Infrared multiphoton dissociation spectrum of CF3Mn(CO)3(NO)−

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Infrared multiphoton dissociation spectrum of $CF_3Mn(CO)_4I^{-*}$

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Abstract

An IR multiphoton dissociation spectrum of $CF_3Mn(CO)_3I^-$ has been obtained using Fourier transform ion cyclotron resonance spectroscopy combined with a line-tunable CW CO_2 laser in the 925–1085 cm^{-1} wavelength range. The trifluoromethyl group in the anion shows two absorption maxima at 1055 and 975 cm^{-1}, which correspond to a C–F stretch of A_1- and E-type symmetry respectively. From comparisons of the ligand effect on the stretching force constant of CO in place of CF_3 in cis and trans isomeric $CF_3Mn(CO)_4I^-$ ions, it is suggested that a cis isomer is responsible for the observed C–F stretching frequencies.

INTRODUCTION

Spectroscopic study of molecular ions has been of great experimental interest in recent years [1–3]. Various techniques have been employed to observe the electronic and vibrational spectra of molecular ions [2]. Modern developments in high-resolution IR spectroscopy made it possible to study the individual vibration–rotation levels of relatively simple ions such as HD^+, HeH^+, CH^+ and H_3^+ [2,3]. In addition, the IR spectra of rather complex ions such as $C_2H_7^+$ and $H_3O^+(H_2O)_n$ ($n=1,2,3$) have been successfully obtained with a radio-frequency octopole ion trap combined with a two color laser scheme consisting of a tunable CW infrared laser to excite the C–H or O–H stretching vibrations and a CW CO_2 laser to dissociate the vibrationally excited ions through a multiphoton process [4,5]. However, there have been only a few experimental observations of IR spectra of organometallic ions in the gas phase.

We have recently explored the technique of multiphoton dissociation [6–10] using a low power CO_2 laser in a trapping ion cyclotron resonance cell [11,12] to obtain IR frequencies for the C–F stretching modes of the trifluo-

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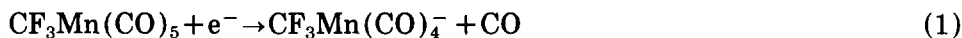*Contribution No. 8217.

romethyl ligand in (trifluoromethyl)manganese tetracarbonyl and (trifluoromethyl)manganese tricarbonyl-nitrosyl anions [13,14]. The trifluoromethyl group in the anions exhibits two IR absorption maxima at 1052 and 945 cm^{-1} for the (trifluoromethyl)manganese tetracarbonyl anion [13] and 1045 and 980 cm^{-1} for the (trifluoromethyl)manganese tricarbonyl-nitrosyl anion [14]. The higher frequency is assigned as a C–F stretch of A_1-type symmetry and the lower one is ascribed to a C–F stretch of E-type symmetry.

Comparison of the IR spectrum of a six-coordinate d^6 complex $CF_3Mn(CO)_5$ (1063 and 1043 cm^{-1} for C–F stretches of A_1- and E-type symmetry respectively) with the IR multiphoton dissociation spectra of the five-coordinate d^7 complex $CF_3Mn(CO)_4^-$ and the five-coordinate d^8 complex $CF_3Mn(CO)_3$ (NO)$^-$, leads to the interesting observation that the C–F stretching frequencies of the anionic species have decreased from those of the neutral molecule and NO substitution in place of an equatorial CO increases a C–F stretching force constant in going from $CF_3Mn(CO)_4^-$ to the $CF_3Mn(CO)_3(NO)^-$ ion [13,14].

In the present paper, we have investigated the IR multiphoton dissociation of the six-coordinate d^6 complex $CF_3Mn(CO)_4I^-$ to see how each C–F stretching mode varies with ligand substituent and the coordination number.

