Two-color, two-photon, direct laser-assisted reactions of Xe with Br_2, I_2, CCl_4, CCl_3Br and CCl_2Br_2

J. Qin and D.W. Setser

Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA

Received 30 May 1991; in final form 1 July 1991

The fundamental plus the doubled output of a pulsed dye laser have been used to induce two-photon, laser-assisted reactions in low pressure gas mixtures of Xe with Br_2, CCl_4, CCl_3Br, CCl_2Br_2 and I_2. The products are XeCl(B, C), XeBr(B, C) or XeI(B, C) following two-photon promotion to the reactive ion-pair potentials. The utilization of a two-color scheme enhances the two-photon, laser-assisted reactions because of better match with an intermediate state of the reagent molecule. Product selectivity with a propensity for XeCl(B, C) formation from CCl_3Br and CCl_2Br_2 by the laser-assisted reactions, relative to the full collisions with Xe(6s) or Xe(6p) atoms, is demonstrated.

1. Introduction

The difficulty of inducing the one-color, two-photon, laser-assisted reaction (LAR) of Xe/Br_2 pairs has been a puzzle because the location of the $V(Xe^+; Br_2^-)$ potential should be very similar to that for $V(Xe^+; Cl_2^-)$ and the LAR of Xe/Cl_2 is facile [1–4]. Boivineau and co-workers [5,6] did successfully use two-color, two-photon excitation via the bound $Br_2(B\,^3\Pi_{0_u^+})$ intermediate state to observe $XeBr^*$ formation from bound $Xe{\cdot}Br_2$ van der Waals molecules. The two colors were the fundamental (λ_1) from a pulsed dye laser plus the doubled frequency (λ_2). The excitation spectrum in $\lambda_1=543$–553 nm range was continuous and the excitation spectrum began at the threshold energy for XeBr(B) formation, $\lambda_1=584$ nm. In the one-color, two-photon experiments of Ku and Setser [1], resonance two-photon absorption giving Br_2 Rydberg states were found, but there was no LAR. Koenders et al. [7] recently reported five Br_2 Rydberg states of g symmetry in the 272–294 nm range. Boivineau [5,6] did not report Rydberg state excitation from absorption of two UV photons in their experiments. Boivineau's observations [5,6] of XeBr(B, C) formation is best interpreted as proceeding by sequential photon absorption through the bound $Br_2(B\,^3\Pi_{0_u^+})$ state; indeed this was the author's explanation [5,6]. The 10 ns pulse provides time for extension of $R(Br_2^*)$ before the UV photon is absorbed and $Xe{\cdot}Br_2^*$ is transferred to the reactive potential. This double resonance process can give access to the reactive potential for large $R(Br\text{–}Br^-)$.

We report the LAR of Xe/Br_2 in dilute gas mixtures by direct two-color, two-photon excitation to $V(Xe^+; Br_2^-)$; the one-photon intermediate state is the repulsive limb of the $Br_2(C\,^1\Pi_u)$ potential. Also, we report the direct two-color, two-photon resonant excitation to $Br_2(f0_g^+)$ levels [8] for $\lambda_1=440$–550 nm through the same intermediate states. Neither Br_2^* emission nor LAR of Xe/Br_2 was observed when only the UV laser beam ($\lambda_2=220$–275 nm) was used. The $Br_2(f)$ molecules can react with Xe to give $XeBr^*$ [9]. However, the relative intensities of the Br_2^{**} and $XeBr^*$ fluorescence at low Xe pressure could be used to distinguish LAR from excitation of Br_2^{**} followed by collision with Xe. The time profile for $XeBr^*$ formation could not be used to distinguish LAR from excitation of Br_2^{**} followed by reaction with Xe, because the short lifetime (10–29 ns) [10] of the Br_2^{**} states controls the kinetics rather than the collision rate with Xe.

The successful two-color, two-photon LAR of Xe with Br_2 demonstrates the importance of a resonant intermediate state; one photon must match the energy difference between the van der Waals potential and the intermediate state and the second photon promotes the system to the ion-pair potential, $V(Rg^+; X_2^-)$. To have a large LAR cross section, both photons must be close to resonance. According to this view, the LARs of a wide range of halogen containing molecules (RX) with Xe should be possible, if the two colors match the energy difference between the van der Waals potential, $V(Xe; RX^*)$ and $V(Xe^+; RX^-)$. In addition to Br_2, we report the direct LAR of Xe with I_2, CCl_4, CCl_3Br and CCl_2Br_2 molecules using two-color, two-photon excitation. Comparison also is made with the one-color, two-photon LAR in some cases.

