

Two-Photon Excitation and Fluorescence Lifetimes of Silver Atoms in Rare Gas Matrices

A. Mehreteab,[†] J. R. Andrews,[‡] A. B. Smith, III,^{*§} and R. M. Hochstrasser*

Department of Chemistry and Laboratory for Research on the Structure of Matter, The University of Pennsylvania, Philadelphia, Pennsylvania 19104 (Received: October 5, 1981)

Two-photon excitation spectra of silver in neon, argon, krypton, and xenon was accomplished by means of a tunable dye laser. The excitation spectra expose bands distinctly different from the one-photon absorption spectra, and these are interpreted as $^2S \rightarrow ^2D$ transitions occurring through two-photon absorption. This interpretation is supported for silver in argon by the long (1.8 μ s) lifetime of the fluorescence emission from the lowest band observed in absorption. The role of these states in the dynamical steps that follow light absorption and end with the well-known broad Stokes-shifted fluorescence of the Ag:Ar system is discussed in relation to these results and new lifetime measurements following selective excitation.

Introduction

There were many previous UV absorption studies of silver-rare gas matrices, making the assignment of the $^2S_{1/2} \rightarrow ^2P$ transitions in the 300-nm region rather complete.¹⁻⁵ Matrix isolated silver atoms show at least three bands (four and five in Xe and Ne matrices, respectively) instead of the two lines, $^2P_{3/2} \leftarrow ^2S_{1/2}$ and $^2P_{1/2} \leftarrow ^2S_{1/2}$, observed in the gas phase. The splitting into more than two transitions is expected from the nonspherical symmetry of the rare gas-silver potential, and the first-order spin orbit coupling. The bands of Ag in a matrix show matrix shifts to higher energy with respect to the $^2P \leftarrow ^2S$ gas-phase transitions.

On the other hand, the relaxation process of excited Ag in matrices were not yet fully understood. Fluorescence studies showed that the emission spectra of Ag in the different rare gas matrices were completely different from each other with respect to the magnitude of the Stokes shift, the spectral width, and the number of observed emission bands. It was suggested that the emission spectra arise from exciplexes formed between excited silver atoms with the nearby rare gas atoms.^{6,7} Recently, Mitchell et al.⁸ have proposed that the excited-state surfaces determining the motion of silver and rare gas atoms and hence the relaxation dynamics could be modeled using Jahn-Teller effect arguments. In addition to the 2P excited states, there also exist 2D states of Ag in the same spectral region.⁹ Lines seen in the fluorescence excitation spectra of Ag in krypton and xenon⁸ were proposed to be $^2D \rightarrow ^2S$ consistent with previous suggestions regarding the presence of D states.⁶ Obviously, such transitions must be considered in the relaxation pathways leading to the broad emission bands.

There is clearly need for further spectroscopic and dynamical studies on these systems, in particular to assign the states involved by more direct methods. As to dynamics, there was until very recently⁸ no information on the decay and buildup times of the various emissions. In this note we present new spectroscopic information by means of two-photon induced fluorescence spectroscopy¹⁰ of silver in Ne, Ar, Kr, and Xe, and direct measurements of the lifetimes of various states considered as crucial in

the ensuing dynamical events.

Experimental Section and Results

A beam of atomic silver (99.999% purity) from Alfa division of Ventron Corp. and rare gas from Airco, Welders Supply Inc. were codeposited onto a cryosurface. The cryostat used was a Heli-Tran Model LT-3-110 from Air Products and Chemical Inc. The beam of atomic silver was generated from a Knudsen cell made of Al_2O_3 surrounded by electrically heated tungsten wire connected to water-cooled copper electrodes. The oven, which was designed and constructed by us, is shown in Figure 1. From the oven temperature, Knudsen cell orifice, and amount of rare-gas used during deposition, the rare gas to silver ratio was estimated to be at least 500. UV absorption measurements of silver deposited under such conditions showed only bands of monomeric silver.

