Optical spectra of the triplet molecules $^4He_2^*$ in superfluid helium in a magnetic field

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The absorption spectra of the transitions $a\rightarrow b$ and $a\rightarrow c$ of the triplet excimer molecules $^4He_2^*$ in superfluid helium have been investigated in the range of temperatures 1.4–2.1 K and in magnetic fields of 0–5.5 T. The molecules were generated as a result of recombination in opposite streams of negative and positive ions. The lifetime of the excimers was determined by the rate of their mutual recombination. It was found that even at the maximum lifetime of 50 μs the molecules were not completely thermalized with respect to the rotational and vibrational degrees of freedom. The vibrational relaxation time was determined. It was found that the rotational relaxation is significantly faster than the vibrational relaxation. No slowing down of the excimer recombination in the magnetic field was found for any of the experimental conditions. This may be due to a long magnetic relaxation time; if so, the maximum lifetime of the molecules in our experiments gives a lower bound for this time. © *1995 American Institute of Physics.*

1. INTRODUCTION

Interest in the electron excited states in condensed helium first arose in connection with the discovery by Surko and Reif[1] of so-called neutral currents. Ionizing liquid helium with a radioactive source and studying the currents through the experimental cell in the presence of various electric fields, they discovered that a new type of excitation of helium exists: A neutral type, which, however, has an energy sufficient for the ionization of helium. As a result of a series of subsequent studies, including spectroscopy,[2] these excitations were identified as triplet excimer molecules of helium.

The excimer molecules $^4He_2^*$ exist by virtue of the presence of a fairly deep minimum ≈ 2 eV of the interaction energy of the helium atoms in their ground and excited states at a distance of ≈ 1 Å (Ref. 3). As is well known, for the first excited triplet state 2^3S of atomic helium the transition to the ground state is very strongly forbidden, and it is metastable with a uniquely long lifetime of ~ 8000 s (Ref. 4). For the lowest triplet state $a^3\Sigma_u^+$ of the excimer molecules, the situation is similar, and although the transition in the molecule is allowed to a significantly greater extent in consequence of the spin-orbit and interatomic electrostatic interaction the radiative lifetime of the molecules in such a state is completely macroscopic: ~ 10 s (Ref. 5).

In condensed helium, on the other hand, it is precisely the triplet molecules that live the longest and therefore are the most important type of neutral electronic excitation. This is due to the fact that, as a consequence of the attraction to the atom in the ground state, an excited helium atom forms a molecule rather quickly:

$$\mathrm{He}(2^3S)+\mathrm{He}(1^1S)\rightarrow \mathrm{He}_2^* .$$

The characteristic time for this process in liquid helium is $\sim 10^{-5}$ s (Ref. 6).

Such molecules in condensed helium are interesting objects, different from similarly investigated charges and isotopic impurities, and they are a possible candidate for a new low-temperature quantum-mechanical system. The most important properties of these molecules established so far are the following:[6–8]

1. The main source of the triplet molecules in condensed helium is the recombination of positive and negative ions, for example:

$$e^- + \mathrm{He}^+ + \mathrm{He} \rightarrow \mathrm{He}_2^*$$

(other processes are also possible, including, for example, He_2^+, etc.). This follows from the observation of the dynamics of the spectral lines corresponding to the different atomic and molecular states of helium at the times of switching on and off of the source of ionization.[6] An estimate of the concentration of molecules from the observed spectrum for different methods of ionization in liquid and solid helium[6,7,9] indicates that the probability of the formation of a molecule in an ion recombination event is close to one.

2. The spectra of electronic transitions and their vibrational and rotational structure for excimers in condensed helium are practically the same as the spectra in the gaseous phase. In order to explain this fact, Hickman and Lane[10] suggested that triplet molecules (and atoms) are localized in liquid helium in bubbles in the same way as electrons. The reason for the formation of the bubbles is the repulsion of the outer excited electron away from the surrounding helium atoms. As a consequence of the interaction of this electron with the ion core, the diameter of such a bubble is ~ 10 Å, i.e., significantly smaller than for a free electron. Working on this assumption, Hickman and others[11] calculated the widths of the lines and the shifts relative to the vacuum values for a series of atomic transitions and obtained satisfactory agreement with experiment. Similar calculations were not carried out for the molecules; however, it can be assumed that in view of a similar structure (a compact ionic core and excited outer electron) the situation for the molecules is similar.

