Zero Kinetic Energy (ZEKE) Photoelectron Study of Fluorobenzene−Argon van der Waals Complexes

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Received: February 25, 1997; In Final Form: May 15, 1997⊗

Two kinds of van der Waals (vdW) complexes of fluorobenzene (FB) with argon, FB−Ar and FB−Ar_2, produced in supersonic jets were studied by mass-selected ion-current spectra and zero kinetic energy (ZEKE) photoelectron spectra by using two-photon resonant ionization through the first singlet electronic excited states (S_1). The results obtained from the ZEKE photoelectron spectra may be summarized as follows. (1) The adiabatic ionization energies have been determined as I_a(FB) = 74 238 ± 4 cm^{-1} (9.2043 ± 0.0005 eV), I_a (FB−Ar) = 74 011 ± 4 cm^{-1} (9.1762 ± 0.0005 eV), and I_a (FB−Ar_2) = 73 816 ± 4 cm^{-1} (9.1521 ± 0.0005 eV). (2) The decreases in I_a have been found to be 227 and 422 cm^{-1} for FB−Ar and FB−Ar_2, respectively, this fact indicating that the increases in the dissociation energy upon photoionization are 227 and 422 cm^{-1}, respectively. (3) Well-resolved vibrational progressions with frequencies of 12 and 9 cm^{-1} have been observed for the vdW cations $(FB-Ar)^+$ and $(FB-Ar_2)^+$, respectively, and assigned to the vdW bending vibrations b_x^{+1} and b_{xs}^{+1}, respectively, along the *x* axis (the C−F bond), by selecting some appropriate S_1 vdW vibrational levels as intermediate resonant states. (4) Two more bands appearing at 31 and 50 cm^{-1} above the origin for $(FB-Ar)^+$ may be assigned to the vdW bending (b_y^{+2}) and the vdW stretching (s_z^{+1}), respectively. (5) From Franck−Condon calculations, it has been found that Ar is shifted by 7° and 6° for $(FB-Ar)^+$ and $(FB-Ar_2)^+$, respectively, with respect to their neutral S_1 states.

1. Introduction

One of the important advantages in the laser photoelectron spectroscopy of resonantly enhanced multiphoton ionization (REMPI) with a pulsed UV laser is that ‘cation spectroscopy’ can be carried out by means of a photoelectron spectroscopic technique based on state-selected photoionization for various neutral molecular species.[1] This technique is especially efficient for studying very weakly bounded van der Waals (vdW) complexes formed in supersonic jets, since a specific vdW species can be selected out from a mixture of various analogous species, as was earlier demonstrated for the vdW complex of NO with Ar.[2]

A technique of measuring zero kinetic energy (ZEKE) photoelectrons as a function of laser wavelength in two-color REMPI experiments is powerful for carrying out high-resolution cation spectroscopy for various vdW complexes,[3] as earlier indicated from several ZEKE studies by Chewter *et al.*,[4] Takahashi *et al.*,[5,6] and Zhang *et al.*[7] It is interesting to study vdW complexes, because of their low binding energies, large equilibrium distances, and low-frequency vibrational modes. Concerning these subjects, three review papers have recently been published by Müller-Dethlefs *et al.*,[8] by Hobza *et al.*,[9] and by Neusser and Krause.[10]

In this laboratory, we have earlier developed a very compact high-brightness cm^{-1}-resolution ZEKE photoelectron analyzer with a short flight distance[11] and recently further improved it by introducing a two-pulsed field technique.[12] Very recently we have found large differences in adiabatic ionization potentials and vdW vibrational progressions upon the complex formation for the vdW complexes of benzonitrile with Ar and Ar_2, where benzonitrile is a typical monosubstituted benzene with an electron-accepting group.[13] Similar ZEKE photoelectron studies have been earlier reported for the vdW complexes of aniline with Ar and Ar_2,[6,7] where aniline is a typical monosubstituted benzene with an electron-donating group.

Fluorobenzene (FB) studied in the present work is another typical monosubstituted benzene containing a fluorine atom with the strongest electron affinity. Very recently, fluorobenzene and its vdW complex with argon (FB−Ar) have been studied by Grebner and Neusser[14] and by Lembach and Brutschy[15] with mass-analyzed threshold ion (MATI) spectroscopy. In the present paper we want to report a ZEKE photoelectron study of a series of FB, FB−Ar, and FB−Ar_2. So far no ZEKE study has been reported on FB−Ar_2.

