[10]C. Tavard, D. Nicolas, and M. Rouault, J. Chem. Phys. 64, 540 (1967).
[11]This fact has been recognized by several authors [cf., Ref. 12; R. M. Gavin and L. S. Bartell, J. Chem. Phys. 45, 4700 (1966) and earlier papers]; K. Kim and M. Inokuti, Phys. Rev. 165, 39 (1968).
[12]D. A. Kohl and R. A. Bonham, J. Chem. Phys. 47, 1634 (1967).
[13]D. A. Kohl and L. S. Bartell, J. Chem. Phys. (to be published).
[14]D. A. Kohl and L. S. Bartell, J. Chem. Phys. (to be published).
[15]M. Fink and J. Kessler, J. Chem. Phys. 47, 1780 (1967).
[16]R. A. Bonham and M. Fink, Rev. Sci. Instr. (to be published).
[17]M. Fink, Nucl. Instr. Methods (to be published).
[18]There is abundant experimental data which indicates that the first Born description of inelastic cross sections at high energies is exceedingly good [cf., E. N. Lassettre *et al.*, J. Chem. Phys. 48, 5066 (1968); and earlier papers].

PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

Deexcitation of Helium 2^1S and 2^3S Atoms in Fast Collisions with Normal Helium Atoms*

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Cross sections for deexcitation of helium 2^1S and 2^3S atoms in collisions of a helium metastable atomic beam with normal helium atoms have been measured in the laboratory energy range 150–2200 eV. The singlet cross sections are from 20 to 75% larger than the triplet cross sections. Both cross sections were found to obey the general relationship $Q^{1/2}=a-b\ln v$ with an oscillatory structure superimposed upon this monotonic velocity dependence. The magnitude of the triplet cross sections compare favorably with calculated values of the cross section for the symmetric excitation-transfer reaction between 2^3S and 1^1S atoms.

INTRODUCTION

The interaction between metastable and normal helium atoms has received considerable attention because of the repulsive barriers in the interaction potentials at intermediate values of the internuclear separation, and because the He_2 system is simple enough to allow a meaningful detailed comparison between experimental and theoretical data on the interaction of a metastable and a ground-state atom.

There have been several theoretical determinations of potentials for the interaction between normal and metastable helium atoms.[1–5] Total cross sections for scattering,[6,7] diffusion,[8–10] and excitation transfer[11] of 2^3S helium atoms in normal helium have been measured at thermal energies. Experimental results at thermal energies have also been used to make adjustments in the $^3\Sigma_u^+$ and $^3\Sigma_g^+$ potentials of He_2.[8,12] The theoretical potential curves for the interaction of normal and metastable helium atoms have been used to calculate diffusion and excitation-transfer cross sections for 2^1S and 2^3S atoms in their parent gas.[8,12–14] Utterback[15] has observed a resonance in the production of metastable helium atoms in charge-transfer collisions between He^+ and He near threshold. Measurements of cross sections for deexcitation of fast (100–1000 eV) metastable helium atoms have been determined from Penning ionization measurements (where there is no selection between singlet and triplet states).[16] However, no previous measurements of cross sections for production of, excitation by, or deexcitation of 2^3S or 2^1S helium atoms have been carried out at higher than thermal energies or by using molecular beam techniques.

We have measured the cross sections for deexcitation of helium atoms in the 2^1S and 2^3S states in fast (150–2200 eV) collisions with normal helium atoms. The over-all features of the optical excitation and some preliminary results[17] have been

reported elsewhere. Metastable helium atoms are formed by near-resonant charge transfer of He^+ with Rb and Cs. The metastable population is monitored by observing optical emission preferentially excited by the metastable atoms. Triplet and singlet emissions of He are each monitored and deexcitation cross sections for 2^1S and 2^3S atoms can be determined separately by measuring the degradation of each metastable component of the beam in the target gas.

