra. Fluorescence excitation spectra of N_2^+ and CO_2^+ have been recorded for free jet expansions of pure N_2, pure CO_2, as well as mixtures of N_2 with Ar at concentrations of 10% N_2/Ar and 1% N_2/Ar. As a result of the recent publication by Johnson et al.[14] of a detailed analysis of the cold spectrum of CO_2^+, further work on CO_2^+ has not been pursued. A representative excitation spectrum of the N_2^+ X state produced by 80-eV electrons intersecting a free jet expansion of 10% N_2/Ar composition is shown in Figure 1. For these experiments, the nozzle was positioned nominally more than 20 nozzle diameters (>1.5 mm) upstream of the center of the electron beam (the electron gun is fixed in position in the chamber), while the laser intersected the jet another 3–5 mm beyond the electron beam.

The relative intensities of the rotational lines in the 0–0 band of the B–X system are quite strong for the lowest few rotational states followed by a weak tail of lines extending to high J values. The spectrum is cold as evidenced by the lack of a significant band head on the

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long-wavelength edge of the P branch.

N_2^+ Rotational Distribution. A rotational temperature can be obtained from the observed relative line intensities by plotting ln $[I_{N'N''}/d(N'+N''+1)]$ vs. $N''(N''+1)$ where N' and N'' are the upper and lower quantum numbers of the transition, respectively,[19] and d is the spin degeneracy. This plot, Figure 2, yields a linear slope only for $N'' \leq 5$. A straight line is indicative of a Boltzmann distribution for the levels. For low N ($\simeq$5) values the distribution can be characterized by a rotational temperature (T_{rot}) of ~30 K. A slight increase in the rotational temperature deduced from the lowest N'' values was observed with decreasing electron energy. For example, $T_{rot}(N_2^+)$ was calculated to be 31.3 K at 80 eV and 37.6 K at 50 eV.

The rotational distribution obtained for the N_2^+ state is very analogous to the distribution observed for the N_2^+ B state through emission studies.[7] The electron-excited fluorescence emission results from N_2^+ ions formed directly in the B state. In the present experiments, with the electron gun operated in a pulsed mode, any N_2^+ formed in the B state (or other excited electronic states) has relaxed to the ground state ($\tau_{rad}(B^2\Sigma_u) = 6.6 \times 10^{-8}$ s)[20] prior to the laser-induced fluorescence probe. Thus, LIF experiments are a sensitive probe of the rotational distribution of N_2^+ ions formed directly in the X state and the N_2^+ ions formed in other electronic states which have cascaded into the ground state. The similar rotational distributions found for the X and B states confirm that rotational excitations from the two processes

$$N_2 + eV\ (80\ eV) \rightarrow N_2^+(B^2\Sigma_u^+) + 2e^-$$

$$N_2 + eV\ (80\ eV) \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$$

are nearly identical within the experimental uncertainity.

The rotational distribution of ions in the ground electronic state can be fitted by a Boltzmann distribution for the first four or five rotational levels *only* with a characteristic temperature of approximately 30 K followed by a long tail extending to higher rotational levels. This is approximately the same rotational temperature obtained for the lowest rotational levels of the N_2^+ B state in the emission studies of DeKoven et al.[7] Rotational distributions for the B state which are characterized by slightly lower rotational temperatures for the first few rotational levels, but probably relatively more population in higher levels, have also been reported.[8,9] Since different jet expansion conditions were used in various experiments, the range of results observed is not surprising. The changes in this distribution as a function of parameters such as electron-impact energy, pressure, etc. have been described for convenience in terms of a changing temperature.[7]

In none of the reported data could the rotational distribution be fitted to a *single* temperature Boltzmann distribution for all rotational levels. In one case, however, the distribution of the B-state rotational levels was fitted to a two-temperature Boltzmann distribution. Although this functional form could characterize the data, the physical significance of the fit is not known. Clearly, though, every experiment to date has demonstrated some overall non-Boltzmann behavior. However, if one's attention is restricted to the lowest five of six N levels, it is often useful, and numerically correct, to describe their populations by a temperature, as we have previously done.[7]

