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Structure and Dynamics of the $\mathrm{He}_2^*\left(a^3\Sigma_u^+\right)$ Molecular Complex in Condensed Phases of Helium

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Abstract—An investigation is made of the absorption spectra of triplet metastable helium molecules in the $a^3\Sigma_u^+$ state in liquid ^{4}He and ^{3}He at various pressures and in dense ^{3}He gas. An analysis of the spectrum corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition confirms the conclusion that there is a microscopic bubble surrounding the molecule in liquid helium. A simple approximation is proposed for the wave function of the valence electron of the molecule and the parameters of the bubble are determined for various experimental conditions. The coefficient of molecular recombination in liquid ^{3}He and ^{4}He was determined experimentally at various pressures and in dense cold ^{3}He gas. The results show good agreement with the theory of mutual recombination limited by molecular diffusion under conditions of strong van der Waals interaction. It is shown that in the condensed phases of helium the polarization of the molecules under the action of the magnetic field does not lead to suppression of their mutual recombination, and this is confirmed experimentally. © *2000 MAIK “Nauka/Interperiodica”.*

1. INTRODUCTION

Numerous experimental and theoretical studies have been devoted to the neutral triplet excitations of helium. The lowest triplet atomic (2^3S) and molecular ($a^3\Sigma_u^+$) states are metastable having intrinsic lifetimes of approximately 8000 s [1, 2] and 15 s [3, 4] and energies of 19.82 and 17.86 eV, respectively. When helium is excited by fast particles, an appreciable fraction of the energy is dissipated in the formation of triplet atoms and molecules. As the helium density increases, the ratio of the steady-state molecular concentration to the concentration of excited atoms increases [5] which can be attributed to an increase in the probability of three-body collisions when a triplet atom may capture an unexcited atom and form a dimer [6]. In dense helium gas ($n \geq 3 \times 10^{20}$ cm^{-3}) [5] and in liquid helium [7], triplet molecules in the $a^3\Sigma_u^+$ state are the predominant type of neutral excitations.

The main mechanism for the loss of triplet molecules in condensed helium [5, 7, 8] and triplet atoms in the low-density gas [9] is their mutual recombination which takes place via a Penning ionization scheme

$$\begin{gathered}\mathrm{He}_2^*(a^3\Sigma_u^+) + \mathrm{He}_2^*(a^3\Sigma_u^+) \longrightarrow 2\mathrm{He}(1^1S) + \mathrm{He}_2^+ + \bar{e}, \\ \mathrm{He}^*(2^3S) + \mathrm{He}^*(2^3S) \longrightarrow \mathrm{He}(1^1S) + \mathrm{He}^+ + \bar{e}.\end{gathered} \quad (1)$$

The characteristic lifetime of the molecules decreases as their concentration increases $\tau = 1/(\alpha n)$ (α is the mutual recombination coefficient) and is a few milliseconds at concentrations of approximately 10^{13} cm^{-3}.

In condensed helium the excimer decay process is limited by diffusion:

$$\alpha = 4\pi D R_I, \quad (2)$$

where R_I is the characteristic distance between the molecules for which the ionization takes place with a probability of the order of unity. This distance is determined from the condition that the characteristic diffusion time R_I^2/D and the characteristic time of reaction (1) are equal.

Detailed calculations of the interaction between a triplet helium atom and a surrounding liquid were made in [10]. The calculated shift of the absorption line for the $2^3S \longrightarrow 2^3P$ transition relative to the position at low pressure showed good agreement with the experiment [7]. Similar calculations have not yet been made for triplet molecules.

In the present study we give the molecular absorption spectra corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ and $a^3\Sigma_u^+ \longrightarrow b^3\Pi_g$ transitions measured in liquid ^{3}He and ^{4}He at various pressures and in dense cold ^{3}He gas. The integrated intensities of the spectra were used to determine the ratio of the oscillator strengths of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ and $a^3\Sigma_u^+ \longrightarrow b^3\Pi_g$ transitions whose value

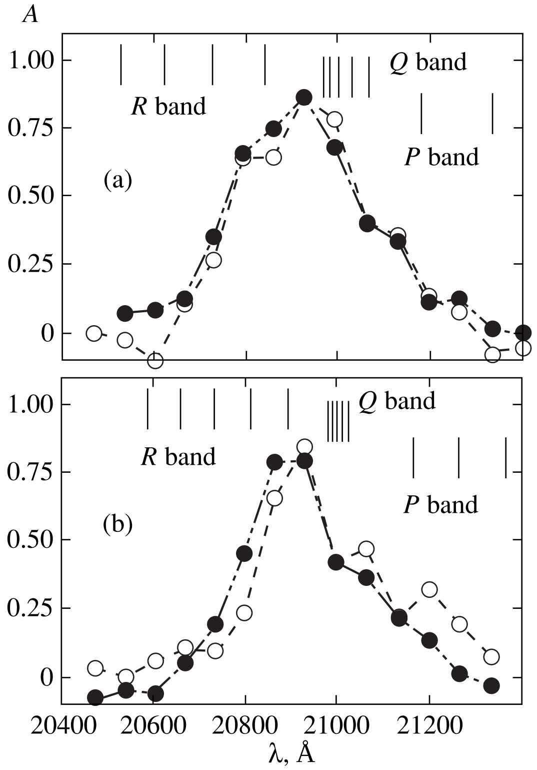

Fig. 1. Absorption spectra of molecules corresponding to the $a^3\Sigma_u^+ \longrightarrow b^3\Pi_g$ transition: (a) in liquid ^{4}He (○—1.0 atm, 2.1 K; ●—23.9 atm, 1.9 K); (b) in liquid ^{3}He (○—1.0 atm, 1.8 K; ●—14.4 atm, 1.8 K). The spectra are normalized to the absorption at the maximum.

