lation of the principal terms. If we make the natural assumption that the small quantities have a smooth dependence on the radiation frequency, then the small corrections, by interfering with the principal terms, lead to a shift of the calculated minimum. On the other hand, if the small corrections give an additive increment to the absorption cross section, then the entire frequency dependence of the absorption coefficient shifts upwards with practically no deformation. Thus, the qualitative conclusion that the absorption coefficient has a deep minimum remain unchanged.

The author thanks V. M. Buĭmistrov for remarks and V. N. Kolesnikov for interest in the work.

[1)] To prove this fact it must be recognized that the Green's function of the atom at a negative value of the energy attenuates exponentially outside the atom, just as the wave functions of bound states.[10]

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Translated by J. G. Adashko

Interaction potential of He(2^3S_1) atoms with H_2 molecules at thermal energies

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(Submitted 22 January 1979)
Zh. Eksp. Teor. Fiz. 77, 52–59 (July 1979)

Optical orientation of the atoms was used to investigate the ionization of H_2 molecules by He(2^3S_1) atoms. The temperature dependence of the reaction rate constant $\bar{C}(T)$ is determined in the interval 77–400 K. Analytic expressions for $\bar{C}(T)$ are obtained within the framework of the classical treatment of the chemo-ionization process for the case of an exponential representation of the real and imaginary parts of the complex interaction potential $V^* - i\Gamma/2$. This has made it possible to obtain for this potential parameters that agree with the obtained experimental $\bar{C}(T)$.

PACS numbers: 82.20.Pm, 82.20.Kh, 82.30.Cf, 34.20.Be

INTRODUCTION

The excitation energies of metastable helium atoms, 19.8 eV for 2^3S_1 and 20.6 eV for the 2^1S_0 state, are sufficient for the ionization of most atoms (with the exception of helium and neon in the ground state) and molecules. The investigation of the ionization reactions with participation of metastable helium atoms has received much attention of late.[1-7] The simplest molecule that can be ionized by a helium atom in a metastable state is hydrogen. In the case of He*(2^3S_1), this reaction proceeds via the following channels:

$$He^* + H_2 \to He + H_2^+ + e^-, \tag{1a}$$

$$He^* + H_2 \to HeH_2^+ + e^-, \tag{1b}$$

$$He^* + H_2 \to HeH^+ + H + e^-, \tag{1c}$$

$$He^* + H_2 \to He + H + H^+ + e^-, \tag{1d}$$

where (1a) is Penning ionization and its contribution is >80%[8]; (1b) is associative ionization with a contribution ~3%[8]; (1c) is ionization with restructuring, with a contribution ~15%[8]; (1d) is dissociative ionization with the smallest contribution, <1%.[1]

The total ionization cross section σ_{H_2}, which is the sum of the cross sections of all the channels of the reaction (1), was determined in experiment by investigating a decaying plasma[9-11] using atomic and molecular beams[12,13] as well as with the aid of optical orientation of atoms.[14-16]

The He*–H_2 system contains a small number of electrons, so that rather exact calculations could be performed for it by various methods.[17,18] The complex or optical potential was found to be

$$W(R, \theta)=V^*(R, \theta)-{}^1/_2 i\Gamma(R, \theta),$$

where $V^*(R, \theta)$ is the potential energy surface for the He*–H_2 system, $\Gamma(R, \theta)$ is the width of the autoionization level, and R and θ are the polar coordinates. It was shown that in the calculation of the total cross section of the reaction (1) it suffices to retain the spherically symmetrical part of the potential $W(R, \theta)$. It turned out that the dependence of the autoionization width on the distance R between H_2 and He* has an exponential character

$$\Gamma(R)=A \exp(-\alpha R), \tag{2}$$

and the potential $V^*(R)$ is repulsive at almost all R, with the exception of very large R, when a van der Waals attraction takes place and results in a small energy minimum at $R\sim 13a_0$ (a_0 is the radius of the first Bohr orbits). This behavior of the potential $W(R)$ corresponds to an increase of the cross section σ_{H_2} with increasing temperature, in agreement with the general experimental course $\sigma_{H_2}(T)$.[11,14–16] However, the values of σ_{H_2} calculated on the basis of these potentials are much smaller than the experimental ones, especially at low temperatures. It is therefore of interest to determine the potential $W(R)$ which agrees with the experimental $\sigma_{H_2}(T)$ dependence.