The rotational distribution which characterizes the relative line intensities of the higher N'' states ($N'' > 5$) corresponds to a "warm" rotational temperature. An extensive discussion on the origin and analyses of this distrubution has been previously presented[7] for N_2^+ B-state emission. Some of these sources incude the following: ionization of background gas, nitrogen dimer formation, relaxation of vibrationally and electronically excited species during supersonic expansion, secondary electron excitation, a warm tail on the parent N_2 distribution, collisional interactions of N_2^+ with neutral N_2 or carrier gas, and a collisional interaction of Ar^+ formed by electron impact. (The latter mechanism is not expected to contribute significantly since the electron gun–nozzle separation is large compared to the $C_6F_6^+$ experiment; see below.)

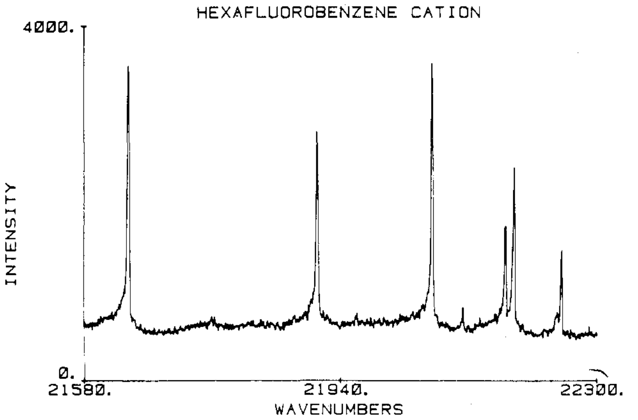

Figure 3. Laser-induced fluorescence spectrum of $C_6F_6^+$, produced by electron impact ionization in the free jet expansion.

Laser-Induced Fluorescence of $C_6F_6^+$. Spectral Features. Laser-induced fluorescence excitation spectra have been observed for hexafluorobenzene cations produced by electron impact ionization of a seeded supersonic jet containing the parent hexafluorobenzene molecule in Ar. Figure 3 shows a sample spectrum generated by this technique at low stagnation pressures ($P_0(Ar) \leq 3$ atm). This spectrum is characterized by vibronic transitions with line widths limited by the 1-cm^{-1} resolution of the dye laser positioned on a flat base line. Hot band transitions originating from vibrationally excited levels of the ground state are completely absent in the spectrum.

The intensity of the origin band grew uniformly with stagnation pressure for $P_0(Ar) \leq 2$ atm. The signal increases at an approximately linear rate with increasing cathode voltage from 40 to 120 eV (collected current was not constant). For electron energies greater than 120 eV, the line intensity increases more slowly as it approaches a limiting value.

The $C_6F_6^+$ origin signal optimized further by decreasing the separation distance between the nozzle and the electron beam along the jet center line. The optimum position occurs when the center of the electron beam is $\lesssim$5 nozzle diameters (~0.75 mm) from the nozzle surface. At this point, the electron current reaching the collector of the electron gun is reduced by ~10% due to electron losses to the nozzle. The relative intensity of the origin signal decreases by approximately 1 order of magnitude as the separation distance is increased by ~10 nozzle diameters from the optimum position. The 0_0^0 signal drops rapidly from electron beam–nozzle separation distances of less than 5 nozzle diameters due to increasing blockage of the electron beam by the nozzle.

As the source pressure is increased ($P_0(Ar) \sim 3.5$ atm), a new weak feature becomes apparent in the spectrum. The new feature has a broad line width (~75 cm^{-1}) centered ~105 cm^{-1} to the red of the origin band. The behavior of this feature at even higher source pressures is

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unknown due to pumping speed limitations. This feature is tentatively assigned as a hexafluorobenzene ion complexed with Ar and is discussed in more detail below.

