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Energy disposal in the two-photon laser-assisted reaction in xenon and chlorine gas mixtures

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The two-photon laser assisted reaction (LAR) in low pressure xenon and chlorine gas mixtures has been studied over a broad range of excitation wavelengths in order to characterize the role of the entrance channel in determining the vibrational state distribution of the reaction products. We measure a high degree of vibrational excitation in the XeCl* product, confirming observations from previous studies of the LAR of Xe+Cl₂ collision pairs [Ku *et al.*, J. Phys. Chem. **87**, 2989 (1983)], and in distinct contrast with the vibrationally cold excimer observed following laser excitation in molecular beam experiments [Boivineau *et al.*, Chem. Phys. Lett. **128**, 528 (1986)]. The mean vibrational energy in the XeCl excimer depends strongly on laser wavelength, increasing with decreasing wavelength. Moreover, an increasing fraction of the available energy from the reaction is observed as vibration in the XeCl* product as the laser is tuned toward shorter wavelengths. The reaction outcomes are interpreted in terms of a selectivity of initial conditions on the ionic potential surface that mediates the reactive collision. © 2000 American Institute of Physics. [S0021-9606(00)71447-4]

I. INTRODUCTION

The two-photon laser-assisted reaction (LAR) of Xe with Cl₂ can be classified under a general category of laserinduced "harpoon" reactions. A common feature of the harpoon reactions between rare gas atoms (Rg) and halogen molecules (X₂) is the presence of an intermediate charge transfer complex {Rg⁺X₂}. This charge transfer state (CTS) leads to formation of the RgX(*B*,*C*) exciplex with near unit probability. The Rg+X₂ harpoon reactions have been the subject of considerable research interest as useful systems for fundamental studies of bimolecular reaction dynamics, and are also of practical interest due to the role of the {Rg⁺X₂⁻} CTS in neutral channels contributing to formation of the excimer states involved in rare gas-halide (excimer) lasers and UV lamps.

The LAR of rare gases with halogens has previously been demonstrated using one- or two-photon excitation in experiments involving transient "collision pairs" in the gas phase, ¹⁻⁸ van der Waals (vdW) complexes formed in supersonic expansions, ^{9–11} as well as liquid or solid rare gas/halogen mixtures.^{12–17} The entrance channel to the Xe+Cl₂ LAR is unique from other laser-induced reactions between Xe and Cl₂ in that it involves a coherent two-photon excitation of the transient Xe-Cl₂ collision pair (or bound vdW complex) to the {Xe⁺Cl₂} CTS,

$$Xe+Cl_2 \xrightarrow{2h\nu} {Xe^+Cl_2^-}^* \rightarrow XeCl^*+Cl.$$
(1)

The above reaction is usually described as a cooperative process, where the excitation involves a *pair* of chemical species rather than a single chemical center.⁸ This reaction is distinct from other harpoon reactions in that the two-photon energy $2h\nu$ is not necessarily resonant with either reagent as an unperturbed species, and the tuning range of the excitation can be very broad. The excitation in Xe/Cl₂ gas mixtures, in particular, is characterized by a broad continuous tuning range between approximately 288–316 nm.^{3,11}

The two-photon excitation in (1) provides a large exoergicity (1.3-2.2 eV) for the reaction; this excess energy will be shared between the translational, rotational, and vibrational degrees of freedom of the reaction products. A significant fraction of the available energy can be expected to appear as internal energy (i.e., vibration and/or rotation) in the excimer product XeCl*. In this work, a large variation in the vibrational energy distributions in the excimer product has been directly measured for the first time as the excitation is tuned through this range. This variation is interpreted in terms of the role of initial conditions in the entrance channel to the reaction. The present experiment is thus of interest as a demonstration of the coherent control of a chemical reaction.

II. EXPERIMENTAL APPROACH

In these experiments, we seek to observe the nascent vibrational distributions in reaction products resulting from the two-photon laser-assisted reaction. By monitoring the bound-free fluorescence of the XeCl* reaction product, the degree of vibrational excitation can be characterized as a function of excitation energy. Detailed analysis of the extent and nature of the diffuse emission spectra, moreover, should ultimately provide an accurate characterization of the distribution of quantum states from which the radiation originates.

The short radiative lifetime of the XeCl(B) product facilitates direct observation of nascent product state distributions in low pressure gas mixtures. Nevertheless, in order that the radiating distribution reflect the nascent distribution, we must ensure that the collision rate is sufficiently low so that vibrational relaxation due to secondary collisions are

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improbable during the radiative lifetime of the product state, i.e., $\nu_{coll} < \nu_{rad}$. This implies the need to work at the lowest possible pressures (P < 3 Torr). These low working pressures also limit, however, the number of collision pairs seen by the excitation laser—the number of collision pairs at a specific collision radius is proportional to the *square* of the total pressure—so that reaction rates and hence signal levels are necessarily limited in our experiment.