EXPERIMENTAL APPARATUS AND PROCEDURE

Details of the apparatus and the experimental method used for measurement of metastable deexcitation cross sections have been described elsewhere.[18,19] He^+ ions are produced in a hot-filament dc discharge by electrons having a maximum energy of 100 eV. Atoms in the 2^1S and 2^3S states of He are then formed by near-resonant charge transfer of the mass-analyzed He^+ ions in an alkali vapor oven filled with either Cs or Rb vapor at pressures from 10^{-4} to 10^{-3} Torr. Any remaining ions are deflected from the beam immediately after it traverses the oven, and the metastable beam passes into the collision chamber, which operates at pressures from 1 to 10 $\times 10^{-4}$ Torr. The 2^1S or 2^3S population in the beam is monitored at two positions in the collision chamber by observing either the singlet (3^1D - 2^1P, 6678 Å) or triplet (3^3D - 2^3P, 5876 Å) emission, respectively, produced by collisions of the beam with the target gas. Measurement of the spatial decay of each metastable component and the collision chamber pressure then yields the respective deexcitation cross sections. The effects of elastic scattering are negligible.

It is important to ensure that possible contributions to the optical signal from states of He other than the metastable state being monitored are not sufficient to produce a large error in the measured deexcitation cross section. Since other excited states of He in the beam will have decayed before the beam enters the observation region, we need only examine the possible effects of ground-state He atoms in the beam. The signal used for monitoring the metastable population is obtained by subtracting the signal produced when the parent ions are deflected before traversing the oven from that obtained by deflecting the ions just after the beam traverses the oven. Thus, the resulting signal arises only from neutral particles formed in the charge transfer of He^+ with the alkali vapor. For charge transfer of He^+ in Cs, the reactions yielding He in the 2^3S, 2^1S, 2^3P (which decays to 2^3S), and 2^1P (part of which decays to 2^1S) have energy defects of 0.88, 0.08, 0.29, and 0.52 eV, respectively, if Cs is in its ground state. For charge transfer in Rb, the energy defects are 0.59, 0.21, 0.58, and 0.81 eV, respectively. On the other hand, all charge-transfer reactions yielding He, Rb^+, and Cs^+ in their respective ground states have energy defects of the order to 20 eV or larger. Therefore, it is most probable that the neutral beam used contains a large fraction of 2^1S and 2^3S atoms.[20] Furthermore, the emission used to monitor the metastable population is much more readily excited by the metastable atoms than by ground-state atoms. The measured optical signal produced by a beam of helium atoms formed by charge transfer of He^+ in Rb or Cs was at least five times larger over the entire energy range of the experiment than the corresponding signal produced by a helium beam of equal intensity (as measured by secondary electron emission from the beam collector) formed by charge transfer in He. As a result of the forementioned considerations, we estimate that contributions from ground-state He can produce no more than a 5% error in the measured deexcitation cross sections.

Excitation of the triplet states by 2^1S atoms in collisions such as He (2^1S) + He (1^1S) → He (3^3D) + He (1^1S) requires a violation of spin conservation and is, therefore, "forbidden."[21] Collisions such as He (2^1S) + He (1^1S) → He (3^3D) + He (2^3S) are not forbidden, but involve two excitations totaling at least 22 eV and will be strongly suppressed. The same is true for excitation of the singlet emission by 2^3S atoms.[21] Each metastable component can thus be monitored separately. This discrimination between triplet and singlet states is confirmed by the result that the deexcitation cross sections obtained from singlet and triplet emissions have significantly different magnitudes. The deexcitation cross-section measurements with beams produced by transfer of He^+ in Cs gave the same results as those obtained with beams produced by transfer in Rb. Since the ratios of singlet to triplet metastable populations in the beam are probably different in these two cases, this result is further evidence of the selection between singlet and triplet states.

RESULTS AND DISCUSSION

The cross sections for deexcitation of helium 2^1S and 2^3S atoms in helium are shown in Fig. 1. The error bars indicate the standard deviation of the data. Any systematic error, due primarily to possible errors in determining the gas number density, is estimated to be less than 25%.

Essentially, all the deexcitation arises from symmetric excitation-transfer reactions between metastable atoms and ground-state helium atoms. The only other deexciting reactions that have small energy defects and are not forbidden by spin con-

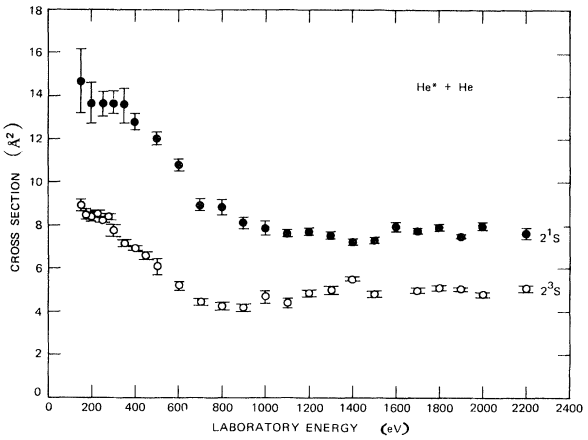

FIG. 1. Cross sections for deexcitation of helium 2^1S and 2^3S atoms in collisions with normal helium atoms.