All experiments were done under dilute gas conditions as described previously [2,3]. The two-color experiments were done with the visible fundamental beam (λ_1) and the frequency-doubled UV beam (λ_2) from a pulsed dye laser pumped by an excimer laser. Both laser beams were focused into the gas cell with a 0.5 m lens. The reaction events were detected by recording the XeX(B–X) fluorescence with a 0.5 m monochromator fitted with an optical multichannel analyzer or a photomultiplier tube and digitizer. The gas handling techniques and data recording methods have been described [2,3].

2. Results

2.1. Excitation of the $Br_2(f0_g^+)$ state

The two-color, two-photon photochemistry of Br_2 in the wavelength range of $\lambda_1 = 440$–550 nm is rather complicated. For photon energies below the onset of the continuum of the $X \to B$ transition (510.8 nm), Br_2 can be pumped with large cross sections to highly excited ionic states (namely E and f) by optical–optical double resonance via the bound levels of Br_2 ($B\,{}^3\Pi_{0_u^+}$) [8]. In a room temperature sample the $Br_2(X)$ vibrational populations extend to $v' \leqslant 2$ and the average J'' is fairly large; thus, a high density of levels exists in the ground state and virtually a continuous absorption spectrum occurs for naturally occurring Br_2 isotopes with a laser band width of ≈ 2 cm^{-1}. Fig. 1a shows a fluorescence spectrum from direct excitation of $Br_2(f)$ by two-color double resonance pumping via the bound Br_2 ($B\,{}^3\Pi_{0_u^+}$) state at $\lambda_1 = 540.6$ nm. The spectrum is dominated by the $Br_2(f0_g^+ \to B\,{}^3\Pi_{0_u^+})$ emission. Boivineau [6] observed sharp bands from excitation to individual vibrational levels from pumping cold Br_2 molecules from a free jet. We estimate that the excitation of $Br_2(f)$ in fig. 1a was to a range of levels near $v' = 15$.

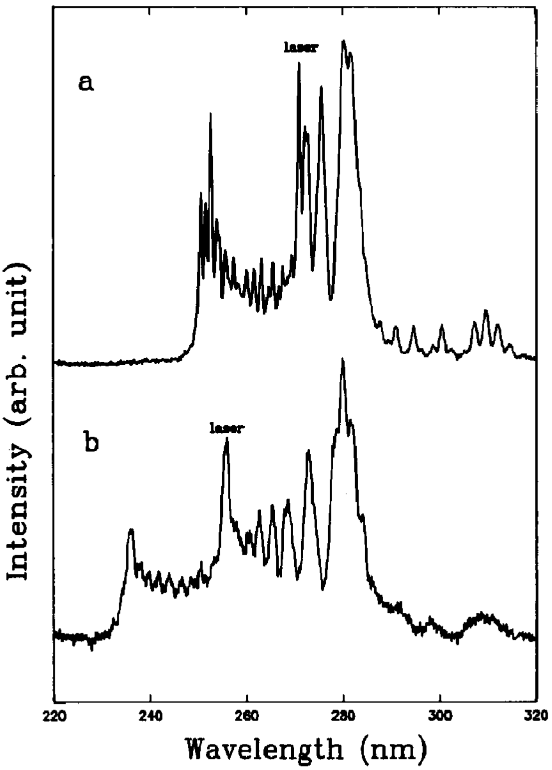

Fig. 1. Fluorescence spectrum, (Br_2(f–B)), from two-color two-photon excitation of Br_2 recorded with an OMA at 0.2 nm resolution. (a) 50 mTorr of Br_2 with $\lambda_1 = 540.65$ nm (1 mJ) and $\lambda_2 = 270.32$ nm (0.05 mJ) giving $Br_2(f, v' \approx 15)$. (b) 2 Torr of Br_2 with $\lambda_1 = 510.0$ nm (3 mJ) and $\lambda_2 = 255.0$ nm (0.15 mJ) giving $Br_2(f, v' \approx 41)$. The feature in the center of the spectrum is scattered laser light.

Direct excitation via the repulsive $Br_2(C\,{}^1\Pi)$ potential at shorter wavelength ($\lambda_1 < 510.8$ nm) also can populate Br_2^{**} states, see fig. 1b; but, the cross section is substantially smaller. We estimated the cross section to be 2–3 orders of magnitude smaller than pumping via the bound intermediate state from comparison of the two Br_2(f–B) spectra obtained from $\lambda_1 = 540.6$ and 510 nm, shown in figs. 1a and 1b. Clearly higher v' levels are populated in fig. 1b than in fig. 1a, and the oscillatory patterns for the emissions are quite different. We estimate $v' \approx 41$ for the $\lambda_1 = 510$ nm excitation.