Given the above limitation on the density of collision pairs, it is especially important to maximize production rates and detection efficiencies for the reaction products. Although two photon transition rates scale quadratically with incident laser powers, saturation effects, including stimulated emission and photoionization, effectively limit increases in useful signal due to increasing laser intensities. We instead utilize a long focal length lens to maximize focal volume, thereby increasing the number of potential collision pairs in the interaction region. We also employ high collection efficiency optics and multichannel detection to improve sensitivity. In addition, long integration times and averages of many spectra are required to obtain acceptable signal to noise ratios.

We also note that, as the laser and continuum emission occur in overlapping spectral regions, we are faced with the technical problems associated with monitoring weak signals in the presence of a strong background. Fluorescence signals are monitored at right angles to the excitation laser beam, and multiple apertures are employed to provide a high degree of rejection of scattered laser light from windows and surfaces. And, most importantly, we employ background subtraction techniques to effectively remove the narrow Rayleigh background signals from the spectra.

A. Experimental apparatus

The xenon and chlorine gas mixtures were prepared by first introducing xenon (Spectra Gases, Inc. 99.999%) into a gas handling system, then cryogenically pumping the gas into a mixing bottle. Chlorine (Matheson Gas Products, research grade) was next released into the same volume in the gas handling system, then also condensed into the mixing bottle. The gas mixture was allowed to thermalize at room temperature within the mixing bottle, and then released into the sample cell.

Excitation of Xe/Cl₂ gas mixtures was provided by the frequency-doubled output of an Nd:YAG-pumped tunable pulsed dye laser system. The laser output was tunable between the range 280–340 nm (using various Rhodamine and DCM laser dyes) with pulse energies up to 7 mJ/pulse. Pulse lengths were 6–7 ns. The UV beam was focused by a 175 mm lens and entered the detection cell via a sapphire window. To avoid the nonlinear effects due to the high laser intensities discussed above, the fluorescence was collected five Rayleigh lengths from the focus of the laser. At this position the beam waist was approximately 240 μ m and the intensity 8–10 MW/cm². A series of three apertures were positioned inside the sample cell both before and after the detection region to reject scattered laser light from the entrance and exit windows.

Fluorescence signals were monitored at right angles to the excitation laser beam, and the broad excimer emission



FIG. 1. Fluorescence spectra as a function of excitation wavelength for the two-photon LAR in 2.7 Torr Xe/Cl₂ (10% Cl₂) gas mixtures. Laser scatter peaks have been subtracted, and peak fluorescence signals have been normalized to the same height for comparison.

was resolved by an optical multichannel analyzer (OMA) with a UV-enhanced, intensified diode array detector (EG&G PARC 1420R-1024-HQ) mounted on a 0.64 m spectrometer (Instruments SA HR640) with f/5.5 imaging optics. The spectrometer includes a 300 g/mm grating blazed for 500 nm in first order. This grating was used in second order to gain greater detection efficiency in the spectral region of interest near 300 nm. The measured quantum efficiency of the diode array detector is 18% at 300 nm.

III. RESULTS AND ANALYSIS

A. Emission spectra

The diffuse emission spectra observed following excitation of the Xe/Cl₂ gas mixture for a range of laser excitation energies are illustrated in Fig. 1. The excitation laser wavelength was tuned from 286 to 313.5 nm in 2.5 nm increments, and the dispersed fluorescence was recorded between approximately 240 and 320 nm for the reaction at each laser wavelength. The recorded spectra were corrected for the measured spectral response of the combined OMA/ spectrometer system (using a D₂ UV radiance standard) as well as the measured "flat field" response¹⁸ of the diode array detector. The Rayleigh scattered laser light was recorded immediately afterward using pure xenon; this peak and a dark noise background were then subtracted from the corresponding LAR spectrum.

The fluorescence spectra were acquired in Xe/Cl₂ gas mixtures at the lowest possible pressures ($P_{tot}=2.6$ Torr, or $n=8.4\times10^{16}$ cm⁻³) in order to minimize collisional relaxation of the nascent vibrational distributions in the reaction products. In order to verify that vibrational relaxation is not significant at this pressure, we consider the vibrational relaxation constant k_{Xe}^{R} determined by Inoue *et al.*¹⁹ for v'=2 $\rightarrow 0,1$ relaxation in XeCl(*B*). From analysis of the timeresolved emission profiles following photoassociative excitation to the XeCl(B, v'=2) level, the authors assigned a value $k_{Xe}^{R} = (2\pm1)\times10^{-10}$ cm³ molecule⁻¹ s⁻¹. Using this value we calculate

$$\nu_{\text{relax}} = k_{\text{Xe}}^{\text{R}} \cdot [\text{Xe}] \approx (60 \,\text{ns})^{-1}.$$
(2)

In comparison, the radiative lifetime for the XeCl(B) state has been measured as $\tau = 11.1 \pm 0.2 \text{ ns.}^{19}$ Hence, $\nu_{rad} = 1/\tau$ $> \nu_{\rm coll}$, and vibrational relaxation can be assumed to be small during the time the excimer fluoresces. The radiative lifetime increases to $\tau \approx 30 \text{ ns}$ for $v' = 100, ^{20}$ but the condition $v_{rad} > v_{relax}$ is still satisfied for these very high vibrational levels. The efficiency, furthermore, of V-T transfer is relatively small for most atom-diatom collisions-10³ or more such collisions are typically required for V-Ttransfer.²¹ We surmise that the rapid vibrational relaxation rate observed by Inoue et al.¹⁹ (nearly equal to the collision frequency) results from exchange and would not be expected to increase significantly for higher vibrational levels. Conclusions from the above analysis were borne out by comparison of emission spectra from the LAR measured at 2.6 Torr with that in 6 Torr gas mixtures: Vibrational relaxation was minimal in the higher pressure spectrum.

