Kinetic Studies Following State-selective Laser Excitation

Final Progress Report

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1. Introduction

The objective of this contract was the study of state-to-state, electronic energy transfer reactions relevant to the excited state chemistry observed in discharges. We studied deactivation reactions and excitation transfer in collisions of excited states of xenon and krypton atoms with Ar, Kr, Xe and chlorine. The reactant states were excited selectively in two-photon transitions using tunable u.v. and v.u.v. lasers. Excited states produced by the collision were observed by their fluorescence.

Reaction rates were measured by observing the time dependent decay of signals from reactant and product channels. In addition we measured interaction potentials of the reactants by laser spectroscopy where the laser induced fluorescence or ionization is measured as a function of laser wavelength (excitation spectra) or by measuring fluorescence spectra at fixed laser frequencies with monochromators. The spectra were obtained in the form of either lineshapes or individual lines from rovibrational transitions of bound states. Our research then required several categories of experiments in order to fully understand a reaction process:

1. High resolution laser spectroscopy of bound molecules or lineshapes of colliding pairs is used to determine potential curves for reactants.
2. Direct measurements of state-to-state reaction rates were measured by studying the time dependent loss of excited reactants and the time dependent formation of products.
3. The energy selectivity of a laser can be used to excite reactants on an excited surface with controlled internuclear configurations. For free states of reactants (as exist in a gas cell) this has been termed laser assisted reactions, while for initially bound states (as chemically bound reactants or dimers formed in supersonic beams) the experiments have been termed photo-fragmentation spectroscopy.

2.0 Relevance to DOE Mission

We measured rates for fundamental processes relevant to the kinetics of various rare gas discharges. These discharges have direct application to understanding the chemistry and energy pathways in discharge lasers, lamps, and plasma processing. As an example, research studying energy transfer from excited rare gases to halogens was directly relevant to a better understanding of excimer lasers. In many cases we studied the research of laser modelers to determine crucial reactions whose rates were unknown.

Since the reaction studies were fundamental, we also developed insight in general to propensity rules controlling reactions in the rare gases. In recent studies of energy transfer from Xe^* , we worked to determine the propensity preserving the state of the ion core during inelastic collisions with krypton and chlorides. Finally, though we may not directly be involved with modeling of other types of discharges, our data often are applicable. Discharges with rare gases and chlorides, for example, are also used in the semiconductor industry for chemical etching.

Recent reviews have emphasized the importance of low temperature plasma processing^{1,2}. The review by Gerardo concludes that many areas of technology that depend upon studies of low temperature plasmas have enormous growth potential and technological importance and are indispensable in many high-value industries. Even though training of new scientists in these fields are severely lacking, only a handful of US universities have active research programs in gaseous electronics. "The level of basic understanding in this branch of science has not progressed significantly in the past 10 years"². "Research bases in low-temperature plasma physics in the U.S. are eroding at an alarming rate. U. S. Scientists trained in this area in the 50s and 60s are retiring or are moving to other areas of science for which support is more likely. Only a handful of U.S. universities receive funding for it and trained new scientists in this branch of science are severely lacking."²

In section 3 we summarize complete measurements of the state-to-state collisional deactivation rates of $\text{Xe}^*(6p,6p',7p)$ and $\text{Kr}^*(5p)$ excited states in collision with Ar, Kr, and Xe atoms. These results are relevant to kinetic models of both excimer lasers and the infrared xenon laser^{3,4}; and we have also obtained a significant improvement in the precision of the known radiative lifetimes. References to detailed descriptions of the experiments and results were contained in previous progress reports and publication reprints and a qualitative summary of observed reaction propensities are included at the end of each section.

In section 4 we describe the importance of similar studies for reactive collisions of the same states of xenon in reaction with chlorine. We also have made model calculation for these reactions which are in good agreement with experiments.

¹H.F. Winters, R.P.H. Chang, C. J. Mogab, J. Evans, J. A. Thornton and H Yasuda, "Coatings and Surface Modifications Using Low Pressure Non-equilibrium Plasmas", *Materials Science and Engineering* **70**, 53(1985).

²J. B. Gerardo and J. T. Verdeyen, "Low-Temperature Plasma Physics: Its Importance and Potential in Technology and Commerce", Sandia National Laboratory Report No. SAND87-1875.

³Mieko Ohwa, Thomas J. Moratz, and Mark J. Kushner, "Excitation mechanisms of the electron-beam-pumped atomic xenon (5d-6p) laser in Ar/Xe Mixtures", *J. Appl. Phys.* **66**, 5131(1989).

⁴W. J. Alford, "State-to-state rate constants for quenching of xenon 6p levels by rare gases", *J. Chem. Phys.* **97**, (1992).

In section 5, we describe experiments studying two-photon laser assisted collisions. The experiments funded by this research were the first direct observation of the effect of inelastic curve crossings on collisional line shapes. In these experiments, the state of xenon is excited while undergoing a collision with a ground state atom

The diabatic potential for excited molecule crosses the potential for a more shallowly bound 0_g^+ potential dissociating to $\text{Xe}^*5d[1/2]_1$. Because the states are of the same symmetry an avoided crossing occurs, and following excitation by the laser to one of the adiabatic potentials two possible products, $\text{Xe}^*6p[1/2]_0$ and $\text{Xe}^*5d[1/2]_1$, are possible. We observed features in the collision lineshape due to this avoided crossing, and we could measure the crossing radius and the difference in the slopes for the two diabatic potential curves.

In section 6 we describe significant progress in the study of the spectroscopy of small molecules and excimers formed in supersonic beams. The molecules being studied are relevant to knowledge of the interaction potentials for our collision studies. We have concentrated in current studies on xenon excimers excited in two-photon transitions. We have also studied larger rare gas clusters both using two-photon transitions at the University of Texas and using synchrotrons at DESY in Hamburg in collaboration with George Zimmerer, at the University of Hamburg, and Thomas Möller, at DESY. As part of our two-photon cluster studies, we measured the first two-photon excitation spectra of even parity excitons in liquid xenon. These results are very interesting in that we have discovered a splitting between the 2s and 2p excitons; this splitting is not explainable by currently accepted models for excitons in liquid xenon.

3. Electronic Energy Transfer in Rare Gas Mixtures

3.1. Experiment

$\text{Xe}^*(6p,6p',7p)$ and $\text{Kr}^*(5p)$ is excited in a two-photon transition⁽⁵⁾ using a frequency doubled, dye laser with a 300 psec pulsewidth. The time dependence of the fluorescent light intensity is determined by the distribution of arrival times for the first photon following excitation. By measuring the exponential decay rates as a function of pressure, we obtain Stern-Volmer plots to determine the reaction rates, $k, \nu = \nu_{\text{rad}} + k[n]$. As an example, we find the decay rates for excited Xe^* in krypton buffers to be described by

$$\nu_q = \nu_0 + k^{(2)}_{\text{Xe}} [\text{Xe}] + k^{(2)}_{\text{Kr}} [\text{Kr}] \quad (3.0)$$

⁵J. Xu and D. W. Setser, "Deactivation rate constants and product branching in collisions of the $\text{Xe}(6p)$ states with Kr and Ar", J. Chem. Phys. **92**, 4191(1990).

where n_0 is the radiative rate and $k^{(2)}_i$ represent bimolecular reaction rates.

3.2. Quenching rates in xenon and argon

The quenching rate constants measured in xenon and argon are summarized in Table 3.1.⁽⁶⁾ These results extended our previous Xe* 6p measurements⁽⁷⁾ to higher pressures in addition to measuring rates for the higher Xe 6p' and 7p configurations. In general, the Xe 6p rates agree well with our previous results.

Table 3.1. Total collisional quench rates for Xe* 5p⁵np, np' (n=6,7) in Xe and Ar.

state	Bimolecular rates (10 ⁻¹² cm ³ /sec)			
	This work xenon	Setser xenon	This Work argon	Setser argon
6p[5/2] ₂	116± 3	96± 3 ^c	82 ± 4.0	82± 5.0 ^c
6p[3/2] ₂	101± 3	82± 5 ^c	40± 2.0	47± 5.0 ^c
6p[1/2] ₀	5.9± 0.5	5.8± 0.5 ^c	200± 4.0 ^a	140± 10 ^c
5d[1/2] ₁	197± 26 ^a		5.9± 0.4 ^b	30± 5.0 ^c
7p[5/2] ₂	462± 9	278± 62 ^d	259 ± 20	240± 20 ^f 340± 70 ^g
7p[3/2] ₂	522± 8	282± 70 ^e	348± 32	230± 20 ^f 300± 30 ^g
7p[1/2] ₀	493± 8	417± 108 ^d	256± 34	190± 30 ^f
6p'[3/2] ₂	426± 10	262± 170 ^d	179± 14	160± 2 ^f 140± 10 ^g
6p'[1/2] ₀	423± 8	262± 170 ^d	247± 14	280± 30 ^f

a) extracted from zero argon pressure intercepts by combining the argon quenching data of the Xe*6p[1/2]₀ at 828.2nm and 5d[1/2]₁ at 125nm. A different intercept for the argon quenching curves was obtained for each different xenon pressure.

b) extracted from the slow component in the Xe* 6p[1/2]₀ decay curves. See Ref.iii

c) Ku and D.W. Setser, J. Chem. Phys. **84**, 4304(1986).

d) Allen, D.G. Jones, and D.G. Schofield, J. Opt. Soc. Am. **59**, 842(1969).

e) Weighted mean value of two measurements of Allen et al.

f) Horiguchi, R.S.F. Chang, and D.W. Setser, J. Chem. Phys. **75**, 1207(1981).

g) Inoue, J.K. Ku, and D.W. Setser, J. Chem. Phys. **81**, 5760 (1984).

The result for Xe*6p[1/2]₀ was unique as it had the smallest quenching rate of all the states measured in xenon, and as in the previous study⁽⁸⁾, the Xe*6p[1/2]₀ Stern-Volmer plot had to be fit using a three-body quenching term (quench rate proportional to pressure squared). We now know from the radiative collision studies described in Section 5 that these three-body rates result from bound states formed by crossings with potentials dissociating to Xe* 5d[1/2]₁.

⁶ M. R. Bruce, Winston B. Layne, Charles A. Whitehead, and J. W. Keto, "Radiative Lifetimes and Collisional Deactivation Rates of Two-photon Excited Xenon in Argon and Xenon", J. Chem Phys. **92**, 2917(1990).

⁷ N. Bowering, M. R. Bruce, and J.W. Keto, "Collisional Deactivation of Two-Photon Excited Xenon 5p⁵6p Atoms: II. Lifetimes and Quench Rates," J. Chem. Phys. **84**, 715-726 (1986).

⁸ Ibid.

We also measured the quench rates in xenon for the higher Xe 7p and 6p' states. Previous studies of these states used charged particle excitation⁽⁹⁾ as opposed to state-selective two-photon excitation used here. The uncertainties in the charged particle measurements exceeded 50%, while the current measurements are under 5% uncertainty. In general, the quench rates by xenon for these states are all very large, on the order $4\text{-}5 \times 10^{-10} \text{ cm}^3/\text{sec}$. The quenching of these states is probably controlled by their orbiting radius⁽¹⁰⁾, as even a weak long range potential similar to what has been measured for Xe*6p states⁽¹¹⁾ produces an orbiting rate on the order of $10^{-10} \text{ cm}^3/\text{sec}$.

Table 3.2. Radiative lifetimes (nsec).

	6p[5/2] ₂	6p[3/2] ₂	6p[1/2] ₀	7p[5/2] ₂	7p[3/2] ₂	7p[1/2] ₀	6p'[3/2] ₂	6p'[1/2] ₀	5d[1/2] ₁
	Experimental								
This work	36±3	31.3±1.8	26.8±0.8	129±6	105±3	69.1±1.3	32.1±0.8	34.1±0.8	111±16
Ref. 2	36±4 ^a	35±3	28±1						
Ref. 13	39±1	36±3	33±1						
Ref. 12 ^b	39±1	31±1		154±9		62±3		40±2	
Ref. 12 ^c		31±2		166±9	115±3	65±2	37±2	38±2	
Ref. 11	40±2	38±2		100±20	120±12				
Ref. 10		33±20	40±12	200±12	152±11 ^d	87±5	39±2	38±2	
Ref. 22			29±4						
VO ^e		48±2	30±4		203±15	115±9	34±2	30±3	
JCS ^f				168±15	107±8	107±8	31±3	31±1	
HMG ^g		39±1					38±1		
CM ^h				310±30	163±10				
KK ⁱ				165±20	150±10	77±3	33±3	33±3	
SS ^j	35±2								
	Theory								
AC ^k	33.0	28.1	22.4	113	75.0	60.1	27.7	28.4	88.9
AC ^l	36.9	31.5	33.2	157	115	74.6	36.0	36.9	218
LG ^m	39.5	34.5	24.5	108	100	153	26.5	18.4	60.5

a) Extracted from the low pressure data.

b) Extracted from Ne data.

c) Extracted from Ar data.

d) Weighted mean of two lifetimes obtained for Xe* 7p[3/2]₂.

e) Ya. F. Verolainen, and A.L. Osherovitch, Opt. Spectrosc. 27, 14 (1969)

f) Jimenez, J. Campos, and C. Sanchez del Rio, J. Opt. Soc. Am. 59, 842 (1969).

g) Husson, and J. Margerie, Opt. Commun. 5, 139 (1972).

h) Chenevier, Compt. Rend. 268, 1179 (1969); M. Chenevier, et P.A. Moskowitz, J. Phys. 35, 401 (1974).

i) Karimov, and V.M. Klimkin, Sov. Phys. J. 14, 308 (1971).

j) T Suzuki, and K. Shimoda, J. Phys. Soc. Jpn. 43, 233 (1977).

k) Aymar, and M Coulombe, At. Data Nucl. Data Tables 21, 537 (1978). Calculated in length formulation.

l) *ibid.*, Calculated in velocity formulation.

m) Loginov, and P.F. Gruzdez, Opt. and Spectrosc. 41, 104 (1976).

