Exchange of metastability in a mixture of ^{3}He and ^{4}He isotopes

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An investigation is made of the process of nonresonant excitation transfer by exchange of metastability in a ^{3}He–^{4}He mixture of helium isotopes at thermal energies. The behavior of the metastability exchange cross sections $\sigma_1(^3\text{He}–^3\text{He})$ and $\sigma_2(^3\text{He}–^4\text{He})$, and of their relative difference $\Delta\sigma=(\sigma_1-\sigma_2)/\sigma_1$ in the temperature range from 77 to 300°K is explained. In a theoretical investigation of the isotopic effect the process of exchange is considered as the result of interference between the *g* and *u* states of a quasimolecule, composed of normal and excited helium atoms.

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1. Elastic scattering of metastable helium atoms by normal atoms has a number of interesting properties associated with the quantum symmetry effects and with the structure of the atomic interactions. Helium is one of the few substances for which sufficiently accurate theoretical calculations have been carried out and, consequently, it is possible to compare quantitatively the theory and experiment.

In addition to the purely elastic scattering, there is also a possibility of resonant excitation transfer:

$$\text{He}^*(2^3S)+\text{He}(1^1S)\rightarrow\text{He}(1^1S)+\text{He}^*(2^3S). \qquad (1.1)$$

In this process there is no exchange of the translational and internal energies between the nuclei. Hence, it follows that the scattering process (1.1) can be regarded as a form of elastic scattering.

2. In investigating the nature of long-range forces of colliding atoms it is particularly interesting to consider the results of the experiments on the elastic scattering at low temperatures.

The first experimental determination of the scattering cross sections of metastable atoms was made by the molecular beam method.[1-5] The cross section of the metastability exchange process (1.1) was determined in Refs. 6 and 7 at low energies. Reliable measurements of the cross sections in the temperature range from 15 to 115 °K and also at 300 °K were made in Refs. 8 and 9, respectively.

The isotopic effect was observed in Ref. 10 and the cross sections $\sigma_1(^3\text{He}–^3\text{He})$ and $\sigma_2(^3\text{He}–^4\text{He})$ were obtained experimentally from the optical orientation and magnetic resonance of metastable helium atoms (2^3S_1) in a mixture of the ^{3}He and ^{4}He isotopes at thermal energies. Figure 1a shows the experimental values of the cross sections σ_1 and σ_2 averaged over the temperature distribution at six temperatures from 77 to 300 °K; the error is within 8%.

The temperature dependence of the relative difference $\Delta\sigma=(\sigma_1-\sigma_2)/\sigma_1$ is shown in Fig. 1b.

It is clear from these figures that a considerable difference between σ_1 and σ_2 appears at a temperature below 300 °K and rises to a factor of 2 at 77 °K; the cross section for the different isotopes becomes smaller.

3. This experimental observation can be explained if we consider, in accordance with the scheme of (1.1), the interaction between two helium atoms, one of which is in the ground state 1^1S_0 and the other in the metastable state 2^3S_1.

Elastic scattering of metastable helium atoms in a gas of unexcited helium atoms is characterized by two interaction potentials which are degenerate at infinity: $V_g(R)$ and $V_u(R)$, corresponding to the symmetric and antisymmetric superpositions of the ground state of one atom and of the metastable state of another atom. In the case of scattering of metastable helium these molecular states are the lowest states $^3\Sigma_g$ and $^3\Sigma_u$ of the quasimolecule He_2^* (Refs. 11 and 12).

The potential $V_u(R)$ corresponds to the antisymmetric wave function of the system and it has a minimum for the internuclear distance $R=2a_0$ ($a_0=0.53\times10^{-8}$ c.m.—Ref. 13).

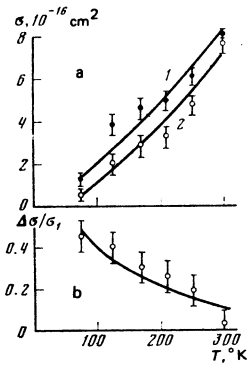

FIG. 1. a) Metastability exchange cross sections σ_1 (^{3}He–^{3}He) (1) and σ_2 (^{3}He–^{4}He) (2) averaged over the thermal distribution and plotted as functions of temperature. b) Relative difference $\Delta\sigma=(\sigma_1-\sigma_2)/\sigma_1$: ○, ●) experimental results; the calculations are represented by a continuous curve. The calculated temperature dependences are close to linear in the investigated temperature range, which makes it easier to average over the energies of the colliding particles.