EXPERIMENTAL

Experimental techniques associated with Fourier transform ion cyclotron resonance spectroscopy [11,15–18] and its modification for IR photochemistry have been previously described in detail [13]. Briefly, the anion of interest is prepared by the reaction of the $CF_3Mn(CO)_4^-$ ion generated from the dissociative electron attachment [19–21] of $CF_3Mn(CO)_5$ (eqn. 1) with trifluoromethyl-iodide (eqn. 2) as shown in Fig. 1 with a rate constant of 1.9×10^{-9} cm^3 molecule^{-1} s^{-1}.

$$CF_3Mn(CO)_5 + e^- \rightarrow CF_3Mn(CO)_4^- + CO \qquad (1)$$

$$CF_3Mn(CO)_4^- + CF_3I \rightarrow CF_3Mn(CO)_4I^- + CF_3 \qquad (2)$$

All ions except $CF_3Mn(CO)_4I^-$ were removed from a trapping ICR cell using a series of ion ejection pulses after 1 s delay from an initial isolation of $CF_3Mn(CO)_4^-$ ion in 2.6:1 mixtures of (trifluoromethyl)manganese pentacarbonyl and trifluoromethyliodide with a total pressure of 1.8×10^{-7} torr. The $CF_3Mn(CO)_4I^-$ ion is unreactive with $CF_3Mn(CO)_5$ and CF_3I. The isolated ion of interest is irradiated with the unfocused output of a line-tunable CW CO$_2$ laser (Apollo Lasers Model 550A). The IR spectrum of the $CF_3Mn(CO)_4I^-$ ion is obtained by monitoring the extent of photodissociation as a function of laser wavelength with laser fluence of 160 mJ cm^{-2}. Irradiation of
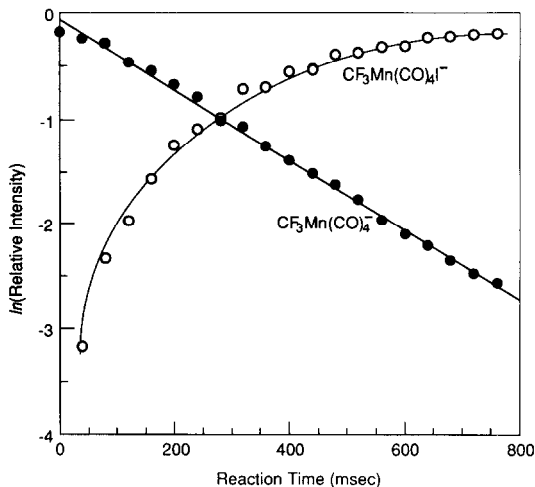
Fig. 1. Temporal variation of $CF_3Mn(CO)_4^-$ generated from dissociative electron attachment of (trifluoromethyl)manganese pentacarbonyl and its reaction product $CF_3Mn(CO)_4I^-$ with trifluoromethyliodide at 1.8×10^{-7} torr. The slope of the disappearance of the reactant ion yields a rate constant of 1.9×10^{-9} cm^3 molecule^{-1} s^{-1}.

$CF_3Mn(CO)_4I^-$ results in loss of CO yielding $CF_3Mn(CO)_3I^-$ (eqn. 3), which undergoes IR multiphoton dissociation to form $CF_3Mn(CO)_2I^-$ (eqn. 4).

$$CF_3Mn(CO)_4I^- + h\nu \rightarrow CF_3Mn(CO)_3I^- + CO \tag{3}$$

$$CF_3Mn(CO)_3I^- + h\nu \rightarrow CF_3Mn(CO)_2I^- + CO \tag{4}$$
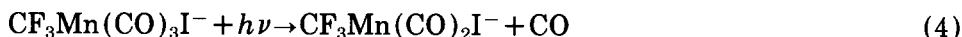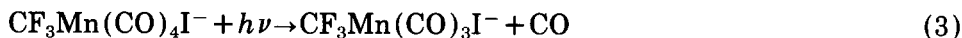
The photodissociation spectrum of $CF_3Mn(CO)_4I^-$ is obtained by the ratio of the parent ion intensity $[CF_3Mn(CO)_4I^-]$ to the total ion intensity $[CF_3Mn(CO)_4I^- + CF_3Mn(CO)_3I^- + CF_3Mn(CO)_2I^-]$ as a function of laser wavelength.