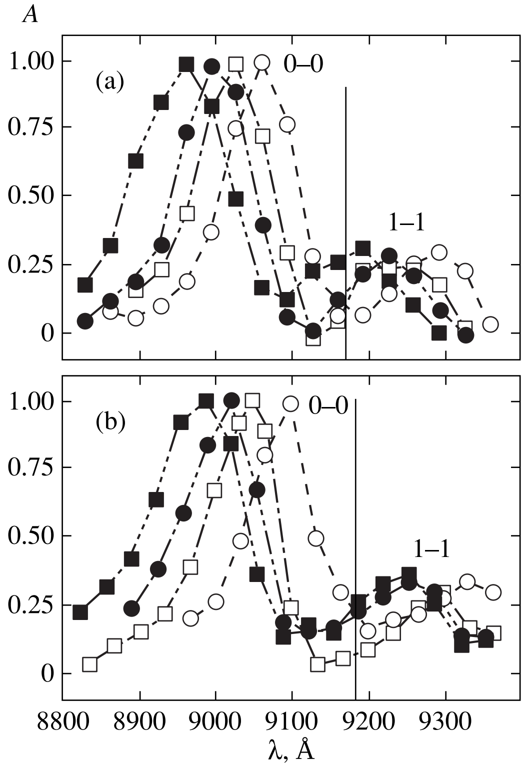

Fig. 2. Absorption spectra of molecules corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition: (a) in liquid ^{4}He (○—0.05 atm, 2.1 K; □—6.3 atm, 2.1 K; ●—10.1 atm, 2.0 K; ■—23.9 atm, 1.9 K; (b) in liquid ^{3}He (○—4.8 atm, 1.8 K; □—14.4 atm, 1.8 K; ●—23.9 atm, 1.7 K; ■—31.5 atm, 1.7 K). The vertical line gives the wavelength corresponding to the (0–0) $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition in vacuum. The spectra are normalized to the absorption at the maximum.

shows good agreement with the calculated value. Quantitative data were obtained on the van der Waals coefficients of the following pair interactions:

$$\mathrm{He}_2^*(a^3\Sigma_u^+) - \mathrm{He}_2^*(a^3\Sigma_u^+),$$

$$\mathrm{He}_2^*(a^3\Sigma_u^+) - \mathrm{He}(1^1S),$$

$$\mathrm{He}_2^*(c^3\Sigma_g^+) - \mathrm{He}(1^1S).$$

We calculated the interaction between a molecule and surrounding helium which leads to a shift and broadening of the absorption lines, using a model of the “bubble” formed by the molecule in liquid helium and we determined the bubble radius under various conditions. The molecular spectra in the gas were described using the standard theory of line broadening in the binary approximation [10, 11].

The theory of diffusion-limited mutual recombination was extended to the case of strong van der Waals interaction. Good agreement was observed between the calculated data and the experimental data obtained in the present study and in [7]. The coefficient of recombination calculated using this model does not depend on the magnetic field and this is confirmed experimentally.

2. ABSORPTION SPECTRA AND THEIR INTERPRETATION

The method of generating molecules and measuring the absorption is similar to that described in [12]. The molecules are formed as a result of the recombination of positive ions and electrons injected into the helium from tungsten tips. Light from a halogen lamp passing through a mechanical chopper and a monochromator is fed along a quartz light guide into an experimental cell from which it is extracted to a photodetector using another light guide. The photodetector signal is amplified and demodulated using a lock-in amplifier. The excimer concentration was modulated at low frequency by periodically varying the current through the cell and the signal from the lock-in amplifier was demodulated using a computer.

Typical absorption spectra observed in liquid ^{3}He and ^{4}He are shown in Figs. 1 and 2. To within experimental accuracy, the $a^3\Sigma_u^+ \longrightarrow b^3\Pi_g$ absorption line does not shift with varying pressure whereas the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ line undergoes an appreciable displacement in the short-wavelength direction and becomes broader as the pressure and particle density increase. Line broadening of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition was observed as a function of temperature (Fig. 3). It is important to note that in the given temperature range at constant pressure, the variation of the helium density is within 1.5% so that we can reliably talk of temperature-induced broadening of the line. Unlike the absorption line width, its shift relative to the vacuum position does not depend on temperature, which suggests that the position of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ line may be used as an indicator of the static interaction between the molecule and the environment, neglecting the temperature fluctuations which lead to additional broadening.

