VOLUME 71, NUMBER 7 PHYSICAL REVIEW LETTERS 16 AUGUST 1993

Spectroscopy of Alkali Atoms and Molecules in Superfluid Helium

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(Received 11 May 1993)

We report on the first laser spectroscopy of alkali atoms (Cs and Rb) and molecules (Na_2 and Li_2) in superfluid helium. General features of the observed spectra can be explained in terms of the spherical atomic bubble model. The excitation and emission spectra for the D_2 lines, however, have double peaked profiles, indicating the importance of the nonspherical density distribution of surrounding helium atoms. The emission spectra for the molecules show well-resolved vibrational structures in the electronic ground states.

PACS numbers: 67.40.Yv, 32.30.Jc, 32.70.Jz, 33.20.Kf

An electron introduced into superfluid helium is known to form a vacant sphere, a so-called electron bubble, with a radius ~17 Å [1]. Foreign neutral atoms in liquid helium are also expected to form spherical bubblelike states. There has been increasing interest in such foreign atoms in liquid helium from the viewpoints of atomic as well as low temperature physics. The pioneering spectroscopic studies of impurity atoms in liquid helium were performed by a group at Heidelberg [2]. Using the recombination method they could successfully implant various kinds of atoms and molecules and could observe their spectra in superfluid helium.

In many respects alkali atoms are considered the best impurity atoms to study. They have one valence electron, so that accurate comparison between theory and experiment is expected to be more straightforward than for other atoms. The D lines are in the visible and near-infrared region, easily accessible by dye and Ti:Al_2O_3 lasers. In addition, optical pumping and optical detection of sublevel resonances can be applied to alkali atoms. The hyperfine constant is a direct measure of the wave function of the outer electron perturbed by the surrounding helium. The spin relaxation times are thought to be very long in liquid helium, which may have various applications. It was reported in the earlier work that no D lines were observed in recombination fluorescence for alkali atoms (Li, Na, K, and Rb) [3] and it was suggested that the nonradiative transition should play an important role in a system with one valence electron in an inert liquid. There is no theory, however, to explain the observed quenching of D line emission.

More recently we have developed a quite efficient method for implantation of foreign neutral atoms; laser sputtering within liquid helium [4]. The method was demonstrated for alkaline earth atoms (Ba and Ca) and the atomic densities were as high as 10^8–10^{10} cm^{-3}. In this Letter we report on the first observation of excitation and emission spectra of neutral alkali atoms (Rb and Cs) and molecules (Na_2 and Li_2) implanted by laser sputtering in superfluid helium.

The experimental conditions were almost the same as those in Ref. [5]. An important point of our method is that the repetition rate of sputtering pulses is as high as about 1 kHz in order to efficiently resputter the clusters, ejected from the metal surface, by successive pulses. For the excitation of Rb and Cs atoms we used a cw Ti:Al_2O_3 laser, and for Na_2 and Li_2 we used single lines of a cw Ar^+ laser. The power of the laser beams was several hundreds of milliwatts before arriving at the helium Dewar. The intensities of laser-induced fluorescence (LIF) signals were as high as those for Ba atoms [4].

First we show the results for alkali atoms. Figure 1(a) shows the excitation spectra of Cs atoms corresponding to the transitions from the ground state $6^2S_{1/2}$ to the excited states $6^2P_{1/2}$ and $6^2P_{3/2}$ (D_1 and D_2). These excitation spectra were observed by detecting the emission light at about 892.1 mm which corresponds to the D_1-emission line [see Fig. 1(b)] and by scanning the wavelength of the excitation Ti:Al_2O_3 laser. As shown in Fig. 1, both excitation spectra are blueshifted by the amount of ~18 nm from the corresponding spectra of free atoms. The lines are considerably broadened, the widths being about 10 nm. The most striking difference between these two D-line excitation spectra is that the D_2 line has a doubly shaped profile [6]. The emission spectra were obtained by scanning the monochromator with the laser wavelength fixed to near the center of the D_1- or D_2-excitation spectrum shown in Fig. 1(a). Figure 1(b) shows the observed emission spectra in the case of the D_2 excitation. The D_1-emission spectrum is almost symmetrical, and the center wavelength is about 2 nm blueshifted and the width is about 2 nm. As shown in Fig. 1(b), the intensity of the D_2 emission is about 1000 times weaker than that of the D_1 emission, which suggests that the atoms in the $6^2P_{3/2}$ state should be quickly relaxed to the $6^2P_{1/2}$ state with a relaxation time ~30 psec. Here we assumed that the radiative lifetime of the 6^2P state was the same as that for a free atom [5] and that there were no other quenching processes for the D_2 emission. Looking at the D_2-emission spectrum, one can see that it consists of two components, one being at about the free atomic spectrum and the other being broader and redshifted. In the case of D_1 excitation, essentially the same D_1-emission spectrum was observed as in the case of D_2 excitation.

