Luminescence of Oxygen Atoms Stimulated by Metastable Helium at Cryogenic Temperatures

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We present investigations of the afterglow of oxygen-helium gas mixtures at cryogenic temperatures. The cooling of a helium jet containing trace amounts of oxygen after passing through a radio frequency discharge zone led to the observation of strong emissions from atomic oxygen. The effect results from the increasing efficiency of energy transfer from metastable helium atoms and molecules to oxygen impurities in the cold dense helium vapor. This effect might find an application for the detection of small quantities of the impurities in helium gas.

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Over the years, many studies have indicated the importance of the transfer of energy from metastable helium to various atoms and molecules. These studies have been performed in gas discharges as well in the afterglow from these discharges over a range of pressures and temperatures [1–7]. Enhancement of the luminescence from impurity species was observed due to the efficient transfer of energy from metastable helium atoms and molecules in Penning ionization (PI) processes [8]. All earlier work on afterglow emission has been performed at temperatures above 77 K.

In the last few decades, remarkable progress has been made in studies of atoms and molecules at temperatures less than a few kelvin [9,10]. Cold metastable helium atoms and molecules were studied in the gas phase, in small helium droplets, and in liquid helium [11–15]. Recently, studies of the collision dynamics of an ultracold (80–200 μK) spin-polarized mixture of metastable helium (He^*) and rubidium atoms have been performed [16]. Cold helium gas was used for cooling a variety of impurity atoms and molecules [17]. The advantages of merged beams for slow molecular collision experiments were discussed recently [18]. In experiments with two merged cold beams, Penning ionization reactions of argon and molecular hydrogen with metastable helium were studied. A sharp absolute ionization rate increase and oscillations were observed when the difference in energy of the beams was changed in the range between a few degrees kelvin and 10 mK [19].

In the early 1970s, a method of injection of a gaseous helium jet containing a small admixture ($\sim 1\%$) of impurities passing through a radio frequency discharge into superfluid helium (He II) was developed [20]. As the jet descends into the helium (Fig. 1), the helium and impurity atoms in the jet are cooled efficiently by the dense helium vapor; the temperature of the atoms in the jet is decreased from 150 K near the orifice to 1.4 K near the surface of the He II. The process of cooling occurs over a distance of ~ 2.5 cm. This method was successfully used for the injection of nanoclusters of impurities into He II [21]. In the present work, we found that reducing the concentration of impurities in a helium gas jet from 10^{-2} to 10^{-5} allows one to avoid the impurity clustering process in the cold helium gas and to enter the regime for studying cold atoms and molecules in the gas phase. Via this method, the impurities and helium atoms in the jet are moving in same direction in the dense cold helium gas. During the cooling process, the velocities of atoms in the jet are reduced substantially. Relative velocities between helium atoms and impurities become negligible, and it is possible to study the processes of energy transfer and chemical reactions in the gas phase at low temperatures. Thus, a study of the energy transfer from metastable helium atoms and molecules to the

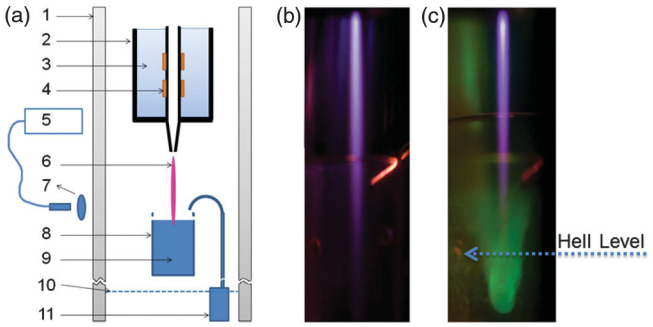

FIG. 1 (color). (a) Scheme of the setup for the spectroscopic study of the afterglow in cold helium vapor: 1, helium dewar; 2, quartz tube; 3, space filled with liquid nitrogen; 4, electrodes for radio frequency discharge; 5, system for registration of optical spectra; 6, gas jet; 7, lens; 8, quartz beaker; 9, superfluid helium in the beaker; 10, level of liquid helium in the main helium bath; and 11, fountain pump. (b) Photo of the jet when liquid helium is absent from the beaker. (c) Photo of the jet when the beaker is filled with liquid helium. The arrow shows the level of He II in the beaker. Note that the jet creates a crater in the helium surface, as evidenced by the cone of green light emanating from the vapor below the indicated helium level.