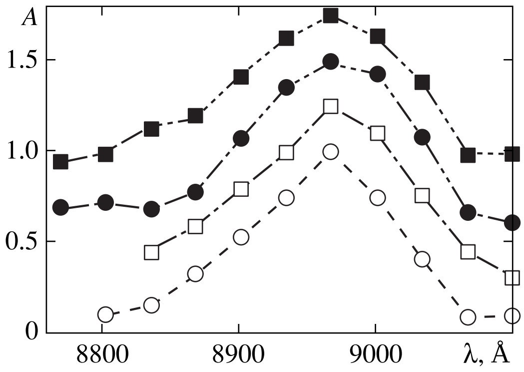

Fig. 3. Line broadening of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition in liquid ^{4}He as a function of temperature at 23.9 atm (○—1.55 K; □—1.75 K; ●—1.95 K; ■—2.1 K; T_λ = 1.88 K). The spectra are normalized to the maximum and are shifted along the ordinate by 0.25 relative to each other.

In order to describe the pressure dependence of the (0–0) $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ line shifts, we used a model which assumes that a microscopic bubble surrounds the molecule in liquid helium. This approach was used in [10] which was devoted to the $\mathrm{He}_2^*(2^3S)$ metastable triplet helium atoms. It is assumed that the bubble is formed as a result of the repulsion of an excited electron from the surrounding helium atoms. This mechanism may lead to the formation of a bubble around the metastable molecule since the size of the outer electron orbit is comparable with the interatomic distance in liquid helium [13].

The equilibrium bubble radius R_0 is determined by minimizing the total energy of the complex $E(R)$ which consists of the total energy of the interaction between the molecule and the surrounding helium atoms E_{ma}, the potential energy of the cavity in the liquid pV, the potential energy at the bubble interface E_{sur}, and the kinetic energy of the molecule E_m which is associated with the oscillations of the molecule in the bubble.

We shall make an assumption which will be justified by the following calculations, that the size of the bubble is considerably greater than the internuclear distance in the molecule (around 1 Å [14]). To a first approximation the interaction of the molecule with the surroundings reduces to the repulsion of the outer electron from the helium atoms at short distances and van der Waals interaction of the molecule with the atoms. In the widely used optical model the energy of the interaction between an electron and a helium atom is written in the form

$$\varepsilon_{ea} = \frac{2\pi\hbar^2 a_0}{m_e}|\psi(\mathbf{R})|^2,$$

where a_0 is the scattering length of the electron on the helium atom in the pseudopotential approximation (a_0 = 0.62 Å) and $\psi(\mathbf{R})$ is the electron wave function [15]. Calculation of the electron wave function of a helium molecule is a complex theoretical problem. However, we are merely interested in its behavior at comparatively large distances from the nuclei. Calculations made for the $A^1(\Sigma_u^+)$ and $C^1(\Sigma_g^+)$ singlet molecular states by Guberman and Goddard [16] show that at distances greater than 5 Bohr radii the wave functions of the outer electron are accurately approximated by hydrogen-like functions of the $2S$ and $2P_0$ type, respectively with the effective charges of the molecular core $Z(A^1) = 1.08$ and $Z(C^1) = 0.69$. We shall assume that the wave functions of an excited electron in the $a^3\Sigma_u^+$ and $c^3\Sigma_g^+$ states are also essentially $2S$ and $2P_0$ hydrogen-like functions and the effective core charges will be fitting parameters.

We do not know of any experimental or theoretical data on the coefficient of the van der Waals interaction between a molecule and a helium atom. In order to estimate this we can use the following simple reasoning: the dipole moment of a molecule is mainly determined by the outer electron whose characteristic frequency of motion is low compared with the frequencies of electrons in the 1^1S ground state of the helium atom. Assuming that the motion of the outer electron relative to the molecular core is classical, at each instant the energy of the interaction between a molecule and a helium atom is $-\alpha\mathbf{E}^2(\mathbf{R})/2$ where $\mathbf{E}(\mathbf{R})$ is the electric field induced by the molecule and α is the polarizability of the helium atom in the ground state (α = 1.383 au [17]).

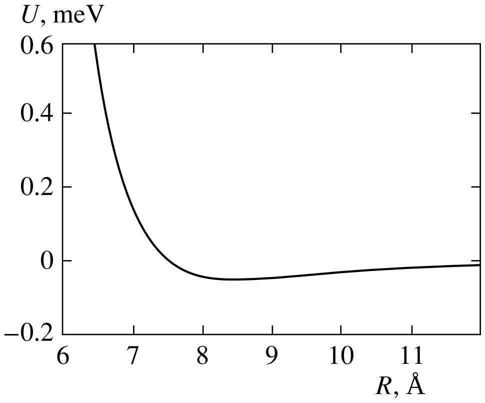

Fig. 4. Energy of interaction between an $He_2^*(a^3\Sigma_u^+)$ molecule and a 1^1S helium atom at large distances.

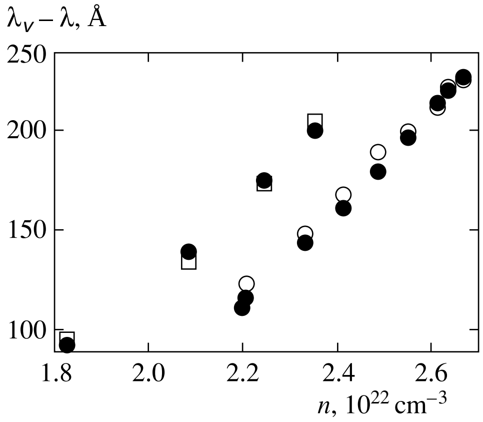

Fig. 5. Shift of the maximum of the (0–0) $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ absorption line relative to the vacuum position in liquid helium [□—^{3}He, ○—^{4}He, ●—fitting using bubble model (see text)].

