Radiative decay of the metastable \( \text{He}_2(a^{3}\Sigma_u^+) \) molecule in liquid helium


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Long-lived phosphorescence has been observed emanating from superfluid helium following excitation by ionizing radiation. This extreme ultraviolet light is predominantly from the radiative decay of metastable \( \text{He}_2(a^{3}\Sigma_u^+) \) molecules and is detected through frequency down-conversion and photon counting techniques. This allows measurement of the phosphorescence lifetime in a low-molecular-density regime that is not dominated by two-body reactions. A phosphorescence lifetime of \( 13 \pm 2 \) s is observed.

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I. INTRODUCTION

The study of impurities in superfluid helium (He II) has produced a wealth of knowledge about ion and electron mobilities, the creation and behavior of vortex rings, micro-environments around impurities, and the spectroscopy of electrons, atoms and molecules [1–6]. Considerable work [7–17] has centered on one molecule in particular: \( \text{He}_2^+ \).

There is renewed interest in this species, spurred by proposals for experiments to magnetically trap ultracold neutrons [18] and to search for the electric dipole moment of the neutron [19]. In these proposed experiments, ionizing radiation released from neutron \( \beta \) decay or the \(^3\text{He}(n,p)^3\text{H}\) reaction produce excited \( \text{He}_2^+ \) molecules within liquid helium. Singlet \( \text{He}_2^+ \) molecules subsequently undergo radiative decay in the extreme ultraviolet (EUV), producing an emission peak centered around 80 nm, known as the Hopfield continuum [7,9]. The EUV light is then frequency down-converted to visible light, which is optically transported out of the apparatus to a detector. Because both experiments rely upon these EUV scintillations to provide precise timing of nuclear decay events, understanding the decay events involved with the \( \text{He}_2^+ \) is important for determining the promise and limitations of this scintillation detection method.

The metastable helium molecule state \( \text{He}_2(a^{3}\Sigma_u^+) \) is unique for its long lifetime in liquid helium and the interactions and decay of this molecule are the most likely sources for the slowly decaying components observed following helium ionization. Past studies [8,13] have shown that ionization of helium within the liquid results in the efficient formation of \( \text{He}_2(a^{3}\Sigma_u^+) \) molecules. These molecules are the end result of complex recombination processes involving metastable helium atoms, \( \text{He}_2^+ \) and \( \text{He}_3^+ \) ions, and the surrounding ground-state helium [13,20]. According to the theory of Hickman, Streets, and Lane [21], \( \text{He}_2(a^{3}\Sigma_u^+) \) exists in liquid helium within a bubble of diameter approximately equal to 1 nm. Helium atoms near the bubble encounter a strong repulsion, produced by the outerlying electron of the molecular state. The molecules in liquid helium have spectroscopic characteristics similar to those in vacuum, with spectral lines that are somewhat shifted. The metastable \( \text{He}_2(a^{3}\Sigma_u^+) \) molecule can be deexcited by radiative decay, reactions with other helium metastables, and collisions with the container walls. Movement of the molecule through the liquid is limited by diffusive scattering with rotons, phonons, and \(^3\text{He}\) impurities [11]. The density of phonons and rotons within the liquid depends strongly on temperature. This causes the molecular diffusion constant \( (D) \) to also change markedly.

The radiative decay of \( \text{He}_2(a^{3}\Sigma_u^+) \) in vacuum is suppressed for several reasons. Radiative decay to the ground state (two free helium atoms) is forbidden since transitions from triplet excited states to the singlet ground state involve a spin flip. Also, the approximately 2-eV deep triplet molecular potential is minimum at an internuclear distance of about 0.1 nm. At this distance, two ground-state helium atoms repel each other strongly, giving a correspondingly small Franck-Condon factor. The radiative lifetime of the \((\nu=0)\) level of the \( \text{He}_2(a^{3}\Sigma_u^+) \) state in vacuum has been calculated [22,23] to be 18 s. When the molecule decays radiatively, emission can be expected to occur in a continuum peaked in the extreme ultraviolet, similar to the Hopfield continuum.

Nonradiative deexcitations of this molecule in liquid helium that is free of metastable He are relatively rare. This stands in contrast to metastable triplet atomic helium (radiative lifetime \( \tau \sim 8000 \) s [24]), which has been shown to survive only 15 \( \mu \)s in the liquid for temperatures in the range 1.4–2.2 K [12]. After a few milliseconds, the only electronic helium excitations left are molecules in the \( \text{He}_2(a^{3}\Sigma_u^+) \) state. As a result, these molecules are the dominant long-lived electronic excitations in liquid helium.

