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TWO-PHOTON LASER-ASSISTED REACTIONS OF Xe WITH HALOGEN CONTAINING MOLECULES⁽¹⁾

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The two-photon, laser-assisted reactions between Xe (or Kr) and several halogen containing molecules have been observed by focusing the output of a pulsed dye-laser into dilute gas mixtures of Xe and the reagent. The occurrence of the reaction is detected from the B-X fluorescence of the XeCl⁺, XeBr⁺ and XeI⁺ products. Results from studies with SOCl₂, CCl₄, CCl₃Br, CCl₂Br₂, Br₂ and I₂ are emphasized. In some instances the utilization of laser pulses of different frequency to drive the reaction enhanced the two-photon cross section, relative to one-color experiments, because of a more favorable energy resonance with the one-photon RX^{*} intermediate state. Direct excitation from bound and free Xe/RX pairs on the van der Waals potential to the ion-pair, Xe⁺RX⁻, reactive potential explains most aspects of these laser-assisted reactions. One application of these laser-assisted reactions is as a very rapid generation source for XeCl⁺ and KrF⁺ molecules in order to study their quenching and relaxation kinetics.

The two-photon, photo-excitation of Xe⁺⁵ and halogen (X) containing molecules (RX) to the reactive ion-pair potential, V(Xe⁺;RX⁻), has now been documented with more than 15 molecules. Upon reaching the ion-pair potential, the expected bimolecular reaction occurs with formation of XeX(B,C) + R. In addition to the Xe reactions, the laser-assisted reactions (LAR) between Kr and halogen molecules also are possible and two examples are Kr/F₂ and Kr/CCl₄.² The LAR of Kr/RX requires shorter wavelength because the laser ionization energy of Kr raises the V(Kr⁺;RX⁻) relative to V(Xe⁺;RX⁻). The two-photon cross section is greatly enhanced by an intermediate RX^{*} resonance state and in general the LAR of Xe/RX requires a RX^{*} state.³ For this reason two-color, two-photon LAR is much easier to accomplish, unless the intermediate state fortuitously lies midway between the ground van der Waals potential and the reactive ion pair potential. A summary of the systems that have been studied in our laboratory for dilute gas conditions is given in Table I.^{2,3}

The single color, two-photon LAR for Xe/Cl₂ and Xe/ClF is very facile in dilute gases (10-50 Torr of Xe and 1-3 Torr of Cl₂) for laser pulses of 1 mJ focused with a 0.5 m lens.^{1,4} The excitation spectra are unstructured bands with half-widths of ~ 0.3 eV. However, the single color LAR for Xe/Br₂ and Xe/I₂ is very difficult to observe, even though the V(Xe⁺;Br₂⁻) and V(Xe⁺;I₂⁻) ion-pair potentials are known.^{1,4} This puzzle has been resolved by the use of two-color, two-photon excitation.³ If one laser is tuned to the Br₂(X-A(¹Π_g)) absorption band in the 440-510 nm range and the frequency of the second laser adjusted to match the energy required to reach V(Xe⁺;Br₂⁻), LAR giving XeBr(B,C) is easily observed. In practice the same dye laser was used for the two colors and the fundamental plus the doubled outputs of the laser were focused into the laser cell. The same strategy was used for Xe/I₂, and LAR giving XeI(B,C) was observed for excitation at 455.0 + 227.5 nm.³ The maximum in the excitation spectra for Xe with diatomic halogens is fixed by the vertical electron affinity of X₂ and the position of the minimum on the van der Waals potential. The width

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TABLE 1 SUMMARY OF LASER ASSISTED REACTIONS

| Systems | One-color | Two-color | Systems | One-color | Two-color |
|-------------------------------------|-----------|-----------|-----------------------------------|-----------|-----------|
| Xe/Cl ₂ | yes | | Xe/CClHBr ₂ | yes | yes |
| Xe/ClF | yes | | Xe/CBr ₄ | yes | yes |
| Xe/F ₂ | yes | | Xe/CHBr ₃ | yes | yes |
| Xe/Br ₂ | no | yes | Xe/CFBr ₃ | yes | yes |
| Xe/I ₂ | no | yes | Xe/CH ₂ I ₂ | yes | yes |
| Xe/SOCl ₂ | yes | | Xe/CH ₃ I | weak | |
| Xe/CCl ₄ | yes | yes | Xe/CF ₃ I | weak | |
| Xe/CCl ₃ Br | yes | yes | Kr/F ₂ | yes | |
| Xe/CCl ₂ Br ₂ | yes | yes | Kr/CCl ₄ | yes | |

of a spectrum is largely determined by the gradient of the potential in the R(X-X) coordinate. Thus, the excitation spectra for LAR provide a way to probe the properties of the radical anion.

