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Fluorescence Excitation Spectroscopy of Ionic Clusters Containing the C $_{6}$F$_{6}^{+}$ Chromophore [and Discussion]

C.-Y. Kung, T. A. Miller, R. A. Kennedy and H.-J. Foth

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Fluorescence excitation spectroscopy of ionic clusters containing the $C_6F_6^+$ chromophore

BY C.-Y. KUNG[1], T. A. MILLER[1] AND R. A. KENNEDY[2]

[1] *The Ohio State University Laser Spectroscopy Facility, Department of Chemistry,*
The Ohio State University, 120 *West* 18*th Avenue, Columbus, Ohio* 43210, *U.S.A.*
[2] *Department of Chemistry, Birmingham University, P.O. Box* 363, *Birmingham B*15 2*TT, U.K.*

Fluorescence excitation spectra of the ion–molecule complexes $C_6F_6^+\cdot X_n$ (X = He, Ne, Ar or N_2) are reported. It is shown that such data can be used to test model potentials for these complexes. For $n = 1$ and X = He and Ne, a simple long-range model of the interaction potential is nearly adequate, but for X = Ar it appears that a substantial charge-transfer component to the interaction is required.

INTRODUCTION

The spectroscopy of ion–molecule clusters potentially offers a very direct probe of the interactions between an ion and one or more neutral species. An understanding of these forces is crucial to the development of models for such fundamental processes as nucleation about ions (e.g. the cloud chamber) and the solvation of ions. Ionic clusters are also known to be involved in the chemistry of the upper atmosphere (Smith & Adams 1980), and play a role in some discharge processes (Kaufman *et al.* 1980).

The success of the spectroscopic approach to the investigation of intermolecular forces is amply demonstrated by the many studies of neutral clusters (Levy 1981; Beswick & Jortner 1981). Although ion–molecule complexes have attracted considerable experimental attention (Märk & Castleman 1985), detailed spectroscopic information concerning them is extremely sparse. Schwarz (1977; 1980) has published low-resolution infrared (IR) spectra of charged H_2O and NH_3 clusters, and Okumura *et al.* (1985, 1986) have observed vibrational predissociation spectra of H_5^+, H_7^+ and H_9^+ and of $H_7O_3^+\cdot H_2$ and $H_9O_4^+\cdot H_2$. DiMauro *et al.* (1984) have reported the red shift of the origin of the $\tilde{B}$–$\tilde{X}$ band of $C_6F_6^+$ on complexation by one or more He, Ne or Ar atoms. This paper describes more recent work on the $C_6F_6^+\cdot X_n$ system in which vibrational structure associated with the motion of the neutral relative to the ion has been observed. These experimental observations are being supported by the development of theoretical methods for the calculation of the vibrational levels of these complexes from model potentials. It will be shown how the combination of the experimental observations and the theoretical calculations is leading to the spectroscopic determination of potentials for these complexes. A preliminary report of work on $C_6F_6^+\cdot$He has been published (Kennedy & Miller 1986).

EXPERIMENTAL METHODS

The intermolecular bonds in neutral and ionic clusters are relatively weak. To obtain adequate quantities of these species for their spectroscopic characterization, it is necessary to work in an environment in which there are few collisions that may break up the clusters after their formation. For neutral clusters the unique properties of supersonic expansions have proved to be ideal (Levy 1981). Precursor molecules of interest are seeded into an inert carrier gas and the mixture expanded through a small orifice. The clusters are formed in the high-pressure region of the expansion close to the nozzle in three-body collisions. Further downstream in the expansion there are very few collisions, and the collision energies are extremely low, being characterized by translational temperatures of only a few kelvin. Once formed, the clusters will not be destroyed until they encounter the background gas in the chamber at a shock front, or the walls of the chamber.