Metastable helium molecules were first detected in liquid helium as unidentified neutral excitations, which for temperatures less than or equal to 0.6 K would travel ballistically through the liquid and cause ions to be emitted from the liquid-vapor interface. In one of these experiments, Surko and Reif [25] found that these neutral excitations could be created with an \( \alpha \) source within the liquid. Subsequent studies measured the times of flight to various detectors and...
found that the neutral excitations could be consistently identified as metastable \( \text{He}_2(a^3\Sigma_u^+) \) molecules [11,26,27]. Lower limits on the molecule lifetime have continued to increase. Most recently, Mehrotra et al. [14] placed a lower bound of 10 s on the lifetime of the triplet state in liquid helium by measuring the time of flight from a field emission discharge to a submerged surface ionization detector.

Other experiments used weak \( \alpha \) and \( \beta \) sources to create scintillations in liquid helium and used wave-shifting fluors to convert the resulting EUV scintillations into visible light [10,28–30]. It was observed that each ionizing particle produced a brief burst of scintillation. This pulse was presumably caused primarily by the prompt decay of singlet states. However, the variation of pulse size with temperature in \( \alpha \)-induced scintillations indicated that reactions of metastable states with other constituents of the ionization track also contributed. It was also observed that a significant amount of light was emitted at later times. The intensity of this slow phosphorescence was found to vary with the size of the container at low temperatures [10], suggesting that the slow emitters of light [presumably \( \text{He}_2(a^3\Sigma_u^+) \) molecules] could be quenched when they hit the walls of the container. Despite the intrinsic interest of the highly forbidden \( \text{He}_2(a^3\Sigma_u^+) \) decay, to our knowledge, the radiative decay of molecular triplet helium has never before been continuously observed in the liquid. This is because the high concentration of helium molecules needed to perform spectroscopy results in a high rate of bimolecular recombination through exchange-dipole Penning ionization:

\[
\text{He}_2(a^3\Sigma_u^+) + \text{He}_2(a^3\Sigma_u^+) \rightarrow ^3\text{He}(1^1S) + \text{He}^+ + e^- \\
\rightarrow ^2\text{He}(1^1S) + \text{He}_2^+ + e^-.
\]  

(1)

If a high density of molecules \( n_0 \) is created in the liquid and allowed to decay through this two-body reaction, the density of helium molecules \( n \) will at first vary as

\[
1/n = 1/n_0 + \alpha(T)t,
\]

(2)

where \( \alpha \) is the bilinear reaction coefficient. Experimental studies [12,13] indicate that \( \alpha(T) \) varies inversely with the number density of rotons or as \( e^{-\Delta T} \), where \( \Delta \approx 8.6 \) K. With \( \alpha \) on the order of \( 10^{-10} \) cm\(^3\) s\(^{-1}\), triplet molecule decay in liquid helium is dominated by this diffusion limited process for \( n \approx 10^9 \) cm\(^{-3}\). Cryogenic experiments using infrared spectroscopy to monitor the molecular state populations in the liquid (these experiments require relatively high molecule densities for detection) have so far been unable to observe the molecules for longer than 100 ms [13,16]. In solid helium, however, where the diffusion of molecules is much slower, the lifetime of the \( \text{He}_2(a^3\Sigma_u^+) \) state has successfully been measured [15] using infrared spectroscopy to be approximately equal to 15 s.

We have developed experimental cell designs that use frequency down-conversion of EUV light to allow highly sensitive detection of liquid-helium scintillations within a geometrically constrained cryogenic environment. While developing these detectors, we found that a significant portion of scintillations in the liquid helium occurred on a time scale comparable to the theoretically predicted molecular triplet lifetime. Our explanation for the observed slow phosphorescence is that the high sensitivity of these detection systems has allowed us to observe molecular decay in a density regime that is dominated by radiative decay rather than Penning ionization.