The dependence of the laser-induced fluorescence on laser fluence was also investigated. Integrated fluorescence signals were recorded at right angles to the incident laser as the laser fluence at the focus in the optical cell was varied from approximately 3 to 30 MW/cm². The measured fluorescence signals were found to be proportional to I^y , where y = 1.7-1.8 for the current focus conditions. By further defocusing the incident laser beam, the power dependence was seen to approach I^2 , as is expected for two-photon transitions. We note that our detection geometry is not sensitive to stimulated emission, and so the measured deviation from quadratic dependence at higher incident laser intensities is consistent with the large cross section for stimulated emission in the upper XeCl state.⁶

The gross trends in energy disposal are evident from inspection of the spectra in Fig. 1. As the excitation laser is tuned to shorter wavelengths, the blue wings of the emission spectra are enhanced, indicating greater vibrational excitation in the XeCl excimer. The excess energy from the reaction ΔH_0^0 increases from 1.4 eV at an excitation wavelength of 313.5 nm to 2.2 eV at 286 nm, and much of this energy can be expected to appear as vibration in the excimer product. In order to provide a more quantitative analysis of energy disposal in the LAR, we model the observed spectral emission. The techniques used to simulate the emission spectra and determine the corresponding vibrational distributions are the subject of the following section.

B. Simulation and analysis method

The vibrational distributions in the reaction products were determined by simulation of the emission from the XeCl* excimer. Determining an unambiguous solution for the populations of the individual vibrational levels P(v') is made difficult by the vast number of energetically accessible vibrational levels in the upper radiating state (up to $v' \sim 140$) and the overlapping nature of the broad continua emission to the repulsive ground state from each of these rovibrational levels in the upper state. The simulation technique is described below, and the inversion approach is detailed in Sec. III B 2.

1. Spectral simulations

To accurately model the observed emission spectrum, we have simulated the bound-free and bound-bound emission resulting from the XeCl($B, v' \rightarrow X$) transition. The dominant contribution is from bound-free transitions due to the largely repulsive character of the ground state potential. The bound-free emission spectrum resulting from transitions between a single rovibrational state $|v'J'\rangle$ and all lower states $|\varepsilon''J''\rangle$ in the vibrational continuum is given by²²

$$I_{v'J'}^{\text{bf}}(\lambda) = \frac{64\pi^4}{3h} \nu^5 |\langle \varepsilon'' J'' | \mu_{\text{e}}(R) | v'J' \rangle|^2.$$
(3)

The emission wavelength is a function of the continuum energy, $\lambda = 1/(G_{v'J'} + T_e - \varepsilon'')$, where T_e is the energy difference between the minima of the excited and ground state potentials, and $G_{v'J'}$ is the rovibrational energy in the excited state. Similarly, the bound-bound contribution is calculated as

$$I_{v'J'}^{bb}(\lambda) = \frac{64\pi^4}{3h} \nu^5 |\langle v''J''|\mu_e(R)|v'J'\rangle|^2,$$
(4)

where $\lambda = 1/(T_e + G_{v'J'} - G_{v''J''})$. Therefore the total emission spectrum from a single rovibrational level is

$$I_{v'J'}(\lambda) = I_{v'J'}^{bf}(\lambda) + I_{v'J'}^{bb}(\lambda).$$
⁽⁵⁾

The above spectral distributions $I_{v'J'}(\lambda)$ are expressed in terms of a quantum flux per wave number in order to facilitate comparison to the experimental spectrum recorded per unit wavelength. The wave functions $\psi_{vJ}(R) = \langle R | vJ \rangle$ and $\psi_{\varepsilon J}(R) = \langle R | \varepsilon J \rangle$ are normalized solutions of the radial Schrödinger equation,

$$d^{2}\psi/dR^{2} + (2\,\mu/\hbar^{2})[E - U_{J}(R)]\psi(R) = 0, \qquad (6)$$

where $E = G_{vJ}$ ($E = \varepsilon$) for the bound (unbound) states and U_J are the effective potentials defined as

$$U_J(R) = V(R) + (\hbar^2/2\mu R^2)J(J+1).$$
(7)

V(R) are the rotationless potentials V'(R) and V''(R) associated with the $B(\frac{1}{2})$ and $X(\frac{1}{2})$ electronic states of XeCl, respectively, and μ is the reduced mass for the XeCl molecule. The potentials and dipole transition moment $\mu_e(R)$ used in this work are described in the Appendix.