⁹ L. Allen, D.G. Jones, and D.G. Schofield, J. Opt. Soc. Am. 59, 842 (1969).

¹⁰ See for instance James T. Yardley, *Introduction of Molecular Energy Transfer* (Academic Press, New York 1980), p. 126.

¹¹ T.D. Raymond, N. Bowering, Chien-Yu Kuo and J.W. Keto, "Two -Photon Laser Spectroscopy of Xenon Collision Pairs," Phys. Rev. 29A, 721-734 (1984).

The radiative lifetimes determined from this work are summarized in Table 3.2 along with theoretical and previous measurements.

The Xe*6p' lifetimes (32-34 nsec) were very similar to the lifetimes of the Xe*6p states (28-36 nsec). The Xe*7p states had a relatively long lifetime (69-129 nsec) and required significantly greater laser power to excite by two-photon excitation than the Xe*6p and 6p' states. An attempt to excite the Xe*8p states was made; at 1000 Torr of xenon, weak fluorescence was produced at 173nm (Xe₂* excimer band) when the laser was tuned to 8p resonances. No direct fluorescence was observed from these states in the visible even at low pressures. It is likely that the Xe*8p states associatively ionize before they radiate. Details of these experiments were included in previous DOE progress reports DOE/ER/13191-8, DOE/ER/13191-9, and DOE/ER/13191-10. Details are also provided in publications referenced and previously provided DOE as reprints.

3.3. Radiative lifetimes and total quenching rates for Xe* and Kr* in krypton and xenon

We have measured the radiative lifetimes and state-to-state quenching rates for Xe*(5p⁵6p, 5p⁵6p', 5p⁵7p; J=0,2) and Kr*(4p⁵5p) in krypton and xenon buffer gases.¹² The measured radiative lifetimes and quench rates are summarized in Table 3.3 and 3.4.

Table 3.3: Radiative lifetimes in nanoseconds of the Xe(6p,6p',7p) and Kr(5p) levels.

Level (Racah)	Experimental values			Theoretical values	
	Present work	Ref. a	Ref. b	Ref. e	Ref. f
Xenon					
6p'[1/2] ₀	33.1±1.2	34.1±0.8	-----	23	28.4
6p'[3/2] ₂	31.2±1.1	32.1±0.8	-----	28	27.7
7p[1/2] ₀	63.6±4.9	69.1±1.3	-----	118	60.1
7p[3/2] ₂	108.0±2.1	105.3±2.9	120±12	112	75.0
7p[5/2] ₂	140.0±15	128.6±5.6	100±20	140	113.
6p[1/2] ₀	25.9±0.7	26.8±0.8	-----	27	22.4
6p[3/2] ₂	28.0±1.2	31.3±1.8	38±2	27.1	28.1
6p[5/2] ₂	37.7±1.9	36.0±2.8	40±2	45	33.0

¹² C. A. Whitehead, M. R. Bruce, Hong Cai, J. Kohel, W. B. Layne, and J. W. Keto, "Deactivation of Two-Photon Excited Xe(5p⁵6p, 6p', 7p) and Kr (4p⁵5p) in Xenon and Krypton", to be published, J. Chem. Phys.

Krypton	Present	Ref. c	Ref b	Ref. g	Ref. c	Ref. d
5p[1/2] ₀	23.5±0.1	22.8±2	-----	-----	23.5	23.4
5p[3/2] ₂	26.4±0.5	21.5±2	25.4±0.8	27.35±0.06	24.5	25.2
5p[5/2] ₂	-----	32.±1.5	26.5±2.0	32.10±0.09	33.0	33.8

a) M. R. Bruce, W.B.Layne, C. A. Whitehead, and J. W. Keto, J. Chem. Phys. **92**, 2917 (1990)

b) H. Horiguchi, R. S. F. Chang, and D. W. Setser, J. Chem. Phys. **75**, 1207 (1981)

c) M. V. Fonseca and J. Campos, Phys. Rev. A **17**, 1080 (1978)

d) R. A. Lilly, J. Opt. Soc. Am. **66**, 245 (1976)

e) L. Allen, D. G. C. Jones, and D. G. Schofield, J. Opt. Soc. Am. **59**, 842 (1969)

f) M. Aymar and M. Coulombe, At. Data Nucl. Data Tables **21**, 537 (1978)

g) H. Schmorangee, U. Volz, R. Henkel, private communication.

Table 3.4. Total bimolecular reaction rates for Kr*4p⁵ 5p and Xe*5p5np in krypton and xenon.

Bimolecular rates (10 ⁻¹² cm ³ /sec)				
State	Xenon		Krypton	
	This work		This work	
Kr*	5p[5/2] ₃		170±8 ^a	
	5p[5/2] ₂	408±5	349±34	
	5p[3/2] ₂	299±6	24±2	
	5p[1/2] ₀	420±6	42±4	
		Ref. c	This work	Ref. d
Xe*	6p[5/2] ₂	116±3	38±2	45±5
	6p[3/2] ₂	101±3	28±1	22±3
	6p[1/2] ₀	5.9±0.5	132±4	110±5
	7p[5/2] ₂	462±9	405±16	
	7p[3/2] ₂	522±8	311±5	
	7p[1/2] ₀	493±8	396±6	
	6p'[3/2] ₂	426±10	294±5	
	6p'[1/2] ₀	423±8	286±5	

a) Extracted from mixed decay of Kr 5p[5/2]₂.

c) Bruce et. al.

d) Xu and Setser

e) Estimate of lower bound found from integrated intensity measurements. See text.

Note: Error bars shown are twice the standard deviation.

3.4 State-to-state reaction rates

We have measured state-to-state reaction rates for excited states of xenon and krypton described above. For our previous studies of deactivation of xenon in argon and xenon, only intramultiplet and intermultiplet deactivation of the excited state is energetically allowed. For krypton buffers excitation transfer between the reactants is also expected:

The state-to-state reaction rates were found from measurements of the relative integrated fluorescence intensities of the collisionally populated and laser excited states. The integrated intensity of the states fluorescence was measured for all states simultaneously using an EG&G intensified OMA mounted to a JY 620 spectrograph. In the vuv, a separate monochromator is used with a solar blind detector. All detector systems are absolutely calibrated using NIST traceable standard lamps. The relative integrated populations N_j are determined by

$$N_j = \frac{v_{ij}}{v_i} N_i \quad (3.3)$$

where N_i and N_j are the populations of the initially excited state $li>$ and the collisionally populated product state $lj>$, respectively. Here v_{ij} is the product formation rate from $li>$ to $lj>$ and v_i is the total quench rate of $li>$. The population N_i can be determined from the measured integrated intensity

$$I_{ik} = \eta_{ik} A_{ik} \frac{N_i}{v_i} \quad (3.4)$$

where η_{ik} is the quantum efficiency of the optical system and A_{ik} is the radiative transition probability from $li>$ to $lj>$. Finally, the product formation rate can be written as

$$v_{ij} = \frac{I_{jk} \eta_{ik} b_{ik} A_i}{I_{ik} \eta_{jk} b_{jk} A_j} v_j, \quad (3.5)$$

hence by measuring the relative integrated fluorescence intensities, branching fractions, optical transition rates, and total loss rates, we can obtain the state-to-state reaction rate v_{ij} .

Fig. 3.1. Fluorescence scan following excitation of Xe*7p[5/2]₂ in 50 Torr xenon.

Example data showing product fluorescence is shown in Fig. 3.1. At sufficiently high pressure, product states may be quenched to other levels leading to secondary population of those levels. The amount of this production depends upon the quench rates of these products compared to their spontaneous decay rates. Secondary production is a source of systematic error in the measurement of the direct state-to-state reaction rate, and it may be detected both by observing the time dependence of the product state or by observing the pressure dependence of the integrated intensity of a product state. If the lifetime of the adjacent state leading to secondary production is sufficiently different from the observed product state, then the latter state will have a time dependence different from the expected two-exponential decay,

$$N_j(t) = \frac{N_i(0)v_{ij}}{(v_i - v_j)} [\exp(-v_j t) - \exp(-v_i t)] . \quad (3.6)$$

It will also have an intensity which increases linearly with pressure at low pressures and then increases more rapidly at higher pressures due to the contribution from the secondary channel. Fig. 3.2 demonstrates a product channel with no secondary channel while Fig. 3.3 clearly indicates production through an intermediate state, likely Xe* 5d[3/2]₁. By measuring the slope of the linear portion of the curve, the state-to-state rate v_{ij} can be measured without interference from the secondary channel. Data similar to Figs. 3.2 and 3.3 have been obtained for all product channels observed for the eleven laser excited states of krypton and xenon.

Fig. 3.2 Intensity resulting from $\text{Xe}^*6p'[1/2]_0 \rightarrow 6p[1/2]_0$ in krypton.

Fig. 3.3 Intensity resulting from $\text{Xe}^*6p[1/2]_0 \rightarrow 6p[3/2]_1$ in krypton.

We have found that stimulated emission can be another major source of error in these experiments. Many spectra were taken in 1990 on a apparatus employing a detector at right angles to the laser beam propagation. Subsequent data analysis showed an erratic pressure dependence and an anomalous production of states with large oscillator strengths to the laser excited states. Data for $\text{Xe}^*6p[1/2]_0$, $\text{Xe}^*(6p', 7p)$, and $\text{Kr}^*(5p)$ were retaken using an apparatus and detector which collects fluorescence in a 30° cone in the back direction relative to the laser beam. This apparatus can then observe stimulated emission in the form of coherent fluorescence (bursts of photons). We required very low laser powers to avoid stimulated emission for these states. We also obtained product intensities which accurately increased linearly with pressure. Stimulated emission greatly distorts the branching fractions in that significant populations of states in the lower state are produced and these states in turn undergo collisional relaxation.

The state-to-state rates are summarized in Tables 3.5, 3.6, and 3.7. The results summarized in these tables represents a significant amount of work. Each entry in the tables is obtained from an analysis of a Figure such as Fig. 3.2. Each data point in Fig. 3.2 represents a spectra such as Fig. 3.1. Since each state-to-state rate in the table is an absolute measurement as indicated by Eq. 3.5, the sum of all the state-to-state quench rates should equal the total quench rate measured in our previous time dependent studies. The sums are compared with the directly measured quench rates at the bottom of each table. Note that the sums could be less if dark products occur. Most states agree surprisingly well. For the $\text{Xe}^* 7p$ states we obtain sums larger than the quench rates, indicating a systematic error. One possible error would be double counting, eg flux appearing in one product state is quenched to a second, where it is measured again. Time dependent studies of product channels were made while directly exciting $\text{Xe}^* 7p$. This data did verify secondary channels. (note 5d and 6d transitions occur in the region $1.73\text{-}3.51 \mu\text{m}$ where detection with photomultipliers is not possible). Additional research is necessary to completely unravel quenching from $\text{Xe} 7p$ states.

Table 3.5 State-to-state reaction rates for excited states of xenon in a xenon buffer. States excited by two-photon absorption are listed across the top while product states are listed in the first column. All values are in 10^{-12} cm³/sec. very fast decay rates.

Laser Excited State of Xenon								
	Ref. 13			This work				
Product	6p[5/2] ₂	6p[3/2] ₂	6p[1/2] ₀	7p[5/2] ₂	7p[3/2] ₂	7p[1/2] ₀	6p'[3/2] ₂	6p'[1/2] ₀
6p'[1/2] ₀	b	b	b	b	b	b	b	*
6p'[1/2] ₁	b	b	b	b	b	b	b	b
6p'[3/2] ₂	b	b	b	b	b	b	*	53±4
6p'[3/2] ₁	b	b	b	b	b	b	b	b
7p[1/2] ₀	b	b	b	b	b	*	b	b
7p[3/2] ₂	b	b	b	b	*	b	b	b
7p[5/2] ₂	b	b	b	*	b	b	b	b
6p[1/2] ₀	b	b	*	334±47	139±10	366±73	60±14	95±4
6p[3/2] ₂	0.069±.1	*	1.46±0.3	396±21	220±13	367±40	61±11	89±15
6p[3/2] ₁	0.34±0.3	6.4±1.5	0.96±0.3	316±32	158±42	150±37	61±4	32±8
6p[5/2] ₃	8.6±3.3	22.4±3.1	1.74±0.6	397±25	242±16	188±14	114±18	63±10
6p[5/2] ₂	*	26.5±6.9	1.42±1.0	293±18	187±33	429±78	77±16	45±9
6p[1/2] ₁	46±18	b	b	214±46	170±37	261±16	97±32	44±19
6s'[1/2] ₁	22±8	32±14	0.99±0.7	b	b	b	a	a
ΣK _{ij}	77±18	87±16	6.6±1.5	1950±126	1116±101	1760±172	471±63	420±46
K _{total}	87±5.9	92.2±4.7	5.9±3.3	462±9	522±8	493±8	426±10	423±8

a) Fluorescence here was attributed to radiative decay to the Xe*6s'[1/2]₁ state and not collisional quenching.

b) No fluorescence was detected.

¹³J.E. Velazco, J. H. Kolts, and D. W. Setser, J. Chem. Phys. 69,4357(1978)

Table 3.6 State-to-state reaction rates for excited states of xenon in a krypton buffer. States excited by two-photon absorption are listed across the top while product states are listed in the first column. All values are in $10^{-12}\text{cm}^3/\text{sec}$.