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The potential energy $V_u(R)$ has a maximum at a relatively large internuclear distance ($R = 4.5a_0$). This is explained by competition between the various exchange forces.[14] The existence of a potential barrier is closely related to the existence of an excitation energy in the metastability exchange reaction.[11,15] Although the existence of the excitation energy has been confirmed in optical pumping experiments,[16] there is still a large discrepancy with the results of Ref. 11. Since the most probable source of error is in calculation of the term $^3\Sigma_u$, much theoretical work has been done on this topic[17-19] and the results of Ref. 19 are in good agreement with the experiments.[8]

The existence of a potential barrier in the case of both potential curves $V_g(R)$ and $V_u(R)$ of an investigated pair of atoms has the effect that the metastability exchange cross sections decrease when the kinetic energy increases.

The long-range interaction is governed by the van der Waals forces; it has the form $-30.5/R^6$ expressed in atomic units for both terms. (The coefficient 30.5 follows from a calculation based on a variational approach in perturbation theory.[13]) This interaction gives rise to a minimum of both potential curves at $R \sim 6-7$ Å with a depth less than 1 meV, which is unimportant for the process in question.

It should be stressed that the results of calculations of the potential curves are very sensitive to the nature of the wave functions. Therefore, the behavior of the terms (particularly in the case of large distances between the nuclei) must be checked and refined experimentally.

Figure 2 shows the potential curves obtained recently by Brutschy and Haberland.[20] A qualitative explanation of the temperature dependences of σ_1 and σ_2 in the range from 77 to 300 °K is given in Ref. 10.

The metastability exchange cross section is governed by the difference $\Delta V = V_g - V_u$ averaged during the time

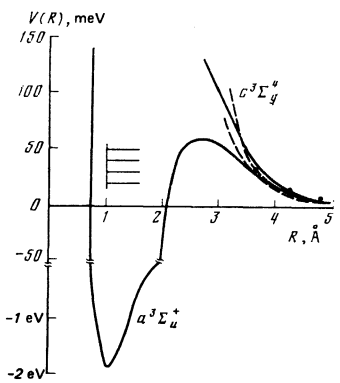

FIG. 2. Potential curves for the He(2^3S) + He(1^1S) process.[20] The barrier height of the symmetric term is approximately four times that of the antisymmetric term. The points were obtained in Ref. 21 and the dashed curves in Ref. 19. The density of the population of a potential well with quasistationary states is shown schematically. The average distance between the levels in the well is of the order of 10^{-2} eV, whereas the width of the levels does not exceed 10^{-7} eV.

of interaction between helium atoms and multiplied by the interaction time, i.e., the time during which atoms are in a region of considerable divergence between the potentials.[22] When temperature is lowered, the cross section decreases because of the repulsive nature of the terms. Conversely, when temperature is increased, the effective interaction range and, consequently, the average value of the potential difference ΔV increases considerably (Fig. 2). This causes the cross sections σ_1 and σ_2 to rise steeply.

It is clear from Fig. 1b that the relative difference $\Delta\sigma$ is fairly large in a wide range of temperatures.

4. In a theoretical investigation of the isotopic effect we can employ the usual representation of the process as the result of interference between the g and u states of a quasimolecule[23,24] allowing for the factors listed below.

a) The number of partial waves from which cross sections are formed in the investigated temperature range varies from 20 to 40. Hence, it follows that the approximation of classical trajectories can still be used, but partial waves have to be summed to reveal fine effects.

b) In the classical trajectory approximation the velocity of motion in the ^{3}He–^{3}He system, which is characterized by the smaller reduced mass, is greater for a given energy than in the ^{3}He–^{4}He system. Therefore, the integral $\int_{-\infty}^{\infty} \Delta V dt$ is somewhat larger in the latter case than in the former and $\sigma_2(^3\text{He}-^4\text{He})$ is greater than $\sigma_1(^3\text{He}-^3\text{He})$, which is contrary to the experimental results; hence, it follows that this factor does not predominate.

