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# The Laser Induced Fluorescence Spectrum of the *sym*-Trichlorotrifluorobenzene Radical Cation in the Gas Phase

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**Abstract:** The laser induced fluorescence excitation spectrum of the trichlorotrifluorobenzene radical cation in the gas phase has been obtained. The spectrum is analyzed in terms of excitation to both $a_1'$ and e′ species vibrational modes in the $\tilde{B}\ ^2A_2''$ state, consistent with the presence of Jahn–Teller perturbations in the ground $\tilde{X}\ ^2E''$ state of the ion. Comparison of the spectrum with that previously obtained in the Ne matrix environment suggests that there is little matrix perturbation.

## I. Introduction

Molecular ions are an important class of compounds for which little spectroscopic information was available until quite recently. Experimental advances during the past few years, however, have enabled the study of the electronic spectra of many ionic species, and particular interest has been shown in the spectra of halogenated benzene radical cations. Maier and co-workers,[1-3] using electron impact ionization techniques, showed that the excited electronic states of these molecular ions fluoresce with high quantum efficiency and lifetimes of around 50 ns. We have previously reported[4-9] vibrationally resolved laser excitation and fluorescence spectra of several fluorinated and chlorinated benzene cations in both the gas phase and rare gas matrices. In the presence paper we report the laser excitation spectrum of the gaseous 1,3,5-trichlorotrifluorobenzene radical cation.

Symmetrically substituted benzene ions are of special interest because their nominally degenerate ground electronic state is liable to be subject to a Jahn–Teller-type distortion leading to a splitting of the potential function. Previous work on $C_6Cl_3H_3^+$ and $C_6F_3H_3^+$ and their deuterated analogues[7,8] has shown that the benzene ring in this type of molecule probably distorts from a regular hexagon primarily via changes in the C–C–C bond angles and C–C bond lengths. The spectra reported here also show convincing evidence for such a distortion. These studies are complementary to matrix work on the same ion reported recently.[9] Previous work on the traditional emission spectroscopy of the halobenzene cations has been performed by the Orsay group.[11-13]

## II. Experimental Section

The experimental techniques used have been fully described elsewhere[5,6] and only a brief outline is given here. The ion was generated by the reaction of argon metastables, formed in a dc discharge at liquid-nitrogen temperature[10] in a mixture of a few percent argon in several torr of helium. The reaction at liquid-nitrogen temperatures produces the ions at a much lower effective vibrational temperature than does an ambient-temperature discharge. This has the effect of reducing the sequence band congestion in the spectrum and narrowing the line width to ~15 cm$^{-1}$ fwhm.

Table I. Measured Line Positions (cm$^{-1}$) and Assignments in the Laser Induced Fluorescence Excitation Spectrum of Gaseous $C_6Cl_3F_3^+$