The Schrödinger equation (6) is integrated numerically using the Numerov finite difference method as described by Cooley²³ (see also Ref. 24) to obtain the eigenenergies and normalized wave functions. The continuum wave functions were energy normalized by matching the amplitude at large R to the asymptotic solution

$$\psi_{\varepsilon}(R) \xrightarrow{R \to \infty} \sqrt{2\mu/\pi\hbar^2 k} \sin(kR + \delta), \qquad (8)$$

where $k = \sqrt{2\mu\epsilon}/\hbar$ and δ is a phase term dependent on the form of the dissociative lower potential.

Once the wave functions have been obtained, the Franck–Condon integrals (3,4) are evaluated for the dipoleallowed transitions $\Delta J \equiv J' - J'' = 0, \pm 1$ and over a range of continuum energies ε'' . The observed spectra are modeled as superpositions of the radiative transitions originating from all possible rovibrational levels in the upper state, i.e.,

$$I(\lambda) = \sum_{v'=0}^{v'_{\max}} \sum_{J'=0}^{J'_{\max}(v')} P(v', J') I_{v'J'}(\lambda),$$
(9)

where P(v',J') is the population in the initial state $|v'J'\rangle$, v'_{max} is the maximum energetically allowed vibrational level, and $J'_{max}(v')$ is the maximum allowed rotational level within the vibrational manifold v'. As noted, the summations in Eq. (9) are over very large numbers of vibrational and rotational levels due to the large reaction exoergicity in the laser-assisted reaction.

2. Inversion method

Once the emission spectra $I_{v'J'}(\lambda)$ have been calculated for all energetically accessible levels in the upper state, it should be possible to determine the product state distribution from which the observed spectra originates by directly solving Eq. (9) for the populations P(v',J'). This approach, however, is computationally expensive, and in practice is also limited by the finite instrumental resolution and by the presence of noise in the experimental spectrum. These limitations make a unique determination of the individual populations P(v',J') difficult if not impossible. A more expedient and reliable approach is to seek a histogram representation of the actual distribution, i.e.,

$$I(\lambda) \simeq \sum_{i=1}^{N} \bar{P}_{i} I_{i}(\lambda), \qquad (10)$$

where \overline{P}_i is the mean population number for the *i*th group of rovibrational levels, N is the total number of bins of vibrational levels, and $I_i(\lambda)$ is the sum of the contributions to the spectra from all rovibrational levels within the *i*th group,

$$I_{i}(\lambda) = \sum_{v' \in i} \sum_{J'=0}^{J'_{\max}(v')} P(J'|v') I_{v'J'}(\lambda).$$
(11)

 $P(J'|v') \equiv P(v,J)/P(v)$ is the conditional probability for the level J' in the rotational manifold of the vibrational level v'.

The binned populations \overline{P}_i were determined using a nonlinear regression technique^{25,26} in which the amplitudes were constrained to non-negative values. The optimal size and number of bins were determined through trial and error. Best results were typically obtained using 5–7 equal sized bins containing approximately 20 vibrational levels each smaller bin sizes resulted in less reliable histogram representations while larger bin widths resulted in obvious loss of resolution and a degraded fit to the observed spectrum. The simulated spectra $I_i(\lambda)$ are largely insensitive to rotational contributions—although the summation over J may include a very large number of rotational levels, the effect of angular momentum is largely to smooth out the highest frequency (noiselike) components in the generated spectrum. Hence the rotational distributions P(J'|v') were adequately represented by the rotational "prior distribution,"²⁷

$$P^{0}(f_{\rm R}|f_{\rm V}) = \frac{3}{2}(1 - g_{\rm R})^{1/2} / (1 - f_{\rm V}), \qquad (12)$$

where f_V , f_R are the reduced energies defined as $f_V \equiv E_v/E$, $f_R \equiv E_R/E$; and g_R is the reduced rotational energy defined as $g_R \equiv f_R/(1-f_V)$. The summation over *J* in Eq. (11) was also approximated by including fewer than a dozen levels (i.e., every 80th *J*) for computational expediency.

The sensitivity of the direct inversion method was first tested by applying this procedure to the analysis of a simulated spectra generated for a known vibrational distribution. Toward this end, a three-body linear surprisal distribution,²⁷

$$P(f_{\rm V}) = P^0(f_{\rm V}) \exp[-\lambda_0 - \lambda_v f_{\rm V}], \qquad (13)$$

where $f_V \equiv E_v / E$, and $P^0(f_V)$ is the vibrational prior distribution

$$P^{0}(f_{\rm V}) = \frac{5}{2} (1 - f_{\rm V})^{3/2}, \tag{14}$$

was chosen to represent a typical rovibrational distribution involving very high vibrational levels. The inversion algorithm quickly converged to a stable solution, independent of initial conditions, for the amplitudes \overline{P}_i . The size and number of vibrational bins were varied to confirm the invariance of the fit, and the self-consistency of this approach was also verified by recalculating the simulated spectrum from the derived population histogram.