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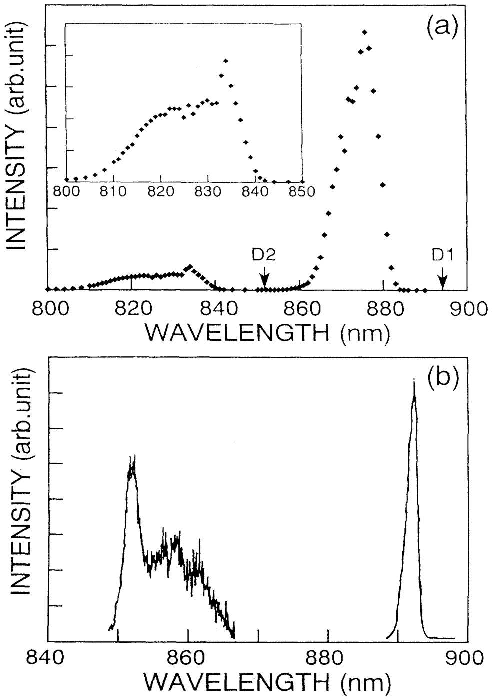

FIG. 1. Excitation (a) and emission (b) spectra of Cs atoms in liquid helium. The excitation spectrum (a) was obtained for the D_1-emission line at 892.1 nm. The inset is the magnification of the D_2-excitation spectrum. The arrows represent the positions of corresponding spectra of the Cs atoms in vacuum. The emission spectrum (b) was obtained with the D_2 excitation at 837 nm. The resolution was about 0.2 nm. The D_2-emission signal indicated in the left part is magnified 1000 times.

The spectral features observed for Rb atoms were not basically different from those of Cs. The features of the observed spectra for Rb and Cs atoms are summarized in Table I. The intensities of the LIF signals were about the same for both atoms, but for Rb atoms the D_2-emission signals have not been detected so far.

It is known that a spherical bubble model can be applied to alkaline-earth atoms in liquid helium [4,7] just like an electron bubble model. In the atomic bubble model, outer electrons of the atoms push out surrounding helium by the Pauli exclusion force and the atoms form spherical structures of surrounding helium. The optical excitation, i.e., absorption, occurs at the bubble radius determined by the ground state wave function, whereas the emission occurs after the bubble is expanded due to the larger extent of the excited state wave function. Our preliminary calculations show that the features of the excitation and emission spectra of D_1 lines of the alkali atoms can rather quantitatively be explained by using configuration coordinate diagrams based on a simplified spherical atomic bubble model, except for the precise values of the excitation linewidths. This is the first experimental evidence of the bubble structure of the alkali atoms which was suggested theoretically in Ref. [8]. However, the spectral structure of the D_2 line cannot be explained by this model. Although we have not yet made quantitative studies, we consider that such a doubly peaked profile can be explained by the nonspherical density distribution of surrounding helium atoms. In the emission process the symmetry of the density distribution of helium may be lowered to axial symmetry according to the distribution of the wave function of the excited P state, which removes the degeneracy of the $m_J = \pm \frac{1}{2}$ and $m_J = \pm \frac{3}{2}$ states as in the static Jahn-Teller effect. The doubly shaped profile of the D_2-excitation spectrum was also observed for Ba ions [6]. As was speculated there, the dynamical Jahn-Teller effect might be responsible for the observed structures.