Mechanism of Organic Ion Production. There are several possible mechanisms for producing $C_6F_6{}^+$ in the free jet expansion. They include (i) direct ionization of C_6F_6 (or a cluster involving C_6F_6) by the electron beam, (ii) Penning ionization via collisions between C_6F_6 and metastable Ar* produced by electron impact, and (iii) charge-transfer reaction through collisions of Ar^+ produced by electron impact with C_6F_6 molecules.

First the likely relative efficiencies of mechanism i and ii will be considered. For direct electron impact ionization,[21]

$$N^{e}{}_{B^+} = n_e{}^0 \sigma_{B^+} \rho_B x \tag{1}$$

where $N^{e}{}_{B^+}$ = number of hexafluorobenzene ions produced per second by electron impact, σ_{B^+} = cross section for ionization of C_6F_6, $n_e{}^0$ = number of electrons intersecting the beam per second, ρ_B = density of hexafluorobenzene neutrals at the point of intersection, and x = path length traversed by the electron beam. For the Penning ionization mechanism, the number of $C_6F_6{}^+$, $N^{P}{}_{B^+}$, generated by collisions with Ar* is given by

$$N^{P}{}_{B^+} = N^{e}{}_{Ar^*} P_{Ar^*\text{-}B} \tag{2}$$

where $N^{e}{}_{Ar^*}$ = number/s of Ar metastables, produced by electron impact and $P_{Ar^*\text{-}B}$ = probability function (0–1) that a given Ar is destroyed before the observation region by an ionizing collision with C_6F_6. $N^{e}{}_{Ar^*}$ is given by an equation identical with that for $N^{e}{}_{B^+}$, except that the density and cross section are now for Ar* production rather than $C_6F_6{}^+$ production.

Therefore, to find the ratio, R, of $C_6F_6{}^+$ produced by Penning ionization to $C_6F_6{}^+$ produced by direct electron impact, the following expression must be evaluated:

$$R = N^{P}{}_{B^+}/N^{e}{}_{B^+} = (\rho_{Ar}/\rho_B)(\sigma_{Ar}{}^*/\sigma_{B^+})P_{Ar^*\text{-}B} \tag{3}$$

Equation 3 depends on the ratio of the Ar and C_6F_6 densities and the relative cross sections for electron impact production of Ar* and $C_6F_6{}^+$. The ratio of the densities (ρ_{Ar}/ρ_B) at any point in the expansion is equal to the ratio of the partial stagnation pressures which for a typical experiment is ~45. Actually this represents a minimum value for this ratio because the partial pressure of C_6F_6 may be lower than its vapor pressure if equilibrium is not reached behind the nozzle.

The ratio of cross sections is somewhat more difficult to estimate. The cross section for production of Ar* is known to vary[22] from 0.35 to 0.06 Å^2 as the electron energy is varied from 22 to 100 eV. While the experimental cathode voltage was near the high end of this range, in an electron gun of this design there are known to be large numbers of electrons with low energies. Hence, the maximum value for the cross section, $\sigma_{Ar^*} \approx 0.35$ Å^2, was assumed.

No information is currently available on the exact cross section for ionization of C_6F_6. However, Kr has a typically large cross section for ionization of 2.5 Å^2 at 100 eV.[23] Then, assuming $\sigma_{B^+} \simeq 2.5$ Å^2, R becomes

