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Emission Spectrum of Tri-*B*-fluoroborazine Radical Cation in the Gas Phase: $\tilde{A}^2A_2'' \rightarrow \tilde{X}^2E''$ Band System

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Received December 15, 1978

The optical emission spectrum of the tri-*B*-fluoroborazine radical cation in the gas phase has been obtained. The band system is assigned to the $\tilde{A}^2A_2'' \rightarrow \tilde{X}^2E''$ electronic transition of the cation by reference to the photoelectron spectrum of tri-*B*-fluoroborazine which was recorded under higher resolution. A vibrational analysis of the emission band system yields the frequencies of three of the four A_1' (under D_{3h} symmetry classification) fundamentals for the $\tilde{X}^2E''$ state whereas the Ne I photoelectron spectrum allows the corresponding three frequencies for the $\tilde{A}^2A_2''$ state of tri-*B*-fluoroborazine cation to be deduced.

Introduction

Optical emission spectra of polyatomic radical cations in the gas phase have recently been obtained for several groups of organic species.[1,2] These radical cations range from tetraatomic systems such as the haloacetylenes[3] to the 18-atomic octatetraene.[4] In the case of inorganic radical cations, however, the detection of the radiative relaxation channel has been limited to the triatomic cations N_2O^+,[5] H_2S^+,[6] H_2O^+,[7] and SO_2^+.[8] In this work we report the emission spectrum of the first large inorganic radical cation, tri-*B*-fluoroborazine, in its first excited cationic state.

The observation of the emission spectrum allows us to infer the frequencies of three of the four totally symmetric fundamentals (A_1' under D_{3h} classification) for the ground state of the tri-*B*-fluoroborazine radical cation from the analysis of the band system. In addition, the frequencies of these vibrational modes have also been obtained for the first excited cationic state from the photoelectron spectrum of tri-*B*-fluoroborazine which was recorded under high resolution. For the molecular ground state the corresponding frequencies have not been given in the literature as only the bands in the gas-phase IR spectra have hitherto been reported.[9]

Experimental Section

The emission spectrum was measured by using the apparatus and techniques which have been described in an earlier work.[3] The spectra shown in Figure 1 were obtained by an electron beam of ~40 eV in energy, ~450 μA in current, impacting on an effusive sample beam at a pressure of $\sim 10^{-3}$ torr. The emitted radiation was dispersed with an optical resolution of 1.6 nm in the first run and 0.8 nm in the second, during which the sample was exhausted. The resolution used was dictated by the weakness of the emission. The data were accumulated on-line with a computer and then corrected for the optical transmission function of the apparatus and converted to a wavenumber, cm^{-1}, scale. The sample was introduced into the instrument from a glass vessel held in a bath at room temperature. The sample of tri-*B*-fluoroborazine was prepared according to the procedure given in the literature and purified by vacuum distillation.[9] The high-resolution photoelectron spectra were obtained with a spectrometer incorporating a $\pi/2^{1/2}$ cylindrical sector analyzer.[10] The resolving power of the instrument was ~250 and the spectrum shown in Figure 2 was excited with the Ne I (16.85 eV) photon resonance line in order to resolve more distinctly the low-frequency vibrational fine structure on the lowest ionization energy bands. The energy scale was internally calibrated by using xenon.

Results and Discussion

The emission spectrum which is attributed to the $\tilde{A} \rightarrow \tilde{X}$ electronic transition of the radical cation of tri-*B*-fluoroborazine is shown in Figure 1. The assignment is made on the basis of the photoelectron spectrum of tri-*B*-fluoroborazine[11,12] which shows that the separation of the first two bands corresponds to the energy region spanned by the emission band system, ~1.9–2.4 eV. In Figure 2 is reproduced a high resolution Ne I photoelectron spectrum in the region from 10 to 15 eV. The photoelectron spectrum, at lower resolution, has been reported earlier by two groups and an assignment of the bands was proposed.[11,12] In the case of the ground and first excited electronic state of tri-*B*-fluoroborazine cation the symmetries $^2E''$ and $^2A_2''$, respectively, have been deduced.