Concerning the vdW complexes FB−Ar and FB−Ar_2, the following studies have been published. In a REMPI study through the S_1 state, Gonohe *et al.*[16] have obtained two-color (1 + 1′) ion-yield curves to find their adiabatic ionization potentials for these vdW complexes. From a REMPI study, Bieske *et al.*[17,18] have successfully observed a total of three vdW vibrational frequencies for FB−Ar in the S_1 state. From a study of rotational spectra with a molecular beam microwave Fourier transform spectrometer in the region 7−18 GHz, Stahl and Grabow[19] have determined the rotational constants of FB−Ar in the neutral ground state, indicating that Ar is located 3.553 Å above the center of mass of FB and shifted by 0.460 Å in the direction opposite to the fluorine atom along the C−F axis. Furthermore, from a study of *ab initio* structural calculations on FB−Ar in the neutral ground state, Hobza *et al.*[20] have obtained theoretical results consistent with those obtained experimentally, indicating that Ar is not localized directly above the center of the mass but is shifted between 0.33 and 0.43 Å in the direction opposite to the fluorine atom.

2. Experimental Section

The apparatus used in the present work is essentially the same as that described previously.[12,13] Briefly, it consists of a main vacuum chamber, a sample inlet system for producing a

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)00698-1 CCC: $14.00

supersonic free jet, a system for detecting cations and ZEKE electrons, and a data acquisition system. The supersonic free jet was produced by a pulsed valve (General Valve, P/N 9-279-900) with an orifice diameter of 0.8 mm. The pulsed nozzle was driven by a valve driver (General Valve, IOTA-1) and synchronized with each laser shot (10 Hz) by a delay pulse generator (Princeton Applied Research, Model 9650). The background pressure in the chamber during experiments was $(6-9) \times 10^{-6}$ Torr.

Two dye lasers (Quanta-Ray, PDL-3) pumped by a nanosecond Nd:YAG laser (Quanta-Ray, GCR-190) were used for two-color experiments. The outputs of the dye lasers were frequency-doubled by BBO and KD*P crystals, using Coumarin 500 for the first laser ($\omega_1 = 261-265$ nm), and Rhodamine 575 for the second laser ($\omega_2 = 272-278$ nm). The counter-propagating laser beams intersected the pulsed jet at a right angle. The wavelength calibration was carried out with a UV wavemeter (Burleigh Instruments, WA-5500).

Prior to ZEKE photoelectron measurements, mass-selected ion-current spectra of one-color (1+1) REMPI were measured to obtain spectroscopic information about the S_1 origins, as well as several low-frequency vibrational levels for fluorobenzene (FB) and its vdW complexes with argon (FB−Ar and FB−Ar_2), using a time-of-flight mass analyzer of the Wiley−McLaren type[21] with a field-free drift tube of 20 cm in length.

Measurements of ZEKE photoelectrons were carried out by two-color (1+1′) resonant ionization combined with two-pulsed-field ionization (2PFI).[12] In the first step, a positive discrimination pulsed field ($F_1 = +0.7$ V/cm, 200 ns duration) was applied at 50 ns after each laser shot to remove all the electrons ejected by two-photon direct ionization and fast autoionization. This discrimination pulse also field ionizes upper Rydberg states. In the second step, a negative collecting pulsed field ($F_2 = -1.0$ V/cm, 700 ns duration) was applied shortly after the first pulse to field ionize deeper Rydberg states. The electron signal detected by an electron multiplier (Murata, Ceratron) was averaged by a boxcar integrator (Stanford Research Systems, SR 250), and then transferred to the data acquisition system equipped with a personal computer (NEC PC-9821). The observed ionization energies were corrected for the pulsed electric field by extrapolating the plots of the two-color energies producing the ZEKE origin peaks against several different pulsed electric fields. The slope of the plots was found to be −4.08, indicating that the correction is $4.08(F)^{1/2}$, where F is the field strength.