It should be noted that the experimental results on the reaction (1), obtained out by various workers, differ substantially. This is clearly seen in the summary of the results given in Ref. 17. Thus, according to Ref. 11 $\sigma_{H_2}=(1.3\pm 0.4)\,\text{Å}^2$, while according to Ref. 12 this quantity is 2.5 times larger. This difference between the experimental results can be attributed to the difficulty of separating the interaction of H_2 with the helium atoms in the 2^1S_0 and 2^3S_1 states, as well as to the need for estimating the degree of deviation of the particle velocity distribution from Maxwellian. These difficulties, which are inherent in experiments with atomic beams and afterglow, can be circumvented by investigating the reaction (1) by the method of optical orientation of the atoms.[14]

The present paper is devoted to a determination of the complex potential $W(R)$ of the He*–H_2 system on the basis of results of experiments on optical orientation of atoms in the temperature interval 77–400 K. In the first part of the paper we describe the procedure for determining the rate constants of the reaction (1) and present the experimental results. In the second part, on the basis of quasiclassical description of the chemo-ionization process Smirnov's,[19] we obtain analytic expressions for the rate constants of the reaction (1), which are used to obtain for the complex potential $W(R)$ parameters that agree with the experimental results.

1. DETERMINATION OF THE RATE CONSTANT OF THE REACTION OF IONIZATION OF H_2 BY He* ATOMS BY THE METHOD OF OPTICAL ORIENTATION OF THE ATOMS

The experimental investigations were performed with the apparatus described in detail earlier.[20]

The absorption chamber, filled with a mixture of He^4(0.36 Torr) and H_2(0.019 Torr) at 300 K, was placed in a homogeneous constant magnetic field $H_0 \parallel Z$ produced by a system of Helmholtz coils. A weak high-frequency gas discharge in the absorption chamber excited a fraction of the atoms ($\sim 10^{-5}$–10^{-6}) from the ground state 1^1S_0 to the metastable state 2^3S_1. The metastable atoms optically oriented by circularly polarized light of wavelength $\lambda = 10\,830$ Å (the transition $2^3S_1 \to 2^3P$) directed along Z (Fig. 1). Application of an oscillating magnetic field $H_1 \cos\omega t$ perpendicular to H_0 makes it possible to produce magnetic resonance in the system of the 2^3S_1 helium atoms.

We determined the width of the magnetic-resonance line of the He* atoms in the temperature interval 77–400 K. The absorption chamber was placed in a dewar through which cooled nitrogen vapor (in the interval 77–300 K) or hot air (in the interval 300–400 K) was pumped. The temperature was regulated by varying the gas flow. The stability of the temperature setting during the measurement time was not worse than 3 K.

Addition of hydrogen to the helium leads to a noticeable broadening of the resonance line compared with the case of pure He^4, owing to the disintegration of the 2^3S_1 state of the helium as the result of process (1). To separate the contribution made to the width of the resonance line by (1), we determined, under identical experimental conditions, both the line width in the mixture He^4+H_2 (Δf_{He+H_2}) and the line width of the magnetic resonance in pure He^4 (Δf_{He}). The mean value of the rate constant for the given temperature $\bar{C}=\langle\sigma v\rangle$ was obtained from the relation

$$\pi\Delta f_{H_2}=N_{H_2}\langle\sigma v\rangle, \tag{3}$$

where N_{H_2} is the concentration of the hydrogen molecules, v is the average collision velocity of the He^3

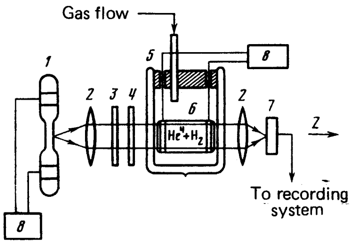

FIG. 1. Diagram of the experimental setup for the investigation of the optical orientation of helium atoms in the mixture He^4+H_2. 1— Capillary helium lamp; 2— lenses; 3— PPI-1 polaroid; 4— quarter-wave mica plate; 5— dewar; 6— absorption chamber; 7— silicon photodetector FD-7K; 8— high-frequency generator.

