brational resonances are broadened beyond recognition in the dimeric B state due to lifetime shortening. Furthermore, to rationalize the dramatic difference in branching ratios, the lifetime shortening in the dimer cannot be entirely ascribed to predissociation but rather to efficient nonradiative relaxation from the B to the X states bypassing the A and A' manifolds.

On the basis of the observed emission lifetimes, we are led to conclude that the A' manifold in the dimeric species is essentially unperturbed. On the other hand, the absence of structure in the excitation spectrum to the B state indicates that the B state is strongly perturbed in the dimer or at least that the vertically accessed states in the B manifold undergo rapid relaxation. This observation is also consistent with the notion that there is a significant difference between the ground- and excited-state intermolecular potentials of the dimer, as previously argued on the basis of the $(A' \rightarrow X)$ emission line widths. A consideration of the molecular orbitals involved in these states gives clues as to the structure of the excited- and ground-state intermolecular potentials. The ground-state potential is due to interactions between closed-shell molecules and therefore expected to be determined by the balance between dispersive attractive forces and electron-electron repulsion between the filled orbitals. A parallel or a D_{2d} geometry would be expected to minimize the energy of such a dimer. Quadrupolar interactions, which would favor a "T" geometry, are known to be unimportant from structure analyses of Cl_2 crystals.⁸ Excitation into the ³ Π manifold (B, A, and A' states) involves the promotion of a nonbonding π electron into

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the antibonding σ^* orbital, reducing the molecular binding by a bond order of one-half. Accordingly, reduction in electronic repulsion for side-on intermolecular binding, and therefore a tighter geometry in the excited state, is to be expected. These considerations rationalize the observed differential binding and the large change in intermolecular coordinates that was inferred from the emission and excitation line shapes. However, it is not possible to ascertain the dimer geometry at present. As a further probe of structure and dynamics, we have carried out polarization measurements in the crystalline samples. No net polarization is observed in emission. This null result does not lead to unique interpretations.

Work is presently in progress to put some of the above conclusions on a firmer footing. It should, however, be clear that a wealth of information regarding intermolecular dynamics can be extracted from such studies and that extension of such studies to clusters of unlike species should be particularly useful for probing reactive dynamics. The present results also indicate that, due to the very rapid relaxation of the vibronic states in the B manifold, it may be difficult to observe Cl₂ clusters in molecular beams if the B state is used as detection intermediate. Finally, we point out that despite the very high dilution (1:50 000), the dominant emission in the crystal is due to dimers. While this may vary as a function of conditions of crystal growth, this observation illustrates the danger in assumptions of molecular isolation based on dilution arguments alone.

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Two-Photon Direct Laser-Assisted Reaction between Xe and CIF

J. Oin, T. O. Nelson, and D. W. Setser*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506 (Received: March 12, 1991; In Final Form: May 16, 1991)

The two-photon, laser-assisted reaction between Xe and CIF under dilute gas conditions is demonstrated. The only product is XeCl(B,C) in contradistinction to the reactions of Xe(6s) and Xe(6p) atoms with CIF or the reaction of $ClF(4s^{1.3}\Pi)$ with Xe, which give both XeCl(B,C) and XeF(B,C). The excitation spectra from the laser-assisted reaction of Xe/ClF and Xe/Cl₂ are compared. Arguments based upon product-state distributions and the laser intensity dependence are summarized to favor a direct, rather than a stepwise, mechanism for the laser-assisted reactions of Xe with halogens under dilute gas conditions.

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I. Introduction

There has been considerable interest in the one-color, twophoton, laser-assisted reaction (LAR) of rare-gas atoms with halogen molecules as a direct probe of the reactive ionic potential with respect to the ground-state van der Waals potential. Experiments have been done with Xe/Cl₂, Xe/ICI, Xe/CCl₄,¹ Xe/F_2 ,² and Kr/F_2 ³ in dilute gases, as well as with Xe-Cl₂ van der Waals complexes generated in a free jet expansion.⁴ LAR of Xe/Cl_2 also has been employed to generate XeCl(B,C) for subsequent kinetic studies of $XeCl^*$ and $Xe_2Cl^{*,5}$ The two-photon

LAR in liquid or solid mixtures of rare gases and halogen also has drawn attention,⁶ and there is some correspondence with gas-phase processes. We will report the excitation spectrum for the two-photon LAR of Xe/ClF and demonstrate that product specificity can be achieved. This opens a new dimension for study of sterochemical constraints to entrance channels in bimolecular reactions.7