RESULTS AND DISCUSSION

The IR multiphoton dissociation spectrum of $CF_3Mn(CO)_4I^-$ is presented in Fig. 2(a). Those of $CF_3Mn(CO)_4^-$ and $CF_3Mn(CO)_3(NO)^-$ are shown in Fig. 2(b) for comparison. The IR spectrum of the neutral precursor, $CF_3Mn(CO)_5$, is also shown in Fig. 2(c). The difference in intensity of the IR multiphoton dissociation spectra reflects different experimental conditions and not the oscillator strengths of the CF_3 groups. The peaks at 1055 and 975 cm^{-1} in Fig. 2(a) are assigned as C–F stretches of A_1- and E-type symmetry respectively, from comparisons with results for $CF_3Mn(CO)_5$, $CF_3Mn(CO)_4^-$ and $CF_3Mn(CO)_3(NO)^-$ [13,14].

Comparison with the IR spectrum of $CF_3Mn(CO)_5$ reveals that the symmetric C–F stretching mode changes little in frequency from 1063 cm^{-1} for

CF$_3$Mn(CO)$_4$I$^-$

(a)

Relative Intensity

Wavenumber (cm^{-1})

▲ CF$_3$Mn(CO)$_4^-$ ○ CF$_3$Mn(CO)$_3$(NO)$^-$

(b)

Relative Intensity

Wavenumber (cm^{-1})

CF$_3$Mn(CO)$_5$

(c)

Transmission (%)

Wavenumber (cm^{-1})
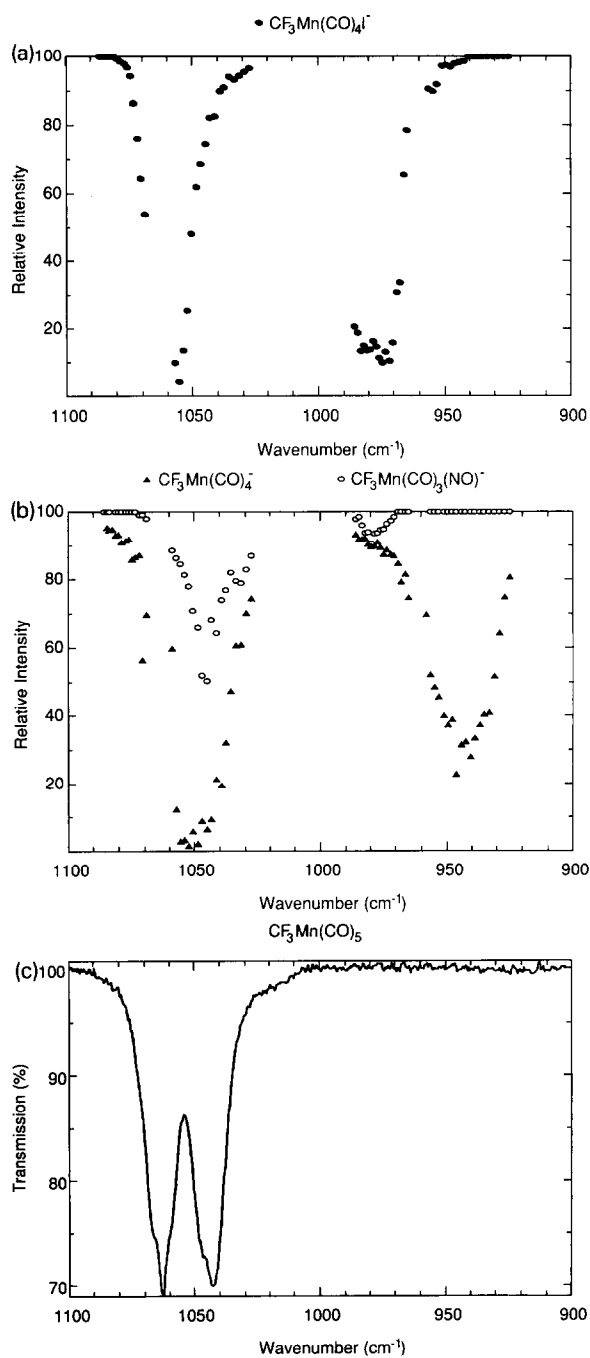
$CF_3Mn(CO)_5$ to 1055 cm^{-1} for $CF_3Mn(CO)_4I^-$, while the C–F stretching frequency of E-type symmetry decreases from 1043 cm^{-1} for the 18 e$^-$ neutral precursor to 975 cm^{-1} for the 18 e$^-$ anion. In comparison with the IR multiphoton dissociation spectrum of $CF_3Mn(CO)_4^-$ we observe that both C–F stretches of A_1- and E-type symmetry increase from 1052 and 945 cm^{-1} for the five-coordinate d^7 complex $CF_3Mn(CO)_4^-$ to 1055 and 975 cm^{-1} for the six-coordinate d^6 complex $CF_3Mn(CO)_4I^-$ respectively. It is also interesting to observe that the symmetric C–F stretching mode increases in frequency from 1045 cm^{-1} for the five-coordinate d^8 complex $CF_3Mn(CO)_3(NO)^-$ to 1055 cm^{-1} for $CF_3Mn(CO)_4I^-$, while the degenerate C–F stretching bands overlap with each other within experimental uncertainties.

