

Formation of AgHe₂ Exciplex in Liquid Helium

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We report the first experimental confirmation of a metal-atom-He exciplex formation in liquid helium. Following the excitation of the *D2* line of an Ag atom, we have observed the atomic *D1* line emission and a broadband emission to the red of the *D1* line. The band has been assigned to the $\tilde{A}^2\Pi_{3/2} - \tilde{X}^2\Sigma^+$ bound-free transition of the He-Ag-He linear exciplex trapped in a microcavity in liquid helium. The assignment has been confirmed by an *ab initio* calculation on the AgHe₂ molecule. The absence of the atomic *D2* emission as well as an emission from AgHe indicates that the $^2P_{3/2} \rightarrow ^2P_{1/2}$ relaxation and the formation of AgHe₂ in the $\tilde{A}^2\Pi_{3/2}, v' = 0$ state occur on a subnanosecond time scale.

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In recent years much interest arose in spectroscopic studies of impurity particles in liquid helium. The interest was stimulated by the development of new experimental techniques for dispersing atoms and molecules in the liquid [1–4]. The dispersed neutral species are usually trapped in microscopic bubblelike cavities formed by a strong repulsive force between the impurity electron cloud and closed shells of surrounding helium atoms [5]. The coupling of the trapped neutral atoms with the helium bubbles (or soft cages) usually produces a large blueshift and broadening for absorption lines [3,6,7], while emission lines show shifts and broadening on the order of only 1–2 nm or less. Such behavior of the absorption lines has been related to the Franck-Condon principle. The liquid configuration around the impurity atom does not change during the excitation, thus immediately after the excitation, the excited atom finds itself still in the bubble equilibrated for the ground state. The stronger interaction of the liquid with the excited atom, which usually has an electron cloud larger than that of the ground state, induces a large blueshift and broadening for the absorption lines. Such shift and broadening have been extensively studied for Ba, Cs, and Rb in a pressure range of up to 30 atm (solid helium), and reproduced by a calculation based on metal-atom-He pair potentials [8–10].

Although remarkable progress has recently been made in spectroscopy of neutral atoms in liquid helium [11], there remain a number of phenomena for which no clear interpretation has been given. One of them is the absence of laser induced fluorescence (LIF) from light alkali atoms (Li, Na, and K) [6]. Also for heavy alkalis (Rb and Cs), LIF in the *D2* line is missing or very weak despite the fact that the excitation spectra clearly show *D2* absorption. An attempt to explain these observations has been made by Dupont-Roc [12]. Using a simple model based on a continuous and local description of liquid helium, he analyzed a configuration of liquid helium around an alkali atom impurity in the lowest *p* state. According to his model, a light alkali atom in the *p* excited state attracts

5–6 helium atoms in a nodal plane, forming a helium *ring* localized near the atomic core ($1.9 < R < 3 \text{ \AA}$). Such a configuration can produce a large redshift of the emission lines, or even quench the excited *p* state by a nonradiative relaxation to the ground state.

For heavy alkaline atoms like Cs, he has discussed two fine structure components separately because the magnitude of the spin-orbit splitting in the *6p* state is not negligible as compared to the Cs-He interaction energy. The $6p^2P_{1/2}$ state, which has a spherical charge distribution, shows a repulsive potential against helium atoms. On the other hand, the $6p^2P_{3/2}(M = \pm 3/2)$ state has a *doughnut-shaped* electron density distribution, and only two helium atoms can be attracted to the Cs ion core along the nodal line. Unlike for Na, the total energy shift by the bonding of two helium atoms is not sufficient for the quenching of emission. Instead, an emission redshifted with respect to the atomic *D2* line is expected. Despite extensive searches by several groups, such emission has not been reported yet.

