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Kinetic Studies Following State-selective Laser Excitation

Progress Report

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I. Introduction

During the past year, we have made measurements of state-to-state energy transfer cross sections and radiative lifetimes for Xe*(6p,6p',7p) and Kr*(5p) states in xenon and krypton buffer gases. These results are relevant to kinetic models of both excimer lasers and the infrared xenon laser; and they are a significant improvement in the precision of the known radiative lifetimes.

II. Measured quench rates

Xe* and Kr* is excited in a two-photon transition[1] 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 decays as a function of pressure, we obtain a Sturm-Volmer plot, $\nu = \nu_{rad} + k[n]$, whose slope determines the reaction rate k. We find the decay rates for excited Xe* in krypton buffers to be described by

$$\nu_q = \nu_0 + k^{(2)}_{xe}[Xe] + k^{(2)}_{Kr}[Kr] \qquad (2)$$

where ν_0 is the radiative rate and $k^{(2)}_i$ represent bimolecular reaction rates.The measured quench rates for Xe*(6p,6p',7p) and Kr*(5p) are shown in Table I. All states except Xe*6p[1/2]$_0$ and Kr*5p[5/2]$_2$ exhibit simple bimolecular quenching characteristics. Xe*6p[1/2]$_0$ has been determined to be collisionally mixed with the Xe*5d[1/2]$_1$ state

Table I. Radiative Lifetimes and quench rates for Xe* and Kr*

State	Lifetimes (nsec)	Bimolecular Quench Rates (10^{-12} cm^{3}sec^{-1})		
		Xenon	Krypton	Krypton,Ref.1
Kr* 5p[5/2]$_3$			40±4[a]	
5p[5/2]$_2$	23.5±0.3	408±5	248±6[b]	
5p[3/2]$_2$	26.2±0.3	299±6	24±2	
5p[1/2]$_0$	22.7±0.3	420±6	42±4	
Xe* 6p[5/2]$_2$	36.0±2.8	116±3	38±2	45±5
6p[3/2]$_2$	31.3±1.8	101±3	28±1	22±3
6p[1/2]$_0$	26.8±0.8	5.9±0.5	132±4	110±5
6p'[1/2]$_0$	34.1±0.8	423±8	286±5	
6p'[3/2]$_2$	32.1±0.8	426±10	294±5	
7p[5/2]$_2$	128.6±5.6	462±9	405±16	
7p[3/2]$_2$	105.3±2.9	522±8	311±5	
7p[1/2]$_0$	69.1±1.3	495±8	396±6	

a) Extracted from slow component of Kr 5p[5/2]$_2$ decay.
b) Extracted from fast component of Kr 5p[5/2]$_2$ decay.
Error bars shown are twice the standard deviation.

approximately 132 cm-1 below it in energy. We determined that the time dependent fluoresence of Kr*5p[5/2]$_2$ is described by a minimum of three exponentials. This state is most probably mixed with both Kr* 5p[5/2]$_3$ and a nearby state in the Kr*4d manifold.

III. Measured state-to-state reaction rates

The state-to-state reaction rates can be found from measurements of the relative integrated fluorescence intensities of the collisionally populated and laser excited states combined with the measured deactivation rates of Table I. The integrated intensity of the state's fluorescence is 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 uv detector (EMR #?). All detector systems are absolutely calibrated using NIST traceable standard lamps. The relative integrated populations N_i and N_j are related by

$$N_j = \frac{\nu_{ij}}{\nu_i} N_i \tag{3}$$

where N_i and N_j are the populations of the initially excited state $|i\rangle$ and the collisionally populated product state $|j\rangle$, respectively. Here ν_{ij} is the product formation rate from $|i\rangle$ to $|j\rangle$ and ν_i is the total quench rate of $|i\rangle$, measure by procedure of section II. The integrated populations N_i and N_j can be determined from the measured integrated intensities

$$I_{ik} = \eta_{ik} A_{ik} \frac{N_i}{\nu_i} \text{ and } I_{jk} = \eta_{jk} A_{jk} \frac{N_j}{\nu_j} \tag{4}$$