A detailed model for the excitation mechanism of the one-color, two-photon LAR reaction of Xe with halogen molecules (X_2) remains to be developed. Ku and Setser¹ proposed a direct mechanism based on low-pressure experiments with Xe/Cl_2 :

$$Xe + Cl_2 \xrightarrow{h\nu} Xe \cdot Cl_2(^{1}\Pi_u) \xrightarrow{h\nu} Xe^+ Cl_2^- \rightarrow XeCl(B,C) + Cl$$
(1)

A second-order dependence for generation of vibrationally excited XeCl(B,C) molecules was observed for a wide range of laser

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Chem. Phys. Lett. 1986, 128, 528; 1986, 130, 208. (c) These authors studied the two-photon excitation of bound Xe-Cl₂ van der Waals molecules. The reaction dynamics apparently differ from our dilute gas experiments because low vibrational energy XeCl(B,C) molecules were generated starting from the bound $XeCl_2$ van der Waals molecules.

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intensity, 90-290 MW/cm², at 313 nm. On the other hand, McCown and Eden⁸ suggested a sequential mechanism from experiments at high pressure (\geq 300 Torr of Xe) when a Xe/Cl₂ mixture was irradiated at 308 nm with a excimer laser giving 7-70 MW/cm^2 :

$$\operatorname{Cl}_2 \xrightarrow{h_{\nu}} \operatorname{Cl}_2({}^1\Pi_u) \rightarrow 2\operatorname{Cl}$$
 (2)

$$Xe + Cl \xrightarrow{h_{F}} XeCl(B)$$
 (3)

Depending on the Xe pressure and the length of the laser pulse, there may or may not be intervening collisions of the hot Cl atom with other Xe atoms before (3). Their conclusions were based, in part, on the observation of a first-order laser intensity dependence for the formation of Xe₂Cl^{*}, which was the monitor for XeCl^{*} formation. Schloss and Eden⁹ more recently performed a two-color experiment with Kr/F_2 using a variable time delay between the two lasers to ensure sequential excitation. Since the two-photon LAR process involves a real intermediate, the $X_2(^{1}\Pi_u)$ state, the distinction between direct two-photon excitation vs sequential excitation largely depends upon whether the R(X-X)distance changes or is fixed at $R_e''(X_2)$ for the duration of the excitation process. One diagnostic difference between the sequential and coherent mechanisms is that only XeX(B) is a primary product from reaction 3, whereas reaction 1 generates both XeX(B) and XeX(C). The two mechanisms also differ in their predictions about the nascent XeX(B) vibrational distribution with reaction 1 giving higher vibrational energy for excitation of collision pairs (but not necessarily from bound Xe-Cl₂ pairs; see ref 4c). Although subsequent collisions between Xe and XeCl* molecules rapidly mix the B and C states and change the vibrational distribution, 5,10 monitoring XeX(B,v) at low pressure can give clues about the formation process.

The dependence of XeX* formation on laser intensity provides an additional test between direct and sequential one-color excitation. Schloss and Eden⁹ modeled the two-color, two-photon Kr/F₂ system at high pressure taking into account the stimulated emission of KrF(B) and the absorption of Kr_2F^* . According to this model, the saturation threshold for KrF(B) formation by step 3 should increase with Kr pressure in the intermediate-pressure regime because the three-body Kr₂F* formation rate will overcome the KrF* stimulated emission rate. This conclusion also should apply to the Xe/Cl₂ system, since Xe₂Cl* formation occurs at high pressure.⁵ But the following discussion will show the opposite result; i.e., the threshold for saturation of XeCl(B) formation decreases with increasing Xe pressure because of the role of XeCl(B.C) vibrational relaxation. For our experimental conditions, the direct mechanism seems to be dominant.