As an attempt to understand this unexplained problem of missing LIF from heavy alkalines (Rb and Cs), we recently studied the optical spectrum of an Ag atom in liquid helium. Members of the IB group including Ag have spectral properties similar to alkaline atoms (IA group). Thus their interactions with helium atoms were expected to be similar as well. The experiment was done in a metal Dewar containing superfluid helium at a temperature of about 1.6 K under a saturated vapor pressure (5 torr) [13]. The Dewar was equipped with quartz windows for optical access to the liquid helium. An Ag sample immersed in liquid helium was ablated by a focused pulsed YAG laser beam (10 Hz, 10–20 mJ/pulse, 532 nm) to produce Ag particles in the liquid. Neutral silver atoms were dispersed into liquid helium by subsequent photodissociation of the particles with an unfocused XeCl excimer laser beam (10 Hz, 10 mJ, 308 nm). A pulsed dye laser beam, spatially overlapped with the excimer laser beam, excited the Ag atoms with a few microseconds delay from the dissociation

laser pulse. The LIF was detected with a photomultiplier through a 25 cm grating monochromator. The signal was gated and averaged with a boxcar integrator.

Figure 1 shows the emission spectrum recorded by pumping the $D2$ absorption line of Ag atoms in liquid helium (322.5 nm). The $D1$ emission line exhibits a very small shift (~ 0.2 nm) with respect to the free atom line, while the $D2$ emission line is missing. At the same time, a broadband fluorescence peaked near 382 nm is observed. The integrated intensities for the $D1$ and broadband emission are approximately equal. In order to find an origin of the band, two absorption spectra were recorded by detecting fluorescence at the atomic $D1$ line and the broad emission band, respectively. The spectrum taken with the $D1$ line detection [Fig. 2(a)] reveals two asymmetric absorption bands, blueshifted with respect to the free atom lines, corresponding to the excitations through the $D1$ and $D2$ transitions. The observation of the $D1$ emission line following the $D2$ excitation indicates a fast (subnanosecond) nonradiative relaxation from the $^2P_{3/2}$ to the $^2P_{1/2}$ state, a phenomenon which has been known for Cs and Rb atoms [6]. The absorption spectrum [Fig. 2(b)] taken by monitoring the broadband emission shows a marked difference. The $D2$ absorption line is very strong while the $D1$ absorption line is about 2 orders of magnitude weaker. Thus, we conclude that the broad emission at 381.5 nm is correlated with the preparation of the $^2P_{3/2}$ state of Ag atom in liquid helium.

Inspired by Dupont-Roc's discussion [12], we hypothesized that the broad emission originates from the AgHe_2 exciplex formed in a bubble after an excitation of the Ag atom to the $^2P_{3/2}$ state. To verify the hypothesis, we calculated the *ab initio* potentials for the ground states

and several lowest excited states of AgHe and AgHe_2 . The calculations were carried out with the GAUSSIAN 94 program [14]. Ground states were calculated at the UHF+MP4 level (unrestricted Hartree-Fock followed by the fourth order Möller-Plesset perturbation theory) while excited states were obtained using the configuration interaction with single substitution followed by the second order Möller-Plesset perturbation theory (CIS+MP2). The basis set and the effective core potential (ECP) of Andrae *et al.* [15] were used for the Ag atom. The spin-orbit-averaged relativistic ECP replaced 28 core electrons of Ag, significantly simplifying the calculation and reducing its cost. The energy-optimized $(8s7p6d2f)/[6s5p3d2f]$ Gaussian-type orbital (GTO) basis set was used for the Ag atom. For the He atom we applied the cc-pVQZ $((7s3p2d1f)/[4s3p2d1f])$ basis set of Woon and Dunning [16].