The formation of ion–molecule clusters by this approach is complicated by the fact that molecular ions are highly reactive species. Ions seeded into the carrier gas before the expansion will be destroyed both by ion–molecule reactions and by neutralization on the walls of the metal nozzle before they pass through the expansion orifice. The ions must instead be formed within the supersonic expansion, and neutral species attached in subsequent collisions.

$C_6F_6^+$ was chosen as the ion for these experiments for a number of reasons.

1. The ion is cleanly formed from the neutral by nonresonant photoionization with two photons from an excimer laser operating on the ArF (193 nm, $2h\nu = 104000\ \text{cm}^{-1} = 12.8\ \text{eV}$) transition. The ionization potential of $C_6F_6^+$ is about 9.9 eV.

2. C_6F_6 is easily entrained in the expansion by passing the carrier gas, helium of HP grade (+Ne, Ar, N_2 ..., if desired) over the liquid held in a temperature-controlled bath at or below room temperature.

3. C_6F_6 is an excellent chromophore for the observation of fluorescence excitation spectra. The $\tilde{B}$–$\tilde{X}$ system of the bare ion is very strong, has a fluorescence quantum yield of unity, and is easily accessible in the blue region of the spectrum ($\tilde{\nu}_0 = 21616\ \text{cm}^{-1}$).

Details of the experimental method have been given elsewhere (Di Mauro *et al.* 1984). The formation of ionic clusters depends critically on the point at which photoionization occurs. From the results of experiments in which the number of ionic clusters present in the expansion was monitored as a function of the distance from the tip of the nozzle to the excimer laser crossing point, it appears that a number of steps are involved in the formation of an ion cluster.

1. Formation of a neutral cluster, which occurs very close to the nozzle (within 10 nozzle diameters).

2. Photolysis of the neutral cluster to leave a bare ion. Fragmentation of the neutral cluster during photolysis disposes of the excess energy deposited in the organic molecule, thereby lessening fragmentation of the parent molecule during or after photoionization.

3. Attachment of one or more neutral species to the bare ion in three-body collisions. Note that direct photoionization of a neutral cluster to form an ionic cluster does not appear to be a significant process. The optimum nozzle–excimer distance was found to be about 10 nozzle diameters (*ca.* 1.5 mm). Moving the nozzle closer to the excimer leads to the appearance of a variety of photolysis fragmentation products including C_2, whereas pulling the nozzle away does not allow the bare ions to undergo three body collisions to form clusters. The distance of 10 nozzle diameters applies for a helium reservoir pressure of *ca.* 15 atm†. This was found to be the optimum pressure for forming small ionic clusters such as $C_6F_6^+\cdot He$. Higher pressures cause more collisions to occur after the bare ion is formed, leading to the formation of larger clusters (Di Mauro *et al.* 1984).

The best approach to generating $C_6F_6^+\cdot X$ (e.g. X = Ne, Ar, N_2) is first to produce good

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† 1 atm ≈ 10^5 Pa.

spectra of $C_6F_6^+\cdot He$, and then add a small amount (at most a few percent, by mass) of the species, X, to be attached to $C_6F_6^+$ to the carrier gas. The formation of $C_6F_6^+\cdot X$ may well proceed by displacement of the He atom

$$C_6F_6^+\cdot He + X \rightarrow C_6F_6^+\cdot X + He.$$

Addition of larger quantities of X (especially Ar and N_2) leads to the formation of larger clusters $C_6F_6^+\cdot X_n$, and also quenches the generation of $C_6F_6^+$ by excimer laser photoionization.

SPECTROSCOPY AND THEORY OF $C_6F_6^+\cdot He$

The original spectroscopic investigations of the ion–atom complex $C_6F_6^+\cdot He$ were restricted to the determination of the red shift (*ca.* 38 cm^{-1}) of the origin of the $\tilde{B} \leftarrow \tilde{X}$ system on attaching a helium atom (Di Mauro *et al.* 1984). The data on this ion have now been greatly extended through the observation of a vibrational progression in the modes corresponding to the motion of the He atom with respect to the chromophore ion (Kennedy & Miller 1986). The analysis of this progression is leading to the determination of a model potential for this ionic cluster. This experiment is believed to be the first to so-directly probe the potential surface of an ionic cluster.