Averaging over the state of the outer electron in the molecule, we can easily obtain

$$\varepsilon_{\text{vdW}}(2S) = -\frac{\alpha\bar{e}^2\langle r^2\rangle_{2S}}{R^6},$$

$$\varepsilon_{\text{vdW}}(2P_0) = -\frac{\alpha\bar{e}^2\langle r^2\rangle_{2P_0}}{R^6}\left(\frac{4}{5} + \frac{3}{5}\cos^2\Theta\right),$$

where the angular brackets denote averaging over the state. We note that the expression for $\varepsilon_{\text{vdW}}(2P_0)$ is the same as the result of the approximate quantum-mechanical calculations [18]. Figure 4 gives the interaction potential between a molecule in the $a^3\Sigma_u^+$ state and a helium atom in the ground state. It can be seen that the characteristic scale of the region of major variation in the potential is smaller than the interatomic distance in the liquid. Thus, the helium density was subsequently assumed to be equal to its value at infinity everywhere outside the bubble and

$$E_{ma} = n\int\limits_{R > R_0}\{\varepsilon_{ea}(\mathbf{R}) + \varepsilon_{\text{vdW}}(\mathbf{R})\}d^3R.$$

We write the energy associated with the presence of a liquid–vacuum interface at the bubble surface in the form $E_{\text{sur}} = 4\pi R_0^2\gamma$. The value of γ was assumed to be equal to $\sigma_0(n/n_0)$, where σ_0 and n_0 are the coefficients of surface tension at the liquid–saturated vapor interface and the liquid density at the saturated vapor pressure, respectively, when $T \longrightarrow 0$. When calculating the kinetic energy of the molecule we assumed that the configuration of the surrounding liquid remains the same under the molecular oscillations since the attached mass of the bubble is considerably greater than the molecular mass and the characteristic frequencies of the bubble oscillations are relatively low. Under this assumption the change in the potential energy of the interaction of the molecule with the surroundings when the molecule is displaced by $\delta\mathbf{r} = \{\delta x, \delta y, \delta z\}$ relative to the center of the bubble is

$$\delta E(\delta\mathbf{r}) = n\int\limits_{R > R_0}\{\varepsilon_{ea}(\mathbf{R} - \delta\mathbf{r}) + \varepsilon_{\text{vdW}}(\mathbf{R} - \delta\mathbf{r})\}d^3R. \quad (3)$$

Expanding (3) as a series in powers of δx, δy, and δz as far as quadratic terms and integrating, we find the frequencies of the molecular oscillations in the corresponding directions. For a bubble radius of 6–7 Å these frequencies correspond to temperatures of 10–15 K and consequently the kinetic energy of the molecule is simply the energy of its zero-point oscillations.

In the adiabatic approximation the frequency shift of the transition is $\Delta\omega = (E_c(R_0) - E_a(R_0))/\hbar$, where $E_a(R_0)(E_c(R_0))$ is the total energy of the "bubble + molecule in state $a^3\Sigma_u^+$ $(c^3\Sigma_g^+)$" complex, and R_0 is the equilibrium radius of the bubble formed by the molecule in the initial state $a^3\Sigma_u^+$. In our model, the shift of the absorption line only depends on the unknown effective charges of the molecular core Z_a and Z_c in the initial and final states which were determined by fitting the experimental values. It can be seen from Fig. 5 that the proposed model accurately describes the interaction between the molecule and the surrounding liquid.

The values of $Z_a = 1.04 \pm 0.05$ and $Z_c = 0.78 \pm 0.04$ thus determined are close to the effective charges Z_A and Z_C determined for, respectively, the $A^1(\Sigma_u^+)$ and $C^1(\Sigma_g^+)$ singlet states from Guberman and Goddard's calculation[16]. The bubble radius varies between 7 Å at low pressure and 6.4 Å at pressures close to solidification.

The absorption spectra corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition were also measured in cold ^{3}He gas at densities of 1.3×10^{21}–1.1×10^{22} cm^{-3} (Fig. 6). In order to describe the observed line shifts relative to the vacuum position we used the standard theory of line broadening in the binary limit (see, e.g., [11]) assuming that the energy of the interaction between the molecule and the surroundings can be reduced to the sum of the energies of two-particle interactions between the molecule and isolated atoms. Then, in the adiabatic approximation the frequency dependence of the absorption intensity is given by

$$I(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\varphi(\tau)d\tau,$$

where

$$\varphi(\tau) = \exp\left[-\int\left\{1 - \exp\left[-\frac{i\tau(U_c(\mathbf{R}) - U_a(\mathbf{R}))}{\hbar}\right]\right\}n(\mathbf{R})d^3\mathbf{R}\right]. \tag{4}$$