Single-photon excitation and emission fluorescence spectra of Ag in argon matrix were taken with a Perkin-Elmer MPF4 spectrofluorometer. Figures 2 and 3 show the resulting emission and excitation spectra, respectively.

Lifetime and two-photon excitation experiments were done with an N_2 laser pumped dye laser as a source of excitation. The two-photon excitation spectrum from 560 to 670 nm (rhodamines 6G, B, and 640) with emission monitored at 331 nm was recorded for the Ag/Ne matrix. Two excitation bands were observed at 575 and 628 nm (Figure 4). Excitation spectra from 625 to 670 nm (rhodamine 640) were recorded for the other silver rare gas matrices. Emission wavelengths monitored were 326, 521, and 557 nm for the Ar, Kr, and Xe matrices, respectively. Figure 5 shows absorption spectra and smoothed two-photon excitation spectra for the different Ag-rare gas matrices.

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[†] Colgate-Palmolive Research and Development Center, 909 River Rd., Piscataway, NJ 08854.

[‡] National Eye Institute Post Doctoral Fellow; Webster Research Center, Xerox Corporation, Webster, NY 14580.

[§] Camille and Henry Dreyfus Teacher-Scholar, 1978-1983; National Institutes of Health (National Cancer Institute) Career Development Awardee, 1980-1985.

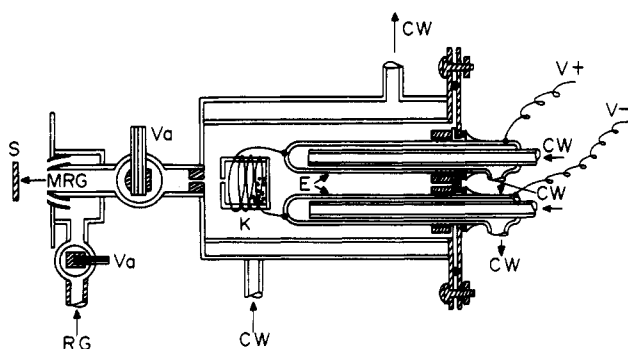


Figure 1. Oven used to evaporate metal: CW, cooling water; E, water cooled electrodes; K, Knudsen cell; MRC, metal-rare gas mixture; S, cold finger inside helitran where sample is deposited; RG, rare gas; Va, valve.

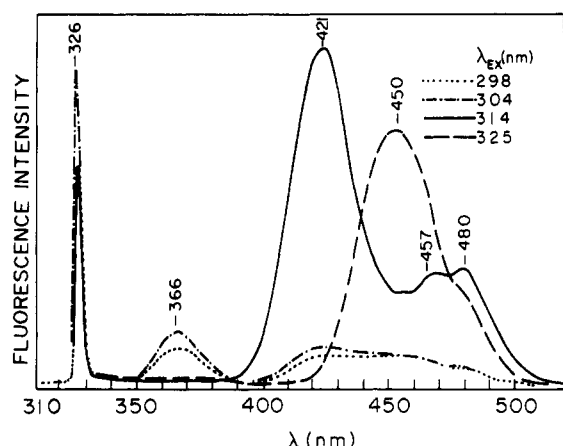


Figure 2. Emission spectra with excitation wavelengths at 298 nm (·····); 304 nm (·-·-·-·); 314 nm (X3) (—); 325 nm (X5) (---).

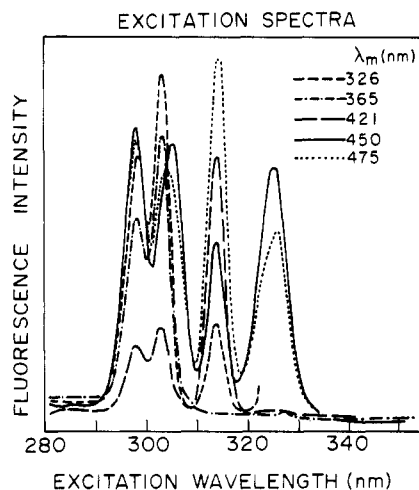


Figure 3. Excitation spectra of Ag in Ar matrix with emission wavelength monitored at 326.2 nm (---); 365 nm (·-·-·-·); 421 nm (---); 450 nm (—); 475 nm (·····).

