Temperature Dependence of Helium Metastability Exchange Cross Section

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The cross section for exchange of metastability in collisions between He^3 atoms in the ground (1^1S_0) state and metastable (2^3S_1) state has been measured as a function of temperature by optical pumping techniques. The exchange cross section decreases from about 5.5×10^{-16} cm^2 at 500°K to less than 10^{-17} cm^2 at 4.2°K. These results suggest a thermally activated exchange process in qualitative agreement with the predicted existence of a long-range repulsive interaction between metastable and ground-state helium atoms as proposed by Buckingham and Dalgarno.

INTRODUCTION

WHEN a weak electrodeless discharge is excited in a low-pressure helium gas a steady state is maintained in which a few atoms (about one in 10^6) are in the 2^3S_1 metastable state. The lifetime of this state is determined primarily by diffusion to the walls of the containing vessel, collisions with ions and electrons, and in three body collisions. In the two-body collision between a metastable and a ground-state atom the 2^3S_1 "state" is not usually destroyed but the metastability may be transferred from one atom to the other as a result of exchange of electrons between the colliding atoms. Thus at low pressures the metastability can be transferred from atom to atom many times before this excited state suffers a destructive collision. By the method described in this paper the metastability exchange process,

$$He^* + He = He + He^*$$

(where* denotes an atom in the 2^3S_1 metastable state), can be singled out for study and the cross section measured. These measurements were made in the temperature range 4.2 to 500°K and verify the important qualitative features of previous theory.

Detailed calculations by Buckingham and Dalgarno[1,2] in 1952 predicted the existence of a long-range repulsive interaction between a normal helium atom and one in the 2^3S_1 state. An energy barrier of 0.29 eV was calculated to occur at a separation of about 2 Å (see Fig. 1). When account was taken of the van der Waals interaction, the barrier height was reduced to about 0.18 eV; however, the contribution of van der Waals forces was considered to be extremely uncertain. At closer range, the interaction becomes attractive, with the calculations indicating a potential minimum at 1-Å separation. This accounts for the metastable $2^3\Sigma_1$ helium molecule which is known to exist as a bound state with a lifetime of about 50 msec at room temperature.[3]

The predicted long-range repulsion will cause significantly different behavior for thermally activated processes in the helium gas compared to similar phenomena in many other gases. The usual view is that the force between the two atoms forming a molecule is attractive even for large separation as, for example, in the case of hydrogen atoms also shown in Fig. 1. Therefore, the cross section for any collision-induced transfer of excitation between the atoms will increase monotonically with decreasing temperature approaching a maximum at or very near absolute zero.[4,5] In contrast to this usual temperature dependence, Buckingham and Dalgarno showed that the metastability exchange cross section in helium should *decrease* rapidly at low temperatures, approaching zero at the absolute zero of temperature.[2] Based on the results of their interaction energy calculations they determined qualitatively the expected temperature dependence of the exchange cross section. The result is shown as the solid curve in Fig. 2.

The physical basis of the theory is briefly as follows. The probability of electron transfer during a collision, hence the exchange cross section, depends upon the distance of closest approach of the colliding atoms and the difference in energy between the symmetric and antisymmetric $^3\Sigma$ states of the helium molecule. The energy difference ΔE decreases rapidly as the approach distance increases; thus at low temperatures, where the thermal energies of the colliding atoms are generally

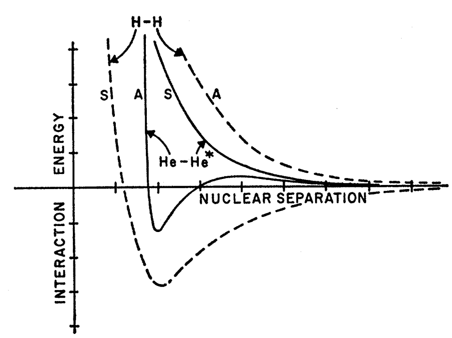

FIG. 1. Predicted symmetric (S) and antisymmetric (A) potentials between a helium atom in the 1^1S_0 state and one in the 2^3S_1 state (solid curves—Ref. 1) and between two hydrogen atoms (dashed curves—Ref. 4). The scales are arbitrary.