3. Despite the comparatively long radiative lifetime, the real lifetime of the molecules $^4He_2^*$ in superfluid helium with

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concentration necessary for the optical measurements is significantly shorter and is limited by the mutual recombination of the molecules:[6]

$$He_2(^3\Sigma_u^+)+He_2(^3\Sigma_u^+)\begin{array}{l}\nearrow 3He(1\,^1S)+He^+ + e^-,\\ \searrow 2He(1\,^1S)+He_2^+ + e^-.\end{array}\qquad (1)$$

This is the thresholdless process of Penning ionization. It occurs with a probability close to one when the molecules in the process of diffusive motion approach to separations r_0 of the order of the bubble radius.[5] The characteristic decay time is $\tau=1/\alpha n$ (n is the concentration, $\alpha\approx 4\pi r_0 D$ is the recombination coefficient, and D is the diffusion coefficient for triplet molecules). This process is very effective: near the λ point, the lifetime is $\tau\sim 1$ ms at concentrations $n\sim 10^{13}$ cm^{-3}. When the temperature is lowered, it decreases because of the acceleration of diffusion.[6] In solid helium, the lifetime of the molecules was approximately 15 s for all concentrations up to 10^{15} cm^{-3}. This was interpreted as the radiative lifetime.[8] Such a short lifetime in liquid limits the possibilities of research into excimer molecules and leads to the need to dissipate a high power to ionize the helium, the molecules remaining in highly excited nonthermalized states.

In 1991, Konovalov and Shlyapnikov[5] showed that the process (1) brought about by exchange interaction is forbidden if the original molecules are completely polarized: it is easy to see that the initial spin in this case will be equal to two, while the final one will not exceed one. Decay through the channel (1) will only occur when weak dipole interaction is allowed for and will be significantly slower: the authors[5] estimated the time of decay for $n\sim 10^{17}$ cm^{-3} as $\tau\sim 1$ s in the case of complete polarization. The aim of our experiment was an attempt to find the predicted slowing down of the recombination of the molecules in liquid when polarized in a magnetic field.

2. THE EXPERIMENT

A schematic representation of our experiment is shown in Fig. 1. As mentioned above, in order to obtain excimer molecules in condensed helium it is necessary to ionize it and let the charges recombine. Various methods of excitation of helium have been used in research into the molecules: a radioactive source,[1,8] a discharge near a point in a strong electric field,[9,12] and a high energy electron beam.[6] In the majority of cases, the triplet molecules are formed inside the region of the excitation of helium together with a great number of different excited atomic, ionic, and molecular states of helium. This leads to the presence in the spectra of a large number of additional lines and also to the possibility of interaction between the triplet molecules and other atomic and ionic states. We used a method which does not have this deficiency. In our experimental cell, two discharge points were set up opposite each other. With a high voltage between them, it was possible to extract ions of the corresponding sign from the discharge region near the points to the center of the experimental cell. At the same time, excimer molecules were formed as a result of the recombination of ions throughout the complete volume occupied by the current far from the region of excitation of helium near the points, which measured ~30 μm.[9] The discharge points were made from tungsten wire with a diameter of 0.2 mm by means of electrochemical etching in a KON solution (see, for example, Ref. 13). The radius of the curvature was checked in a scanning electron microscope and was approximately 0.1 μm. The distance between the points was varied in the range 3–4 mm, and the applied voltage was 5–9 kV. At the same time, the current through the cell could be varied in the range 200–500 nA. The calculations of the recombination of the charges in a very simple model allowed us to assume that the recombination would be almost complete in such geometry. Since there is a minimum stable current for the emission of charges from a point, which is particularly well expressed for positive ions, to permit operation at lower currents in our experimental cell we designed an arrangement with detachable metallic diaphragms with openings of differing diameters which carried away part of the current from the discharge points. For the modulation of the concentration of the excimers, the current through the cell was switched on and off with the frequency 1 Hz.

