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Electronic Spectra of Tetrafluorobenzene Cations Produced by Pulsed Glow Discharge in a Supersonic Free Jet

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Cold ions of tetrafluorobenzene isomers were produced by pulsed glow discharge in a supersonic free jet and the electronic spectra due to D_2–D_0 transitions were observed. The vibrational frequencies of the ions were determined for the ground and electronically excited states through observations of the fluorescence excitation and dispersed fluorescence spectra under collision-free conditions. The vibronic bands observed in the spectra were assigned to totally symmetric vibrations. The difference in the vibrational frequencies between the ion and neutral molecules is very small in spite of the ejection of an electron from the π orbital. A very small frequency change is observed in the electronic excited state of the ions. The frequencies observed for the ions show that the bonding π orbitals are less effective for chemical bonds of the molecules. The electronic spectra of the 1,2,4,5-tetrafluorobenzene cation, whose neutral parent molecule is distorted in the S_1 state along the fluorine-wagging normal mode, gave no sign of such a structural change in the electronic excited D_2 state.

A spectroscopic study of the ion or the free radical is very important because many chemical reactions occur through the ion or radical as an intermediate. Since vibrational spectroscopy is an effective method to determine the potential surface of a molecule, observations of the vibrational structure of such unstable molecular species in various electronic states may give important information to understand chemical reactions. Because a chemical reaction occurs along the potential surface of the reactant, and occasionally proceeds through an unstable molecule, such as a radical or cation as a reactive intermediate. However, a spectroscopic study of unstable molecular species is very difficult due to the high reactivity and short lifetime. A collision-free condition enables us to study unstable molecules. The supersonic free-jet technique is an ideal method to study unstable molecule, because it attains the collision-free condition, and also simplifies the vibrational and rotational fine structures in electronic spectra because of low the vibrational and rotational temperatures.

Fluorobenzene cations are known as fluorescent molecular ions. This is due to the 'perfluoro effect', which stabilizes the σ orbital and causes the (σ, π) state to be higher in energy in the cations.[1] Because of this effect, the (π, π) state becomes the D_2 state and nonradiative relaxation into the ground state is diminished. Therefore, the emission spectroscopy of the cations of fluorobenzenes has been studied in a rare-gas matrix,[2—5] in the gas phase,[6—10] and in a jet.[3,5,11—14] Miller et al. observed the fluorescence excitation spectra of tetrafluorobenzene cations in the vapor phase and determined the vibrational frequencies in the D_2 states.[9] In their study, the cation was produced by electric discharges in the gas phase and vibrational hot bands and broad rotational contours were observed. They concluded that the bands in the spectra are due to totally symmetric vibrations and that the frequencies are similar to those of the neutral molecules. Cossert-Magos et al. observed the dispersed fluorescence spectra of three tetrafluorobenzene cations in the gas phase, and determined the vibrational frequencies of the ions in the ground states.[8] However, the emission from the vibrationally excited states in the D_2 state might give extra bands and a congested band structure because of a gas-phase experiment at room temperature.

Tuckett has observed the dispersed fluorescence spectra of fluorobenzene cations by electron impact in a molecular beam.[11] The spectra gave a vibrational fine structure of the cations. Because the spectra gave only bands from the zero vibrational level of the D_2 state, the vibrational frequency in the ground states could be determined from the spectra.

In the present study, fluorescent tetrafluorobenzene cations were produced in a supersonic free jet by electric discharge. The fluorescence excitation and dispersed fluorescence spectra were both measured and used to determine the vibrational correspondence between the ground and excited states of the ions.

For 1,2,4,5-tetrafluorobenzene (1245TFB), the molecular structure in the S_1 state is distorted along the fluorine wagging vibrational mode, the butterfly vibration,[15] although the ion is planar in the ground state, as determined from a measurement of the pulsed field ionization zero kinetic electron (PFI-ZEKE) spectroscopy.[16] The planarity of the molecule by electronic excitation in the ion gives interesting information that can help to understand the origin of the distortion by electronic excitation in a neutral molecule.

In our previous paper,[17] an effective production of a triplet-state molecule was observed in a supersonic free jet by pulsed glow discharge. Pyrazine and benzophenone were directly excited into the lowest triplet states by electric discharge, and the dispersed phosphorescence spectra were observed in a supersonic free jet without using a laser. The study also showed the effective production of an electronically excited CN radical by the electric discharge of pyrazine. This fact indicates that pulsed glow discharge is one of the effective methods to create unstable molecular species in a jet. In this paper, the effectiveness of an electric discharge to produce molecular ions in a supersonic free jet will be shown, and the fluorescence excitation and dispersed fluorescence spectra of tetrafluorobenzene cations are reported. Also, the molecular structure of the ions is discussed based on an observation of the vibrational structure in the electronic spectra.