Here, ω is the frequency shift, $U_a(\mathbf{R})$ and $U_c(\mathbf{R})$ are the energies of the interaction of the molecule with an isolated atom in the initial and final states, $n(\mathbf{R})$ is the coordinate distribution function of the helium atoms. Taking into account the slope of the interaction potential $U_a(R)$ and the smallness of the van der Waals minimum compared with temperature (see Fig. 4), we approximated the real potential by an infinite wall located at a distance $R_{\min}$ from the molecule. The value of $R_{\min}$ is determined from the condition $U_a(R_{\min}) = T$ (classical turning point) and depends weakly on temperature. If three-body "molecule + atom + atom" collisions are neglected, we can easily calculate the coordinate distribution function of the atoms:

$$n(R < R_{\min}) = 0,$$

$$n(R > R_{\min}) = n_\infty\left(1 - \exp\left\{-\frac{2mT(R - R_{\min})^2}{\hbar^2}\right\}\right).$$

Figure 7 shows measured shifts of the maximum of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ absorption line from the vacuum position in ^{3}He at various densities and results of calculations using the bubble model and in the binary approximation. On comparing the experimental data with the calculations, we can conclude that at densities $\gtrsim 1.5 \times 10^{22}$ cm^{-3} the molecule is localized in a bubble (for comparison, the critical ^{3}He density is 8.3×10^{21} cm^{-3} [19]).

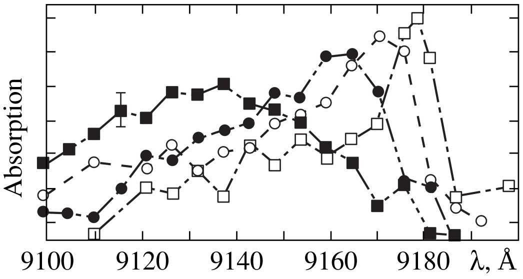

Fig. 6. Absorption spectra of molecules corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition in cold ^{3}He gas at various densities (□—0.7 atm, 2.9 K, 0.0064 g/cm^3; ○—1.8 atm, 4.2 K, 0.017 g/cm^3; ●—2.2 atm, 4.2 K, 0.033 g/cm^3; ■—2.1 atm, 3.4 K, 0.057 g/cm^3).

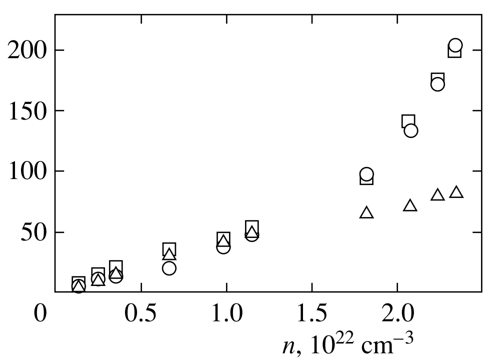

Fig. 7. Shift of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ absorption line relative to the vacuum position in liquid and gaseous ^{3}He at various densities [○—experiment, □—calculations using bubble model, △—calculations using binary approximation (see text)].

3. KINETICS OF MOLECULAR DECAY

Triplet $\mathrm{He}_2^*(a^3\Sigma_u^+)$ molecules are the longest-lived neutral excitations in condensed helium and thus the question of the processes leading to their decay is of considerable interest. The dominant mechanism of excimer loss in liquid and dense gaseous helium is the binary Penning ionization reaction (1) [5, 7, 8]. In cases where the total electron spin of the interacting triplets does not exceed unity, reaction (1) takes place to the extent of exchange interaction between the outer electrons of the reacting particles and its rate at maximum convergence (2.5–3 Å [20]) is $W_{ex} \approx 10^{14}$ s^{-1} [20, 21]. If the electron spin of the reacting triplets is two, ionization as a result of total spin-conserving exchange interaction is forbidden since the spin of the reaction products does not exceed unity. In this case, a nonzero Penning ionization probability only occurs when weak spin dipole interaction is taken into account. The rate W_{ex-d} of the reaction taking place by this exchange dipole mechanism is seven orders of magnitude lower than W_{ex} [4]. Konovalov and Shlyapnikov [4] predict that recombination will be appreciably suppressed when the triplets are strongly polarized.

The dynamics of the loss of molecules as a result of mutual recombination may be described by the following relationships:

$$\begin{aligned}\dot{n}_\uparrow &= -\alpha_{\uparrow\uparrow}n_\uparrow^2 - \alpha_{\uparrow 0}n_\uparrow n_0 - \alpha_{\uparrow\downarrow}n_\uparrow n_\downarrow,\\ \dot{n}_0 &= -\alpha_{0\uparrow}n_0 n_\uparrow - \alpha_{00}n_0^2 - \alpha_{0\downarrow}n_0 n_\downarrow,\\ \dot{n}_\downarrow &= -\alpha_{\downarrow\uparrow}n_\downarrow n_\uparrow - \alpha_{\downarrow 0}n_\downarrow n_0 - a_{\downarrow\downarrow}n_\downarrow^2,\end{aligned} \tag{5}$$

where $n_\uparrow$, n_0, and $n_\downarrow$ are the concentrations of molecules having different spin projections and α_{ij} are the recombination coefficients. If, following Konovalov and Shlyapnikov [4], we assume that free molecular diffusion takes place, the rate of recombination is determined by