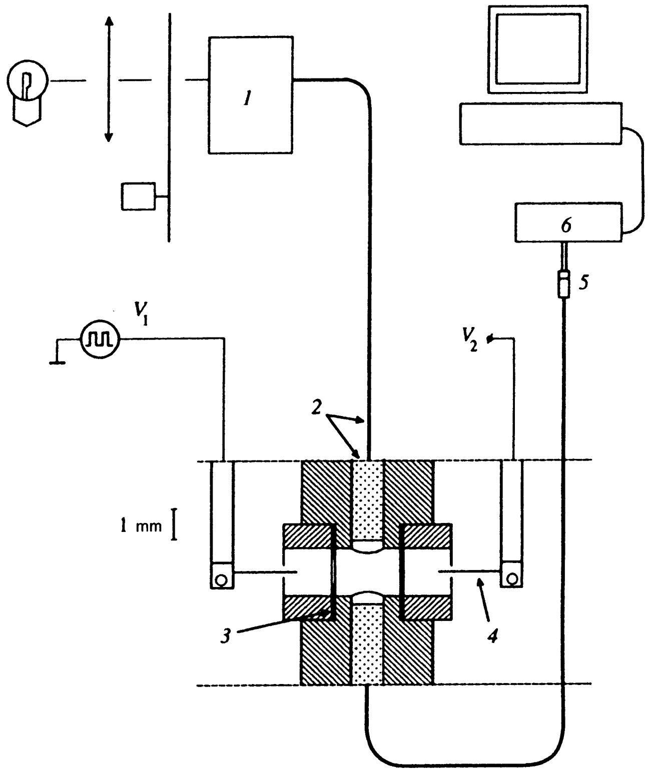

FIG. 1. Schematic representation of the experimental setup: *1*) lattice monochromator, *2*) light pipe, *3*) detachable diaphragm, *4*) discharge point, *5*) photodetector, *6*) the lock-in amplifier.

Molecules were detected on the basis of the absorption spectra in the center of the experimental cell. The light source for the optical measurements was a halogen lamp with a power of 100 W. After the mechanical chopper, the light was incident on a lattice monochromator. The width of the monochromator band was 30 Å near 1 μm and 60 Å near 2 μm, i.e., significantly narrower than the width of the observed spectra. After the monochromator, the light was incident on the experimental cell and was extracted to the pho-

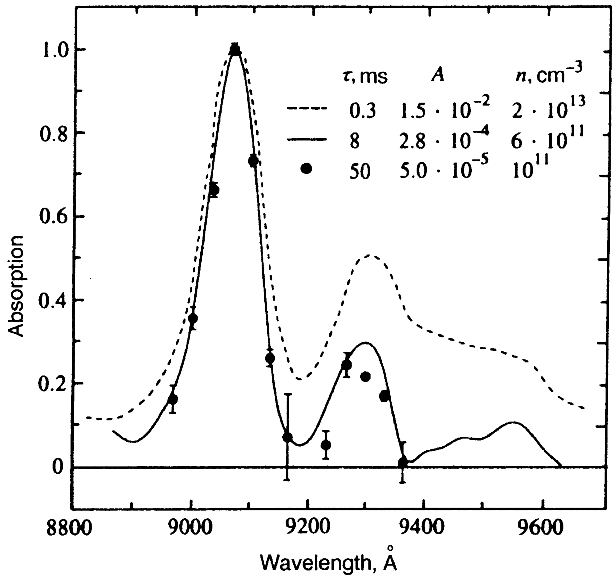

FIG. 2. Absorption spectra of the transition $a^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+$ measured at temperature 2.1 K in a zero magnetic field and normalized to the maximum absorption. The data for the lifetime 0.3 ms are taken from Ref. 6.