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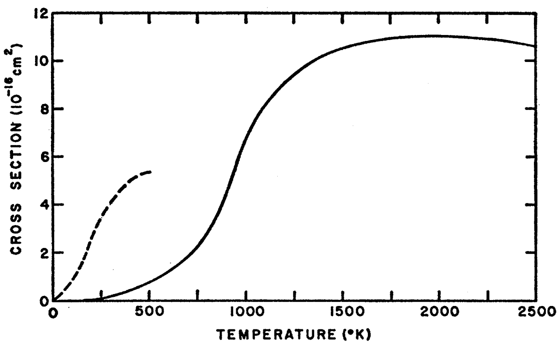

FIG. 2. Predicted temperature dependence of excitation transfer cross section (Ref. 2). Dashed curve indicates values derived from our measurements.

lower than the repulsive barrier height, the interaction occurs only at relatively long range. The exchange cross section is then small and is proportional to $\Delta Et/\hbar$, where t is the collision duration and ΔE is the energy difference averaged over the effective scattering range. The cross section will increase with increasing temperature due to the rapid increase of ΔE as the distance of closest approach decreases.

At high temperature where the colliding particles have energy much larger than the potential barrier, the cross section will decrease with increasing temperature in the usual manner expected in cases where no barrier exists.[2] At these energies ΔE becomes almost constant for small inpact parameters and the electrons can be considered to exchange at the rate $\Delta E/\hbar$ during the collision while for larger impact parameters both ΔE and t decrease with increasing relative velocity of the particles. Several calculations of the interaction energy between a helium atom in the ground state and one in the metastable state have recently been made and agreement has been found in all the qualitative aspects of Buckingham and Dalgarno's work, although the potential barrier was generally found to be smaller.[6,7]

Prior experimental work has not provided a good test for the theory outlined above, though limited evidence which tended to support the existence of a long-range repulsive interaction was reviewed by Burhop in 1954[8] and discussed recently by Tanaka and Yoshino.[9]

The experiments reported here were undertaken as a definitive test of the Buckingham-Dalgarno theory. In the following sections we will give measured values of the metastable He^3 resonance linewidth which is directly related to the product of the relative collision velocity and the cross section for metastability exchange. This relationship and the experimental procedures will be described and the results discussed in relation to existing theory.

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[7] R. D. Poshusta and F. A. Matsen, Phys. Rev. **132**, 307 (1963).
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PRINCIPLES OF THE EXPERIMENT

The technique of optical pumping can be used to control relative populations of the magnetic sublevels of the 2^3S_1 metastable helium atom and to observe changes in distribution that occur among these levels. In the usual optical pumping experiment metastable atoms are created in pure helium gas by a weak discharge and are polarized by the absorption of circularly polarized resonance radiation. Transitions between the metastable magnetic sublevels can be induced by means of an alternating transverse magnetic field with the appropriate resonance frequency. Detection of the resonance and measurement of the resonance linewidth are accomplished by monitoring the intensity of the pumping radiation transmitted through the experimental absorption cell.

The experimental parameters can be adjusted in such a way that the most frequent "event" in the life of a metastable atom is metastability exchange with a ground-state atom. The duration of these encounters ($<10^{-12}$ sec) is much shorter than any precession periods involved. During such collisions between a ground-state atom and one in the 2^3S_1 metastable state the total angular momentum and its z component must be conserved. When the exchange occurs between two He^4 atoms, the emerging metastable is in all respects identical to the incident metastable since He^4 has zero nuclear spin and the magnetic properties of the metastable depend only on the electron spin. The resonance linewidth is then unaffected. However, the mass three isotope of helium has nuclear spin $\frac{1}{2}$, hence two magnetic sublevels associated with the ground state and six with the metastable state; i.e., the magnetic properties of the He^3 metastable are determined by the hyperfine interaction between the electron and nuclear spins. Consequently, each metastability exchange is a dephasing, or lifetime limiting, process for a metastable spin state, and the resonance linewidth depends directly

