

Kinetic Study on the Low-lying Excited States of Ga Atoms in Ar

Kuntack Lee, Ju Seon Goo, and Ja Kang Ku*

Department of Chemistry, Pohang University of Science and Technology, Pohang, Kyungbuk 790-600, Korea

Received April 11, 1994

Decay kinetics of Ga(5s), Ga(5p) and Ga(4d) atoms in Ar were studied by laser induced fluorescence technique. The ground state gallium atoms in the gas phase were generated by pulsed dc discharge of trimethyl gallium and argon mixtures. Both pulsed discharge and YAG-DYE laser system were controlled by a dual channel pulse generator and the delay time between the end of discharge and laser pulses was set 3.0-6.0 ms. The Ga(5s) and Ga(4d) atoms were generated by single photon excitation from the ground state Ga atoms and radiative lifetimes as well as the total quenching rate constants in Ar were obtained from the pressure dependence of the fluorescence decay rates. The Ga(5p) atoms were populated by a two-photon excitation method and the cascade fluorescence from Ga(5s) atoms were analyzed to extract quenching rate constant of Ga(5p) atoms by Ar in addition to radiative lifetimes of Ga(5p) state. The magnitudes of the quenching rate constants by Ar for the low-lying excited states of Ga atoms are $1.6-3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which are much larger than those for alkali, alkaline earth and Group 12 metals. Based on the measured rate constants, kinetic simulations were done to assign state-to-state rate constants.

Introduction

Organometallic compounds having considerable vapor pressures at a relatively low temperature have drawn substantial interests because these compounds provide an easy way to produce temporally well defined pulses of free metal atoms by UV/VIS multiphoton dissociation (MPD) technique.¹⁻⁶ Among the various species of organometallic compounds, trimethyl gallium (TMGa) has been one of the target molecule for investigation, since gallium is an important element for compound semiconductor technology, and since the generation of free Ga atoms in the gas phase by MPD of TMGa provides one to investigate physical and chemical properties of Group 13 metal atoms at low temperature. Mitchell and Hackett⁷ have studied the MPD of TMGa and shown that the free Ga atoms are liberated by pulsed UV/VIS laser photolysis using multiphoton ionization (MPI) technique. Mitchell and coworkers also have studied MPD mechanism for TMGa,⁸ fine structure changing collisions for Ga(4p 2P_{3/2}) state and branching ratios for chemical reactions in collisional quenching of Ga(5s) state.⁹ Baughcum and coworkers¹⁰ have shown that the photolysis of TMGa with an excimer laser produces various excited states of Ga atoms.

In this work, we have generated gas phase Ga atoms by pulsed dc discharge of TMGa/Ar mixtures and investigated collisional energy flow among the low-lying excited states of Ga atoms in Ar using single and two-photon laser induced fluorescence technique. Radiative lifetimes for those low-lying excited states of Ga atoms have been studied by several groups using various experimental techniques.¹¹⁻²⁵ Nevertheless, the collisional energy transfer processes among the low-lying excited states have not been reported. This work is motivated by the observation of substantial fluorescence quenching of the low-lying excited states of Ga atoms and intermultiplet mixing by Ar. Since it is well known that fluorescence emissions from those low-lying excited states of alkali metals are virtually not quenched by rare gases,²⁶ the fluorescence quenching of Ga atoms by Ar is interesting. The energy levels relevant to this work is shown in Figure 1.

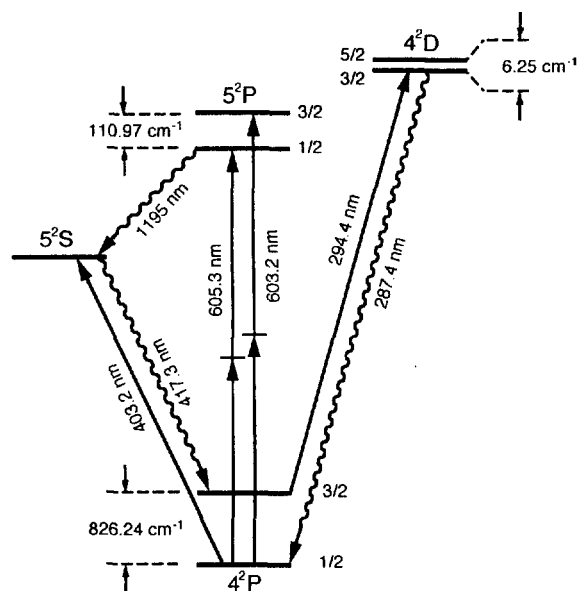


Figure 1. Schematic energy level diagram for the low-lying excited states of Ga atom.

Experimental Section

A schematic diagram of the experimental set up is shown in Figure 2. The cell was made of a 2 l pyrex bulb and two pairs of 1" pyrex O-ring joints were attached to allow laser beam path as well as to install electrodes for pulsed discharge. The electrodes for pulsed discharge were made of Ta foil and tungsten rods. The sample gas (0.5-2% TMGa in Ar) was premixed and stored in a storage bulb in the vacuum rack. The partial pressures of the TMGa in the cell were kept constants (~ 30 mTorr) by varying the contents of TMGa (0.5-2%) in the sample gas to investigate the quenching of Ga(5s) and Ga(4d) atoms by Ar. The gas mixture was slowly flowed through the cell and the flow rate (~ 0.5 mmoles/min) was controlled by adjusting the openings of the inlet needle valve and exit teflon valve. The ground state