$$R = 6.3\ P_{Ar^*\text{-}B}$$

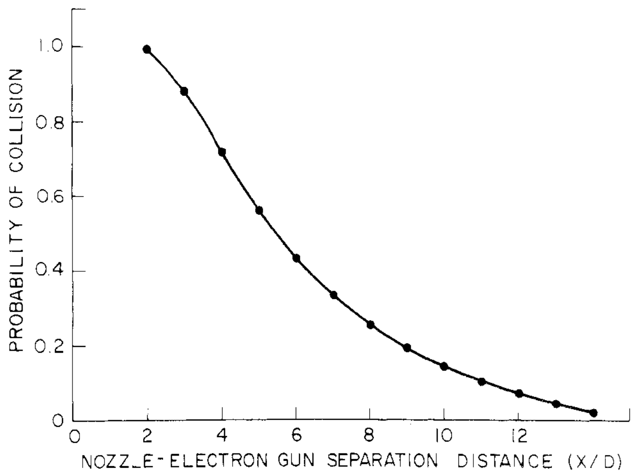

Figure 4. Plot of probability function for Ar* decay due to collisions with C_6F_6.

If $P_{Ar^*\text{-}B}$ is of the order of unity, the production of $C_6F_6{}^+$ by Penning ionization will be more than 6 times more favorable than direct electron impact ionization. Considering the approximations made in the calculation it is probably best to simply note that any value of $P_{Ar^*\text{-}B}$ near unity should ensure that a significant fraction of the $C_6F_6{}^+$ produced is via the Penning mechanism.

Lubman, Rettner, and Zare[24] have done extensive calculations to determine the mean number of collisions with a given cross section that a molecule suffers per second in a free jet expansion as a function of distance along the stream axis at a given backing pressure. From this information the average number of collisions that an Ar* suffers resulting in Penning ionization of a C_6F_6 can be calculated as a function of position downstream of the nozzle, assuming a Langevin type cross section (~100 Å^2) for this process.[25]

The total number of collisions was determined by summing all effective collisions between the electron beam position and the observation point. The probability $P_{Ar^*\text{-}B}$ of an Ar* suffering at least one collision with a C_6F_6 prior to the detection zone can be calculated, assuming a Poisson distribution,[26] from

$$P_{Ar^*\text{-}B} = 1 - e^{-\mu} \tag{4}$$

where μ is the mean number of collisions. The probability $P_{Ar^*\text{-}B}$ is plotted as a function of nozzle–electron gun separation distance in Figure 4. For Ar* production positions less than 5 nozzle diameters downstream $P_{Ar^*\text{-}B} > 0.55$. Hence, the relative production of $C_6F_6{}^+$ via Penning ionization to direct electron impact is

$$R \gtrsim 3.5$$

The collision mechanism appears to be more effective in generating $C_6F_6{}^+$ until the position of Ar* production is on the order of 10 nozzle diameters downstream of the nozzle. The relative efficiencies of production of $C_6F_6{}^+$ by mechanisms i and ii are shown as a function of nozzle–electron gun separation in Figure 5. While some uncertainty exists in the exact value of R, the above calculations

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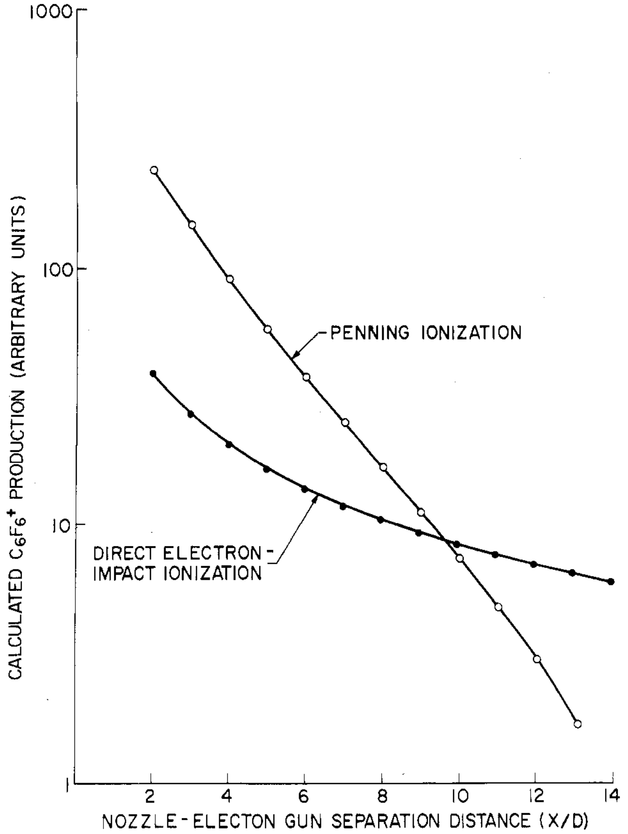