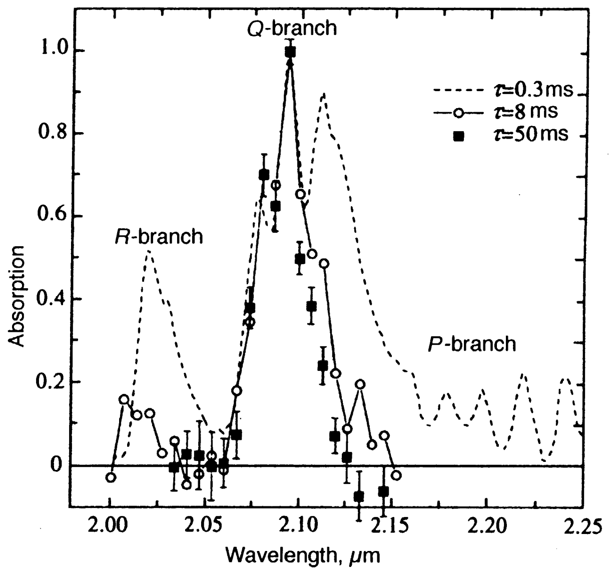

FIG. 3. Normalized absorption spectra for the transition $a^3\Sigma_u^+ \rightarrow b^3\Pi_g$. The conditions of observation were the same as for Fig. 2.

todetector through quartz light pipes with a diameter of 1 mm and a red transmission limit of 2.2 μm. In the experimental cell, the ends of the light pipes were secured at a distance of 2 mm from each other between the discharge points. A silicon photodiode was used as photodetector for measurements in the vicinity of 1 μm and a PbS photoresistor was used in the vicinity of 2 μm. After the photodetector, the signal was first detected at the frequency of the mechanical chopper, and after that at the frequency of the modulation of the current through the cell. The second detection was carried out digitally with the aid of a computer. The double modulation allowed a sensitivity to absorption better than 10^{-5} to be achieved.

A magnetic field of up to 5.5 T was generated by a superconducting solenoid.

3. THE ABSORPTION SPECTRA

The majority of the measurements were carried out at a temperature of 2.1 K, where the recombination coefficient of the excimers is at a minimum of $\alpha \approx 2 \cdot 10^{-10}$ cm^{-3}s^{-1} (Ref. 6). We studied the absorption spectra for the transitions $a^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+$ and $a^3\Sigma_u^+ \rightarrow b^3\Pi_g$ in wavelength ranges in the vicinity of 1 μm and 2 μm, respectively. The spectra that we obtained for the excimer lifetimes $\tau \approx 8$ ms and 50 ms are presented in Figs. 2 and 3. For comparison, the spectra from the Ref. 6 which correspond to $\tau \approx 0.3$ ms, are also shown. We determined the lifetime on the basis of the absorption in the maximum of the transition $a \rightarrow c$:

$$\tau = \frac{1}{\alpha n} = \frac{\sigma d}{\alpha A},$$

where A is the absorption, $d = 2$ mm is the path of the light in the experimental cell, and $\sigma = 2.4 \cdot 10^{-15}$ cm^2 is the absorption cross section, corrected to our line width (100 Å).

The structure of the spectra is similar to the structure observed in Ref. 6; however, we see an obvious decrease in the intensity of the transitions from excited rotational and vibrational levels. In addition, we did not see any unidentified lines, and we also did not see lines of the absorption spectra of any other objects except triplet molecules. Nevertheless, it is noteworthy that even at the lifetime 50 ms the intensity of the transition from the first excited vibrational state ($E \approx 2500$ K) was fully observable.

The intensity distribution in the observed absorption bands is determined by the fact that the molecules are formed in various excited states and are then partly thermalized during their lifetime. Thus, in a steady situation there is a flux of molecules from the upper to the lower energy levels. This leads to a strongly non-Boltzmann distribution of the molecules with respect to these levels, which can be determined from our spectra.

The distance between the individual rotational components of the transition $a \rightarrow c$ is less than their width for the molecules in liquid helium; therefore, the rotational structure cannot be resolved in the spectrum of the transition $a \rightarrow c$, whereas the vibrational bands (0–0) and (1–1) are well resolved. For the transition $a \rightarrow b$ on the other hand, the bands (0–0) and (1–1) overlap, whereas the rotational components are well separated. Therefore, it is possible to find the distribution of the molecules with respect to the excited vibrational and rotational levels by a simultaneous fitting of both spectra. In the process of fitting, we assumed that the individual components have a Gaussian form with FWHM equal to 100 and 115 Å for the transitions $a \rightarrow c$ and $a \rightarrow b$, respectively. (In fact, these components have a slightly asymmetric form as in the atomic transitions.) The shifts of the spectra as a whole in relation to the vacuum position were also free parameters. The result of the least-squares fitting of the spectra corresponding to a lifetime of 50 ms allowing for the condition of the nonnegativity of the occupancy numbers is shown in Fig. 4. Independently of the number of components