In the first step we calculated spin-orbit-averaged potentials. For AgHe and AgHe_2 , we obtained one nondegenerate antibonding (σ) and one doubly degenerate bonding (π) potential curves correlating with the $\text{Ag}(5p^2P) + \text{He}(^1S)$ limit. In the second step, we introduced the spin-orbit interaction operator of the form, $H = \xi \vec{l} \cdot \vec{s}$, where ξ was taken as 2/3 of the experimental value of the $^2P_{3/2} - ^2P_{1/2}$ splitting [17]. This semiempirical technique assumed that the spin-orbit coupling is independent of the Ag-He internuclear distance R . We believe that this assumption is valid in the range of $R > 2 \text{ \AA}$, covering the entire region of interest in the present model. Finally, the potential curves were shifted so that, in the $R \rightarrow \infty$ limit, they coincided with the energy levels of free Ag atoms. The potential curves of the ground and p excited states of AgHe_2 are presented in Fig. 3. Only a linear symmetric

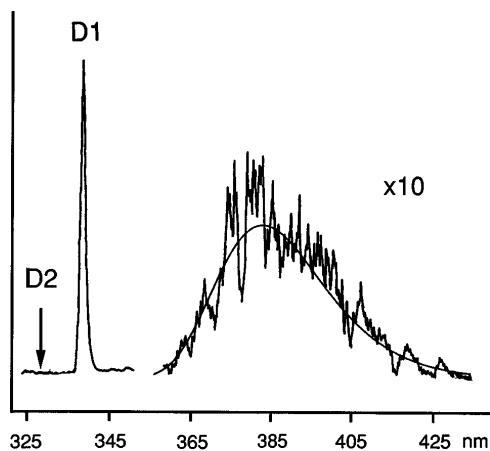


FIG. 1. The LIF spectrum recorded following the $D2$ excitation (322.5 nm in liquid helium). The intensity of the broad band at 381.5 nm is presented with 10-fold magnification. The *ab initio* bound-free transition profile (a smooth curve) is superimposed with the experimental spectrum. The integrated intensity of the calculated profile was set equal to the experimental integrated intensity of the broad emission band. The integrated intensity of the $D1$ emission line is approximately equal to the integrated intensity of the band.

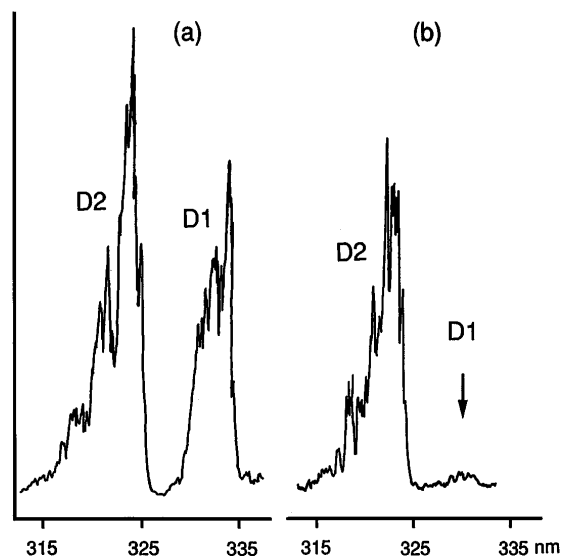


FIG. 2. The absorption spectra recorded by monitoring the $D1$ emission line (a) and broad emission band (b). The signal intensity is not normalized by the laser power. The broad emission is observed only when the $D2$ line of the Ag atom is excited.