The experimental observations of Kennedy & Miller provide the location of four excited vibrational levels of $C_6F_6^+(\tilde{B})\cdot He$. This information can be used to test and refine model potentials for the complex. Jortner *et al.* (1983) have proposed a potential for systems of this type, consisting of a sum of pairwise Lennard–Jones 12–6 interactions for the helium atom with the carbon and fluorine atoms

$$V_{LJ}(\boldsymbol{r}_{He}) = \sum_i A_i \left\{ \frac{-1}{r_{iHe}^6} + \frac{\frac{1}{2}(r_{iHe}^0)^6}{r_{iHe}^{12}} \right\}, \tag{1}$$

where

$$r_{iHe} = |\boldsymbol{r}_i - \boldsymbol{r}_{He}|, \tag{2}$$

and a charge-induced dipole term describing the interaction of the distribution of the net positive charge on the $C_6F_6^+$ ion with the polarizability of the helium atom

$$V_{cid}(\boldsymbol{r}_{He}) = -\tfrac{1}{2}\alpha_{He} e^2 |\boldsymbol{F}(\boldsymbol{r}_{He})|^2, \tag{3}$$

where

$$F_\xi = \sum_i \frac{(e_i/e)}{r_{iHe}^3}(\xi_i - \xi_{He}); \quad \xi = x, y, z. \tag{4}$$

The total potential

$$V_{tot}(\boldsymbol{r}_{He}) = V_{LJ}(\boldsymbol{r}_{He}) + V_{cid}(\boldsymbol{r}_{He}) \tag{5}$$

$$= V(x, y, z) \tag{6}$$

is a function of three spatial variables that were chosen as z, the height of the helium atom above the ring, and the orthogonal displacements (x, y) of the atom from the C_6 axis through the centre of the ring. The x-axis is chosen to lie 15° from the direction of a C–F bond, so that the potential cuts $V(x, 0, z)$ and $V(0, y, z)$ are identical.

If the $C_6F_6^+$ ring is assumed to be infinitely massive compared to the helium atom, the hamiltonian describing the motion of the atom relative to the fixed ring may be written as

$$H = \frac{-\hbar^2}{2m_{He}}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) + V(x, y, z). \tag{7}$$

The assumption is also made that the $C_6F_6^+$ chromophore may be treated as a rigid body. This assumption is supported by the observation that the cluster spectra associated with different vibrational levels of $C_6F_6^+(\tilde{B})$ are identical.

Plots of the total potential, $V(x,y,z)$, with reasonable values for the various parameters show two interesting features (see figure 1). First, the minimum is located above the centre of the ring, and secondly, the minimum energy path for moving the helium atom away from the C_6 axis keeps the height of the atom above the ring approximately fixed at the equilibrium value for quite substantial displacements. The hamiltonian (7) may usefully be expressed as the sum

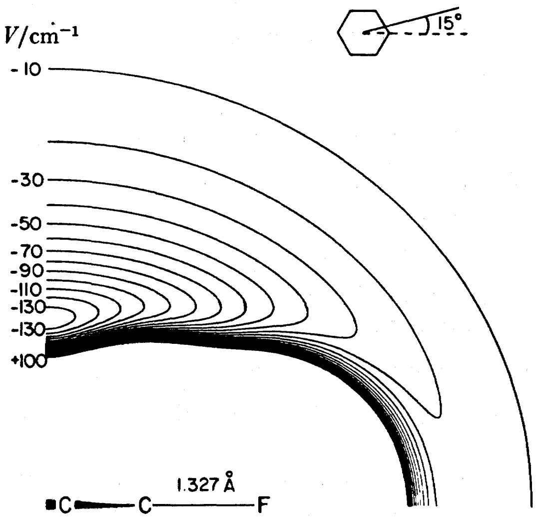

FIGURE 1. Contour plot of the $V(x,0,z)$ cut of the potential for $C_6F_6^+\cdot He$ described in the text. The minimum is located 2.43 Å above the plane of the $C_6F_6^+$ ring. Contours are plotted every 10 $\mathrm{cm^{-1}}$.

