Absorption Spectra of Intermolecular Charge-Transfer Transitions between Xenon and Halogen Molecules \((\text{F}_2, \text{Cl}_2, \text{Br}_2)\) in Liquid Xenon

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The intermolecular charge-transfer transitions between molecular halogens, \(X_2\), and \(\text{Xe}\) can be observed in UV spectra of \(\text{Xe}:X_2\) liquid solutions \((X_2 = \text{F}_2, \text{Cl}_2, \text{Br}_2)\). In all cases the spectra occur near the UV cutoff of the spectrometer \((187 \text{ nm})\). The absorption coefficients at 200 nm are \(6.9 \times 10^{-18}, 1.2 \times 10^{-18}\), and \(2.0 \times 10^{-18} \text{ cm}^2\) for \(\text{F}_2\), \(\text{Cl}_2\), and \(\text{Br}_2\), respectively. Implications with respect to one-photon- and two-photon-induced cooperative photoproduction of rare gas halides in gas and condensed phases are discussed.

**Introduction**

Gas-phase laser-assisted reactions of halogens, \(X_2\), with rare gas atoms, \(\text{Rg}\), to yield the rare gas halides

\[
\text{Rg} + X_2 + h\nu \rightarrow \text{Rg}^*X_2^* \rightarrow \text{Rg}^*X^+ + X
\]

(1)

were among the first systems advanced as models for the study of radiative collisional processes\(^1\) and were subsequently demonstrated experimentally by several groups.\(^2-5\) Even in the case of xenon as the rare gas atom, to which all of the studies to date have been limited, the accepted thresholds for these photoinduced halogenating processes is in the vacuum-UV.

The two-photon version of the same process

\[
\text{Rg} + X_2 + 2h\nu \rightarrow \text{Rg}^*X_2^* \rightarrow \text{Rg}^*X^+ + X
\]

(2)

is then more convenient for study with readily available radiation sources and has been characterized in both bulb studies\(^6\) and \(\text{Xe}:X_2\) \((X_2 = \text{Cl}_2 \text{ or Br}_2)\) van der Waals complexes formed in molecular beams.\(^7\)

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The two-photon reaction of eq 2 for \( R_g = Xe \) and \( X_2 = Cl_2 \) and \( HCl \) has also been studied in rare gas matrices and liquid solutions. The studies have since been extended to \( X_2 = F_2, Br_2, HBr, \) and \( R_g = Xe \) and \( Kr \) (solid and liquid). The anticipated enhanced cross sections (due to large number densities of \( R_g \) and \( X_2 \) complexes) and the lowering of photon thresholds (due to solvation of the charge-transfer complex by the polarizable medium) were verified. The condensed-phase studies are particularly interesting since they provide a means of studying many-body dynamics. Moreover, due to the large exciplex densities created in these processes, the mechanisms of eq 1 and 2 may serve as a general scheme for optically pumped condensed-phase exciplex lasers.

A knowledge of the optical threshold for these charge-transfer transitions is obviously of great interest. In the past this has been estimated based on theoretical grounds. The simplicity of the system clearly yields itself to reliable estimates. Yet there is wide discrepancy between the observed and rationalized thresholds. To estimate the threshold wavelengths for these cooperative transitions, a knowledge of the vertical electron affinities of the halogens is necessary. The most reliable source of vertical electron affinities is charge-transfer absorptions in electron-donating solvents. Such studies were initiated by Mulliken and have been recently revised to produce the most complete set of \( X_2^- \) potentials.

The charge-transfer transitions between xenon and molecular halogens can be directly observed in UV absorption spectra of \( Xe \) solutions. These spectra are presented and discussed in this report. Their relevance to the condensed-phase studies is direct; the data also shed light on the gas-phase studies. Extension of these studies to the vacuum-UV could provide the clearest source of \( X_2^- \) ground- and excited-state potentials.