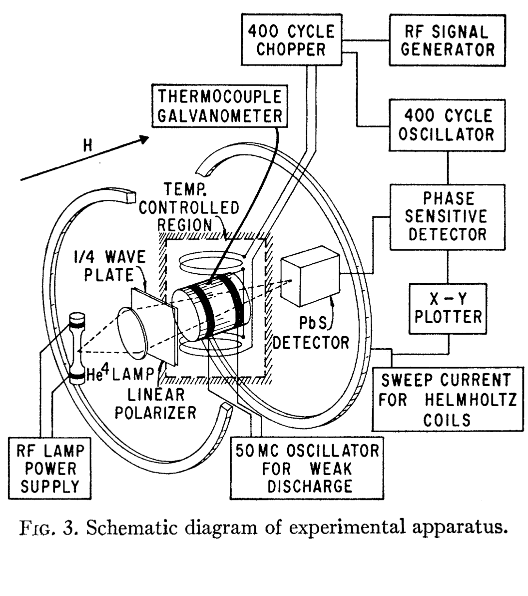


FIG. 3. Schematic diagram of experimental apparatus.

on the rate at which such exchange collisions occur. The nuclear moment of the ground-state atom is almost completely unaffected by the applied alternating magnetic field. Consequently, when an exchange takes place, the emerging metastable is uncorrelated with the incident metastable. In fact the magnetic quantum number of the ground state may change by ± 1 with a corresponding change of the metastable state ∓ 1, so that the emerging atoms may have different magnetic quantum numbers than the incident ones.

The procedure for studying the temperature dependence of the exchange cross section is to perform a resonance experiment on the polarized metastables at each temperature and measure the resonance linewidth

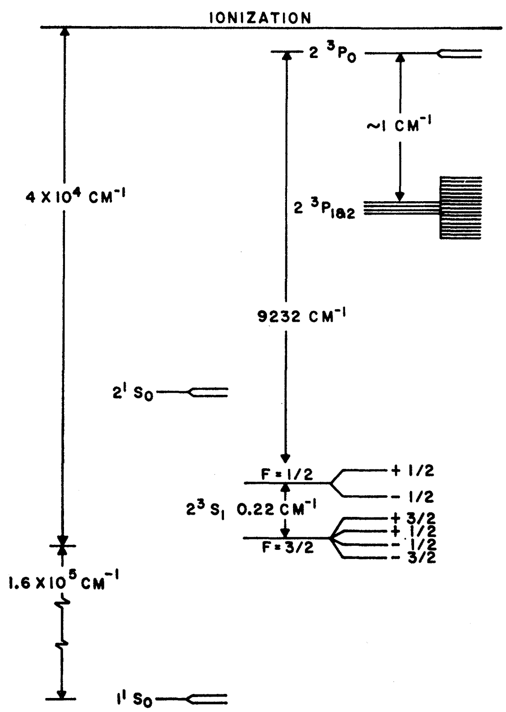
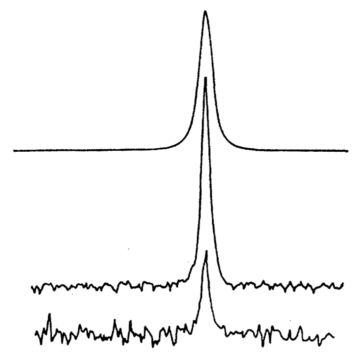


FIG. 4. Energy levels of He^3 atoms in external magnetic field (not to scale).

$\Delta\nu$. The lifetime of a metastable in a particular state before it is disturbed is then simply $\tau = 1/\pi\Delta\nu$. If the magnetic field gradient across the sample volume is ΔH, the linewidth is increased by $\gamma\Delta H$ and the linewidth used to determine τ may be obtained by subtracting this constant amount.