Product	Laser Excited State of Xenon					Ref. 6		
	This work							
	6p[5/2] ₂	6p[3/2] ₂	6p[1/2] ₀	6p'[3/2] ₂	6p'[1/2] ₀	6p[5/2] ₂	6p[3/2] ₂	6p[1/2] ₀
Xe6p'[1/2] ₀	a	a	a	a	*			
Xe6p'[1/2] ₁	a	a	a	c	c			
Xe6p'[3/2] ₂	a	a	a	*	78±6 ^d			
Xe6p'[3/2] ₁	a	a	a	c	c			
Xe7p[1/2] ₀	a	a	a	a	a			
Xe7p[3/2] ₂	a	a	a	a	a			
Xe7p[5/2] ₂	a	a	a	a	a			
Xe6p[1/2] ₀	a	d	*	7±29 ^d	9±4 ^d			*
Xe6p[3/2] ₂	c	*	41±4 ^d	26±4 ^d	38±7 ^d		*	≤10
Xe6p[3/2] ₁	c	14±1	16±2 ^d	42±2 ^d	19±2 ^d		6±2	≤10
Xe6p[5/2] ₃	11±2	4±1	0±1 ^d	33±6 ^d	11±5 ^d	15±2	6±2	≤10
Xe6p[5/2] ₂	*	14±3	2±1 ^d	36±3 ^d	10±4 ^d	*	10±2	≤10
Xe6p[1/2] ₁	24±9	4±1	0±1 ^d	14±1 ^d	2±4 ^d	30±2		≤10
Xe6s[1/2] ₁	c	a	a	b	b			
Kr5s[3/2] ₂	a	a	73±6 ^d	a	a			100±20
Kr5s[3/2] ₁	a	a	a	85±10	169±25			
ΣK _{ij}	36±7	36±4	132±10 ^d	243±19 ^d	336±38 ^d	45	22	110
K _{total}	38±2	28±1	132±4	294±5	286±5	45	22	110

a) No fluorescence was detected.

b) Fluorescence here was attributed to radiative decay to the Xe*6s'[1/2]₁ state and not collisional quenching.

c) Fluorescence was detected but was too weak for reliable measurement. State-to-state rates for these states are believed to account for <1% of the total quench rate.

d) Contributions from both pathways, Xe6p[1/2]₀→Xe6p and Xe6p[1/2]₀→Kr5s[3/2]₂→Xe6p, were deconvolved for these values.

3.5 Conclusions

The collisional deactivation cross sections observed in the tables for xenon excited states below $6p[1/2]_0$ are all on the order of $20 \times 10^{-12} \text{ cm}^3/\text{sec}$ for collisions with both xenon and krypton. The actual magnitudes of these cross sections involve the details of curve crossings between potential curves and the coupling mechanisms; but the magnitude of the cross sections are consistent, qualitatively with the expected internuclear separation for the crossings. Specific comparisons of the cross sections require detailed many body calculations as recently done for collisions of excited states of xenon with argon and helium.¹⁴

Table 3.7. State-to-state reaction rates for excited states of krypton in xenon and krypton buffers. States excited by two-photon absorption are listed across the top while product states are listed in the first column. All values are in $10^{-12} \text{ cm}^3/\text{sec}$.

Product	in Krypton			in Xenon		
	Kr5p[5/2] ₂	Kr5p[3/2] ₂	Kr5p[1/2] ₀	Kr5p[5/2] ₂	Kr5p[3/2] ₂	Kr5p[1/2] ₀
Kr5p[1/2] ₀	b	b	*	b	b	*
Kr5p[3/2] ₂	b	*	26±4	b	*	b
Kr5p[3/2] ₁	18±4 ^e	0.73	1.3±0.2	b	b	b
Kr5p[5/2] ₂	*	5±2	5±2	*	b	b
Kr5p[5/2] ₃	262±18	22±4	7±1	a	b	b
Kr5p[1/2] ₁	81±16 ^e	0.2	0.5	b	b	b
Xe6p'[1/2] ₀	b	b	b	d	d	d
Xe6p'[3/2] ₂	b	b	b	d	d	d
Xe6p[1/2] ₀	b	b	b	31±6	19±3 ^c	28±2
Xe6p[3/2] ₂	b	b	b	46±5	119±29 ^c	101±18
Xe6p[3/2] ₁	b	b	b	33±5	0±12 ^c	d
Xe6p[5/2] ₃	b	b	b	53±4	0±3 ^c	19±6
Xe6p[5/2] ₂	b	b	b	44±4	0±1 ^c	18±8
Xe6p[1/2] ₁	b	b	b	41±10	b	11±1
Xe6s'[1/2] ₁	b	b	b	b	b	b
ΣK _{ij}	357±25	28±5	39±5	247±23	131±32	150±20
K _{total}	347±34	24±2	42±4	408±5	299±6	420±6

- Product formation rate was independent of xenon pressure for this state indicating that quenching was due to krypton and not xenon.
- No fluorescence was detected.
- Contributions to the state-to-state rates due to an intermediate Kr metastable channel have been subtracted off using the rates obtained from analysis of Xe*6p[1/2]₀.
- Fluorescence was detected but was too weak for reliable measurement. State-to-state rates to these states are believed to account for <1% of total quench rate.
- The energy lost to (Kr5p[3/2]₁) and (Kr5p[1/2]₁) from (Kr5p[5/2]₃) is energy transferred from the mixed state. The state-to-state rates measured for Kr5p[5/2]₂→Kr5p[3/2]₁ and Kr5p[5/2]₂→Kr5p[1/2]₁ is actually the rate, $(1+\chi)^{-1}\chi k_{10} + (1+\chi)^{-1}k_{20}$, from the mixed state to these product states.

¹⁴A. P. Hickman, D. L. Huestis, and R. P. Saxon, J. Chem. Phys. **96**, 2099 (1992).

For the higher lying states of xenon in the 6p' and 7p manifolds the cross sections are much larger, on the order of $100\text{-}300 \times 10^{-12} \text{ cm}^2/\text{sec}$. As was observed for reactions with argon,¹⁵ these reaction rates are consistent with the classical orbiting model for excitation transfer. This model assumes the reactants move in a long range dispersive potential $V(R) = -C_n/R^n$; any pair of reactants which surmounts the centrifugal barrier will react. The maximum impact parameter

$$b_{\max} = (nC_n/2E)^{2/n} [(n-2)/n]^{(2-n)/n} \quad (3.7)$$

Any collision of energy E , with $b < b_{\max}$ will react. Outside this $b_{\max}$, the reaction probability is zero. Therefore the reaction cross section is $\sigma = \pi b_{\max}^2$.

To obtain reaction rate k from this cross section, we assume a Maxwellian velocity distribution and integrate

$$k = \langle \sigma v \rangle = \int_0^\infty dv (\sigma v) f(v) v \quad (3.8)$$

The k resulting from a van der Waals ($n=6$) potential is¹⁶

$$k = (\pi/\mu)^{1/2} (2)^{11/6} (C_6)^{1/3} (kT)^{1/6} \Gamma(2/3) \quad (3.9)$$

In a more quantum mechanical picture, this model will be good if there is a sufficient number of reaction channels with reaction probability near unity once the centrifugal barrier is crossed. For "typical" $C_6 \sim 10^7 \text{ cm}^6$ (value for $6p[1/2]_0$, Ref. 17), $k = 306 \times 10^{-12} \text{ cm}^2/\text{sec}$. The relative rates for different buffer gases can be obtained from the ratio

$$\frac{k_{\text{Xe}^*-\text{Xe}}}{k_{\text{Xe}^*-\text{Rg}}} = \sqrt{\frac{m_{\text{Xe}-\text{Rg}}}{m_{\text{Xe}-\text{Xe}}}} \left(\frac{C_6 \text{ Xe}^*-\text{Xe}}{C_6 \text{ Xe}^*-\text{Rg}} \right)^{1/3} \quad (3.10)$$

where Rg is Ar or Kr. The nature of the long range forces ($C_6 \sim D_e$, the well depth) is expected to follow the systematic decrease in the bonding energy of the ionic series:

	Xe_2^+	XeKr^+	XeAr^+
$D_e(\text{eV})$	1.02	0.385	0.176

Averaging over the rates in Table 3.5 and 3.6, and previous rates for argon, we obtain the comparisons:

¹⁵M. R. Bruce, W. B. Layne, C. A. Whitehead, and J. W. Keto, *J. Chem. Phys.* **92**, 2917(1989).

¹⁶Harold S. Johnston, *Gas Phase Reaction Rate Theory*, (Ronald Press, New York 1966) p.144.

¹⁷T. D. Raymond, N. Böwering, Chien-Yu Kuo, and J. W. Keto, *Phys. Rev. A* **29**, 721 (1984).

Table 3.8. Comparison of reaction rates with and without the orbiting model in different buffer gases.

	$\frac{k_{\text{Xe}^*-\text{Xe}}}{k_{\text{Xe}^*-\text{Kr}}}$	$\frac{k_{\text{Xe}^*-\text{Xe}}}{k_{\text{Xe}^*-\text{Ar}}}$
Calc.	1.42	1.54
Exp ^a .	1.5±0.2	1.8±0.3

a) Based on the higher states Xe* 6p', 7p

Finally, we find rates for state-to-state reactions involving excitation transfer from Xe* to Kr and Kr* to Xe which are on the order of $50\text{--}100 \times 10^{-12} \text{ cm}^3/\text{sec}$. These rates are significantly larger than the collisional deactivation rates.

4.0 Reactions of excited xenon with chlorine

4.1. The harpoon reaction

We made complete studies of state-to-state electronic energy transfer from excited atoms of xenon to chlorine. In general, an understanding of energy transfer from excited xenon atoms to chlorides is relevant to the modeling the kinetics of the XeCl excimer laser. Energy transfer from excited rare gases to chlorides are expected to occur by a harpoon reaction,

where transfer from the reactant channel to the ionic intermediate occurs by charge transfer. If the ionization potential of the excited atom and the potentials for the negative chloride ion are known, the potential surface for the reaction can be easily constructed and is shown in Fig. 4.1. Though most chloride excimer lasers use HCl as the fuel gas; we chose Cl₂ for experiments because experiments are cleaner (Secondary reaction products are avoided; while for HCl, H₂ and Cl₂ are gradually produced in static reaction cells.) and theoretical potentials for the negative ion states are better known. By comparing the experiments with theoretical models, we can obtain a fundamental understanding of how the properties of the reactants control the reaction.

In the intermediate state of the harpoon reaction described by Eq. 4.1, the potential between Xe⁺ and Cl₂ at fixed chlorine internuclear separation is a simple coulomb potential, while the potential between the reactants Xe* and Cl₂ outside of the charge transfer crossing is only very weakly attractive. As the ionization energy of the xenon atom is increased by exciting more highly excited states, the radius of the crossing between the entrance channel for the reactants and the ionic intermediate potential (again at fixed Cl₂ separation) is expected to increase in radius; hence one might expect in a simple model that the reaction rate would be larger for higher lying excited states. However, as the radius of the crossing R_c increases, the probability for charge transfer at the crossing decreases as exp(-αR_c). To study this in detail, we measure reaction rates for excited atoms over a broad range of ionization potential and made direct comparison between the measurements and quantum calculations of the reaction rates. The details of both the experiments and the calculations were explained in detail in several publications^(1,2) and in a review written with DOE support.⁽³⁾ We only summarize them here.

1M. R. Bruce, Winston L. Layne, Enno Meyer, and J.W. Keto, "Reactive Quenching of Two-photon Excited Xenon Atoms by Cl₂", J. Chem. Phys. 92, 420(1990).

2M. R. Bruce, Winston B. Layne, and J.W. Keto, "A Multichannel Harpoon Model for Reactive Quenching of Xe 5p⁵np by Cl₂", J. Chem. Phys. 92, 428(1990).

3J. W. Keto, W. B. Layne, and M. R. Bruce, "Harpooning Reactions of Excited Rare Gas Atoms", Gas-Phase Metal Reactions, A. Fontijn, ed., Elsevier(Amsterdam), 1992, p. 435-466.

Fig. 4.1. Adiabatic potential energy surface for the Xe 6p[1/2]0 atom and chlorine. The surface was calculated by numerically diagonalizing the diabatic surfaces. The potentials were treated as isotropic with respect to orientation of the chlorine molecule.

4.2. Experiment

Xe* was excited in a two photon transition⁽⁴⁾ using a frequency doubled dye laser. The time dependence of the fluorescent light intensity was determined by the distribution of arrival times for the first photon following excitation. An example of this decay is shown in Fig. 4.2. The time response of the detector and laser was measured separately and deconvolved from the data. By measuring the exponential decay as a function of pressure, we obtained a Stern-Volmer plots to determine the reaction rates, k , $\nu = \nu_{\text{rad}} + k[n]$, as shown in Fig. 4.3. The decay rates for excited Xe* are described by

$$\nu_q = \nu_0 + k^{(2)}_{\text{Xe}} [\text{Xe}] + k^{(3)}_{\text{Xe}} [\text{Xe}]^2 + k^{(2)}_{\text{Cl}} [\text{Cl}_2] \quad (4.2)$$

Fig. 4.2. Time dependent laser induced fluorescence of Xe* 6p[1/2]₀. The line is a least square fit including the instrument response.

where ν_0 is the radiative rate and $k^{(2)}_i$ represent bimolecular reaction rates. In Table 4.1, we summarize the rates measured for energy transfer to Chlorine⁽⁵⁾. As observed in the table, the reaction rates were measured with high accuracy because of the small errors in the lifetime measurements, accurate pressure measurements, and careful of the the sample chamber.⁽⁶⁾ Shown for comparison are reaction rates calculated from cross sections equal to πR_c^2 , where R_c is the crossing radius of the Xe* + Cl₂ potential curve and the Xe⁺ + Cl₂⁻ curve which is determined using the electron affinity at the Cl₂ equilibrium distance (often termed the vertical electron affinity). The data agree nicely with this simple harpoon model for excited states with higher ionization energies. For states of the 5p⁵6p manifold the agreement of the experiment with the simple model is within a few percent! For states with smaller ionization potentials, this simple model grossly overestimates the cross sections when compared with the experiment. This clearly shows the effect of the reduced charge transfer probabilities expected at larger crossing radii.

⁴T.D. Raymond, N. Böwering, Chien-Yu Kuo, and J.W. Keto, Phys. Rev. A 29, 721 (1984).

⁵M. R. Bruce, W. B. Layne, Enno Meyer, and J. W. Keto, "Reactive Quenching of Two-Photon Excited Xenon Atoms by Cl₂", J. Chem Phys. 92, in press.