The fluorescence of the silver/argon matrix at 326 nm generated by the laser at 649 nm was recorded for various laser powers. It was found that the signal intensity was proportional to the laser intensity *squared* in the intensity regime used for the reported experiments (slightly more than one decade range of laser intensities were studied). We can be confident then that the observed signals represent two-photon induced fluorescence, and that the intensities of the excitation spectra are dependent on the product of the two-photon absorption coefficient and the fluorescence yield corresponding to the particular choice of excitation and detection wavelengths. We believe that

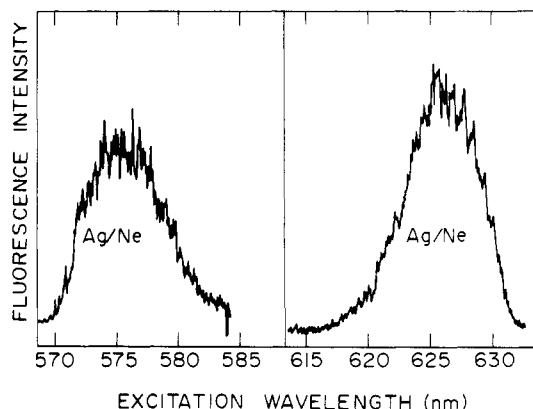


Figure 4. Two-photon excitation spectra of silver in neon matrix.

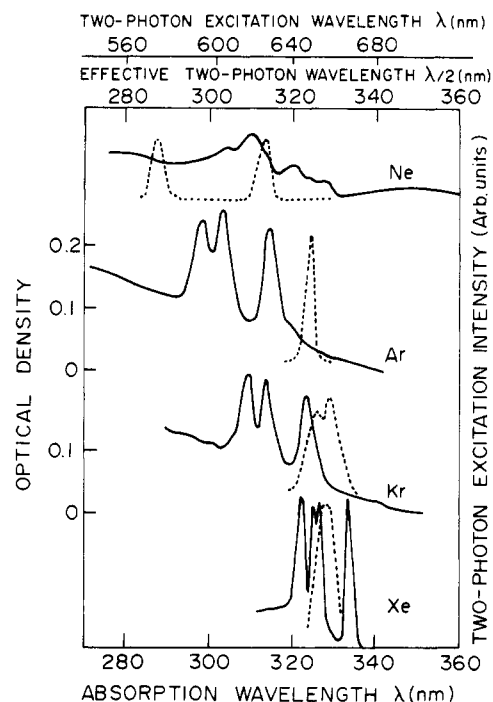


Figure 5. Two-photon excitation spectra (---) and absorption spectra (—) of silver in the different rare gas matrices. The excitation bands have been smoothed and scaled down from the original spectra such as in Figure 4.

TABLE I: Fluorescence Decay Times (ns) for Silver Atoms in Argon

λ_E , nm	λ_M , nm				
	326	366	420	450	475
298	1800 ± 300	5			
304	1800	~5	15		
315	1800		15	15	15
325				15	

these might be the first two-photon spectra obtained from matrix-isolated systems.

Lifetime measurements were carried out only for the Ag/Ar system. Decay curves of single shots were taken from a storage oscilloscope. All emission signal rise times were pulsed limited, that is <2 ns. Exponential decay times are reported in Table I (λ_E is the excitation wavelength, nm; λ_M the monitoring wavelength, nm).

