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Kinetic Studies Following State-selective Laser Excitation

Progress Report

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DISCLAIMER

I. Introduction

We have made measurements of state-to-state deactivation 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. This type of experiment can now be compared with recent calculations of state-to-state collisional relaxation in rare-gases by Hickman, Huestis, and Saxon.[1]

We have also made significant progress in the study of the electronic spectra of small molecules of the rare gases. Spectra have been obtained for Xe_2, Xe_3, Xe_4, and larger clusters. As guidance for the larger clusters of the rare gases we have obtained the first multiphoton spectra for excitons in condensed xenon.[2] In collaboration with research on the multiphoton spectra of the rare gases, we have continued experiments using synchrotron radiation in collaboration with the University of Hamburg.[3] In experiments there we have observed excitation and fluorescence spectra for single xenon atoms at the surface, within the second layer, and within the bulk of large argon clusters.[4,5]

II. Electronic Energy Transfer in Rare Gas Mixtures: Experiment

Xe* and Kr* is excited in a two-photon transition(6) 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 to determine the reaction rates,k, $\nu = \nu_{rad} + k[n]$. 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) were reported in last years abstract. 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 approximately 132 cm-1 below it in energy. Kr*5p[5/2]$_2$ is most probably mixed with a similar nearby Kr*5d state.

III. 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. The integrated intensity of the states 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 solar blind detector. All detector systems are absolutely calibrated using NIST traceable standard lamps. The relative integrated populations N_j are determined by

$$N_j = \frac{\nu_{ij}}{\nu_i} N_i \qquad (3)$$

where N_i and N_j are the populations of the initially excited state |i> and the collisionally populated product state |j>, respectively. Here ν_{ij} is the product formation rate from |i> to |j> and ν_i is the total quench rate of |i>. The population N_i can be determined from the measured integrated intensity

$$I_{ik} = \eta_{ik} A_{ik} \frac{N_i}{\nu_i} \qquad (4)$$

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

$$\nu_{ij} = \frac{I_{jk}\,\eta_{ik}\,b_{ik}\,A_i}{I_{ik}\,\eta_{jk}\,b_{jk}\,A_j}\,\nu_j, \tag{5}$$

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 ν_{ij}.

Example data showing product fluorescence is shown in Fig. 1. At sufficiently high pressure product states may be quenched to other levels leading to secondary population of those levels. The amount or 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,

$$N_j(t) = \frac{N_i(0)\nu_{ij}}{(\nu_i - \nu_j)}[\exp(-\nu_j t) - \exp(-\nu_i t)]\,. \tag{6}$$

and it will have an intensity which increases linearly with pressures at low pressures and then increases more rapidly at higher pressures due to the contribution from the secondary channel. Fig. 2 demonstates a product channel with no secondary channel while Fig. 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 ν_{ij} can measured without interference from the secondary channel. Data similar to Figs. 2 and 3 have been obtained for all product channels observed for the eleven laser excited states of krypton and xenon. The state-to-state rates are summarized in Tables I , II, and III. 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