⁶Ibid.

4.3. The Harpoon model

We developed⁽⁷⁾ a harpoon reaction model employing multiple crossings based on the formalism of Bauer et al⁽⁸⁾ and Gislason and Sachs⁽⁹⁾. The multiple crossing model essentially reflects the Cl₂ vibrational wavefunction onto the reactant coordinate (internuclear separation between xenon and chlorine) via the seam between the reactant potential surface and the ionic surface. This seam is seen as the precipice of the cliff observed in Fig. 4.1. The model calculates the Landau-Zener transition probability for each crossing for a particular impact parameter and velocity for the reactants. The transition matrix element H₁₂ used at each crossing is represented as a product of the electronic interaction (modeled by the empirical result of Olson et al⁽¹⁰⁾) and a

Fig. 4.3. Decay rates measured as a function of Cl₂ pressure for 6p[1/2]₀.

Table 4.1. Bimolecular quench rates ($k^{(2)}_{Cl}$) for Xe* in Chlorine.

state	IP (eV)	Bimolecular rates (10^{-10} cm ³ /sec)		
		(This work)	(Setser) ^a	(calc. πR_C^2)
6p[5/2] ₂	2.44	12.8 ± 0.3	13.3 ± 1.0	12.5
6p[3/2] ₂	2.31	15.5 ± 0.2	14.5 ± 1.0	15.0
6p[1/2] ₀	2.19	17.9 ± 0.2	14.6 ± 1.0	17.8
6p'[3/2] ₂	2.38	18.6 ± 0.5		13.5
6p'[1/2] ₀	2.29	21.9 ± 1.0		15.2
7p[5/2] ₂	1.17	30.7 ± 1.9		1,051
7p[3/2] ₂	1.13	36.1 ± 1.2		1,938
7p[1/2] ₀	1.11	29.5 ± 0.8		2,898
5d[1/2] ₁	2.21	9.2 ± 0.5		17.7

J.K. Ku and D.W. Setser, Appl. Phys. Lett. 48, 689 (1986).

Frank-Condon factor for the Cl₂ → Cl₂⁻ transition. The model predicts near unit probability for a transition to the ionic surface for impact parameters less than 20 Bohr, and once transfer occurs, the pair is captured by dissociation of Cl₂⁻ to form XeCl*. A summary of the cross sections for the Olson model is presented in Table 4.2.

⁷M. R. Bruce, W. B. Layne, and J. W. Keto, "A Multichannel Harpoon Model for Reactive Quenching of Xe by Cl₂", J. Chem Phys. 92, in press.

⁸E. Bauer, E. R. Fisher, and F. R. Gilmore, J. Chem. Phys. 51, 4173(1969).

⁹E. A. Gislason and R. Sachs, J. Chem. Phys. 62, 2678(1975).

¹⁰R. E. Olson, F. T. Smith, and E. Bauer, Appl. Opt. 10, 1848(1971).

Table 4.2. Reaction Cross-Sections for Xe* with Cl₂

State	IP(eV)	$\sigma(\text{\AA}^2)$					
		v = 0 Olson	v = 1 Olson	(300°K) Olson	H12 fitted	(πR_c^2)	Experiment this work
6p[5/2] ₂	2.44	384	422	386	397	321	329± 8
6p[3/2] ₂	2.30	457	442	456	468	393	406± 5
6p[1/2] ₀	2.19	551	461	545	566	472	474± 5
6p'[1/2] ₀	2.29	475	449	474	488	403	593± 27
6p'[3/2] ₂	2.37	418	432	419	430	366	504± 13
7p[5/2] ₂	1.17	108	574	136	840	27,838	831± 52
7p[3/2] ₂	1.13	80	491	105	744	52,433	978± 32
7p[1/2] ₀	1.11	69	453	92	697	76,748	799± 22
5d[1/2] ₁	2.21	534	457	529	546	472	282± 10

For the states with lower ionization potential, we find that the reaction probability approaches one, nearly as a step function in impact parameter. Detailed examination of plots of the reaction probability as a function of impact parameter⁽¹¹⁾ shows that the onset of the reaction is controlled by crossing of dissociative levels of Cl₂⁻ with the reaction channel. As long as the charge transfer rate at the crossings is above a threshold level the large density of crossings in the continuum causes a rapid increase in reaction probability toward one. For these cases, the reaction cross section is given by πR_c^2 , where R_c is the distance of the reactants where the continuum of crossings begin. The model also demonstrates that the exponential decrease in H₁₂ begins to decrease the cross section relative to πR_c^2 for the higher lying states. While it agrees remarkably well with experiment for Xe* (6p), the Olson empirical model produces cross sections which decrease too rapidly with decreasing ionization probability because of the leading factor $\sqrt{(EA \text{ IP})}$. (see Eq. 10 of Olson) This dependence causes the cross section to converge to zero as the ionization energy approaches zero, while the cross section should converge to the attachment cross section as seen in the experiment (high rydberg state acts as free electron). We have fitted an exponential coefficient using the form $A \exp(-\alpha R)$. This model gives better agreement with experiment over the whole energy range. A better model should use quantum defect calculations to determine the charge transfer probabilities ab-initio. Such a model should also predict the angular momentum dependence of the charge transfer rate observed in the experiment (see Table 4.2).

4.4. Termolecular Reactions

We have discovered that harpoon reactions of Xe* 6p with Cl₂ are termolecular in xenon buffer gases:

¹¹ See Fig. 7, Bruce et al, "A Multichannel Harpoon..", preprint enclosed.

This reaction has the effect of increasing the effective reactivity with increasing buffer gas pressures. If the effect persists with the buffer gases (Ar and Ne) and reactants (HCl) used in the XeCl laser, the overall rate of transfer from excited states of the rare gases to chloride would have made these neutral channels essential to the modeling of the laser. We have now completed measurements of the termolecular rates in argon buffers and find a significantly smaller rate than for xenon buffers. The termolecular rates are measured by repeating measurements of the bimolecular reactivity, demonstrated by Fig. 4.3, at different xenon pressures. By measuring the increase in the reaction rate as the xenon pressure is increased, we measure the termolecular rate of the reaction in Eqn. 4.3. These rates are summarized in Table 4.3 for both xenon and argon buffers.

Table 4.3. Termolecular rates ($k^3_{\text{Cl-Xe}}$) for $\text{Xe}^* 5p^5 6p$ with Cl_2

State	Termolecular rates ($10^{-28} \text{ cm}^6/\text{sec}$)	
	(This work, Xenon)	(This work, Argon)
$6p[1/2]_0$	3.5 ± 0.5	<0.5
$6p[3/2]_2$	1.4 ± 0.5	<0.1
$6p[5/2]_2$	1.8 ± 0.5	<0.1

4.4 Products: a test for conservation of the state of the ion core

We measured the branching fractions for product states formed in reactions of 5 states of $\text{Xe } 6p, 6p'$, and $7p$ with Cl_2 . The motivation of the work was to test the propensity for ion core conservation during the reaction. The $\text{Xe}^*(6p')$ quench rates were found to be considerably larger than estimated by the simple πR^2_c reaction model involving electron transfer at the $\text{Xe} + ({}^2P_{1/2}) + \text{Cl}_2 - ({}^2\Sigma_u)$ reaction surface. This model works extremely well for the $\text{Xe}^*(6p)$ states. In principle, $\text{Xe}^*(6p')$ atoms should involve the $\text{Xe}^+ 5p^5[{}^2P_{1/2}]$ ionization limit (13.433eV); therefore, they should have about the same crossing radii as the $\text{Xe}^*(6p)$ states. However, the magnitudes of the measured reaction rates for $\text{Xe}^*(6p')$ indicate significant charge transfer through the lower $\text{Xe}^+ 5p^5[{}^2P_{3/2}]$ ionization limit (12.127eV). This is in contrast to the observation by Sadeghi *et al.*¹² of the propensity for ion-core conservation. Their conclusions were based on spectroscopic measurements from the metastable states $\text{Ar } 4s({}^3P_0)$ and $\text{Ar } 4s({}^3P_2)$. They observed D-X emission from reactions of halogens with $\text{Ar}({}^3P_0)$ and not with $\text{Ar}({}^3P_2)$ (the D state is correlated with ${}^2P_{1/2}$ core states while the Band C states are primarily correlated with ${}^2P_{3/2}$ core states). They obtained similar results for Krypton.

4.5 Experiment

For the branching fraction experiments we used a Questek 2400 v-beta series XeCl excimer laser to pump a three stage dye laser. The frequency doubled (BBO crystal) output of this dye laser was typically kept at or below 500 micro-joules per pulse, to avoid non-linear effects. A cooled,

¹² N. Sadeghi, M. Cheaib, and D.W. Setser, J. Chem. Phys. **90**, (1988) 219.

gated, optical multichannel analyzer (OMA) was mounted to a JY Hr 640 monochromator. With the OMA we were able to take long (800 angstrom) spectra in a single frame, without having to scan the monochromator.

In the branching fraction measurements, we excite the six two-photon resonances in the 6p' and 7p manifolds, and measure the resultant (XeCl)* fluorescence. The five accessible states are shown in Table 4.4.

Table 4.4. Xenon states directly excited in this study. The excitation wavelength for each state is listed also. The state labels are in Racah notation.

Laserexcited state	LaserWavelength(Å)
7p[5/2] ₂	2263.7
7p[3/2] ₂	2255.1
7p[1/2] ₀	2251.2
6p'[3/2] ₂	2243.1
6p'[1/2] ₀	2225.7
6p[1/2] ₀	2496.7

4.7 Results

The wavelength ranges for the transitions were defined to be B-X 320-270nm, C-A 320-390nm, D-X 230-242nm. In earlier work¹³ we searched for energy disposal in other product channels such as

but found no other fluorescence. For the experiments presented here the ratios of the xenon and chlorine pressures were chosen so that at least 90% of the transitions of the excited states would result from direct reactive quenching by chlorine. Besides this simple criterion, we should examine the collisional rates at these pressures, and what reactive processes we should therefore consider. For a collisional model including the B, C states only, the deactivation and transfer mechanisms are:

¹³M. R. Bruce, W. B. Layne, Enno Meyer, and J. W. Keto, J. Chem. Phys. 92, 420(1989)

The rate constants for reactions 7-10 are τ^{-1} , k_{BC} , K^{B}_{Xe} , and $k^{\text{B}}_{\text{Cl}_2}$ respectively. There is of course a corresponding set of reactions for the XeCl(C) state as well. These are similarly denoted, the subscripts and superscripts B and C being interchanged. To determine which processes should be considered in our model, we compared the corresponding reaction rates with the lifetime of the fluorescing state. For the B state, the rate τ^{-1} is relatively rapid, τ being near 11 nsec. Taking a value $5 \cdot 10^{-12} \text{ cm}^3/\text{sec}$ ¹⁴, we can see that Xe quenching is negligible for the B state. Using values of k^{BC} of $18 \cdot 10^{-11} \text{ cm}^3/\text{sec}$ (Ref. 15), $k^{\text{B}}_{\text{Cl}_2}$ of $5.8 \cdot 10^{-10} \text{ cm}^3/\text{sec}$ (Ref. 16), and substituting nominal experimental pressure values of 5 torr Xe and 2 torr Cl_2 , we find total rates of B to C mixing by Xe and quenching by Cl_2 which are each 35-40% as great as that for simple radiative decay.

For the C state, the radiative rate is an order of magnitude smaller, the lifetime being 130 nsec. This means that the Xe quenching is greater relative to the radiative process but is still minor (10%) at our pressures. The k_{CB} , and k_{Cl_2} rates are now in fact the faster processes, the k_{Cl_2} rate for the C state being the same as for the B state, and the k_{CB} transfer rate being $15 \cdot 10^{-11} \text{ cm}^3/\text{sec}$ ¹⁷.

The great majority of the fluorescence comes from highly excited XeCl(C,B) . We were also able to see D-X transitions in reactions involving the 6p, states, but the integrated intensity was quite low. Example spectra are shown in Figs. 4.4 and 4.5.

We considered the B-X, C-A system alone, without coupling it to the D-X levels. In the first instance, this is because only the 6p' prime levels show any D-X activity at all, and only in very small proportion. As we shall see later, small raw intensities are not always indicative of a small initial population except in the low pressure, collisionless limit. However, the relatively small intensity, coupled with the short lifetime (11 nsec) persuade us to discount the D level in our coupled state model. The B-X/C-A intensity ratios from this work are shown below in Table 4.5.

¹⁴E. Quinones, Y.C. Yu, D.W. Setser, and G. Lo, "Decay kinetics of XeCl(C,B) in Xe and in Mixtures of Xe with Kr, Ar, Ne, and He", J. Chem. Phys. 93 (1), 1990.

¹⁵Gen Inoue, J.K. Ku, and D.W. Setser, "Photoassociative laser-induced fluorescence of XeCl^* and kinetics of XeCl(B) and XeCl(C) in Xe", J. Chem. Physics 80 (12) 6006, (1984).

¹⁶J. Le Calve, M.C. Castex, B. Jordan, G. Zimmerer, T. Moller, and D. Haaks, in *Photophysics and Photochemistry above 6 eV*, Edited by F. Lahmani (Elsevier, Amsterdam, 1985) p. 639.

¹⁷Quinones et al., *opere citato*.

Figure 4.4. Normalized XeCl(C-A, B-X) spectra resulting from the direct laser excitation of the $6p'[1/2]_0$ state of xenon and subsequent reaction with chlorine.

Table 4.5. Integrated ratio of intensities for the XeCl(B) and XeCl(C) measured for the gas pressures specified in the table. The integration range was 270-320 nm for B-X and 320-390 nm for C-A.

Excited State	P_{Xe}/P_{Cl_2} (torr/torr)	I_{B-X}/I_{C-A}
$6p'3/2]$	5/25	5.8
$6p'[1/2]_0$	5/2	3.1
$7p[1/2]_0$	5/2.4	1.7
$7p[3/2]_2$	4/5	1.6
$7p[5/2]_2$	4/5	1.5

Figure 4.5. Normalized XeCl(D-X) spectrum resulting from laser excitation of the $6p'[3/2]_2$ state of xenon and the subsequent reaction with chlorine. The large peak on the right is scattered laser light.