impurities present in the jet can be made at low relative velocities. In this work, we have studied the influence of temperature on the spectra of oxygen atoms excited by the metastable helium atoms and molecules. For thermalization of oxygen atoms by cold helium gas from 150 K to a temperature of 1.4 K, approximately 30 collisions are needed [17]. Near the surface of He II in a cold dense helium gas, oxygen atoms undergo 300 collisions in 1 μs [22], so that all atoms in the jet should be effectively thermalized. It was found that the intensities of oxygen atomic lines were increased drastically as the jet was cooled to temperatures $\sim$1.4 K. A striking example of this effect is the intense green glow associated with atomic oxygen lines shown in Fig. 1(c).

The overall experimental arrangement is shown in Fig. 1(a). The gas mixture consisting of helium and small concentrations of oxygen enters the helium bath region via a quartz capillary cooled by liquid nitrogen. Electrodes placed around the quartz capillary provide a 53 MHz, 90 W radio frequency discharge to form metastable helium atoms and dissociate the oxygen molecules. In the experiment, we used research grade helium from Linde Electronics & Specialty Gases with 99.9999% purity. The oxygen content in the discharge space (1 ppm) results from contamination of the helium gas. The content of oxygen in the oxygen-helium mixture can be adjusted by adding trace amounts of oxygen to the helium gas or by purifying the helium gas in a cold trap at liquid helium temperatures. Under a small gradient of pressure ($\Delta p \sim 2$ Torr) between the discharge zone and the cryostat, a well-formed jet is created after the passage of the gas mixture through a small orifice (0.75 mm diameter) in the quartz capillary [Figs. 1(b) and 1(c)]. The flux of 5×10^{19} atoms/s of the oxygen-helium mixture entering the cryostat is measured by a Brooks Instrument 5850E flow controller. A temperature of 1.4 K of the liquid helium in the cryostat is maintained by pumping the main helium bath and was measured by a germanium thermometer. A collection beaker was placed below the orifice with a distance of 2.5 cm between the orifice and the top of the beaker. The spectra of the gas jet afterglow were studied when the beaker was empty and also when the beaker was filled with superfluid helium by the fountain pump shown in Fig. 1. A photo of the jet with no He II in the beaker is shown in Figs. 1(b) and 1(c) shows the helium jet when the beaker was filled with superfluid helium. We studied the dependence of spectra on the pressure of helium gas in the helium dewar by varying the pumping speed on the main bath. In this experiment, the light of the jet afterglow was collected near the top of the collection beaker at a distance of 2.5 cm below the orifice by a lens which focused it onto the end of an optical fiber [see 7 in Fig. 1(a)]. The fiber splits into two separate channels, one of which was attached to an Ocean Optics spectrometer and the other to an Andor Shamrock SR500 spectrograph. The Ocean Optics spectrometer

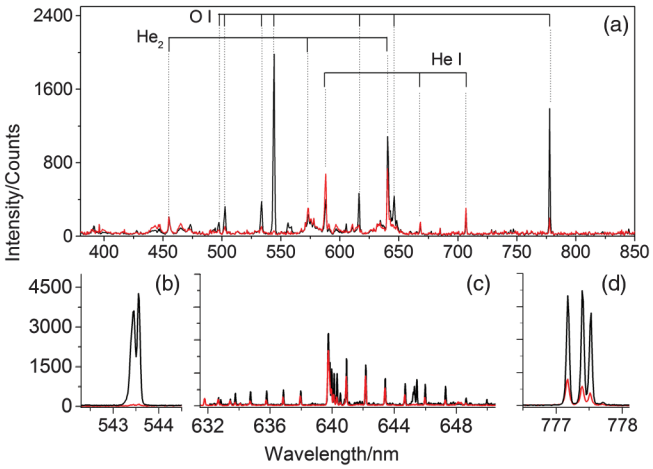

FIG. 2 (color). (a) Spectrum of the helium jet with traces of oxygen, when the beaker is empty (red curve) and after it is filled with He II (black curve). Light was collected at the top of the beaker. (b) Spectrum of the atomic oxygen lines near 543.6 nm. (c) Spectrum of the He_2 band near 639.6 nm. (d) Spectrum of the oxygen lines near 777.4 nm.

(HR2000+) was used for detecting spectra over a broad wavelength range (200–1100 nm) with spectral resolution 1.3 nm, whereas the Andor spectrograph with a Newton EMCCD camera was used to obtain high resolution (0.05 nm) spectra.

