Luminescence of Ion-Pair States of Halogens in Liquid Perfluorocarbons.

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ABSTRACT: The I2(D′→A′) luminescence in liquid C7F16, C8F18, C9F20, and C12F26 has been observed following irradiation with visible (within the I2 X → B band region) and UV (λ < 300 nm) lasers. The band is shifted by ~2000 cm⁻¹ to the red relative to the gas phase and is significantly broader (fwhm ≈ 3000 cm⁻¹ vs 500 cm⁻¹ in the gas phase). Two-color excitation of other halogens in C6F2n+2 solvents revealed similarly shifted and strongly broadened D′→A′ bands of Br2, IBr, and BrCl. The stability of the ion-pair states of halogens in room temperature liquids opens new experimental opportunities for condensed phase studies and may be of applied interest considering the increasing industrial applications of perfluorocarbons.

1. INTRODUCTION

The I2 molecule has strongly bound ion-pair states correlating to 1P → 1D + 1S dissociation asymptotes. These states may be accessed optically by one photon absorption from the ground state or via the intermediate valence state I2(B) using optical–optical double resonance,

I2(X 0⁺g) + hν₁ → I2(B 0⁺u) + hν₂ → I2(E 0⁺g)

When an ion-pair state is excited in a mixture with gaseous or condensed rare gases, interactions with the environment transfer population to the lowest ion-pair state D′ 2g, which decays radiatively to the valence A′ 2g state. In pump–probe studies of energy relaxation processes, the I2(D′ → A′) transition provides a monitor of transient population in the B state. On the other hand, solvation of I2 D′ in condensed Rg gases is of interest in its own right and has been the subject of several experimental and theoretical investigations.

Perfluorocarbons (PFC), C6F2n+2, are known as inert solvents, which weakly interact with the excited states of the solute molecules. Early studies revealed exceptionally small solvation shifts in PFC in comparison with other molecular solvents, including in particular linear hydrocarbons C6H2n+2.

I2 is weakly soluble in the perfluorocarbons, and upon addition of I2 crystals the originally colorless liquids acquire a faint violet color. It is known from early studies that the solution color depends on the strength of interaction between I2 and solvent molecules. The interaction with C6F2n+2 is very weak as evidenced by the fact that the envelope of I2(X → B) absorption band in these solvents is nearly the same as in the gas phase.

In this contribution we report on studies of halogen in C6F2n+2, n = 7–9,12, liquids using the optical–optical double resonance technique. Observation of I2(D′→A′) luminescence in PFC solvents has been briefly reported in ref 14. This contribution discusses studies of iodine in PFC solvents in detail and reports on the observation of the D′→A′ luminescence bands of Br2, IBr, and BrCl in PFC solvents. Stability of the ion-pair states of halogens in room temperature liquids opens new experimental opportunities for condensed phase studies and is of applied interest considering the increasing industrial applications of perfluorocarbons.

2. EXPERIMENTAL SECTION

The I2(D′) luminescence was observed following simultaneous irradiation with visible (within the X → B band region) and UV (λ < 300 nm) lasers. The visible laser was either the second harmonic of a Nd:YAG laser (Quantel, YG 980E-10), 532 nm, or the fundamental output of a dye laser (Quantel TDL-90), and the UV beam was the frequency doubled output of the dye laser. Samples were contained in a 1 cm quartz cell positioned in front of the entrance slit of a 0.5 m Acton Research SP500i monochromator. Time-resolved luminescence spectra were recorded using an Andor Technologies iStar DH720 iCCD (intensified charge coupled device) detector. Details of the optical arrangement and detection system have previously been presented.

The measurements on the solutions of other halogens in PFC liquids were performed using a Lambda Physik laser...
system consisting of a LEXTRA50 excimer laser pumping an LPD3002 tunable dye laser. In these experiments, the visible fundamental of the dye laser (typically in the 500 nm region) was used in combination with the UV beam obtained by frequency doubling. In some of the experiments, a small fraction of the XeCl pump laser beam ($\lambda = 308$ nm) was used instead of the second harmonic. Spectra were recorded using an Acton 0.30 m SP-300i scanning monochromator equipped with a 955 Hamamatsu photomultiplier.

3. RESULTS AND DISCUSSION

Figure 1 shows the electronic states of the I$_2$ molecule discussed in the present work. Luminescence spectra of I$_2$ in liquid PFC following two-color laser excitation are shown in Figure 2a. The spectra display two bands at 370 and 560 nm attributed to the D$'\rightarrow$A transitions in the gas phase and in solutions.

![Figure 1](Image 106x403 to 255x592)

**Figure 1.** Potential curves of some electronic states of the I$_2$ molecule. The dashed curves schematically show potential curves in solution. In contrast to the ion-pair states, the valence states in condensed environment have no dipole moment, and for the equilibrium I$_2$(D$'\rightarrow$PFC liquids is red degraded implying that in the Franck–Condon region the I$_2$(A$'\rightarrow$C$_n$F$_{2n+2}$ interaction is repulsive. The vertical dotted lines schematically show D$'\rightarrow$A$'$ transitions in the gas phase and in solutions.