It is apparent that the negative charge decreases the C–F stretching frequencies compared with the neutral molecule and the extra iodine ligand increases the C–F stretching frequencies compared with the five-coordinate anions. The observed C–F stretching frequencies for $CF_3Mn(CO)_4I^-$ compared with other complexes may afford the possibility of differentiating their structural isomers.

The structure of the d^6 complex $CF_3Mn(CO)_5$ is octahedral (**I**) and that of the five-coordinate d^7 complex $CF_3Mn(CO)_4^-$ is presumed to be square-based pyramidal (**II**) with CF$_3$ in the basal plane from comparisons with the structures for other five-coordinate d^6 and d^7 complexes. An IR spectroscopic study of the five-coordinate d^6 complex, $CH_3COMn(CO)_4$, in methane matrix at 12 K indicates the square-based pyramidal structure with η^1-acetyl bonding [22]. Spectroscopic studies of the d^7 complex, $Mn(CO)_5$, generated in $Cr(CO)_6$ crystals or in low-temperature solid matrices, support a square pyramidal structure with C_{4v} point group [23–29]. Extended Hückel calculations by Elian and Hoffmann [30] also suggest the square pyramidal structure for the five-coordinate d^7 complex carrying its odd electron in a relatively high-lying, directional orbital of A_1 symmetry. The five-coordinate d^8 complex $CF_3Mn(CO)_3(NO)^-$ is considered to have a trigonal-bipyramidal structure with a linear Mn–NO bond in the equatorial position from comparisons with the structures of the five-coordinate d^8 complexes $Mn(CO)_4NO$ and $Mn(CO)_5^-$. Frenz et al. [31] have determined the crystal structure of $Mn(CO)_4(NO)$, revealing that the nitrosyl group is in an equatorial position