Because of the different lifetimes of the B, C states and collisional mixing of the B, C states¹⁸, the raw intensity ratios do not translate directly into the original B, C product distribution. To get this distribution, we first wrote a set of coupled differential equations to relate the two initial state populations to the observed intensity ratios. Because only the B, C states needed to be considered, we fit the process by the a three state kinetic scheme.¹⁹

where

$$K_1 = 1/\tau_B + k_{Q_{Cl_2}}^{Cl_2} [Cl_2] \quad (4.11)$$

$$K_2 = k_{BC}^{Xe} [Xe]$$

$$K_{-2} = k_{CB}^{Xe} [Xe]$$

$$K_3 = 1/\tau_C + k_{Q_{Cl_2}}^{Cl_2} [Cl_2]$$

and

$k_{Q_{Cl_2}}^{Cl_2}$ is the quenching rate constant for XeCl(B,C)

k_{BC}^{Xe} is the B to C transfer rate constant

k_{CB}^{Xe} is the C to B transfer rate constant

¹⁸Quinones et al., opere citato.

¹⁹J.T. Yardley, *Introduction to Molecular Energy Transfer* (Academic, New York, 1980), Chap. 3.

Following the same procedure as in Yardley, the coupled differential equations were written as

$$\frac{d[B]}{dt} = -(K_1 + K_2)[B] + K_{-2}[C] + \delta(t)N^B_0 \quad (4.12)$$

$$\frac{d[C]}{dt} = K_2[B] - (K_{-2} + K_3)[C] + \delta(t)N^C_0$$

Integrating,

$$N^B_0 = -(K_1 + K_2)I_B\tau_B + K_{-2}I_C\tau_C \quad (4.13)$$

$$N^C_0 = K_2I_B\tau_B - (K_{-2} + K_3)I_C\tau_C$$

where $I_{B,C}$ are the total integrated intensities for the B-X, C-A transitions. Dividing these two equations, one by the other, and dividing the resulting ratio by I_C allowed us to relate the measured intensity ratios to the original branching ratios from the Xe^* , Cl_2 collision. These branching ratios are given in Table 4.5.

As mentioned, we saw D-X fluorescence only in the $6p'$ manifold. This was expected, as the D states correlate with the $^2P_{1/2}$ state of the ion core, and the C, B states primarily with the $^2P_{3/2}$ states. However, the degree of core conservation appears to be small. The raw intensity ratios are shown below in table 4.6.

Table 4.5. Branching ratios for the states excited in this study.

Excited State	$P_{\text{Xe}}/P_{\text{Cl}_2}$ (torr/torr)	$\text{XeCl}(C)/\text{XeCl}(B)$
$6p'3/2]_2$	5/25	3.6
$6p'[1/2]_0$	5/2	7.2
$7p[1/2]_0$	5/2.4	200
$7p[3/2]_2$	4/5	5.7
$7p[5/2]_2$	4/5	15

Table 4.6. Integrated ratio of intensities for the XeCl(B-X), XeCl(D-X) transitions measured for the gas pressures specified in the table. The integration range was 320-270 nm for B-X and 230-242 nm for D-X.

Excited State	P_{Xe}/P_{Cl_2} (torr/torr)	XeCl(B)/XeCl(D)
$6p'[3/2]_2$	5/2.5	19
$6p'[1/2]_0$	5/2	13

The D-X emission is quite weak and appears to be a minor partner in Xe-Cl₂ energy transfer. This result is consistent with observed large reaction rates for states of Xe*6p' which appear to react strongly with the Xe⁺(²P_{3/2}) ion surface. This result is different from that observed for Setser for reactions of Xe* with HCl.²⁰

²⁰D. W. Setser, private communication.

5.0 Observation of curve crossings in optical collision of xenon atoms

5.1 Introduction

In recent years, lasers have stimulated interest in photochemistry because of the greater variety and selectivity of reactions which can be studied. In traditional photochemistry, most reactions proceed by inelastic or reactive energy transfer following dipole-allowed photoexcitation of the reactant. An example of simple atomic excitation transfer is given by

When using the greater intensities of a laser, less probable reactions can be induced in systems where dipole transitions occur only during the collision and neither A nor B resonate with the laser independently. Cases where both reactants A and B change state have been termed "radiative collisions". Such reactions were first described by Gudzenko and Yakovlenko ⁽¹⁾ and studied experimentally by the group of Harris ⁽²⁾. Gallagher and Holstein ⁽³⁾ have shown how these reactions can be described as dipole-induced transitions between (AB)* molecular potential surfaces. Reactive collisions have also been probed with lasers ^(4,5). By changing the laser frequency, the initial conditions for a reaction can be changed and its outcome can be selectively controlled.

In experiments described here, xenon atoms were excited to 5p⁵6p during a collision by two-photon laser excitation. The pair excitation rate can be measured directly by observing the laser induced fluorescence in the vuv from the lowest bound excimer; hence by simultaneously measuring LIF in infrared 6p-6s transitions of dissociated product states and forming the ratio of ir/vuv intensities, we measured the probability for collision pairs to dissociate to specific product channels following the half-collision on the excited potential curve. Within the quasistatic range of the absorption line, the initial internuclear separation for this half-collision can be directly controlled by the laser detuning. As we tune the laser so as to excite pairs with smaller internuclear separation, we observe a sudden decrease in the probability for formation of the diabatic dissociative channel. A Landau-Zener model for the first half-collision is in qualitative agreement with the data.

¹L.T. Gudzenko and S.I. Yakovlenko, Sov. Phys. JETP **35**, 877 (1972).

²R.W. Falcone, W.R. Green, J.C. White, J.F. Young, and S.E. Harris, Phys. Rev. A **15**, 1333 (1977).

³A. Gallagher and T. Holstein, Phys. Rev. A **16**, 2413 (1977).

⁴B.E. Wilcomb and R.E. Burnham, J. Chem. Phys. **74**, 6784 (1981).

⁵T.C. Maguire, P.R. Brooks and R.F. Curl, Jr., Phys. Rev. Lett. **50**, 1918 (1983).

5.2 Experimental Approach

$\text{Xe}^* (5p^5 6p)$ is excited at various positions on the excited potential curve by two-photon transitions

The inset of Fig. 1 shows schematically the relevant molecular potentials and the laser-induced transitions observed. Pressure broadening was studied to extract bound excited state potentials at intermediate and long range using both unified phase-shift (6) and quasistatic (7) calculations. According to the theory of spectral line shapes (8), the broadening of the line wings arises from the perturbation of the excited atom by a collision partner. In the quasistatic theory, the shape of the line wing is mapped into the difference potential (difference between ground and excited state potential) by applying the Franck-Condon principle to atom-perturber pairs and taking into account the distribution of nearest neighbors. The largest contribution to the overlap of the translational wavefunctions comes from points where the photon energy equals the energy difference. Thus different frequencies in the line wing correspond to excitation of the excited atom and its perturber at different internuclear separations.

Avoided crossings of these states occur at long range with the repulsive $0g^+$ and $1g$ symmetries of $\text{Xe } 6s'[1/2]_1$ as is shown in Fig. 5.1 for the $6p[1/2]_0 0g^+$ state. According to the two-photon selection rules, excitation of this state is allowed while excitation of $6s'[1/2]_1 0g^+$ is forbidden. The line profile is thus expected to be primarily described by the diabatic potential of the $6p[1/2]_0 0g^+$ state. The diabatic potential curve for this state was measured in previous work (9), where the state was found to be attractive at long

Fig. 5.1 Potential curves for $\text{Xe } 6p[1/2]_0 0g^+$ and for $\text{Xe } 6s'[1/2]_1 0g^+$.

⁶T.D. Raymond, N. Böwering, C.Y. Kuo, and J.W. Keto, Phys. Rev. A29, 721 (1984).

⁷N. Böwering, C.Y. Kuo, T.D. Raymond, and J.W. Keto, *Spectral Line Shapes*, Vol. 2, ed. K. Burnett, 927 (de Gruyter, Berlin 1983).

⁸For a recent review, see: Nicole Allard and John Kielkopf, Rev. Mod. Phys. 54, 1003 (1982).

⁹ibid, Raymond, et. al.

range with a well depth of 326 cm^{-1} at $4.25 \text{ \AA}$. The potential curve for $6s'[1/2]_1 0g^+$ was taken from the calculation of Ref. 10. Upon excitation, the $6p[1/2]_0$ state either radiates in an infrared transition to $6s[3/2]_1$ at 828 nm or is collisionally deactivated to lower levels. At the high pressures ($p > 1000 \text{ Torr}$) of these experiments, the resonant states are radiation trapped and primarily lost by excimer formation.⁽¹¹⁾ No fluorescence was observed from product states radiating to the ground state in the range from 100 to 200 nm , except the continuum at 173 nm . Since rates for deactivation directly to the ground state are small compared to excimer formation rates, laser-induced fluorescence observed at 173 nm represents an accurate measure of the number of excited states produced by the laser. Schematically, the avoided crossing is shown in Fig. 5.2. Excitation transfer can be described using the Landau-Zener model^(12,13). For sufficiently slow collisions, the atoms remain on the adiabatic curves (shown as full drawn lines). As the excited pair approaches the crossing radius R_c during the inward half of the collision, there is a probability P that the state will jump to the lower adiabatic curve. In the outward half of the collision the excited pair can jump back to the upper curve or remain on the lower. The probability of dissociating to the upper curve is thus $(1 - P)^2 + P^2$. On the other hand, a pair excited on the outward half of a collision with $R \geq R_c$ will always dissociate. However, if the laser is tuned so as to create the excited pair at separations shorter than the crossing radius R_c , the crossing is encountered only once during the collision and the resulting probability for dissociation to the upper curve is only P . The total probability P_{rad} for the pair to dissociate and give rise to radiation in the infrared is then given as a function of excitation radius by

$$\begin{aligned} P_{\text{rad}}(R) &= 1 - P + P^2 & R \geq R_c ; \\ &= P , & R \leq R_c . \end{aligned} \quad (5.1)$$

According to the Landau-Zener formula, the probability P depends on the interaction energy E_{12} , the relative velocities of the collision partners v_r , and the difference of the slopes of the potentials crossing each other:

$$P = \exp \left\{ - \frac{2\pi}{\hbar v_r} \frac{E_{12}^2}{|d/dR (V_1 - V_2)|} \right\} . \quad (5.2)$$

¹⁰ O. Vallee, N. Tran Minh, and J. Chapelle, J. Chem. Phys. 73, 2784 (1980).

¹¹ T.D. Bonifield, F.H.K. Rambow, G.K. Walters, M.V. Mc Cusker, D.C. Lorents and R.A. Gutscheck, J. Chem. Phys. 72, 2914 (1980).

¹² L. Landau, Phys. Z. Sowjet Union 2, 46 (1932).

¹³ C. Zener, Proc. Roy. Soc. A137, 696 (1932).

5.3 Results

Plotted in Fig. 5.3 is the dependence of the ratio of the ir to vuv signals on excitation frequency for the $6p[1/2]_0$ state at 2800 Torr and 296 K. The data shown are an average of seven scans in the line wing for a total of 3750 laser shots per spectral sample. Care was taken to avoid problems caused by stimulated emission in the transition to $\text{Xe } 6s[3/2]_1$ (14), which was observed at high laser powers. The scale for internuclear separation in Fig. 5.3 was obtained from the corresponding difference potential (15). The figure shows that the probability for radiation decreases strongly with increased detuning into the red wing of the line (corresponding to absorption at shorter internuclear separations) and that the decrease has an approximate staircase structure with a dip in the center, the satellite; yet only a minor change in the ratio spectra was observed.

The structure of the ratio is qualitatively in agreement with what was expected from a Landau-Zener model. If the transfer occurs primarily in the vicinity of a crossing, the probability for quenching during the first half-collision is expected to remain constant as the initial internuclear separation is decreased toward a crossing and to increase near the crossing radius. After dissociation, the free, excited atom can radiate or undergo subsequent elastic or inelastic collisions. These subsequent full collisions are assumed to occur identically for all dissociating states independent of where on the potential curve they were created. The decrease in probability for radiation is interpreted as due to an increase in quench rate.

Fig. 5.3 Ratio ir/vuv as a function of laser frequency for the red line wing of $\text{Xe } 6p[1/2]_0$. Also shown as a short dashed line is the static model, dashed-dot is a model by M. O'Callaghan, et. al. with $s = .9$, while the solid line is for $s = 1.25$.

5.4 Effect of Bound States

A different explanation for the data of Fig. 5.3 was considered by examining the contribution from bound-bound and free-bound transitions in which bound excited states are created. In the absence of collisions these states would be unable to dissociate and would radiate as molecules; hence they may not fluoresce within the bandpass (~ 2 nm) of the ir monochromator which was tuned to the atomic resonance. The

¹⁴ A.W. McCowan, M.N. Ediger, and J.G. Eden, Phys. Rev. A26, 2281 (1982).

¹⁵ *ibid*, Raymond et. al.

fluorescence line shape for the $6p[1/2]_0 \rightarrow 6s[3/2]_1$ transition was measured with the laser fixed on resonance and when detuned to various positions in the red line wing as shown in Fig. 5.4. (This is the line shape in the "infinite pressure limit" of Ref. 16.) Even when the laser was detuned 70 cm^{-1} into the absorption line wing, no significant difference was found in the line shape, especially no increase of the line wings. As demonstrated in Fig. 5.4, states excited at both large and small internuclear separations radiate with the same spectral dependencies but with different integrated probabilities.