Fluorobenzene vapor mixed with argon (2.0−3.0 atm.) at room temperature was expanded into the vacuum chamber through a pulsed nozzle to produce its vdW complexes with argon in supersonic free jets. Fluorobenzene (Nacalai Tesque, Extra Pure Grade) was used without further purification.

3. Results and Discussion

3.1. Mass-Selected MPI Spectra and S_1 Origins. One-color (1+1) MPI spectra were obtained for the series of FB, FB−Ar, and FB−Ar_2 to confirm their S_1 origins and low-frequency vibrational bands. The observed origin bands (S_1 0^0) are shown in the inset in Figure 1, appearing at 37 818, 37 794, and 37 771 cm^{-1}, respectively (within ±2 cm^{-1}). The shifts in the S_1 origin from bare FB are −24 and −47 cm^{-1} for FB−Ar and FB−Ar_2, respectively. All these values of the S_1 origins are summarized in Table 1. together with literature values for comparison.[14−17,22−25]

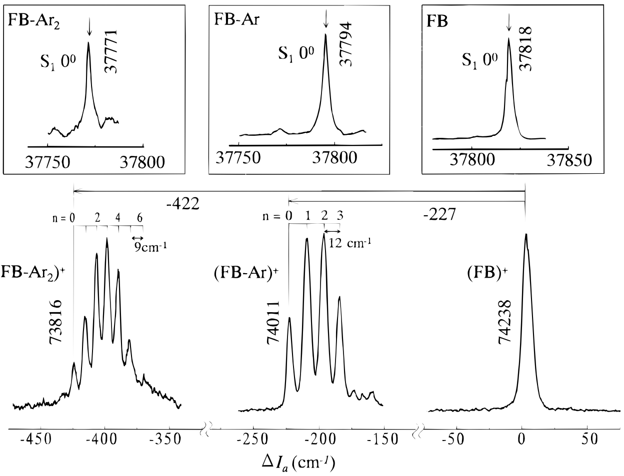

Figure 1. ZEKE photoelectron spectra of fluorobenzene (FB) and its vdW complexes (FB−Ar and −Ar_2), obtained in the region around the cation D_0 origins through the S_1 origins (indicated by allows in the REMPI spectra in the inset). The observed shifts in the D_0 origins are 227 and 422 cm^{-1} for FB−Ar and FB−Ar_2, respectively. Well-resolved progressions attributable to the cation vdW bending vibrations (b_x^+ and b_{xs}^+) are clearly observed.

TABLE 1: Adiabatic Ionization Energies I_a and S_1 0^0 Energies $E(S_1)$ of Fluorobenzene−Ar and −Ar_2 (in cm^{-1})

	this work[a]	refs
$E(S_1)$		
FB	37 818	37 814,[b] 37 816,[c,d] 37 816.2,[f] 37 818[g]
FB−Ar	37 794	37 790,[b] 37 791[c]
FB−Ar_2	37 771	
ΔE		
(FB)−(FB−Ar)	24	24[b−e]
(FB)−(FB−Ar_2)	47	47,[d] 50[e]
I_a		
FB	74 238	74 222,[b] 74 229,[c] 74 230,[d] 74 217[h] 74 000 (9.18 eV)[g]
FB−Ar	74 011	74 000,[b] 74004[c]
FB−Ar_2	73 816	
ΔI_a		
(FB)−(FB−Ar)	227	222,[b] 224,[c] 200,[d]
(FB)−(FB−Ar_2)	422	389[d]

[a] $E(S_1)$ and I_a values obtained within ±2 and ±4 cm^{-1}, respectively. [b] Reference 14 (Grebner and Neusser, REMPI, MATI). [c] Reference 15 (Lembach and Brutschy, REMPI; MATI). [d] Reference 16 (Gonohe *et al.*, REMPI, ion-yield curve). [e] Reference 17 (Bieske *et al.*, REMPI). [f] Reference 22 (Seliskar and Lipp, UV absorption). [g] Reference 23 (Walter *et al.*, REMPI photoelectron, TOF). [h] Reference 24 (Smith and Raymonda, vacuum UV absorption; Rydberg states).