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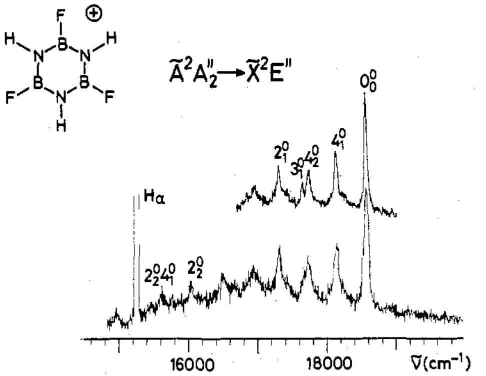

Figure 1. Emission spectra of the tri-*B*-fluoroborazine radical cation: $\tilde{A}^2A_2'' \rightarrow \tilde{X}^2E''$ band system, recorded with an optical resolution of 1.6 and 0.8 nm for the bottom and upper traces, respectively. The proposed vibrational assignments are indicated (cf. Table I).

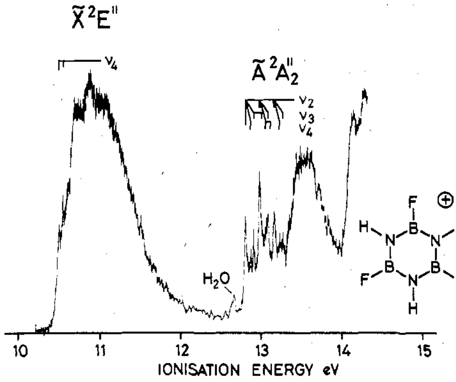

Figure 2. Ne I excited photoelectron spectrum of the first two bands of tri-*B*-fluoroborazine. A vibrational assignment of the bands is marked.

In the spectrum shown (Figure 2) the low-frequency vibration at the onset of the first band and three vibrational progressions on the second band are now discernible. Thus, the adiabatic ionization energy leading to ground state of the tri-*B*-fluoroborazine cation is now well defined and is found to be 10.49 ± 0.02 eV, as compared to the value given originally of 10.46 ± 0.01 eV.[11] The adiabatic ionization energy for the first excited cationic state is determined to be 12.78 ± 0.02 eV, in agreement with one of the two values reported previously (12.74 eV),[12] whereas the value reported first (12.85 ± 0.01 eV)[11] is too high. Because the difference between the first and second adiabatic ionization energies is 18 470 ± 160 cm^{-1} (cf. Figure 2), the most intense band in the emission spectrum (maximum at 18 580 ± 10 cm^{-1}) is assigned as the 0_0^0 component of the $\tilde{A}^2A_2'' \rightarrow \tilde{X}^2E''$ electronic transition of the tri-*B*-fluoroborazine radical cation.

The bands which lie to lower energy of the 0_0^0 band in the emission spectrum are assigned to transitions from the zeroth vibrational level of the $\tilde{A}^2A_2''$ state to excited vibrational levels of the cationic ground state. These levels correspond to the excitation of the totally symmetric fundamentals (A_1') and their overtone and combination bands. As has been pointed out previously,[11] for the four A_1' fundamentals the frequency of the ν_1(N–H$_{\text{str}}$) mode is expected around 3500 cm^{-1}, of the ν_2(B–F$_{\text{str}}$) around 1200 cm^{-1}, and of the two ring modes around 900 cm^{-1} (ν_3) and 400 cm^{-1} (ν_4). In Figure 1 an assignment of some of the prominent bands is indicated by using the numbering for the four A_1' fundamentals given in Table I. The vibrational frequencies of three of the four A_1' modes are inferred and are collected in Table I. From the photoelectron spectrum only the frequency of the ν_4 mode (Table I) can be deduced for the $\tilde{X}^2E''$ state from the two sharp peaks resolved (cf. Figure 2). The frequency of 1050 ± 160 cm^{-1} given in the earlier study[11] for the ν_1 band of the cationic ground state is slightly low in view of the value of 1260 ± 10 cm^{-1} obtained from the emission spectrum.