servation are:

$$2^1S + 1^1S \rightarrow 2^1P + 1^1S, \quad (1)$$

$$2^1S + 1^1S \rightarrow 1^1S + 2^1P, \quad (2)$$

$$2^3S + 1^1S \rightarrow 2^3P + 1^1S, \quad (3)$$

$$2^3S + 1^1S \rightarrow 1^1S + 2^3P. \quad (4)$$

The energy defect is 0.60 eV for reactions (1) and (2), and 1.17 eV for reactions (3) and (4). Such inelastic reactions are expected to have cross sections small compared to the symmetric excitation-transfer reactions at these velocities. Furthermore, since 2^3P decays rapidly to 2^3S, reaction (3) does not remove excited triplet particles from the beam and will not contribute to the measured deexcitation cross section.

Since the symmetric excitation transfer for 2^1S and 2^3S atoms in normal helium involves an s-s transition, the excitation-transfer cross sections should have the general velocity dependence given by [22]

$$Q_t^{1/2} = a - b \ln v \quad (5)$$

for a limited range of energies. This result is also obtained for symmetric excitation transfer by using the procedure described by Bates and McCarroll[23] for symmetric charge transfer. However, as was pointed out by Smith[24] and further developed by others[25,26] for symmetric charge transfer, if the difference between gerade and ungerade potentials passes through an extremum, oscillations in the total cross section will be superimposed on the monotonic behavior, the positions of the maxima increasing linearly with v^{-1}. Furthermore, at energies below 1 eV the excitation-transfer cross section is expected to fall rapidly with decreasing energy because of the repulsive barrier in the normal-metastable helium interaction potentials.

Figure 2 shows the square roots of our measured deexcitation cross sections plotted as a function of $\ln E$, displaying the general dependence on velocity given by (5), upon which is superimposed an oscillatory structure. It is possible that the oscillatory structure arises from a maximum in the difference between gerade and ungerade potentials for the interaction between normal and metastable helium. However, structure can occur even in the absence of such a maximum. It is possible that the dip in the measured cross sections is not part of an "oscillation" due to an extremum in the gerade-ungerade difference potentials, but is instead the effect of a loss in the symmetric resonant-transfer reaction channel to one or more inelastic channels.[27] The partial cross sections for such inelastic channels may be fairly large for certain diabatic crossings of potential curves. (Some of these crossings exist near the repulsive hump in the $^3\Sigma$ curves of He_2.) Additional measurements at higher energies may clear up this point.

A detailed analysis of our data is being carried out[27] to settle some of these problems and to obtain new values for the difference between the gerade and ungerade potentials for the $^1\Sigma$ and $^3\Sigma$ interactions of normal and metastable helium atoms. The results will be published separately.

Calculations of total and excitation-transfer cross sections for 2^3S atoms have been made by Evans and Lane[28] over an extended energy range between 2×10^{-2} and 10^3 eV. They used potentials of Klein, Greenawalt, and Matsen,[5] modified in the long-

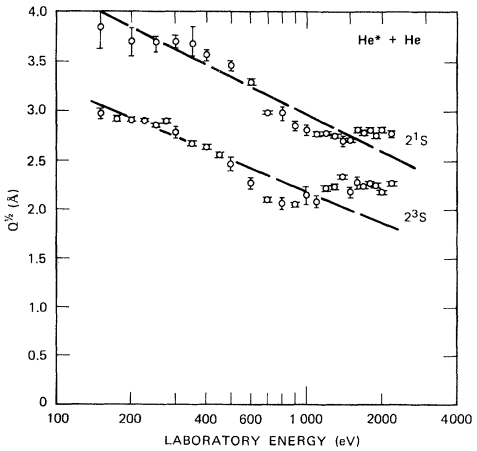

FIG. 2. Square roots of the cross sections for deexcitation of helium 2^1S and 2^3S atoms in normal helium, shown as a function of $\ln E$.

range tail to fit thermal diffusion data of Fitzsimmons, Lane, and Walters[8]. Our results are compared with their calculated cross-section curve in Fig. 3. There is a reasonable agreement in magnitude between our data and the theoretical values, which also agree well with some thermal deactivation rate measurements.[11] However, the structure in our cross-section curve does not match that of Evans and Lane. This difference in structure may arise from loss to inelastic channels as mentioned above or from a small error in the interaction potentials used by Evans and Lane. (Small adjustments in the interaction potentials make a considerable difference in the predicted structure.)