We have observed these scintillations in liquid helium using an apparatus that employs a \( \beta \) source. The effect has also been confirmed by measurements with a second apparatus that uses \( ^3\)He neutron capture to create scintillations [31]. Both experiments have in common the creation of \( \text{He}_2(a^3\Sigma_u^+) \) molecules with ionizing radiation and the frequency down-conversion of the resulting EUV light to blue light at about 440 nm using tetraphenyl butadiene (TPB), an efficient frequency down-converter of EUV radiation. A thorough study of the fluorescence efficiency of this and other such fluors as well as the techniques we use to make thin scintillating films is published elsewhere [32].

II. MEASUREMENTS USING A \( \beta \) SOURCE

A diagram of the fiber-based apparatus is shown in Fig. 1. Briefly, \( \beta \) particles from a radioactive source cause scintillations within the liquid helium. This EUV light impinges on the sides of the cell, which are coated with TPB. The emitted blue light is reflected within the cell until it is absorbed by wavelength shifting fiber. A portion of the green light is then trapped in the fiber and travels out of the cell to be detected via a photomultiplier tube.

The experimental cell is hung vertically along the cylindrical axis of a standard metal cryostat. The main body of the cell is a 114-cm-long tube of epoxy coated G-10 plastic, with a 41-mm outer diameter and a 1.6-mm-thick wall. This tube is connected at the bottom by an indium O-ring seal to a copper end cap. This end cap provides a thermal link from the liquid helium surrounding the cell to the inside of the cell.
itself. The cell is first evacuated and the cryostat filled with liquid helium. Then helium gas from the boiloff of a storage Dewar is condensed into the cell. The temperature of the liquid helium within the cell is controlled by pumping on the helium outside the cell and monitored by measuring the helium vapor pressure within the cell.

Helium molecules are created using a 100-nCi \( ^{36}\text{Cl} \) \( \beta \) source, originally chosen by us to closely mimic the \( \beta \) decay spectrum of the neutron. This isotope decays predominantly by electron \( \beta \) decay, with an end-point energy of 763 keV. The activity of the source is quite small; we estimate that no more than 2000 \( \beta \) particles per second enter the helium. The source is held facing down and \( \beta \) particles travel on average 5 mm through the liquid. Normally held in the center of the active detection region of the cell, it can be moved mechanically in less than 1 s into a small copper cup at the bottom of the cell, well out of the detection region.

The inner wall of the experimental cell is lined with a 1.6-mm-thick sheet of expanded Teflon, upon whose inner surface is evaporated a thin (~0.2-mg cm\(^{-2}\)) layer of TPB. Coiled inside this Teflon tube are two Y11 frequency down-converting optical fibers, wound in a helix with loops spaced approximately 6 mm apart [33]. These fibers absorb in the blue (absorption peaked at 430 nm, width 75 nm) and emit in the green (emission peaked at 490 nm, width 70 nm). About 10% of the emitted green light is trapped within the fiber. Half of this trapped light travels up the fiber and out of the cell. The other half travels down to the end of the fibers, where it leaves the fibers and is lost. Of the light that travels up the fibers, about 30% is lost through attenuation in the fiber. The fibers pass through vacuum feedthroughs to room temperature [34]. Light from the fibers is detected using a cooled Hamamatsu R943-02 photomultiplier (quantum efficiency of 19% at 500 nm and \( \approx 1 \) Hz dark count rate). Light that exits the fiber ends is focused onto the photocathode with about 80% efficiency using a 10-mm-diam optical quality ball lens. Single photoelectron pulses from the photomultiplier anode are counted and binned in time. We estimate a total conversion efficiency of EUV photons to single photoelectrons in the photomultiplier to be between 0.04% and 0.14%.

At the beginning of each run, the source is placed in the middle of the cell. The source is then mechanically removed from the detection region and the decay of counts is recorded. The phosphorescence spectrum, with a constant 42-Hz background level subtracted, is shown in Fig. 2. The measured decay is not purely exponential; this will be discussed below.

We checked that this slowly decaying signal originates from processes within the helium by performing runs in which blue light (from a light-emitting diode) or ultraviolet light (from a UV lamp) were shone into a liquid helium filled cell. Turning off the light resulted in a sharp drop in photomultiplier tube counts; the signal dropped to a constant background level within our timing bin size of 100 ms.