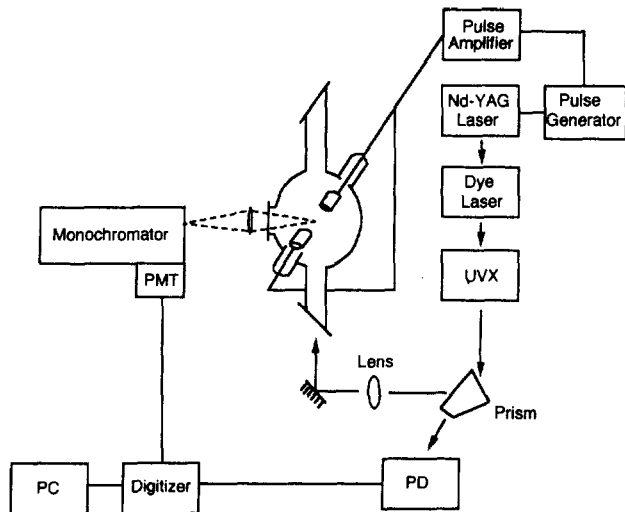


Figure 2. Schematic diagram of the experimental set up.

gallium atoms were generated by a pulsed dc discharge (2-3 kV, 5 mA) of the gas mixture. The discharge pulse width was 4-5 ms and the delay time between the discharge and laser pulses (8 ns FWHM) was 5-6 ms to allow the excited species to decay. The Ga(5s) and Ga(4d) atoms were generated by single photon excitation at 403.2 and 294.4 nm, respectively, and the fluorescence from the laser excited states was monitored at 417.3 and 287.4 nm, respectively. On the other hand the Ga(5p) atoms were generated by two-photon excitation at either 605.3 or 603.2 nm and the cascade fluorescence from Ga(5s) state was monitored at 417.3 nm. The line width of our laser (Quantel YG681-TDL 60 with NBP and DGO) was narrow ($<0.1 \text{ cm}^{-1}$) enough to excite single spin-orbit state selectively.

The fluorescence from the excited Ga atoms was detected at 90° from both the laser beam and discharge directions through 0.5 m monochromator (Spex) equipped with a Hamamatsu R928 photomultiplier tube. The signal from the PM tube was digitized with a transient digitizer (Tektronix 7912 HB) and transferred to a laboratory computer for signal averaging and storage.

Results

Decay behavior of Ga(5s) and Ga(4d) atoms. The fluorescence time profiles from the Ga(5s) atoms in pure TMGa and in the Ar mixtures showed fast rise and decay following the laser excitation pulse. The decaying part of the fluorescence signal after the termination of the laser pulse showed clearly single exponential decay with strong enough amplitude for the analysis. The decay constants of the decaying part of the Ga(5s) emissions at different gas pressures are plotted in Figure 3(a).

The radiative lifetimes as well as the quenching rate constants obtained from the intercepts and slopes of the plots are shown in Table 1 with those previously reported values. The radiative lifetime for Ga(5s) state in this work is in good agreement with the previously reported values,^{9b, 15-18} but substantially longer than that from Lindgard *et al.*²¹

The radiative lifetimes and decay behavior of Ga(4d) atoms have been reported in the previous paper.²⁵ It has been re-

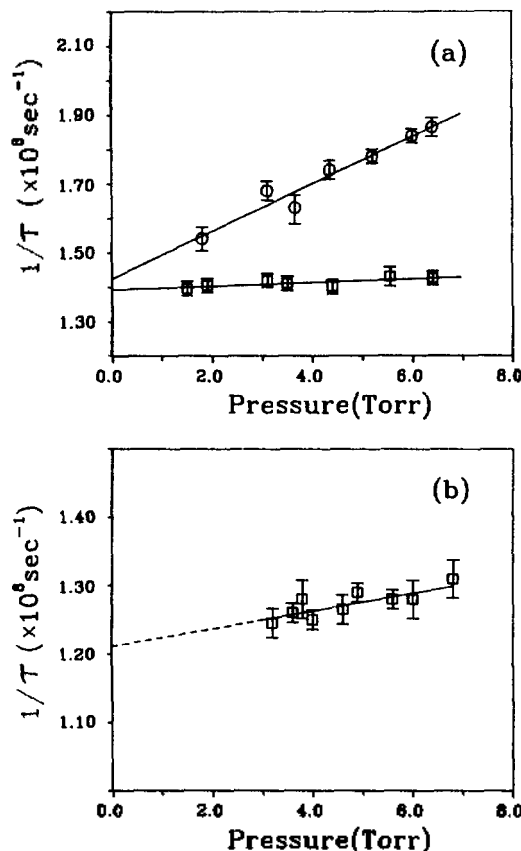


Figure 3. The pressure dependence of fluorescence decay rates; (a) Ga(5s) atoms in pure TMGa (○—○) and in Ar (□—□), (b) Ga(4d) atoms in Ar (□—□).