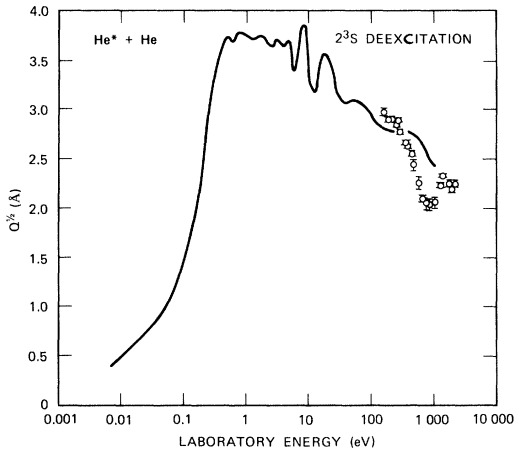

FIG. 3. A comparison of our measured cross sections (O) with the calculated values of Evans and Lane (solid line), Ref. 29.

SUPPLEMENTARY OBSERVATIONS

The lower limit of the beam energies used in these studies (150 eV) was established by two factors, both of which ultimately led to a loss of detectable signal from the metastable component in the beam as the energy was decreased. On one hand, the product of the incident-ion beam current and the charge-transfer cross section falls off rapidly toward lower beam energies. At the same time, the collisional excitation cross sections such as $He(2^3S) + He(1^1S) \rightarrow He(3^3D) + He(1^1S)$, which produce the emissions used to monitor the metastable components of the beam, also decrease with decreasing beam energy.

It was of some interest to explore another method of monitoring the metastable populations of the beam. We had found earlier[16] that the Penning ionization cross sections are quite large ($\sim 10^{-15}$ cm^2) at low energies.

It is also known that the reaction $He^* + N_2 \rightarrow He(1^1S) + N_2^+ + e$ yields the $B^2\Sigma_u^+$ state of N_2^+, resulting in emission of the N_2^+ first negative bands. Therefore, we performed a short experiment to test the practicality of using N_2^+ first negative emissions from a small admixture ($\sim 1\%$) of N_2 in the He target gas to monitor the metastable He in the beam. We had reasoned that the slight amount of N_2 would not seriously affect the total deexcitation of He* in the beam, but the light signal could be considerably larger than from He I lines at lower energies. At the same time it was recognized that the singlet-triplet discrimination would be lost. We found indeed that the light signals were sufficient to permit measurements below 150 eV. The deexcitation cross sections measured in this manner agreed (within experimental error) with the cross sections shown in Fig. 1 for the deexcitation of the singlet metastables. This result probably indicates that the He* beam (formed by $He^+ + Cs$ charge transfer) contained mostly He (2^1S) at these energies, since He (2^3S) also produces $N_2^+(B^2\Sigma_u)$ in collisions with N_2. One might expect He(2^1S) to dominate a low-energy neutral beam formed from $He^+ + Cs$ charge transfer, since the energy defect (0.08 eV) is smaller than for He(2^3S) production (0.29 eV) via He(2^3P).

We have also measured apparent cross sections for deexcitation of the 2^3S state of helium by using another triplet line, the 3389 Å emission from 3^3P-2^3S rather than the 5876 Å emission to monitor the triplet population in the beam. The cross sections so measured were from 10 to 30% larger than those shown in Fig. 1. This discrepancy probably arose as a result of contributions to the signal from unwanted line or band emission. If there are trace impurities of N_2 in the system, emission from the first negative, 3914 Å band of N_2^+ would be detected. Also the 3965 Å (4^1P-2^1S) emission of helium falls within the transmission of the filter used. Under the conditions of our experiment, contributions from either of the above emissions would be representative of the singlet rather than the triplet population in the beam and would therefore tend to increase the deexcitation cross section.

ACKNOWLEDGMENTS

We gratefully acknowledge the skillful help of George M. Conklin in performing measurements and of Ralph Leon in maintaining the apparatus.