Preliminary results from the reactions of $Xe(6p[5/2]_2)$ and $[1/2]_0$) atoms with CIF and of the CIF*(4s^{1,3}II) Rydberg states with Xe atoms are presented for comparison with the LAR; the Xe(6p) and ClF(4s) states also were prepared by two-photon excitation. The reactive quenching of Xe(6s) and Xe(6p) atoms via the $V(Xe^+;X_2^-)$ potential is well understood,¹¹ and energytransfer channels giving Cl_2^* or F_2^* are not competitive with reactive quenching. Reactive quenching is dominant for collisions



Figure 1. Fluorescence spectra from two-photon excitation. (top) Xe-(6p[1/2]₀ or 2p₅) excitation at 256 nm with 1.5 Torr of ClF and 5 Torr of Xe. The weak features at 231 and 257 nm are emission bands from ClF ionic states. (center) ClF($4s^3\Pi$, v'=8) state excitation at 256.2 nm for 5 Torr of CIF, 15 Torr of Xe, and 250 Torr of Ar. The weak feature at 257 nm is a new ClF* emission system. (bottom) Xe/ClF pair excitation at 307 nm for 2 Torr of Xe and 2 Torr of CIF. The sharp feature at 307 is the residual scattered laser light, which has been subtracted. Note the vibrational excitation in the XeCl(B-X) spectrum.

of Xe(6p) with ClF, but formation of ClF* ion pair is observed too. Relaxation and reactive quenching are about equal from interaction of $ClF(4s, {}^{1,3}\Pi)$ states 13a with Xe.

II. Experimental Methods

The Xe/ClF experiments at 300 K were done in the stainless steel cell used previously to study the F_2/Kr system;^{2.3} the Xe/Cl₂ experiments were carried out in a Pyrex glass reactor. The fundamental from a Lambda-Physik FL2002 dye laser, pumped (308 nm) by an excimer laser, was doubled by a KDP-B,C or BBO-B crystals in a Inrad autotracker II and focused by a 0.5-m focal length lens. The laser pulse had a Gaussian shape with a half-width of 12 ns. The laser pulse energy was measured by a Precision power meter (RJP-735) and averaged with a digital oscilloscope. The unfocused laser beam spot size was measured by the burn pattern to have an area of 1.3×10^{-3} cm²; the focused spot size was estimated to be 5 times smaller than that of the unfocused beam. The XeCl(B-X) and XeF(B-X) fluorescences were monitored for low and medium Xe pressure experiments, and the $Xe_2Cl(4^2\Gamma \rightarrow 2^2\Gamma)$ fluorescence was monitored for 1000-Torr Xe experiments. All spectra were obtained with a 0.5-m monochromator equipped with either a 1200 or 300 groves/mm grating both blazed at 3000 Å. Either the fluorescence signal was detected by a photomultiplier tube, with amplification and digitization by a Biomation waveform recorder, or the spectra were recorded by a Princeton Instrument optical multichannel analyzer. Generally \geq 2500 laser pulses were required to obtain a waveform or a spectrum.

III. Results

The LAR experiments were done with 2 Torr of ClF and 70 Torr of Xe to identify the products and record the excitation spectrum. Only XeCl(B,C) emission (see Figure 1) was found in the 200-360-nm region.¹⁴ Special searches for XeF(B,C)

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Figure 2. Excitation spectrum (\bullet) for XeCl(B,C) formation from LAR of Xe/ClF. The data were acquired by monitoring the XeCl(B) fluorescence from mixtures of 2 Torr of ClF and 72 Torr of Xe. The solid line is the excitation spectrum for Xe/Cl₂ taken from ref 1. The Cl₂ and ClF excitation spectra are not normalized to each other. The inset shows the one-photon extinction coefficients for Cl₂ and ClF; the latter was measured in our laboratory.¹⁴

formation were made from 340 to 360 nm, where XeF(B,C) formation might be expected based upon the LAR of Xe/F_{2} .² However, XeF(B,C) formation was never observed. Time profiles for XeCl(B,C) formation showed that the XeCl(B) product was from LAR and not from excitation of CIF* followed by chemical reaction with Xe; the arguments are exactly as described for Kr/F_{2} ³ A waveform taken with 1 Torr of ClF and 10 Torr of Xe showed double-exponential decay (the lifetime of the first component is 28 ns and that of the second is 44 ns) indicative that both XeCl(B) and XeCl(C) are formed by LAR. Significant XeCl(B) vibrational excitation could be observed at low Xe pressure, as illustrated by the 2-Torr spectrum shown in Figure 1. Figure 2 shows the Xe/ClF excitation spectrum that was obtained by changing the laser wavelength and recording the integrated intensity of the $XeCl(B \rightarrow X)$ emission monitored at 308 nm. The excitation spectrum from Xe/Cl_2 also is shown for ease of comparison.¹ The Xe/ClF spectrum drops more abruptly on both the long- and short-wavelength sides than does the Xe/Cl₂ spectrum. The Xe/ClF excitation spectrum has a weak shortwavelength tail, and in fact, the LAR spectrum probably extends into the range where the CIF Rydberg states are excited. The feature at 298 nm that exists in both the Xe/Cl_2 and Xe/ClFspectra matches the energy of $Xe(6s, {}^{3}P_{2})$.