Experimental

The experimental details concerning how to produce molecular ions were the same as for the experimental setup reported previously.[17] For observing the fluorescence excitation and dispersed fluorescence spectra of ions, a pulsed dye laser (Spectra Physics PDL-II) pumped by a frequency-tripled Nd-YAG laser (Spectra Physics DCR-11) was used with a suitable delay with respect to a high-voltage electric pulse for the electric discharge. The high-voltage pulse was synchronized with respect to the electric pulse for the nozzle opening. Optical and spatial filters were inserted between the collimation lens and the photomultiplier tube in order to decrease laser scattering and discharge emission. A photomultiplier tube of Hamamatsu Photonics (R928) was located perpendicular for both the laser and the molecular jet axes in the same way as observed for the usual fluorescence excitation spectrum.[18]

The fluorescence from the excited state of ions was dispersed with a 1.26 m monochromator (Spex 1269) and detected by a photomultiplier tube (EMI-9789QB). The output from the photomultiplier tube was processed with a boxcar integrator (SRS-250) and recorded with a strip-chart recorder. The intensity change of the dye laser was monitored with a photo diode and recorded during the experiment.

Tetrafluorobenzenes were purchased from Aldrich Chemical Co. and used without further purification.

Results and Discussion

Figure 1 shows a typical oscilloscope trace of metastable emission and the LIF signal from 1,2,4,5-tetrafluorobenzene (1245TFB) cation, where the discharge was made in a jet with 2 atm of Ar carrier gas. The laser wavelength was tuned to the band origin of the D_2–D_0 transition of the 1245TFB cation.[8,9,11] The peak indicated by the arrow is due to LIF from the cation. The other peaks could be caused by emission from metastable molecules created by the discharge. The first sharp peak might be due to discharge emission at the nozzle exit. The LIF signal of the ion was observed only when the laser was fired on the third broad peak. These observations show that the third broad peak was due to the emission of metastable molecules with a long lifetime, traveling from the nozzle exit to the laser-irradiating region. As the LIF signal was observed only when the laser was fired on the third peak of the discharge emission, the baseline of the excitation spectrum changed as the intensity fluctuation of the third broad peak. The intensity of the third broad peaks changed during the experiment, which means that the discharge emission is very sensitive to the condition of the nozzle and/or electrodes. The spectral structure of the excitation spectra showed that the cations were effectively cooled in the jet because hot bands were not observed.

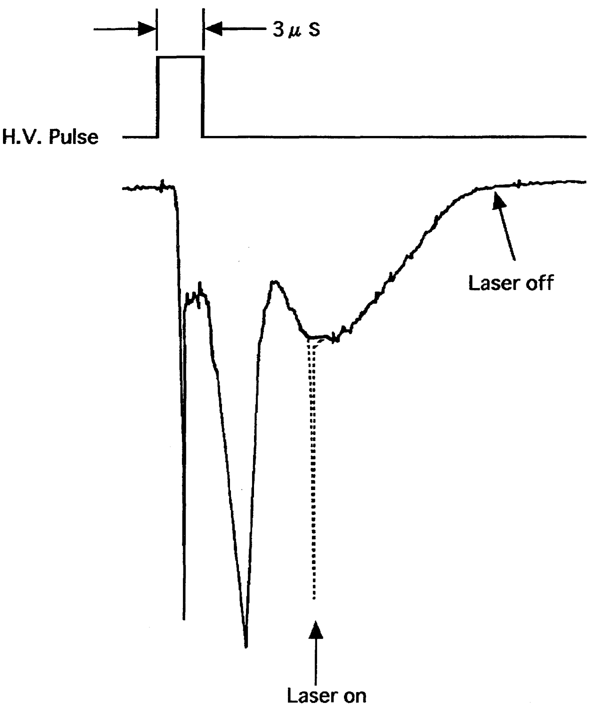
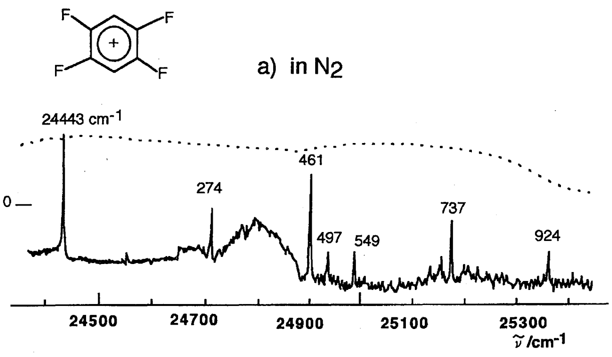


Fig. 1. Oscilloscope trace of the discharge emission and laser induced fluorescence of 1245TFB cation with laser (dotted line) and without laser (solid line).