If τ_2 is defined as the average time between excitation transfer for a metastable, then when this process is predominant, $\tau \approx \tau_2$ and the metastability exchange cross section σ is related to the thermal velocity of the atoms v and the density of ground-state atoms N by the equation: $\sigma v = 1/(\tau_2 N)$. Since v will have a Boltzmann distribution and σ is an unknown function of v, the cross section alone can not be measured at a given

FIG. 5. Zeeman resonance lines of the 2^3S_1 metastable state of He^3 for different values of the oscillating magnetic field.



temperature. However, except where σ is a rapidly varying function of v, an approximate value can be obtained by dividing by the mean velocity.

EXPERIMENTAL PROCEDURE

The polarization of He^3 by optical pumping and the observation of resonance transitions between the magnetic sublevels have been described in detail in earlier papers.[10–12] The experiment may be described briefly by reference to the schematic of Fig. 3 and the He^3 energy level diagram of Fig. 4. A Pyrex vessel is filled with He^3 to a pressure between 0.1 and 5 mm Hg at room temperature and sealed. The vessel is then placed in a Dewar or oven. Circularly polarized light from a bright

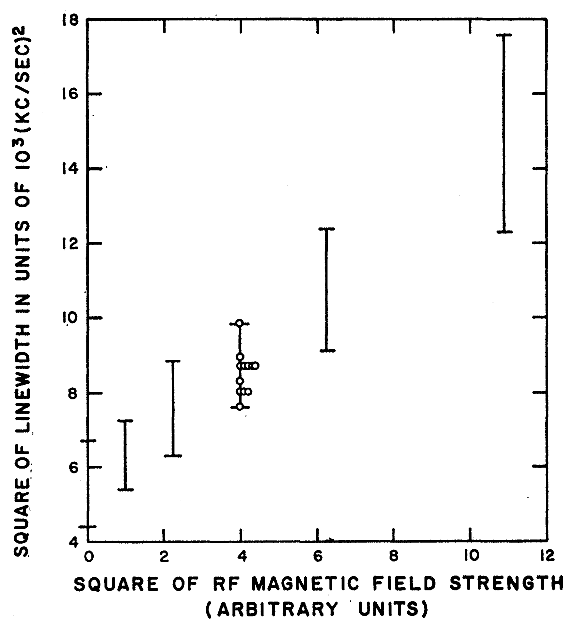


FIG. 6. Dependence of linewidth on strength of oscillating magnetic field.

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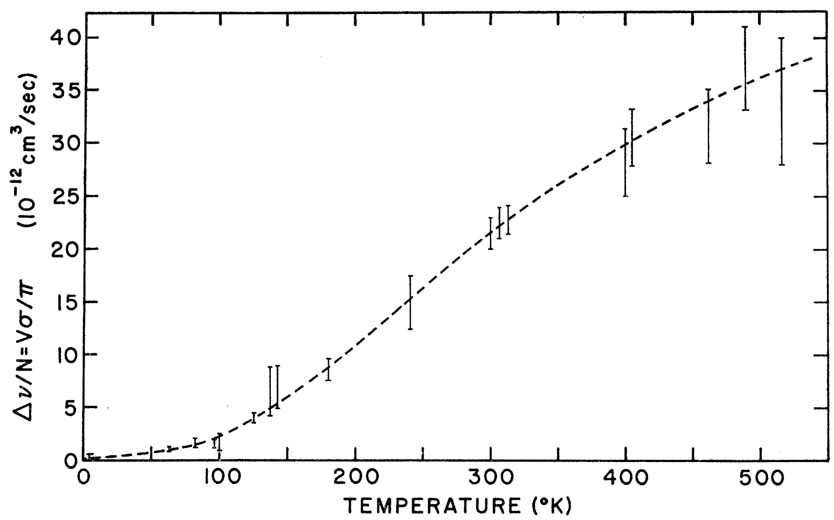

FIG. 7. Temperature dependence of the product of metastability exchange cross section and relative collision velocity.