$$\alpha = 4\pi D R_I, \tag{6}$$

where the ionization radius is determined by the condition $R_I^2/D \approx 1/W(R_I)$ ($W(R)$ is the probability of recombination event (1) per unit time). The molecular diffusion coefficient can be estimated in the τ approximation using the calculated bubble radius (see previous section). Typical values of the diffusion coefficient in a normal liquid are around 10^{-5} cm^2/s, increasing in a superfluid liquid as the density of the normal component decreases. As a result of an exponential decrease in the recombination probability W with distance, the characteristic ionization radius varies weakly as the diffusion coefficient varies. Under our experimental conditions the ionization radius of a spin-allowed reaction was 7–10 Å. The characteristic time of an ionization reaction by the exchange–dipole mechanism is several orders of magnitude greater than the diffusion time at all distances and in the approximation under study we find $\alpha_{\uparrow\uparrow} \ll \alpha_{\uparrow\downarrow}, \alpha_{\uparrow 0}$.

However, the assumption of free diffusion is not consistent with the real situation because of the presence of strong van der Waals interaction between the molecules. Allowance for this interaction yields the conclusion that molecules having converged to a distance at which the van der Waals energy is comparable with the temperature, do not diverge but form a bound state having a short intermolecular distance (≈3 Å) and react within times much shorter than the diffusion convergence time even when the total molecular spin is two. The van der Waals capture radius is [22]

$$\begin{aligned}R_{\text{vdW}} &= \left[\int_{R_I}^{\infty}\exp\left(-\frac{C_6}{r^6 T}\right)\frac{dr}{r^2}\right]^{-1}\\ &= \left[\frac{1}{6}\left(\frac{T}{C_6}\right)^{1/6}\int_0^{C_6/(TR_I^6)} e^{-t}t^{-5/6}dt\right]^{-1}.\end{aligned} \tag{7}$$

We use the following formula to estimate the van der Waals coefficient (see, e.g. [23])

$$C_6 = \frac{3\hbar e^4}{2m^2}\sum_{k,k'}\frac{f_{ak}f_{ak'}}{(\omega_{ak}+\omega_{ak'})\omega_{ak}\omega_{ak'}}, \tag{8}$$

where f_{ak} and ω_{ak} are the oscillator strength and frequency of the $a^3\Sigma_u^+ \longrightarrow k$ transition, respectively, and summation is performed over all possible transitions. The oscillator strength of the $a^3\Sigma_u^+ \longrightarrow b^3\Pi_g$ transition is known, $f_{ab} = 0.205$ [5]. The oscillator strength of the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ transition can easily be calculated using the matrix elements of the dipole moment operator calculated by Yarkony [24] and the calculations give $f_{ac} = 0.307$.

Using the well-known relationship (see, e.g., [25])

$$f_{kk'} = \frac{c^2 m}{\pi\bar{e}^2}\int\sigma(\nu)d\nu,$$

where $f_{kk'}$ is the oscillator strength of the $k \longrightarrow k'$ transition, $\sigma(\nu)$ is the cross section for absorption of light at frequency ν, and the integral is taken along the entire absorption line corresponding to this transition, we obtain from the integrated intensities of our measured spectra: $f_{ac}/f_{ab} = 1.5 \pm 0.2$ which agrees with the calculated data.

Having retained only the principal terms with $k, k' = b, c$ in the sum (8), we obtain the lower constraint on the van der Waals coefficient $C_6^{\min} = 6020$ au. For the upper constraint on C_6 we assume $f_{ae} = 1 - f_{ab} - f_{ac}$ (the $a \longrightarrow d$ transition is parity-forbidden), $f_{ak} = 0$ for $k \neq b, c, e$, which gives $C_6^{\max} = 7940$ au. Thus, we have $C_6 = 7000 \pm 1000$ au.

Bearing in mind that $R_I \lesssim 10$ Å we have $C_6/(TR_I^6) \gg 1$ and integration in (7) can be extended to infinity, which gives

$$R_{\text{vdW}} = \frac{6}{\Gamma(1/6)}\left(\frac{C_6}{T}\right)^{1/6} = 15\text{–}18\ \text{Å} \tag{9}$$

at temperatures of 1.5–4.2 K. Thus, at low temperatures we find $R_{\text{vdW}} > R_I$ so that the van der Waals capture radius should be taken as the characteristic ionization radius:

$$\alpha = 4\pi D R_{\text{vdW}}. \tag{10}$$

Thus, in this model the polarization of the molecules has no influence on their decay dynamics.

Formula (10) obtained in the diffusion approximation holds for short mean free paths $l \ll R_{\text{vdW}}$. If the molecule is situated in a liquid, it is localized in a bubble and direct estimates in the τ-approximation give $l \approx R_0/6$ (R_0 = 6.4–7.0 Å is the bubble radius); for a superfluid liquid we have $l \approx (R_0/6)(n/n_{\mathrm{norm}})$ where n_{norm} is the density of the normal component. If the molecule is situated in a low-density gas, we find $l \approx 2/\sigma n$ where the cross section for scattering of a helium atom at a molecule is $\sigma = 1\text{–}2 \times 10^{-14}$ cm^2 at 2–4 K (the factor 2 appears as a result of a difference between the atomic and molecular masses which has the result that for a molecule a single collision with an atom is insufficient to reverse its momentum). Thus, we find that the result (10) is valid in normal liquid helium, in superfluid ^{4}He at temperatures above 1.7 K, and also in gases at densities $n \gg 10^{21}$ cm^{-3}, and under all the conditions listed above polarization does not influence the recombination of excimers.