Experimental Section

Spectra were recorded with a Perkin-Elmer 330 UV–vis spectrometer with a UV cutoff at 187 nm. The onset of atmospheric absorptions results in a usable spectral region extending down to approximately 195 nm.

The following gases, with their stated purities, were used without further purification: xenon (Cryogenic Rare Gas, Research Grade), 99.995%; chlorine (Matheson, Research Grade), 99.96%; 10% fluorine in helium (Spectra Gases). In addition, bromine (Aesar, 99.9%) was subjected to one vacuum distillation over barium oxide.

The solutions were prepared in a high-pressure cryocell kept at 205 K; the design of the cell has been previously described. The cell was first partially filled with liquid xenon, after which a fixed volume of a gaseous \( Br_2-Xe \) mixture of known \( Br_2 \) concentration was admitted. Finally, the remaining volume of the cell was filled with liquid xenon.

Absorption spectra of the halogens were recorded both in the gas phase and in liquid xenon solution. Concentrations of gas-phase samples were calculated simply from the cell temperature (205 K) and the sample pressure, as determined with an MKS Baratron. Prior to scans of halogen-liquid xenon solutions, a scan of pure liquid xenon was obtained to serve as a background.

The major source of error in the reported solution-phase cross sections involves determining the halogen concentration in liquid xenon. This is due to the fact that a fraction of the halogen molecules added to the cell in the course of sample preparation adsorb on the cell walls as evidenced by a gradual drop in halogen pressure with time. When liquid xenon is added to the cell, some adsorbed halogen molecules may dissolve along with those that were in the gas phase. Considering the relatively low concentrations employed in the present experiments (as necessitated by the relatively large cross sections measured), dissolution of adsorbed species may be significant.

Since both \( Br_2 \) and \( Cl_2 \) possess molecular absorptions in the visible (peaking around 420 and 330 nm, respectively) which are sufficiently strong to be observed at the solution concentrations employed, a knowledge of the cross sections for these transitions could be used to determine accurate solution-phase concentrations. To a first approximation, the gas-phase cross sections for \( Br_2 \) and \( Cl_2 \) can be expected. However, the gas-phase cross sections would only be expected to approximate the actual solution-phase cross sections. Minimally, it would be expected that the solution-phase cross section would differ from the gas phase due to the differences in dielectric constant of the medium. The nature of the correction term is of the well-known form: \[
\frac{1}{n} \left[ \frac{n^2 + 2}{3} \right]^{12}
\]

where \( n \) is the index of refraction of the medium. For liquid xenon this predicts an enhancement of 22% in the absorption cross section versus the gas phase.

Obviously, an exact determination of the solution-phase visible cross section requires an exact knowledge of the solution-phase concentration of the halogen which is fraught with the previously indicated problems. Nevertheless, more accurate measurements of concentrations can be made for more concentrated solutions. This has been done for \( Cl_2 \), and the peak extinction coefficient of the visible absorption of \( Cl_2 \) in liquid Xe (at 327 nm) is found to increase by 35%, versus the gas phase. This measured liquid-phase cross section is thus within ~10% of that predicted by simply multiplying the gas-phase cross section by the dielectric correction.

Thus, the \( Cl_2 \) and \( Br_2 \) concentrations used in calculating solution-phase cross sections at 200 nm were determined by using the intensity of the visible transitions in the liquid phase and reported gas-phase cross sections for these transitions corrected for the dielectric effect of liquid Xe. This procedure is expected to produce a lower limit for the reported 200-nm solution-phase cross section.

Fluorine possesses a weak molecular absorption near 300 nm. At the concentrations of \( F_2 \) employed in this study, the strength of this transition is not accurately measurable. Thus, the concentration of \( F_2 \) in \( F_2-Xe \) liquid xenon solution was estimated based on the pressure of \( F_2-Xe \) mixture used. Assuming complete passivation of the cell and complete solubility of all gas-phase \( F_2 \), one obtains an upper limit for the 200-nm cross section of \( F_2 \) in liquid xenon using this concentration.