He^4 lamp is passed through this bulb in the direction of an applied magnetic field and is monitored by a lead sulfide detector. When a weak electrical discharge is maintained in the He^3 gas, 2^3S_1 metastables are created and equally distributed among the six magnetic sublevels. These metastables are polarized by the optical pumping process. The amount of light passing through the sample cell and reaching the detector is related to the polarization of the metastables.[10] Therefore, the degree of polarization can be monitored with the detector.

A coil with its axis in the plane perpendicular to the constant magnetic field is provided to destroy the metastable polarization by exciting transitions among the $^3S_1$ Zeeman levels. The resonance line is obtained by setting the oscillating field at a fixed frequency (between 1 and 10 Mc/sec), chopping this oscillating field at 400 cps, and slowly sweeping the external magnetic field through the resonance value with Helmholtz coils. The signal from the detector is amplified by a 400-cycle phase detector and placed on the vertical input to an X-Y plotter. The horizontal input is the voltage across the sweep coils. Several resonance lines for different values of the oscillating magnetic field strength are shown in Fig. 5. These were obtained at low temperatures where the signal to noise is good.

The width of the resonance lines is measured at half-maximum and τ is determined from the relation $\Delta\nu=(1/\pi\tau)$. In general, the lifetime of a metastable atom in a given spin state, hence the measured resonance linewidth, is determined by several independent physical processes. Each may be characterized by a relaxation time τ_i, which would determine the linewidth if none of the other processes were acting, and $1/\tau=\Sigma_1/\tau_i$. The average time of existence of a metastable atom before it undergoes an exchange process with a ground-state atom τ_2 is the quantity of interest in this study.

Also contributing to the linewidth are lifetime limiting processes characterized by τ_p, the reciprocal rate at which a metastable atom absorbs photons from the pumping light, and τ_r, the metastable spin-lattice relaxation time (excluding metastability exchange processes) in the absence of pumping light. τ_r is determined primarily by collisions of metastable atoms with ions and electrons present in the discharge.

These relaxation times have been fully discussed in Ref. 12, where it was shown that $\tau_2 \ll \tau_r$, τ_p at room temperature. The experimental conditions in the present study were such that the inequality held at all temperatures; hence $\tau \simeq \tau_2$. Verification of the inequality is accomplished simply by demonstrating that the linewidth is independent of pumping light intensity, and that the resonance line measured under identical conditions for a He^4 sample bulb (in which τ_2 processes cannot alter the metastable spin-state lifetime) is much narrower than that of the corresponding He^3 resonance line.

The effect of the oscillating magnetic field which induces transitions among the $^3S_1$ sublevels is to broaden the line so that the actual width measured when the oscillating magnetic field strength is H_1 is $\Delta\nu=(1/\pi)[(1/\tau_2)^2+\gamma^2H_1^2]^{1/2}$. The data was analyzed by plotting $(\Delta\nu)^2$ as a function of H_1^2 for a particular temperature and extrapolating to $H_1=0$. The example shown in Fig. 6 is from data taken at 241°K and is fairly typical. The error bars indicate that all measured line widths at that particular rf magnetic field strength fell within those limits (measured values are shown on one of the bars). The linewidth limits used to calculate $\Delta\nu N=\sigma\nu/\pi$ are indicated on the vertical scale.

The temperature measured is that of the vessel walls. There is always some doubt about the true temperature of atoms in a gaseous discharge. It is easily seen that the temperature of the metastables will be very nearly that of the gas as a whole since many collisions and exchanges occur during the period of existence of a particular metastable atom. It is not so easy to say with certainty that the gas is at the temperature of the container walls.

An estimate can be made of the maximum temperature difference that can occur between the center and walls of the discharge cell by considering the temperature distribution in a sphere of the same volume. If Q calories/cm^3 are generated uniformly throughout the helium gas which has a thermal heat conductivity K, then the temperature at equilibrium will satisfy Poisson's equation $\nabla^2 T = -Q/K$. For a sphere of radius R and the vessel walls kept at temperature T_0, the solution is $T = T_0 + Q[6K(R^2 - r^2)]^{-1}$. The temperature difference between the walls and center is then $T - T_0 = QR^2/6K$. The thermal conductivity of helium at the temperature and pressures considered is always greater than 1.1×10^{-4} cal/sec cm°C and the radius of an equivalent volume sphere is about 3 cm.