C. Simulation and analysis of the LAR

The series of emission spectra recorded following the two-photon excitation in low pressure Xe/Cl_2 gas mixtures (Fig. 1) were analyzed using the direct inversion technique as described above to determine the vibrational distributions in the XeCl* reaction product. Each spectrum was analyzed using multiple combinations of vibrational bin size and number in order to confirm that the algorithm converges to a consistent and physical result. Optimal results were obtained using 5–7 bins containing between 15 and 21 vibrational levels each—larger numbers of bins typically resulted in less smooth histogram distributions and larger uncertainties.

Typical simulated and observed emission spectra are illustrated in Figs. 2-4. The simulated spectra are seen to reproduce the profile of the experimentally obtained spectra well, particularly the oscillations at shorter wavelengths. Direct inversion using the histogram representation gave qualitatively similar results to those obtained using a linear vibrational surprisal representation (13) in which the vibrational distribution is described by the single parameter λ_{v} —in fact, in most cases the simulated spectra from the two methods could not be distinguished although the direct inversion result indicated greater population in the highest vibrational levels. A comparison of the simulated spectra obtained using these two representations and the resulting vibrational distributions is provided in Fig. 2. Differences in the population numbers determined by these two representations were within the fitting errors for the histogram amplitudes returned by the direct inversion algorithm. We also noted problems in both methods in reproducing the sharpness of the main peak in certain spectra. We were unable to determine the reason for this discrepancy.

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FIG. 2. Comparison of observed emission spectra from the Xe/Cl₂ LAR for excitation at 311 nm (crosses) to simulated spectra obtained by direct inversion using histogram (solid line) and linear surprisal (dashed line) representations for the vibrational populations, as described in the text. The populations determined using each models are shown in the inset. The asterisk above the wavelength axis indicates the two-photon laser excitation wavelength for this reaction.

The vibrational population histograms returned by the direct inversion method are shown in Figs. 5 and 6, and the energy disposal trends determined by inversion of the observed spectra using both the histogram and linear surprisal representations of the vibrational distributions are summarized in Table I. Vibrational energy disposal in the LAR was characterized by the mean reduced vibrational energy

$$\langle f_{\rm V} \rangle = \langle E_v \rangle / E = \sum_{v,J} P(v,J) E_v / E,$$
 (15)

where P(v,J) is the normalized vibrational distribution determined from the simulation of the observed spectrum, E_v



FIG. 3. Comparison of observed emission spectra from the Xe/Cl₂ LAR for excitation at 301 nm (crosses) to simulated spectra (solid line) obtained by direct inversion. The asterisk above the wavelength axis indicates the two-photon excitation wavelength for the reaction.



FIG. 4. Comparison of observed emission spectra from the Xe/Cl_2 LAR for excitation at 293.5 nm (crosses) to simulated spectra (solid line) obtained by direct inversion. The asterisk indicates the two-photon excitation wavelength for the reaction.

are the eigenenergies in the upper potential, and E is the maximum energy available to the reaction products in the LAR,

$$E = \Delta H_0^0 = 2h \nu_{\rm ex} - T_{\rm e}({\rm XeCl}) - D_{\rm e}({\rm Cl}_2).$$
(16)



FIG. 5. Calculated vibrational distributions, as determined by direct inversion of the emission spectrum recorded following excitation at (a) 313.5 nm, (b) 311 nm, (c) 308.5 nm, (d) 306 nm, (e) 303.5 nm, and (f) 301 nm.

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FIG. 6. Calculated vibrational distributions, as determined by direct inversion of the emission spectrum recorded following excitation at (g) 298.5 nm, (h) 296 nm, (i) 293.5 nm, (j) 291 nm, and (k) 288.5 nm.

The analysis results (Table I) show that the mean vibrational energy in the excimer product $\langle E_v \rangle$ increases (from 0.48 to 1.13 eV) as the excitation laser is tuned from 313.5 nm to 288.5 nm. Moreover, the average *fraction* of the available energy entering vibration $\langle f_V \rangle$ is seen to increase from approximately one-third at the longest excitation wavelengths

TABLE I. Summary of analyses results for energy disposal in the twophoton laser-assisted reaction of Xe with Cl_2 . Fitting results using a linear three-body surprisal model are also shown for comparison to direct inversion results using histogram representations for the distributions of vibrational levels. (See text for details.)

			Linear surprisal		Histo	gram	
$_{(nm)}^{\lambda_{ex}}$	ΔH_0^0 (eV)	$v_{\rm max}$	λ_v	$ \begin{array}{c} \langle E_v \rangle \\ (\mathrm{eV}) \end{array} $	$\langle f_{\rm V} \rangle$	$\langle E_v \rangle$ (eV)	$\langle f_{\rm V} \rangle$
286.0	2.167	138		•••			
288.5	2.092	131	-2.87	1.02	0.49	1.13	0.54
291.0	2.018	123	-1.87	0.86	0.43	0.99	0.49
293.5	1.946	116	-2.12	0.86	0.44	1.03	0.53
296.0	1.874	110	-3.16	0.94	0.50	1.05	0.56
298.5	1.804	104	-2.71	0.85	0.47	0.98	0.54
301.0	1.735	98	-1.91	0.73	0.42	0.97	0.56
303.5	1.667	92	-2.64	0.77	0.46	0.92	0.55
306.0	1.601	87	-2.86	0.75	0.47	0.87	0.55
308.5	1.535	83	-0.32	0.50	0.33	0.60	0.39
311.0	1.470	78	-0.43	0.49	0.33	0.55	0.37
313.5	1.407	74	-0.41	0.46	0.33	0.48	0.34



FIG. 7. Mean vibrational energy $\langle E_v \rangle$ and mean fraction of available energy entering vibration $\langle f_V \rangle$ in the XeCl* reaction product as a function of the available energy ΔH_0^0 from the LAR.