The MPI spectrum of the FB−Ar complex shows four additional bands at 17, 32, 35, and 43 cm^{-1} above the S_1 origin (not shown in Figure 1), attributable to the vdW vibrational levels (b_x^1, b_y^2, b_x^2, and s_z^1), as already assigned by Bieske *et al.*[18] Here, the vdW bendings along the y axis and the x axis (the C−F bond) are denoted by b_y and b_x, respectively, and the vdW stretching along the z axis (perpendicular to the FB plane) is denoted by s_z.

3.2. ZEKE Photoelectron Spectra. Figure 1 shows the ZEKE photoelectron spectra of FB, FB−Ar, and FB−Ar_2, which were obtained in the region around the cation origin (D_0 0^{+0}) by two-color (1+1′) resonant ionization through the S_1 origins. In the spectrum due to $(FB)^+$, a single peak appearing at 74 238 cm^{-1} is attributable to the origin of the ground-state cation, corresponding to the adiabatic ionization energy (I_a). In the spectra due to both $(FB-Ar)^+$ and $(FB-Ar_2)^+$, well-resolved vibrational progressions are observed with the first peaks at 74 011 and 73 816 cm^{-1}, respectively, which may be attributed to the origin peaks. From the cation origin peaks, we have determined the adiabatic ionization energies as follows: I_a(FB) = 74 238 ± 4 cm^{-1} (9.2043 ± 0.0005 eV), I_a (FB−Ar) =

74 011 ± 4 cm^{-1} (9.1762 ± 0.0005 eV), and I_a (FB−Ar_2) = 73 816 ± 4 cm^{-1} (9.1521 ± 0.0005 eV).

All these I_a values are summarized in Table 1, compared with several literature values.[14−16,23,24] After we completed the present work, we noticed that our I_a values of FB and FB−Ar are considerably larger than those of the MATI studies.[14,15] Therefore, in order to check our I_a values, we carried out remeasurements of ZEKE spectra. As a result, our original I_a values have been confirmed. As mentioned in section 2, in the present work the I_a values were corrected for the pulsed electric field by extrapolating the plots of the ZEKE peak energy against the field strength.

It is interesting to note that the I_a value of bare FB (74 238 cm^{-1}, 9.2043 eV) is almost identical to its vertical ionization energy (I_v = 9.20 eV) earlier reported in a HeI photoelectron study.[25]

The shifts in I_a from bare FB are $\Delta I_\mathrm{a} = -227$ and -422 cm^{-1} for FB−Ar and FB−Ar_2, respectively. The I_a shift of FB−Ar_2 is 32 cm^{-1} smaller than twice that of FB−Ar. This relationship is contrast to the aniline−Ar and −Ar_2 complexes, in which the additivity rule holds almost strictly; namely, ΔI_a(aniline−Ar) = −111 cm^{-1} and ΔI_a(aniline−Ar_2) = −219 cm^{-1}.[6] It is also interesting to see how the shift in I_a is affected by the substituents or by the molecular size. The following two examples may be mentioned: (1) The shifts in I_a are 252, 227, and 116 cm^{-1} for the vdW complexes benzonitrile−Ar,[13] FB−Ar, and styrene−Ar,[26] respectively. (2) The shifts in I_a are 172, 85, and 65 cm^{-1} for the vdW complexes benzene−Ar,[4] naphthalene−Ar,[27] and anthracene−Ar,[28] respectively.

