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Charge-Transfer Interactions between Transition Metal Hexafluorides and Xenon[†]

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Received July 5, 1977

Abstract: Charge transfer transitions are reported for MF_6 (M = W, Mo, U, Re, Ir) with Xe. The nature of the charge transfer complexes is discussed. Based on spectroscopic data new estimates of MF_6 electron affinities are presented.

I. Introduction

In the course of spectroscopic studies of paramagnetic transition metal hexafluorides, it became apparent that additional information might be obtained if a high-symmetry host material for mixed crystals could be found. Such systems would be particularly useful for the study of the Γ_{8g} ($O_h{}^*$) states, in which the Jahn–Teller interaction is of particular interest.[1,2] It was thought that xenon might serve as a good host; it has no crystal vibrational frequencies in the range of intramolecular MF_6 vibrations, and size and orientation considerations indicate that MF_6 might go into the Xe lattice substitutionally. However, it was found that when IrF_6, which is yellow, is dissolved in liquid Xe, the solution is totally opaque, although purple in reflection. It is the purpose of this paper to demonstrate that the new absorption band for the IrF_6–Xe system is due to a low-lying intermolecular charge transfer (CT) transition between Xe and MF_6:

$$\mathrm{Xe} + \mathrm{MF_6} \xrightarrow{h\nu} \mathrm{Xe^+MF_6^-}$$

Such CT transitions and associated complexes with MF_6 are known,[3] but have not been previously observed for the rare gases.

Several experiments have been carried out to verify these conclusions and to increase understanding of this phenomenon. The absorption spectra of MF_6–Xe (M = Ir, Re, W, Mo, U) at liquid nitrogen temperature have been taken. An IrF_6–Kr sample and a gas-phase IrF_6–Xe sample were also prepared and investigated. Besides demonstrating the CT nature of the new transitions, these experiments also give valuable information on the exceptionally high electron affinities of the hexafluorides. Observation of "local" (intramolecular) IrF_6 transitions in the near IR also permits conclusions to be drawn concerning stability of the IrF_6–Xe complex.

II. Experimental Section

Handling of hexafluorides has been previously described.[1] Research grade xenon and krypton (Linde) were used and were further purified by distillation to remove any traces of H_2O, a very serious impurity for the hexafluorides.

Crystals were grown from the melt by suspending the sample cell a few centimeters above the surface of liquid nitrogen in a closed Dewar. Although crystals grown this rapidly (~20 min) are certainly not high-quality single crystals, they are of adequate quality to allow spectra to be taken. Visible and near-UV absorption spectra were taken on a McPherson 285 monochromator with photoelectric detection. Near-IR spectra were obtained on a McPherson 2051 with a 77K InAs (Texas Instruments) detector. Some preliminary spectra were also obtained on a Cary 17.

III. Theory

The theory of CT transitions and complexes is well known[4] and will be outlined only briefly here. For 1:*n* complexes (in this case *n* is either 12Xe or 1Xe), the energy of the CT transition is

$$h\nu_{\mathrm{CT}} = I_{\mathrm{d}} - E_{\mathrm{a}} + (G_1 - n'G_0) + (X_1 - n'X_0) \qquad (1)$$

in which I_{d} = ionization potential of the donor D (Xe), E_{a} = electron affinity of the acceptor A (MF_6), G_1 = "normal" interaction of D^+ and A^-, specifically neglecting the CT interactions, G_0 = "normal" interaction of D and A, X_1 = additional interaction between D^+ and A^- due to proximity of D–A configuration, X_0 = additional interaction between D and A due to proximity of the D^+–A^- configuration, n = number of donors in the complex, and in the limit of weak complexes, $n' = n$. For stronger complexes $n' < n$ due to saturation effects.[5]

X_0 can be approximated by second-order perturbation theory as

$$X_0 \sim -\frac{\beta_0{}^2}{\Delta} \qquad (2)$$

[†] Supported in part by the Office of Naval Research.