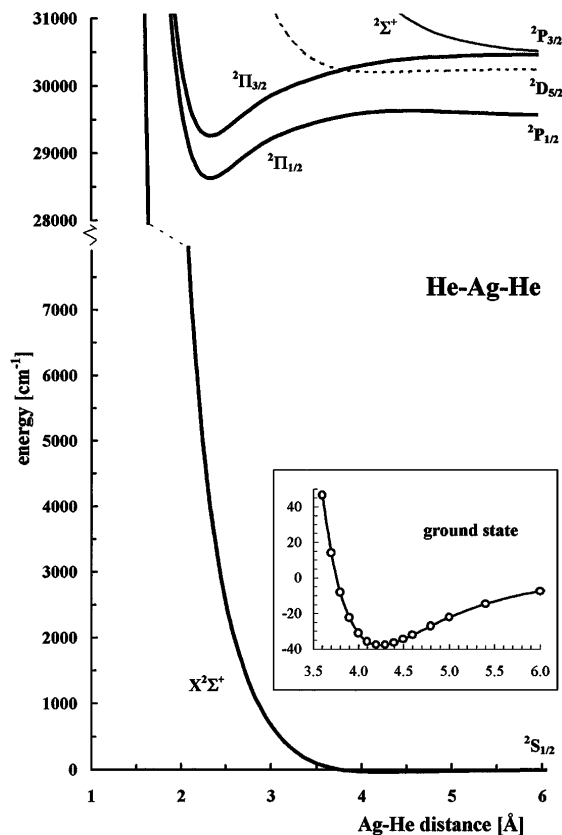


FIG. 3. *Ab initio* potential curves for the $5p\ ^2\Pi_{1/2}$, $5p\ ^2\Pi_{3/2}$, $5p\ ^2\Sigma^+$, and the ground state $5s\ ^2\Sigma^+$ (solid lines). A potential curve for states correlating with the $4d^95s^2\ ^2D_{5/2}$ state of the Ag atom is also shown with a broken line. In the inset, the minimum of the ground state potential is presented in an expanded energy scale.

He-Ag-He configuration was considered in accordance with the expected cylindrical symmetry of the p -electron cloud in the $^2P_{3/2}(M = \pm 3/2)$ state of a free Ag atom.

The ground state potential curve for AgHe₂ exhibits the minimum at 4.25 Å and the depth of 38 cm⁻¹, while the one for AgHe has the minimum at 4.3 Å and the depth of 19 cm⁻¹. For both AgHe and AgHe₂, the doubly degenerate $^2P_{3/2}$ atomic state correlates with repulsive $^2\Sigma^+$ and attractive $^2\Pi_{3/2}$ states at a shorter internuclear distance. The $^2\Pi_{3/2}$ potential of the AgHe exciplex has the potential minimum at 2.55 Å with the depth of ~417 cm⁻¹. In the AgHe₂ exciplex, the $^2\Pi_{3/2}$ state has the potential minimum at 2.35 Å with the depth of 1215 cm⁻¹. The Ag $^2P_{3/2}$ state is more stabilized by the attachment of two helium atoms than only one helium atom. We also verified *ab initio* that the AgHe_{*n*} (*n* > 2) exciplexes in symmetric nonlinear configurations exhibit no potential minima in molecular states correlating with the $^2P_{3/2}$ state of Ag. This leaves AgHe₂ as the most stable exciplex. The AgHe₂ exciplex is vibrationally cooled rapidly to the $\nu' = 0$ state by collisions with the helium bath as observed in Cu₂ and Ca₂ [4]. The AgHe₂ exciplex in the $^2\Pi_{3/2}, \nu' = 0$ state decays radiatively to

the repulsive wall of the ground $^2\Sigma^+$ state, resulting in the broad bound-free emission. In both AgHe and AgHe₂ exciplexes, the $^2\Pi_{1/2}$ states correlating with the $^2P_{1/2}$ state of Ag have potential minima at around 2.3 Å and potential barriers at 4.1 Å (AgHe) and 4.6 Å (AgHe₂). The heights of the potential barriers are 66 cm⁻¹ for AgHe and 75 cm⁻¹ for AgHe₂. These potential barriers will be sufficient to prevent the He atoms from reaching the potential minima when the Ag atom is excited or relaxing from the $^2P_{3/2}$ state to the $^2P_{1/2}$ state in the liquid helium. As is evident from Fig. 3, the $^2\Pi_{1/2}$ potential curve for the AgHe₂ exciplex neither crosses nor closely approaches the potential curve for the $^2\Pi_{3/2}$ state. Thus the $^2P_{3/2} \rightarrow ^2P_{1/2}$ relaxation by a (near) crossing of the two levels seems to be unlikely in the present case.