| $\bar{\nu}$ | $\Delta\bar{\nu}$ | assignment |
|---|---|---|
| 16 364 | −584 | $\nu_3''$ |
| 16 542 | −409 | $\nu_{12}''$ |
| 16 634 | −318 | $\nu_{13}''$ |
| 16 855 | −93 | |
| 16 896 | −52 | $\nu_{13}' \leftarrow \nu_{12}''(^3/_2)^a$ |
| 16 948 | 0 | origin |
| 17 042 | 94 | $\nu_{13}' \leftarrow \nu_{13}''(^3/_2)$ |
| 17 097 | 149 | $\nu_{13}' \leftarrow \nu_{14}''(^3/_2)$ |
| 17 128 | 180 | $\nu_{14}'$ |
| 17 146 | 198 | $\nu_{12}' \leftarrow \nu_{13}''(^3/_2)$ |
| 17 194 | 246 | $\nu_{12}' \leftarrow \nu_{14}''(^3/_2)$ |
| 17 242 | 294 | $\nu_{13}'$ |
| 17 278 | 330 | $\nu_{13}' + \nu_{12}' \leftarrow \nu_{12}''(^3/_2)$ |
| 17 341 | 393 | $\nu_{12}'$ |
| 17 381 | 433 | $2\nu_{13}' \leftarrow \nu_{14}''(^3/_2)$ |
| 17 392 | 444 | |
| 17 435 | 487 | $\nu_{13}' + \nu_{12}' \leftarrow \nu_{13}''(^3/_2)$ |
| 17 492 | 544 | $\nu_{13}' + \nu_{12}' \leftarrow \nu_{14}''(^3/_2)$ |
| 17 524 | 576 | $\nu_3'$, $2\nu_{13}'$ |
| 17 562 | 614 | |
| 17 586 | 638 | $\nu_9'$ |
| 17 638 | 690 | $\nu_{13}' + \nu_{12}'$ |
| 17 671 | 723 | |
| 17 722 | 774 | $2\nu_{12}'$ |
| 17 767 | 819 | $2\nu_{13}' + \nu_{12}' \leftarrow \nu_{14}''(^3/_2)$ |
| 17 821 | 873 | $\nu_3' + \nu_{13}'$, $3\nu_{13}$ |
| 17 920 | 972 | $2\nu_{13}' + \nu_{12}'$ |
| 18 032 | 1084 | $2\nu_{12}' + \nu_{13}'$ |
| 18 057 | 1109 | $\nu_{10}'$ |
| 18 094 | 1146 | $2\nu_3'$, $\nu_2'$ |
| 18 129 | 1181 | $3\nu_{12}'$ |
| 18 161 | 1213 | |
| 18 214 | 1266 | $\nu_3' + \nu_{13}' + \nu_{12}'$ |
| 18 423 | 1475 | $\nu_9'$ |
| 18 477 | 1529 | $\nu_8'$ |
| 18 511 | 1563 | |

[a] $\nu_{12}''(^3/_2)$, etc., refers to the $j = {}^3/_2$ component of the Jahn–Teller split vibration in the ground electronic state (see text).

All experiments were performed by using a Molectron DLII dye laser pumped by a UV24 nitrogen laser. The excitation spectrum was obtained by monitoring the total fluorescence as a function of laser wavelength, using suitable cutoff filters to prevent discharge light from reaching the photomultiplier tube. The phototube signal was processed by a LRS gated integrater and stored on a H.P. 9825 computer which also controlled the laser scan.

## III. Results

Previous observations[4-7] of the spectra of related halogenated benzene cations strongly suggest that, under the conditions of our

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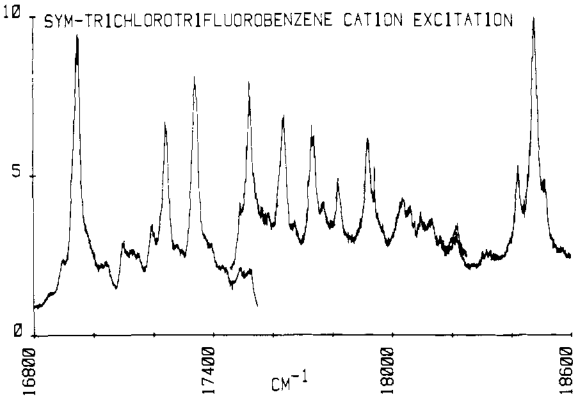

**Figure 1.** The experimental gas phase laser excitation spectrum of *sym*-$C_6Cl_3F_3^+$. The discontinuities occur because the spectrum was taken with three different laser dyes. No correction has been made for changes in laser power across the spectrum.

Table II. Observed Mode Frequencies for $C_6Cl_3F_3$ Ion and Neutral (cm$^{-1}$)

| | | ion | | | |
|---|---|---|---|---|---|
| | | $\tilde{X}$ | | $\tilde{B}$ | |
| | neutral molecule[14,15] | gas phase | matrix[9] | gas phase | matrix[9] |
| | | A. $a_1'$ Modes | | | |
| $\nu_1$ | 1408 | | | | |
| $\nu_2$ | 1167 | | | 1146 | 1148 |
| $\nu_3$ | 579 | 584 | 585 | 576 | 581 |
| $\nu_4$ | 380 | | | | |
| | | B. e′ Modes | | | |
| $\nu_8$ | 1598 | | 1629[a] | 1529 | 1538 |
| $\nu_9$ | 1452 | | 1428[a] | 1475 | 1483 |
| $\nu_{10}$ | 1088 | | 1128[a] | 1109 | 1111 |
| $\nu_{11}$ | 800 | | | | |
| $\nu_{12}$ | 397 | 409[a] | 429[a] | 393 | 398 |
| $\nu_{13}$ | 299 | 318[a] | 324[a] | 294 | 298 |
| $\nu_{14}$ | 182 | | 182[a] | 180 | 186 |