Figure 5. Efficiency of production of $C_6F_6^+$ (arbitrary units) by electron impact and Penning ionization mechanisms as a function of nozzle-electron gun separation distance (x/D).

demonstrate that the production of $C_6F_6^+$ by collisional Penning ionization is at least competitive with production by direct electron impact under some conditions in the jet.

To this point we have not considered mechanism iii, production of $C_6F_6^+$ via charge exchange from Ar^+. This process will be governed by an expression like eq 3 but with Ar* replaced by Ar^+. The cross section for electron impact ionization of Ar is $\sigma_{Ar^+} \approx 2$ Å^2 at 100 eV, which is considerably larger than $\sigma_{Ar^*} \approx 0.35$ Å^2. One can estimate the overall cross section for charge exchange from Ar^+ to $C_6F_6^+$ to be >10 Å^2, i.e., only slightly less than that assumed for the Penning ionization process. On these grounds one might expect that charge exchange would be the most efficiency mechanism for the production $C_6F_6^+$.

However, somewhat further reflection suggests that mechanism iii contributes only insignificantly to the cold $C_6F_6^+$ detected in the LIF experiment. Our reasoning is as follows. In the Penning ionization mechanism, it was implicitly assumed that, if an Ar* collided with a C_6F_6, a resulting cold $C_6F_6^+$ was produced. This is probably valid as consideration of Franck–Condon factors and angular momentum conservation imply that cold ions are likely formed from cold neutrals because the departing electron can ensure energy conservation.

In contrast for a collision of Ar^+ with C_6F_6, the production of a cold $C_6F_6^+$ seems rather unlikely. The ionization potentials of Ar and C_6F_6 are 15.76[28] and 9.9 eV,[29] respectively, while the fragmentation threshold for the latter is 15.3 eV.[30]

Production of C_6F_6 ionic fragments from reaction with Ar^+ is a definitive, and perhaps the most likely, possibility. However, assuming parent $C_6F_6^+$ is produced by charge exchange, some 5.8 eV of energy must be partitioned between internal excitation of $C_6F_6^+$ and translational energy between $C_6F_6^+$ and Ar. Since partitioning of large amounts of energy into translation is usually unfavorable, several electronvolts of energy would likely be deposited into the internal degrees of freedom of $C_6F_6^+$. To produce the cold $C_6F_6^+$ ions observed, this energy must be disposed of into translation and rotation. At energies ≥ 4 eV above the $\tilde{X}$ state, the quantum yield[28] for emission from $C_6F_6^+$ drops to $\leq 1\%$ thus leaving no available route for relaxation of internal energy. Hence, we conclude that the most likely products from Ar^+ charge exchange would be ionic fragments or highly excited $C_6F_6^+$, not the cold $C_6F_6^+$ observed in the LIF experiment.

Identification of Satellite Peak. The Penning mechanism may also provide an explanation for the relative broad and weak satellite peaks seen in the spectrum. These bands are located ~ 105 cm^{-1} to the low-frequency side of the bare ion transitions. This may be contrasted to the satellite lines ascribed[11,32] to Ar clusters ($n \geq 2$) of halobenzene cations. For the case of $C_6F_6^+$ these shifts are of the order of 230 cm^{-1}. Approximately equal shifts would be expected for an aromatic ion as the first two Ar atoms bond above and below the ring, with all subsequent Ar atoms added resulting in much smaller shifts.