Results and Discussion

Spectra of \( X_2 \) and \( X_2-Xe \) solutions (\( X_2 = F_2, Cl_2, Br_2 \)) are collected in Figure 1. In all cases, upon addition of xenon a very intense absorption is observed near the UV limit of the spectrometer (upper traces in Figure 1). The fact that this absorption is absent in the halogens and that there are no xenon absorptions in this spectral range clearly establishes that the absorption is due to an intermolecular transition between \( X_2 \) and \( Xe \). Since in none of the cases is it clear that the absorption maximum is observed, we report the absorption cross sections at 200 nm. They are 6.9

Transitions between Xenon and Halogen Molecules


Figure 1. UV-vis spectra of F$_2$ (a), Cl$_2$ (b), and Br$_2$ (c) in liquid xenon solution (upper traces) and in the gas phase (lower traces). Gas-phase concentrations are $1.8 \times 10^{17}$, $1.0 \times 10^{17}$, and $4.2 \times 10^{17}$ molecules/cm$^3$ for F$_2$, Cl$_2$, and Br$_2$, respectively. Solution-phase concentrations are estimated (see text) to be $4.5 \times 10^{16}$, $5.3 \times 10^{16}$, and $1.4 \times 10^{16}$ molecules/cm$^3$ for F$_2$, Cl$_2$, and Br$_2$. The cell path length is 3.81 cm.

Figure 2. Cl$_2$(1$^1\Sigma^+$) and Cl$_2$(2$^2\Sigma^+$) potentials according to Chen and Wentworth (ref 13) are shown. The vertical electron affinity from $v = 0$ of Cl$_2$ obtained in the reflection approximation is shown along the ordinate. X$_lo$ = 1.2, 2.0, and 3.0 for Xe:F$_2$, Xe:Cl$_2$, and Xe:Br$_2$, respectively. Such intense absorptions are characteristic of charge-transfer transitions. It can be safely assumed that the observed portion of the spectrum is at best half the entire band; thus, lower limits on oscillator strengths can be established as

$$f \geq 1.202 \times 10^{12} \Delta \lambda / \lambda_{\text{max}}^2$$

in which $\Delta \lambda$ corresponds to the full width at half-maximum (2 $\times$ hwhm). It can then be estimated that $f \geq 0.01, 0.017$, and 0.05 for Xe:F$_2$, Xe:Cl$_2$, and Xe:Br$_2$, respectively. For a single-electron transition in which a full charge is transferred an oscillator strength of near unity is to be expected. It is then difficult to establish whether the true maximum is observed in any of the spectra based on the estimated minimal oscillator strengths.

We may estimate the maxima in these charge-transfer transitions and their expected minimal widths based on simple arguments. For a Xe:X$_2$ pair at contact distance $r_c$, the optical transition energy is given as

$$E_{\text{opt}}(r_c) = IP(Xe) - EA'(X_2) + \Delta V(r_c)$$

in which $EA'(X_2)$ is the vertical electron affinity of the molecular halogen and $\Delta V(r_c)$ is the difference in ionic excited-state and neutral ground-state potentials.

The vertical electron affinities of all molecular halogens are broad, since the $v = 0$ of the neutral ground state $X_2(\Sigma_u^+)$ maps out the repulsive wall of the negative ion ground state, $X_2^- (\Sigma_u^-)$. The pertinent potentials for Cl$_2$, taken from ref 13, are shown in Figure 2. The vertical electron affinity distribution, calculated as a reflection of the $v = 0$ harmonic wave function on the $3\Sigma^-_g$ potential, is shown along the ordinate. The calculated electron affinities of all three halogens by the same method, including all thermally populated states at 200 K are shown in Figure 3. In all cases both negative and positive electron affinities are possible due to the crossing of the $3\Sigma^-_g$ repulsive wall with the $v = 0$ wave function in $X_2$. The breadths of these distributions are mainly a reflection of the steepness of the $X^-_2$ repulsive wall.