The Br_2^{**} ionic states readily react with Xe to produce XeBr*, as do most other X_2^{**} states [9], and a XeBr(B–X) emission from $Br_2(f)$ with different pressures of Xe is given in fig. 2 for excitation at $\lambda_1 = 540.6$ nm in 0.05 Torr of Br_2. One interesting difference, relative to ion-pair states of most other halogens, is that very little $Br_2(D')$ is formed by collisions of $Br_2(f)$ with Xe, in contrast to the reactions of Cl_2^{**}, I_2^{**} and ICl** with Xe, which give ≈30% $X_2(D' \to A')$ emission. Fig. 2 compares the emission from 10 Torr of Xe versus 10 Torr of Ar. Note the large increase of the $Br_2(D' \to A')$ emission around 291 nm for the Br_2/Ar experiment. Evidently collisions between Br_2(f, high v') and Xe are very effective in producing XeBr*. Fig. 2 also shows several spectra from experiments with increasing Xe pressure. Half quenching of $Br_2(f)$ by Xe requires nearly 10 Torr of Xe, because of the short radiative lifetime of $Br_2(f)$.

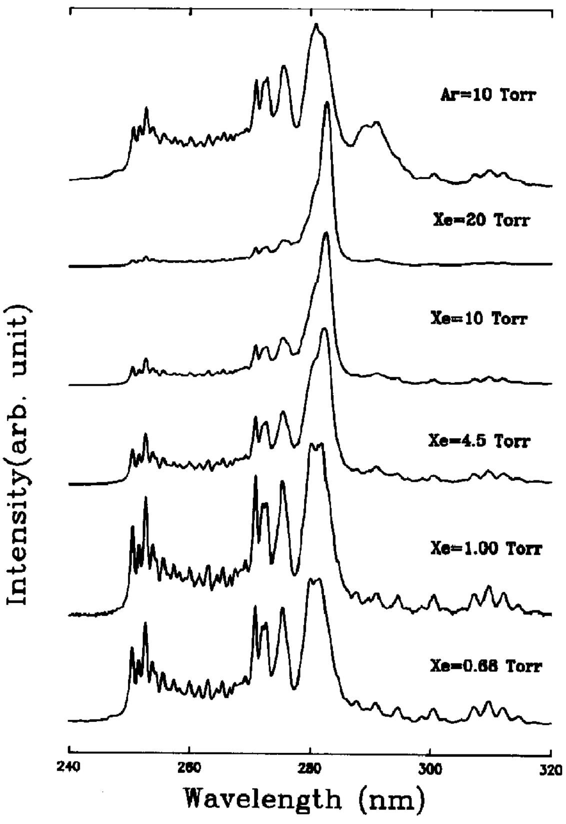

Fig. 2. Fluorescence spectra for excitation, 540.65 (2 mJ) + 270.32 (0.1 mJ) nm of Br_2(f, $v' = 15$) in 50 mTorr of Br_2 and various pressure of Xe or Ar.

2.2. LAR of Xe/Br_2 mixtures

Direct two-photon LAR was observed from Br_2/Xe mixtures for $\lambda_1 = 440$–510 nm plus $\lambda_2 = 220$–255 nm, see fig. 3. That is, XeBr* (B–X) from LAR could be observed even though very weak Br_2^{**} emission from two-photon excitation of Br_2 also exists in this wavelength range. We assign the observed XeBr* fluorescence in fig. 3 to LAR rather than to reaction of $Br_2(f)$ with Xe based on the following arguments.