The SOCl₂, CCl₄, CCl₃Br, and CCl₂Br₂ molecules have one-photon intermediate states with absorption beginning about 280 nm. One-photon LAR is observed in each case for mixtures of ≥ 10 Torr Xe and ≥ 2 Torr of reagent.³ The two-color experiments gave somewhat higher product yields than one-color experiments, in part because of higher laser pulse energy for the fundamental dye laser pulse, but also the intrinsic cross section seems larger.³ The one-color excitation spectra for SOCl₂ and CCl₄ are shown in Figure 1. These are shifted to shorter wavelengths than for Cl₂ or ClF because (i) The $R_e(Xe-CCl_4)$ is larger in the lower state than for $R_e(Xe-Cl_2)$, and (ii) The EA(CCl₄) is smaller than for Cl₂. The increased breadth and apparent broad structure in the excitation spectra probably reflect the availability of electronically excited radical anion states, as well as a larger range of Franck-Condon factors for the polyatomic systems.

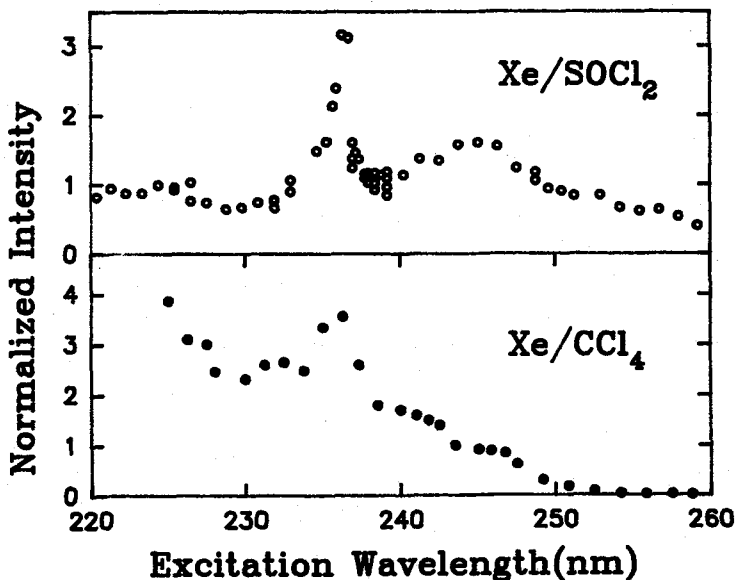


Figure 1. The two-photon, single-color excitation spectra for the LAR of CCl₄ and SOCl₂.

The CCl₃Br and CCl₂Br₂ reactions are especially interesting because both XeCl(B,C) and XeBr(B,C) can be formed. The full collision of Xe(6s,³P₂) with CCl₃Br₂ and CCl₃Br favors XeBr(B,C) by ratios of $\sim 5/1$ and $2/1$, respectively. This is the expected result because the ground state of CCl₃Br⁻ has the extra electron in the C-Br antibonding orbital.^{6,7} Since XeBr(B,C) + CCl₂Br is the most exoergic channel (by ~ 0.3 eV), the XeBr(B,C) channel correlates directly to the

ground state of the radical anion. The $\text{XeCl(B,C)} + \text{CBr}_2\text{Cl}$ channel correlates to an excited radical anion state. The electron attachment data⁶ show that two excited CCl_3Br^- states exist and these are expected to have more electron density on the Cl atoms. The product fluorescence spectrum from a one-color (253 nm) LAR experiment is shown in Figure 2A; the XeCl(B,C) product is strongly favored, in contrast to the Xe(6s) reactions. These data provide a clear demonstration that controlling the initial conditions of a bimolecular reaction can greatly affect the end result, not only for energy distributions, but also the chemical product branching. The LAR results for CCl_2Br_2 , not shown here, are very similar to those for CCl_3Br .

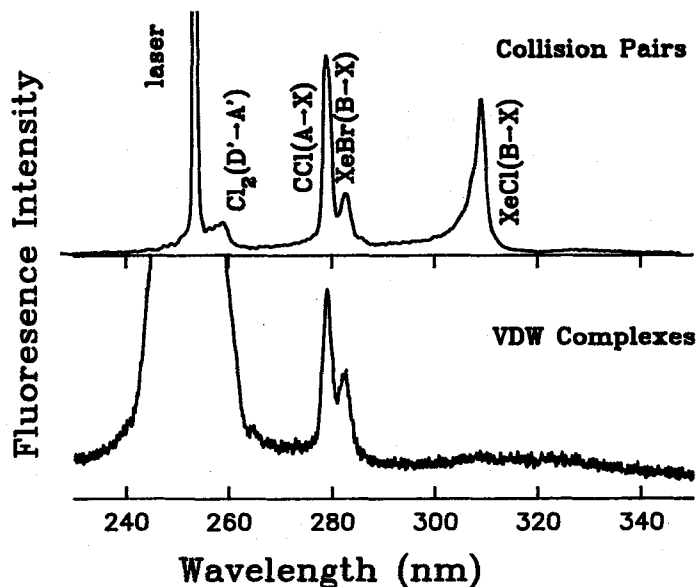


Figure 2. Product fluorescence spectra from LAR of Xe with CCl_3Br in a dilute gas mixture and from van der Waals molecules formed in a free-jet expansion.