where η_{ik} is the quantum efficiency of the optical system and A_{ik} is the radiative transition probability from $|i\rangle$ to $|k\rangle$. An example spectra showing the excited state and various product state fluorescences is shown in Fig. 1. The state-to-state optical transition rate can be related to the measured total transition rate,

$$A_i = \tau_i^{-1} = \sum_{k=1}^{m} A_{ik} = \sum_{k=1}^{m} b_{ik} A_i, \tag{5}$$

where b_{ik} is the optical branching fraction from $|i\rangle$ to $|k\rangle$. Finally, the product formation rate can be written as

$$\nu_{ij} = \frac{I_{jk}\, \eta_{ik}\, b_{ik}\, A_i}{I_{ik}\, \eta_{jk}\, b_{jk}\, A_j} \nu_j; \tag{6}$$

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 ν_{ij}.

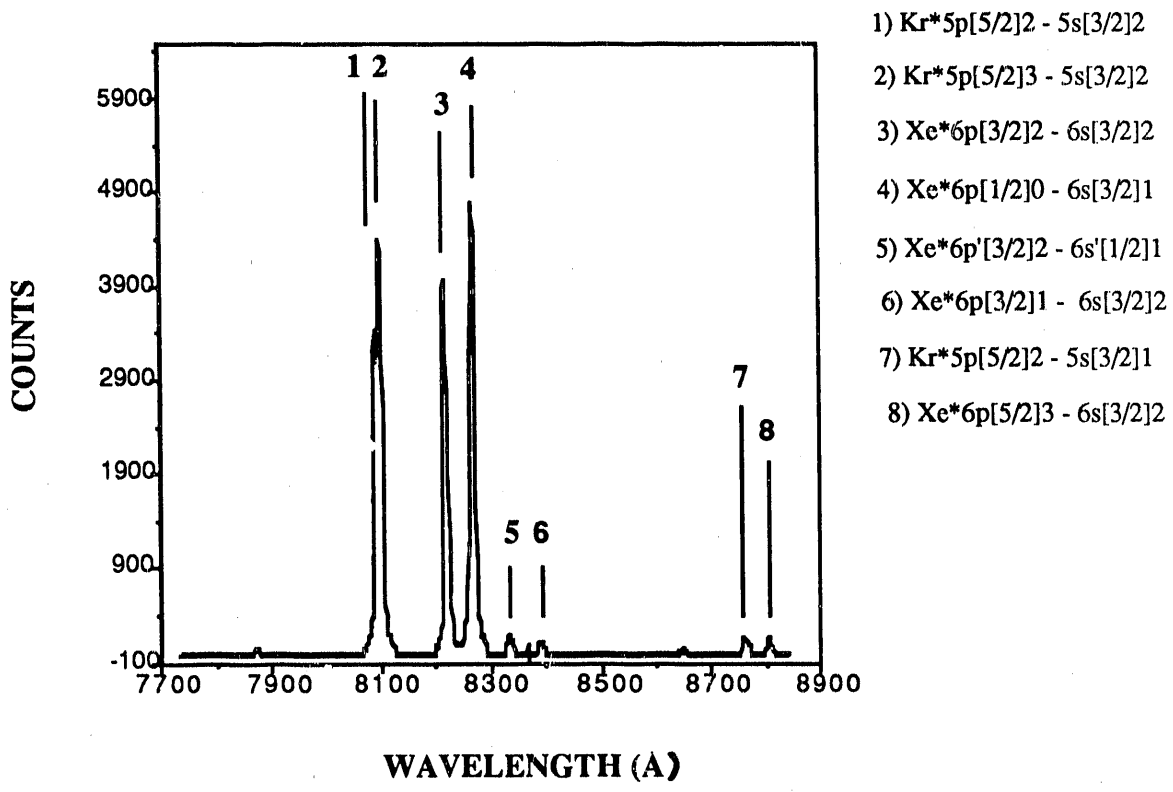

Fig. 1. Fluorescence spectra of 1 Torr krypton in 10 Torr xenon, while exciting Kr* 5p[5/2]$_2$.