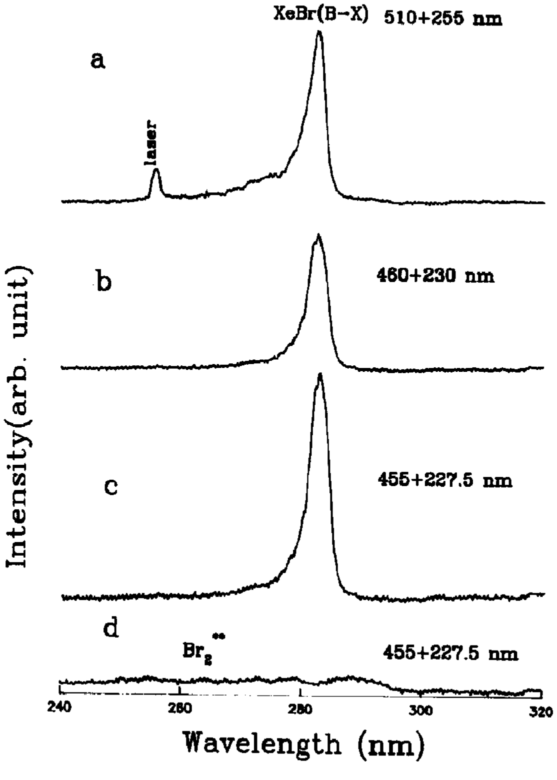

Fig. 3. XeBr(B–X) fluorescence spectra from LAR of Br_2/Xe mixtures. (a) XeBr(B→X) fluorescence from 2 Torr of Br_2 and 20 Torr of Xe, $\lambda_1 = 510$ nm (4 mJ) $+ \lambda_2 = 227.2$ nm (0.4 mJ). (b) XeBr(B–X) fluorescence from 2 Torr of Br_2 and 61 Torr of Xe with $\lambda_1 = 460$ nm (4 mJ) $+ \lambda_2 = 230$ nm (0.4 mJ). (c), (d) Comparison of the Br_2(f–B) emission from 1.9 Torr of Br_2 versus the XeBr(B→X) emission from 1.9 Torr of Br_2 plus 71 Torr of Xe at the same pulse energy with $\lambda_1 = 435.0$ nm (4 mJ) $+ \lambda_2 = 227.5$ nm (0.4 mJ). Both spectra are plotted on the same scale for ease of comparison.

(i) At modest pressure (<80 Torr Xe), quenching of XeBr(B) is negligible. Therefore, the XeBr(B→X) emission intensity from quenching of Br_2^{+*} could never be stronger than the Br_2^{+*} spectra when there is no Xe present. Fig. 3 shows the Br_2^{+*} and XeBr(B→X) emissions recorded at 71 Torr of Xe and 1.7 Torr of Br_2 versus the Br_2^{+*} emission at 1.7 Torr of Br_2 with no Xe; the integration time was 0–250 ns. The wavelengths were $\lambda_1 = 455$ and $\lambda_2 = 227.5$ nm and the pulse energies were the same for each experiment. The $XeBr^*/Br_2^{+*}$ intensity ratio for the two experiments is greater than 100, thus $XeBr^*$ cannot be formed from Br_2^{+*} to any significant extent. Similar experiments were done for $\lambda_1 = 510$ and 460 nm, and the results are shown in fig. 3.

(ii) At low pressure, Xe = 2 Torr for example, there is little reaction with Br_2^{+*} because most of the Br_2(f) radiatively decays before encountering a Xe atom. Fig. 4b shows the fluorescence spectrum from a Xe/Br_2 mixture with 2 Torr each of Xe and Br_2 when pumped at 460+230 nm. At this pressure, the formation of XeBr(B) can be seen clearly. This $XeBr^*$ emission can be compared to the Br_2^{+*} emission at 2 Torr of Br_2 with no Xe present in fig. 4a. Fig. 4c shows the subtraction of figs. 4a and 4b, which should represent the net LAR from the Xe/Br_2 mixture. The short wavelength part of the XeBr(B→X) emission extends to ≈235 nm suggesting significant vibrational energy disposal to XeBr(B) from LAR [11,12].

Obtaining a two-color LAR excitation spectrum of Xe with Br_2 was not feasible using only one dye-laser because energy normalization of the fundamental and doubled laser pulses was too difficult. These two-color experiments were typically done with energies of 4 and 0.4 mJ for λ_1 and λ_2; the corresponding intensities for the focused beams are 400 and 40 MW cm^{-2}, respectively. We were able to show that the XeBr(B) intensity scaled as the product of $I_1 I_2$. For the present experiments, the combined excitation energy of the two photons was in the 7.2 to 8.4 eV range. This is consistent with the expected LAR excitation spectrum of Xe/Br_2, which should be red-shifted relative to that for Xe/Cl_2, because $EA(Br_2) > EA(Cl_2)$.