[a] These are the positions of the $v = 1, j = 1/2$ levels (see text).

experiments, the ions are thermalized and the lowest vibrational level of their ground electronic state is most populated by the time they reach the irradiation region of the sample chamber. Under these circumstances the information which may be derived from the excitation and emission spectra is to a large extent complementary. The strongest features of the excitation spectrum are associated with transitions from the vibrationless level of the ground electronic state and thus primarily give information concerning the vibrational structure of the excited electronic state. Some information on the ground state vibrational level structure can be gleaned from weaker "hot-band" structure in the spectrum.

**1. The Excited State.** Figure 1 shows the experimental excitation spectrum. It is somewhat congested and in this respect shows greater similarity with the spectrum of the hexafluorobenzene cation[5] than with either the trichloro[6]- or trifluorobenzene[5] cations, whose spectra appear more clearly resolved in the gas phase. The strongest feature in the spectrum is a band at 16 948 cm$^{-1}$ which is identified as the origin. Table I shows a complete list of the observed line positions and assignments. The assignments given in Table I were arrived at following comparison with the infrared spectra of the parent compound[14,15] and by comparison with the spectra of the related trifluoro- and trichlorobenzene cations.[5,6]

Leaving aside the origin band, the most prominent features in the spectrum are associated with $\nu_{12}'$, $\nu_{13}'$, and $\nu_9'$, which are identified roughly as the C–C–C angle bend, the C–F bend, and the C–C stretch, respectively, and are of e′ symmetry, and $\nu_3'$, which is an $a_1'$ mode. The spectrum shows several weak bands close to the origin which are identified as arising from absorption by vibrationally hot ground-state molecules. These line positions give us information about the lower vibrational frequencies of the ground state and are important in the interpretation of the Jahn–Teller effect in the compound.

The notation used for these "hot bands" requires some amplification. In the linear Jahn–Teller coupling theory outlined by Longuet-Higgins[16] each Jahn–Teller active mode is characterized by a value of a distortion parameter $D$ and the unperturbed mode frequency $\omega$. In the linear approximation, the $v = 1$ vibronic level is split into two components labeled by a quantum number $j$ which may take the values $^1/_2$ and $^3/_2$. Various selection rules imply that levels with $j = {}^3/_2$ are inaccessible from totally symmetric upper state levels, e.g., the vibrationless level in the $\tilde{B}\ {}^2A''$ state. Therefore they cannot be observed in the laser induced emission spectrum in the matrix[9] where emission invariably occurs from the vibrationless level due to very fast vibrational relaxation prior to emission. Transitions from these $j = {}^3/_2$ ground state levels are, however, allowed to non-totally-symmetric vibrational levels in the upper state and it is this type of transition which is observed in the present case.

It is noticeable that $\nu_{13}'$, the low-frequency C–X bending mode, appears anomalously strong in the spectrum of this compound as compared to the corresponding bands in the spectra of the trihalobenzene ions.[6-8] A similar conclusion was reached[5] in the analysis of the hexafluorobenzene cation, where the corresponding mode ($\nu_{18}$) appears to participate to greater extent in the Jahn–Teller activity. A possible reason for this lies in the reduced frequency of the C–C–C angle bend ($\nu_{12}$ in $C_6Cl_3F_3^+$ and $\nu_{17}$ in $C_6F_6^+$) which is perhaps an indication of greater normal-coordinate mixing in the hexahalogenated species.