$$H = H_s(z)+H_b(x)+H_b(y)+\Delta V(x,y,z), \tag{8}$$

where the 'stretching' hamiltonian is

$$H_s(z) = \frac{\hbar^2}{2m_{\mathrm{He}}}\frac{\mathrm{d}^2}{\mathrm{d}z^2}+V_s(z),\ V_s(z) = V(0,0,z) \tag{9}$$

and the 'bending' hamiltonian is

$$H_b(x) = \frac{\hbar^2}{2m_{\mathrm{He}}}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V_b(x),\ V_b(x) = V(x,0,z_m), \tag{10}$$

(z_m is such that $(\mathrm{d}V_s/\mathrm{d}z)_{z=z_m} = 0$, i.e. z_m is the height of the atom above the ring at the minimum of the stretching potential), $H_b(y)$ is similar to $H_b(x)$, and

$$\Delta V(x,y,z) = V(x,y,z)-V_s(z)-V_b(d), \tag{11}$$

where $|d| = (x^2+y^2)^{\frac{1}{2}}$. The determination of the vibrational energy levels for the model potential $V(x,y,z)$ now breaks down into three stages.

(*a*) Calculation of the zeroth-order stretching and bending vibrational energy levels and wavefunctions by numerically solving the separated Schrödinger equations for the vibrational coordinates z and x (or y)

$$\left[\frac{-\hbar^2}{2m_{\mathrm{He}}}\frac{\mathrm{d}^2}{\mathrm{d}z^2}+V_{\mathrm{s}}(z)\right]X_{\mathrm{s}}(z) = E_{\mathrm{s}}X_{\mathrm{s}}(z) \tag{12}$$

and

$$\left[\frac{-\hbar^2}{2m_{\mathrm{He}}}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V_{\mathrm{b}}(x)\right]X_{\mathrm{b}}(x) = E_{\mathrm{b}}X_{\mathrm{b}}(x). \tag{13}$$

These equations were solved by using the Numerov–Cooley algorithm (Cooley 1961).

(*b*) Evaluation of the first-order corrections, E', to the combined stretching and bending energy levels from the difference potential perturbation, ΔV,

$$E' = \langle sb_1 b_2 |\Delta V| sb_1 b_2\rangle, \tag{14}$$

where

$$(sb_1 b_2) = X_{\mathrm{s}}(z)\, X_{b_1}(x)\, X_{b_2}(y). \tag{15}$$

The required matrix elements were evaluated by three-dimensional numerical quadrature with Gauss–Legendre weights and abscissae; up to 192 × 192 × 192 points were employed to ensure convergence.

(*c*) Evaluation of the off-diagonal matrix elements of ΔV:

$$\Delta V^{mn} = \langle s^m b_1^m b_2^m |\Delta V| s^n b_1^n b_2^n\rangle \tag{16}$$

followed by the construction and diagonalization of the numerically generated hamiltonian matrix. The matrix elements were again computed by three-dimensional Gauss–Legendre quadrature. Symmetry considerations show that off-diagonal matrix elements with Δb_1 and/or Δb_2 odd must be zero. For levels that are doubly degenerate through first order, $(sb_1 b_2)$, $(sb_2 b_1)$, $b_1 \neq b_2$, symmetric and antisymmetric combinations can be formed

$$\sqrt{\tfrac{1}{2}}[(sb_1 b_2)+(sb_2 b_1)] \text{ and } \sqrt{\tfrac{1}{2}}[(sb_1 b_2)-(sb_2 b_1)].$$

The transition observed in the fluorescence excitation spectrum from the vibrationless level of the ground state must be to totally symmetric vibrational levels of the excited state. These levels are constructed from the singly degenerate basis functions $(s00)$ and $(s2b_1 2b_1)$, together with the symmetric combination of the stretch-bend functions with both b_1 and b_2 even, i.e. $\sqrt{\tfrac{1}{2}}[(s\,2b_1\,2b_2)+(s\,2b_2\,2b_1)]$. The hamiltonian matrix for these levels is set up, including basis functions up to a fixed energy above (000), and diagonalized.