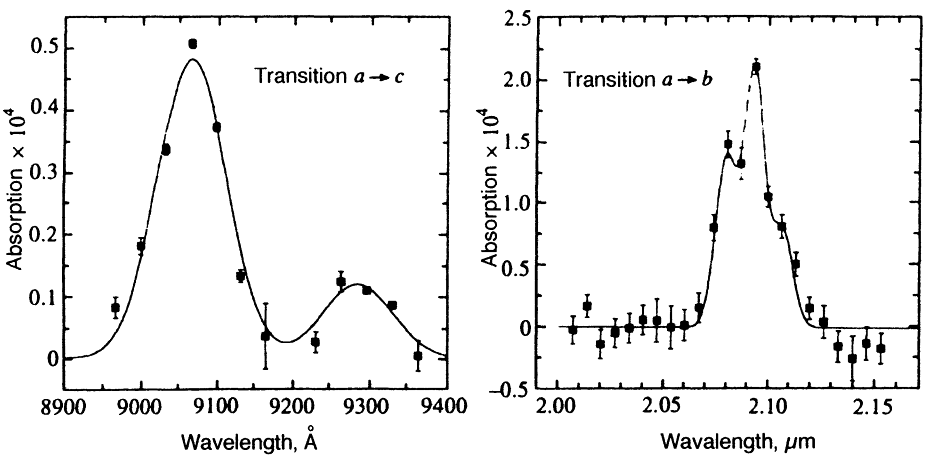

FIG. 4. Fitting of the absorption spectra corresponding to the lifetime 50 ms. Nonzero occupancy numbers were obtained only for the levels $v=0$, $J=1$, and $v=1$, $J=1$ in the ratio 1:0.23.

taken into account in the fitting, it was practically possible to obtain significant deviations from zero for the occupancy numbers, for only a few of the first excited levels. Moreover, since even for short lifetimes the intensity of the lines associated with transitions from excited rotational levels is comparable with the sensitivity of our apparatus, the errors in the obtained occupancy numbers are very great. Only the occupancy n_3 of the first rotational level ($J=3$) relative to the ground level ($J=1$) and also the total number of levels with observable occupancy (i.e., the maximum observable rotational quantum number J_m) can be determined relatively accurately.

At the lifetime 50 ms and sensitivity limit achieved in our experiment, the transitions from excited rotational states are absent in the spectra: $n_3=0$ and $J_m=1$. At the lifetime 30 ms, $n_3 \approx 0.12$, and the levels with a higher J are not occupied: $J_m=3$. Thus, approximately 20% of the molecules are in excited rotational states. For the lifetime 8 ms, we obtained $n_3 \approx 0.18$ and $J_m \approx 15$. The estimate of the fraction of molecules in excited rotational states for that lifetime is 60%. The relative errors in the results presented for the occupancy numbers are ≈30%. For comparison, we note that in Ref. 6 for the lifetime 0.3 ms approximately 80% of the molecules were in excited rotational states and $J_m \approx 19$. Taking into account that the fraction of molecules in the excited vibrational state $v=1$ decreases very slowly to 25% as the lifetime is increased to 50 ms, we can conclude that the vibrational relaxation of excimer helium molecules in the liquid occurs significantly slower than the rotational relaxation. Qualitatively, this may be due to the fact that because the vibrational quantum (2500 K) is significantly larger than the rotational quantum (100 K) the energy transfer process in superfluid helium, which requires the generation of a large number of excitations, is significantly less probable for vibrational transitions.

The vibrational relaxation time can be determined from the dependence of the fraction of excited molecules in the first vibrational state on the lifetime. For two levels with exponential relaxation with time τ_v and mutual recombination in the steady state, we have

$$p - n_2/\tau_v - \alpha n_2(n_1+n_2) = 0 \quad \text{(excited level)},$$

$$kp + n_2/\tau_v - \alpha n_1(n_1+n_2) = 0 \quad \text{(ground level)},$$

where n_2 and n_1 are the concentrations, and p and kp are the rates of generation in the excited and ground levels, respectively. From this we find

$$\frac{n_1}{n_2} = \frac{k+1}{\tau_v}\,\tau + k, \tag{2}$$

where $\tau = 1/[\alpha(n_1+n_2)]$ is the lifetime determined by recombination. The corresponding graph is shown in Fig. 5. From it, we obtain $\tau_v \approx 140 \pm 40$ ms. The basic source of the relatively large error in τ_v is the error in the measurement of the absorption for the weaker transition (1−1).

