Emission Spectrum of the C_2 Radical Embedded in Superfluid Helium around 1.5 K

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The C_2 $d^3\Pi_g$-$a^3\Pi_u$ $(v' - v'')$ Swan band emission spectrum induced by the laser ablation of graphite in the superfluid helium around 1.5 K, was observed. Only the vibrational progression of $\Delta v = v' - v''$, where Δv less than 0 are observed, indicating fast ($\tau < 100$ ns) vibrational relaxation in superfluid helium. This result also indicates a unique characteristic of superfluid helium as a circumstance of chemical processes.

We are currently interested in dynamical chemical processes including vibrational and rotational relaxation as well as chemical reactions in the liquid helium environment at extremely low temperatures. Liquid helium provides a unique matrix environment due to its quantum nature. Also, helium atoms can be an ideal solvent for chemical processes since the solute-solvent interaction is generally very small and low-temperature helium atoms act as efficient thermal bath.

In this letter, we present the spectroscopic measurements of the C_2 radical in bulk helium liquids. This radical is known to be very reactive and many important reactions concerning C_2 have been studied. C_2 can be detectable by a spectroscopic technique in the visible region. Most of previous studies are restricted to metallic dimmers and this is the first measurement on the highly reactive organic radical in superfluid helium. Although we have obtained only spectroscopic information about the C_2 radical in this study, we believe that the present study would be a starting point for future investigations on chemical reactions.

Recently, a liquid helium droplet technique using molecular beams has extensively been applied to spectroscopic studies of atoms, molecules and radicals embedded in, or attached to large helium clusters.[1] The most important feature of this technique is that one can easily introduce impurity species into helium clusters combined with a pickup cell method. Several unusual but interesting phenomena due to the quantum mechanical nature of helium clusters have been reported so far. For example, it has been found that rotational constants of molecules embedded in superfluid ^{4}He clusters are much smaller than those in the gas phase.[2] This result demonstrates that molecular spectroscopy can be a new probe of microscopic manifestations of quantum superfluidity of liquid helium.

On the other hand, the most advantageous points to use bulk liquid helium is that we can artificially control the temperature and pressure of liquid helium. However, unlike the helium droplet method as mentioned above, it is generally difficult to introduce impurity species into liquid helium since the affinity of impurities with helium is usually small. Nevertheless, some experimental methods to introduce impurity species into bulk liquid helium have been proposed so far. Yabuzaki and coworkers applied laser ablation of metal solids and extensively measured electronic spectra of many metal atoms and a few metal dimers in bulk superfluid helium.[3–6] We employ in this study the same technique to produce the C_2 radical in liquid helium. Very recently, in our research group, tritium atoms were directly produced in liquid helium containing ^{3}He atoms using nuclear reaction, $^3\mathrm{He} + \mathrm{n} \rightarrow \mathrm{T} + \mathrm{p}$, by neutron irradiation.[7] This technique was used in the study of atomic recombination reactions in liquid helium. Benderskii et al. have recently employed intense femtosecond laser excitation to produce excited and ionized species although pure liquid helium has been used in their experiment.[8,9]

The C_2 radical was produced by laser ablation of graphite rod. The second harmonic output of Nd:YAG laser (Spectra Physik INDI-40) at about 10 mJ/pulse with 10 Hz repetition was used for ablation. The cryostat was equipped with quartz optical windows in five directions. The ablation laser light was focused on the rotating rod with a 20 cm focus lens. Note that ablation is possible only when superfluid is attained, or boiling bubbles in liquid helium interfere laser light. The emission at the plume was corrected by lens outside the cryostat and focused on the optical fiber inlet of a medium resolution multichannel spectrometer (Hamamatsu C7473). The energy resolution and sampling gate width of the spectrometer are 2 nm and 19 ms, respectively. The temperature was controlled at around 1.5 K by evaporative cooling method using pumping system.

A typical emission spectrum accumulated during 19 ms just after ablation pulse in bulk superfluid helium around 1.5 K is shown by bold solid line in Figure 1. The extremely intense signal centered at 532 nm comes from scattered light of the ablation laser. The structures seen around 520, 560 and 610 nm can be assigned as $d^3\Pi_g$-$a^3\Pi_u$ $(v' - v'')$ Swan band of the C_2 radical;[10] these three bands correspond to $v' - v'' = 0$, -1, and -2, respectively. The observed structures have a relatively broad feature, indicating that the rotational distribution of the C_2 radical