5.5 Landau-Zener Model

In the following section the model based on the Landau-Zener formula (eq. 5.1,5.2) for the first half-collision in the binary regime is considered in more detail. In the data of Fig. 5.3 a staircase shape (see eq. 5.1) is observed; however, is it seen "smeared out" over a range of internuclear separations. Taking the limits at small and large R , P_{rad} is seen to decrease by a factor of ten. In general, the relative velocity v_r depends on the impact parameter b , the kinetic and potential energy at the excitation radius R of the colliding pair. In the Landau-Zener approximation, all the parameters of eq. (5.2) are taken at the crossing radius R_c . The relative kinetic energy available at the crossing can be obtained from the kinetic energy at excitation E , the potential energy gain or loss from the excitation radius to the crossing radius and the centrifugal energy term. With μ denoting the reduced mass of the xenon collision pair, one has:

$$v_r(b,E,V_u(R)) = \left\{ \frac{2}{\mu} \left(E - V_u(R_c) + V_u(R) - \frac{Eb^2}{R_c^2} \right) \right\}^{1/2}. \quad (5.3)$$

The additional term $V_u(R)$ to the usual expression (17) arises because half-collisions are considered here ($V_u(R) = V_u(\infty) = 0$ for full collisions). Assuming that the kinetic energies are

Fig. 5.4. Fluorescence line shapes obtained as a function of detuning into the red line wing of Xe $6p[1/2]_0$. The data are shown shifted on arbitrary intensity scales.

¹⁶ G. York, R. Scheps, and A. Gallagher, J. Chem. Phys. 63, 1052 (1975).

¹⁷ L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, (Pergamon Press, London 1958).

thermalized at all separations of interest on the ground state potential and that the kinetic energy does not change at excitation, the energies E are distributed according to a Boltzmann distribution. Using equation (1), the fact that the ratio data decrease by a factor of ten, and integrating over impact parameter while taking mean thermal energies (for ease of computation), one has:

$$10 \int_0^{b_{\max}} P b db \big|_{R=4\text{\AA}} = \int_0^{b_{\max}} (1-P+P^2) b db \big|_{R=10\text{\AA}}, \quad (5.4)$$

where $b_{\max}$ is determined by the condition $v_r(b_{\max}, E, V_u(R)) = 0$. For the potentials of Fig. 1, $d/dR|V_1 - V_2| \cong 1000 \text{ cm}^{-1} \text{ \AA}^{-1}$. Evaluating P with v_r of eq. (5.4) at $R = 4 \text{ \AA}$ or $10 \text{ \AA}$, respectively, and using numerical integration and a root finding program, an interaction energy of $E_{12} = 60 \text{ cm}^{-1}$ was calculated. In the Landau-Zener model described by Eqns. 5.1 and 5.2, the probability P describes the probability for a pair hopping from one adiabatic curve to another as it moves through the crossing region from a large distance. As the pair is excited closer to the crossing in our experiment, it is created in a linear combination of adiabatic states. Independent of R , only one of the diabatic states, $6p[1/2]_0$, has transition rate. For R in the vicinity of the crossing, however, the diabatic states are mixed. This mixing can be described for a two level system

Ψ_i = adiabatic state

χ_i = diabatic state

$$\langle \chi_1 | H | \chi_1 \rangle = E_c + F_1(R - R_c)$$

$$\langle \chi_2 | H | \chi_2 \rangle = E_c + F_2(R - R_c)$$

$$\langle \chi_1 | H | \chi_2 \rangle = V_{12} = V_{21}.$$

Diagonalizing at $\Delta R = R - R_c$.

$$\Psi_1 = \cos\theta \chi_1 + \sin\theta \chi_2, \quad \Psi_2 = -\sin\theta \chi_1 + \cos\theta \chi_2$$

$$\theta = \tan^{-1} \left\{ \frac{\Delta F \Delta R}{V_{12}} \pm \left(\frac{\Delta F \Delta R}{V_{12}} + 1 \right)^{1/2} \right\}$$

From this initial set of states the system evolves as the pair move through the crossing arriving at t_1 :

$$i\hbar \dot{|\Psi_1\rangle} = F_1 v_r t |\Psi_1\rangle + V_{12} |\Psi_2\rangle$$

$$i\hbar \dot{|\Psi_2\rangle} = F_2 v_r t |\Psi_2\rangle + V_{12} |\Psi_1\rangle$$

Landau and Zener originally integrated these equations for $t_0 \rightarrow \infty$, and calculated the hopping probability between adiabatic states.

At the beginning of the experiment, where R is defined by the laser, only the state χ_2 with transition rate is excited. Then $\chi_2(t=0) = 1$ and $\chi_1(t=0) = 0$; hence $\Psi_1 = \sin\theta$ and $\Psi_2 = \cos\theta$. If we ignore the energy spread caused by the finite $\Delta t = t_1 - t_0$ and treat the initial amplitudes incoherently:

$$\begin{aligned} R \leq R_c: \quad P|\Psi\rangle(\infty) &\cong P \cos^2\theta + (1-P) \sin^2\theta \\ R \geq R_c: \quad P|\Psi\rangle(\infty) &\cong P(1-P) \cos^2\theta + (1-P+P^2) \sin^2\theta. \end{aligned}$$

we obtain $P(\Psi_2)(R)$ as shown in the dashed curve of Fig. 5.3. This static model neglects the finite time between the pair's creation and its arrival at the crossing. M. O'Callaghan and coworkers⁽¹⁸⁾ solved for the absorption and emission of radiation in the vicinity of a crossing by fourier transforming the coupled equations to obtain

$$\begin{aligned} i \frac{\partial C_{10}}{\partial \beta} &= \frac{2\gamma}{S_0-1}(-\beta C_{10} + C_{20}) \\ i \frac{\partial C_{20}}{\partial \beta} &= \frac{2\gamma}{S_0+1}(C_{10} - 2\beta C_{20}) \\ S_0 &= \frac{F_{20} + F_{10}}{F_{20} - F_{10}}, \quad \beta = \frac{\hbar(\omega - \omega_c)}{V_{12}}. \end{aligned}$$

Their single crossing calculations apply directly to our experiment. For the potentials described earlier, their calculations give the dashed-dot line of Fig. 5.4; this result is similar to our static model although a satellite is clearly visible. This satellite is due to the zero in the difference potential of the upper adiabatic curve as we have speculated earlier, and is in disagreement with the data. Better agreement is obtained for O'Callaghan's parameter, $s = (F_{20}-F_{10})/(F_{20}+F_{10}) = -1.25$. For this value, the crossing diabatic potentials must both have positive slope in the vicinity of the crossing. This suggests that the $6s'[1/2]_1$ state is not the state involved; but rather our crossing is with an attractive potential from more highly excited 5d states.

¹⁸ M. O'Callaghan, T. Holstein, and A. Gallagher, Phys. Rev. 32A, 2754(1985).

6.0. Two-photon spectra of excitons in liquid xenon

6.1 Introduction

Although one-photon absorption has been studied previously in condensed xenon,^{1,2,3,4} we have just measured the first two-photon excitation spectra through the band edge of liquid xenon in which direct excitation of the even-parity exciton levels is observed. Justification for measurements of the excitonic structure of condensed rare gases lies mainly in the close correspondence between the fluorescence of the trapped exciton in the liquid and the excimer in the gas. Liquid rare gases have been studied as possible excimer lasers systems, both as pure systems⁵ and doped with halogens.⁶

The one-photon excitation scans of Beaglehole²² and Subtil, et. al.⁷ in liquid xenon yield linewidths consistent with those of the data reported here, but, while the 2s, odd-parity excitons observed in those experiments are shifted by approximately 0.03eV to the red^{22,27,8} relative to the 2s exciton in the solid at 160K, the even-parity bands excited by two-photon absorption in the liquid are shifted approximately 0.085eV towards the blue. We present a model estimating the shift between the 2s and 2p excitons due to central cell corrections which is consistent with the measured shift of 0.115 eV.

6.2. Experiment

Xenon was condensed to a liquid in a stainless steel sample cell by flowing the nitrogen vapor at 77K through 1/8 inch copper tubing silver-soldered around the outside of the sample cell. The temperature was regulated using a Lakeshore Cryogenics Model DRC 80C to within 0.1K with a Lakeshore Model DT-500 silicon diode supplying the temperature feedback. The controller adjusted the temperature to within the desired range by heating with nichrome wire wrapped around the body of the sample cell.

VUV fluorescence following laser excitation passed through a MgF₂ window mounted on top of the cell and was analyzed using a modified Seya 1meter monochromator to which was attached an EMR Model 541N-09-13-03900 phototube. Laser light passed into the sample cell

¹G. Baldini, Phys. Rev. **128**, 1562 (1962)

²D. Beaglehole, Phys. Rev. Lett. **15**, 553 (1965)

³E. Roick, R. Gaethke, G. Zimmerer, Solid State Communic. **47**, 333 (1983)

⁴P. Laporte, N. Damany, and J.-L. Subtil in *Photophysics and Photochemistry above 6 eV*, edited by F. Lahmani (Elsevier Science Publishers, Amsterdam, 1985)

⁵N. Schwentner, "Photodissociation of small molecules and generation of laser radiation in rare-gas crystals", J. Mole. Struct. **222**, 151 (1990).

⁶K. Okada and V. A. Apkarian, "Electronic relaxation of Xe₂Cl in gaseous and supercritical fluid xenon", J. Chem. Phys. **94**, 133 (1991).

⁷J. L. Subtil, P. Laporte, R. Reininger, and V. Saile, Phys. Stat. Sol. (b) **143**, 783, (1987).

⁸B. Sonntag, "Dielectric and Optical Properties", Rare Gas Solids Vol II, M.L. Klein and J. A. Venables, eds., Academic Press, London, New York, 1977, p. 1049.

through sapphire windows sealed onto flanges on either end by gold O-rings. Radiation tunable between 245-300nm was generated by frequency doubling the output of a Hansch type dye laser pumped by a Spectra-Physics DCR-2 pulsed Nd:YAG laser. Three dyes(Coumarin 500, Coumarin 540, and Rhodamine 610) were pumped by the tripled output of the YAG to cover the range of excitation of the exciton states and band edge. Frequency doubling was achieved with a beta-Barium Borate(BBO) crystal to obtain 0.5mJ of horizontally polarized UV radiation which was focussed in the center of the cell to a spotsize of ~ 15 microns. Pulsewidths were 6 nanoseconds and the laser bandwidth at the doubled wavelength was approximately 0.4 cm^{-1} ($5 \times 10^{-5} \text{ eV}$). Fluorescence measurements following laser excitation were normalized to the square of the measured laser energy in order to remove the variations in laser energy over the large tuning range and the pulse-to-pulse fluctuations in laser energy.

6.3. Results and Discussion

After absorption of two quanta of energy from the focussed laser, an exciton consisting of an electron and hole bound one to the other are created. This exciton is free to move throughout the crystal; however, Roick et. al.²³ have shown that the rate of trapping of these excitons in solid xenon to form quasi-molecular centers is rapid and limited in the high temperature limit by the Debye frequency of the lattice. After creation, these excitons are trapped immediately into a local lattice deformation whose fluorescence is similar to that of the excimer in the dense gas at $1730\text{\AA}$ but is Stokes shifted by roughly $30\text{\AA}$. By monitoring this quasi-molecular fluorescence and scanning the laser as a function of energy, we obtain the two-photon excitation scan shown in Fig. 6.1. The

stepsize of the frequency-doubled light for this scan was 0.01eV and 500 laser shots were taken at each spectral point. Indicated in the figure are the positions of the $\Gamma(3/2) n=1,2,3$ excitons in solid xenon at 160 K as determined by Subtil, et. al.²⁷; also indicated is the band edge observed in the solid. The small bands at 8.8, 9.55, and 9.75eV have been reproduced in subsequent scans but are currently unassigned. We have fitted the two features between 9.0 and 9.5eV with a Gaussian line shape using a nonlinear least square fit. The best fit is shown as the solid line in Fig. 4.1 and the mean energies and widths are reported in Table 6.1.

Fig. 6.1 Two-photon excitation spectra of liquid xenon at 162K. Indicated are the positions of the 1s, 2s, and 3s excitons in solid xenon at 160K as measured by Subtil, et. al., Ref. 27. Also shown is the band gap for the solid at 160 K.

Table 6.1 Liquid Xenon, T=162 K. Reported errors are 2σ .

State	Energy (eV)	FWHM (eV)	Reference
1s $\Gamma(3/2)$	8.145	0.3	2,7,13
2s $\Gamma(3/2)$	8.97	0.15 ± 0.01	7,12
2p $\Gamma(3/2)$	9.085 ± 0.022	0.149 ± 0.011	This work
3p $\Gamma(3/2)$	9.257 ± 0.034	0.172 ± 0.022	This work

At the G point in the Brillouin zone of the xenon lattice, the valence band is comprised of atomic p orbitals of the ground state atom while the lowest conduction band is made up of s orbitals of the first excited states. Direct two-photon transitions from the valence to lowest conduction band are therefore not allowed. This explains the absence of a band edge in the excitation scan. The conduction band at the X point of the Brillouin zone, which is thought to comprise mainly p orbitals, has a band gap of approximately 12eV⁹ and would be another good argument for scans to shorter wavelengths. Two-photon excitation scans in the alkali halides exhibit no excitonic structure, while the band edge is readily apparent. Frohlich and Stagninus⁵ suggest two possibilities for the appearance of the band edge in alkali halides under two-photon absorption: 1. forbidden transitions at the Γ point, and 2. allowed transitions to bands of different symmetry. Neither of these models accounts for the absence of the band edge in xenon. A more detailed study of the symmetry of the valence and conduction bands would have to be undertaken to explain this disparity.

6.4 Rydberg Model for Excitons

Models for excitons in condensed rare gases have been recently reviewed.^{10,11} The Wannier model has been shown to accurately model the energies for s-exciton in the rare gases for $n \geq 2$.

$$E_{n,j} = E_{\infty,j} - \frac{B_j}{n^2} \quad (6.1)$$

Here the exciton is modeled as an electron bound by the Coulomb attraction to the valence hole with either $j = 1/2$ or $j = 3/2$ at the center of the Brillouin zone (often referred to as $\Gamma(1/2)$ and $\Gamma(3/2)$ excitons). E_{∞} is the Rydberg convergence limit and B_j is the exciton binding energy,

⁹U. Rossler, *Phys. Status Solidi* **42**, 345 (1970)

¹⁰G. Zimmerer, *Excited-State Spectroscopy in Solids*, XCVI Corso, Soc. Italiana di Fisica, Bologna, Italy, 1987.