Table II lists the gas phase mode frequencies for the two states of the ion and the parent compound[14,15] together with values derived from the Ne matrix study.[9] There is clearly very good agreement between the matrix and gas-phase values, which strengthens the views expressed in ref 7 and 8 that the spectra taken in a Ne matrix show little perturbation. There may be a very slight tendency for the gas phase vibrational frequencies to be lower, but it is comparable to experimental error. If the effect is real, it may well reflect a more or less systematic shift between band heads (measured in the gas phase) and band origins (measured in the matrix). The origin of the spectrum in the matrix shifts to 16 779 cm$^{-1}$, corresponding to a matrix shift of 169 cm$^{-1}$ or ~1%.

**2. Jahn–Teller Distortion of the Ground State.** In previous work[7-9,11-13] on the highly symmetric halobenzene radical cations $C_6F_6^+$, $C_6H_3F_3^+$, and $C_6H_3Cl_3^+$, we and others have argued that their spectra are affected by Jahn–Teller distortions in the ground state of the ion. The strong appearance of the $\nu_{12}$, $\nu_{13}$, and $\nu_9$ modes as well as the weaker $\nu_8$ and $\nu_{10}$ modes, all of e′ species in $D_{3h}$ symmetry, indicates clearly that a Jahn–Teller effect occurs in the isolated molecule.

Our "hot-band" transitions give the fundamental frequencies in the ground state for the two strongest Jahn–Teller modes, $\nu_{12}$ and $\nu_{13}$. The "hot-band" spectrum does not extend far enough to get information on the overtones to determine Jahn–Teller distortion parameters directly from our excitation spectrum. However, the relatively close agreement between the frequencies derived for $\nu_{12}''$ and $\nu_{12}''$ from the gas-phase "hot-bands" and the Ne matrix study indicates that these levels are basically unperturbed in the matrix. This is a particularly important result, as the relative softness of the Jahn–Teller distorted potential makes it an ideal candidate for further perturbation by crystal field effects.

Besides the transitions of the form $\nu_0' \leftarrow \nu_i''$ ($v = 1, j = {}^1/_2$) for $i$ = 3, 12, 13, there are many bands close to the origin which are missing from the matrix excitation spectrum[9] and which must therefore be assigned to transitions originating in vibrationally

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"hot" ground state levels. Following our analyses of the trifluoro- and trichlorobenzene cations[17] we expect that these features are to be associated with transitions from the lower levels in the $j = {}^{3}/_{2}$ stack which are predicted to be very intense.[17] We defer detailed discussion of the assignments given in Table I until a future publication[18] dealing with the theory and calculation of the Jahn–Teller effect.

However, it is appropriate to point out here that the assignment of these combination bands is crucial to the understanding of the Jahn–Teller effect in this compound. We showed[17] that in the case of $C_6H_3Cl_3^+$ and $C_6H_3F_3^+$ the simple single mode model of the Jahn–Teller effect used in the earlier work on these compounds[5-7,11-13] was inadequate and gave misleading results. Not surprisingly, this appears to be the case in $C_6Cl_3F_3^+$ also and the assignments given in Table I are based on preliminary calculations using the model involving mode coupling as outlined previously.[17]

For $C_6H_3F_3^+$ and $C_6H_3Cl_3^+$, key factors in the reappraisal of their Jahn-Teller effects were the recent availability of laser excited wavelength resolved fluorescence data and the observations of vibrationally unrelaxed emission in the matrix. Similar experiments are planned for $C_6F_3Cl_3^+$ to give more information on the ground state vibrational frequencies and Jahn–Teller splittings. Such data together with the more sophisticated analysis should resolve the remaining ambiguities with respect to the Jahn–Teller distortion in this compound.

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# Phosphorescence and Delayed Fluorescence of 1-Chloronaphthalene in Micellar Solutions

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**Abstract:** Phosphorescence, delayed monomer fluorescence, and delayed excimer fluorescence of 1-chloronaphthalene are readily observable in conventional anionic and cationic micelles. The delayed luminescences are shown to arise predominantly from triplet–triplet annihilation within a single micelle. A kinetic analysis of the data allowed evaluation of the rate constant for intramicellar triplet–triplet annihilation and the rate constant for exit of 1-chloronaphthalene from a micelle.