3.3. Cation van der Waals Vibrations. In $(\mathrm{FB{-}Ar})^+$ with C_s symmetry, there are three vdW vibrations; "totally symmetric bending" $\mathrm{b}_x^+(\mathrm{a}')$, "non-totally symmetric bending" $\mathrm{b}_y^+(\mathrm{a}'')$ and "stretching" $\mathrm{s}_z^+(\mathrm{a}')$. In $(\mathrm{FB{-}Ar_2})^+$ with $\mathrm{C}_{2\mathrm{v}}$ symmetry, there are six vdW vibrations: Namely, two "symmetric (in-phase) bendings" $\mathrm{b}_{xs}^+(\mathrm{a}_1)$ and $\mathrm{b}_{ys}^+(\mathrm{b}_2)$, two "antisymmetric (out-of-phase) bendings" $\mathrm{b}_{xa}^+(\mathrm{b}_1)$ and $\mathrm{b}_{ya}^+(\mathrm{a}_2)$, and "symmetric and antisymmetric stretchings" $\mathrm{s}_{zs}^+(\mathrm{a}_1)$ and $\mathrm{s}_{za}^+(\mathrm{b}_1)$. The vibrational progressions due to $(\mathrm{FB{-}Ar})^+$ and $(\mathrm{FB{-}Ar_2})^+$ in Figure 1 consist of several vibrational peaks with nearly equal spacings of 12 and 9 cm^{-1}, respectively. These vibrational progressions are very similar in intensity distribution to those previously reported by Araki *et al.*[13] for the benzonitrile−Ar and −Ar_2 vdW complexes whose vibrational spacings are also 12 and 9 cm^{-1}, respectively. These cation frequencies have previously been assigned to the vdW bending mode (b_x^+) and the vdW symmetric bending (b_{xs}^+), respectively.[13] Therefore the vibrational progressions shown in Figure 1 may reasonably be assigned to the vdW cation bending modes $\mathrm{b}_x^+(\mathrm{FB{-}Ar})^+$ and $\mathrm{b}_{xs}^+(\mathrm{FB{-}Ar_2})^+$, respectively. These assignments have been confirmed from our Franck−Condon calculations, as described in section 3.4.

Figure 2 shows three additional ZEKE photoelectron spectra b−d of FB−Ar, which were obtained through the three S_1 vibrational levels attributable to b_y^2, b_x^2, and s_z^1. Here, s_z means the vdW stretching mode. Spectrum a in Figure 2 is the same as that in Figure 1 (the lower middle), already interpreted in terms of b_x^{+n}. Spectra b and d in Figure 2, obtained through S_1 b_y^2 and S_1 s_z^1, respectively, are similar in vibrational progression to spectrum a, consisting of four peaks with the same spacing (12 cm^{-1}), but shifted 31 and 50 cm^{-1} from the origin peak, respectively. These frequencies (31 and 50 cm^{-1}) may be attributed to the vdW vibrations (b_y^{+2} and s_z^{+1}, respectively) of $(\mathrm{FB{-}Ar})^+$, since there are a total of three vdW vibrations (b_y, b_x, and s_z). Therefore it may be concluded that the vibrational progressions in spectra b and d are due to $\mathrm{b}_x^{+n}\mathrm{b}_y^{+2}$ and $\mathrm{b}_x^{+n}\mathrm{s}_z^{+1}$, respectively, as indicated in Figure 2.

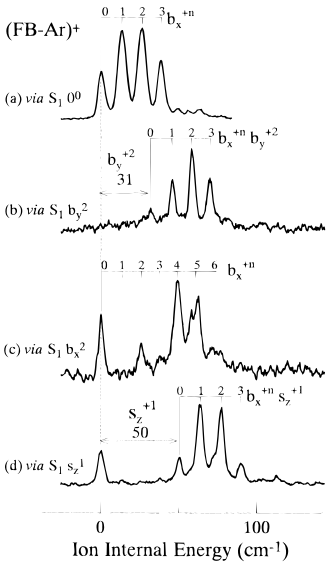

Figure 2. Four kinds of ZEKE photoelectron spectra of FB−Ar, obtained in the low-frequency region through the S_1 vibrational levels: (a) 0_0^0, (b) b_y^2, (c) b_x^2, and (d) s_z^1. All the observed vibrational structures may be interpreted in terms of the three vdW vibrations (b_y^+, b_x^+, and s_z^+).

Spectrum c in Figure 2, which was obtained through S_1 b_x^2, shows a somewhat complicated structure with almost the same spacings (12 cm^{-1}) as in spectrum a. In other words, spectrum c seems to be interpreted again in terms of b_x^{+n}. This has been confirmed also from our Franck−Condon calculations (see section 3.4.) All the assignments of the observed vdW vibrational peaks of FB−Ar in the cationic state are summarized in Table 2, together with those in the S_1 state. Spectra a and d in Figure 2 are similar in spectral pattern to those of the corresponding MATI spectra. However, spectra b and c in Figure 2 have been obtained for the first time.