¹¹Irene Ya. Fugol, "Excitons in rare-gas crystals", *Advances in Physics* Vol. 27, p1. (1977).

$$B = \frac{\mu R}{\epsilon^2} \quad (6.2)$$

where $\mu = m_e m_h / (m_e + m_h)$, m_e and m_h are the effective masses of the electron and hole, R is the Rydberg, and ϵ is the relative dielectric constant for the solid or liquid. For the 2p and 3p excitons listed in Table I, $B = 1.24 \pm 0.3$ eV and $E_\infty = 9.39 \pm 0.29$ eV. Using $\epsilon = 1.94$, as measured by Sinnock for liquid xenon near the triple point¹², we estimate the reduced effective mass for the exciton, $\mu = 0.34 \pm 0.08$. These values compare to $E_\infty = 9.30$ eV and $\mu = 0.36$ for the solid near the triple point.^{27,13}

In liquid xenon, Reshotko, et. al.³³ estimated the effective mass of the 2s exciton over a range of densities. Since the 3s exciton is not observed in liquid xenon,^{21,27,33} they estimated the binding energy for the Rydberg series limit from measured threshold values E_{th} for photoconductivity.¹⁴ In solid xenon at the triple point, E_∞ exceeds the threshold value, $E_{th} = 9.265$ eV, by 0.38 eV; presumably because of thermal ionization of photoexcited excitons near the conduction band.³³ Assuming that the same difference $E_\infty - E_{th}$ applies to the liquid at the same temperature, Reshotko, et. al. estimated $E_\infty = 9.22$ eV and $\mu = 0.27$ for liquid xenon at the triple point. We find the 2p and 3p excitons observed by two-photon excitation to be closer to the solid than to the liquid, when comparing these simple Wannier models.

The blue shift between the 2p and 2s exciton observed in the liquid and compared in Table II suggests a breakdown of the Wannier model, since the energies of the hydrogenic model described by Eq. 6.1 are independent of ℓ . Such a shift is common in alkali atoms because of decreased screening of the ion core caused by greater penetration of the s orbital compared to the p orbital. In the alkali atoms the screening is accurately accounted for by a quantum defect model of the Rydberg series,

$$E_n = E_\infty - \frac{R}{(n' - \delta_\ell)^2} \quad (6.3)$$

where n' is the principle quantum number for the valence electron.

In atomic systems, the screened effective charge Ze seen by the valence electron falls rapidly with increasing radius decreasing to $Z=1$ at $r=r_0$. For the region $r < r_0$ (on the order of one Bohr (0.53 Å) for xenon) where $Z(r) > 1$, the kinetic energy term dominates the solution of

¹²A. C. Sinnock, J. Phys. C 13, 2375 (1980).

¹³M. Reshotko, U. Asaf, G. Ascarelli, R. Reininger, G. Reisfeld, and I. T. Steinberger, Phys. Rev. B 43, 14,174(1991).

¹⁴R. Reininger, U. Asaf, I. T. Steinberger, V. Saile, and P. Laporte, Phys. Rev. B 28, 3193(1983).

Schroedinger's equation,¹⁵ giving nearly the same radial wavefunction (within a normalization factor) for $r < r_0$ for all n (given the same ℓ). For the region $r > r_0$, the potential is Coulombic with a hydrogenic solution shifted to $n' = n - \delta_\ell$ in order to match the interior wavefunction at r_0 . As the eigenenergy increases, n' increases by 1, giving nearly the same quantum defect for all n .

These effects would also apply to the interaction of the electron with the hole in the exciton. Indeed the higher energy observed for the 2p exciton compared to the 2s exciton might naively be attributed to lesser penetration into screened charge of the multielectron hole; but for excitons, the problem is considerably more complicated. Just outside of r_0 (on the order of one atomic unit, 0.53 Å, for xenon, the potential seen by the electron is Coulombic, $V = -e/r$, but by two atomic units the potential converges to $-e/\epsilon r$ due to the dielectric screening of the solid.¹⁶ This change in dielectric constant has been modeled by Hermanson, et. al.³⁶ In reducing the potential, the dielectric screening spreads the electron wavefunction to larger r , which in turn decreases the expected quantum defect. Because of large dielectric constant for xenon, one expects that for $n \geq 2$ the quantum defects are small and that the Wannier model is approximately correct. Additional effects in the solid such as polarization of the hole and the change in the effective mass for radii inside of the central cell further complicate a calculation. The effective mass converges from the atomic value at small r to the effective mass over a range of 5 Å. In contrast to the above picture, the Wannier model assumes the effect of both the dielectric and effective mass continues to $r=0$.

Central Cell Corrections

Because of the dielectric screening, the radius for an $n=2$ exciton is approximately 3 times the nearest neighbor distance. This greatly decreases the amplitude for the wave function within the ion core, and greatly decreases the expected quantum defect for these states. One might reasonably assume that the expected shifts for the $n=2$ excitons would be significantly smaller and that the 2s and 2p states should be degenerate. This is in disagreement with the experimental results.

Because of this discrepancy between an intuitive understanding and the experiment, we have estimated the central cell corrections for the 2s and 2p excitons in liquid xenon using the results of Hermanson.³⁶ In his calculations, he considered three contributions: 1. an effective local repulsive potential V_R (Eq. 6.8c of Ref. 20), 2. a perturbation of the Wannier model due to the change in dielectric constant within the central cell V_{DB} (Eq. 6.8a of Ref. 36), and 3. a perturbation due to the nonparabolic nature of the energy bands V_{KE} (Eq. 6.8b of Ref. 36). Since we find the latter is the most significant for the $n=2$ excitons, we reproduce it here (with the removal of a typographical minus sign):

¹⁵John C. Slater, *Quantum Theory of Atomic Structure* Vol. I, McGraw-Hill Co. (New York, Toronto, London) 1960, p. 229-232.

¹⁶J. Hermanson, Phys. Rev. 150, 660(1966).

$$V_{KE} = \frac{\hbar^2}{2m} \left(\frac{m}{\mu^*} - 1 \right) \left(\frac{\exp(-r/a)\nabla^2 + \nabla^2\exp(-r/a)}{2} \right), \quad (6.4)$$

where a is a radial cutoff parameter for the change in effective mass,

$$m/\mu(r) = m/\mu^* - (m/\mu^* - 1)\exp(-r/a). \quad (6.5)$$

Before making a pseudopotential calculation for the $n=1$ exciton, Hermanson first estimated the shift using perturbation theory. Since we expect that the perturbation approach is reasonably accurate for the $n=2$ excitons, we have used a similar model by numerically integrating the perturbations of Eq. 6.8 of Ref. 36 for the $n=1$ and $n=2$ exciton states for liquid xenon. We used hydrogen atom wavefunctions expected from the Wannier picture as the first order solution. In Table 6.2 we compare our results for the total energy shift for solid xenon using the equations and parameters of Hermanson's paper, and we obtain results consistent with Hermanson's results in Ref. 36; energies are listed in atomic units rather than the fractional shift relative to the energy of the $1s$ exciton, as was used by Hermanson. For the liquid calculations, we used the reduced exciton mass $\mu^* = 0.34$ and dielectric constant $\epsilon = 1.94$. Note that the electrostatic perturbations V_R and V_{DB} are small for the $n=2$ excitons as expected, but the perturbation due to Eq.6.4 is significant. Table 4.2 predicts the $2p$ exciton lies higher in energy than the $2s$ exciton by 0.064 eV compared with the experimental difference of 0.114 ± 0.029 eV observed in Table 4.1. This is reasonable agreement considering the lack of an accurate estimate for μ^* in liquid xenon and expected deficiencies in Eq. 6.4.³⁶ More exact calculations require detailed models for the conduction bands in solid xenon similar to the calculations of Rössler.¹⁷

Table 6.2. Central cell correction for the $n=1$ and $n=2$ excitons for liquid xenon at the triple point. Energies are in atomic units, μ/ϵ Hartrees.

	V_R	V_{DB}	V_{KE}	$\Delta E(\text{liquid})$	$\Delta E(\text{solid})^a$
$1s$	+0.361	-0.0155	-0.276	+0.069	-0.021
$2s$	+0.043	-0.0014	-0.090	-0.048	
$2p$	+0.001	-0.0004	-0.023	-0.022	

a) Hermanson, Ref. 36 obtained $\Delta E = -0.025$ a.u. for the solid. For the Eqns.6.8 of Ref. 36, we used the parameters $a = (0.86)^{-1}$ a.u., $Q = 0.5$ (a.u.)⁻¹, and the atom radius, $r_0 = 4.2$ a.u. For solid xenon, $\epsilon = 2.23$, $\mu^* = 0.31$, while for liquid xenon, $\epsilon = 1.94$, $\mu^* = 0.34$.

6.5. Conclusion

Though a more precise value of the effective mass for the exciton is needed for a definite conclusion, the Wannier model with central cell corrections appears to reasonably predict the shift in energy between the $2s$ and $2p$ excitons of the liquid. This model for liquid xenon is limited by

¹⁷U. Rössler, Rare Gas Solids Vol. I, M. L Klein and J. A. Venables, editors, Academic Press (London, New York, San Francisco) 1976, p. 503-557.

the large widths and small number of resonances observed in the liquid which results in an uncertainty in both E_∞ and the exciton mass; a more accurate picture may be possible for the solid. While data for even parity excitons in the solid is needed to fully understand the exciton structure, the first observation of even parity excitons in condensed rare gases has been achieved.

7.0 Laser Spectroscopy of Dimers in a Supersonic Jet

7.1 A Search for Fluorescence

We proposed to measure the structure of excimers bound in potentials dissociating to the Xe^* $6p[1/2]_0$, $6p[3/2]_2$, and $6p[5/2]_2$ by exciting dimers formed in supersonic beams. In similar experiments, Dehmer et al.⁽¹⁸⁾ have found resonances in the photoionization spectrum which they interpret as a vibrational sequence described by a Morse potential dissociating to the same levels. These potentials do not describe the linebroadening we have measured for the same states⁽¹⁹⁾; however, the shape of the Morse potential depends upon an absolute assignment of the vibrational sequence (eg. Is the lowest energy peak $v = 0, 1$, or 2 ?). Dehmer et. al. could not make this assignment. We proposed to excite the same lines and observe simultaneously the ionization rate and fluorescence. By measuring the fluorescence spectra of the $6p[1/2]_0 0g^+ \rightarrow 6s[3/2]_1 1_u$ transition, we hoped to be able to assign the sequence absolutely. In a bound-bound spectra, the Frank-Condon factors are modulated by the upper state potential. By counting the nodes in the modulation, the upper state vibrational assignment can be made. Similar modulations can be observed in bound-free spectra.

7.2 Apparatus

The supersonic beam apparatus employs four differentially pumped chambers. The first houses a pulsed supersonic nozzle. A skimmer isolates this stagnation chamber from the second, laser interaction chamber. The third chamber houses a quadrupole mass spectrometer (Extranuclear, Inc.) with a mass range of 400 and resolution of better than one amu. The vacuum system has been designed for ultra high vacuum in order to minimize ionization of the background gas when using u.v. lasers and resonance ionization detection. The laser is focussed diagonally into the laser interaction chamber through a baffled window and is dumped into a high-quality Wood's horn to minimize scattered laser light. Experimental tests have measured less than 3 photons of scattered light per 1000 laser shots.

The ion detector is a deflection, time-of-flight mass spectrometer for use with ions produced by a two-photon, resonance excited, one-photon photoionization process ($2+1$ REMPI). This

¹⁸P. M. Dehmer, S. T. Pratt, and J. L. Dehmer, J. Chem. Phys. **85**, 13 (1986).

¹⁹T. D. Raymond, N. Bowering, Chien-Yu Kuo, and J. W. Keto, Phys. Rev. **29A**, 721 (1984).

technique is very sensitive and enables the measurement of excitation spectra of excited molecules and clusters unstable for fluorescence. Since the detection is mass selective, excitation bands can be assigned to specific clusters. Note that though a given size of cluster can fragment into several specific ion masses, the combination of mass analysis, an analysis of the laser excitation spectra, and a measurement of pressure dependences should be sufficient to identify the cluster size. The fluorescence spectra can then be measured for these selectively excited clusters. In the apparatus constructed, we can obtain fluorescence from the excited state in both the IR, visible or VUV simultaneously while obtaining time-of-flight spectra from ions photoionized from other molecules resonantly excited to the same level.

In Fig. 7.1 we show the Xe^+ signal, detected in the time-of-flight mass spectrometer plotted as a function of laser frequency. The peak at 2496.25 Å is the $6p[1/2]_0$ atomic resonance. The ratio of the integrated monomer to dimer intensities was estimated to be approximately 100/1. There is good agreement between our ion spectrum and that of Dehmer et al.

In Fig. 7.2 we also show the laser induced spectrum in the infrared. We used an optical design with a collection lens and mirror with $F = 1$ aperatures situated transverse to the supersonic beam.

A multiple lens system was used to match the collection optics to a Jarrel-Ash 1/4 meter monochromator with $F = 3.5$. The slit of the monochromator was arranged so as to collect light for a 1 cm distance along the molecular beam. The laser is focused normal to the molecular beam and at a 45° angle relative to the collection optics. The laser beam is stopped by a Woods horn positioned 1 cm after the point of intersection of the laser and molecular beams. Scattered light from the entrance window (which is shielded from view of the monochromator by a stack of 5 aperatures), woods horn, and the gas jet define the background of 0.002 photons/laser shot. We observed in Fig. 7.2 only fluorescence from excited atoms; no fluorescence from excited dimers in the vicinity of $6p[1/2]_0$ has been observed.