In contrast to the LAR, reactive quenching of $Xe(6p[5/2]_2 \text{ or } [1/2]_0)$ by CIF gave XeCl(B,C) (70%) and XeF(B,C) (20%), as well as CIF^{*} ($\leq 10\%$). A descriptive spectrum is shown in Figure 1 for 5 and 1.5 Torr of CIF. The branching between XeCl^{*} and XeF^{*} formation for the Xe(6p) reactions resembles that for Xe(6s, ³P₂) with CIF.^{11a} The CIF(4s^{1.3}\Pi, v'=4-8) Rydberg states interact with Xe to give XeCl^{*} and XeF^{*}, as well as the CIF^{*} ion-pair states. The relative emission from these product channels is illustrated in Figure 1. At high Xe pressure, the CIF(D'-A') band is dominant, but at intermediate Xe pressure emission from other CIF^{*} ion-pair states is observed.¹⁴ The full description of



Figure 3. Laser intensity dependence of XeCl(B,C) formation at 291 nm from Xe/Cl₂ mixtures using 1-2 Torr of Cl₂ with the Xe pressures stated in the figure. The XeCl(B,C) formation was measured from the integrated (B-X) fluorescence waveforms observed at 308 nm. The change from second- to first-order dependence is defined by eqs 11 and 14 as I_{mail} and I_{math} . The saturation thresholds are 85, 10 and 6.5 MW/cm² for Xe pressures of 7, 50, and 1000 Torr, respectively. A second 50-Torr data set obtained without a focusing lens is shown in the upper log-log plot. In the plots the points are the experiment data and the solid lines are the best fits.

the CIF* Rydberg state quenching by rare gases is rather involved, and these details will be given in a separate report.¹⁴

Experiments to demonstrate the dependence of the LAR on laser intensity were done with Xe/Cl₂ rather than Xe/ClF because of greater ease of gas handling. A laser wavelength of 291.5 nm was selected, and three series of experiments were done using 1 Torr of Cl₂ and Xe pressures of 7, 50, and 1000 Torr; see Figure The plot for the 1000-Torr data (obtained from observing Xe₂Cl^{*}) clearly shows second- and first-order regimes at low and high laser intensity, respectively. The change occurs at about 6.5 MW/cm^2 , according to the fit to eq 14 (see below). The change in order for the 50-Torr data occurs at a somewhat higher laser intensity, 10 MW/cm². A second data set, obtained without the focusing lens, also is shown in the log-log plot of Figure 3, and the dependence was second order up to 18 MW/cm². For the 7-Torr experiments saturation occurs only at very high laser intensity, $\sim 85 \text{ MW/cm}^2$, according to the fit to eq 11 (see below). The $XeCl(B \rightarrow X)$ fluorescence was used as the monitor for the 7- and 50-Torr experiments.

IV. Discussion

By analogy to Kr·ClF,¹⁵ the Xe·ClF van der Waals molecule was assumed to have linear geometry with Cl toward Xe; a bond energy of 350 cm⁻¹ and $R_e'' = 3.5$ Å were estimated; see Figure 4. LAR at 300 K consists of absorption by the bound [Xe·ClF] plus a larger contribution from the free pairs with $R \leq 1.3R_e''$ -(Xe·ClF); the majority of the transitions will occur from the vicinity of $R_e''(Xe$ -ClF). If the maximum in the excitation spectrum is associated with transitions from $R_e''(Xe$ -ClF), the vertical EA(ClF) must be ~0.5 eV. There are no definitive vertical EA values for ClF, but 0.5 eV is a reasonable estimate. Although the maxima in the Cl₂ and ClF excitation spectra both

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Figure 4. A potential energy sketch for the van der Waals Xe-CIF molecule and the upper Xe⁺(CIF)⁻ state for collinear geometry. But the ion-pair energy was calculated as point charges with the electron placed at the center of mass of CIF for a vertical EA(CIF) of 0.5 eV. The ordinate is the distance between the Xe and Cl atoms. The van der Waals potential was drawn for $r_e = 3.5$ Å and $D_e = 350$ cm⁻¹. The edges and maximum positions of the excitation spectrum have been placed at the $R_e(Xe-CIF)$ that matches the energy; however, the width of the excitation spectrum probably is governed more by the Franck-Condon factors for $CIF(^{1}\Sigma^{+}) \rightarrow CIF^{-}(^{2}\Sigma^{+})$.