The energies obtained at the different stages in the calculation are reported in table 1, together with the experimental results for comparison. The parameters used in generating the model potential were obtained from various sources. The geometry of $C_6F_6^+(\tilde{B})$ was assumed to be the same as for the ground state of neutral $C_6F_6^+$, $r_{\mathrm{CC}} = 1.394$ Å†, determined by electron

Table 1. Results of theoretical calculations on the vibrational energy levels of $C_6F_6^+\cdot He$

level $(sb_1 b_2)$	zeroth-order energy/cm^{-1}	first-order energy/cm^{-1}	energy from diagonalization/cm^{-1}	experimental/cm^{-1}
(000)	0.0	0.0	0.0	0.0
(100)	48.5	45.3	47.7	41.5
(020) + (002)	43.6	44.0	33.8	48.4
(040) + (004)	67.0	66.5	57.4	66.4
(200)	77.9	70.8	72.3	75.3

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† 1 Å = 10^{-10} m = 10^{-1} nm.

diffraction (Almenningen *et al.* 1964). The polarizability of the He atom is $\alpha_{\mathrm{He}} = 0.204\,956 \times 10^{-24}\ \mathrm{cm}^3$ (Miller & Bederson 1977). The Lennard–Jones parameters for C–He and F–He were extrapolated from those used for previous model calculations on aromatic – rare-gas systems (Ondrechen *et al.* 1981), $A_{\mathrm{C}} = 4000\ \mathrm{cm}^{-1}$, $r^0_{\mathrm{CHe}} = 3.3$ Å, $A_{\mathrm{F}} = 3800\ \mathrm{cm}^{-1}$, $r^0_{\mathrm{FHe}} = 3.2$ Å. The net positive charge on the $C_6F_6^+$ ion was distributed according to the scheme proposed by Jortner *et al.* (1983); $e_{\mathrm{C}}/e = \frac{1}{6}$, $e_{\mathrm{F}}/e = 0$. Basis functions up to $120\ \mathrm{cm}^{-1}$ above the (000) level were included in the construction of the full hamiltonian matrix.

The comparison of the calculations with the experimental results is quite appealing. The most obvious discrepancy is that the bending level (002) + (020) is predicted to lie below the stretching level (100), whereas the experimental results suggested the reverse order. Attempts at reversing the order predicted by theory through variations in the four Lennard–Jones parameters have so far proved to be unsuccessful. A relatively small shift of the zeroth-order levels is required; once (100) is below (002) + (020) the substantial Fermi resonance between these levels will push (002) + (020) up still further. The calculations did reveal the anticipated Fermi resonance between the pairs of levels, (100) with (002) + (020) and (200) with (004) + (040), through which transitions to the bending levels borrow intensity from the allowed stretching progression. Inspection of the eigenvector coefficients obtained by diagonalization of the hamiltonian matrix showed that there was also substantial mixing of (002) + (020) with (102) + (120) and of (004) + (040) with (104) + (140). It is believed that these mixings reflect the fact that there is a tendency for the height of the He atom above the ring to decrease as it moves away from the centre (see the contour plot of the potential in figure 1). In the limit, the He atom may orbit the ion, making the method used in these calculations inadequate.