Discussion

Spectroscopy of Ag in a Rare Gas Matrix. The strongest two-photon excitation band of Ag in Ar occurs

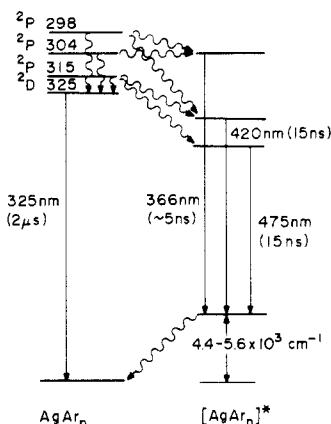


Figure 6. Schematic diagram of the energy levels and vertical transitions of silver in argon matrix.

at 324.5 nm. This is very close to and significantly overlaps the emission band at 326.2 nm. (The discussion will be more readily followed with reference to Figure 6.) The two-photon peak is within a few angstroms of a peak in the one-photon excitation spectrum. This peak is not apparent in the absorption spectrum. These results all point to there being a weakly dipole-allowed but strongly two-photon-allowed transition in this region. The most obvious interpretation is that these experiments locate either the $^2D_{3/2}$ or $^2D_{5/2}$ state of Ag. For gaseous Ag atoms the $^2D_{3/2} \leftarrow ^2S_{1/2}$ transition is found around 288 nm,⁹ at higher energy than $^2D_{5/2} \leftarrow ^2S$. We therefore assign the transitions near 325 nm to $^2D_{5/2} \leftarrow ^2S$. The reason for this choice is our experimental observation that rapid relaxation occurs between all the optically accessible levels, so that it is unlikely that there are any atomic-like transitions at lower energy than 325 nm. We then assume that the matrix shift does not cause a change in the ordering of the atomic D states. These experiments confirm the suggestion⁶ that the 326-nm emission line occurs after an inner atomic relaxation from the P to D states.

Ag in Ne, Kr, and Xe Matrices. Single-photon excitations of silver in Kr and Xe show broad emission bands at 521 and 545 nm, respectively. These bands have been previously explained to be due to the silver 2P states forming exciplexes with the rare gas atoms.^{6,7} Since there were no emission bands that were attributed to the 2D states of silver in these matrices, the above wavelengths were used to monitor the emission in obtaining the two-photon excitation spectra of the Kr- and Xe-silver matrices (Figure 5). The observed Ag/Kr two-photon excitation bands at 651 and 657 nm corresponding to 325.5- (i.e., 651/2) and 328.5-nm (i.e., 657/2) one-photon transitions, respectively, do not match any of the 2P transition which are at 309, 313, and 322 nm as observed in the absorption spectrum. Likewise, the two-photon excitation band in Ag/Xe at 658 nm which would correspond to a one-photon transition at 329 nm does not match any of the transitions of silver involving 2P in this matrix which are at 323, 326, 327, and 334 nm. The spectral location of the $^2S \rightarrow ^2D_{5/2}$ transition of Ag/Xe is therefore suggested to be at 329 nm, and for Ag/Kr it may be at either 325.5 or 328.5 nm.

The excitation spectrum of the Ag/Ne matrix was different in that the two-photon excitation band was observed at ~629 nm which is at a much higher energy than the two-photon transitions of the other silver-rare gas matrices. This would correspond to a one-photon transition at 315 nm (630/2). Two photon excitation of the Ag/Ne matrix at still higher energy showed another band at 575 nm (one-photon transition at around 287.5 nm). This

might be the $^2S_{1/2} \rightarrow ^2D_{3/2}$ transition which in gaseous silver is located at 288 nm.⁹ The band at 315 nm is then the transition to the $^2D_{5/2}$ state.

The lifetime measurements relating to the emission in Ag/Ar at 326 nm clearly indicate that the transition involved is moderately forbidden. The $^5P_{3/2}$ state of silver atoms has a lifetime of 7.3 ± 0.4 ns¹¹ so that the observed 1.8- μ s lifetime could not reasonably correspond to a $^2P \rightarrow ^2S$ transition. The microsecond lifetime is nevertheless confirmatory of the involvement of a 2D state in the transition. The symmetry of the atomic states is expected to be lowered by matrix interactions leading to a mixing of P and D states. Such mixing will cause $^2D \leftarrow ^2S$ transitions to occur weakly in one-photon absorption (or excitation), and serve to shorten their lifetimes in relation to the atomic values.