occur at \sim 308 nm, the EA(Cl₂) corresponds to \sim 1 eV, because $R_{e}^{\prime\prime}(Xe-Cl_{2})$ is larger (and the geometry is C_{2v}). According to Figure 4, the LAR excitation should be located largely inside the $V(Xe({}^{3}P_{2});ClF) - V(Xe^{+};ClF^{-})$ crossing distance. The one-photon ClF and Cl_2 absorption spectra are also shown in Figure 2. The more abrupt decrease in the Xe/ClF excitation spectrum toward longer wavelength, relative to that for Xe/Cl_2 , can be explained by the declining extinction coefficient of the $ClF(^{1}\Pi)$ absorption spectrum. According to this argument, the short-wavelength end of the LAR excitation spectrum, which corresponds to large R(Xe-ClF), should be aided by the increasing one-photon extinction coefficient for CIF. However, it declines even more rapidly than the Xe/Cl_2 excitation spectrum. The short-wavelength limit to the excitation spectrum probably is governed by the dependence of the transition dipole of the second matrix element upon R-(Xe-CIF) and the Franck-Condon factors for $V(CIF(X)) \rightarrow$ V(ClF(X)). The similar widths of the Cl₂ and ClF excitation spectra may be a consequence of these Franck-Condon factors. The small resonance corresponding to the $Xe({}^{3}P_{2})$ energy exists for both Cl_2 and ClF spectra.

Since Xe-ClF has a linear geometry with the Cl atom toward Xe, the Xe-ClF configuration will be somewhat favored over Xe-FCl even at 300 K, and the two-photon LAR would favor formation of Xe⁺(ClF)⁻ rather than Xe⁺(FCl)⁻. Furthermore, the ClF(¹II) state has a higher electron density on the Cl atom, which in the second photon step leads to Xe⁺(ClF⁻). The radical anion with the electron localized on F corresponds to an excited (ClF⁺)⁻ state, and reaching Xe⁺(FCl⁺)⁻ through ClF(¹II) will be more difficult. The full collision involving Xe(6s or 6p) proceeds via all orientations, and the electron-transfer probability depends on the localized crossing of potential curves; ^{11a} the first crossing is with $V(Xe^+;(ClF)^-)$. The ClF⁺(4s) Rydberg state has nearly the same energy as Xe(2p₂). As the Cl-F distance stretches in the $V(Xe^+;ClF)^-$ entrance channel, the trajectory that starts from Xe(2p₂) + ClF can cross to V(Xe;ClF(4s)), leading to energy transfer, as well as continue on the ion-pair potentials to give XeCl^{*} or XeF^{*}. The interactions between the states of Xe and

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CIF in the ~ 10 -eV range will be of continued interest.¹⁴

Consider next the laser intensity dependence for the sequential and direct mechanisms. Equations 4–9 can be used with eqs 1-3to model the mechanism; the role of stimulated emission and Xe₂Cl^{*} absorption should be noted. Consider first the excitation

$$XeCl(B) \rightarrow Xe + Cl + h\nu$$
 (4)

XeCl(B) + Xe ≓ XeCl(C) + Xe B, C mixing and vibrational relaxation (5)

$$XeCl(B) \xrightarrow{n r_L} Xe + Cl + 2h\nu$$
 stimulated emission (6)

$$\operatorname{AeCl}(B,C) + 2Xe \to Xe_2\operatorname{Cl}(4^2\Gamma) + Xe \tag{7}$$

$$Xe_2Cl(4^2\Gamma) \rightarrow Xe_2Cl(2^2\Gamma) + h\nu$$
 (8)

$$Xe_2Cl(4^2\Gamma) \xrightarrow{n_L} Xe_2Cl(9^2\Gamma) \qquad Xe_2Cl^* absorption (9)$$