The satellite line appears at an appropriate position for a $C_6F_6^+\cdot Ar$ (single Ar) cluster, which has not been previously observed. Such a species could be produced by direct electron impact ionization of $C_6F_6\cdot Ar$. However, if this were the predominate mechanism, $C_6F_6^+\cdot Ar_2$ and higher clusters shifted downward by ~ 230 cm^{-1} should also have been detected. Furthermore, some question exists as to whether a neutral van der Waals aggregate will survive electron impact ionization without fragmentation.

In contrast if Penning ionization collisions are occurring with Ar*, the associative ionization process

$$Ar^* + C_6F_6 \rightarrow C_6F_6^+\cdot Ar + e^-$$

should also occur. This process would likely produce the single, but not higher, ionic clusters. The broadness of the peak could be explained as sequence congestion caused by vibrational excitation in the ionic cluster created in the associative step. Since the electron produced can leave the collision with a near continuum of possible energies, the resultant complex could be formed with a broad distribution of internal energies.

Laser-Induced Fluorescence of Other Organic Cations. As mentioned earlier, several other organic ions have been produced by electron impact and observed in the jet by laser-induced fluorescence. These include other fluorobenzene cations and the $C_4H_2^+$ ion. The $C_4H_2^+$ spectrum is much less congested than those previously obtained at room temperature. This spectrum analyzed in conjunction with spectra taken at liquid-N_2 temperature and in a solid Ne matrix will hopefully unravel the Renner–Teller effect present in this molecule. Such work is now in progress and will be reported at a later date.

The spectrum of $C_6F_5H^+$ closely resembles that just described for $C_6F_6^+$. As is the case with $C_6F_6^+$, the $C_6F_5H^+$ spectrum is very clean, essentially devoid of hot bands, sequence structure, and rotational contours. The spectrum obtained of $C_6F_5H_+$ is particularly valuable since, unlike

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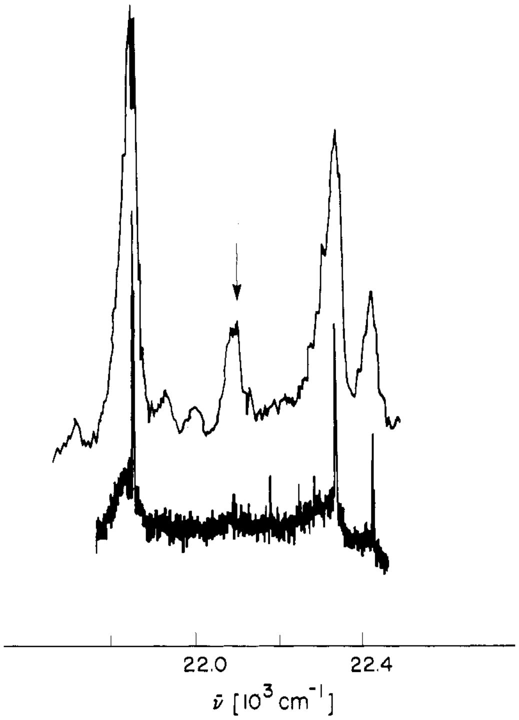

Figure 6. Laser-induced fluorescence spectrum of $C_6F_3H_3^+$. The top trace is a laser excitation spectrum taken with the $C_6F_3H_3^+$ produced in rom temperature by Penning ionization (see ref 44). The lower trace is the excitation spectrum of $C_6F_3H_3^+$ produced by electron impact at very low temperature in the free jet expansion. The arrow indicates the transition whose assignment has been in question.

$C_6F_6^+$, the molecule shows no Jahn–Teller effect. Thus, the spectrum of $C_6F_5H^+$ can serve as a "control" for understanding effects in a Jahn–Teller-active molecule like $C_6F_6^+$.