Using the potential curves described above, we calculated the $^2\Pi_{3/2} - ^2\Sigma^+$ emission spectra for the AgHe and AgHe₂ exciplexes. For both the $^2\Pi_{3/2}$ and the ground $^2\Sigma^+$ state, we solved the vibrational Schrödinger equations and calculated the bound-free Franck-Condon densities, $f(\nu', \epsilon)$. Using the *ab initio* transition dipole matrix elements, we calculated $^2\Pi_{3/2} - ^2\Sigma^+$ bound-free transition intensity as a function of transition energy. All the molecules in the $^2\Pi_{3/2}$ state are assumed to have relaxed to the lowest vibrational level before photoemission. The calculated bound-free band profile is shown in Fig. 1 as a smooth line superimposed with the experimental spectrum. The integrated intensity of the calculated AgHe₂ emission band is set equal to the experimental one. The band profile for the AgHe₂ bound-free emission agrees very well with the observed spectrum. The peak position of the simulated band is at 382.5 nm. The *ab initio* radiative lifetime, 9.7 ns, for the $^2\Pi_{3/2}, \nu' = 0$ state can be compared with the 7.69 ns lifetime of the $^2P_{3/2}$ state of a free Ag atom [18]. We confirmed that the emission occurs from the $\nu' = 0$ level of the $^2\Pi_{3/2}$ state because an incomplete vibrational relaxation of AgHe₂ in the $^2\Pi_{3/2}$ state (for example, 5% population in the $\nu' = 1$ level at 187 cm⁻¹ above the $\nu' = 0$ level) would result in an experimentally detectable difference in the emission profile.

It has been known for many years that collisions of excited alkali atoms with helium gas induce the $^2P_{3/2} \rightarrow ^2P_{1/2}$ relaxation [19]. A temperature dependence of the relaxation rate has been studied extensively for Cs and Rb atoms in the range of 300 to 900 K [20]. Unfortunately, the extrapolation of these data to 1.6 K is not reliable. Nevertheless, if one takes the collisional relaxation cross section of $\sigma = 10^{-21}$ cm² as an upper limit for Cs, one can estimate the relaxation rate in liquid helium to be $\sim 2 \times 10^5$ s⁻¹ by assuming that the liquid is a high density (0.145 g/cm³ or 2.2×10^{22} atoms/cm³) gas at 1.6 K. This rate is too low to compete with the formation of exciplex in a subnanosecond time scale because the probability of collisional relaxation per 1 ns is only on the order of 10^{-4} . For an Ag atom, this value would be even a few orders of magnitude smaller because the fine structure splitting for Ag (921 cm⁻¹) is substantially larger than the

splitting for Cs (554 cm^{-1}). Thus, neither an atom-atom collision model nor the (near) crossing mechanism provides a satisfactory explanation for the fast ${}^2P_{3/2} \rightarrow {}^2P_{1/2}$ relaxation. An alternative model for the relaxation, a dynamic collective quenching model, is under development in our group.

In this Letter we report the first evidence of the formation of an impurity atom-helium exciplex in liquid helium. The broadband emission, the signature of the AgHe_2 exciplex, has been attributed to the bound-free $\tilde{A}^2\Pi_{3/2} - \tilde{X}^2\Sigma^+$ transition. Similarly, our preliminary *ab initio* calculation on Cs predicts that the CsHe_2 exciplex, formed after the excitation of the ${}^2P_{3/2}$ state of a Cs atom, should exhibit a broad bound-free emission band centered to the red of 1080 nm, just outside the region surveyed in Ref. [10]. Also we believe that the present model can be applied to the unassigned broadband emission followed by the laser excitation of the $D2$ line of Ba^+ in liquid helium [2]. The emission band is due most likely to the ${}^2\Pi_{3/2} - {}^2\Sigma^+$ transition in $\text{Ba}^+\text{-He}_2$.

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