at modest Xe pressure such that Xe₂Cl* formation is not important. For the sequential mechanism, a large fraction of the XeCl(B) will be in low vibration levels and these levels can be depleted by stimulated emission at 291.5 nm. For laser intensities sufficiently large that stimulated emission becomes important, the intensity dependence (photon order) will become one rather than two. Eden and co-workers9 showed that saturation arising from step 6 occurs at low intensity, 0.44 MW/cm^2 , for KrF(B) molecules formed by direct photoassociation of Kr with F atoms at low pressure (<10 Torr). Therefore, for the 7- and 50-Torr experiments a change from a second- to first-order dependence should have been observed for intensities of $\sim 0.5-1.0$ MW/cm², if stepwise excitation was the dominant mechanism. This, however, is not demonstrated in Figure 3. We will develop some steady-state equations to document the above argument and to address the direct mechanism, which gives XeCl(B,C) with higher vibrational energy.

The steady-state [XeCl*] for sequential excitation will follow eq 10. I is the laser intensity, σ_d and σ_a are photodissociation

$$[XeCl(B)] = \frac{I^2[Xe][Cl_2]\sigma_d\sigma_a}{\tau_B^{-1} + \sigma_s I + k_7[Xe]^2}$$
(10)

and photoassociation cross sections for (2) and (3), respectively, σ_s is the stimulated emission cross section at the excitation wavelength, and k_7 is the formation rate constant of Xe₂Cl^{*}. For modest [Xe] and high laser intensity, the denominator will be dominated by $\sigma_s I$, and the formation of XeCl(B) will be first order in I as mentioned above. Define $I_{sat,l}$ for modest pressure as the intensity for which the depletion of XeCl(B) caused by stimulated emission is equal to the sum of radiative decay and three-body quenching rates of XeCl(B,C). For these conditions, the steady-state concentration is first order in laser intensity, but $I_{sat,l}$ should increase with Xe pressure.

$$[XeCl(B)]_{l} = \frac{I^{2}[Xe][Cl_{2}]\sigma_{d}\sigma_{a}}{\sigma_{s}(I + I_{sat,l})}$$
(11)

Vibrationally excited XeCl(B and C) molecules are formed in the direct mechanism. An intrinsic characteristic of a bound-free transition is that the stimulated emission cross section is proportional to $\lambda^2 g(\nu) A$. In addition to the Einstein coefficient for spontaneous emission (A), the continuum line shape factor, g(v), which measures how the emission is distributed among the final continuum states, must be considered. The emission spectrum for XeCl(B,v) extends over a range of kinetic energy, as has been demonstrated by several groups from computed Franck-Condon factors for XeCl(B,v).⁵ So, only a fraction, f, of the XeCl(B,v)population can be lost by stimulated emission, and this fraction depends on pumping wavelength and on the pressure, which governs the vibration relaxation rate. For 100 Torr of Xe, collisions of XeCl(B,C) molecules formed by LAR give a 300 K Boltzmann XeCl(B,C) distribution after ~ 30 ns.⁵ For Xe pressure below the range where Xe₂Cl^{*} formation is important, eq 12 is the appropriate steady-state expression, where the stimulated emission

$$[XeCl(B)] = \frac{I^{2}[Xe][Cl_{2}]\sigma_{1}K_{eq}}{\tau_{B}^{-1} + f\sigma_{ee}I}$$
(12)

A

cross section has been multiplied by the fraction, f. The absorption cross section of Xe/Cl₂ pairs is σ_1 , and K_{eq} is the equilibrium constant for van der Waals molecules. Now f has the property of approaching unity as relaxation to a 300 K distribution becomes complete and being very small at low pressure. Thus, the observed tendency for the saturation limit to become smaller, rather than larger, with increasing Xe pressure can be explained by the direct mechanism.

At higher pressure the LAR usually is monitored by Xe₂Cl*. The kinetics are dominated by Xe₂Cl* formation and photoabsorption and the laser intensity dependence provides no information about (1) vs (2) plus (3). The steady-state concentration of Xe_2Cl^* will be given by (13) because $k_7 [Xe]^2 > \tau_B^{-1} + \sigma_s I$.

$$[\mathbf{X}\mathbf{e}_{2}\mathbf{C}\mathbf{I}^{*}] = \frac{I^{2}[\mathbf{X}\mathbf{e}][\mathbf{C}\mathbf{l}_{2}]\sigma_{d}\sigma_{a}}{\tau_{\mathbf{X}\mathbf{e}_{2}\mathbf{C}\mathbf{I}}^{-1} + \sigma_{\mathbf{X}\mathbf{e}_{2}\mathbf{C}\mathbf{I}}I}$$
(13)