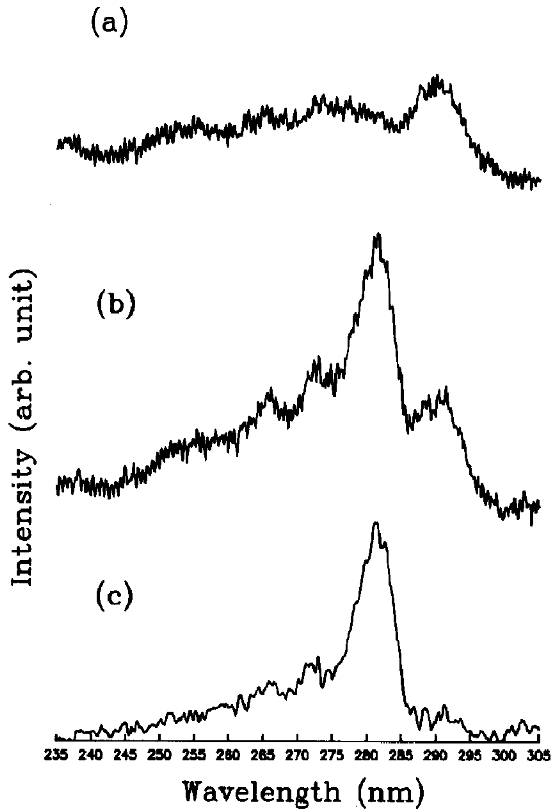

Fig. 4. Emission spectrum of XeBr(B→X) from LAR of 2 Torr of Xe and 2 Torr of Br_2 with $\lambda_1 = 460$ nm (5 mJ) + $\lambda_2 = 230$ nm (0.5 mJ). The emission spectrum from Br_2 alone (a) was subtracted from the Xe/Br_2 spectrum (b) to obtain the LAR spectrum (c), which was smoothed before plotting.

2.3. *LAR of Xe/I_2*

The LAR of Xe with I_2 has never been observed to our knowledge. Boivineau et al. [5] attempted to use single color UV photons to excite Xe·I_2 van der Waals molecules, but XEI^* formation was not observed. Donovan and co-workers [9] has demonstrated the reaction of $I_2(D_{0_u^+})$, excited by VUV radiation, with Xe to give XeI^*; electronic quenching of I_2(D) also occurred and the ratio of XeI^* to I_2(D′→A′) emission was about 2 for <100 Torr of Xe.

The fluorescence from the two-photon excitation of I_2 alone with the XeI^* fluorescence from LAR of a Xe/I_2 mixture when both were excited at 455.0+227.5 nm is shown in fig. 5A. The ratio of XeI^*/I_2^{+*} (without Xe) is >20, which provides con-

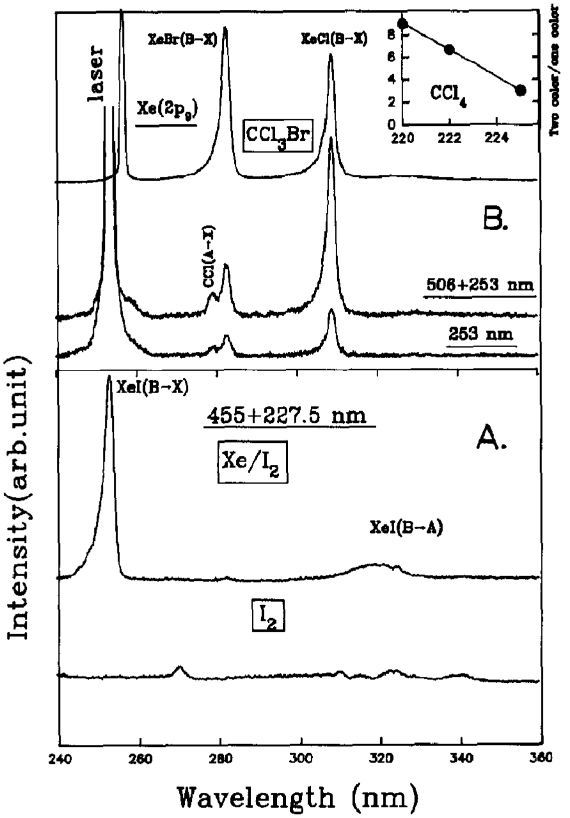

Fig. 5. (A) A comparison of XeI(B→X) and I_2 emission spectra from I_2/Xe mixtures. I_2 = 1 Torr, Xe = 150 Torr with $\lambda_1 = 455$ nm (4 mJ) and $\lambda_2 = 227.5$ nm (0.4 mJ). The XeI(B→A) band also is evident. (B) Comparison of XeCl(B–X) and XeBr(B–X) emission spectra from Xe/CCl_3/Br. Reaction of Xe(2p$_9$) with CCl_3Br for Xe and CCl_3Br pressures of 15 and 1.0 Torr, respectively, and two-color and one-color LAR of Xe/CCl_3Br with 80 Torr of Xe and 2 Torr of CCl_3Br. The plot in the upper right hand corner shows the ratio of XeCl(B–X) intensity from Xe/CCl_4 for two-color versus one-color LAR at 220, 222 and 225 nm; the UV pulse energy was the same for the two- and one-color experiments.