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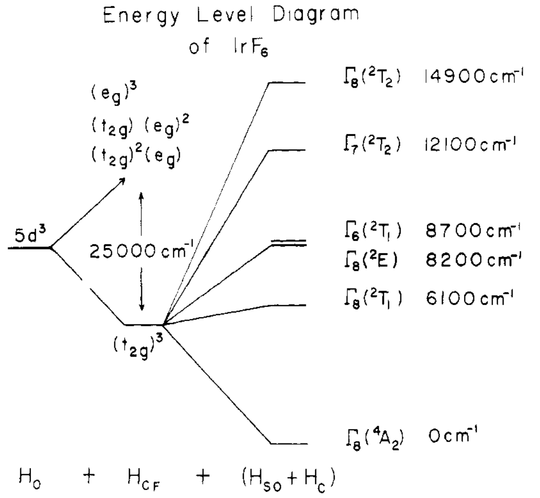

Figure 1. Energy levels of IrF_6. Rigorous symmetry labels (O_h*) for each electronic state are given along with the cubic Russell-Saunders state which correlates with the state for vanishing spin-orbit coupling. Since all the final states are gerade, the g label has been omitted in the right-hand column.

Table I. Onset Frequency for Inter- and Intramolecular Charge-Transfer Transitions [$\sigma_{CT}(MF_6\text{-}Xe)$, $\sigma_{CT}(MF_6)$] and Estimated Electron Affinities (E_a) for MF_6[b]

MF_6	$\sigma_{CT}(MF_6\text{-}Xe)$, cm^{-1}	$\sigma_{CT}(MF_6)$, cm^{-1}	E_a, kcal/mol
IrF_6	9 800	20 000	181
ReF_6	>22 000	22 000	<146
WF_6	36 600	52 000	(104)[a]
MoF_6	26 300	50 000	133
UF_6	>26 000	26 000	<134

[a] Reference 8. [b] A literature value for E_a (WF_6) is used in conjunction with eq 3 to determine the other E_a (MF_6) (see text).

Table II. Observable Near-IR Transitions of 0.1% IrF_6-Xe. Frequencies Are Determined to ±1 cm^{-1}

MF_6	Vacuum wavenumber, cm^{-1}	Fwhh, cm^{-1} [a]	Assignment
IrF_6	5724	205	$\Gamma_8(^2T_1)$
	6016	168	$\Gamma_8(^2T_1)$ + bv[b]
	6404		$\Gamma_8(^2T_1)$ + sv[c]
	6641		$\Gamma_8(^2T_1)$ + bv + sv
	7814	203	$\Gamma_8(^2E)$
	8036		$\Gamma_8(^2E)$ + bv
	8324	207	$\Gamma_6(^2T_1)$
	8575		$\Gamma_6(^2T_1)$ + bv

[a] Fwhh = full width at half height. [b] bv = bending vibrations (ν_4, ν_5, ν_6). [c] sv = stretching vibrations (ν_1, ν_2, ν_3).

Table III. Shifts in Near-IR Origins between Neat IrF_6 and 0.1% IrF_6-Xe

	Neat IrF_6, cm^{-1}	0.1% IrF_6-Xe, cm^{-1}	Δ, cm^{-1}
$\Gamma_8(^2T_1)$	6114	5724	−390
$\Gamma_8(^2E)$	8177	7814	−363
$\Gamma_6(^2T_1)$	8701	8324	−377

for which $\Delta = I_d - E_a + (G_1 - n'G_0)$ and $\beta_0 = \langle\psi(D,A)|\mathcal{H}|\psi(D^+,A^-)\rangle$.

For the purpose of estimating electron affinities, the following approximate equation is useful:

$$h\nu_{CT} = I_d - E_a + G_1 \qquad (3)$$

Location and character of excited electronic states of the donor and acceptor are of importance in more detailed considerations. The excited electronic states of Xe are so high in energy as to have a negligible effect in this regard and will be ignored here. The onset of intramolecular CT transitions for the hexafluorides is given in Table I. The lowest energy ligand-field states of IrF_6 are shown in Figure 1. Note that in the above considerations solvent effects have been neglected.