We shall now consider the opposite limit of long mean free paths $l \gg R_{\mathrm{vdW}}$. The coefficient of molecular recombination in this case is determined by

$$\alpha = \sigma v_T, \qquad (11)$$

where σ is the cross section of reaction (1) and v_T is the thermal velocity. The limit of long mean free paths obtains in superfluid helium at ≲1.3 K and in gas at densities $\ll 10^{21}$ cm^{-3}. In superfluid helium as the molecules converge to distances $R \lesssim 2R_0$ (R_0 is the bubble radius), a bound state of two molecules localized in a single bubble forms so that the cross section is $\simeq \pi(2R_0)^2$ and the recombination coefficient also does not depend on the polarization of the molecules.

We note that an electron–ion pair formed as a result of the excimer ionization reaction (1) may recombine to form a "secondary" molecule. If the probability of this process γ is not low, the recombination coefficient (10), (11) should be multiplied by (1 – γ). The experimental setup in the present study can be used to estimate γ. The lifetime of the molecules in liquid helium under the conditions used to observe the absorption spectra was several milliseconds which is much shorter than the characteristic vibrational and rotational relaxation times (~300 ms and 15 ms, respectively [8]). Consequently, the molecular distribution over excited vibrational and rotational states corresponds to the probability of the formation of a molecule in a particular excited state. However, the characteristic relaxation times of the He_2^+ and He_3^+ molecular ions are relatively short as a result of the absence of an excited electron which suppresses the interaction of the ion core with the surroundings in the case of a molecule. Hence, molecules generated in highly excited rotational states are formed as a result of recombination of an electron–ion pair which occurred when the helium atom was ionized, and attachment of one or two atoms to an atomic ion. Such a pair is comparatively short-lived (the characteristic distance of maximum separation during expansion is $R \lesssim 10^{-5}$ cm, the time of convergence and pair recombination is $\tau_{ei} \sim R^3/(\mu \bar{e}) \lesssim 10^{-7}$ s) and the ion core does not have time to relax.

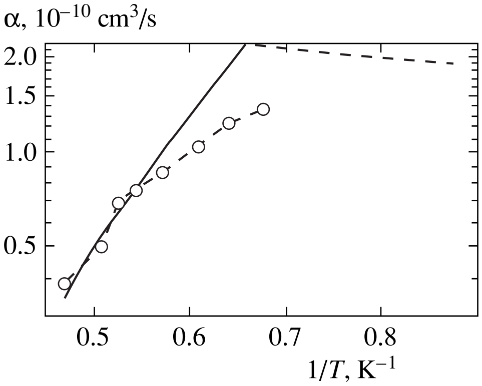

Fig. 8. Temperature dependence of the coefficient of recombination of molecules in superfluid ^{4}He: ○—Fitzsimmons experimental data [7], corrected allowing for the calculated [5] oscillator strength f_{ab}; the solid curve gives the calculations using the diffusion approximation, the dashed curve gives the calculations using the long mean free path limit (see text).

An analysis of the spectra shows that the fraction of molecules formed in this process is (20 ± 10)%. Thus, using the measured spectra we can estimate the probability γ of the formation of a single molecule in a mutual recombination event involving two molecules: let n_1 and n_2 be the concentrations of unexcited (primary) and excited (secondary) molecules and then the rate of generation of secondary molecules is $\gamma\alpha(n_1 + n_2)^2$ and their rate of recombination is $\alpha n_2(n_1 + n_2)$. Consequently in the steady-state regime we have $\gamma = n_2/(n_1 + n_2) \approx 0.2$ and allowance for the factor (1 – γ) in estimates of the recombination coefficient is needlessly accurate.

The calculated values (10) and (11) and the Fitzsimmons experimental data [7] measured in superfluid ^{4}He at temperatures of 1.4–2.1 K are compared in Fig. 8.

Thus, the suppression of recombination by a strong magnetic field can only be observed in a gas in the long mean free path regime. The condition $l \gg R_{\mathrm{vdW}}$ is equivalent to the absence of three-body "molecule + molecule + atom" collisions. Then, as they converge, these

Table 1

Phase	T, K	P, atm	$\mu_B H/(kT)$
Superfluid ^{4}He	2.12	0.05	3.5
Superfluid ^{4}He	1.76	28.1	4.2
Superfluid ^{4}He	1.43	0.004	5.2
20% ^{3}He–^{4}He solution	1.8	14.4	4.1
^{3}He, liquid	1.8	14.4	4.1
^{3}He, liquid	1.8	31.5	4.1
^{3}He, gas	2.9	0.7	1.4