We could also observe the signals of alkali dimers. In order to excite Na_2 molecules from the ground electronic state $X^1\Sigma_g^+$, we used single lines of a cw Ar^+ laser whose wavelength could be changed discretely in the range 450–500 nm. Figure 2(a) shows the intensity of the fluorescence at 618 nm normalized by the laser intensity at five wavelengths: 457.9, 465.8, 472.7, 476.5, and 488.0 nm. The state excited is assigned to the $B^1\Pi_u$ state. The spectrum has about the same profile as that of the transition from $X^1\Sigma_g^+(v''=0)$ to $B^1\Pi_u(v')$ of a free molecule, and the peak is blueshifted by about 700 cm^{-1}. v' and v'' represent vibrational quantum numbers of Na_2 in the excited and ground states, respectively. Figure 2(b)

TABLE I. Spectroscopic results of Cs and Rb atoms. The properties (shift and width) of D_1-emission line were independent of the excitation line used (D_1 or D_2). The properties of D_2-excitation line were also independent of whether D_1- or D_2-emission line was monitored. For Rb atoms the D_2-emission signals have not been detected so far.

		Free	Excitation in He II		Emission in He II	
Atom	Line	λ (nm)	Shift (nm)	HWHM (nm)	Shift (nm)	HWHM (nm)
Rb	$D1$	794.76	−16.8 ± 0.5	4.0 ± 0.5	−1.2 ± 0.2	0.9 ± 0.2
	$D2$	780.03	−16.0 ± 0.5	3.0 ± 0.5		
			−24.0 ± 0.5	8.0 ± 0.5		
Cs	$D1$	894.35	−18.4 ± 0.5	5.5 ± 0.5	−2.1 ± 0.2	1.2 ± 0.2
	$D2$	852.11	−18.1 ± 0.5	2.8 ± 0.5	6 ± 2	12 ± 2
			−30.1 ± 0.5	8.0 ± 0.5	0 ± 1	1 ± 1

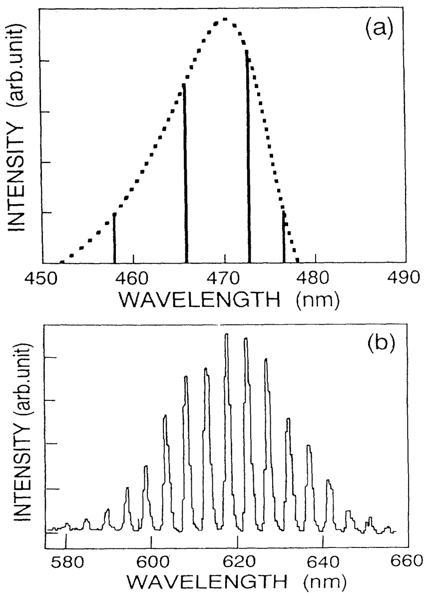

FIG. 2. Excitation (a) and emission (b) spectra of Na_2 molecules in liquid helium. The excitation spectrum (a) was obtained through the emission line at 618 nm. The signal at 488 nm was about 2 orders of magnitude smaller than those at other wavelengths. The dotted line represents the spline-fitted curve of the signal intensities. In the fitting the signal intensity was arbitrarily set to zero at 452 nm. The emission spectrum (b) was obtained with each excitation line, and was found to be essentially the same. The resolution was about 0.2 nm.

shows the emission spectrum observed when the molecules were excited at 457.9 nm. It was found that the emission spectrum was independent of the excitation wavelength. This indicates that Na_2 molecules excited to various vibrational states of the $B\,^1\Pi_u$ state relax to the $v'=0$ state during the excited state lifetime [9]. It is unclear whether the observed emission originates from the $B\,^1\Pi_u(v'=0)$ state or from the lower electronic state $A\,^1\Sigma_u^+(v'=0)$ state. In the former case, the observed spectrum is redshifted by an amount of about 4000 cm^{-1} from that of the free molecule. In the latter the shift is about 2000 cm^{-1} and is negative.

Whichever the initial state is of the emission process, the spectrum shown in Fig. 2(b) represents the energy structure of the vibrational states of the ground electronic state $X\,^1\Sigma_g^+$. Unfortunately we could not assign the vibrational quantum number v'' for each emission line. We could not detect the band edge corresponding to the emission from the excited $v'=0$ state to the ground $v''=0$ state, due to the low S/N ratio in the shorter wavelength side of the emission spectrum. If we could know the values of v'' by some means, the vibrational oscillation frequency would be accurately determined, which might furnish the information regarding the effective mass of a Na atom in liquid helium.

As seen in Fig. 2(b), the envelope of the emission lines is much more symmetrical than that of the corresponding free molecular spectra which show a short-wavelength cutoff. According to the Franck-Condon principle this means that the molecular size, i.e., the interatomic distance giving the minimum of the adiabatic potential of the molecule, of the excited state differs from that of the ground state much more in liquid helium than in vacuum.