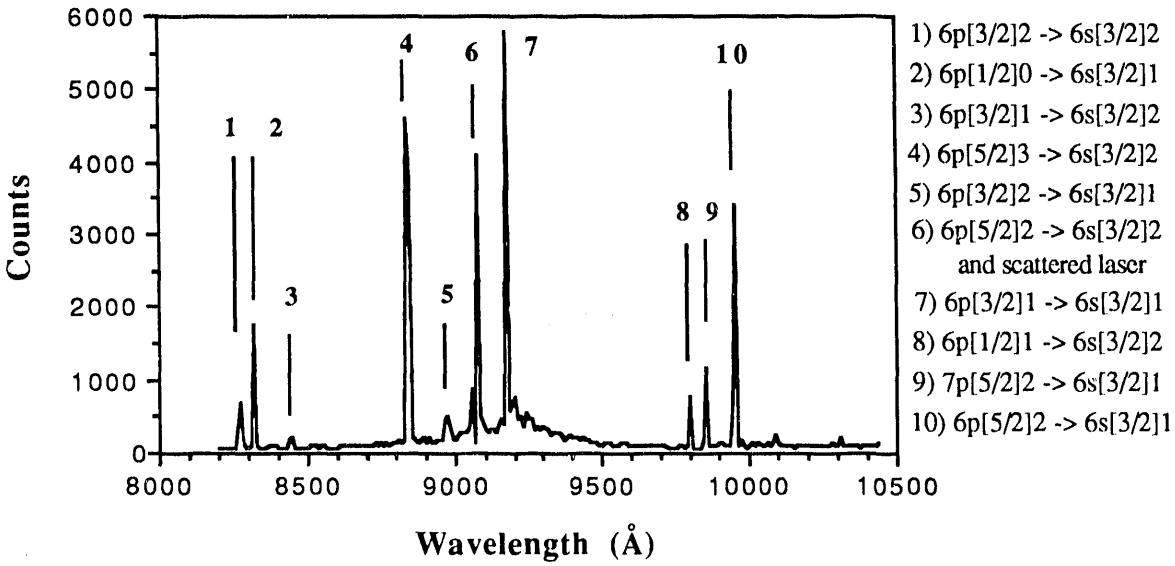

Fig. 1. Fluorescence scan following excitation of Xe*7p[5/2]$_2$ in 50 Torr xenon.

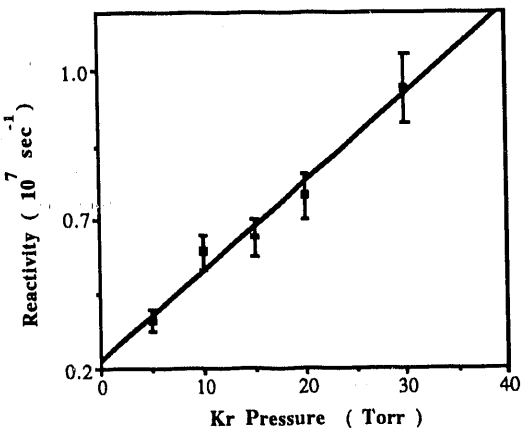

Fig. 2 Intensity resulting from Xe*6p'[1/2]$_0$→6p[1/2]$_0$ in krypton.

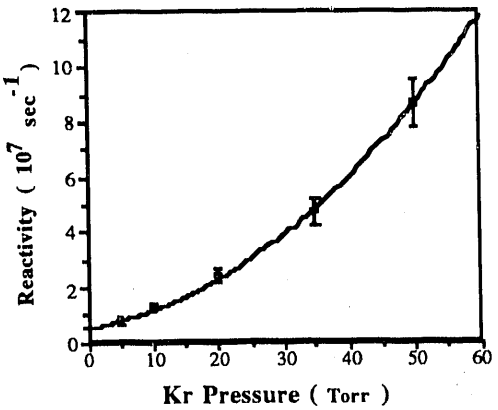

Fig. 3 Intensity resulting from Xe*6p[1/2]$_0$→6p[3/2]$_1$ in krypton.

as Fig. 2. Each data point in Fig. 2 represents a spectra such as Fig. 1! We required computerized spread sheets just to organize this tremendous amount of data. Since each state-to-state rate in the table is a absolute measurement as indicated by Eq. 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. Most states agree surprisingly well. For the 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 Xe* 7p. This data did verify secondary channels with

Table I 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} cm^3/sec.

Laser Excited State of Xenon

	Ref. 7			This work				
	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]$_0$
Product								
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.

very fast decay rates. Because the formation rates for the intermediated states (possibly Xe* 6d) could not be measured directly the data of Table I cannot be corrected for these intermediate channels (note 5d and 6d transitions occur in the region 1.73-3.51 μm where detection with photomultipliers is not possible. Additional research is necessary to completely unravel quenching from Xe 7p states. The data in Table II for krypton buffers also indicated sums too large for Xe* 6p'. These experiments are being repeated in attempts to resolve the problem.

These experiments represented the major part of the thesis of Andy Whitehead, who received his PhD under DOE support in the fall semester. We are now preparing a manuscript discribing these results. A preliminary draft is included as an appendix.

Table II 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 10-12cm^3/sec.