![Figure 2](Image 343x269 to 546x422)

**Figure 2.** (a) Luminescence spectrum following two photon excitation ($\lambda_1 = 595$ nm and $\lambda_2 = 297.5$ nm) of I$_2$ dissolved in (1) C$_8$F$_{18}$ at $T = 300$ K (spectrum in C$_8$F$_{18}$ solvent is identical in the scale of plot), (2) C$_{13}$F$_{26}$ at $T = 300$ K, and (3) C$_3$F$_{16}$ at $T = 360$ K (spectra in C$_3$F$_{16}$ and C$_{13}$F$_{26}$ solvents at this temperature have nearly identical shape). The feature marked with $*$ is the scattered laser light. (b) Luminescence spectra of (1) gas phase mixture of I$_2$ with C$_3$F$_{16}$, P = 1 bar, and (2) pure C$_3$F$_{16}$ liquid, one photon excitation $\lambda$ = 286.615 nm.

![Figure 3](Image 365x523 to 524x749)

**Figure 3.** Intensity of D$'\rightarrow$A$'$ luminescence as a function of time following two photon excitation ($\lambda_1 = 595$ nm and $\lambda_2 = 297.5$ nm) of I$_2$ in C$_3$F$_{16}$, C$_{13}$F$_{26}$ solutions, I$_2$ + Ar gas phase mixture (P$_{I_2}$ ≈ 0.3 mbar, P$_{Ar}$ = 1.5 bar) at $T = 300$ K. Results for C$_9$F$_{18}$ and C$_{13}$F$_{26}$ solvents at this temperature have nearly identical shape. The feature marked with $*$ is the scattered laser light.
Along with experiments at room temperature, solutions were also studied at elevated temperatures, including solution in C12F26, which melts at T = 350 K. Experiments showed that the D′ → A′ band has a nearly identical shape as in C8F18 and C9F20 solvents at the same temperature (Figure 2a). The D′ state lifetime is also approximately the same. When a solution of iodine in C12F26 is cooled, its color changes from violet in the liquid to brown in the solid state. A similar effect was observed upon cooling solutions of I2 in C6F14 and C8F18 below the freezing point. Two-color excitation of I2 in C8F18 solids (n = 7–9, 12), prepared by cooling liquid solutions, yields no D′ luminescence. The effect of temperature on color of iodine solutions has been known for a long time.11 A further study of this effect for iodine solutions in perfluorocarbons appears of interest.

Following successful observation of the I2(D′) luminescence, we studied solutions of other halogens in PFC liquids. A spectrum of Br2 in the C8F18 solvent is shown in Figure 4a. Like the case of I2 (Figure 2), the spectrum displays a shifted and broadened band assigned to the Br2(D′ → A′) transition. The shift relative to the gas phase is 2000 cm⁻¹, that is, approximately the same as for I2(D′ → A′). Figure 3b shows spectra recorded after adding I2 to saturated Br2 solution in C8F18. Along with the D′ → A′ bands of I2 and Br2, spectra display a new broad band at 440 nm assigned to the IBr(D′ → A′) transition. Finally, the spectrum in Figure 3c was recorded after bubbling Cl2 gas through a saturated Br2 solution. A broad band at 375 nm is assigned to BrCl(D′ → A′) transition. However no ClI(D′ → A′) luminescence in the PFC solvents was observed in the present experiments. Search for ICl(D′ → A′) luminescence was also unsuccessful. It should be noted that the present test experiments were conducted within a short time span and were mainly aimed to confirm the stability of the D′ state of other halogens in PFC solutions. A more systematic study would likely yield a wealth of new, interesting results.

4. SUMMARY AND OUTLOOK

The present study has shown that chemically reactive high-lying ion-pair states of halogens are stable with respect to chemical reaction and fast predissociation in liquid perfluorocarbons at room temperature. Along with the exceptional chemical inertness, a peculiar property of PFC liquids is their transparency in the UV and Vac UV regions, which extend down to 160 nm.17 The absorption spectrum of I2 vapor in the Vac UV displays a broad quasi-continuum in the 175–210 nm region corresponding to the transition to the ion-pair state D′.18 and test experiments have already demonstrated population of the D′ state following one photon excitation in this spectral region.19

The stability of the ion-pair states in room temperature liquids enables the application of the pump–probe method supplemented with sensitive luminescence detection techniques to study energy relaxation in the valence states, recombination of halogen atoms following photodissociation via excitation to a repulsive valence state, long-range photoinduced charge-transfer between atoms, and solvation dynamics. An applied aspect of the present study concerns the lasing properties of the D′ → A′ transition. An optically pumped I2(D′ → A′) gaseous laser has been demonstrated many years ago.20 The large spectral width of the charge-transfer bands of halogens in PFC solvents and their bound–free character (due to repulsive guest–host interaction in the lower state) make these solutions potentially interesting as novel media for tunable lasers, pulse amplifiers, and broad band luminophors.

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