(1) 1,2,4,5-Tetrafluorobenzene (1245TFB). Figure 2 shows the fluorescence excitation spectra of the 1245TFB cation in a supersonic free jet with carrier gases of N_2 (Fig. 2a) and Ar (Fig. 2b). The vibronic bands commonly observed in both spectra should be assigned to the bands due to the D_2–D_0 transition of the 1245TFB cation. The fluctuation of the base lines in the spectra is considered to be due to a change in the discharge emission intensity during the experiment. In spite of the fluctuation, the relative intensity of the bands was kept unchanged in the spectra. The band appearing at 24443 cm^{-1} coincides with the 0–0 band of the 1245TFB cation observed in the literatures.[8,9,11] The bands with frequencies of 274 and 461 cm^{-1} form the main progressions in the spectra. The overtone bands of the 274 and 461 cm^{-1} bands are also observed at 549 and 924 cm^{-1}, respectively. The combination band of the two vibrations is also observed at 737 cm^{-1}. The frequencies of the overtone and combination bands show that the potential surface of the ion is harmonic in the excited state for the observed totally symmetric normal vibrations. A weak band at 497 cm^{-1} might be observed through a Fermi resonance with the ν_{6a} vibration in the excited state; the appearance of this band is discussed later.

Figure 3 shows the dispersed fluorescence spectra obtained by exciting the bands in the LIF spectrum of the 1245TFB cation in Ar carrier gas. The band intensities observed around the exciting position could not be determined due to strong laser-light scattering. The spectrum excited to the band ori-



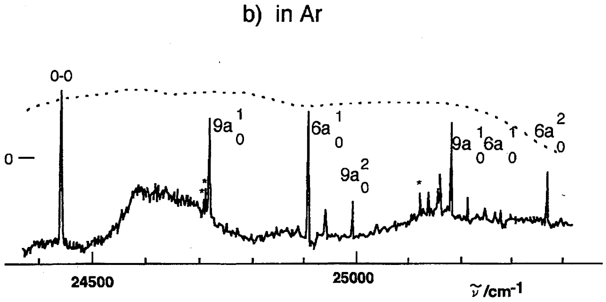


Fig. 2. Fluorescence excitation spectrum of 1245TFB cation in a supersonic free jet. The dotted lines indicate the laser intensity during the experiments and "0" indicates baseline for the laser intensity. The upper trace is observed with the carrier gas with nitrogen and lower one with Ar. In the lower spectra, the transitions due to Ar are marked by *.

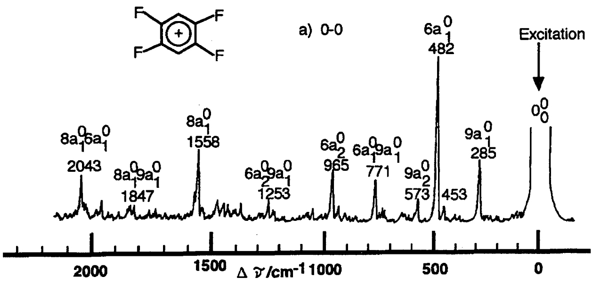
gin (Fig. 3a) gives three main fundamental bands, whose frequencies are 285, 482, and 1558 cm^{-1}, respectively. The other bands could be assigned as overtone or combination bands of the three vibrations. The vibrational frequencies of the overtone and combination bands suggest that the potential surface of the 1245TFB cation is harmonic in the ground state, as observed in the excited state.

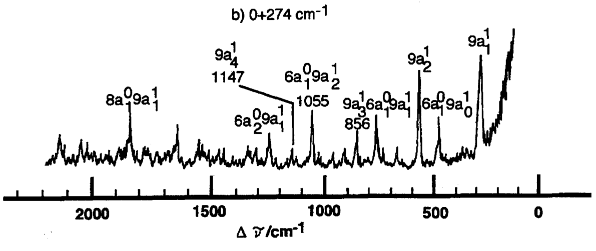
For the neutral 1245TFB molecule, two totally symmetric vibrations are expected below 500 cm^{-1} in the ground state.[19—21] One is the ring-deforming ν_{6a}, and the other is fluorine bending, with frequencies of 486 and 411 cm^{-1}, respectively. In the pulsed field ionization zero kinetic energy (PFI-ZEKE) photoelectron spectrum of the 1245TFB, Takazawa et al. observed the ν_{6a} vibration in the D_0 state with a frequency of 491 cm^{-1}.[16] This frequency corresponds to the band at 482 cm^{-1} in the dispersed fluorescence spectra. The discrepancy of the frequencies was due to the uncertainty of the broad band in the ZEKE spectrum. The frequency of the overtone band is observed at 965 cm^{-1} (Fig. 3a), and is closer to twice the frequency of 482 cm^{-1}, rather than 491 cm^{-1}. Therefore, the ν_{6a} vibration, whose frequency is 486 cm^{-1} in the neutral molecule, becomes 482 cm^{-1} in the ground state of the 1245TFB cation. This fact indicates that the vibrational frequency of the cation is similar to that of the neutral ground state for ν_{6a}.