	Laser Excited State of Xenon							
	This work					Ref. 6		
	$6p[5/2]_2$	$6p[3/2]_2$	$6p[1/2]_0$	$6p'[3/2]_2$	$6p'[1/2]_0$	$6p[5/2]_2$	$6p[3/2]_2$	$6p[1/2]_0$
Product								
$Xe6p'[1/2]_0$	a	a	a	a	*			
$Xe6p'[1/2]_1$	a	a	a	c	c			
$Xe6p'[3/2]_2$	a	a	a	*	66±8(?)			
$Xe6p'[3/2]_1$	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	*	32±9(?)	9±3(?)			*
$Xe6p[3/2]_2$	c	*	41±4[d]	66±15(?)	74±12(?)		*	≤10
$Xe6p[3/2]_1$	c	14±1	16±2[d]	80±18(?)	48±18(?)		6±2	≤10
$Xe6p[5/2]_3$	11±2	4±1	0±1[d]	25±6(?)	23±3(?)	15±2	6±2	≤10
$Xe6p[5/2]_2$	*	14±3	2±1[d]	85±17(?)	35±10(?)	*	10±2	≤10
$Xe6p[1/2]_1$	24±9	4±1	0±1[d]	24±20(?)	8±8(?)	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(?)			
ΣKij	36±7	36±4	132±10[d]	397±63	432±58	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, $Xe6p[1/2]_0 \rightarrow Xe6p$ and $Xe6p[1/2]_0 \rightarrow Kr5s[3/2]_2 \rightarrow Xe6p$, were deconvolved for these values.

Table III. 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 $10^{-12}cm^3/sec$.

	in Krypton			in Xenon		
	$Kr5p[5/2]_2$	$Kr5p[3/2]_2$	$Kr5p[1/2]_0$	$Kr5p[5/2]_2$	$Kr5p[3/2]_2$	$Kr5p[1/2]_0$
Product						
$Kr5p[1/2]_0$	b	b	*	b	b	*
$Kr5p[3/2]_2$	b	*	26±4	b	*	b
$Kr5p[3/2]_1$	4±2	0.73	1.3±0.2	b	b	b
$Kr5p[5/2]_2$	*	5±2	5±2	*	b	b
$Kr5p[5/2]_3$	190±11	22±4	7±1	a	b	b
$Kr5p[1/2]_1$	34±16	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
ΣKij	228±19	28±5	39±5	247±23	131±32	150±20
K_{total}	231±16	24±2	42±4	408±5	299±6	420±6

a) Product formation rate was independent of xenon pressure for this state indicating that quenching was due to krypton and not xenon.
b) No fluorescence was detected.
c) 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 $Xe^*6p[1/2]_0$.
d) 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.

IV. Spectra of Small Molecules

In a separate apparatus,we are measuring high resolution, photoionization and laser induced fluorescence spectra of rare gas dimers, clusters, and diatomic molecules formed in a supersonic jet. In these experiments a pulse supersonic nozzle is crossed with a pulsed uv laser tuned to near two-photon transitions of atomic xenon. A second green or infrared laser is used to photoionize the excited state. The resulting ion is then collected in a time-of-flight mass spectrometer. The spectra of small molecules dissociating to Xe_2^+, Xe_3^+, Xe_4^+, or large can then be obtained as a function the two-photon frequency. Previously we assumed that the spectra the larger molecules would be similar to Xe_2^+ except for small splittings to additional vibrational frequencies of the larger molecules. Indeed, we observe the dimer spectra in the production of larger ions, in addition to the observation of additional "weak" lines.

In order to improve the signal-to-noise of these weaker features we have attempted to obtain greater numbers of the triatomic molecules. Using non-resonant two-photon excitation using 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. After comparing this data with similar data obtained for cw nozzles with identical nozzle geometries in synchrotron experiments in Hamburg[3], we concluded that we were not achieving steady state conditions in our Laser Technics pulsed supersonic nozzle. We have determined that the axial opening Δz of this nozzle is insufficient to achieve the stagnation pressure across the full area of

the nozzle throat. We are now using a solenoid opened nozzle with a larger axial opening. At opening times of 2 msec we achieve mean cluster sizes within 50% of cw nozzles. We now achieve significantly greater numbers of $Xe_3^+$and Xe_4^+.