c) On the other hand, the same difference between the reduced masses has the result that the ^{3}He–^{3}He system penetrates deeper under the potential barrier where ΔV increases and this factor tends to increase the cross section for the ^{3}He–^{3}He pair.

d) In principle, we can also expect some influence of the resonant effects associated with the presence of quasistationary states, particularly in the case of the term $^3\Sigma_u$, when the barrier height is of the order of 0.1 eV.

e) Finally, we can allow for the nonresonant nature of the excitation transfer process. We must bear in mind that in the case of large internuclear distances the terms $^3\Sigma_g$ and $^3\Sigma_u$ will be different only is we allow for the nonadiabatic corrections, which take into account the motion of nuclei in each of the atoms so that the potential curves should be considered here in the generalized sense.

However, calculations show that neither the subbarrier penetration nor resonances can give any significant contribution to the excitation transfer cross section. In fact, the average distance between quasidiscrete levels inside a well is of the order of 10^{-2} eV, whereas the level width is of the order of 10^{-7} eV (Ref. 22) at temperatures ~300 °K. Consequently, the probability of formation of quasistationary states corresponding to levels in a well is negligible.

The integral $\int_{-\infty}^{\infty} \Delta V dt$ for the ^{3}He–^{4}He system is several percent higher than the corresponding integral for the ^{3}He–^{3}He system, but this difference is not significant.

Estimates indicate that the difference between the excitation energies of the state 2^3S_1 for the ^{3}He and ^{4}He isotopes makes the process of metastability exchange between atoms of different helium isotopes strongly nonresonant.[10] The resonance defect $\Delta = \Delta_2 - \Delta_1$ appears mainly because of the difference between the masses[1)] of the ^{3}He and ^{4}He atoms.

5. Theoretical calculations[14,19] relating the cross section $\sigma_1 = \sigma_1(^3\text{He}-^3\text{He})$ and its temperature dependence to V_g and V_u have already been made, but similar calculations have not been carried out for the interaction between ^{3}He and ^{4}He and for the cross section $\sigma_2 = \sigma_2(^3\text{He}-^4\text{He})$. Had the results of such calculations been available, it would have been possible to determine more accurately the potentials V_g and V_u from the values of σ_1 and σ_2 and their temperature dependences found experimentally. Clearly, the potential curves V_g and V_u should allow for the above splitting at infinity; the exact solution of the problem goes beyond the adiabatic theory framework.

We shall use the adiabatic approach to deal with the process (1.1). We shall assume that the velocity of atoms is much less than the velocity of the outer electrons and that their kinetic energy is much greater than the kinetic energy of electrons (in our case these conditions are satisfied). The case of resonant excitation transfer is considered in Refs. 23 and 24. Here, we shall discuss a small resonance defect, i.e., a small difference between the electron energies of the initial and final states.

We shall also assume that nuclei move along classical trajectories; we shall represent the wave function of the system approximately in the form

$$\psi(t) = a(t)\varphi_A + b(t)\varphi_B, \tag{5.1}$$

where φ_A and φ_B are the wave functions of electrons in the states near atoms A and B in the process

$$A^+ + B \to A + B^+$$

or in the excitation transfer process corresponding to the scheme (1.1). This case of two-level approximation was considered by Demkov[25] using adiabatic theory.

The probability of nonresonant charge exchange is given by

$$w = \left(\sin^2 \int_{-\infty}^{\infty} H_{12}\, dt\right) \Big/ \operatorname{ch}^2(\pi\alpha/\gamma), \tag{5.2}$$

where

$$H_{12} = \int \varphi_A \cdot \hat{H} \varphi_B d\mathbf{r},$$

where integration is carried out over the electron coordinate; $\hat{H}$ is the Hamiltonian of the system; $\alpha = \Delta/2$; $\gamma t = \sqrt{2I}R$; I is the lowest ionization potential of a helium atom; R is the internuclear distance.

The limits of validity of the above formula are also discussed in Ref. 25; they correspond to the experimental conditions of Ref. 10.

The square of the hyperbolic cosine in the denominator of Eq. (5.2) allows for the resonance defect in the excitation transfer process. If $\alpha = 0$, there is no splitting and Eq. (5.2) reduces to the formula for the usual resonant charge exchange.