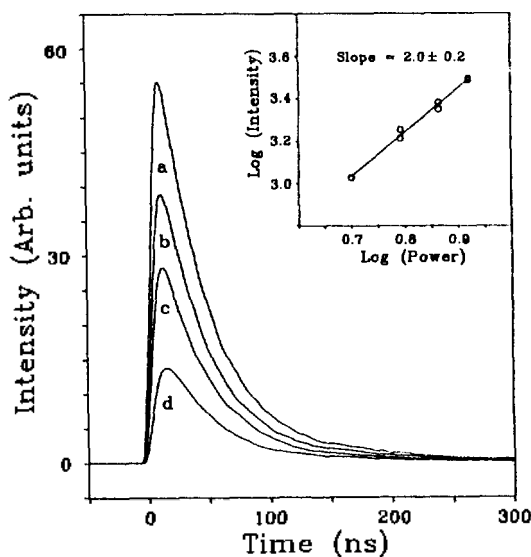


Figure 4. Laser power dependence of cascade fluorescence from Ga(5s) state following two-photon excitation of Ga(5p) state. Laser pulse energies were (a) 8.3, (b) 7.3, (c) 6.2 and (d) 5.0 mJ.

ported that the radiative lifetimes of the two spin-orbit states are substantially different from each other. However, collisional mixing between the two states is found to be very efficient in Ar and the Ga(4d) atoms show a coupled decay with

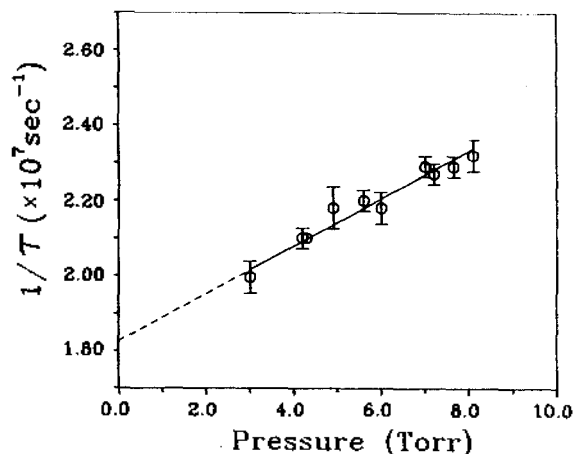
Table 1. Radiative lifetimes and quenching rate constants for the low-lying excited states of Ga in Ar and TMGa

States	Radiative lifetimes (ns)			Quenching rate constants (10^{-11} cm ³ molecule ⁻¹ s ⁻¹)	
	This work	Others	<Ref.>	This work	Others ^a
5s ² S _{1/2}	7.0 ± 0.2	9.9 ± 0.2	11	20 ± 3 (TMGa)	
		6.4 ± 2.4	12	1.6 ± 0.6 (Ar)	
		11.4 ± 1.7	13		<0.1 (H ₂)
		7.6 ± 0.4	14		38 ± 4 (CH ₄)
		6.8 ± 0.3	15		5 ± 1 (N ₂)
		6.9 ± 0.5	16		
		6.8 ± 0.5	17		
		6.8 ± 0.4	18		
		7.0 ± 0.4	19		
		7.0 ± 0.4	20		
	5.7 ± 0.6	21			
	7.1 ± 0.2	9b			
5p ² P _{1/2}	55 ± 2	55 ± 5	22	1.9 ± 0.2 (Ar)	
		50 ± 4	23		
		56 ± 4	24		
5p ² P _{3/2}	51.7 ± 0.9	24			
4d ² D _{3/2}	6.6 ± 2.4	12	3 ± 1 (Ar)		
	8.3 ± 0.3 ^b	13			
4d ² D _{5/2}	9.7 ± 1.4	13			
	7.7 ± 0.3	14			
	6.4 ± 0.5	16			
	6.9 ± 0.5	17			
	5.8 ± 0.6	18			
	7.4 ± 0.3	22			

^a Ref. 9b (Reported quenching rate constants for many polyatomic species). ^b Effective lifetime of the coupled states: The radiative lifetimes are 7.5 ± 0.2 ns for the ²D_{3/2} state and 9.0 ± 0.3 ns for the ²D_{5/2} state.

an effective radiative lifetime of 8.3 ± 0.3 ns above 3.0 Torr as shown in Figure 3(b). Since the purpose of this work is aimed at investigation of the collisional energy flow among the low-lying excited states of Ga atoms, the effective lifetime of the coupled state is shown in Table 1, which is used for the kinetic simulations for the Ga(4d) atoms.

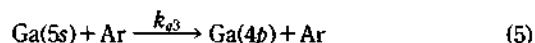
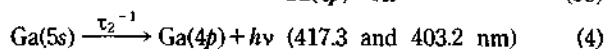
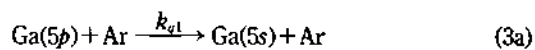
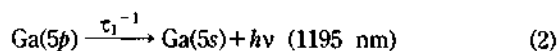
Kinetics of Ga(5p) atoms. The Ga(5p) atoms were prepared by two-photon excitation of the ground state Ga(4p) atoms and the fluorescence from the Ga(5s) state was monitored to investigate the radiative lifetimes as well as the quenching rate constants of the Ga(5p) states. Typical time profiles of the cascade fluorescence from the Ga(5s) atoms at different laser pulse energies at 605.3 nm are plotted in Figure 4, and the power dependence of the fluorescence intensities is shown in the insert. Since the strong fluorescence from Ga(5s) state was observed only at specific laser wavelengths (603.5, 605.3, 618.5 and 620.6 nm) corresponding to $2h\nu = \Delta E[\text{Ga}(5p) - \text{Ga}(4p)]$, and since the fluorescence intensities showed clearly second order for the laser power, the fluorescence from Ga(5s) state must be originated from the Ga(5p) atoms excited by two-photon absorption of the ground

**Figure 5.** The pressure dependence of the decay rates of the cascade fluorescence from Ga(5s) state following Ga(4p) excitation.

state Ga atoms.