atoms, and Δf_{H_2} is the contribution made to the width of the resonance line by the process (1) and is equal to

$$\Delta f_{H_2}=\Delta f_{He+H_2}-\Delta f_{He}. \tag{4}$$

The expression (4) for Δf_{H_2} is quite reasonable, inasmuch as in the case of pure helium the width of the resonance line is determined mainly by the diffusion of the metastable atoms towards the absorption-chamber wall, by the inhomogeneity of the constant magnetic field, and by the presence of uncontrollable impurities, and all these factors remain practically unchanged when H_2 is added. At the same time, the line broadening due to the collision of He* with electrons, He*, and He_2^* is very small, so that the possible change of the concentration of these particles following the addition of H_2 does not affect the accuracy with which Δf_{H_2} is given by Eq. (4). The possible difference between the optical broadening in pure He^4 and in the He^4+H_2 mixture, due to the decrease of the concentration of He* following the addition of the hydrogen, is negligible and can be accounted for at small Δf_{H_2} by extrapolating the resonance-line widths Δf_{He} and Δf_{He+H_2} to zero pump-light intensity.

Next, the disintegration of He* can be the result of not only the reaction (1), but also of collisions of He* with H, H_2^+, H_3^+, HeH^*, etc. Although the rate constants of these reactions can reach values of the order of 10^{-9} cm^{3}sec^{-1}, their contribution to the line width Δf_{H_2}, compared with the reaction (1), is very small, since the concentration of these particles is ~10^{10} cm^{-3}, whereas $N_{H_2}\approx 10^{15}$ cm^{-3}. The small role of these particles was verified also in experiment by determining Δf_{He+H_2} at different discharge intensities. The amounts of H, H_2^+, H_3^+, HeH^+ change when the discharge intensity is increased, so that if these particles were to play a noticable role one should expect an additional broadening of the line in this case. This was not observed, so that the role of the atomic hydrogen and of the different molecular ions in the disintegration of He* is small compared with the role of molecular hydrogen.

Finally, it was shown[18] that the cross section of the inelastic process connected with the rotational excitation of H_2 (for example, from a state with rotational quantum number $j=0$ into a state with $j=2$), at low energies of the relative motion of the particles, is not more than 1% of the total cross section for the ionization of H_2 by the He* atoms, i.e., the contribution of this process to the broadening Δf_{H_2} can also be neglected.

Thus, the cross section of ionization of molecular hydrogen via reactions (1) practically coincides with the cross section for the disintegration of He* by addition of hydrogen. This makes it possible in principle to determine the rate constant of the reaction (1) with an accuracy of several percent.

The experimental results are given in Table I. The error in the determination of $\bar{C}$ is due to the errors in the determination of the width of the resonance line and in the measurement of the hydrogen pressure in the absorption chamber, and does not exceed 15%. A comparison with the previously reported results shows that at $T=300$ K the value of $\bar{C}$ reported in the present paper are close to the data of Refs. 10, 11, and 13, and differs substantially from the value given in Refs. 9 and 12.

TABLE I. Experimental values of the rate constant of the reaction of ionization of H_2 molecules by helium atoms in the 2^3S_1 state.

T, K	$\bar{C}(T)$, 10^{-11} cm^{3}sec^{-1}
77	0.75±0,11
162	1.76±0.21
220	2.57±0.29
300	3.36±0.36
353	4.14±0.53
400	5.31±0.72

The rate constant of the process (1) increases monotonically with increasing temperature. This makes it possible to approximate $\bar{C}(T)$ by a sufficiently simple analytic function, and this will be done subsequently when the parameters of the complex potential $W(R)$ are determined.

2. DETERMINATION OF THE PARAMETERS OF THE INTERACTION POTENTIAL OF THE He(2^3S_1) ATOM WITH THE H_2 MOLECULE

The ionization process (1) can be described either by using the methods of quantum theory of scattering or classically, i.e., by assuming the presence of a trajectory of the relative motion of the Me* atom and the H_2 molecule (Fig. 2). However, the quantum-mechanical method of partial waves is most inconvenient for the calculation of the ionization cross section, inasmuch as at the relative-motion energies investigated in the experiment a large number of scattering phase shifts (of the order of 20) contributes to the value of this cross section. In the classical description of ionization by collision of a metastable atom with an atom or molecule the expression for the rate constant of the reaction is[19]

$$C=4\pi\int_{R_0}^{\infty}\Gamma(R)\,(1-V^*(R)/E)^{1/2}R^2dR. \tag{5}$$

Here R is the distance between the H_2 molecule and the He* atom, and R_0 is the closest approach of the col-