Relaxation Pathways in Ag/Rare Gas Matrices. Figure 6 shows the relative energies of the states of atomic Ag and those for vertical transitions of Ag in argon. On the extreme right of the figure are shown a proposed disposition of equilibrated states into which the system relaxes after light absorption. This part of the figure is schematic in as much as we have assumed that all the relaxed excited forms correspond to the same ground-state energy. More likely each excited distorted region will correspond to a different equilibrium structure.

The fluorescence risetimes were, in every case, too short to measure with our equipment. This result indicates that all the interstate relaxation times involved are less than ca. 1 ns. Excitation at 298 nm yielded emission at 366 nm having a lifetime of ~5 ns, but emission at 325 nm ($\tau = 1.8$ μ s) also results from this excitation. These results, together with the risetimes, show that a 2P state (298 nm) relaxes by two independent paths: one to states giving Stokes shifted diffuse emission, the other to atomic-like D states. The latter path is most likely a "conventional" relaxation occurring with little or no change in the equilibrium structure of the system. The D-state emission also arises when the system is pumped at 304, 315, or 325 nm. On the other hand, a small amount of short-lived emission at 450 nm was observed for 325-nm excitation.

In Figure 6 those relaxation processes that are known to occur are indicated as solid wavy lines. These processes all occur on the subnanosecond timescale. The radiative processes are shown as solid lines. The 2D state giving rise to the 325-nm emission (1.8 μ s) clearly does not undergo the same dynamic interactions with argon as the 2P states. The $^2D_{5/2} \rightarrow ^2S$ emission overlaps the absorption significantly so that the emitting and absorbing states must both be essentially atomic silver states modified by the crystal field. The weak binding of Ag ($^2D_{5/2}$) with Ar (1S) is presumably the result of the inner-shell nature of the $4d^9 5s^2$ configuration that composes the 2D states; the $4d^{10} 5p$ configuration of the P states is apparently much more effective in bonding to the surrounding argon atoms.

The energy separations between the 1P states are in the range from 600–1100 cm^{-1} . These gaps are an order of magnitude larger than the Debye cutoff frequency of argon (65 cm^{-1}) so that a direct coupling of an essentially atomic electron and lattice vibrations of the medium requires the involvement of many (ca. 10) phonons. Since such a process would seem unlikely to occur on the picosecond timescale for a purely substitutional Ag atom, we suggest that the Ag ($5P$) atoms must significantly distort the surrounding lattice even along coordinates that do not correspond to exciplex formation. The relaxation between the atomic-like states is then envisaged as first involving

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these higher frequency local Ag-Ar modes. The dissipation of this localized lattice excitation into delocalized lattice modes is considered as a second step in the overall process. The distortion leading to the formation of the Stokes-shifted luminescent states provides the other pathway for decay of the photoexcited atomic state. The results indicate that both channels for decay of the atomic states occur with rates much faster than the nanosecond radiative decay. Our results do not provide any sharp information on the specific excited-state forces involved in the gener-

ation of the distorted states. Nevertheless the concepts of exciplex^{6,7} and Jahn-Teller effect⁸ are not mutually exclusive in our view, and the actual surfaces determining the motion of the atoms are likely to be dependent on more than one excited state of silver and argon.

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Gas-Phase Two-Photon Spectroscopy of Polyazines. Pyrimidine

I. Knoth, H. J. Neusser, and E. W. Schlag*

Institut für Physikalische Chemie der Technischen Universität München, 8046 Garching, West Germany (Received: August 12, 1981)

The two-photon excitation spectrum of gas-phase pyrimidine in the region of the $S_1 \leftarrow S_0$ transition is presented. Two vibrational frequencies in the 1B_1 electronic state, not obtainable from one-photon spectra, have been obtained. This is possible although symmetry selection rules are similar to those in one-photon absorption.