Saturation now occurs if the loss of [Xe₂Cl^{*}] by photoabsorption equals that from radiative decay; $\sigma_{Xe_{2}Cl}I_{sat,h} = \tau_{Xe_{2}Cl}I_{sat,h}$

$$[Xe_2C|^*] = \frac{I^2[Xe][Cl_2]\sigma_d\sigma_a}{\sigma_{Xe_2Cl}(I+I_{sat,h})}$$
(14)

Equations 11 and 14 both predict a first-order laser intensity dependence, but for different laser fluence regimes, because Isat,h probably is larger than Isat, Our 1000-Torr data based on monitoring Xe₂Cl* are consistent with this result but proves nothing about the XeCl(B,C) formation mechanism.

These arguments using steady-state analysis for simplicity have been confirmed by more elaborate calculations based upon numerical integration of rate equations using a master equation formulation that included several vibrational levels for the XeCl(B) and XeCl(C) states.14

V. Conclusions

The one-color, two-photon LAR between Xe/ClF pairs has been demonstrated. The LAR gives only the XeCl(B,C) product, whereas the reactions of $Xe(6s, {}^{3}P_{2} \text{ or } {}^{3}P_{1})$ and Xe(6p) atoms with CIF give both XeCl(B,C) and XeF(B,C). The excitation spectrum for Xe/ClF is similar to that for Xe/Cl₂, but it is slightly narrower and shifted to shorter wavelength. The two-photon LAR cross section for Xe/ClF is 2-3 times smaller than Xe/Cl_2 in accord with their similar one-photon extinction coefficients. The generation of high vibrational levels of XeCl(B and C) provides support for the direct excitation mechanism for the conditions of these experiments. The interplay between stimulated emission rates and vibrational relaxation rates of XeCl(B,C) upon the apparent laser intensity dependence of LAR is discussed. If the excitation wavelength is >308 nm for which σ_s is negligible (e.g. the experiments of ref 1 for which the excitation wavelength was 313 nm and the pressure was <10 Torr), the second-order intensity dependence would hold even for intensities as high as 300 MW/cm^2 . But, if the laser wavelength is ≤ 308 nm, stimulated emission must be considered because the stimulated emission cross section is very large, $\sigma_s = 4.0 \times 10^{-16} \text{ cm}^2 \text{ at } 308 \text{ nm}.^{16}$

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Influence of Potential on Metal-Adsorbate Structure: Solvent-Independent Nature of Infrared Spectra for Pt(111)/CO

Si-Chung Chang,[†] Xudong Jiang, Joseph D. Roth, and Michael J. Weaver*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (Received: April 16, 1991)

In situ infrared spectra are reported in the C–O stretching (ν_{CO}) region for saturated CO adlayers on Pt(111) in four nonaqueous solvents; acetonitrile, dimethylformamide, dichloromethane, and tetrahydrofuran, each containing tetraalkylammonium cations, over wide electrode potential ranges, ca. -2.0 to 1.5 V vs SCE. Notably, the spectral features (vco frequencies, CO site occupancies, etc.) are sensitive only to the applied potential, being virtually independent of the solvating medium. Comparisons with spectra obtained in the presence of different cations, and in corresponding aqueous electrochemical and ultrahigh-vacuum environments, demonstrate that the adlayer properties are controlled in each case by the surface potential drop across the adsorbate layer.

A fundamental topic in electrochemical surface science concerns the manner and extent to which the adsorbate bonding and adlayer structure are influenced by the applied potential. Although not always recognized as such, this issue is also of relevance to adsorption at metal-ultrahigh vacuum (uhv) interfaces, especially in the presence of ionizable and strongly dipolar coadsorbates. The recent development of infrared reflection-absorption spectroscopy (IRAS) for the in situ examination of ordered monocrystalline metal-solution interfaces is enabling molecular-level information on adsorbate structure to be obtained in a manner previously exclusive to uhv surface science. The adsorption of

carbon monoxide is of particular interest in this regard, given the sensitivity of the C–O vibration (ν_{CO}) to the details of surface bonding.

We have recently undertaken a series of in situ IRAS studies of the adsorption and electrooxidation of CO at ordered low-index platinum and rhodium surfaces in aqueous media.¹⁻⁶ One im-

[†]Current address: Analytical Sciences Laboratory, Dow Chemical Co., Midland, MI 48674.

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