Table I. Vibrational Frequencies (cm^{-1}) of the Totally Symmetric Fundamentals, A_1' (under D_{3h} Symmetry Classification), for the Ground, $\tilde{X}^2E''$, and First Excited, $\tilde{A}^2A_2''$, States of Tri-*B*-fluoroborazine Radical Cation Deduced from the Emission and Photoelectron Spectra[e]

	$\tilde{X}^2E''$			$\tilde{A}^2A_2''$	
vibration[a]	emission[b]	PES[c]	PES[d]	PES[c]	PES[d]
ν_1(N–H str)					
ν_2(B–F str)	1260		1050	1450	1500
ν_3(ring brth)	840			800	750
ν_4(ring brth)	430	400		500	

[a] Approximate description of the modes. [b] Values ±10 cm^{-1}. [c] This work, values ±80 cm^{-1}. [d] Reference 11, values ±120 cm^{-1}. [e] The assigned bands in the emission spectrum (Figure 1) are labeled according to the numbering of the modes given.

In case of the $\tilde{A}^2A_2''$ state of the tri-*B*-fluoroborazine radical cation, the frequencies of three A_1' vibrational modes have been obtained from the resolved fine structure on the second photoelectron band (Table I). The interpretation of the peaks is indicated in Figure 2. The two frequencies given in the first photoelectron spectroscopic study,[11] which are included in Table I, are in agreement with the values obtained in this work. On the basis of the comparison of the photoelectron values (±80 cm^{-1}) for the $\tilde{A}^2A_2''$ state and the emission values (±10 cm^{-1}) for the $\tilde{X}^2E''$ state, the emission sequence bands 3_1^1 and 4_1^1 are predicted to fall under the band marked 0_0^0, and the 2_1^1 band is expected on the high-energy tail of the 0_0^0 band.

A decay curve was accumulated for the 0_0^0 band of the $\tilde{A} \rightarrow \tilde{X}$ emission of tri-*B*-fluoroborazine radical cation by gating the electron beam and detecting single photons in delayed coincidence.[3] The lifetime of the zeroth vibrational level of the $\tilde{A}^2A_2''$ state, which was extracted from these data in the usual manner,[3] yielded only an upper limit, 6 ns, which represents the time resolution of the apparatus. However, from the weakness of the emission intensity relative to previous observations,[2] it appears that the nonradiative pathway depleting the $\tilde{A}^2A_2''$ state proceeds at a rate about 3 orders of magnitude faster than the radiative rate. Fragmentation decay can be excluded as the electron impact excited lowest fragment appearance potential is found to be more than 3 eV above the parent ion onset.[13] Thus the intramolecular nonradiative relaxation for the $\tilde{A}^2A_2''$ state of tri-*B*-fluoroborazine radical cation is dominant.

The observation of the radiative transition $\tilde{A} \rightarrow \tilde{X}$ confirms that the $\tilde{A}$ state of tri-*B*-fluoroborazine radical cation is generated by a π^{-1} process as is clearly the case for the $\tilde{X}(\pi^{-1})$ state. This follows by analogy with the results obtained earlier for the fluoro-[14] and chlorobenzene[15] radical cations. With the latter, emission spectra were only observed for the case where the excited state was formed by a π^{-1} ionization process whereas on the other hand for a state formed by a σ^{-1} process dominant nonradiative decay "quenched" the quantum yield of emission below the detection limits ($>10^{-5}$). Thus, for the 1,3,5-trifluorobenzene radical cation[14] the symmetry of the $\tilde{A}$ state is $^2A_2''(\pi^{-1})$ as is the case with the tri-*B*-fluoroborazine cation. In fact the corresponding photoelectron bands for these two species are similar. In contrast the generation of the $\tilde{A}$ states of the radical cations of benzene[16] and borazine[11,12] is by a σ^{-1} process and consequently the radiative relaxation is not expected to be detected. This has been confirmed experimentally for the benzene cation.[14]

Acknowledgment. This work is part E 15 (part E 14, ref 4) of Project No. 2.719-0.77 of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Ciba-Geigy SA, Sandoz SA, and F. Hoffmann-La Roche & Cie. SA, Basel, are thanked for financial support.

Registry No. Tri-*B*-fluoroborazine radical cation,, 70160-55-3.