4. THE INFLUENCE OF THE MAGNETIC FIELD

We also made measurements of the absorption spectra in a magnetic field up to 5.5 T at temperatures 2.1 and 1.4 K. In the case of equilibrium polarization of the molecules, the slowing down of their recombination should lead to a significant increase in the steady concentration for an unchanged generation rate: by 3.7 and 8.8 times at 2.1 and 1.4 K, respectively, in the field 5.5 T. Even if we assume that the molecules in the excited states are completely unpolarized

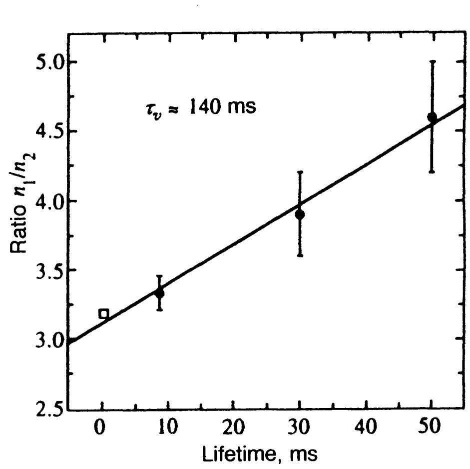

FIG. 5. The dependence of the ratio of the number of molecules in the ground and first vibrational states determined from the intensity of the bands (0–0) and (1−1) in the spectrum of the transition $a \to c$ as a function of the recombination lifetime. The straight line is the fitting according to Eq. (2): ☐ is the data from Ref. 6, and ● is our data.

(25% for 50 ms), the effect should nevertheless still be significant (>2). Of course, one of the conditions for its observation is that the lifetime of the molecules is really determined by their recombination. Other possibilities that can be considered are diffusion and destruction of the molecules on the walls, as well as blowing out due to motion of the liquid entrained by moving charges. The diffusion coefficient of the excimers in the investigated range of temperatures is in the range $10^{-3}-10^{-4}$ cm^2/s (Ref. 6), and thus the distance traveled because of diffusion during the lifetime is considerably smaller than the range of observation and the distance to the walls ~1 mm. As far as the motion of the normal component of the liquid is concerned, the force acting on unit volume $f=j_+/\mu_+ - j_-/\mu_-$ ($j_\pm$ and $\mu_\pm$ are the current densities of the positive and negative ions and their mobilities, respectively) is sufficiently great for turbulent motion to set in quickly when the current is switched on. The connection between the body force and the steady velocity in superfluid turbulence is well known,[14] and estimates show that in our case the motion with the normal component of the liquid does not cause the molecules to travel in their lifetime distances that exceed the dimensions of the region of observation.

Because of the small amplitude of the absorption signal, we were not able to observe the time dependence of the concentration of the molecules after the switching off of the generation source (the dependence should be proportional to $1/t$ in the case of decay due to mutual recombination). However, we could measure the dependence of the steady concentration n on the rate of generation p of the molecules, which in this case should be $p=\alpha n^2$. The generation rate p can be determined from the current I through the experimental cell under the assumption of complete recombination of the ions, equality of the currents of the positive and negative ions, and also of probability one of generation of a molecule in a recombination event as $p=I/(V\cdot 2e)$, where V is the volume of the ion recombination. (In fact, this is a somewhat too large estimate.) Taking into account also the relationship between the concentration and the absorption $n=A/(\sigma d)$, we obtain

$$A=\frac{\sigma d}{\sqrt{\alpha V\cdot 2e}}\sqrt{I}. \tag{3}$$

The graph of the dependence of the absorption on the square root of the current through the experimental cell is shown in Fig. 6. The points at the high currents obtained in the absence of diaphragms in the path of the current actually lie on a straight line, whose slope $2.1\cdot 10^{-5}$ nA$^{-1/2}$ agrees well with the value $2.4\cdot 10^{-5}$ nA$^{-1/2}$ calculated according to Eq. (3). The points at the low currents were obtained with diaphragms and have a different and less definite geometrical factor included in Eq. (3). With allowance for this, they do not contradict the relation (3).