For Li_2 molecules we also used single lines of a cw Ar^+ laser for excitation. With the excitations at wavelengths below 476.5 nm, we could observe twelve emission lines in the region from 536.5 to 648.0 nm at bout 10 nm separation. The S/N ratio was so poor that we could not obtain the accurate shape of the excitation and emission spectra so far. From our data, assignment of the electronic and vibrational states for Li_2 are similar to the case of Na_2.

In this paper we have reported on the results of the laser spectroscopy of alkali atoms and dimers in superfluid helium. It was previously reported that no D lines were observed in recombination fluorescence [3]. In Ref. [6] the authors were sure that alkali atoms were formed with the recombination method [10]. From the fact that the LIF signals were observed in the present work, one can infer the existence of some quenching mechanism associated with the recombination of an electron bubble and an alkali-ion snowball.

There still remain some problems to be solved. First of all, LIF signals for alkali atoms lighter than Rb have not been observed so far. We looked for LIF signals of lighter atoms (K, Na, and Li), changing the excitation wavelength over almost the entire visible and near-infrared region, but we could not observe any signals. Instead the emission signals at the moment of the cluster sputtering could be observed. These emission signals were observed without excitation lasers and are considered to originate from the atoms initially created in the excited states due to laser sputtering. We think that the existence of these signals indicates the successful implantation of the atoms just after the laser sputtering. Inferring from the observed excitation spectra of Rb and Cs, the excitation spectra of lighter alkali atoms should not be greatly shifted to the violet or far-infrared region inaccessible to our present system. In addition there is no reason to believe that nonradiative transition rates are too high for the emission to be observed only for lighter alkali atoms. The emission signals at the moment of sputtering were as strong for lighter atoms as those for heavier ones. Thus we are forced to conclude that within a few microseconds [11] after the laser sputtering the density of produced lighter atoms should become extremely small, at least 3 orders of magnitude smaller than for the case of Rb and Cs atoms. It is also noted that LIF signals of lighter alkali molecules such as Li_2 and Na_2 were observed while heavier alkali molecules were not detected, whereas only the heavier alkali atoms were detected. This suggests that rather rapid molecular formation might occur for the lighter alkali atoms. This seems to be supported by the fact that there appeared no emission light for Na_2 or Li_2 at the moment of laser sputtering. There is no theory, however, predicting such rapid molecular formation for lighter alkali atoms. In addition to alkali atoms no LIF signals were observed for lighter alkaline-earth ions and atoms (Mg^+, Ca^+, Sr^+, and Mg). This puzzling problem might be solved by considering the novel behavior of atomic and molecular impurities in liquid helium. The second problem left is the quantitative explanation of the doubly shaped profile of the emission and excitation spectra of D_2 lines. The time-resolved spectra and the spectra of atoms in pressurized liquid helium offer important information for a quantitative explanation of the behaviors of the D_2 lines. These experiments are now underway. In addition it must be noted that the excitation rate of the D_1 line was higher than that of the D_2 line (see Fig. 1), which is opposite to the case of free atoms. It is not known whether the partial quenching of the emission from the $P_{3/2}$ state occurs or the oscillator strength of the D_2 line is reduced in liquid helium.

Finally, it is mentioned that quite recently we have made an optical pumping experiment with Rb and Cs atoms in liquid helium and obtained a sizable spin polarization. The magnetic resonance of these atoms could also be detected. Details of this experiment will be reported elsewhere.

We thank Professor T. Tsuneto, Professor T. Ohmi, and Professor T. Mizusaki for useful discussions and comments. This work was partially supported by the Matuo foundation and the Grant-in-Aid for Scientific Research (04554010).

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[5] We have measured lifetimes of $5d6p\,^3P_J$ states of Ba in liquid helium by the correlated single photon counting method, and they turned out to be about the same as those in vacuum (10 ns). This is the basis of our assumption.

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[9] We have measured the lifetime of the optically excited state of Na_2 by the correlated single photon counting method, and it turned out to be about 10 ns or less. The results will be published elsewhere.

[10] This should be checked experimentally by the observation of the LIF signals.

[11] The time for the photon counting was delayed by more than 5 μsec from the time of sputtering in order to avoid counting the scattered and recombination light as well as the emission at the moment.