In Fig. 3a, a band at 1558 cm^{-1} in the dispersed fluorescence spectrum from the band origin in the excited state is assigned to a totally symmetric fundamental vibration because no overtone or combination band is expected at this frequency. In the neutral molecule, the totally symmetric vibration of ν_{8a} (C–C stretching vibration of the ring) was observed in these regions with a frequency of 1644 cm^{-1}. Therefore, the 1558 cm^{-1} vibration in the cation ground state could be assigned to the ν_{8a} vibration, with taking into account the frequency decrease due to the ejection of an electron from the bonding π orbital. The dispersed fluorescence spectrum excited to the band origin of the cation is consistent with the result obtained by Tuckett,[11] except for emission from the metastable state of the carrier gas in their spectrum.

The dispersed fluorescence spectrum excited to the 0+274 cm^{-1} band (Fig. 3b) gives a progression with a frequency of 285 cm^{-1} up to the 4th quanta. The intensity distribution of the band could be assigned as a totally symmetric vibration. The spectral structure shows that the 274 cm^{-1} vibration in the excited state corresponds to vibration with a frequency of 285 cm^{-1} in the ground state.

The dispersed fluorescence spectrum excited to 0+461 cm^{-1} is shown in Fig. 3c. The vibronic structure of the low-energy region of the spectrum could not be observed because





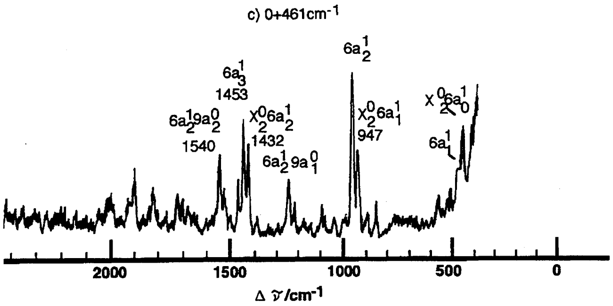


Fig. 3. Dispersed fluorescence spectra from electronically excited state of 1245TFB cation in a supersonic free jet. The exciting levels are a) 0–0 and b) 0+274 and c) 0+461 cm^{-1} bands, respectively. The exciting positions contain strong scattering of the exciting laser.

of strong laser scattering. Although the band at 482 cm^{-1} is weakly observed as a shoulder band of the strong 453 cm^{-1} band, the overtone bands at 965, 1451, and 1920 cm^{-1} are clearly observed. The observed intensity distribution shows that the 461cm^{-1} vibration in the excited state corresponds to the 482 cm^{-1} vibration in the ground state. In the spectrum excited to the band origin, a weak band at 453 cm^{-1} is clearly observed. In Fig. 3c, the 453 cm^{-1} and its combination bands with 483 cm^{-1} vibration become very strong in the spectrum. As mentioned above, the 453 cm^{-1} band might be active through a Fermi resonance with the ν_{6a} vibration in the excited state, because the corresponding vibration in the ground state is observed in the spectrum excited to the 0+461 cm^{-1} band. The interaction could be confirmed by an observation of the SVL spectrum excited to the 497 cm^{-1} band in the excitation spectrum; however, the dispersed fluorescence from the level was too weak to be observed. The mode of the 453 cm^{-1} vibration in the ground state should be a totally symmetric fundamental vibration or an overtone of the anti-symmetric vibration. Totally symmetric vibrations of neutral 1245TFB in the lower frequency region are observed at 275, 486, and 746 cm^{-1}; these modes were assigned to the ν_{9a}, ν_{6a}, and ν_1 vibrations, respectively. As discussed for other molecules later, the frequencies of the cations are similar to those of the corresponding neutral molecule. The vibrations with frequencies of 285 and 482 cm^{-1} in the ground state are assigned to the ν_{9a} and ν_{6a} modes, respectively. It is unreasonable that the frequency of the ν_1 vibration (746 cm^{-1} in the neutral molecule) decreases to 453 cm^{-1} in the ion. Therefore, the 453 cm^{-1} vibration could be assigned to the overtone vibration of the anti-symmetric vibration of the fluorine bending or wagging vibration.