Preliminary spectra are shown in Fig.4a and 4b. These are sections of a long spectra from 245-266nm. Shown in the Xe_2^+ intensity is a strong spectral feature at 256.34 nm which has previously been assigned as a dimer transition to the 0_g state dissociating to Xe* 6p[5/2]$_2$. Note that this feature is clearly absent from the Xe_3^+ and Xe_{4-5}^+ spectra. This confirms the assignment as a transition of the xenon dimer. Because of predissociation of the excited molecule, predissociation of the ion (we here photoionize well above threshold), and subsequent photodissociation by the absorption of a fourth photon, spectral features of the larger molecules can produce smaller sized ions. This is shown clearly in Fig. 4b. Here the spectral features at 262.52, 262.54, 262.67, and 262.82nm in the Xe_{4-5}^+ spectra are clearly apparent (though weaker) in the Xe_2^+ signal because of dissociation. Fig. 4b demonstrates that the larger clusters have absorption bands which are significantly shifted to the red from dimer bands, suggesting a different electronic structure. This red shift is consistent with our recently measured two-photon spectra of liquid xenon, where exciton bands peaked near 272 nm. We are now improving the signal-to-noise and testing reproducibility of the spectra by averaging several independent spectral scans. We are also obtaining spectra over a range of Xe/He ratios with varying mean cluster sizes.

V. Future Work

We will measure the rates for harpoon reactions of Xe and Cl_2 in krypton buffers. These measurements will test a harpoon model for termolecular reactions.

VI. References

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[3]M. Joppien, F. Grotelueschen, T. Kloiber, M. Lengen, T. Moeller, J. Woermer, G. Zimmerer, J. Keto, M. Kykta, and M. C. Castex, "Some Aspects of the Photoluminescence Properties of Solid Argon: Solids Versus Clusters in a Supersonic Beam", J. of Luminescence **48-49**, 601(1991).

[4]T. Moller, "Optical propperties and electronic exciations of rare gas clusters", Z. Phys. D. 20,1(1991).