Good resonance signals are obtained only in comparatively weak electrodeless discharges—at room temperature and below the best signals are generally observed for the weakest self-sustaining discharge that can be produced. The heat dissipated in the discharge tube is estimated by comparison with dc discharges of similar intensity to be less than a half watt or $Q \cong 10^{-3}$ cal/sec cm^3. Even if all heat losses other than conduction are neglected, the maximum temperature difference between the hottest point at the center and the walls should then be less than 14°C. The average temperature of the gas would be no more than 3°C above the walls. Further evidence that no large changes in temperature exist due to the discharge is the fact that no increase in linewidth outside of experimental error is observed when the discharge intensity is varied from the lowest level to the brightest at which reasonable resonance signals are still observed.

RESULTS

Figure 7 graphically presents the results of this research with a suggested curve drawn through the data points. The error limits represent about a 90% confidence level. The error spread depends upon the number of resonances measured at a given temperature (between 10 and 60) and the signal to noise. In general the signal to noise is worse for broad lines, i.e., at high temperature or high pressures. The approximate curve of cross section as a function of temperature is obtained by dividing σv by the mean velocity at a given temperature. While this cross section is not accurate due to the velocity distribution at any particular temperature, it is shown in Fig. 8 to demonstrate that the product σv is decreasing much more rapidly with temperature than does the mean velocity.

Most of the data were taken with a sample cell that had been initially filled to a pressure of 0.145 mm Hg since this was the lowest pressure at which an electrodeless discharge could conveniently be excited in our geometry. The points at 82 and 63°K were taken with a 0.95-mm Hg cell. At these temperatures the linewidth at the lower pressure would have been determined almost entirely by field inhomogeneity. The field gradient across the sample volume was determined to be about 4×10^{-3} G by measuring the inhomogeneity broadened linewidth of a metastable He^4 resonance. This correction ($\gamma \Delta H \cong 8$ kc/sec) was small in most cases, however it was subtracted from the extrapolated ($H_1 \rightarrow 0$) linewidth at each temperature. A sample filled at 5 mm Hg had a linewidth at 4.2 °K of about 14 kc/sec. This would indicate a $\sigma v/\pi$ value at this temperature of about 4×10^{-14} cm^3/sec; however, this must be considered only an approximate upper limit since both the field inhomogeneity linewidth and line broadening effects due to the spin-lattice relaxation τ_r are of the same order of magnitude.

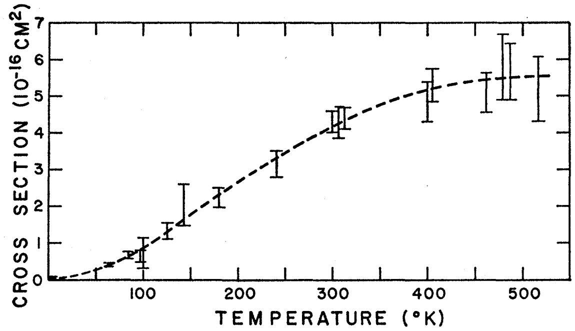

FIG. 8. Approximate cross section as a function of temperature computed by using the mean velocity for a given temperature.

With some modification of the experimental apparatus, it should be possible to extend these measurements to higher temperatures. Data obtained at temperatures at and above the point at which the cross section reaches a maximum would be particularly interesting. However, this may require considerably higher temperatures and, therefore, a complete redesign of the absorption cells and ovens.

The experimental data presented in Figs. 7 and 8 show that the metastability transfer cross section decreases monotonically below 500°K. This provides direct confirmation of the long-range repulsive interaction predicted in Refs. 3 and 4. The results of this study should provide a basis for new efforts to improve the interaction energy calculations.

ACKNOWLEDGMENTS

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