**III. MEASUREMENTS USING NEUTRON ABSORPTION BY \( ^{3}\text{He} \)**

The existence of helium phosphorescence has been confirmed using a different setup, which uses a detector made of an acrylic tube that is coated on its inner surface with a thin layer of TPB doped polystyrene [32]. The tube is filled with helium that is doped with \( ^{3}\text{He} \). Neutrons are introduced into the cell by means of a neutron beam and are absorbed by the \( ^{3}\text{He} \), which results in proton and triton emission with 764 keV of total kinetic energy. This decay ionizes the helium, causing subsequent recombination and EUV scintillation. The EUV light is down-converted to blue light by the transparent layer of TPB-doped polystyrene and the emitted light is guided within the acrylic tube wall to light guides and a photomultiplier tube. This detection scheme used here is more efficient than the method used in the previous setup. This allows us to distinguish light in the main pulse (created largely by singlet molecule decay immediately upon neutron absorption) from single photoelectron afterpulses (created by triplet molecule decay). When the neutron beam is turned off, the main pulses abruptly stop, but the afterpulses decay with time, with a lifetime that is similar to that observed in the previous experiment. The decay is not perfectly exponential; we attribute deviation from exponential decay at early times (\( \approx 5 \) s) to bilinear interactions. If in spite of the non-exponential nature of the decay curves we fit an exponential to a limited region we arrive at the values shown in Table I. These estimates of the observed decay times are consistent with the results of the \( \beta \) source experiments.

**TABLE I.** Molecule lifetimes measured by exciting helium through the reaction. \( T \) is the sample temperature, \( \rho \) is the helium density, and \( \tau \) is an estimate of the phosphorescence decay lifetime (see the text).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T ) (K)</th>
<th>( \rho ) (cm(^{-3}))</th>
<th>( \tau ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-mbar He gas</td>
<td>4.2</td>
<td>( 8.6 \times 10^{20} )</td>
<td>8</td>
</tr>
<tr>
<td>750-mbar He gas</td>
<td>4.2</td>
<td>( 1.3 \times 10^{21} )</td>
<td>9</td>
</tr>
<tr>
<td>1000-mbar He gas</td>
<td>4.2</td>
<td>( 1.7 \times 10^{21} )</td>
<td>12</td>
</tr>
<tr>
<td>liquid helium</td>
<td>4.2</td>
<td>( 1.9 \times 10^{22} )</td>
<td>14–15</td>
</tr>
<tr>
<td>liquid helium</td>
<td>1.8</td>
<td>( 2.2 \times 10^{22} )</td>
<td>14–15</td>
</tr>
</tbody>
</table>

**FIG. 2.** Count rate \( N \) of detected \( ^{3}\text{He}(a^{3}\Sigma_{u}^{+}) \) decays versus time. A \( ^{36}\text{Cl} \) \( \beta \) source is placed in the center of the detection region and then removed in a time \( \Delta t < 1 \) s. This measurement was performed at a temperature of 1.8 K and resulted in a measured decay rate \( \tau = 13 \pm 2 \) s.
IV. DISCUSSION

The roton collision limited diffusion coefficient [35] for the triplet helium molecules in liquid helium is about $3 \times 10^{-4}$ cm$^2$s$^{-1}$ at a temperature of 1.8 K. As a result, the molecules travel less than 1 mm before decaying and are unlikely to hit the walls of the cell. Molecules could, however, hit the stainless-steel rod that holds the $\beta$ source used in one of the experiments, producing a decay curve that is not a pure exponential.

A possible explanation for the nonexponential behavior at early times is extremely slow vibrational relaxation of the triplet molecules. Since the calculated radiative lifetime of the molecule in vacuum decreases with increasing vibrational quantum number [22], a significant population of vibrationally excited molecules surviving to long times would clearly contribute to nonexponential decay. Vibrational relaxation of the molecules has already been found to be very slow in the liquid; Eltsov et al. [17] measure a ($v = 1$) to ($v = 0$) vibrational relaxation time of $0.3 \pm 0.2$ s. Since our detection method cannot differentiate between molecules of different vibrational states, the measured phosphorescence lifetime can only be strictly interpreted as a lower limit on the lifetime of the longest-lived molecular state in liquid helium.

The decay curves could also be rendered nonexponential by two-body recombination with other metastable helium molecules. In a given ionization track, the molecule density can be quite high relative to the surrounding helium and the resulting Penning ionization could lead to singlet molecule formation. This could lead to nonexponential fluorescence timing curves, especially at short times or high liquid temperatures at which diffusion is slow.