(lowest ΔH_0^0) to over one-half at the shorter wavelengths. The vibrational energies determined using the linear surprisal representation were consistent with the direct inversion results. These energy disposal trends are illustrated in Fig. 7.

IV. DISCUSSION

A large degree of vibrational energy disposal characterized the LAR's in Xe/Cl₂ gas mixtures studied in this work. The mean vibrational energy $\langle E_v \rangle$ in the excimer product varied from slightly less than 0.5 eV for the LAR at 313.5 nm to greater than 1 eV for the reaction at 288.5 nm. Furthermore, the average fraction of available energy entering vibration $\langle f_{\rm V} \rangle$ was also found to increase with decreasing laser wavelength from an initial value of one-third for λ_{ex} = 313.5 nm to over one-half for wavelengths $\lambda_{ex} \leq 306$ nm. The mean reduced energy $\langle f_{\rm V} \rangle$ is approximately constant for excitation wavelengths below 306 nm. The mean vibrational energy appears to be significantly less, however, for the LAR in the current experiment than for the reactive quenching of metastable Xe* by Cl₂—compare, for example, $\langle f_V \rangle = 0.77$ measured for the Xe(${}^{3}P_{2}$) + Cl₂ reaction (ΔH_{0}^{0} = 1.865 eV) (Ref. 28) with the mean energy $\langle f_{\rm V} \rangle = 0.56$ for the LAR at 296 nm ($\Delta H_0^0 = 1.874 \,\mathrm{eV}$)—although the quenching reactions were investigated at substantially lower pressures (0.1 Torr vs 2.6 Torr in the current experiment).

The entrance channel to the Xe+Cl₂ LAR, unlike the quenching reaction, involves a direct two-photon excitation to the ${\rm Xe^+Cl_2^-}$ CTS via a cooperative photoabsorption by the initial Xe+Cl₂ complex. One of the difficulties associated with demonstrating this cooperative excitation process is in isolating this reaction from competing reaction pathways, particularly that of the photodissociation of Cl₂ followed by photoassociation of Xe with Cl,

$$\operatorname{Cl}_2 \xrightarrow{h\nu} \operatorname{Cl}_2(A^{-1}\Pi_u) \rightarrow 2\operatorname{Cl},$$
 (17)

$$Xe+Cl \longrightarrow XeCl(B).$$
 (18)

This sequential or stepwise process was observed by Mc-Cown and $Eden^{29}$ in the excitation of high pressure (300

hν



FIG. 8. Semiempirical representation of the reactive potential energy surface for the $Xe^+Cl_2^-$ system, assuming a $C_{2\nu}$ geometry. The trajectories represent the classical evolution of the triatomic complex from initial conditions **A**, **B**, and **B**^{*} on the reactive surface. (See text for discussion.)

Torr) Xe/Cl₂ gas pressures. Previous researchers have argued a lack of evidence for this sequential channel in the Xe/Cl₂ reaction in low pressure gas mixtures,⁸ and detailed calculations show that this process is indeed negligible $(\sigma_{seq}/\sigma_{LAR} \approx 10^{-4})$ under the current experimental conditions.³⁰

We note that the two-photon excitation in (1) can also be considered as proceeding via the energy-resonant dissociative $\text{Cl}_2(A \ ^1\Pi_u)$ intermediate state, as recognized by Setser and co-workers.⁸ If the lifetime of this intermediate complex is short, however, the initial conditions still determine the reaction outcome.³¹ Recent two-photon femtosecond studies^{17,32} suggest that this is in fact the case in the reaction originating from collision pairs in low pressure gas mixtures. In the latter study,³² Dedonder-Lardeux *et al.* also identified a second entrance channel occurring some 500 fs after the initial photon absorption in the reaction originating from vdW complexes. This delayed entrance channel is also transient, and therefore is thought to occur within Xe_nCl₂ clusters where cage effects allow a recoil of the dissociating Cl atom.