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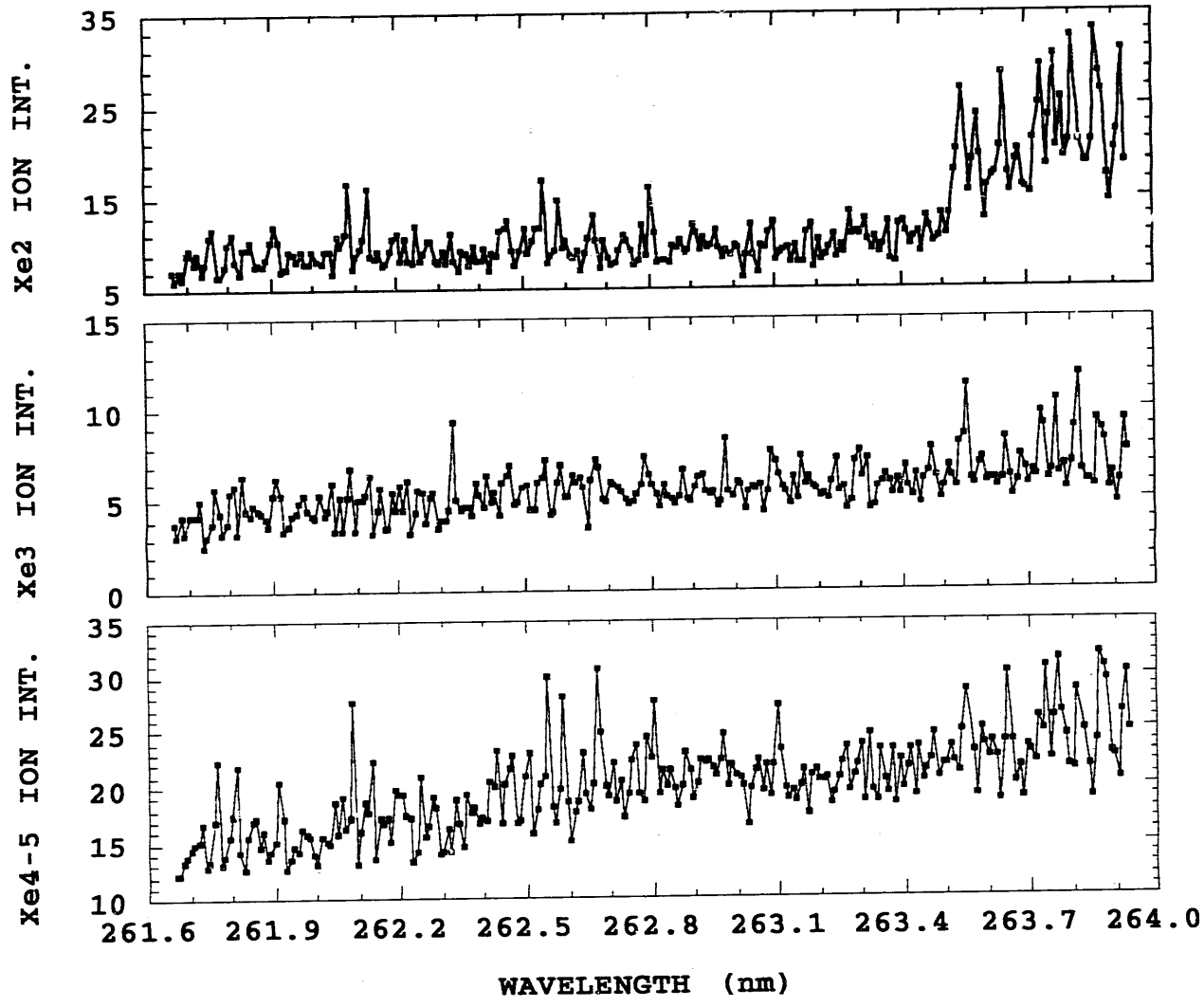
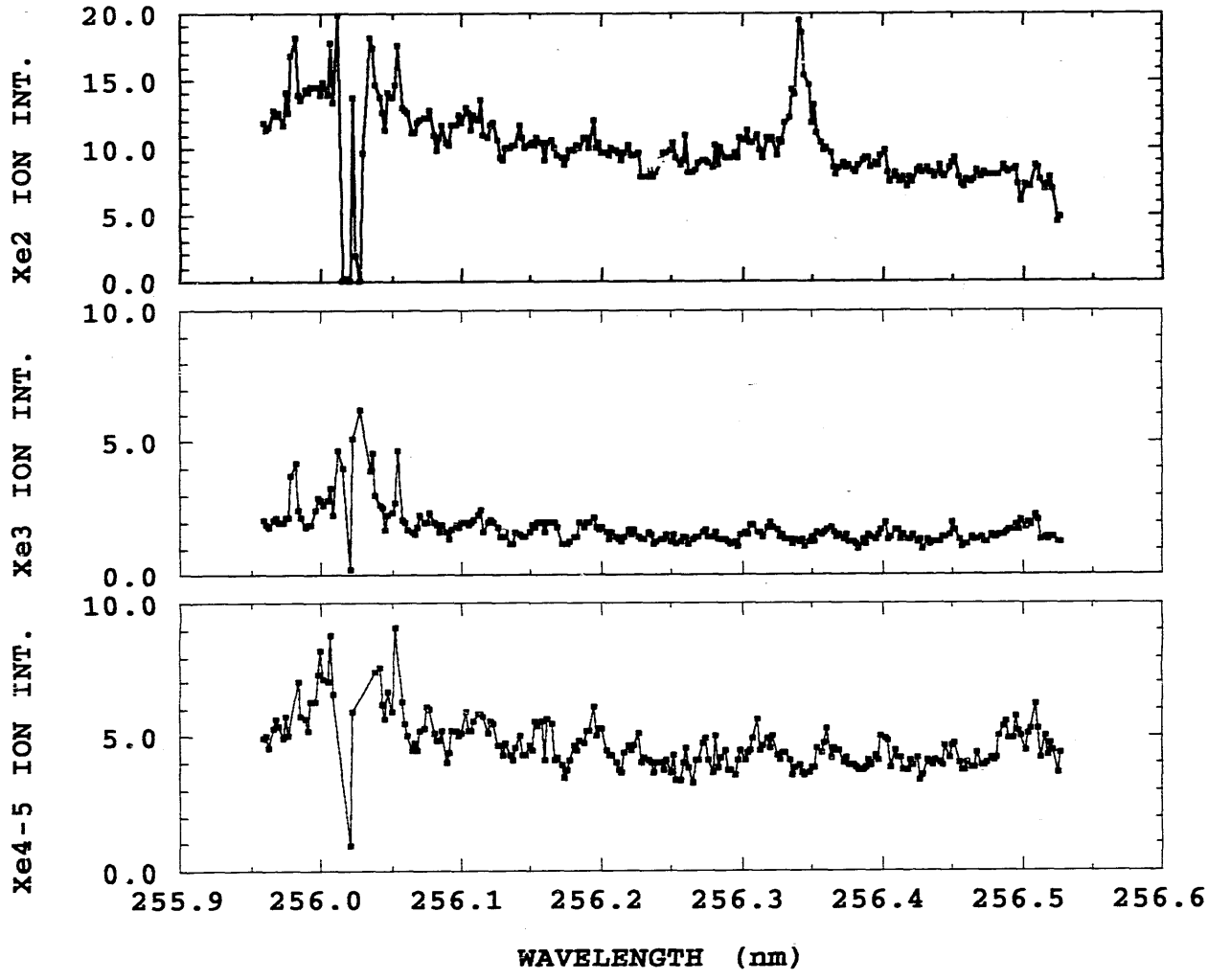
[6]J. Xu and D. W. Setser, "Deactivation rate constants and product branching in collisions of the Xe(6p) states with Kr and Ar", J. Chem. Phys.**92**, 4191(1990).