Fig. 2. The IR multiphoton dissociation spectra of the CF$_3$ group in, (a) $CF_3Mn(CO)_4I^-$, (b) $CF_3Mn(CO)_4^-$ (solid triangles) and $CF_3Mn(CO)_3(NO)^-$ (open circles) over the CO$_2$ laser spectra range, and the IR absorption spectra of (c) (trifluoromethyl)manganese pentacarbonyl. Data points for photodissociation spectra of $CF_3Mn(CO)_4I^-$ are the ratio (in percentage) of the intensity of $CF_3Mn(CO)_4I^-$ to the total ion intensity $[CF_3Mn(CO)_4I^- + CF_3Mn(CO)_3I^- + CF_3Mn(CO)_2I^-]$ as a function of wavelength. The mass-selected ion of interest is irradiated for 20 ms at 8 W cm^{-2}.

in the trigonal bipyramidal structure (**III**) and the Mn–CO and Mn–NO bonds are linear. $Mn(CO)_5^-$ is also trigonal bipyramidal in the solid state [32]. The six-coordinate d^6 complex $CF_3Mn(CO)_4I^-$ has cis (**IV**) and trans (**V**) structural isomers.

(I)   (II)   (III)   (IV)   (V)
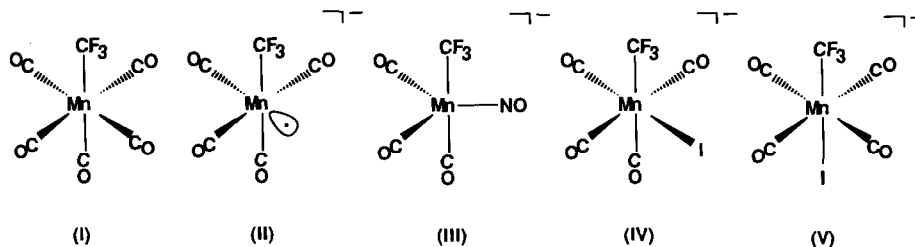
The strength of the C–F stretching force constant depends on the position of the carbonyl and iodine ligands in the octahedral structure. Since the iodine ligand is a strong σ-acceptor and moderate π-donor, the inductive property of the iodine ligand should operate to the C–F stretching force constant in iso-tropic fashion [33] and increase it by reducing the electron density of the σ-donor orbital of the CF_3 group. This means that the cis isomer (**IV**) must have higher C–F stretching frequencies than the five-coordinate d^7 complex $CF_3Mn(CO)_4^-$ (**II**) due to the addition of an inductive iodine ligand to an empty site cis to CF_3. However, the possibility for $CF_3Mn(CO)_4I^-$ of being the trans isomer (**V**) cannot be ruled out because the iodine ligand effect on the stretching force constant of the CF_3 group trans to the iodine would be greater than the cis isomer (**IV**) due to the better overlap of the σ-donor orbital of the CF_3 group with a p_z orbital of the iodine through an empty d_{z^2} orbital of the manganese. However, the carbonyl group trans to the CF_3 group in the cis isomer (**IV**) interacts with CF_3 via two d_π orbitals of Mn while the antibonding orbitals of the carbonyl group cis to the CF_3 group in the trans isomer (**V**) can interact with CF_3 only through a single d_π orbital of Mn [33]. The effect of CO trans to CF_3 would be at least twice as much as the cis carbonyl. Thus it is reasonable to suggest that the cis isomer (**IV**) has a higher C–F stretching force constant than the trans isomer (**V**) because the stronger π-acceptor ability of the carbonyl trans to CF_3 enhances the delocalization of the electron density in the anionic CF_3 group resulting in an increase of the C–F stretching force constant.

In order to quantify the difference in the ligand effect between the cis and trans isomers, we applied the previously reported "ligand effect constant" developed for predicting the carbonyl stretching force constants to the CF_3 stretching force constants. Timney [34] reported ligand effect constants for predicting the C–O stretching frequencies of mononuclear transition metal carbonyl compounds containing CO and other ligands based on the Cotton–Kraihanzel force field approximation [35–39]. Stretching force constants of CO in place of CF_3 are evaluated by using the empirical relationship

$$k_{CO} = k_d + \Sigma_L \epsilon_L^\theta$$

where k_d is the stretching force constant for an isolated $M(CO)$ unit with the appropriate number of d electrons and ϵ_L^θ are ligand effect constants which quantify the effect on k_d of adding a ligand L at an angle θ to the $M(CO)$ unit. The assumption of using this empirical relationship for the stretching force constant of CO in place of CF_3 is that the ligand effect is additive and linearly applicable to the stretching force constant of CF_3.