The observed energy disposal trends support the qualitative interpretation of dynamics in the LAR based on the role of initial conditions on a reactive PES.^{11,31} For laser wavelengths above 306 nm, the direct excitation is predicted to occur for Xe–Cl distances very near the minimum of the "exit seam" in the ionic potential surface [correlating to XeCl(*B*) at large *R*(Cl–Cl)]. Release of the repulsion in the Cl–Cl⁻ bond leads to energy disposal largely as translation between the XeCl and Cl products. This is illustrated in Fig. 8 by the trajectory originating from point A. The low fraction of excess energy found as vibration in the excimer produced by the LAR at this laser wavelength ($\langle f_V \rangle \approx 0.3$) is consistent with this interpretation, and implies that as much as 1.1 eV of kinetic energy is shared between the atom and diatom products. The range of initial conditions probed on the reactive $V(Xe^+;Cl_2^-)$ surface as the laser is tuned from the minimum transition energy is determined by gradients in both the Xe^+-Cl^- and $Cl-Cl^-$ coordinates of the PES. The gradient in the $Cl-Cl^-$ coordinate $[\partial V/\partial R(Cl-Cl^-)\approx -15.7 \text{ eV/Å} \text{ at } R(Cl-Cl^-)=R_e(Cl_2)]$ (Ref. 33) is much larger than that in the Xe^+-Cl^- coordinate $[\partial V/\partial R(Xe^+-Cl_2^-)\approx 0.8 \text{ eV/Å} \text{ at } R(Xe^+-Cl_2^-)=4 \text{ Å}]$, so the vibrational phase in the Cl_2 reagent may have a large role in determining the excitation range for the reaction. In fact, as noted by Setser,⁸ the width of the excitation spectrum can be accounted for entirely by the gradient in the Cl_-Cl^- coordinate of the PES.

As the laser is tuned to more energetic wavelengths, we consider two limiting cases: (a) the reaction proceeds from collision pairs at larger Xe–Cl₂ distances and typical Cl–Cl distances $[R(Cl-Cl) \approx R_e(Cl_2)]$ (point B in Fig. 8), and/or (b) the reaction occurs for $R(Xe-Cl_2)$ near the vdW minimum and for $R(Cl-Cl) < R_e(Cl_2)$ (point B* in Fig. 8). If we follow a typical reactive trajectory originating from point B*, we see that any additional energy is also carried away as translation between the XeCl* and Cl products, so that the degree of vibrational excitation in the excimer differs very little from that resulting from the half collision originating at point **A**.

If, on the other hand, the excitation at the shorter wavelength occurs for an initial geometry corresponding to point **B** on the ionic surface, the subsequent dynamics will exhibit significant motion in the R(Xe-Cl) coordinate as the triatomic complex flies apart, and thus the XeCl excimer will be formed with a high degree of vibrational energy. This interpretation appears to be more consistent with the observations in the current experiment, in which a significant degree of vibrational excitation was measured ($\langle E_v \rangle \sim 1 \text{ eV}$) for the LAR at short laser wavelengths.

The previous analysis assumes a C_{2v} (T-shaped) geometry for the collision pair or vdW complex, as suggested by the spectroscopic studies of Janda *et al.*³⁴ Recent studies of Xe/Cl₂ in Ar matrices imply that this assumption is not necessarily valid, even for the vdW molecule: Their work gives evidence for the existence of a linear ground state for XeCl₂.³⁵ Similar arguments, however, can be presented, *mutatis mutandis*, for the dynamics on a reactive PES appropriate for a linear geometry.

V. SUMMARY AND CONCLUSIONS

The entrance channel to the Xe/Cl₂ LAR is unique from other laser-induced reactions between Xe and Cl₂ in that it involves a direct two-photon excitation to the {Xe⁺Cl₂⁻} CTS. This excitation occurs via a cooperative photoabsorption by the transient Xe–Cl₂ collision pair, and is characterized by a broad continuous excitation spectrum. The continuous range of excitation in the LAR affords an aspect of direct laser control of the reaction. The goal of the present work has been to characterize the energy disposal as a function of excitation wavelength, and thus to relate the measured trends to the role of initial conditions in the entrance channel to the LAR. Toward this end, we have analyzed the continua emission observed following the LAR for a broad range of excitation wavelengths to determine the vibrational distributions in the excimer product. Significant vibrational population inversion is observed in the excimer resulting from the LAR. From analysis of the measured XeCl(B-X) fluorescence spectra we determined the mean vibrational energy $\langle E_v \rangle$ in the newly formed Xe-Cl bond to be approximately 0.5 eV (3900 cm^{-1}) for the reaction resulting from laser excitation wavelength of 313.5 nm. $\langle E_n \rangle$ increases to approximately 1.1 eV (9100 cm^{-1}) for the reaction at 288.5 nm. Furthermore, we found an increasing *fraction* of the available energy from the reaction appears as vibration in the excimer product XeCl* as the laser is tuned from redmost $\langle f_{\rm V} \rangle$ ≈ 0.3 at 313.5 nm) to bluer wavelengths ($\langle f_V \rangle \approx 0.5$ for λ_{ex} \leq 306 nm). As illustrated in Fig. 7, this transition is sudden with increasing exoergicity for the reaction. This sudden increase in vibrational energy disposal is also evident in the sequence of spectra shown in Fig. 1.