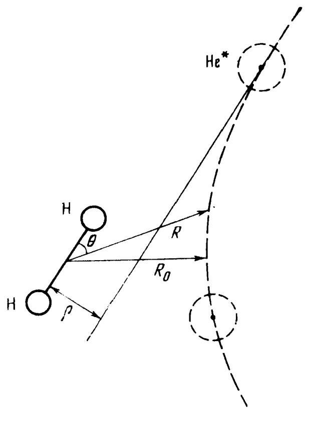

FIG. 2. Trajectory of relative motion of the He* atom and of the H_2 molecule.

liding particles at an impact parameter $\rho=0$, and is determined from the condition

$$V^*(R_0)=E. \tag{5a}$$

In the case of an exponential dependence of the autoionization width $\Gamma(R)$ [in accordance with (2)] and of the potential energy surface of the He*–H_2 system on the distance R:

$$V^*(R)=B\exp(-\beta R), \tag{6}$$

the integration in (5) can be carried through to conclusion, and we obtain the following analytic formula for the rate constant of the chemo-ionization reaction:

$$C=(E/B)^\lambda(A_1\ln^2(B/E)+A_2\ln(B/E)+A_3), \tag{7}$$

where

$$\lambda=\alpha/\beta,\quad A_1=4\pi AD_1/\alpha\beta^2,\quad A_2=8\pi AD_2/\alpha^2\beta,$$
$$A_3=8\pi AD_3/\alpha^3,$$

and $D_i (i=1,2,3)$ are sums of rapidly converging series:

$$D_i=1-\sum_{m=1}^{\infty}\frac{(2m-3)!!}{(2m)!!(1+m\beta/\alpha)^i}. \tag{7a}$$

Equation (7) makes it possible to estimate the influence exerted on the rate constant by various parameters of the complex interaction potential $W(R)$, and also to determine the dependence of the rate constant on the energy of the relative motion of the colliding particles.

For the interaction of He* with H_2 we can estimate the parameters in (7) at $\alpha=2$, $\beta\sim1$ and $\ln(B/E)\gg1$. The $C(E)$ dependence is therefore close to a power-law function whose exponent is equal to the ratio of the slopes of the imaginary and real parts of the complex potential $W(R)$. Thus, by analyzing the experimental dependence [provided, of course, that it can be approximated by (7)], we can determine the value of α/β. In (7), the main contribution (~90%) to the rate constant is made by the first term, so that the coefficient A_1 is in fact a scale factor from which we can determine one more combination of the parameters of the potential $W(R)$. For an unambiguous choice of these parameters it is necessary to use additional considerations. The situation is very similar to that in attempts to choose the correct symmetrical and antisymmetrical interaction potentials in the quasimolecule $He_2^*[He(1^1S_0)\cdot He(2^3S_1)]$ on the basis of only the temperature dependence of the cross section for the metastability exchange between atoms of one and the same helium isotope, when the large divergence of the potential curves could be "compensated" by their large slope.[20]

The transition from the experimental temperature dependence of the rate constant of the reaction $C(T)$ to the energy dependence of this same quantity $C(E)$ was carried out using the calculated dependence of the quantity $\xi=\bar{E}/kT$ on $\lambda=\alpha/\beta$, which are shown in Fig. 3 for different B/kT (k is the Boltzmann constant, T is the absolute temperature, $\bar{E}$ is the average energy for the ionization process (1) and is obtained as the result of averaging (7) in accordance with the Maxwellian particle energy distribution). At $B/kT>10^4$ and α/β taken from Refs. 1 and 2, good accuracy is obtained with curve 1, which corresponds to $B/kT\to\infty$. In this case

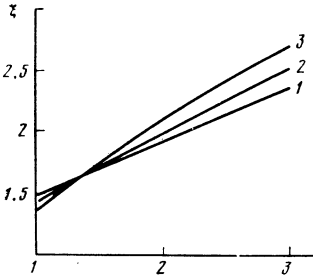

FIG. 3. Depencence of the quantity $\xi=\bar{E}/kT$ on $\lambda=\alpha/\beta$ at different values of B/kT. 1—$B/kT\to\infty$; 2—$B/kT=10^4$; 3—$B/kT=10^2$

$$\xi=[2\pi^{-1/2}\Gamma(\lambda+3/2)]^{1/\lambda}, \tag{8}$$

where the Euler gamma function $\Gamma(x)$ with argument $x=\lambda+\frac{3}{2}$ is used.