Introduction

For molecules of high symmetry (e.g., benzene,¹ D_{6h} , or naphthalene,² D_{2h}) two-photon spectroscopy is now known to be an important method for excitation of hitherto unobservable states. Recently, this has been shown also for pyrazine (D_{2h}).^{3,4} If the molecule contains a center of symmetry, the tensor character of the two-photon transition reverses the one-photon selection rule $g \leftrightarrow u$ into a $u \leftrightarrow u$ and $g \leftrightarrow g$ selection rule. For molecules, however, belonging to the low symmetry point group C_{2v} , the transition symmetries of one- and two-photon excitation are identical (except for an additional in two-photon excitation). Therefore, at first glance one would expect that the spectrum obtained by two-photon excitation should resemble the one-photon spectrum. In this work we would like to demonstrate for pyrimidine which is a molecule of C_{2v} symmetry that, even though selection rules are nearly identical, a two-photon spectrum yields new spectroscopic information.

Pyrimidine, one of the three isomeric diazines, was the subject to extensive absorption and emission spectroscopic studies in the past decades.^{5,6} Uber⁷ was the first to study the pyrimidine absorption in the vapor phase. He found a sharp absorption system near 3200 Å, while a diffuse one was seen near 2400 Å.⁷ As in pyrazine the sharp system belongs to a $n\pi^*$ transition.⁸ A detailed analysis of the 3200-Å vapor-phase ($n\pi^*$) absorption of pyrimidine is given by Innes et al.⁹ A rotational analysis of the 0-0 band shows that this band is of type C. Thus, the electronic transition moment is parallel to the top axis (*c* axis) of the

molecule. The authors found gross irregularities in the vibrational differences in the upper state and proposed that these irregularities are the result of Fermi resonances between $6a_1'$ and $16b_2'$. Surprisingly, in contrast to pyrazine, there is no spectral activity in transitions induced by modes of symmetry b_1 or a_2 which are also allowed in symmetry C_{2v} . Only transitions which belong to the same symmetry as the 0-0 transition (1B_1 , axis convention from ref 10) are seen in the spectrum. These are progressions in a_1 modes or two-quanta excitation of other vibrations with a large Franck-Condon factor.⁹ On the other hand, the corresponding $n\pi^*$ state in pyrazine shows other bands than of type C.¹¹ Thus, the excited-state frequency of ν_{16b} in pyrimidine, a b_1 mode,¹⁰ is not known from a single-quantum excitation.

Recent single-vibronic level fluorescence measurements of Knight et al.¹² give some reassignments of the excited-state vibrational frequencies. The fluorescence spectra generated by pumping each of the bands of the Fermi resonance $6a_1'/16b_2'$ ⁹ show that one component is indeed $6a_1'$ while the other corresponds to a vibration whose ground-state frequency is 621 cm^{-1} . Sbrana et al.¹³ assigned this frequency in their IR data to the vibration ν_{6b} of symmetry b_2 .¹⁰ As in the case of ν_{16b} the frequency of ν_{6b} is not known in the excited state, but the (unperturbed) frequency should be $\sim 320 \text{ cm}^{-1}$ in the excited state.¹² So the mode excited by two quanta, which are in Fermi resonance with $6a_1'$, is reassigned by the authors¹² to ν_{6b} , while the original assignment of a sequence band at $+22 \text{ cm}^{-1}$ is changed from $6b_1'$ to $16b_1'$. Two-photon spectroscopy provides a good tool to test these assignments.

Pyrimidine belongs to the symmetry group C_{2v} . In conventional UV spectroscopy transition symmetries of A_1 , B_1 , and B_2 are allowed which in principal could lead to inducing vibrations of b_1 , a_1 , and a_2 symmetry. In two-photon spectroscopy together with transitions of A_1 , B_1 , and B_2 symmetry additional transitions of A_2 symmetry

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