Figure 2(a) shows the emission spectra observed by the Ocean Optics spectrometer for the cases when the collection beaker was empty (warm jet) and when it contained liquid helium (cold jet). Both spectra contained atomic helium lines and molecular helium bands as well as the atomic oxygen lines listed in Table I. When the beaker was empty and the level of liquid helium was far from the orifice, we had a warm jet, with helium atomic lines and molecular bands dominating the spectra, and with only three very weak oxygen atomic lines present. When liquid helium was introduced into the beaker, the oxygen lines and the molecular helium lines became much stronger [see Fig. 2(a)]. In particular, the 533 nm line and the strong 543.6 nm line of oxygen were present only when the beaker contained liquid helium. High resolution spectra obtained

TABLE I. Identification of observed lines and bands shown in Figs. 2 and 4.

λ, nm	Transition	λ, nm	Transition
844.6	O I ($3s^3S$-$3p^3P$)	728.3	He I ($2p^1P$-$3s^1S$)
777.4	O I ($3s^5S$-$3p^5P$)	706.5	He I ($2p^3P$-$3s^3S$)
645.4	O I ($3p^5P$-$5s^5S$)	667.9	He I ($2p^1P$-$3d^1D$)
615.7	O I ($3p^5P$-$4d^5D$)	587.6	He I ($2p^3P$-$3d^3D$)
543.6	O I ($3p^5P$-$6s^5S$)	501.6	He I ($2s^1S$-$3p^1P$)
533.0	O I ($3p^5P$-$5d^5D$)	639.6	$He_2(d^3\Sigma_u^+ \rightarrow b^3\Pi_g)$
502.0	O I ($3p^5P$-$7s^5S$)	573.2	$He_2(f^3\Delta_u \rightarrow b^3\Pi_g)$
496.8	O I ($3p^5P$-$6d^5D$)	454.7	$He_2(h^3\Sigma_u^+ \rightarrow b^3\Pi_g)$

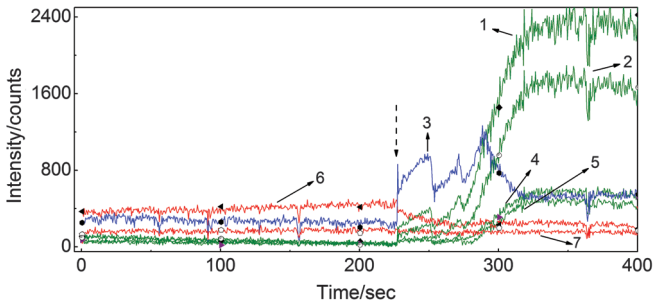

FIG. 3 (color). Dynamics of the intensities of atomic oxygen (green curve: 1, $\lambda = 543.6$ nm; 2, $\lambda = 777.4$ nm; 4, $\lambda = 615.7$ nm; 5, $\lambda = 533.0$ nm) and helium (red curve: 6, $\lambda = 587.6$ nm; 7, $\lambda = 706.5$ nm) atomic lines and also molecular helium bands (blue curve: 3, $\lambda = 639.6$ nm) during the filling of He II in the beaker. (The arrow at $t = 227$ s shows the moment when helium starts to fill the beaker.)