The conclusion can therefore be drawn that in our experiments the lifetime of the excimer helium molecules is in fact determined by their mutual recombination; therefore, when the molecules are polarized in a magnetic field we should observe an increase in their steady concentration. Nevertheless, we did not observe any effect of the magnetic field for any of the experimental conditions. For the maximum achieved lifetime 50 ms, an effect was absent with an accuracy of 10%. By all appearances, we can conclude from this that the time of magnetic relaxation of the triplet helium molecules under our conditions significantly exceeds their lifetime.

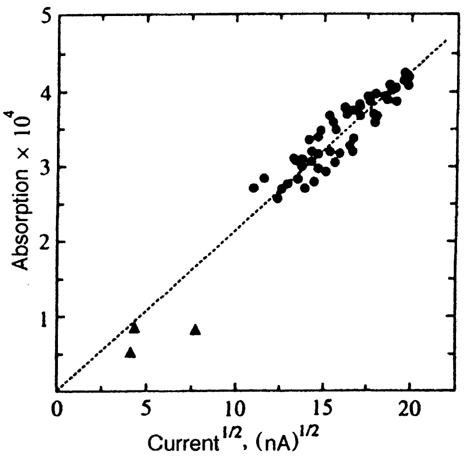

FIG. 6. Dependence of the absorption at the maximum of the transition $a\rightarrow c$ on the square root of the total current through the experimental cell. The black circles represent points obtained in the absence of diaphragms in the path of the current.

Possible channels of magnetic relaxation are the spin–axis interaction within the molecules (the interaction of the molecules with the superfluid helium also plays a role here; it is necessary for the final transfer of energy and angular momentum), the dipole–dipole interaction with the charges that are in the volume of the experimental cell, and the dipole–dipole interaction between the molecules themselves. However, the last process is also responsible for the recombination of the molecules with the same projections of magnetic moments. A specific theoretical description of these mechanisms for triplet excimer molecules in superfluid helium does not exist today. From the published experimental studies which relate to the magnetic properties of these molecules, we know only of an attempt[1] to discover the deflection of these molecules during motion in a magnetic field gradient. The experiment produced an effective value of the magnetic moment not larger than $0.2\mu_B$. Bearing in mind the slow mechanical relaxation of these molecules after their formation that we discovered, we can explain the result of Ref. 1 if we assume that random reversal of the magnetic moment is possible in the process of such relaxation.

5. CONCLUSIONS

As a result of spectroscopic study of the triplet excimer molecules $^4\mathrm{He}_2^*$ in superfluid helium with lifetimes that exceeded those achieved in earlier experiments by two orders of magnitude, we found that these molecules remain incompletely thermalized even at lifetimes of approximately 50 ms. At the same time, the vibrational relaxation occurred significantly slower than the rotational relaxation with a characteristic time 140 ms. Slowing down of the mutual recombination of the molecules in a magnetic field was not discovered; this indicates a long magnetic relaxation time. Thus, relaxation processes play a significantly more important role than was supposed earlier in the attempts to obtain a long-lived spin-polarized state of the triplet molecules in superfluid helium. A theoretical study of these processes is necessary.

Thus, for the successful polarization of triplet molecules it is necessary either to increase the lifetime or to look for means of accelerating the relaxation. A further increase in the lifetime by the decrease of the concentration is coupled with significant difficulties in the detection of even smaller quantities of molecules. A significant increase of this time at high concentrations can be achieved in solid helium; therefore, one of the possibilities is to polarize molecules in a crystal and then melt it. A simple increase in the pressure of the liquid can also accelerate the vibrational–rotational relaxation: In Ref. 6, an exponential decrease in the intensity of the radiation of the molecular transitions was observed when the pressure was increased. An experiment with a ^{3}He–^{4}He solution can give one more possibility, since in this case there is an additional magnetic relaxation channel, while the recombination is somewhat slowed down.[6]

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