The high degree of vibrational excitation observed in the XeCl* product in the current experiment is qualitatively consistent with the previous observations by Setser and coworkers for the LAR of Xe+Cl₂ collision pairs. The significant variation in *degree* of vibrational excitation over the wide range of excitation wavelengths, however, is clearly demonstrated for the first time in the present work. We attribute the increasing vibrational energy disposal to a variation of initial conditions on the reactive $V(Xe^+;Cl_2^-)$ potential energy surface, as discussed. We note, however, that while this predicted trend toward greater vibrational energy disposal with decreasing laser wavelength is clearly demonstrated in the current experiment, the same trend may not necessarily be exhibited in similar experiments in supersonic jets or in solid matrixes, due to the restricted geometries and cage effects in the in vdW complexes and in the solid matrix.

While gross dynamical trends may be inferred from the present work, deconvolution of the data to reveal individual reactive trajectories is far more difficult. A more detailed analysis, furthermore, must consider complications due to a distribution of initial (kinetic and internal) energies and orientations in the reagents. Nonetheless, the above conclusions are believed to be qualitatively correct. Numerical calculations of classical trajectories on the reactive PES using Monte Carlo sampling techniques to integrate over a distribution of initial conditions are also in reasonable agreement with the observed product state outcomes.³⁶ These conclusions differ slightly from that of Setser and co-workers, who calculate that the majority of collision pairs are found in bound levels of the shallow vdW potential $(n_{\rm b}/n_{\rm f}=0.86$ at 300 K) and conclude that the width of the excitation spectrum (0.4 eV) is largely determined by the gradient in the Cl-Cl⁻ coordinate of the PES.⁸ This interpretation, however, would fail to account for the significant variation in energy disposal observed in the present work or, for that matter, the dramatic difference in energy disposal observed for the LAR in gas phase studies and in molecular beam experiments where the initial geometry may be more restricted.

We have noted also that vibrational energy disposal in the LAR appears to be significantly less in the current experiment than that in the quenching reactions of metastable Xe* with Cl₂ studied by Setser *et al.*²⁸ This difference appears to be a significant feature of the LAR, even when accounting for additional relaxation due to the higher pressures in the current study. The exit channels in both the laser-assisted and quenching reactions involve the $\{Xe^+Cl_2^-\}$ CTS, so this apparent difference in energy disposal was previously⁸ attributed to the presence of different pathways for the two reactions.

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APPENDIX: POTENTIAL REPRESENTATIONS

The upper and lower potentials used in the simulations of the excimer emission were taken from Sur et al.³⁷ and the molecular scattering studies of Aquilanti et al.,³⁸ respectively, with slight modifications as necessary to accurately simulate emission spectra from both thermal and highly excited vibrational distributions in the upper state. The XeCl(X) ground state potential was unmodified, while the vertical position of the XeCl(B) excited state potential was determined by the XeCl(B-X) 0⁰ transition energy $\left[\nu(0^{0})\right]$ $= 32495 \pm 1 \text{ cm}^{-1}$] measured by Jouvet *et al.* in a free jet.³⁹ The upper potential was then shifted relative to the lower potential along R in order to accurately simulate the vibrationally-relaxed emission measured in high pressure Xe/Cl₂ gas mixtures (1430 Torr Xe, 10 Torr Cl₂). And finally, the upper repulsive wall was adjusted slightly to give agreement with the oscillations in the blue wing of vibrationally excited low pressure emission spectra observed by Setser and co-workers⁴⁰ following the reactive quenching of $Xe(6s, {}^{3}P_{2})$ by Cl₂. The modified upper potential was recast in the form of a truncated Rittner potential,

$$V'(R) = a \exp(-R/b) - C_1/R - C_4/R^4 + d,$$
 (A1)

and the shape of this potential was verified by comparing the calculated eigenenergies to measured values³⁷ for the lowest dozen vibrational levels.

The XeCl(B-X) transition moment is a slowly varying function of R with a maximum near R'_{e} . The *ab initio* transition moment of Hay and Dunning,⁴¹ however, required slight modification for the best simulation of spectra originating from distributions including large vibrational quanta (which sample transitions at large R). The transition moment was represented in this work by the function

$$\mu_{\rm e}(R) = c_0 \frac{\exp[-\gamma(R-c_1)]}{(1-R/c_1)^2 + c_2}.$$
 (A2)

Parameters for the above transition moment function were adjusted so that the overall "envelope" of the simulated

TABLE II. Parameters for the XeCl(B) Rittner potential function.

$a (10^7 \text{ cm}^{-1})$	b (Å)	C_1 (10 ⁵ cm ⁻¹ Å)	C_4 (10 ⁵ cm ⁻¹ Å ⁴)	d (cm^{-1})
2.185	0.387	1.177	5.456	68 987

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TABLE III. Parameters for the $B \rightarrow X$ transition moment function [Eq. (A2)].

c ₀ (Debye)	с ₁ (Å)	<i>c</i> ₂	$\stackrel{\boldsymbol{\gamma}}{(\text{\AA}^{-1})}$
0.323	3.139	0.122	0.10

spectrum matches that of the low pressure emission spectra from Setser and co-workers.⁴⁰ The final transition moment differs from the *ab initio* function largely in the enhanced shoulder at large R.

Parameters for the upper state Rittner potential (A1) and the dipole moment (A2) are compiled in Tables II and III, respectively.

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