3.4. Franck−Condon Calculations. In order to confirm the assignments of the observed 12 and 9 cm^{-1} progressions, Franck−Condon calculations were carried out for the following three vibrational transitions.

$$\mathrm{D}_0(\mathrm{b}_x^{+n}) \leftarrow \mathrm{S}_1(\mathrm{b}_x^{\,n}, n = 0) \text{ for FB−Ar} \tag{1}$$

$$\mathrm{D}_0(\mathrm{b}_x^{+n}) \leftarrow \mathrm{S}_1(\mathrm{b}_x^{\,n}, n = 2) \text{ for FB−Ar} \tag{2}$$

$$\mathrm{D}_0(\mathrm{b}_{xs}^{+n}) \leftarrow \mathrm{S}_1(\mathrm{b}_{xs}^{\,n}, n = 0) \text{ for FB−Ar}_2 \tag{3}$$

In each case, the same harmonic potential curve except for the potential displacement $D_{\mathrm{b}x}$ was assumed for the lower S_1 and the upper D_0 state. The following expression was used in our Franck−Condon calculations.

$$Q_{\mathrm{b}x}^{+} = Q_{\mathrm{b}x}' + D_{\mathrm{b}x} \tag{4}$$

where $Q_{\mathrm{b}x}^{\,+}$ and $Q_{\mathrm{b}x}'$ represent the normal coordinates along b_x of the cation D_0 and the S_1 states of FB−Ar, respectively, and $D_{\mathrm{b}x}$ represents the displacement along the b_x coordinate between these two states. In these calculations we used an analytical expression for the overlap derived by Smith.[29] For FB−Ar_2, similar Franck−Condon calculations were also carried out to reproduce the observed cation vibrational progression (Figure 1). For the FB−Ar and −Ar_2 complexes, the displacements ($D_{\mathrm{b}x}$ and $D_{\mathrm{b}xs}$) between the lower and the upper curve were taken as adjustable parameters. Figure 3 shows appropriate theoretical

TABLE 2: Frequencies (cm^{-1}) and Assignments of vdW Vibrational Bands of (FB−Ar)$^+$ and (FB−Ar$_2$)$^+$ vdW Complexes

		n						
	vib progression	0	1	2	3	4	5	6
			(FB−Ar)$^+$					
spectrum a *via* S$_1$ O^0	b_x^{+n}	0	12^a	24	36			
spectrum b *via* S$_1$ b_y^2	$b_x^{+n}b_y^{+2}$	31	43	55	67			
spectrum c *via* S$_1$ b_x^2	b_x^{+n}	0		24		48	60	72
spectrum d *via* S$_1$ s_z^1	$b_x^{+n}s_z^{+2}$	50^b	62	74	86			
			(FB−Ar$_2$)$^+$					
spectrum *via* S$_1$ 0^0	b_{xs}^{+n}	0	9	18	27	36	45	

[a] 13 cm^{-1} in refs 14 and 15. [b] 49 cm^{-1} in ref 14, while 51 cm^{-1} in ref 15.

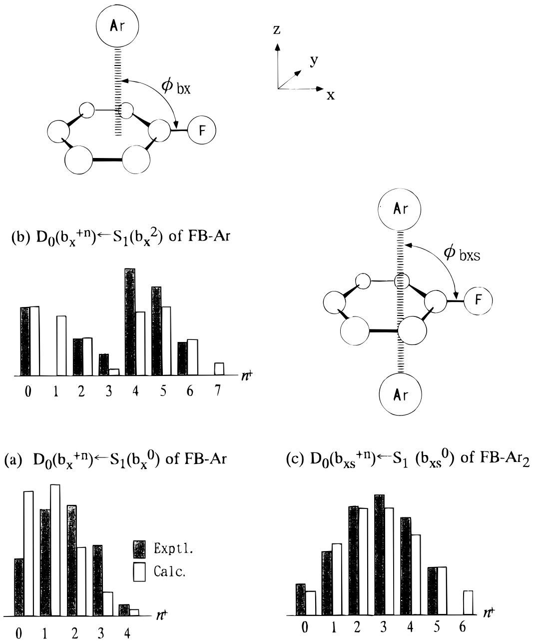

Figure 3. Comparison between the calculated and observed Franck−Condon intensity distributions of the vdW vibrational transitions. (a) D$_0$(b_x^{+n}) ← S$_1$(b_x^0) of FB−Ar, (b) D$_0$(b_x^{+n}) ← S$_1$(b_x^2) of FB−Ar, and (c) D$_0$(b_{xs}^{+n}) ← S$_1$(b_{xs}^0) of FB−Ar$_2$

Franck−Condon intensity distributions calculated with $D_{bx} = 1.45$ and $D_{bxs} = 2.45$, compared with the experimental ones. As seen from Figure 3, the observed vibrational progressions seem to be well reproduced from the Franck−Condon calculations.