Although we were not able to observe the direct emissions from the Ga(5p) levels, we attempted to extract kinetic informations on Ga(5p) levels by analyzing the pressure dependence of the cascade fluorescence time profiles from the Ga(5s) level following Ga(5p) excitation. The time profiles of the cascade fluorescence showed a single exponential decay and the pressure dependence of the decay constants is shown in Figure 5. The zero pressure intercept and the slope are $(1.82 \pm 0.07) \times 10^7$ s⁻¹ and $(1.9 \pm 0.2) \times 10^{-11}$ cm³molecule⁻¹s⁻¹, respectively. Although the magnitude of the slope is not much different from the quenching rate constant of the Ga(5s) state, the apparent radiative decay rate constant from the zero pressure intercept is much smaller than the radiative lifetime of the Ga(5s) state. Indeed, it is found that the zero pressure intercept and the slope in Figure 5 correspond to the radiative lifetime and quenching rate constant for the Ga(5p) state, respectively, based on the kinetic analysis discussed below.

The kinetic scheme for the two-photon excitation of Ga(5p) state can be written as followings.



The formation and decay of the excited states of Ga atoms can be expressed by the following coupled differential equations.

$$\frac{d[\text{Ga}(5p)]}{dt} = F(t) - \left\{ \frac{1}{\tau_1} + (k_{q1} + k_{q2})[\text{Ar}] \right\} [\text{Ga}(5p)] \quad (6)$$

$$\frac{d[\text{Ga}(5s)]}{dt} = \left\{ \frac{1}{\tau_1} + k_{q1}[\text{Ar}] \right\} [\text{Ga}(5p)]$$

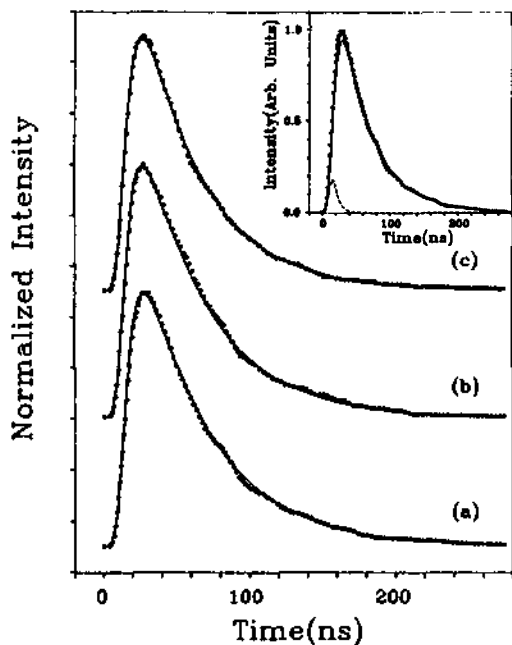


Figure 6. Comparison of the experimental (●—●) and simulated (—) time profiles from Ga(5s) state following two-photon excitation of Ga(5p) atoms including 4-5% of direct formation of Ga(5s) atoms at (a) 4.4 Torr, (b) 5.6 Torr, and (c) 8.1 Torr. The contribution of the directly formed Ga(5s) atoms to the time profile at 4.4 Torr (—) is shown in the insert.

$$-\left\{\frac{1}{\tau_2} + k_{q3}[\text{Ar}]\right\}[\text{Ga}(5s)] \quad (7)$$

where $F(t)$ denotes the formation rates for the laser excited state. If the deactivation rates for the Ga(5p) atoms were much slower than the formation rates, $F(t)$ could be assumed as a δ -function so that it could be dropped out in the rate equation. In that case, the concentrations of the Ga(5p) vs time can be expressed by Eq. (8).

$$[\text{Ga}(5p)](t) = [\text{Ga}(5p)]_0 \exp(-b_1 t) \quad (8)$$

where $b_1 = \tau_1^{-1} + (k_{q1} + k_{q2})[\text{Ar}]$. Substituting Eq. (8) into Eq. (7), and solving for the time dependence of the Ga(5s) concentrations, the following Eq. (9) is obtained.

$$[\text{Ga}(5s)](t) = \frac{b_2}{b_3 - b_1} [\text{Ga}(5p)]_0 \{ \exp(-b_1 t) - \exp(-b_3 t) \} \quad (9)$$

where $b_2 = \tau_1^{-1} + k_{q1}[\text{Ar}]$, and $b_3 = \tau_2^{-1} + k_{q3}[\text{Ar}]$. If $b_3 \gg b_1$, the second exponential term in Eq. (9) could be neglected, and the decay constant of the cascade fluorescence corresponds to b_1 . Thus, the radiative lifetime and the total quenching rate constant for the Ga(5p) states can be obtained from the pressure dependence of the decay constants of the cascade fluorescence. The radiative lifetimes and collisional deactivation rate constants for Ga(5p) states are also given in Table 1. The radiative lifetime of Ga(5p) state obtained from the Stern-Volmer plot in this work is in good agreement with that of Ga(5p $^2P_{1/2}$) state reported by Carlsson *et al.*²² and Buurman and Donszelmann.²⁴ Since the energy difference between the two spin-orbit states of Ga(5p) atoms is only 111 cm^{-1} and the pressure range employed in this