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High-Pressure Nuclear Magnetic Resonance Kinetics. 5. Proton Nuclear Magnetic Resonance Study of the Effect of Pressure on the Exchange of Nonaqueous Solvents on Nickel(II) and Cobalt(II)[1]

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Received February 5, 1979

The effect of pressure (up to 200 MPa) on the solvent exchange of $MS_6(ClO_4)_2$ with M = Ni or Co and S = *N,N*-dimethylformamide (DMF), acetonitrile, or methanol has been studied by utilizing ^{1}H FT NMR T_2 measurements. The derived volumes of activation, ΔV^* ($cm^3\ mol^{-1}$), for the above solvent series with Ni(II) are 9.1 ± 0.3 (297 K), 9.6 ± 0.3 (294 K), and 11.4 ± 0.6 (307 K) and with Co(II) are 6.7 ± 0.3 (296 K), 9.9 ± 0.7 (260 K), and 8.9 ± 0.3 (279 K). These values are in accord with a dissociative interchange mechanism, although they suggest Co(II) exhibits less dissociative character than Ni(II). For both ions, the solvent variation of $\Delta V^*/V^\circ$ mirrors that of ΔG^*; these results may suggest that the faster the reaction, the less dissociative character it has.

1. Introduction

The effect of pressure on the rate of a chemical reaction is now a well-accepted approach in elucidating reaction mechanisms.[4] For the understanding of the mechanisms of complex formation and inner-sphere redox processes, the exchange of solvent molecules between the primary solvation shell of a metal ion and bulk solvent may be considered the fundamental reaction. It is precisely for solvent-exchange reactions, where conventional mechanistic tests such as variation of the nature and the concentration of reacting ligands are not possible, that pressure effects will prove most useful. The parameter derived from the pressure dependence of a reaction rate constant by using transition state theory is the volume of activation $\Delta V^* = -RT(\partial \ln k/\partial P)_T$. It expresses the change in volume during the activation process, i.e., the difference in volume between the transition state and the reactants. ΔV^* primarily consists of two contributions: the intrinsic part, ΔV^*_{int}, and the electrostrictive part ΔV^*_{el}. ΔV^*_{int} represents the intrinsic difference in molecular size between reactants and transition state, due to the effects of bond making, breaking, and stretching. ΔV^*_{el} represents the accompanying change of volume of the surrounding solvent resulting from changes in electrostriction. As discussed by Swaddle[5] and Stranks[6] the electrostriction changes between reactants and transition state must be negligibly small for solvent exchange reactions where no charge separation or cancellation is involved. Therefore ΔV^* is a good measure of ΔV^*_{int}, and it is possible to correlate directly a positive volume of activation with a dissociative activation mode or a negative value with an associative activation mode for the exchange process.

Until recently, the only high-pressure solvent exchange studies have been those of the nonlabile ions cobalt(III), chromium(III), rhodium(III), and iridium(III)[4-6] by means of isotopic labeling. ΔV^* values for the latter three ions are in accord with an associative interchange, I_a, mechanism, whereas a dissociative interchange, I_d, mechanism is indicated for cobalt(III). It has been suggested that I_a mechanisms are the rule for 3+ ions, Co^{3+} being an exception due to its small size.[5] It is widely believed that the 2+ ions exchange solvent via I_d mechanisms;[7] however, for these labile ions no activation volumes are available for solvent-exchange reactions. The experimental technique used to obtain kinetic information on these systems is NMR. We have recently reported the design of a high-pressure proton NMR probe-head,[8] as well as the results on the effect of pressure on the methanol[9] and acetonitrile[2] exchange on nickel(II). In this paper, we report the results of the first systematic study by ^{1}H NMR of the effect of pressure on the methanol, acetonitrile, and dimethylformamide exchange on nickel(II) and cobalt(II). The results show that the solvent exchange on nickel(II) and cobalt(II) are both clearly dissociative interchange, I_d, but suggest that the latter exchange systems have *less* dissociative character than the former.

2. Experimental Section

Solvents. Methanol (Fluka puriss p.a.) was shaken with anhydrous calcium sulfate for 24 h and distilled (water content by Karl-Fischer titration less than 50 ppm). Anhydrous dilute acidic methanol was obtained by adding 65% $HClO_4$ to methanol and removing the water by reaction with a slight excess of methyl orthoformate *N,N*-Dimethylformamide (Fluka puriss p.a.) was distilled from BaO under reduced pressure and stored over previously activated 4-Å molecular