The minimum of the model potential described in the text above is located 2.43 Å above the plane of the ring; the equilibrium-well depth is $136\ \mathrm{cm}^{-1}$. The energies of the vibrational levels that we have observed amount to a very substantial fraction of the well depth, and the potential surface is extensively sampled. The red shift of the cluster origin leads to the conclusion that the well depth for $C_6F_6^+(\tilde{X})\cdot He$ is about $38\ \mathrm{cm}^{-1}$ shallower than for $C_6F_6^+(\tilde{B})\cdot He$, indicating a well depth of *ca.* $100\ \mathrm{cm}^{-1}$ for $C_6F_6^+(\tilde{X})\cdot He$.

SPECTROSCOPY OF $C_6F_6^+\cdot Ne$, $C_6F_6^+\cdot Ar$ AND $C_6F_6^+\cdot N_2$

In addition to $C_6F_6^+\cdot He$, a number of other ion–atoms and ion–molecule complexes containing the $C_6F_6^+$ chromophore have been investigated.

Figure 2 shows the spectrum of $C_6F_6^+\cdot Ne$ around the origin of the bare ion, and for comparison the same region for $C_6F_6^+\cdot He$. The pattern of lines for $C_6F_6^+\cdot Ne$ is very similar to that for $C_6F_6^+\cdot He$. It is possible that there is a transition of $C_6F_6^+\cdot Ne$ concealed beneath the origin of bare $C_6F_6^+$. Table 2 tabulates the results for $C_6F_6^+\cdot Ne$ obtained experimentally, and also gives the results of a preliminary calculation of the vibrational energy levels (parameters $A_{\mathrm{C}} = 11\,100\ \mathrm{cm}^{-1}$, $r^0_{\mathrm{C}} = 3.49$ Å, $A_{\mathrm{F}} = 5000\ \mathrm{cm}^{-1}$, $r^0_{\mathrm{F}} = 3.20$ Å, $\alpha_{\mathrm{Ne}} = 0.395 \times 10^{-24}\ \mathrm{cm}^3$). This potential gives a well depth of *ca.* $210\ \mathrm{cm}^{-1}$, with the Ne atom 2.66 Å above the ring. The match between experiment and theory is again appealing, suggesting that the model potential constructed from considerations of the purely physical interactions within the complex provides a useful description of the system.

A long progression of sharp transitions due to $C_6F_6^+\cdot Ar$ can be recorded by adding *ca.* 1% Ar to the He carrier gas (see figure 3). The preliminary conclusions from the spectra

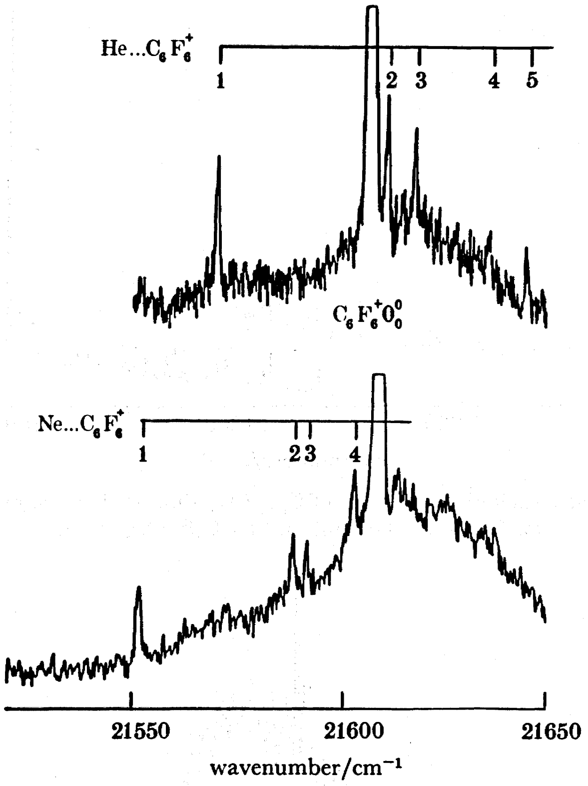

FIGURE 2. Fluorescence excitation spectra of $C_6F_6^+\cdot He$ and $C_6F_6^+\cdot Ne$ associated with the origin transition of $C_6F_6^+$.