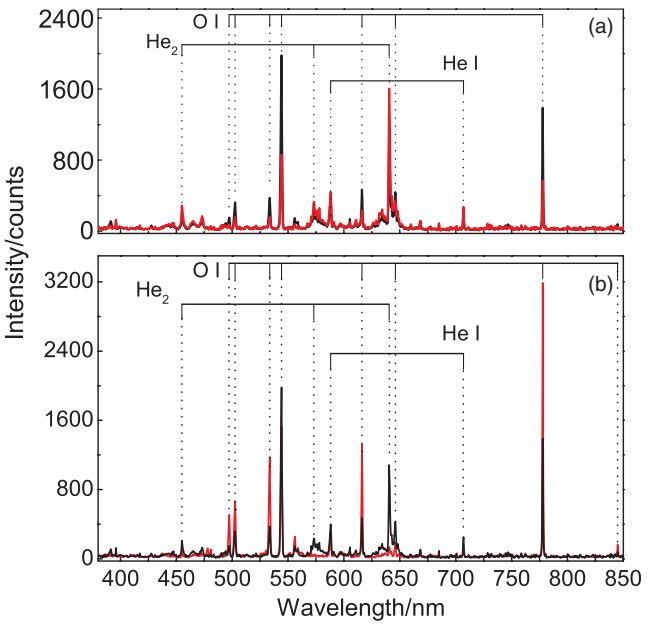

FIG. 4 (color). (a) Comparison of the spectra of helium jets with the 1 ppm trace of oxygen (black curve) and the spectra of helium jets after purification of the helium gas in the trap cooled to liquid helium temperature (red curve). (b) Comparison of the spectra of helium jets with the 1 ppm trace of the oxygen (black curve) and the spectra of helium jets with the 25 ppm trace of the oxygen (red curve).

by the Andor spectrometer in the regions around 543.6, 639.6, and 777.4 nm, respectively, are shown in Figs. 2(b)–2(d). The fine structure obtained helped to definitively identify the spectral lines observed. The dramatic effect on the intensities of the spectral lines upon filling the beaker with superfluid helium is plotted in Fig. 3. The sudden increase in the intensities of the atomic oxygen and molecular helium lines occurs as liquid helium is added, whereas the intensities of the atomic helium lines are almost insensitive to the addition of liquid helium.

In order to understand the influence of oxygen impurities in the spectra, a comparison was made between the spectrum obtained for the normal helium jet (with 1 ppm oxygen) and the spectrum of the jet corresponding to purified helium gas, as shown in Fig. 4(a). Figure 4(b) shows a comparison between the spectrum of the normal helium jet and the spectrum for a helium jet which contains 25 ppm oxygen. The removal of some of the oxygen from helium via purification resulted in a substantial decrease in the intensity of the oxygen lines in the spectrum and in an increase of the He_2^* band intensities. On the other hand, the addition of oxygen to the helium gas led to a significant increase in the intensity of the oxygen lines. The intensity of the He_2^* bands decreases with the increase of oxygen content in the jet. The intensity of the observed atomic He lines is not influenced by the variation of oxygen content.

The spectra shown so far were all obtained at the pressure of helium vapor in the cryostat of 2 Torr. It was found that as the pressure increased up to 12 Torr, the intensity of all of the spectral lines gradually decreased.

The main effect observed is a large enhancement of the oxygen line intensities when the collection beaker contained superfluid helium, which provided efficient cooling of the oxygen-helium jet by the dense ($n_{He} \sim 10^{19}$ cm^{-3}) cold helium vapor.

Helium gas is a simple system, but under excitation, it exhibits a rich array of processes involved in the energy transfer. A detailed scheme of reaction pathways occurring at 4.2 K in a helium plasma was determined during the irradiation of helium gas and its afterglow [14]. Ionic helium species play a very important role in the energy circulation in plasmas of pure helium [14]. They are the main precursors of highly excited helium atoms and molecules observable in the jet (Fig. 2). Ionic helium species are formed in the helium afterglow as a result of processes with participation by metastable helium atoms and molecules present in the jet. In our experiments, the average travel time of an atom or molecule from the orifice to the surface of superfluid helium is of order 100 μs. This means that all atoms and molecules excited in the discharge zone with lifetimes in the range 14–1000 ns should emit light only in the discharge zone and near the orifice. Therefore, the observed emission spectra well below the orifice resulted from processes taking place in the jet. A decrease in the temperature of the jet led to an increase in the intensity of the He_2 molecular bands. The helium and oxygen atoms and the helium molecule energy levels as well as the optical transitions observed in this work are presented in Fig. 5. The energies of ionization potentials (I.P.) for O and He atoms as well for a He_2 molecule are also shown in Fig. 5.

It is well known that metastable helium species easily excite, dissociate, and ionize any admixtures of impurity species in helium plasmas and in the afterglow [4]. The process of the Penning ionization of molecular oxygen by helium atoms and molecules has been intensively studied.