vincing evidence for LAR. At this wavelength the I_2^{**} emission is weak and the much stronger emission from XeI(B→X) must be attributed to LAR of Xe/I_2. The broad band at ≈320 nm is associated with XeI(B→A) emission [12]. Similar results were found for excitation at 513.7+256.9 nm. In this energy range (≈7.1 eV), there is an I_2 state with *g* symmetry [13], which could be excited by two photons (UV+visible). This probably explains the somewhat stronger I_2^{**} emission from 513.7+256.9 nm than from 455.0+227.5 nm. Experiments using the focused UV laser beam alone did not give any observable signal when the Xe/I_2 mixture was irradiated. These preliminary two-color experiments, which probed the 7.1 to 8.5 eV range, have demonstrated the LAR of Xe/I_2.

2.4. *LAR of Xe with CCl_4, CCl_3Br and CCl_2Br_2*

Both two-color and one-color, two-photon LAR experiments were successful with CCl_4, CCl_3Br and CCl_2Br_2. However, interference was observed from fluorescence arising from multiphoton-induced photofragments, e.g. CCl(A–X) emission was observed from CCl_4, CCl_3Br and CCl_2Br_2, as a consequence of multiphoton excitation by the UV laser pulse. The single color, two-photon LAR excitation spectra for Xe/CCl_4 extends from 260 to 220 nm and has a shape similar to that for Xe/Cl_2, Xe/ClF and Kr/F_2 [1–3] plus a rising edge at shorter λ. The insert in fig. 5B shows the ratio of two-color to one-color XeCl(B) formation from CCl_4 for 225, 222 and 220 nm. The two-color enhancement is significant, especially at shorter wavelength because of the increasing extinction coefficient of the one-photon absorption spectrum of CCl_4 in the UV. The CCl(A→X) and Cl_2(D′→A′) emission (not shown here) are a consequence of multiphoton photochemistry of CCl_4 from the UV laser pulse.

The LAR of Xe/CCl_3Br gives both XeCl* and XeBr* (see fig. 5B) with a ratio of 3:1 in favor of XeCl* at $\lambda_1 = 505.8$ nm. The one-color excitation with two UV photons also is possible, but the two-color process is more effective. The LAR of Xe/CCl_2Br_2 also gives both XeCl* and XeBr* (not shown here) with a ratio of 1.2:1.0 in favor of XeCl* at $\lambda_1 = 494$ nm. The two-color enhancement again is significant. The CCl(A→X) and Cl_2(D′→A′) are multiphoton decomposition products of CCl_3Br and CCl_2Br_2. The one-color LAR excitation spectra of Xe/CCl_3Br and CCl_2Br_2 resemble that of Xe/CCl_4. An interesting aspect about CCl_3Br and CCl_2Br_2 is the change in product branching ratio for LAR versus reactions with Xe(6p, 2p$_9$) and Xe(6s, $^3P_2$). The reactions of Xe(2p$_9$) with CCl_3Br and CCl_2Br_2 give XeCl(B, C)/XeBr(B, C) ratios of 0.8 and 0.2, respectively (see fig. 5B) and the ratios for Xe(6s, $^3P_2$) are similar [14], which is expected based upon the Hg($^3P_2$) reactions with these molecules and dissociative electron attachment data [14].

3. Discussion and conclusions

3.1. Direct two-photon excitation of Br_2

Optical–optical double resonance (OODR) is a powerful method for preparing specific final states that require either stretching or compression of bonds of the initial state to access a given final state. In this type of application, OODR is a sequential two-photon event with the intermediate state relaxing to r'_e before the second photon is absorbed. Direct two-photon excitation via a repulsive intermediate state is different in that the process proceeds through the intermediate state with the same geometry as the initial state. The successful excitation of Br_2 (f, $v'=42$) by resonant excitation through a repulsive intermediate state is possible because the inner wall of Br_2(f) potential can be reached via the repulsive $Br_2(C\,^1\Pi_u)$ potential [15]. We also have observed similar two-photon excitation for ClF, but in this case the final states are the ClF($4s\,^{1,3}\Pi$) Rydberg states [3]. Kasatani et al. have observed two-photon absorption in I_2 via dissociative intermediate states using visible light [16].