TABLE 2. $C_6F_6^+\cdot Ne$ EXPERIMENTAL OBSERVATIONS AND PRELIMINARY RESULTS OF THEORETICAL CALCULATIONS

identification	shift relative to bare-ion origin/cm^{-1}	shift relative to cluster origin/cm^{-1}	theory	vibrational energy level
1	−57.4	0.0	0.0	(000)
2	−20.6	36.8	34.0	(100)
3	−17.4	40.0	26.39	(020)
4	−6.5	50.9	48.79	(040)
			63.42	(200)

of $C_6F_6^+\cdot Ar$ are that the dramatic increase in the red shift on going from He (37.5 cm^{-1}) or Ne (57.4 cm^{-1}) to Ar (420 cm^{-1}), and the observed increase in the stretching vibrational spacing to *ca.* 66 cm^{-1} indicate that the binding between an Ar atom and $C_6F_6^+$ ($\tilde{B}$) is much stronger than for the lighter rare gases. Model calculations of the type developed for $C_6F_6^+\cdot He$ support this conclusion, with reasonable values for the Lennard–Jones parameters and the known polarizability of the Ar atom (Miller & Bederson 1977), the stretching frequency is grossly underestimated (calculated 44 cm^{-1}). The increased strength of the attractive interactions between Ar and $C_6F_6^+$ ($\tilde{B}$), compared to the essentially physical binding of the lighter rare gases to this ion, arises from the development of some charge-transfer bonding in the $C_6F_6^+\cdot Ar$ complex, which is facilitated by the lower ionization potential of Ar relative to He and Ne.

Experiments have also been conducted to try to attach molecules, rather than atoms, to

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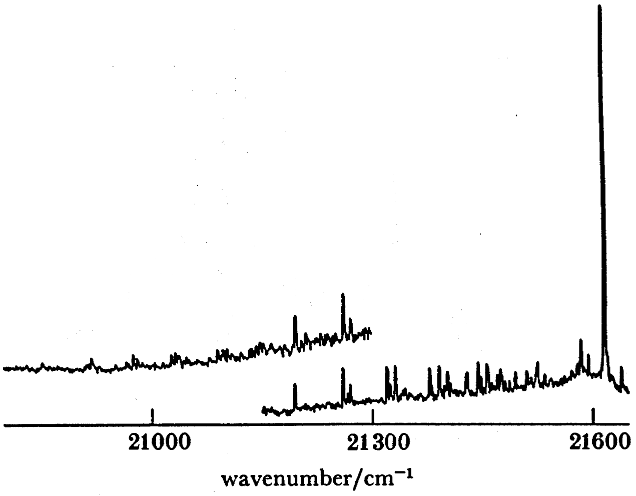

FIGURE 3. Fluorescence excitation spectrum of $C_6F_6^+\cdot Ar_n$ showing long vibrational progressions for $C_6F_6^+\cdot Ar$, (bottom) and for $C_6F_6^+\cdot Ar_2$ (top).