The remaining halobenzene ion studied is the 1,3,5-$C_6F_3H_3^+$ cation. Its LIF spectrum is shown in Figure 6. The spectrum is quite similar to that of $C_6F_6^+$ in general appearance. There is, however, a hint of sequence structure in the $C_6F_3H_3^+$ spectrum which is effectively absent in both $C_6F_6^+$ and $C_6F_5H^+$. The sequence congestion appears as pedestals at the baseline of each vibronic transition line. These pedestals extend primarily to the red of the transition with a width of ~40 cm^{-1}. The sequence congestion in $C_6F_3H_3^+$ may result from inadequate relaxation of the neutral parent molecule prior to ionization. Vibrational relaxation may proceed more slowly as F's are replaced by H's in the series of molecules from C_6F_6 to benzene, the latter of which is known[33] to relax very slowly in a supersonic expansion. Perhaps $C_6F_3H_3$ may be the first member in this series which exhibits this effect. An alternative explanation for the sequence congestion is that the cation is vibrationally excited in the ionization step due to Franck–Condon considerations.

Nonetheless, the present spectrum of $C_6F_3H_3^+$ is certainly cold enough to provide considerable insight into an old problem concerning the Jahn–Teller effect in $C_6F_3H_3^+$. Above the jet spectrum of $C_6F_3H_3^+$ is shown the room-temperature spectrum of $C_6F_3H_3^+$. There have been two previous interpretations[34,35] of the vibronic structure herein and hence the Jahn–Teller effect in $C_6F_3H_3^+$. In one interpretation[34,36,37] the line marked with an arrow in the room-temperature excitation spectrum is the 14_0^1 transition, i.e., a transition from the vibrationless level of the ground electronic state to the $v = 1$ level of mode 14 of the excited state. In our previous interpretation,[38-41] this transition is 13_1^1, i.e., a transition from the $j = {}^3/_2$, $v = 1$ level of mode 13 in the ground state to $v = 1$ in the excited state. In this latter interpretation, this transition is a hot band which should disappear at low temperature while in the former interpretation the transition will increase slightly as the temperature is lowered. In the former interpretations it was suggested[34] that a hot band may overlap the 14_0^1 transition. Thus, the overall intensity may not increase as the temperature is lowered but clearly the 14_0^1 contribution to the transition must remain, even at 0 K.

As Figure 6 demonstrates, the transition in question is a hot band, essentially being totally absent in the cold jet spectrum. This spectrum is certainly not the only evidence for the correctness of the Jahn–Teller analysis $C_6F_3H^+$ in ref 41 but it is the clearest evidence of the hot band nature of the transition in question. Recently the proponents of the alternative interpretation have analyzed[42] the spectrum of $C_6F_3D_3^+$ in great detail and have altered their position on the Jahn–Teller analysis. Now all are in essential agreement with the Jahn–Teller parameters published for $C_6F_3H_3^+$ in ref 41 and 43.

IV. Conclusions

The present work has demonstrated the possibility of using laser-induced fluorescence detection to study molecular ions, ranging from diatomic to organic, formed by the electron impact ionization in a free jet expansion. For all these ions, simple cold spectra have been obtained. For N_2^+, the rotational distribution in the X state closely resembles that found previously for the B state.

For the larger organic ions, the very clean spectra help greatly the interpretation of the molecular energy levels by narrowing lines and eliminating squence congestion and hot bands. Under certain circumstances production of ions in the jet by the Penning process involving metastable inert gas atoms is competitive with direct ionization by electrons. This suggests that reactive collisions may be studied under the very unique conditions of a free jet expansion.

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Registry No. N_2^+, 13966-04-6; CO_2^+, 12181-61-2; $C_6F_6^+$, 34528-23-9; $C_6F_5H^+$, 34528-24-0; 1,3,5-$C_6F_3H_3^+$, 57164-21-3; $C_4H_2^+$, 55468-55-8.

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