Since, as noted above, the analysis of the $C(E)$ dependence does not make it possible to determine uniquely all four parameters of the complex interaction potential

$$W(R)=B\exp(-\beta R)+{}^1/_2 iA\exp(-\alpha R), \tag{9}$$

we can use the values of some of those parameters which are known with sufficiently high degree of reliability from other studies. Thus, the values of the parameters A and α of the autoionization width $\Gamma(R)$, which were calculated earlier,[17,18] are close to each other (see Table II). In addition, according to Ref. 21, the exponential factor α calculated in Ref. 17 is in good agreement with the semiempirical formula for single-electron exchange[22] that can take place also upon ionization of hydrogen molecules by 2^3S_1 helium atoms.[23] Thus, assuming that we know the parameters of the imaginary part of the potential (9), i.e., the width of the autoionization level $\Gamma(R)$, we can, by analyzing the experimental $C(T)$ dependence using (7) and (8), determine the parameters B and β of the real part of this potential, i.e., of the potential energy surface $V^*(R)$ of the He*–H_2 system, or of the potential of the interaction of He* with H_2. These parameters are given in Table II. In the calculation of the rate constant of the reaction (1) by formulas (7) and (8), using the mean values of the parameters B and β listed in Table II, the mean squared deviation from the mean values of the experimental $\bar{C}(T)$ listed in Table I was less than 2%. We can note further that the quantity ξ was equal to 1.65, i.e., the average energy for the ionization process (1) exceeded slightly the average thermal energy of the particles.

In Fig. 4 are plotted the potentials of the interaction of the 2^3S_1 metastable atoms of helium with the hydrogen molecules, obtained in the present paper (curves

TABLE II. Parameters of the potential of the interaction of He* with H_2, determined on the basis of experiments on optical orientation of the atoms (in the atomic system of units).

Parameters of autoionization width	B	β
$A=18.5$; $\alpha=1,95$ [17]	42±2	1.47±0.01
$A=14.008$; $\alpha=2,0177$ [18]	28±1	1.51±0.01

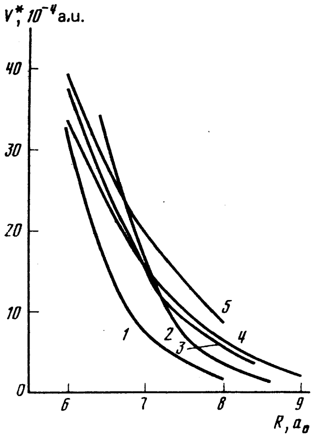

FIG. 4. Potential of the interaction of the He(2^3S_1) atom with the H_2 molecule. 1—Determined on the basis of the experimental $C(T)$ dependence from formulas (7) and (8), using the parameters of the autoionization width $\Gamma(R)$ of Ref. 18; 2—the same using these parameters from Ref. 17; 3—determined in Ref. 24; 4—calculated in Ref. 18; 5—calculated in Ref. 17.

1 and 2), calculated quantum-mechanically in Refs. 17 and 18 (curves 4 and 5), and also determined in Ref. 24 from experiments with atomic and molecular beams (curve 3). It should be noted that in Ref. 24 principal attention was paid not to the exact determination of the potential in the investigated energy interval 20–180 meV, but to a check on the absence of a structure in this (triplet) potential compared with the singlet potential, i.e., the potential of the interaction of He(2^1S_0) with H_2. A comparison of curves 1–5 (Fig. 4) points to a noticable difference between the potentials obtained in the present paper and in Refs. 1, 7, 18, and 24, especially at $R > 7a_0$. The previously obtained potentials are excessively repulsive at large distances between He(2^3S_1) and H_2.

In conclusion, the authors thank R. A. Zhitnikov for interest in the work and for useful remarks.

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Translated by J. G. Adashko