It is known that the molecular structure of 1245TFB in the electronic excited S_1 state is distorted along a normal coordinate of the fluorine wagging vibration, the butterfly vibration, due to a vibronic interaction between closely lying (π, σ^*) states.[15] The experimental result of the PFI-ZEKE spectrum showed that the molecular structure in the D_0 state is planar similar to the neutral ground state.[16] In the fluorescence excitation and dispersed fluorescence spectra of the 1245TFB cation, the vibrational progression has no irregular intensity distribution or frequency interval, as observed in the S_1–S_0 transition of the molecule. This fact clearly indicates that the change in the structure between the D_2 and D_0 states occurs only along the totally symmetric vibrational normal coordinates; that is, the structure of the 1245TFB cation is planar in both the D_0 and D_2 states. Ito et al. concluded that the distortion in the S_1 state is attributed to vibronic coupling between the S_1 (π, π^*) and closely lying (π, σ^*) states, which is lowered in energy by fluorine substitution of benzene. Vibronic coupling between the (π, π^*) and (π, σ^*) states is induced by coupling between the π^* and σ^* orbitals if these electronic excited states are expressed by a single electronic orbital configuration. In the D_2–D_0 electronic transition of the 1245TFB cation, the electronic transition occurs between the bonding π orbitals. Since the σ^* or π^* orbital has no relation to the electronic transition observed in this experiment, the unusual vibrational intensity distribution, as observed in the S_1–S_0 transition, might not be observed in the electronic spectrum in the cation.

(2) 1,2,3,5-Tetrafluorobenzene (1235TFB) Cation. Figure 4 shows the fluorescence excitation spectra of 1235TFB in a supersonic free jet. He (Fig. 4a) and Ar (Fig. 4b) were used as the carrier gases. The bands due to the 1235TFB cation were easily analyzed by comparing with Figs. 4a and 4b. The band at 23324 cm^{-1} is assigned to the 0–0 band due to the D_2–D_0 transition of the ion, and coincides with the literatures.[8,9,11] Weak bands at 311 and 603 cm^{-1}, which were not observed in Miller's experiment, are clearly observed in the spectra.

The dispersed fluorescence spectrum excited to the band origin of the cation is shown in Fig. 5a, which is observed in Ar. The band position and the band intensities are similar to the spectrum observed by Tuckett.[11] Scattering of the exciting laser at the exciting position was too strong to obtain the relative intensity with other bands. The bands at 306, 424, and 585 cm^{-1} are assigned to the totally symmetric fundamental vibration in the ground state of the ion because the combination and overtone bands are not expected to be observed at the positions. The spectrum excited to the 0+301 cm^{-1} band gives strong peaks at 306 and 609 cm^{-1}. Therefore, the 301 cm^{-1} vibration in the excited state corresponds to 306 cm^{-1} in the ground state. In the parent neutral molecule,

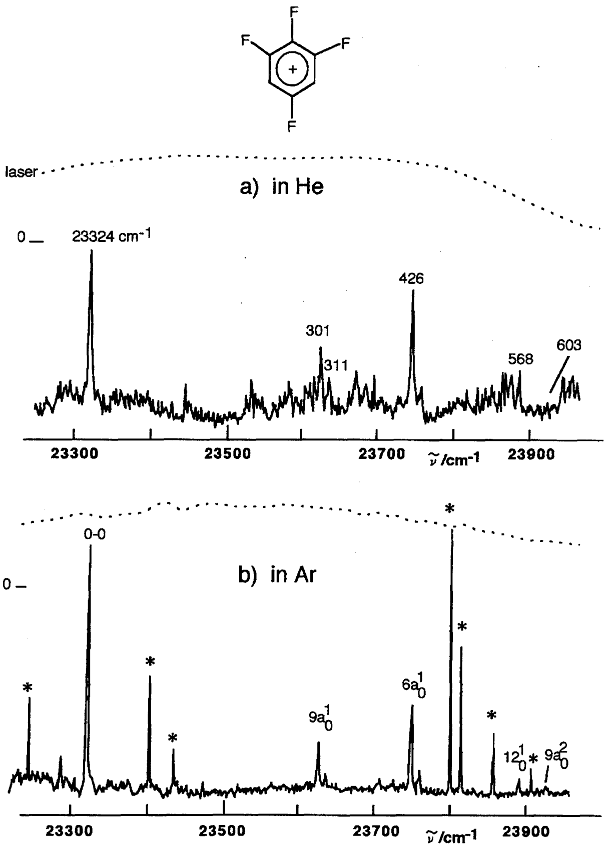


Fig. 4. Fluorescence excitation spectra of 1235TFB cation in a supersonic free jet with the carrier gases with (a) He and (b) Ar, respectively.