The correct explanation of the difference between the full collision and LAR is not so obvious. One possibility is that the XeCl(B,C) channel is partly blocked in the full collision because the approach of Xe(6s) to the chlorine end of the molecule results in excitation-transfer quenching before the curve crossing region between $(\text{Xe}^+; \text{Cl}^- \text{CCl}_2\text{Br})^*$ is reached. In contrast, photo-excitation can directly transport the collision pair at the $\text{R}(\text{Xe}-\text{CCl}_3\text{Br})$ in the van der Waals molecule to the $\text{Xe}^+; \text{Cl}^- \text{CBrCl}_2$ configuration. Apparently, the one-photon CCl_3Br^* intermediate facilitates the charge transfer to the excited radical-anion state. From a statistical point of view, the Xe will have a higher probability for being close to a Cl atom than to the Br atom in the 300K dilute gas. The surprising result is that the $\text{V}(\text{Xe}^+ - \text{Cl}^- \text{CBrCl}_2)$ configuration, which correlates to an excited radical anion state, is as low in energy as implied by the two-color experiment. In the presence of Xe^+ , the ground and excited potentials for the radical anion must be close in energy.

Figure 2B illustrates the dramatic reversal of product channels for LAR of bound van der Waals molecules ($\text{Xe} \cdot \text{BrCCl}_3$) formed in a free jet. In this experiment only XeBr(B) was observed. The CCl(A-X) emission is a consequence of multiphoton dissociation of CCl_3Br . These free-jet experiments are preliminary and they must be confirmed. If they prove to be true, they imply that the bound van der Waals molecule has the $\text{Xe} \cdot \text{Br}-\text{CCl}_3$ structure. Excitation from this configuration then can lead only to $\text{Xe}^+; \text{Br}^- \text{CCl}_3$, which yields XeBr(B,C) . If this is true, the two-color LAR excitation spectra for Xe with CCl_3Br should be different for the bound molecules vs. the free molecules in a 300K dilute mixture because the final $\text{V}(\text{Xe}^+; \text{RX}^-)$ states are different.

The $\text{XeCl}^*/\text{XeBr}^*$ product branching ratio from LAR of CCl_3Br (and CCl_2Br_2) in dilute gases is very wavelength dependent. This is demonstrated by the excitation spectra for the XeCl(B,C) and

XeBr(B,C) channels in Figure 3. The change in the product ratio with wavelength is a consequence of photo-excitation to two different electronically excited CCl_3Br^- states. This interpretation is supported by the energy dependence of the dissociative electron attachment cross sections.^{6,7}

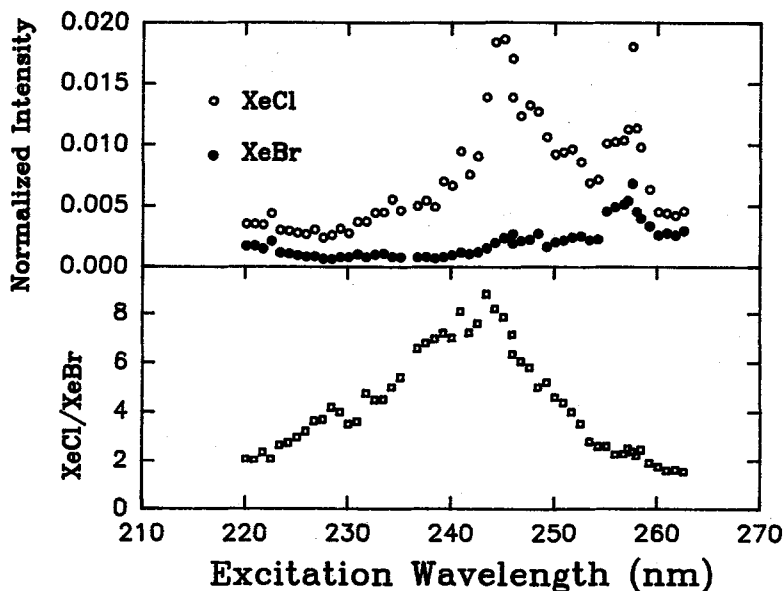


Figure 3. Two-photon, single-color excitation spectra for XeCl^* and XeBr^* formation from Xe (30 Torr) with CCl_3Br (2 Torr). The ratio is plotted in the second panel.

In addition to providing data that illuminate the dynamics of reactions on the $V(\text{Xe}^+;\text{RX}^-)$ potential surface, the LAR generate $\text{XeX}(\text{B,C})$ molecules on the same time scale as the laser pulse. This rapid generation in a clean controllable environment permits the study of quenching kinetics of $\text{XeCl}(\text{B,C})^8$ and $\text{KrF}(\text{B,C})^9$.

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