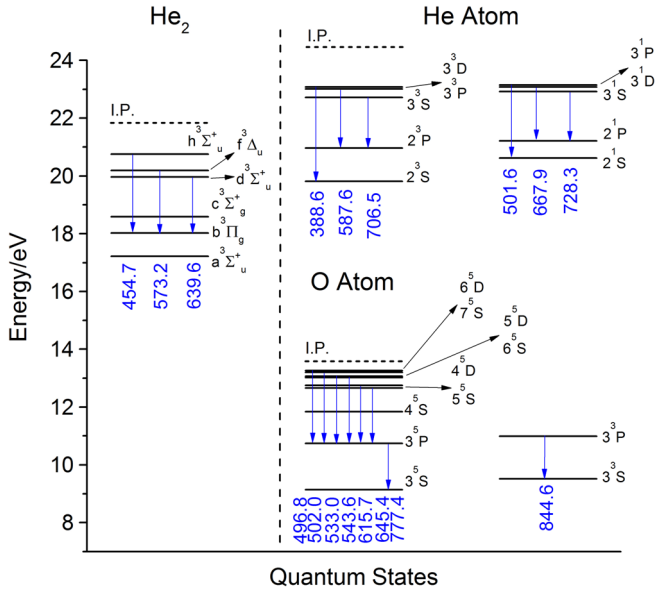

FIG. 5 (color online). Energy transitions between quantum states of molecular and atomic helium, and atomic oxygen with a wavelength of emitted light.

In our experimental condition, the very low content (1–25 ppm) of O_2 molecules in helium gas is completely dissociated in the discharge zone; therefore, all of the oxygen should be in an atomic state in the expanded helium jet. The Penning ionization process of oxygen atoms by helium atoms and molecules is a dominant process in the jet. The formation of highly excited states of oxygen atoms is a result of the Penning ionization of oxygen atoms by helium atoms and molecules followed by electron-oxygen ion recombination. The temperature dependence of the PI process is not well understood, and additional experimental and theoretical work is needed. Qualitatively, the effect of large enhancement of the oxygen line intensities and the appearance of new even more intense oxygen lines in the dense cold helium vapor observed in this work might be explained by an increase in density of the oxygen and metastable helium atoms and molecules as the jet enters the region of dense helium vapor near the surface of liquid helium. The process of the PI of O atoms should be much more efficient in this region. Another possible factor for the enhancement of the oxygen line intensities is the increasing cross sections of Penning ionization processes of oxygen atoms by metastable helium atoms and molecules at low temperatures. In our experiments, the temperature of the atoms and molecules in the jet before entering bulk superfluid helium is close to 1.4 K, and both reacting species, helium and oxygen, are moving in the same direction, representing a situation with cold merged beams, which provides an increasing time for the interaction of reagents. An example of the consequences of these increased interaction times of the slow beams at low temperatures was the observation of quantum effects during the PI process [19].

In the region of cold and dense helium gas, the recombination rate of O atoms is increasing, and therefore, traces of O_2 molecules could be created in the lower part of the jet. The interaction of metastable helium atoms and molecules will lead to the formation of superexcited O_2^* molecules with energies higher than the first ionization limit [23]. An O_2^* molecule could directly dissociate via a curve crossing interaction yielding at least one O atom in a highly excited state and another in the ground state. Another scenario is for a superexcited O_2^* molecule to be autoionized and to form an O_2^+ ion, which subsequently captures an electron and then dissociates into an O atom in the ground state and an O atom in a highly excited state [5,23]. Both processes effectively dissociate O_2 molecules, thus providing oxygen atoms in highly excited and ground states.

The bright green triplet lines of 543.6 nm are emitted from the state $6s^5S$ which has a long decay time (0.259 μs), whereas the final state lifetimes corresponding to these transitions are much shorter ($\sim$ 27 ns). Thus, it might be worthwhile to investigate possible laser action at 543.6 nm under our experimental conditions.

All spectral lines and bands observed in this work correspond to oxygen and helium atoms and helium molecules in the gas phase. We did not observe any sign of the recombination or clusterization of oxygen atoms. This means that we had realized conditions for the creation of an intense cold gas phase oxygen-helium beam in which the flux of oxygen atoms is of order 3×10^{14} atoms/s. This flux is almost 2 orders of magnitude larger than that obtained by using a buffer helium gas method [17,24]. In our experiments, this flux is injected into the volume of superfluid helium, but it is possible to realize a geometry in which the jet will pass the region of cold helium gas near the surface of He II and enter a high vacuum region for further investigations and applications.

In conclusion, the effect of the substantial enhancement of the intensity of atomic oxygen luminescence by the cooling of a helium jet with small traces of O atoms by helium vapor to 1.4 K was observed. The effect was explained by effective energy transfer from metastable helium atoms and molecules to oxygen atoms and molecules under cryogenic conditions. This effect might provide a practical method for the detection of small traces of impurities in helium gas.

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