3.2. Two-color, two-photon LAR with Br_2, I_2, CCl_4, CCl_3Br and CCl_2Br_2

The previously known examples of efficient LAR for rare gas atoms with molecular halogens [1–4] uses the $X_2(C\,^1\Pi_u)$ potential as the intermediate resonant state. Since Br_2 does not have a one-photon absorption band in the UV, the cross section of the single color ($\lambda_1=\lambda_2\approx300$ nm), two-photon process with the necessary energy to reach $V(Xe^+;\, Br_2^-)$ is very small. However, for excitation using visible + UV frequencies, the first photon (λ_1) is resonant with the repulsive $V(Br_2,\, ^3\Pi_{0_u^+}$ or $^1\Pi_u)$ potentials [15] and the UV photon gives $V(Xe^+;\, Br_2^-)$. Subsequently, the system evolves to XeBr(B, C) + Br in less than 0.5×10^{-12} s. This successful demonstration of LAR for Xe/Br_2 and Xe/I_2 by two-color, two-photon excitation is direct proof of the need for a resonant one-photon intermediate state to achieve efficient two-photon LAR of Xe with halogen containing molecules.

Although there will be some vibrational relaxation of XeBr(B, C) at 2 Torr of Xe, the spectrum in fig. 4 shows that XeBr(B) formed by LAR has considerable vibrational energy (the excess energy is ≈1.7 eV for excitation at 460+230 nm). The vibrational excitation of XeBr(B) in the reaction of Xe(6s) with Br_2 is $\langle f_v\rangle\approx0.45$ [11,12], which is qualitatively consistent with the emission spectrum obtained at 2 Torr of Xe.

The vertical electron affinities of CCl_4, CCl_3Br and CCl_2Br_2 are ≈0.0–0.5 eV [17], and R''_e(Xe·RX) is larger than R''_e(Xe·X_2). Thus, the excitation $V(Xe^+;\, CCl_{4-n}Br_n^-)$ are at shorter wavelength than those for Cl_2, Br_2 and I_2. The one-photon intermediate state absorbs in the 260 nm range, so the UV photon accesses the intermediate state and the visible photon gives $V(Xe^+;\, RX^-)$, which is in contrast to Xe/Br_2 and Xe/I_2 for which the visible photon reaches the intermediate state and the UV photon promotes the system to $V(Xe^+;\, X_2^-)$. Since $V(Xe^+;\, RX^-)$ is accessible from a modest range of R(Xe–XR) near R''_e and since the RX^- and $(RX^-)^*$ states are repulsive, the excitation spectra are broad and both two-color and one-color excitations are feasible. The observed two-color enhancement probably is due, in part, to the tenfold larger pulse energy for the visible photons; however, we believe that the two-color cross sections also are larger.

The propensity for XeCl(B, C) formation rather than XeBr(B, C) in the LAR reaction illustrates how changing the initial conditions on a reactive surface can change the outcome of a chemical reaction [17,18]. The propensity for XeCl* formation by LAR, which is opposite to the thermochemically favored product that is favored by the reactive collisions of Xe* (6s or 6p), probably arises because the photo event can start the reaction on a specific ion-pair potential at a smaller $R(Xe^+–RX^-)$ than the full collision. Since the statistically favored starting geometry for pairs in the gas phase will have Xe closer to a Cl atom than the Br atom, the two-photon excitation has a propensity to seek the ion-pair potential with the electron located on chlorine. In contrast, the products from the full collision event are determined by the efficiency of curve crossing in the entrance channel, and the trajectories first encounter the ground state ion-pair potential with the electron mainly located on bromine in the CCl_2Br_2 or CCl_3Br radical anion. In order to obtain XeCl*, the collision must have the chlorine end of the molecule oriented toward the Xe* and the trajectory must reach the second crossing.

In summary, the fundamental plus the doubled outputs of a pulsed dye laser have been used to induce the two-photon, laser-assisted reactions between Xe and Br_2, I_2, CCl_4, CCl_3Br and CCl_2Br_2. The successful observation of these LAR provides direct proof for the importance of a one-photon allowed intermediate state for the two-photon induced LAR. The utilization of two colors enables a wide range of laser-assisted reactions between Xe and halogen containing molecules to be studied. With an independently tunable second dye laser, one laser frequency could be tuned to the center of the absorption band of the intermediate state and the second laser could be scanned to obtain an excitation spectrum. Such excitation spectra should provide more direct information about $V(Xe^+; RX^-)$. In doing such two-color experiments, excitation through a bound intermediate state should be avoided, because such situations can lead to sequential two-photon excitation of a RX** state, which subsequently may react with Xe. These preliminary experiments in dilute bulk gases will be augmented in the future by excitation of bound van der Waals complexes, which will provide even better definition of the starting conditions on the $V(Xe^+; RX^-)$ potentials. For more precise interpretations of the excitation spectra of LAR reactions, more knowledge is needed about the van der Waals potentials.