Fig. 7.1. Two-photon excitation spectra of $6p[1/2]_0$ measured by observing laser induced fluorescence at 828.2 nm and by collecting photoions in the time-of-flight spectrometer from 28-58 μsec (range sufficient for detection of both Xe^+ and Xe_2^+). The spectra are averages of 200 laser shots per spectral point.

7.3 Experimental improvements

To confirm these results, we have sought to improve the signal-to-noise ratio by increasing the dimer-to-monomer ratio. Dimers are formed only in a narrow range of experimental conditions of stagnation pressure, xenon concentration in the He carrier gas, and initial gas temperature.

Echt et. al.²⁰ has shown that nonresonant multiphoton-ionization of xenon clusters using 266 nm (quadrupled YAG) light gives results very similar to electron ionization. Using non-resonant three-photon ionization at 266 nm photons to obtain time of flight spectra we have studied the cluster ion distribution as a function of pushing pressure, Xe/He concentration, and temperature of the nozzle. This distribution does not measure directly the dimer-monomer ratio as larger xenon clusters can contribute to the Xe_2^+ intensity by fragmentation, but the data help to narrow the search for a maximum dimer density. In Fig. 7.2 we show time of flight data for several Xe/He concentration ratios. After comparing this data with similar data obtained for cw nozzles with identical nozzle geometries in synchrotron experiments in Hamburg, we concluded that we were not achieving steady state conditions in our Laser Technics pulsed supersonic nozzle. We use a nozzle geometry similar to the Hamberg group (6.8mm length, 30° cone angle, 500 μm throat diameter).²¹ We determined that the axial opening Δz of this nozzle is insufficient to achieve the stagnation pressure across the full area of the nozzle throat; hence the cluster formation did not agree with nozzles operated continuously (cw rather than pulsed). We are now using a solenoid opened nozzle (General Radio pulsed nozzle) with a larger axial opening. In Fig. 7.3 we plot the mean cluster size calculated from TOF spectra similar to Fig. 7.2 for varying nozzle opening times. At opening times of 2 msec we achieve mean cluster sizes within 50% of that observed for cw nozzles under identical thermodynamic conditions.²² Although this nozzle has an axial opening Δz still insufficient to reach steady state expansions, we achieve conditions similar enough to cw conditions for spectroscopic studie and find that the clusters sizes agree with cw nozzles over a broad range of conditions for temperature and pressure in pure xenon expansions with an effective nozzle diameter of 100 μm .

²⁰O. Echt, P. D. Dao, S. Morgan, and A. W. Castleman, Jr., Chem, Phys. **82**, 4076 (1985).

²¹J. Wörmer, V. Guzielski, J. Stapelfeldt, G. Zimmerer, T. Möller, Phys. Scr. **41**, 490(1990)

²²O. F. Hagen, Z. Phys. D-Atoms, Molecules and Clusters **4**, 291(1987).

Fig. 7.2. Time-of-flight spectra for varying Xe/He concentrations measured at 266 nm. The nozzle was a solenoid actuated valve (30° full angle, 6.8mm long, 0.5mm diameter) with stagnation pressure of 2000 Torr and temperature of 250K.

We have observed a large background which is spread over a mass range from 2-75 for both nozzles. Our first clue as to the origin of this background was the existence of helium peaks in the spectrum. Since we did not believe these were generated by photoionization (>8 photons required) we guessed that the He ions and background might be due to electron impact ionization. The electrons which result from photo-ionization are accelerated by the on extraction field and blown upstream into the denser region of the jet (note we extract ions downstream to avoid the optics for fluorescence). We have now added field grids as shown in Fig. 7.4. In the initial configuration, the first grid was bolted to the vacuum chamber, thus grounding it; hence, we biased the grids as shown in potential (a) of Fig. 7.4. The reduction in background as a function of increasing the voltage on the back grid, V_s , from 0.0 to -0.6V, is shown in Fig. 7.5. When the resulting supersonic ions reach the first grid of Fig. 7.4, the back grid is switched to a negative potential as shown as (a') in Fig. 5.5. Ions produced in the background are then prevented from reaching the the extractor. As observed in Fig. 7.5, background ions trapped in the potential well shown as (a')

in Fig. 7.4 oscillate in the trap, returning periodically to the first grid where they leak through to field lines pushing through the holes in the mesh from the extractor region. The period of oscillation in data similar to Fig. 5.6 was found to vary with the well depth established by the potential on the back grid, as expected.

Fig. 7.4.

Ion potentials for the TOF mass spectrometer. The current configuration is shown as potential (b) which is switched to (b') after the supersonic ions pass the first grid. The initial field between the back grid and first grid is adjusted so as to maximize the mass resolution. Switching to potential (b') removes the background ions.

Fig. 7.5. TOF spectra for 2+1 REMPI of Xe $6p[1/2]_0$. The frequency doubled dye laser was tuned to 249.6272 nm. The grid potentials are shown as curve (a) of Fig. 5.6 where the backgrid is switched to curve (a') after the supersonic ions pass through the first grid. This traps the stationary background ions in a potential well.

Modification of the spectrometer allowing operation at potential (b) in Fig. 7.4 removes these periodic background peaks and improves the signal-to-noise for 2+1 REMPI spectra significantly. In the normal operation of a TOF spectrometer the finite focal volume causes a variation in arrival time at the detector following the drift chamber. By adjusting the initial field between the back and the first grid ions at $z \pm R$ (R being the focal radius of the laser) can be made to arrive at the detector simultaneously improving the mass resolution. By switching the potential to (b') in Fig. 7.4 at the time the supersonic ions pass the first grid then removes the remaining background ions and prevents them from entering the drift chamber. The resulting improvement in mass resolution and

background is observed in Fig. 7.6. We also find significantly improved excimer spectra compared with Fig. 7.2. These are shown in Fig. 7.7.

The spectra of Fig. 7.6 were obtained with the laser tuned to the excimer resonance at 249.9656nm observed in Fig. 7.7. The TOF spectra of Fig. 7.6 were taken for the same nozzle conditions as the spectra shown in Fig. 7.3 for Xe/He = 8%. Surprisingly, for the highest laser powers of Fig. 7.6, very little fragmentation of Xe_2^+ to form Xe^+ is observed in the spectrum.

Two u.v. photons resonantly excite the dimer to a bound excimer state followed by photoionization by a third photon. If this process were to occur vertically, the Frank condon factors from the bound dimer in the ground state should lead primarily to dissociative states of the molecular ion. Since the excimer is excited at the outer turning point of its bound potential, the nuclei move radially inward before photoionization by the third photon. (As will be discussed, the lifetime of the molecule against photoionization is not significantly shorted than the radiative lifetime, hence it is significantly longer than vibrational periods.) The third photon ionizes the molecule at sufficiently small internuclear separations to excite the bound $2\Sigma_u^+$ molecular ion; photoionization is well above threshold, but the electron carries off nearly all the excess energy, leaving behind a stable molecular ion. The remaining ion survives the full flight through the mass spectrometer (lifetime > 60 μsec). As the laser power is decreased, the ion signal decreases as the square of the laser power because of the reduced transition rate to the excimer state. As well one observes that the $\text{Xe}^+/\text{Xe}_2^+$ ratio increases with decreasing laser power. This is consistent with predissociation of the excimer state. As the laser power increases, the probability for photoionization of the molecule before predissociation.

Fig. 7.6. TOF spectra while exciting dimer resonance at 249.9656. Plotted is the normalized ion count/channel plotted as a function of delay time. The curves are organized from low to high power with a fixed offset of 0.5. The peak at 40 μsec is Xe^+ ; that at 55 μsec is Xe_2^+ .

Fig. 7.7 Two-photon excitation spectra of Xe excimers measured by collecting only Xe_2^+ photoions from the TOF spectra. The spectra are averages of 200 laser shots per spectral point.

also increases. These experiments suggest that at the highest laser powers $\tau_{\text{vib}} < \tau_{\text{photoion}} \sim \tau_{\text{diss}} < \tau_{\text{rad}}$ for the excimer state. We also observe that the monomer ion peak is considerably broader than the dimer ion peak. The structure of this peak has been studied as a function of the electric field in the ionization region between the back and first grids. As the fields decrease the dimer ion and the slowest monomer ion decrease in intensity. At a slight negative field only the fastest peak remains. We assign the slowest and fastest monomer peaks to Xe^+ ions formed by photoionization of the excited atoms resulting from predissociation of the excimer. The central peak is formed by photoionization off resonance of supersonic xenon atoms in the jet. In the center of mass motion of the jet, the dissociated ions explode radially at all angles; but the ions exploding transverse to the beam do not reach the ion detector after the drift tube, as we estimate that ions with transverse velocities much above kT will not reach the detector. We shall see these results are consistent with new fluorescence experiments.

From resonant TOF spectra such as Fig. 7.6 at varying Xe/He concentrations we have determined that the maximum Xe_2 concentration occurs from 5-8% concentration. At higher concentration the overall Xe concentration increases, but dimers are lost in the formation of larger clusters. In the 20% concentration nonresonant 266 nm spectra of Fig. 7.3 larger numbers of Xe_2^+ ions are observed per laser shot than the TOF spectra of Fig. 7.6, yet no excimer resonances are observed in 2+1 REMPI spectra over the tuning range of Fig. 7.7. All of the dimer ions observed in Fig. 7.3 result from fragmentation of larger clusters. Either 266 nm photoionization selectively excites larger clusters or the very short lifetime of the intermediated molecular state in nonresonant excitation leads to vertical transitions to dissociative ion states.

7.4 Final Search for Excimer Fluorescence

By measuring the ratio of ions produced by resonant photoionization of excimer versus resonant photoionization of the nearby $\text{Xe}^* 6p[1/2]_0$ state (249.6272 nm in Fig. 7.7), we have measured the Xe/Xe_2 ratio to be 120 at the 8% Xe/He concentration and 1000T stagnation pressure. (This measurement assumes approximately equal two-photon excitation rates and excited state photoionization cross sections for the dimer and monomer.) For the laser tuned to the atomic resonance, we measure 3.06 photons/laser shot fluorescent at 828.2 nm. This signal scales greater than linearly and only slightly less than the square of the laser power suggesting that $\tau_{\text{photoion}} \lesssim \tau_{\text{rad}}$ for the atom.

For these final attempts at observing excimer fluorescence we used a Chromix 0.25 meter spectrograph with a 150 g/mm grating blazed at 600 nm. Photons were detected using a Tektronix model TK512 ccd camera. This detector is back etched and has a calibrated quantum efficiency at 800 nm of 70 %. For each of the strong excimer resonances observed in Fig. 7.7, we searched for fluorescence over the wavelength range from 550 to 980 nm using several overlapping exposures

of the camera. Each exposure covered approximately 150 nm. Binning the camera pixels to a 4x8 superpixel minized the readout noise without loosing too many pixels to hits from cosmic rays. Lead shielding was also used to reduce this background. For 40 minute integration times (24,000 laser shots) the standard deviation of the background due to readout noise was ± 9.2 count (3.7 electrons/count) Within this noise limit no fluorescence photons were observed. When the laser was tune to an atomic resonance we obtained the equivalent of 378,600 counts for the same exposure time (shorter exposures were used). This corresponds to 58 detected photons per laser shot. Combined with the measured atom/dimer ratio, the probability for fluorescence of the excimer, or fluorescence from a product of predissociation, is 2.9×10^3 . This probability the suggest for the excimer, $\tau_{\text{diss}} \lesssim 2.9 \times 10^{-3} \tau_{\text{rad}} \sim 8.7 \times 10^{-11}$ sec. This result is consistent with the data of Fig. 5.7. Since atomic products of the predissociation are themselves not fluorescent in the visible or ir region, these excimer states must predissociate to $\text{Xe}^* 5p^5 6s'$ which fluoresces in the vuv.

7.5. REMPI Spectra of small clusters

We have obtained the 2+1 REMPI spectra for clusters dissociating to Xe_2^+ , Xe_3^+ , or Xe_4^+ - Xe_5^+ , as a function of the wavelength of the exciting laser. Previously we assumed that the spectra of the larger molecules would be similar to Xe_2^+ except for small splittings due to additional low frequency vibrational modes of the larger molecules. We find instead broad bands of complex spectra from wavelengths from 260-266nm(9.53-9.32). A piece of such a spectra is shown in Fig. 7.8 for Xe/He concentrations of 20%. The energy band over which we observe the spectrum of Fig. 7.8 of 9.3-9.5 eV is in reasonable agreement with the exciton band of liquid xenon observed in Fig. 6.1. Spectra similar to Fig. 7.8 have not yet been made for energies less than 9.3 eV because a dye change is required. We are now occupied obtaining spectra with longer scans and over a range of concentrations.

Fig
 . 7.8 Resonant multiphoton ionization spectra leading to Xe_3^+ , and Xe_{4-5}^+ ion channels as a function of laser wavelength in expansions of Xe in He at 20% concentration.

8.0 Publications

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2. N. Bowering and J. W. Keto, "Selective Quenching During Half-Collisions of Laser Excited Xenon Atoms", Lasers 84, San Francisco, Ca., December 1984.
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6. J. W. Keto, "*Dynamics of Multiphoton Excited Xenon Atoms*," Colloquium, University of Wurtzburg, West Germany, May 7, 1985.
7. J. W. Keto, "*Laser Switched Electronic Energy Transfer*," SFB Colloquium, University of Kaiserslautern, West Germany, May 23, 1985.
8. J. W. Keto, "*Dynamics of Multiphoton Excited Xenon Atoms*," Seminar at CNRS-ORSAY, Universite' Paris-Nord, Villetaneuse, France, June 19, 1985.
9. J. W. Keto, "*Laser Physics in Austin, Texas*," Seminar at CNRS, Grenoble, France, June 21, 1985.
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11. J. W. Keto, "*Observation of Curve Crossings in Radiative Collisions of Xenon Atoms*," First International Laser Science Conference of Am. Phys. Soc., November 20, 1985.
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10.0 Degrees:

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