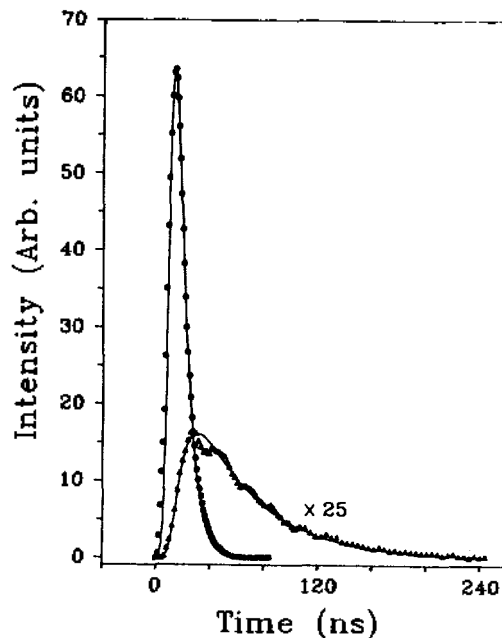


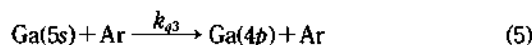
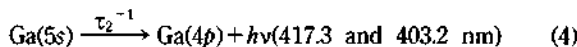
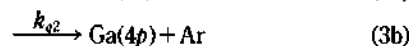
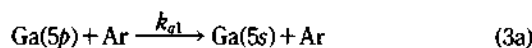
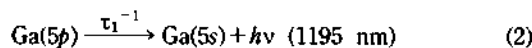
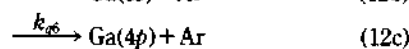
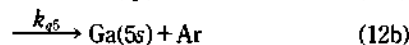
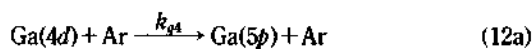
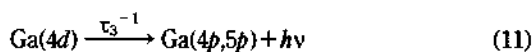
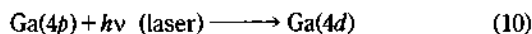
Figure 7. Comparison of experimental (●—●; ▲—▲) and calculated (solid line) time profiles from the laser excited state (●—●) and product state (▲—▲). The Ga(4d $^2D_{3/2}$) level was excited from the Ga(4p $^2P_{3/2}$) level, and emissions from Ga(4d $^2D_{3/2}$) \rightarrow Ga(4p $^2P_{1/2}$) and Ga(5s $^2S_{1/2}$) \rightarrow Ga(4p $^2P_{1/2}$) transitions are monitored. The gas mixture was 5.4 Torr of 2% TMGa in Ar.

work is high enough for the rapid collisional mixing of these states, it is difficult to measure the radiative lifetimes of the two spin-orbit states separately by analyzing the pressure dependence of the decay times of the cascade fluorescence.

We also attempted to assign the magnitude of k_{q1} and k_{q2} by kinetic simulation of the Ga(5s) emissions at several different pressures. For this purpose, Runge-Kutta numerical method was employed and a temporally Gaussian laser pulse shape with 8 ns FWHM was used to simulate the formation rate for the Ga(5p) atoms, *i.e.*, $F(t)$ term in Eq. (6). However, it was unsuccessful to assign definite rate constants for k_{q1} and k_{q2} . It was found that the relative magnitude of the k_{q1} and k_{q2} does not affect on the decay behavior of the cascade fluorescence due to the large radiative transition probabilities between Ga(5p) and Ga(5s) levels, and the later part of the decay curves could be fitted reasonably good using the measured radiative lifetimes and total quenching rate constants for the Ga(5s) and Ga(5p) states, even though the early part of the experimentally observed time profiles showed some discrepancy with the calculated ones as shown in the insert of Figure 6. Since the excitation laser wavelength is far from the observation wavelength, the discrepancy is not believed to be the laser scattered light. Decay curves collected by installing cutoff filters in front of the entrance slit of the monochromator also showed the same magnitude of discrepancy in the early part. Thus, the observed decay curves are emissions from Ga(5s) atoms without doubt and the discrepancy in the early part of the decay curves are attributed to the contributions of the directly formed Ga(5s) atoms by multiphoton dissociation of discharge products of TMGa, most likely GaCH₃^{*}, by the excitation laser beam. When we

included the direct formation of small amounts of Ga(5s) atoms (4-5%) by the excitation laser beam, we were able to fit the whole decay curves at different pressures as plotted in Figure 6.

Kinetics of Ga(4d) atoms. When the Ga(4d) state was excited, weak emissions from the Ga(5s) state was observed at relatively high pressures. Typical time profiles from the Ga(4d) and the Ga(5s) emissions following the Ga(4d) excitation are shown in Figure 7. The emissions from the Ga(5s) atoms are delayed and the magnitude of the Ga(5s) emissions is about 5% of that of the laser excited state. Even though the relative magnitudes of k_{q1} and k_{q2} could not be determined from the kinetic simulations of the Ga(5s) emissions following Ga(5p) excitation, we attempted to assign the magnitude of the state-to-state rate constants among the low-lying excited states of Ga based on the kinetic simulations to fit the shapes and intensities of the Ga(4d) as well as the Ga(5s) emissions following Ga(4d) excitation. Maintaining the same notations used in the decay kinetics for the Ga(5p) excitation except for the formation step, the kinetic scheme for the Ga(4d) excitation can be written as followings.