It is not expected that different ionization tracks interfere significantly in these experiments since the sources of radiation that we use are relatively weak. The distance between tracks is therefore large and the molecular density in the overlap of two expanding tracks is too small to result in many bilinear reactions.

V. CONCLUSION

Radiative decay of the He$_2$(a $3\Sigma_u^+$) has been continuously monitored in a low-density regime using two significantly different methods. Neither apparatus used in this study was originally designed or built with the purpose of studying these molecules and several relatively simple improvements could be made. Obviously, improved statistical precision in the measurement of the lifetime in liquid helium could be accomplished by using a more intense source of ionizing radiation. The metastable densities achieved in this experiment are much less than the densities produced by other techniques where Penning ionization dominates the decay process. A better understanding of how interaction between species in the ionization track influences phosphorescence behavior is desirable.

The potential exists to use these molecules in the investigation of the structure of superfluid helium. It is possible that these molecules will interact with vortices in liquid helium [10]. Because the molecules will probably quench when they hit a wall, the lifetime of the molecules in low-temperature superfluid helium could be heavily influenced by such vortex trapping.

Another simple experiment would involve polarization of He$_2$(a $3\Sigma_u^+$) molecules through application of a large magnetic field. Such polarization has never yet been observed for these molecules because the magnetic relaxation time is longer than the previous maximum observation time [16]. By monitoring the molecule population using wave-shifting methods and photon counting, the effect of a large magnetic field could be extended to much longer time scales. Large initial helium molecule densities could be created with an intense electron beam or a pulsed high-voltage discharge. Two-body loss through Penning ionization would be suppressed by the magnetic field [23] and the effects of polarization could be observed by monitoring the phosphorescence decay.

There also exists the intriguing possibility of magnetically trapping of this molecule within the "mechanical vacuum" of pure superfluid $^4$He. The magnetic moment of the He$_2$(a $3\Sigma_u^+$) state is two Bohr magnetons. Using a superconducting magnetic trap, molecules could be trapped in large numbers if created in cold liquid helium ($T = 0.4–0.6$ K). At this temperature, the diffusion loss to the walls will be small. As the molecules thermalize with the liquid helium, the temperature of the liquid could be lowered, further cooling the trapped molecules. For temperatures less than approximately 0.1 K, the trapped molecules would thermally decouple from the helium bath. Cooling by evaporation to temperatures much lower than that of the bath could be possible. Indeed, it is possible that this "buffer-liquid loading" technique could be applied to other paramagnetic atoms and molecules [36,37]. The trapped population could be studied with laser spectroscopy in either absorption or fluorescence.

The molecules could also be trapped using buffer-gas loading, a method demonstrated to magnetically trap neutral species [37]. In this case the buffer gas, as well as the loaded species, would be $^3$He gas at low temperature ($\sim$ 300 mK). Metastable molecules could be made in the gas with a discharge or ionizing radiation [13,20]. They would then thermalize with the buffer gas and be trapped. Detection of molecular decay could be accomplished through frequency down-conversion, just as we have shown can be done with high efficiency in the liquid and cold gas.

The existence of this slow decay component is relevant to the design of experiments that propose to use liquid helium as a scintillating medium. For example, for the neutron lifetime experiment [18], such long-lived single-photon fluorescence could complicate data analysis. This work has indicated the importance of having a high-efficiency detection system so that the prompt scintillation burst occurring immediately upon neutron $\beta$ decay will result in many photoelectrons in the detector photocathode (thus eliminating the effects of the one-photon triplet scintillation).

Further study of He$_2$(a $3\Sigma_u^+$) decay is clearly warranted. Measurements are currently being conducted at lower temperatures and shorter times. A complete description of the time dependence of the phosphorescence extended from nanoseconds to milliseconds will be presented shortly. These experiments will allow a more thorough understanding of ionizing radiation induced scintillations in liquid helium. Another measurement of interest is the determination of the
He$_2$(a $^3\Sigma_u^+$) decay rate in vacuum. This could be compared with the decay rate in the liquid at various temperatures and pressures, thus extracting the influence of the liquid in the decay rate. More precise theoretical calculation of the radiative lifetime is needed for better comparison of theory with experiment for this unique metastable molecule.

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[33] Y11 scintillating fiber purchased from Kuraray Co., Ltd. 8F, Mauzen Nuilding, 3-10, 2-Chome, Nihonbashi, Chuo-ku, Tokyo, 103-0027, Japan.