## Introduction

The rates of exit from and entrance of aromatic compounds into micelles have been investigated recently by phosphorescence decay and by solubility measurements.[1] The rate constant for triplet energy transfer has been evaluated for aromatic arenes (donor) and rare-earth ions (acceptor). Energy transfer in these systems probably takes place at sites near the micelle–water interface.[2,3] The exit rate constants of aromatic hydrocarbons from the micelle are of the order of $10^3$–$10^4$ s$^{-1}$, whereas values of $10^7$–$10^8$ M$^{-1}$ s$^{-1}$ were reported for intramicellar bimolecular energy transfer processes.[4-6] Thus, in the case of aromatic hydrocarbons as phosphorescence probes, exit from the micelle followed by quenching in the aqueous phase is expected to be an important pathway for triplet deactivation. On the other hand, in the time domain of typical fluorescence decay, the arene molecules usually remain inside of the micelle and do not exit into the aqueous environment.

Relevant to the above investigations we report here the first observation of delayed fluorescence and phosphorescence of 1-chloronaphthalene (Cl-N) in conventional anionic and cationic micelles. We have investigated the time-resolved spectra of Cl-N in micellar solutions and we have observed prompt fluorescence (PF), phosphorescence (P), delayed fluorescence (DF), and delayed excimer fluorescence (DEF). Studies of the relative intensities of DF and P as a function of (1) occupancy number of Cl-N, (2) aqueous quenchers, and (3) dilution with water above the cmc lead to the conclusion that DF results predominantly from intramolecular T–T annihilation. An analysis of the triplet decay by P and triplet–triplet absorption allowed evaluation of the rate constant of triplet–triplet (T–T) annihilation in the micelles in addition to the rate constant of the competing exit of triplet Cl-N from the micelles.

## Experimental Section

**1. Materials.** 1-Chloronaphthalene (Aldrich Chemical Co.) was purified by repeated vacuum distillation. Hexadecyltrimethylammonium bromide (HDTBr), purchased from Sigma Chemicals, was recrystallized twice from methanol after being washed with ethyl ether. Electrophoresis grade sodium dodecyl sulfate (SDS) was used as supplied from Bio-Rad Laboratories. Hexaamminecobalt(III) chloride (Alfa Products) and sodium nitrite were recrystallized twice from water. Spectrograde isooctane was passed through a silica gel column. Micellar solutions were fully degassed by repeated freeze–thaw cycles (~$10^{-5}$ mmHg).

**2. Spectroscopy. a. Measurements of Phosphorescence and Delayed Fluorescence Spectra.** Time-resolved spectra of phosphorescence and delayed fluorescence were measured with a high-sensitivity emission spectrophotometer (Spex Fluorolog) whose operation is based on the photon-counting method. The excitation light source used was a xenon flash lamp (EG & G, FX198U) possessing a half-width of ~3 μs, about 5000 mJ of electrical energy dissipating in each flash. The delay time after a flash excitation was determined by the output of the photomultiplier–amplifier–discriminator circuit of the spectrophotometer. The sampling time is defined as the amount of time over which data excited by a single flash are integrated. By changing the delay time and the sampling time appropriately along the phosphorescence decay curve, time-resolved spectra were obtained in time ranges from 10 μs to 1 s.

**b. Measurements of Phosphorescence Decay.** Phosphorescence decay was monitored by two different techniques.

**(i) Photon Counting–Multichannel Digital Boxcar Technique.** In this case, phosphorescence or delayed fluorescence was observed by means of a photon counting based spectrophosphorimeter which was combined with a multichannel analyzer (MCA). The emission signal at fixed observed wavelength was sent to the MCA with a scaling module (Tracor Northern, TN-1710 and 1710-26). The time resolution of the MCA was 10 μs. Decay curves of the emission were accumulated from $3 \times 10^4$ to $6 \times 10^4$ flashes. The apparatus and technique for the method of phos-

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