The assignments of these vibrational progressions have further been supported by considering the following relationship. If the force constants of the bending b_x^+ and b_{xs}^+ vibrations are the same, the ratio of the two bending frequencies is simply given by the equation[18]

$$\nu_{bxs}^{+}/\nu_{bx}^{+} = (\mu_{bxs}/\mu_{bx})^{-1/2} \tag{5}$$

Here, μ_{bx} and μ_{bxs} are reduced masses (for the vibrational modes of b_x^+ and b_{xs}^+, respectively), which are given by

$$\mu_{bx}\,(\mathrm{FB{-}Ar}) = \{(mR_0^{\,2})^{-1} + (MR_0^{\,2})^{-1} + (I_{yy})^{-1}\}^{-1} \tag{6}$$

and

$$\mu_{bxs}(\mathrm{FB{-}Ar_2}) = \{(mR_0^{\,2})^{-1} + 2(M\,R_0^{\,2})^{-1}\}^{-1} \tag{7}$$

where M and m are the masses of fluorobenzene and Ar, respectively, I_{yy} is the moment of inertia (y axis) of fluorobenzene, and R_0 is the equilibrium distance between fluorobenzene and Ar. Therefore, the reduced masses of FB−Ar and FB−Ar$_2$ are 158.4 and 275.4 amu, respectively.

The term $\nu_{bxs}^{+}/\nu_{bx}^{+}$ in eq 5 is 0.75 from the observed frequencies (12 and 9 cm^{-1}), while the right term $(\mu_{bxs}/\mu_{bx})^{-1/2}$ is calculated to be 0.7584, both terms being very close to each other. This result suggests that the both force constants are essentially the same, further supporting our assignments for the 12- and 9-cm^{-1} progressions. A similar situation has previously been found for the benzonitrile−Ar and −Ar$_2$ cations.[13]

3.5. Structural Information. From the displacements in the potential curves, D_{bx}(FB−Ar) = 1.45 and D_{bxs}(FB−Ar$_2$) = 2.45, the displacements in the location of Ar between the S$_1$ and D$_0$ states were calculated with the following equations.[18]

$$Q_{bx} = (\mu_{bx})^{1/2}\Delta\phi_{bx} \tag{8}$$

$$Q_{bxs} = (2\mu_{bxs})^{1/2}\Delta\phi_{bxs} \tag{9}$$

Here, Q_{bx} and Q_{bxs} are the normal coordinates of the b_x^+ and b_{xs}^+ modes, respectively, and $\Delta\phi_{bx}$ and $\Delta\phi_{bxs}$ are the differences in the angles (in radian) between the C−F bond (x axis) and the line connecting Ar with the center of mass of the FB moiety, respectively. According to a study of the rotational spectrum of FB in the ground state, Stahl and Grabow[19] have indicated that Ar is located at R_0 = 3.553 Å above the center of mass of FB (but shifted 0.460 Å along the x axis in the direction opposite to the F atom). By using eqs 5 and 6, a value of $\Delta\phi_{bx}$(FB−Ar)$^+$ = 7° was obtained from $D_{bx} = 1.45$, and a value of $\Delta\phi_{bxs}$(FB−Ar$_2$)$^+$ = 6° was obtained from $D_{bxs} = 2.45$. A similar situation has also been found in the aniline−Ar and −Ar$_2$ cations (namely, 8° and 9°, respectively) and also in the benzonitrile-Ar and -Ar$_2$ cations (namely, 7° and 6°, respectively).

The change in the vdW interaction energy upon the ionization may be mainly due to the difference in the charge−charge-induced-dipole interaction energy between the neutral ground state (S$_0$) and the cation ground state (D$_0$). According to our *ab initio* molecular orbital calculations in the present work, it was indicated that a negative charge of −0.300 is localized on the F atom and a positive charge of +0.379 is on the adjacent C atom in the fluorobenzene S$_0$ state, whereas in its cation D$_0$ state the F atom negative charge is decreased to −0.159 and the positive charge of the adjacent C atom is increased to +0.455. From our preliminary analysis of the potential energy surface in terms of the charge−charge-induced dipole interaction, it has been indicated that upon the ionization the stable position of Ar is displaced slightly toward the opposite direction of the F atom. A more detailed calculation is now under study.