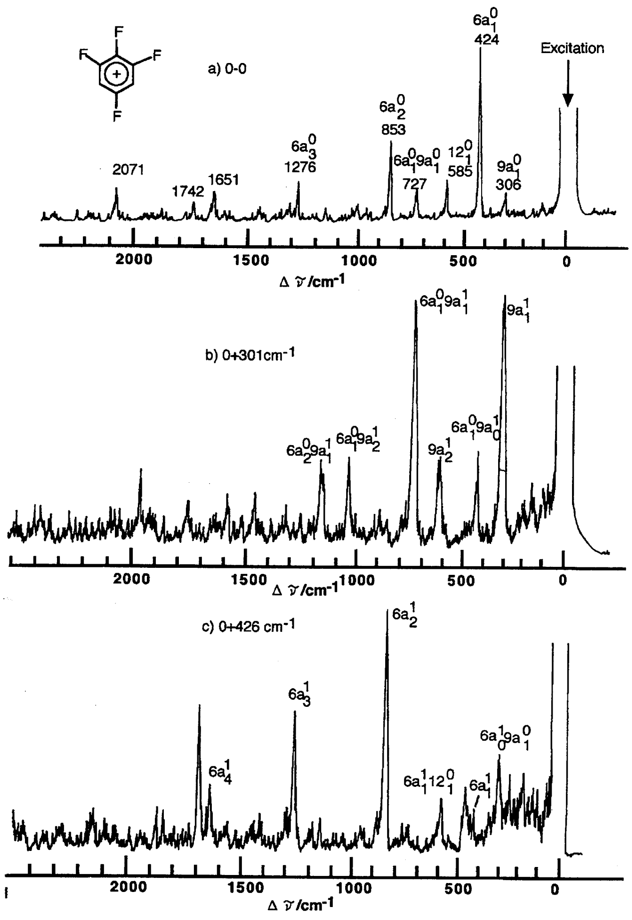


Fig. 5. Dispersed fluorescence spectra of 1235TFB cation in a supersonic free jet with the carrier gas of He.

Eaton et al.[19,20] and Green and Harrison[21] observed totally symmetric vibration at about 305 cm^{-1}, which is the lowest totally symmetric vibration, and assigned it to the fluorine bending vibration. If the fundamental vibrational frequency of the cation is similar to that of the parent neutral molecule, the 301 cm^{-1} vibration in the excited state of the cation is assigned to a C–F bending ν_{9a} vibration.

The dispersed fluorescence spectrum excited to 0+426 cm^{-1} (shown in Fig. 5c) gives a weak band at 424 cm^{-1}; however, the first, second, and third overtones are clearly observed. The intensity distribution of the bands due to a similar potential surface relationship between the states was observed for ν_{6a} in the 1245TFB cation. As a result, a vibrational correspondence between 426 and 424 cm^{-1} in the excited and ground state is established.

The SVL spectrum excited to 0+568 cm^{-1} was too weak to be observed. From the points of view of frequency correspondence between a neutral molecule and a cation, and a mirror-image relation between the LIF and SVL spectra transitions from the zero vibrational levels, this frequency may correspond to vibration with a frequency of 585 cm^{-1} in the ground state. This suggests that the vibration might be assigned to the totally symmetric ν_{12}, ring-breathing vibration.

Analysis of the dispersed fluorescence spectra of the 1235TFB cation shows that C–F bending and ring-deforming vibrations form the main progression in the electronic transition. This fact means that the angle of CCF and/or CCC may change in the electronic excited D_2 state of the cation.

(3) 1,2,3,4-Tetrafluorobenzene (1234TFB) Cation. The fluorescence excitation spectra of the 1234TFB cation in a supersonic free jet are shown in Fig. 6. The 0–0 band is observed at 23291 cm^{-1}.[8,9,11] Weak bands, which could not be observed in the gas-phase experiment,[8,9] are clearly observed in the spectra. The observed bands with frequencies of 271, 320, 434, and 446 cm^{-1} are assigned to the fundamental vibrations based on observations of the dispersed fluorescence spectra.