The multiphoton photochemistry of CCl_4, CCl_3Br and CCl_2Br_2 (and other halomethanes) can lead to strong UV fluorescence from photofragments and often such processes compete effectively with two-photon LAR. We will discuss the multiphoton photoprocesses of the RX molecules in a separate report.

Acknowledgement

This work was supported by the US National Science Foundation (CHE-8822060).

References

[1] J.K. Ku, G. Inoue and D.W. Setser, J. Phys. Chem. 87 (1983) 2989;
D.W. Setser and J.K. Ku, Photophysics and photochemistry above 6 eV, ed. F. Lahmani (Elsevier, Amsterdam, 1985).

[2] T.O. Nelson and D.W. Setser, Chem. Phys. Letters 170 (1990) 430.

[3] J. Qin, T.O. Nelson and D.W. Setser, J. Phys. Chem., in press.

[4] J.C. Jouvet, M. Boivineau, M.C. Duval and B. Soep, J. Phys. Chem. 91 (1987) 5416;
M. Boivineau, J. le Calvé, M.C. Castex and C. Jouvet, Chem. Phys. Letters 128 (1986) 528; 130 (1986) 208.

[5] M. Boivineau, J. le Calvé, M.C. Castex and C. Jouvet, J. Chem. Phys. 84 (1986) 4712.

[6] M. Boivineau, Thesis d'Etat, Université de Paris, Orsay (1987).

[7] B.G. Koenders, G.J. Kuile, K.E. Drabe and C.A. Delange, Chem. Phys. Letters 147 (1988) 310.

[8] T. Ishiwata, H. Ohtoshi and I. Tanaka, J. Chem. Phys. 81 (1984) 2300;
T. Ishiwata, A. Tokunaga, T. Shinzawa and I. Tanaka, Bull. Chem. Soc. Japan 57 (1984) 1317.

[9] B.V. O'Grady and R.J. Donovan, Chem. Phys. Letters 122 (1985) 503;
J.P.T. Wilkinson, E.A. Kerr, K.P. Lawley, R.J. Donovan, D. Shaw, A. Hopkirk and I. Munro, Chem. Phys. Letters 130 (1986) 213.

[10] P.J. Jewsbury, K.P. Lawley, T. Ridley, F.F. Al-Adel, P.R.R. Langridge-Smith and R.J. Donovan, Chem. Phys. 151 (1991) 103;
D.I. Austin, R.J. Donovan, A. Hopkirk, K.P. Lawley, D. Shaw and A.J. Yencha, Chem. Phys. 118 (1987) 91.

[11] K. Johnson, R. Pease, J.P. Simons, P.A. Smith and A. Kvaran, J. Chem. Soc. Faraday Trans. 82 (1986) 1281.

[12] K. Tamagake, D.W. Setser and J.H. Kolts, J. Chem. Phys. 74 (1981) 4286.

[13] A.R. Hoy and A.W. Taylor, J. Mol. Spectry. 126 (1987) 484.

[14] F.M. Zhang, D. Oba and D.W. Setser, J. Phys. Chem. 91 (1987) 1099;
D.P. Zhang and D.W. Setser, to be published.

[15] J.A. Coxon, in: Molecular spectroscopy, Vol. 1, eds. R.F. Barrow, D.A. Long and D.J. Millen, Specialist Periodical Reports (Chemical Society, London, 1973) p. 177.

[16] K. Kasatani, Y. Tanaka, K. Shibuya, M. Kawasaki, K. Obi, H. Sato and I. Tanaka, J. Chem. Phys. 74 (1981) 895.

[17] O.J. Orient, A. Chutjian, R.U. Crompton and B. Cheung, Phys. Rev. 1739 (1989) 4494.

[18] R.D. Levine, J. Phys. Chem. 94 (1990) 8872.

[19] M. Noble, G. Radhakrishnan, H. Reisler, C. Wittig and G. Hancock, J. Phys. Chem. 90 (1986) 1015.