Although the Ga(5p) atoms can be formed by the radiative and collisional processes from the Ga(4d) atoms, the contributions from the radiative process could be negligible considering the short radiative lifetimes of the Ga(4d) atoms and relatively small 'Einstein A' coefficients for Ga(4d)-Ga(5p) transitions (see Discussion) compared to those for the Ga(4d)-Ga(4p). Thus, neglecting the radiative process for the formation of the Ga(5p) atoms, the differential rate eqs. for the Ga(4d) excitation can be written as followings.

$$\frac{d[\text{Ga}(4d)]}{dt} = F(t) - \left\{ \frac{1}{\tau_3} + (k_{q4} + k_{q5} + k_{q6})[\text{Ar}] \right\} [\text{Ga}(4d)] \quad (13)$$

$$\begin{aligned} \frac{d[\text{Ga}(5p)]}{dt} &= k_{q4}[\text{Ar}][\text{Ga}(4d)] \\ &\quad - \left\{ \frac{1}{\tau_1} + (k_{q1} + k_{q2})[\text{Ar}] \right\} [\text{Ga}(5p)] \end{aligned} \quad (14)$$

$$\begin{aligned} \frac{d[\text{Ga}(5s)]}{dt} &= \left\{ \frac{1}{\tau_1} + k_{q1}[\text{Ar}] \right\} [\text{Ga}(5p)] + k_{q5}[\text{Ar}][\text{Ga}(4d)] \\ &\quad - \left\{ \frac{1}{\tau_2} + k_{q3}[\text{Ar}] \right\} [\text{Ga}(5s)] \end{aligned} \quad (15)$$

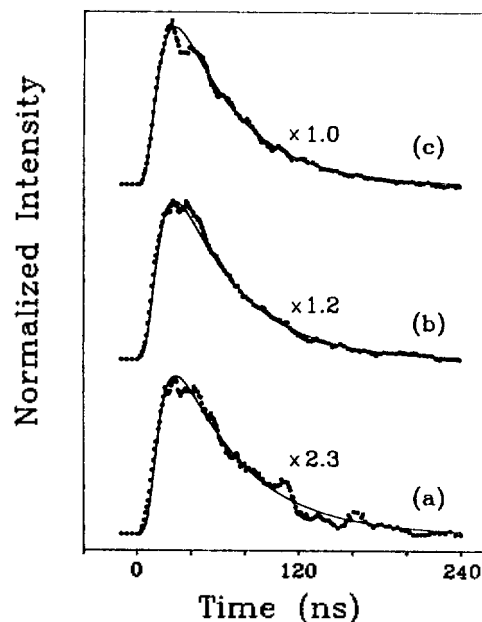


Figure 8. Comparison of experimental (●-●) and calculated (—) time profiles from Ga(5s) state following Ga(4d) excitation at (a) 3.0 Torr, (b) 4.5 Torr and (c) 5.4 Torr.

The concentrations of these low-lying excited states vs time are calculated by the Runge-Kutta numerical method incorporating with a Gaussian laser pulse (8 ns FWHM) for the $F(t)$. Since the emissions from the Ga(5s) state were weak and observed at relatively high pressures, we used the coupled radiative lifetime, 8.3 ns, for the radiative lifetime of the Ga(4d) state to simulate the time profiles. To fit the time profiles from the laser excited state as well as the product state simultaneously at different pressures, it was found that about $57 \pm 5\%$ and 10% of the total quenching rate constant had to be assigned for the Ga(4d)→Ga(5p) and Ga(4d)→Ga(5s) transitions, respectively, and about $33 \pm 5\%$ of the total quenching rate constant was assigned for the Ga(4d)→Ga(4p) transition. The lower limits of Ga(4d)→Ga(5p) rate constant as well as the higher limits of Ga(4d)→Ga(4p) rate constant correspond to the 100% collisional branching for Ga(5p)→Ga(5s), and the higher limits of Ga(4d)→Ga(5p) together with the lower limits of Ga(4d)→Ga(4p) correspond to no collisional transfer between Ga(5p) and Ga(5s) levels. Since the Ga(5p) levels locate about 0.20 eV below the Ga(4d) levels, and since the magnitude of the collisional rate constant for Ga(4d)→Ga(4p) is found to be $(1.0 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, it is assumed that the quenching rate constant for Ga(5p)→Ga(4p) transition could be similar magnitude. Thus, we assigned about 50% of the total quenching rate constant for Ga(5p) level to Ga(5p)→Ga(4p) and remainder to Ga(5p)→Ga(5s) transition. The calculated and experimental time profiles from the Ga(4d) and Ga(5s) states following the Ga(4d) excitation are compared in Figure 8 and the product formation rate constants are also given in Table 2. Since the Ga(4d) atoms are formed by single photon process which occurs at much weaker laser intensities, multiphoton process cannot contribute to the formation of Ga(5s) state.

Table 2. Product formation rate constants and branching fractions in Ar

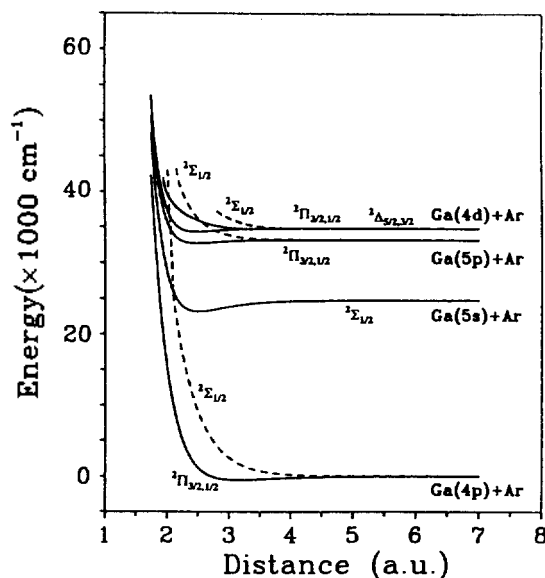
Laser excited state	τ (ns)	process	k_{ij} (10^{-11} cm ³ molecule ⁻¹ s ⁻¹)	Γ (k_{ij}/k_0)
Ga(4d)	8.3	4d→5p	1.7 ± 0.15	0.57 ± 0.05
		4d→5s	0.3 ± 0.02	0.10 ± 0.01
		4d→4p	1.0 ± 0.15	0.33 ± 0.05
Ga(5p)	56	5p→5s	1.0 ± 1.0	0.50 ± 0.50
		5p→4p	1.0 ± 1.0	0.50 ± 0.50