The dispersed fluorescence spectrum excited to the 0–0 band is shown in Fig. 7a. The stronger bands at 273, 343, and 444 cm^{-1} are observed in the low-frequency region. These bands are assigned to the fundamental vibrations, and form the main progression in the dispersed fluorescence spectra. The spectra excited to the 0+271 cm^{-1} (Fig. 7b) and 0+320 cm^{-1} (Fig. 7c) bands give strong bands at 273 and 343 cm^{-1}, respectively, and the overtone band and combination band involving 444 cm^{-1} are also observed. These two fundamental bands could be assigned to fluorine bending vibrations of the cation. In 1245TFB and 1235TFB, there is

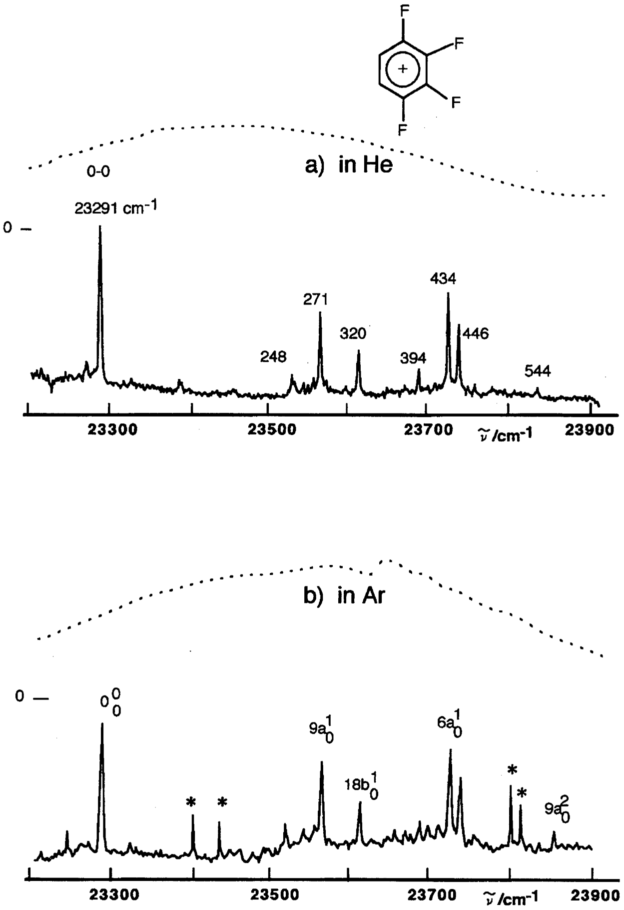


Fig. 6. Fluorescence excitation spectra of 1234TFB cation in a supersonic free jet. The spectra are observed with the carrier gases of (a) He and (b) Ar, respectively.

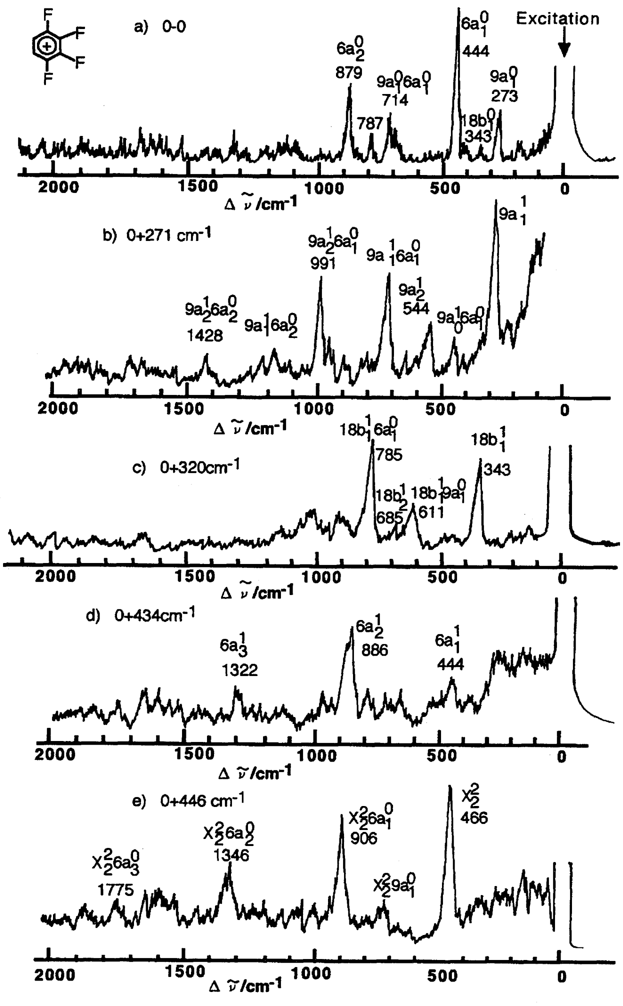


Fig. 7. Dispersed fluorescence spectra of 1234TFB cation in a supersonic free jet with the carrier gas of He.

only one totally symmetric fluorine bending vibration; however, in 1234TFB, there are two totally symmetric fluorine bending vibrations based on a symmetry consideration.