3.6. Dissociation Energies. The differences in the dissociation energies (D_0) between the cation and the neutral ground state for the vdW complexes are equal to the shifts in I_a as follows.

$$D_0(\mathrm{FB{-}Ar})^+ - D_0(\mathrm{FB{-}Ar}) = I_a(\mathrm{FB{-}Ar}) - I_a(\mathrm{FB}) = 227\ \mathrm{cm}^{-1}$$

$$D_0(\mathrm{FB{-}Ar_2})^+ - D_0(\mathrm{FB{-}Ar_2}) = I_a(\mathrm{FB{-}Ar_2}) - I_a(\mathrm{FB{-}Ar}) = 422\ \mathrm{cm^{-1}}$$

In other words, the dissociation energy of $(\mathrm{FB{-}Ar})^+$ is 227 $\mathrm{cm^{-1}}$ larger than that of FB−Ar, while the dissociation energy of $(\mathrm{FB{-}Ar_2})^+$ is 422 $\mathrm{cm^{-1}}$ larger than that of $\mathrm{FB{-}Ar_2}$. Very recently, Grebner and Neusser[14] have found $D_0(\mathrm{FB{-}Ar})^+$ to be 543 $\mathrm{cm^{-1}}$ from the threshold of daughter cations and evaluated $D_0(\mathrm{FB{-}Ar})$ to be 321 $\mathrm{cm^{-1}}$. In the MATI study of Lembach and Brutschy,[15] however, considerably smaller values of 502 and 278 $\mathrm{cm^{-1}}$ are reported as upper limits for $D_0(\mathrm{FB{-}Ar})^+$ and $D_0(\mathrm{FB{-}Ar})$, respectively.

4. Conclusions

In the present work, the two-color (1+1′) ZEKE photoelectron technique has been employed for the vdW complexes FB−Ar and $-\mathrm{Ar_2}$ under jet-cooled conditions to determine their adiabatic ionization energies (I_a) very accurately as well as to observe the vdW vibrations appearing in the low-frequency region up to 100 $\mathrm{cm^{-1}}$ above the D_0 origin. The main results thus obtained are the following. (1) The decreases in I_a for FB−Ar and $-\mathrm{Ar_2}$ have been found to be −227 and −422 $\mathrm{cm^{-1}}$, respectively. These values are very large compared with other mono-substituted benzenes, except for the benzonitrile−Ar and $-\mathrm{Ar_2}$ vdW complexes. (2) The cation vibrational progressions with the spacing of 12 and 9 $\mathrm{cm^{-1}}$ observed for FB−Ar and $-\mathrm{Ar_2}$ have been interpreted in terms of the vdW bending modes (b_x^+ and b_{xs}^+). These vibrational assignments have been supported by considering eq 4 associated with the reduced masses (μ_{bx} and μ_{bxs}). (3) The vibrational frequencies of 15.5 and 50 $\mathrm{cm^{-1}}$ found in the observed cation vibrational structures for FB−Ar have been assigned to the vdW bending mode (b_y^+) and the vdW stretching mode (s_z^+), respectively. (4) From the Franck−Condon consideration for the cation vibrational progressions, it is concluded that the Ar atoms are shifted by 7° and 6° upon the $D_0 \leftarrow S_1$ ionization for FB−Ar and $-\mathrm{Ar_2}$, respectively.

Clearly, the two-color REMPI ZEKE photoelectron spectroscopy with a jet expansion technique has enormous potential to carry out cation spectroscopy in high resolution even for a mixture of large vdW complexes, because individual vdW species can be selected out through the resonant ionization process.

Acknowledgment. The authors thank Mr. Hiroshi Inoue and Mr. Kenji Omiya for their helpful technical suggestions on the experiments in the present work. This was partly supported by a Grant-in-Aid for Scientific Research (C) (Grant 06640468) from the Ministry of Education, Science, Sports and Culture of Japan.

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