*Supported in part by the Advanced Research Projects Agency and monitored by the U.S. Army Research Office, Durham, under Contract No. DA-31-124-ARO-D-446.

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[1]R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) A213, 327 (1952).

[2]E. E. Benton, E. E. Ferguson, F. A. Matsen, and W. W. Robertson, Phys. Rev. 128, 206 (1962).

[3]R. D. Poshusta and F. A. Matsen, Phys. Rev. 132, 307 (1963).

[4]F. A. Matsen and D. R. Scott, Quantum Theory of Atoms, Molecules, and the Solid State (Academic Press Inc., New York, 1966), p. 133.

[5]D. J. Klein, E. M. Greenawalt, and F. A. Matsen, J. Chem. Phys. 47, 4820 (1967).

[6]H. L. Richards and E. E. Muschlitz, Jr., J. Chem. Phys. 41, 559 (1964).

[7]E. W. Rothe, R. H. Neynaber, and S. M. Trujillo, J. Chem. Phys. 42, 3310 (1965).

[8]W. A. Fitzsimmons, N. F. Lane, and G. K. Walters, Phys. Rev. 174, 193 (1968).

[9]M. A. Biondi, Phys. Rev. 83, 653 (1951).

[10]E. Ebbinghaus, Ann. Phys. (Leipzig) 7, 267 (1930).

[11]F. D. Colegrove, L. D. Schearer, and G. K. Walters, Phys. Rev. 135, A353 (1964).

[12]P. L. Pakhomov and I. Ya. Fugol, Dokl. Akad. Nauk USSR 179, 813 (1968) [English transl.: Soviet Phys. – Doklady 13, 317 (1968)].

[13]R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) A213, 506 (1952).

[14]S. A. Evans and N. F. Lane, Bull. Am. Phys. Soc. 14, 262, (1969).

[15]N. G. Utterback, Phys. Rev. Letters 12, 295 (1964).

[16]M. Hollstein, D. C. Lorents, and J. R. Peterson, Bull. Am. Phys. Soc. 13, 197 (1968).

[17]M. Hollstein, D. C. Lorents, and J. R. Peterson, Bull. Am. Phys. Soc. 14, 262 (1968).

[18]M. Hollstein, D. C. Lorents, J. R. Peterson, and J. R. Sheridan, Can. J. Chem. 47, 1858 (1969).

[19]J. R. Sheridan and J. R. Peterson, J. Chem. Phys. 51, (1969).

[20]J. R. Peterson and D. C. Lorents, Phys. Rev. 182, 152 (1969).

[21]Excitation of the 3^3D state could result via cascade from an excitation by 2^1S atoms of the 4^1F state which mixes with the 4^3F state. The 3^1D state could be similarly excited by 2^3S atoms. However, the experimental results indicate that these processes do not contribute significantly.

[22]D. R. Bates, Discussions Faraday Soc. 33, 7 (1962).

[23]D. R. Bates and R. McCarroll, Advan. Phys. 11, 39 (1962).

[24]F. J. Smith, Phys. Letters 20, 271 (1966).

[25]J. M. Peek, T. A. Green, J. Perel, and H. H. Michels, Phys. Rev. Letters 20, 1419 (1968).

[26]R. E. Olson, Phys. Rev. 187, 153 (1969).

[27]R. E. Olson (private communication).

[28]S. A. Evans and N. F. Lane, Phys. Rev. (to be published).

PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

Rotational Excitation of the (H, H_2) System

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(Received 26 May 1969)

An analytic two-body potential, consistent with all available data, is presented for the (H, H_2) system. This potential is then used in the calculation of rotational excitation with the distorted-wave Born approximation. As compared with the results of previous studies, the differential cross sections are drastically different, and the total cross sections are smaller by an order of magnitude. This is because the potential used is different from that used previously.

I. INTRODUCTION

The rotational excitation of hydrogen molecules by the impact of hydrogen atoms has received considerable attention.[1-3] It is physically interesting because it is involved in a variety of relaxation processes,[4] possibly including the cooling of interstellar clouds.[5] Furthermore, it serves as the prototype of the inelastic scattering of molecules by heavy neutral particles.

An exact solution of this many-body problem requires one to consider both the nuclei and the electrons. However, for thermal-energy collisions ($\lesssim$ 1 eV), the Born-Oppenheimer approximation separating nuclear and electronic motion is valid, and a single electronic eigenfunction can