This process is equivalent to extracting the state-to-state rates ν_{ij} from measurements of the time dependence of the product channel. The measured time dependence of the product channel is expected to be described as the excited and product decay rates, ν_i and ν_j, and a ratio of amplitudes related to the ratio of integrated intensities. Integrating the measured time dependence numerically would yield a result similar to Eq. 6 above. Since we gate the photodetector only over the necessary time window to integrate the cascade, the procedures are equivalent. Both procedures are susceptible to population of the product state though secondary channels involving a third state. As we showed earlier, this third channel can often only be detected if the signal-to-noise of the time dependence of the cascade is very good.[2] If the third state decays radiatively, the existance of the secondary population,

$$|i\rangle + Kr \rightarrow |3\rangle + Kr \rightarrow |j\rangle + Kr, \qquad (7)$$

can also be detected by measuring the state-to-state rate ν_{ij} in Eq. 6 as a function of pressure. If secondary channels become important (observed when the collision rates become comparable to the radiative rates), the rates ν_{ij} are not observe to linearly increase with pressure. The effect of secondary production is minimized at the lowest pressures.

For experiments reported here, the rates were measured at 0.1 and 0.5 Torr of the species to be excited and for collision gases pressures from 0.5 to 10Torr. An example plot of a state-to-state transition rate is shown in Fig. 2. Data for excitation of states of Kr* 5p and Xe* 6p' multiplets indicate production by third channels. The product channels observed in fluorescence are indicated for these states by a "?" in the table. These states will require studies of the time dependence of the product channels. The remaining state-to-state rates are shown in Table II. As observed in Fig. 2, the state to state rate of $6p[1/2]_2$ from the excited state $6p[1/2]_0$ (marked by an asterix in the table) increases with xenon pressure indicating two possible secondary channels

$$Xe^* 6p[1/2]_0 + Kr \rightarrow Xe^* 5d[1/2]_1 + Kr \quad (8)$$

$$Xe^* 5d[1/2]_1 + (Kr \text{ or } Xe) \rightarrow Xe^* 6p[3/2]_2 + (Kr \text{ or } Xe) \quad (9)$$

and as suggested by Setser[1]

$$Xe^* 6p[1/2]_0 + Kr \rightarrow Kr^* 5s[3/2]_2 + Xe \quad (10)$$

$$Kr^* 5s[3/2]_2 + Xe \rightarrow Xe^* 6p[3/2]_2 + Kr. \quad (11)$$

Setser prefers the latter mechanism[1], in part because of its obvious xenon dependence. Since it is now known that $Xe^* 5d[1/2]_1$ has a rapid quench rate in xenon[3], reactions 8 and 9 are also expected generate a larger rate for increasing xenon pressures. As futher support of the process described by Eq. 8 and 9, we observe a bright fluorescence of $Xe^* 5d[1/2]_1$ at 125 nm. This is indicated by a large state-to-state rate for $Xe^* 5d[1/2]_1$ in Table II. We have not yet determined that fraction that each of the above processes contibutes to the production of $Xe^*6p[3/2]_2$, and this problem will as well require additional work. The

Table II. Bimolecular state-to-state rates in (10^{-12} cm^3/sec) for Xe* in Krpton and Kr* in xenon. The first column lists the states excited by the laser; each additional column lists the reaction rate for a particular product channel.

State	Xe*	Xe*	Xe*	Xe*	Xe*	Xe*	Xe*	Xe*	Xe*	Xe*	Kr*
Kr*	$6s[3/2]_1$	$6p[5/2]_2$	$6p[5/2]_3$	$6p[3/2]_1$	$6p[3/2]_2$	$6p[1/2]_0$	$5d[1/2]_1$	$6p'[3/2]_2$	$6p'[1/2]_1$	$6p'[1/2]_0$	$5s[3/2]_1$
$5p[5/2]_2$	?				?	?	?				350±175
$5p[3/2]_2$	?				?19±6	?30±8					280±140
$5p[1/2]_0$	?				?25±4	?26±4					280±140
Xe*											
$6p[5/2]_2$	?		?	?	?	?					
$6p[3/2]_2$	17		?	9.1±1.4		1.5±0.8					
$6p[1/2]_0$	57±20				*27±5		48±20				
$6p'[3/2]_2$	193±22				46±9	6±4	7±4		0.8±0.6		41±20
$6p'[1/2]_0$	0±45			38±16	64±16	73±16	3.5±1.7	52±10	7±4		70±35
$7p[5/2]_2$	64±16				24±5	16±3	12±6				280±140
$7p[3/2]_2$	147±80						4±2				160±80
$7p[1/2]_0$	?				?		10±5				280±140