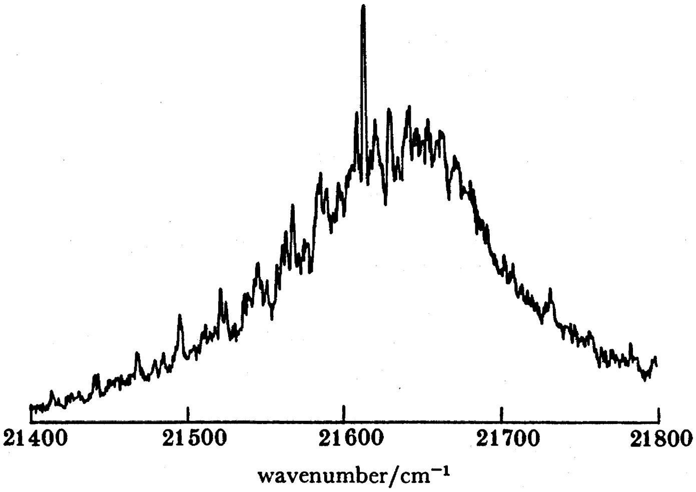

FIGURE 4. Fluorescence excitation spectrum observed close to the origin of $C_6F_6^+$ with a He carrier gas containing *ca.* 2% N_2 (by volume).

$C_6F_6^+$. By using a He carrier gas containing a small amount of N_2 the spectrum shown in figure 4 was obtained. The series of lines starting 200 cm^{-1} to the red of $C_6F_6^+(^0_0)$ is tentatively attributed to $C_6F_6^+\cdot N_2$. The same series of lines can be discerned associated with the 18^1_0 and 17^1_0 transitions of $C_6F_6^+$. As can be seen from the figure, this complex shows a rather more complicated pattern of vibrational structure than seen for the $C_6F_6^+\cdot X$ (X = He, Ne or Ar) clusters. The additional complexity presumably arises from hindered motions of the N_2 within the cluster. The possibility that some of the features are caused by higher clusters $C_6F_6^+\cdot(N_2)_n$ has not been definitely eliminated. One curious feature of this spectrum, when compared to the $C_6F_6^+$–rare-gas clusters, is that the intensity of the cluster vibrational transitions at first shows a considerable, steady increase as the vibrational energy in the cluster modes is raised. This suggests that there is a considerable change in the equilibrium distance of the N_2 from the $C_6F_6^+$ and/or in the equilibrium geometry of the cluster when the $C_6F_6^+$ unit is electronically excited.

The generation of a model potential for the $C_6F_6^+ \cdot N_2$ system must take account of the anisotropy of the polarizability of N_2 and its quadrupole moment, in addition to the terms already described for $C_6F_6^+ \cdot He$. A suitable potential form has not yet been established. The investigation of the vibrational dynamics of the N_2 molecule relative to the $C_6F_6^+$ ion are also more involved than for $C_6F_6^+ \cdot He$. Two new degrees of freedom, hindered rotations of the N_2 unit within the complex, have been added to the problem. The N–N vibration is considered to be of too high a frequency to significantly influence the cluster modes.

CONCLUSIONS

The detailed characterization of the forces between molecules is best accomplished through the spectroscopy of clusters held together by these forces. From the vibrational structure in the fluorescence excitation spectra of $C_6F_6^+ \cdot X$ ion–molecule complexes, it is possible to obtain a substantial amount of data relevant to the ion–molecule forces between a $C_6F_6^+$ ion and a neutral X. These data may be used to test model potentials for these systems. For X = He or Ne, it appears that the results may be adequately accounted for by a purely physical description of the interactions between the ion and the atom. For X = Ar, there is compelling evidence for a substantial charge-transfer component to the binding.

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Discussion

H.-J. FOTH (*University of Kaiserlauten, F.R.G.*). Professor Miller described the low temperature obtained in the adiabatic expansion of the supersonic molecular beam. What can be said about the temperature of the ions? Is photoionization a soft ionization, or are the ionic species heated?

T. A. Miller. It is hard to make a statement that is true for all ions. However, generally speaking, the internal temperature of the ion will approach the translational temperature of the expansion. The example of the CO^+ that was discussed, is typical; its LIF spectrum is indicative of a rotational temperature of a few kelvin.

Conservation of angular momentum requires that there be little difference in the J-states of the precursor and its ion (assuming no fragmentation). Often, the potential function of an ion is sufficiently similar to its parent neutral, that Frank–Cordon considerations dictate little or no change in the vibrational quantum numbers. Therefore, assuming a 'cold' precursor molecule, the ion is also likely to be 'cold'.