Table 2

Phase	T, K	P, atm	α, cm^3/s (±15%) experiment	α, cm^3/s calculated	$l/R_{\rm vdW}$
Liquid ^{4}He	2.10	1.0	3.8×10^{-11}	3.6×10^{-11}	0.086
Liquid ^{4}He	1.98	14.4	3.2×10^{-11}	2.9×10^{-11}	0.072
Liquid ^{4}He	1.76	28.1	2.8×10^{-11}	3.2×10^{-11}	0.080
Liquid ^{4}He	1.76	1.0	1.1×10^{-10}	0.9×10^{-10}	0.23
Liquid ^{3}He	1.64	14.4	3.3×10^{-11}	2.9×10^{-11}	0.086
Gas ^{3}He	3.0	0.7	4.3×10^{-10}	8.5×10^{-10}	0.60

molecules do not form bound states and react with a certain probability which depends on their polarization. The corresponding reaction cross sections for triplet atoms were calculated in [20]: $\sigma(\uparrow\downarrow) \approx \sigma(\uparrow 0) \approx 3.2 \times 10^{-14}$ cm^2, $\sigma(\uparrow\uparrow) \approx 2.9 \times 10^{-15}$ cm^2 at low temperatures.

Unfortunately our method of generating molecules cannot operate at fairly low helium densities since, when $n \lesssim 10^{21}$ cm^{-3}, the electron mobility increases rapidly [15] and breakdown occurs in the cell. Table 1 gives all the experimental conditions used to study the influence of molecular polarization on the recombination coefficient. The molecular lifetimes were 200 ms.

Simple estimates using standard spin–lattice relaxation theory (see, for example [26]) for molecules in helium of appropriate density give longitudinal relaxation times on microsecond scales as a result of “spin–axis” interaction, which suggests that the polarization of the molecules in our experiments is close to equilibrium. Under our conditions it was impossible to observe molecular polarization using the Zeeman effect because in the fairly strong magnetic fields for which multiplet splitting could become appreciable in the absorption spectra, optical transitions accompanied by a change in the spin projection M_S are forbidden as a result of the Paschen–Back effect.

Under all the experimental conditions listed above no influence of the magnetic field on excimer decay was observed, which is in complete agreement with the theory.

In order to determine the numerical values of the recombination coefficient under various experimental conditions, the experimental time dependences of the absorption signal were fitted using the binary reaction equation

$$A(t) = \left(\frac{1}{A(t_0)} + \frac{\alpha(t-t_0)}{\sigma_0 V/S}\right)^{-1},$$

where $A(t) = n(t)\sigma_0 V/S$, σ_0 is the cross section for absorption of light determined from the oscillator strength of the transition and the integrated intensity of the spectrum, V is the volume in which absorption takes place, S is the area of the light beam, and the recombination coefficient α was the fitting parameter. The unknown effective volume V was obtained by comparing our data with the results [7] under similar conditions. The values of the recombination coefficient thus determined and those calculated using formula (10) are given in Table 2.

All the experimental data agree with the calculations within measurement error, except for the coefficient of recombination measured in a gas, where the criterion for the validity of the diffusion approximation ceases to be satisfied. Assuming that the cross section of the ionization reaction is approximately equal to the cross section for the reaction of two triplet atoms at low temperatures (see above), in the long mean free path limit we obtain $\alpha \approx 4.8 \times 10^{-10}$ cm^3/s at 3.0 K which is in good agreement with the experimental value.

4. CONCLUSIONS

The position and shape of the absorption line corresponding to the $a^3\Sigma_u^+ \longrightarrow c^3\Sigma_g^+$ molecular transition exhibits a strong dependence on the helium density which means that the interaction of the $\mathrm{He}_2^*(a^3\Sigma_u^+)$ molecule with the surroundings can be studied using optical measurements. By analyzing the spectra obtained under various experimental conditions, we established that at above-critical densities the molecules are localized in microscopic bubbles similar to the localization of excess electrons. The size of this complex, unlike a bubble, formed by an electron varies weakly with pressure.

We obtained estimates of the coefficients of the van der Waals interaction between a molecule and a ground-state helium atom:

$$C_6(\mathrm{He}_2^*(a^3\Sigma_u^+) - \mathrm{He}(1^1S)) \approx 54 \text{ au},$$

$$C_6(\mathrm{He}_2^*(c^3\Sigma_g^+) - \mathrm{He}(1^1S)) \approx 68(4/5 + 3/5\cos^2\Theta) \text{ au}.$$

We observed appreciable broadening of the absorption line in ^{4}He as a function of temperature. The natural oscillation frequencies of the bubble which are easily estimated correspond to temperatures around 3 K and we ascribe the observed broadening to the excitation of vibrational degrees of freedom of the bubble.

We obtained an estimate of the coefficient of van der Waals interaction of the molecules $C_6 = 7000 \pm 1000$ au. Allowance for the strong attraction of molecules at large distances yields the conclusion that the diffusion-limited rate of excimer recombination does not depend on the molecular polarization. Calculations using the proposed model show good agreement with all the available experimental values measured under conditions when the diffusion approximation is valid (normal ^{3}He and superfluid ^{4}He at temperatures above 1.7 K). The recombination coefficient measured in cold ^{3}He gas agrees with the data [5] obtained in ^{4}He at similar densities and shows good agreement with the results of the theoretical calculations [20] for an extremely low-density gas.

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