* see text

stateto-state rate shown in Table II is the rate determined from extrapolating to zero xenon pressure, and should be free of the secondary production mechanism described by Eq. 10 and 11. Finally, for states of Kr* 5p, Xe* 6p', and Xe* 7p, product channels $Kr^*5s[1/2]_0$ and $Kr^*5s[1/2]_1$ are energetically accessible. The later radiates at 117 nm, and was not observable in the current experiments but is possible in an existing chamber having a LiF window.

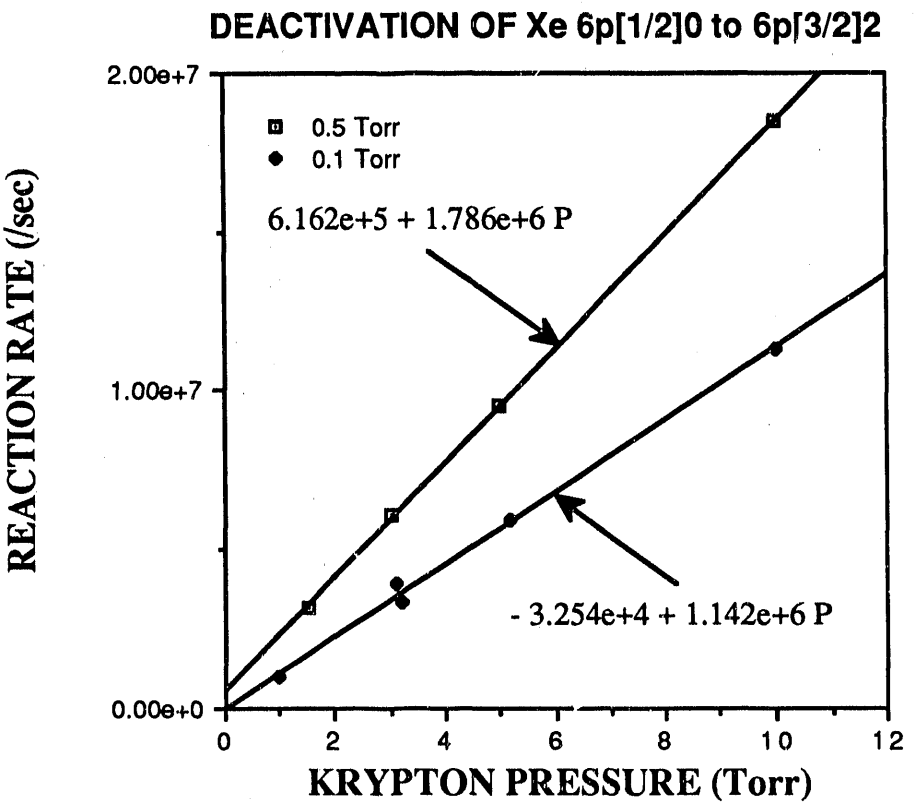

Fig. 2. State-to-state reaction rate. Here the reaction rates are function of xenon pressure, indicating that a third state is contributing to the product in a secondary reaction.

IV. Future work

This study will be completed by the end of this contract period and will be the thesis of Andy Whitehead. For the next contract year, we plan two experiments: (1) a study of energy transfer from Xe* to Cl_2 in krypton buffers and (2) a study of the radiative collisions

$$Xe + Cl_2 + h\nu \rightarrow XeCl^* + Cl \quad (12)$$

and

$$Xe + HCl + h\nu \rightarrow XeCl^* + H \quad (13)$$

$$\rightarrow XeH^* + Cl. \quad (14)$$

In the last process (Eq. 13 and 14), we hope to observe changes in the branching between product channels with photon energy.

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