[7]J.E. Velazco, J. H. Kolts, and D. W. Setser, J. Chem. Phys. **69**,4357(1978)


Xe2 ION INT.
35
25
15
5
Xe3 ION INT.
15
10
5
0
Xe4-5 ION INT.
35
30
25
20
15
10
261.6
261.9
262.2
262.5
262.8
263.1
263.4
263.7
264.0
WAVELENGTH (nm)


Xe2 ION INT.
20.0
15.0
10.0
5.0
0.0
Xe3 ION INT.
10.0
5.0
0.0
Xe4-5 ION INT.
10.0
5.0
0.0
255.9
256.0
256.1
256.2
256.3
256.4
256.5
256.6
WAVELENGTH (nm)

VII. Publications *

i. Lothar Frommhold and J. W. Keto, eds., *Spectra Line Shapes*, Vol 6(AIP, New York) 1991.

ii. M. Joppien, F. Grotelueschen, T. Kloiber, M. Lengen, T. Moeller, J. Woermer, G. Zimmerer, J. Keto, M. Kykta, and M. C. Castex, "Some Aspects of the Photoluminescence Properties of Solid Argon: Solids Versus Clusters in a Supersonic Beam", J. of Luminescence **48-49**, 601(1991).

iii. J. W. Keto, W. B. Layne, and M. R. Bruce, "Harpooning reactions of excited rare gase atoms", *Gas-Phase Metal Reactions*, A. Fontijn, ed., Elsevier (Amsterdan), 1992, to be published.

iv. C. A. Whitehead, H. Pournasr, J. W. Keto, and G. Zimmerer, "Two-photon Absorption in Liquid Xenon", to be published.

v. C. A. Whitehead, M. R. Bruce, Hong Cai, J. Kohel, W. B. Layne, and J. W. Keto, "Deactivation of two-photon Excited Xe ($5p^5 6p,6p',7p$) and Kr($4p^5 5p$) in xenon and krypton," in preparation.

vi. J. W. Keto, "Harpooning reactions of excited rare gas atoms", invited talk at Gas-Phase Metals Symposium, National Congress of the American Chemical Society, New York, N. Y. August 30, 1991.

vii. Jacek Borysow, Hossein Golnabi, Roger H. Taylor, and J. W. Keto, "Techniques for measuring small changes in the intensity of a pulsed laser", to be published in Applied Optics

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