The dispersed fluorescence spectrum excited to the 0+434 cm^{-1} band, shown in Fig. 7d, gives a weak band at 444 cm^{-1} and relatively strong bands at 886 and at 1332 cm^{-1}. These bands are clearly assigned to the fundamental 444 cm^{-1}, overtone and second overtone bands, respectively. The intensity distribution of the spectrum is similar to that observed for the ν_{6a} vibration of the 1245TFB and 1235TFB cations. For neutral 1234TFB, vibration with a frequency of 457 cm^{-1} has been observed in the Raman spectrum, and has been assigned to a totally symmetric vibration based on its depolarization ratio.[21] The vibration could be assigned to the ν_{6a} vibration of 1234TFB. Therefore, the 444 cm^{-1} vibration could be assigned to ν_{6a} in the ground state of the 1234TFB cation and the frequency in the electronic excited state of the cation is 434 cm^{-1}.

The spectrum excited to the 446 cm^{-1} bands is shown in Fig. 7e. The spectrum excited to the 446 cm^{-1} band in the excited state gives a strong band at 466 cm^{-1}, whose frequency is different from that of ν_{6a}, (444 cm^{-1}) and is not observed in the 0–0 band excitation. Therefore, vibrations with frequencies of 434 and 446 cm^{-1} in the excited state correspond to those of 444 and 466 cm^{-1} in the ground state, respectively. The absence of a band in the spectrum excited to the 0–0 band and a small frequency difference with ν_{6a} vibration suggest the band being observed as a result of Fermi resonance with the ν_{6a} vibration. The vibration might be assigned to the overtone of low-frequency F bending or wagging vibration. The small frequency difference between this vibration and the ν_{6a} vibration in both states cause a Fermi resonance. The intensity of the 446 cm^{-1} band in the excitation spectrum comes from the Fermi resonance with the ν_{6a} vibration. Therefore, the main structural change between the ground and excited states is attributed to a deformation of the benzene ring along the normal mode of ν_{6a} and the fluorine bending vibrations.

Conclusion

The vibrational frequencies and assignment of tetrafluorobenzene cations were determined in the electronic ground D_0 and excited D_2 states. The obtained frequencies are shown in the Table 1. The result shows that the vibrational frequencies of the cations observed in this work are similar to those of the neutral parent molecules in the ground state for totally symmetric vibrations. A small frequency change along with ionization has also been obtained for the fluorobenzene[22] and *p*-difluorobenzene[23] observed through ZEKE or mass-analyzed threshold-ionization spectroscopy. A comparison of vibrational frequency in D_2 or D_0 with those in the S_0 states, the frequency change accompanied by the ionization of tetrafluorobenzenes is within 7% for all vibrations determined from this experiment. This fact indicates that the electron occupying the bonding π orbitals is not effective for the vibrational frequency observed in the electronic spectra of the ions, such as totally symmetric ring-deforming ν_{6a} and/or fluorine-bending vibrations. This fact suggests that the vibrational frequency of the totally symmetric vibrations is mainly governed by the σ bond in these cations. The fact that no strong vibronic band due to out-of-plane vibration appears in the D_2–D_0 transition in the cations shows that the

Table 1. Vibrational Frequencies of Tetrafluorobenzenes in the Various Electronic States (cm^{-1})

	Modes	S_0[a)]	S_1[b)]	D_0[c)]	D_2[c)]
1245TFB	ν_{9a}	275	268	285	274
	ν_{6a}	487	430	482	461
	ν_{8a}	1644	—	1558	—
1235TFB	ν_{9a}	305	—	306	301
	ν_{6a}	442	—	424	426
	ν_{12}	577	—	585	568
	ν_{8a}	1642	—	1651	—
1234TFB	ν_{9a}	289	—	273	271
	ν_{18b}	324	—	343	320
	ν_{6a}	457	—	444	434

a) Ref. 21. b) Ref. 15. c) This work.

vibrational frequencies in the electronic states of the cations do not change considerably for the electronic transition from the most stable occupied π to the most unstable occupied π orbitals, because a vibrational frequency change with electronic excitation gives vibronic intensity in the spectrum due to the Franck–Condon principle. However, the totally symmetric ring-deforming vibrations appearing in the D_0–D_2 electronic spectra mean that the molecular structure changes with electronic excitation in the cation in spite of a small vibrational frequency change between the states.

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