IV. Results

The onset frequencies of the intermolecular CT transition for ½% MF_6/Xe (l = 1 cm) are listed in Table I. The observed transitions are found to be broad (>10 000 cm^{-1}), featureless bands, as expected of a CT transition. The frequencies of the near-IR transitions of 0.1% IrF_6-Xe (l = 1 cm) are given in Table II; a comparison of IrF_6-Xe data and neat IrF_6 is given in Table III. The intensities of the near-IR transitions of IrF_6-Xe are estimated to be enhanced by two orders of magnitude over those of neat IrF_6. The band widths are increased by an order of magnitude over the observed band widths in neat IrF_6. Near-IR and visible spectra of gas-phase ½% IrF_6-Xe (10 Torr-L Xe, V = 10 mL, T = 300 K, l = 1 cm) and solid 0.01% IrF_6-Kr (l = 1 cm) show only the intramolecular CT transition at 20 000 cm^{-1} characteristic of IrF_6. Freezing the yellow gas-phase IrF_6-Xe mixture in liquid nitrogen gives an opaque-purple solid; warming the sample to the melting point of Xe gives an opaque-purple liquid which upon warming evaporates, leaving yellow solid IrF_6. With the evaporation of IrF_6, a pale yellow gas is obtained, leaving no residue behind.

V. Discussion

Plausibility of the intermolecular CT transition hypothesis

$$MF_6 + Xe \xrightarrow{h\nu} [MF_6^-Xe^+]$$

can be easily demonstrated. PtF_6 is known to chemically react with Xe,[6] the first step in the reaction being

$$PtF_6 + Xe \rightarrow PtF_6^-Xe^+$$

Since PtF_6 has a higher electron affinity (215 kcal/mol[7]) than the hexafluorides studied here, it is not unreasonable to suspect that the $MF_6^-Xe^+$ electronic configuration would be an excited state rather than the ground state as in PtF_6-Xe. A rough calculation can be used to demonstrate this point quite adequately. The frequency of the CT transition in IrF_6-Xe using eq 3 with I_d = 281 kcal/mol, E_a (IrF_6) ≥ 136 kcal/mol, $G_1 \sim -70$ kcal/mol, is found to be $h\nu_{CT} \leq 26\,000$ cm^{-1}.

Experimental verification of the CT transition hypothesis is given in Table I. These data indicate that E_a (IrF_6) > E_a (MoF_6) > E_a (WF_6), which agrees with the expected trends.[6] Estimates of the electron affinities of MF_6 are made in Table I. The best procedure for estimating these values seems to be to use E_a (WF_6) as determined by the collisional ionization method[8] and to estimate the others through the difference in the onset frequency of the intermolecular CT transition. The main source of uncertainty in this method is neglect of the interaction of the $MF_6^-Xe^+$ electronic configuration with the ground (MF_6Xe) and locally excited (MF_6*Xe) configurations. The latter might be more significant for IrF_6-Xe for which the CT transition occurs in the midst of the low-lying IrF_6 ligand field transitions (see Figure 1) and ~10 000 cm^{-1} from the intramolecular CT band of IrF_6.

Since CT transitions often imply the formation of a CT complex, it is of interest to determine if the MF_6–Xe system forms such complexes. The CT transition in IrF_6–Xe is the closest to the ground state; thus, it is expected that the IrF_6–Xe complex would be the most stable. The usual approach for determining stability of such complexes employs the method of Benesi and Hildebrand[4] to find the equilibrium constant for complex formation. However, the near-IR data obtained for solid IrF_6–Xe (Tables II and III) and the near-IR–visible data for gas-phase IrF_6–Xe allow a simpler, though perhaps more approximate, alternative method to be utilized.

The fact that there is no evidence of the IrF_6–Xe complex in the room temperature vapor indicates that the 1:1 complex is not strongly bound. The observed frequency shifts, increased line widths (see Table III), and intensity enhancements in the 0.1% IrF_6–Xe solid samples indicate that there is significant CT interaction between IrF_6 and Xe in the ground state. However, the solid state data pertain to an $IrF_6 \cdot 12Xe$ complex, whereas information on the 1:1 complex is of more intrinsic interest. Equation 1 and the assumption that the complex is weak enough to allow n' to be set equal to 12 provide an approximate relationship between the 1:12 and the 1:1 complexes.