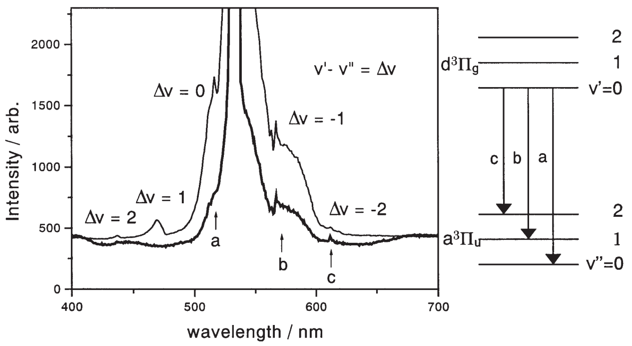

Figure 1. Emission spectra of the $d^3\Pi_g$-$a^3\Pi_u$ Swan band of the C_2 molecule. v' and v'' are vibrational quantum numbers of upper and lower electronic states, respectively. The bold solid line corresponds to the spectrum recorded in superfluid liquid helium at 1.5 K while the thin solid line to the spectrum recorded in helium gas (<1 Torr).

in the $d^3\Pi_g$ electronic state may be relatively hot and the rotational temperature of the C_2 produced by ablation is much higher than the bulk temperature of 1.5 K. Note that the observed broad structures make it difficult to assign an each vibrational quantum number of upper or lower electronic state. This is simply because the vibrational frequency difference between the $d^3\Pi_g$(1788 cm^{-1}) and $a^3\Pi_u$(1641 cm^{-1}) electronic states is small. Therefore, we can assign only the value of $\Delta v = v' - v''$. For comparison, we have also measured the emission spectrum of the C_2 radical in the gas phase with the helium pressure below 1 Torr and the result is plotted by thin solid line in Figure 1. The peak positions measured in superfluid liquid helium were found to be exactly the same as those measured in the gas phase. However, an important difference is apparent. We can see the additional two bands, $\Delta v = 1$ and $\Delta v = 2$, in the emission spectrum measured in vacuum. In contrast, these bands are completely absent in the spectrum measured in superfluid helium. The relative intensity of each vibrational progression is determined by Franck–Condon Factors (FCFs). The gas phase value of FCFs for $d^3\Pi_g$-$a^3\Pi_u$ $(v' - v'')$ of $\Delta v = 1$ are 0.24085, 0.36218, and 0.41370 for $v'' = 0$, 1, and 2, respectively.[11] Because the FCF for $v' = 1 \rightarrow v'' = 0$ is sufficiently large, if the $v' = 1$ state is populated, the $v' = 1 \rightarrow v'' = 0$ transition should be observed. The fact that $\Delta v = 0$ does not appear in the superfluid helium indicates that the vibrational relaxation in $d^3\Pi_g$ electronic state occurs prior to the $d^3\Pi_g$-$a^3\Pi_u$ electronic transition, which was measured to be about 100 ns.

Nauta and Miller observed the vibrational relaxation process of HF in helium droplet.[12] They showed the vibrationally excited HF ($v = 1$) does not relax within the experimental time scale of 0.5 ms. Our observation, on the other hand, suggests very fast vibrational relaxation. The difference could presumably be explained by the difference in the production process of the C_2 radical in bulk liquid helium. In droplet experiments, HF is attached in the pick-up cell and then excited by IR laser to the $v = 1$ state. The excited HF molecule relaxes to the ground state and the elementary excitation of surrounding helium occurs. They concluded that the vibrational energy gap is so large compared to elementary excitation that the relaxation is very slow. In the bulk experiment, the vibrationally excited state of C_2 is generated during the ablation process. After ablation, high temperature plasma is generated on the surface of graphite and nearby superfluid helium is vaporized. It is expected that both the temperature and pressure are very high in this temporary plasma. After the collision of C_2 with helium atoms, the vibrationally excited states are quickly quenched to the ground vibrational state. The gaseous plasma is then cooled by surrounding superfluid helium and again condensed to liquid. Therefore, all C_2 radicals are quenched to the vibrationally ground state and the emission from only the $v' = 0$ state is observed. The above mechanism is justified if the vibrational relaxation occurs much faster than the radiative lifetime of the $d^3\Pi_u$ electronic state, which is about 100 ns. However, for example, collisional vibrational relaxation rates of CO ($v = 1$) with helium were measured to be 10 µs at 1500 K and 1 atm.[13] Therefore, this mechanism cannot explain very fast vibrational relaxation of C_2.

In order to understand the generation and relaxation mechanisms of C_2 in superfluid helium in detail, other electronic states including singlet states should be also investigated. Measurement of time resolved LIF spectra of C and C_2 will be useful for understanding generation and relaxation mechanisms of C_2. The ground state C atom and C_2 can be probed by two-photon excitation at 280 nm[14] and $D^1\Sigma_u{}^+$-$X^1\Sigma_g{}^+$ transition at 230 nm,[15] respectively. These studies are currently in progress.

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