Values of stretching force constants of CO in place of CF_3 for five complexes are listed in Table 1 with the observed C–F stretching frequencies. The stretching force constant of CO in place of CF_3 is descending in the order of $I > IV > III > II > V$. The stretching force constant for the neutral molecule (I) is the highest, that for the cis isomer (IV) is higher than those for the five-coordinate anions (II and III), and that for the trans isomer (V) is the lowest. This ordering of stretching force constant among complexes I, II and III is in good agreement with the observed ordering of C–F stretching frequency. As shown in Fig. 3 plotting the C–F stretching frequencies as a function of k_{CO}, the cis isomer (IV) with a higher k_{CO} linearly fits to the stretching force constant–frequency relationship obtained with the other three complexes, whereas the trans isomer (V) shows even lower k_{CO} than the five-coordinate d^7 complex (II) and deviates significantly from linearity. Therefore, the cis isomer (IV) is considered to be responsible for the observed C–F stretching frequencies from the IR multiphoton dissociation spectrum of $CF_3Mn(CO)_4I^-$.

In conclusion, the C–F stretching mode of the CF_3 group bonded to the transition metal center, which is sensitive to the net charge of the complex and ligand substituents, is used to explore IR photochemistry of organometallic complexes. The observed C–F stretching frequency shift, combined with the previously reported "ligand effect constant", is a valuable guide in differentiating the structures of complexes.

TABLE 1

Stretching force constants and C–F stretching frequencies of CF_3X molecules

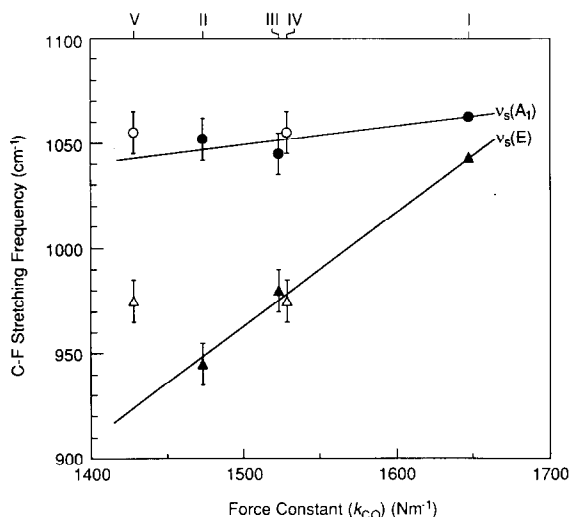| Molecule	d^n	k_{CO} (N m^{-1})	$\nu_s(A_1)$ (cm^{-1})	$\nu_s(E)$ (cm^{-1})
$CF_3Mn(CO)_5$ (I)	d^6	1647	1063	1043
$CF_3Mn(CO)_4^-$ (II)	d^7	1474	1052	945
$CF_3Mn(CO)_3(NO)^-$ (III)	d^8	1523	1045	980
cis-$CF_3Mn(CO)_4I^-$ (IV)	d^6	1529	1055	975
$trans$-$CF_3Mn(CO)_4I^-$ (V)	d^6	1428		

Fig. 3. The C–F stretching frequencies of CF_3X molecules as a function of the stretching force constant of CO in place of CF_3 obtained using ligand effect constants: circle, A_1-type symmetry; triangle, E-type symmetry. Solid symbols, refs. 13 and 14; open symbols, this work.

ACKNOWLEDGMENTS

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