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The last term in eq 4 is the difference between excited state and ground state of the pair at contact. The ground state can be calculated as a sum of pairwise additive contributions in the liquid phase. The upper state is dominated by the Coulombic interaction between the charged pair; however, a contribution due to Cl$_2$−Xe and Xe$^+$−Xe van der Waals potentials is also present. Little error is made by ignoring the van der Waals energies in both states since they nearly cancel each other and individually
they are a minor contribution to the overall energies.\(^{17}\) Thus, \(\Delta V(r_o)\) can be reduced to

\[
\Delta V(r_o) = V(Xe^+X_2^-) - \left( \frac{\epsilon^2}{r_o} - \frac{8(\epsilon - 1)}{(2\epsilon + 1)} \right) d^3
\]

(5)

in which only the Coulombic attraction between \(Xe^+\) and \(X_2^-\) and the solvation of the \(Xe^+X_2^-\) dipole in a continuum dielectric are retained \((d = \text{diameter}, \mu = \text{molecular dipole})\). If we further make the assumption that \(d = 2r_o\) and that \(\mu = \epsilon r_o\) \(\Delta V(r_o)\) can be estimated. Using for \(r_o\) the sum of van der Waals radii, we can calculate \(E_{\text{m}}\) of eq 4. These estimates are collected in Table 1.

The agreement between estimated maxima and the observed spectra is acceptable given the very crude approximations that were made. The UV cutoff of the spectrometer is predicted to be very near the band maxima. The true bandwidths should be as large as the vertical electron affinity distributions, \(-4\text{ eV}\) in the case of \(Xe^+F_2^-\). There should be further broadening on the blue edge due to the distribution of \(Xe^+X_2^-\) distances. A convolution of \(E_{\text{m}}\) of eq 4 over the \(X_2^-\)-\(Xe\) radial distribution, weighted by the distance-dependent transition dipole, is the most appropriate representation of the experimental line shape. In the absence of a more complete spectrum such a treatment is not warranted.

The observation of these contact charge-transfer absorption thresholds and a knowledge of their expected minimal widths have significant implications with respect to photoinduced exciplex formation in condensed phases, in the gas phase, and in \(X_2^-\)-Rg complexes or clusters.\(^{8-10}\) The implications with respect to liquid-phase exciplex formation is obvious. All halogens in liquid xenon at 200 K, calculated from the known saturated liquid density of xenon at 200 K.

**Conclusions**

Intense charge-transfer transitions between xenon and \(X_2\) \((X_2 = F_2, Cl_2, Br_2)\) are observed in \(X_2\)-\(Xe\) solutions. These absorptions occur near the UV cutoff of our spectrometer; nevertheless, it is believed that the absorption maxima are near this cutoff \((-187\text{ nm})\). The peak positions are justified based on solvation of the charge-transfer complex in the polarizable liquid. It is, however, clear that due to the broad distribution of electron affinities, the charge-transfer bands of all \(Rg^+X_2^-\) \(\rightarrow RgX_2\) absorptions overlap. Since the solvation energies of all \(Rg^+X_2^-\) complexes in a given solvent are similar \((-0.5\text{ eV for }Xe\)) the latter conclusion should hold for the gas phase also. Extended vacuum-UV spectra of these solutions would be indeed useful for the determination of \(X_2^-\) ground and excited potentials. Due to the simplicity of the atomic solvents, rigorous analysis of such spectra via radial distribution functions should be possible. The latter would yield the effective many-body \(Rg^-X_2^-\) intermolecular potentials. The same absorptions should be detectable in the gas phase since a large fraction of the halogens in \(X_2\)-\(Xe\) mixtures should be complexed.

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**Registry No.** Xe, 7440-63-3; F\(_2\), 7782-41-4; Cl\(_2\), 7782-50-5; Br\(_2\), 7726-95-6.