6. The metastability exchange cross section in the resonant case can be calculated from

$$\sigma_{trans} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\eta_l^g - \eta_l^u). \tag{6.1}$$

The nature of the interaction of colliding particles is such that the sum in Eq. (6.1) has a finite number of terms representing partial cross sections. Then, l_{max} (maximum value of the orbital quantum number) is governed by the difference ΔV in the long-range parts of the potential curves and by the kinetic energy of the atoms. At $T = 300\,^\circ$K the sum (6.1) contains about 40 terms.

The phases are calculated using the familiar Jeffreys formula:

$$\eta_l^{g,u} = \int \left[k^2 - 2\mu V_{g,u}(R) - \frac{(l+1/2)^2}{R^2} \right]^{1/2} dR - \int \left[k^2 - \frac{(l+1/2)^2}{R^2} \right]^{1/2} dR, \tag{6.2}$$

where the lower limits of the integrals are the largest zeros of the integrands. Figure 3 shows typical dependences of the difference $\eta_l^u(k) - \eta_l^g(k)$ on the orbital quantum number obtained for three values of the energy of the ^{3}He–^{3}He system. It should be pointed out that the behavior of the $\eta_l^u - \eta_l^g$ system as a function of l is governed not only by the value of ΔV but also by the difference between the classical turning points for the symmetric and antisymmetric terms and, consequently, by the steepness of these terms. Therefore, the less steep terms would have made a somewhat greater contribution to the cross section than the steeper terms with the same divergence ΔV, but this difference is compensated to some extent by the fact that in allowing for the difference between the turning points the scattering phases are governed not only by the divergence ΔV but also by the potentials V_g and V_u.

Clearly, if we neglect the difference between the turning points, the steeper potentials with a smaller diver-

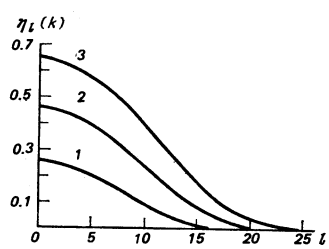

FIG. 3. Characteristic dependence of the difference $\eta_l(k) = \eta_l^u(k) - \eta_l^g(k)$ on the orbital quantum number for different energies: 1) $k = 1.850$ a.u. ($E = 16.90$ meV); 2) $k = 2.356$ a.u. ($E = 27.42$ meV); 3) $k = 2.732$ a.u. ($E = 36.87$ meV); $k = \mu v_\infty$, where v_∞ is the thermal velocity of a system of a colliding atoms. The calculations are made for the ^{3}He–^{3}He system.

gence and the less steep potentials with a larger divergence will make the same contribution to the excitation transfer cross section. (This becomes particularly true if we can ignore also the difference between pairs of classical turning points of the corresponding pairs of terms.)

The cross section $\sigma_2(^3\text{He}-^4\text{He})$ in the nonresonant case can also be calculated from Eq. (6.2) if the final result is multiplied by the average value of the square of the hyperbolic secant.

The cross sections were calculated and averaged over the temperature scale on a computer. The results are shown in Figs. 1a and 1b (continuous curves). As pointed out earlier,[10] an increase in the potential difference $\Delta V = V_g - V_u$ at low values of R causes the metastability exchange cross sections to increase with the kinetic energy. They begin to oscillate[20] when the energy of the system exceeds the antisymmetric potential barrier ($T > 300\,^\circ\text{K}$). The calculated temperature dependences of the cross sections are fairly close to linearity in the investigated range of temperatures, which makes it easier to average $\sigma_1(T)$ and $\sigma_2(T)$ over the energies of the colliding particles and then the relative difference $\Delta\sigma(T)/\sigma_1(T)$ agrees well with the experimental results of Ref. 10.

We shall conclude by noting that the approximation employed is not fully self-consistent because the σ_2 ($^3\text{He}-^4\text{He}$) cross section is first calculated in the approximation of resonant metastability exchange, and then only multiplied by a factor allowing for the resonance defect and the corresponding head-on collisions. It would be more correct to allow this factor in each partial wave, solving a system of two second-order differential equations, which would have reduced additionally the effective cross section. It is possible that in this case the calculated cross sections can be made to agree better with the experimental results and can reproduce an inflection in the region of 100–250 °K (Fig. 1). One should also bear in mind that in the case of cross sections not averaged over the temperature scale the nonmonotonicity in this range should be even steeper, so that the problem of theoretical explanation is still urgently in need of solution.

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