Discussion

The quenching rate constants for Ga(5s), Ga(5p) and Ga(4d) atoms by Ar are not large. The collisional cross sections ($\sigma = k_{ij}/\langle v \rangle$) calculated at 300 K for Ga(5s), Ga(5p) and Ga(4d) atoms correspond to 3.2 ± 1.2 , 4.0 ± 0.4 and 6.0 ± 2.0 Å², respectively. Nevertheless, they are much larger than those for low-lying excited states of alkali, alkaline earth and Group 12 metals, which is smaller than 0.1 Å² for most cases.²⁶ The relatively small but much larger quenching rate constants for these low-lying excited states of Ga in comparison with alkali metals by Ar could be explained qualitatively in terms of the shapes of the interaction potentials.

Recently, Stanggassinger *et al.*²⁷ reported spectroscopic results for Ga-rare gas van der Waals molecules and discussed about the shapes of the interaction potentials of Ga(4p)-Ar and Ga(5s)-Ar pairs. They have shown that the binding energy of the $B^2\Sigma_{1/2}$ state arising from Ga(5s)-Ar pair is 0.056 eV (455 cm⁻¹). The binding energies of those from Ga(5p)-Ar as well as Ga(4d)-Ar pairs are not expected to be large, either. Based on the work of Stanggassinger *et al.*²⁷, schematic potential energy curves of Ga-Ar pairs are drawn in Figure 9. The Ga(5p)-Ar potentials are drawn by assuming that they might have similar shapes with the Ga(4p)-Ar potentials, and those of Ga(4d)-Ar pair are just a sketch because reliable ab initio potentials for these states are not available yet. Although the potentials for Ga(5p)-Ar and Ga(4d)-Ar pairs in Figure 9 are merely sketches, they are helpful to explain the substantial fluorescence quenching of the low-lying excited states of Ga atoms by Ar observed in this work. As shown in Figure 9, the strongly repulsive $A^2\Sigma_{1/2}$ potential arising from Ga(4p)-Ar pair crosses those potentials from the low-lying excited states of Ga-Ar pairs at short internuclear distances, and may provide better exit channel for the Ga(5s) and Ga(5p) atoms colliding with Ar. On the other hand, such a potential is absent for the alkali metal-rare gas system, where the fluorescence quenching of the low-lying excited states is not observed.²⁸ Thus, the fluorescence quenching for the low-lying excited states of Ga atoms observed in this work could be ascribed to those curve crossing shown in Figure 9. Since the energy difference between the Ga(4d) and Ga(5p) atoms is 0.20 eV, about two times larger quenching rate constant for Ga(4d) atoms could be due to the another strongly repulsive potential arising from Ga(5p)-Ar pair which crosses the Ga(4d)-Ar potential at longer distance than that from Ga(4p)-Ar.

The assignment of the collisional branching fractions for Ga(4d) atoms is based on the neglect of the radiative

**Figure 9.** Schematic potential energy curves of Ga-Ar system drawn by extrapolating the repulsive walls appeared in ref. 27.

decay from Ga(4d) to Ga(5p) level which is allowed by the selection rule. The relationship among the oscillator strength, Einstein A coefficient and the fluorescence wavelength is given by Eq. (16).²⁹

$$A_{ij} = \frac{f_{ij} g_i}{1.51 g_j (\lambda_{ij})^2} \quad (16)$$

where A_{ij} is the Einstein A coefficient between i and j levels, f_{ij} represents oscillator strength, g_i and g_j are degeneracy, and λ_{ij} is the transition wavelength in centimeters. Using Eq. (16), the ratio of A_{4d5p} and A_{4d4p} is given by Eq. (17).

$$\frac{A_{4d5p}}{A_{4d4p}} = \frac{g_{5p} f_{4d5p} (\lambda_{4d4p})^2}{g_{4p} f_{4d4p} (\lambda_{4d5p})^2} \quad (17)$$

Using the theoretical oscillator strengths ($f_{4d4p} = 0.309$, $f_{4d5p} = 0.246$) reported by Carlsson and coworkers²² and the wavelengths corresponding to the energy separations, A_{4d5p} is estimated to be 2.2×10^5 s⁻¹ based on the measured radiative lifetime of Ga(4d) atoms. This is an order of magnitude smaller than the collisional deexcitation rates of Ga(4d) atoms at high pressures and neglect of the radiative process in the kinetic simulations could be justified.

Conclusion

We have investigated the collisional energy transfer rate constants among the low-lying excited states of Ga atoms in Ar at room temperature. The pulsed discharge of a mixture of an organometallic compound with a rare gas turned out to be an appropriate method to generate high concentrations of metal atoms in the gas phase and enabled us to investigate kinetics of the excited states of metal atoms at low temperature. Even though the overall magnitude of the quenching rate constants of the low-lying excited states of Ga atoms are not large in Ar, they are much larger than those of excited states of alkali metals investigated at high temperatures. The large difference in the quenching rate constants

nts for the low-lying excited state of Ga atoms and alkali metals are ascribed to the strongly repulsive potential arising from the ground state electron configuration.

Acknowledgement. This work is financially supported in part by Korean Science and Engineering Foundation through the Center for Molecular Science at KAIST and in part by RIST through basic science program.