The stabilization energy of the ground state $[12X_0(\Gamma_8(^4A_2))]$ of the $IrF_6 \cdot 12Xe$ complex can be estimated by assuming that eq 2 can be applied to the frequency shift data for the $\Gamma_8(^2T_1)$ state to find $\beta_0(\Gamma_8(^2T_1))$, and that $\beta_0(\Gamma_8(^4A_2))$ is roughly the same since both states stem from the $(t_{2g})^3$ configuration. These considerations lead to a value for $12X_0$ $(\Gamma_8(^4A_2))$ of $\sim$300 cm^{-1}. The stabilization energy of the ground state $X_0(\Gamma_8(^4A_2))$ of the 1:1 complex is then $\sim$25 cm^{-1}. One would certainly expect this to be a lower limit since saturation effects[5] have not been taken into account. The original assumption that the ground state complex is weak thus appears well justified.

The general picture that emerges for these weak charge transfer complexes between Xe and MF_6 molecules is then as follows. The ground state is neutral probably with a shallow broad potential minimum somewhere near $r^\circ \sim 4$ Å, the Xe–Xe approximate distance in a crystal lattice or a liquid. It is possible that there are a few vibrational quanta in this well but this is not a necessary condition imposed by our data. The excited state potential well is much deeper and more narrow, and the potential minimum is such that $r^*(MF_6{}^-Xe^+) < r^\circ(MF_6Xe)$. These considerations also account nicely for the very broad (>10 000 cm^{-1}) Franck–Condon envelope observed for the CT transitions in all systems.

VI. Conclusion

The new electronic transitions which appear when certain transition metal hexafluorides are dissolved in liquid xenon can be assigned as intermolecular charge-transfer transitions. The concomitant charge-transfer complexes are weakly bound.

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Flash Kinetic Spectroscopic Studies of Dinuclear Rhodium(I) Complexes

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Received April 11, 1977

Abstract: Excitation of concentrated acetonitrile solutions of $[Rh(tol)_4]PF_6$ (tol is *p*-methylphenyl isocyanide) at 562 nm, where strong absorption attributable to $[Rh_2(tol)_8]^{2+}$ occurs, produces emission (λ_{max} 697 nm) with a quantum yield of 0.0065 and a lifetime of ≤2 ns. Excitation of $[Rh_2(bridge)_4](BPh_4)_2$ (bridge is 1,3-diisocyanopropane) in acetonitrile solution at 553 nm gives emission at 656 nm with a quantum yield of 0.056 and a lifetime of ≤2 ns. The emission is assigned to $^1A_{2u} \rightarrow {}^1A_{1g}$ $(2a_{1g} \rightarrow 1a_{2u})$ in both dinuclear Rh(I) complexes. Excitation also gives rise to long-lived transient absorptions attributable to the following dinuclear and trinuclear species: $\sim$8 μs, $Rh_2(bridge)_4{}^{2+}$; 0.09 μs, $[Rh_2(tol)_8]^{2+}$; and 0.14 μs, $[Rh_3(tol)_{12}]^{3+}$. In the dinuclear complexes, this transient is most likely $^3A_{2u}$, which is the triplet excited-state partner of $^1A_{2u}$. The results suggest that the spin-orbit components of $^3A_{2u}$ possess very little singlet character.

Introduction

In recent work it has been established[2-4] that planar Rh(I) isocyanide complexes oligomerize in solution, through formation of weak metal-metal bonds. The oligomerization can be followed conveniently by monitoring electronic absorption spectra, as transitions attributable to dimers, trimers, and higher oligomers occur at progressively lower energies. As part of our continuing study of the physical and chemical properties of Rh(I) oligomers, we have performed flash kinetic spectroscopic experiments on solutions of $[Rh(tol)_4]PF_6$, where tol is *p*-methylphenyl isocyanide, and on the dinuclear complex, $[Rh_2(bridge)_4](BPh_4)_2$,[3] where bridge is 1,3-diisocyanopropane.

0002-7863/78/1500-0485$01.00/0