References

1. Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33.
2. Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *Chem. Phys.* **1979**, *44*, 415.
3. Gerrity, D. P.; Rothberg, L. J.; Vaida, V. *Chem. Phys. Lett.* **1980**, *74*, 1.
4. Engelking, P. C. *Chem. Phys. Lett.* **1980**, *74*, 207.
5. (a) Leutwyler, S.; Even, U.; Jortner, J. *Chem. Phys. Lett.* **1980**, *74*, 11; (b) *J. Phys. Chem.* **1981**, *85*, 3026.
6. Gedanken, A.; Robin, M. B.; Kuebler, N. A. *J. Phys. Chem.* **1982**, *86*, 4096.
7. (a) Mitchell, S. A.; Hackett, P. A. *J. Chem. Phys.* **1983**, *79*, 4815; (b) *Chem. Phys. Lett.* **1984**, *107*, 508.
8. Mitchell, S. A.; Hackett, P. A.; Rayner, D. M.; Humphries, M. R. *J. Chem. Phys.* **1985**, *83*, 5028.
9. (a) Mitchell, S. A.; Hackett, P. A. *J. Phys. Chem.* **1985**, *89*, 1509; (b) Mitchell, S. A.; Hackett, P. A.; Rayner, D. M.; Flood, M. *J. Chem. Phys.* **1987**, *86*, 6852.
10. (a) Baughcum, S. L.; Oldenberg, R. C.; Winn, K. R.; Hof, D. E. *SPIE* **1985**, *50*, 314; (b) Baughcum, S. L.; Oldenberg, R. C. *SPIE* **1986**, *669*, 90.
11. Demtröder, W. Z. *Physik* **1962**, *166*, 42.
12. Penkin, N. P.; Shabanoba, L. N. *Opt. Spectrosc. (U. S. S. R.)* **1965**, *18*, 504.
13. Lawrence, G. M.; Link, J. K.; King, R. B. *Astrophys. J.* **1965**, *141*, 293.
14. Cunningham, P. T.; Link, J. K. *J. Opt. Soc. Amer.* **1967**, *57*, 1000.
15. Norton, M.; Gallagher, A. *Phys. Rev. A* **1971**, *3*, 915.
16. Andersen, T.; Sorensen, G. *Phys. Rev. A* **1972**, *5*, 2447.
17. Erdevdi, N. M.; Shimon, L. L. *Opt. Spectrosc. (U. S. S. R.)* **1976**, *41*, 640.
18. Gough, W.; Griffiths, S. B. *J. Phys. B* **1977**, *10*, 817.
19. Havey, M. D.; Balling, L. C.; Wright, J. J. *J. Opt. Soc. Amer.* **1977**, *67*, 491.
20. Reader, J.; Corliss, C. H.; Wiese, W. L.; Martin, G. A. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U. S.)* **1980**, *68*.
21. Lindgard, A.; Mannervik, S.; Jelenkovic, B.; Veje, E. Z. *Phys. A* **1981**, *301*, 1.
22. Carlsson, J.; Lundberg, H.; Peng, W. X.; Persson, A.; Wahlstrom, C. G.; Brage, T.; Fisher, C. F. *Z. Phys. D* **1986**, *3*, 345.
23. Buurman, E. P.; Donszelmann, A.; Hansen, J. E.; Snoek, C. *Astron. Astrophys.* **1986**, *164*, 224.
24. Buurman, E. P.; Donszelmann, A. *Astron. Astrophys.* **1990**, *227*, 289.
25. Lee, K.; Goo, J. S.; Ku, J. K. *Chem. Phys. Lett.*, **1993**, *216*, 483.
26. Breckenridge, W. H.; Umemoto, H. *Adv. Chem. Phys.* **1982**, *50*, 325.
27. Stangassinger, A.; Scheuchenflug, J.; Prinz, T.; Bondybey, V. E. *Chem. Phys. Lett.* **1993**, *209*, 372.
28. Edward, M. G. *J. Phys. B (Atom. Molec. Phys.)*, **1969**, *2*, 719.
29. Steinfeld, J. I. *Molecules and Radiation*; MIT Press: Cambridge, U. S. A., 1985; p 29.

Diaminoplatinum(II) Complexes of Glutamic Acid: Obvious Chelating Isomerization

Young-A Lee, Jongki Hong[†], Ok-Sang Jung*, and Youn Soo Sohn*

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

[†]*Molecular Structure Laboratory, Korea Basic Science Center, Taejon 305-600, Korea*

Received April 25, 1994

Coordination isomers of *cis*-(N-N)Pt(Glu) prepared by reaction of *cis*-(N-N)Pt(SO₄) (N-N=2NH₃, ethylenediamine(en), (R,R)-1,2-diaminocyclohexane (DACH), N,N,N',N'-tetramethylethylenediamine (TMEDA)) with barium glutamate in water have been monitored and characterized by ¹H-NMR, ¹³C-NMR, IR, and mass spectra. The reaction at room temperature affords the mixture of O,O'- and N,αO-chelated platinum(II) complexes. The O,O'-chelate initially formed isomerized to N,αO-chelate on standing for a long time or increasing temperature. The ratio of the two isomers at room temperature depends on the nature of the nitrogen donor coligand (N-N).

Introduction

In order to overcome the drawbacks of *cis*-platin such as

nephrotoxicity, nausea/vomiting, and myelosuppression along with development of resistance in the tumor cell,¹⁻⁵ new type of platinum complexes have been synthesized and