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Chemi-ionization in Collisions between Helium Metastable Atoms and Argon*

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We have measured cross sections for chemi-ionization in thermal energy collisions of He(2^1S) and He(2^3S) metastable atoms with argon using both crossed-beams and gas-cell techniques. The results indicate that several earlier measurements of these cross sections were in error.

In recent years there has been a resurgence of interest, both theoretical and experimental, in collision processes involving chemi-ionization. The present state of knowledge regarding these processes has recently been reviewed by Rundel and Stebbings.[1] The majority of interest has centered around thermal energy collisions of He(2^1S) and He(2^3S) metastables with various target gases. For a given gas, measured cross sections for He(2^3S) metastables have generally been in agreement, while those for He(2^1S) metastables have differed greatly.[2-6]

In the present experiment, both a crossed-beams technique and a beam–gas-cell technique have been used to measure the thermal-energy cross sections for chemi-ionization in collisions of He(2^1S) and He(2^3S) with argon.

The apparatus in the crossed-beams configuration is shown in Fig. 1. A collimated beam of He atoms is excited by electron impact. It then passes through a region where it may be irradiated with light from a helium discharge lamp, which causes the He(2^1S) metastables to be quenched via transitions of the type $2^1S \rightarrow n^1P \rightarrow 1^1S$.[7] The He($2^3S$) metastables are not quenched since the 2^3S state is the lowest state of the triplet system. By this means, greater than 99% of the 2^1S atoms may be quenched, and the resulting beam then consists only of He(1^1S) and He(2^3S). Measurements appropriate to each of the two metastable species may thus be carried out by making observations with the quench lamp alternately on and off.

After removal of charged particles, the He beam intersects a modulated crossed beam of Ar, and then strikes a metal surface where the metastable atoms are detected via secondary electron ejection. Ions formed in the region of intersection of the two beams are extracted by an electric field and focused into a particle multiplier. Ion counts are registered by two scalers, gated by a reference signal from the beam chopper, such that one scaler counts only when the target beam is on while the other counts only when the target beam is off. The difference in the two scaler count rates then gives the count rate due to the presence of the Ar beam.

The cross section Q for chemi-ionization is then given by

$$Q = kS/F\rho l_m, \tag{1}$$

where S is the signal count rate due to collisions of He metastables with Ar, F is the flux of metastable atoms, ρ is the Ar beam density, l_m is the effective path length of metastables through the Ar beam, and k is the efficiency with which signal ions are detected.

A further measurement is then made in which the metastable beam is replaced by a 1-keV electron beam, and the count rate S' of ions produced

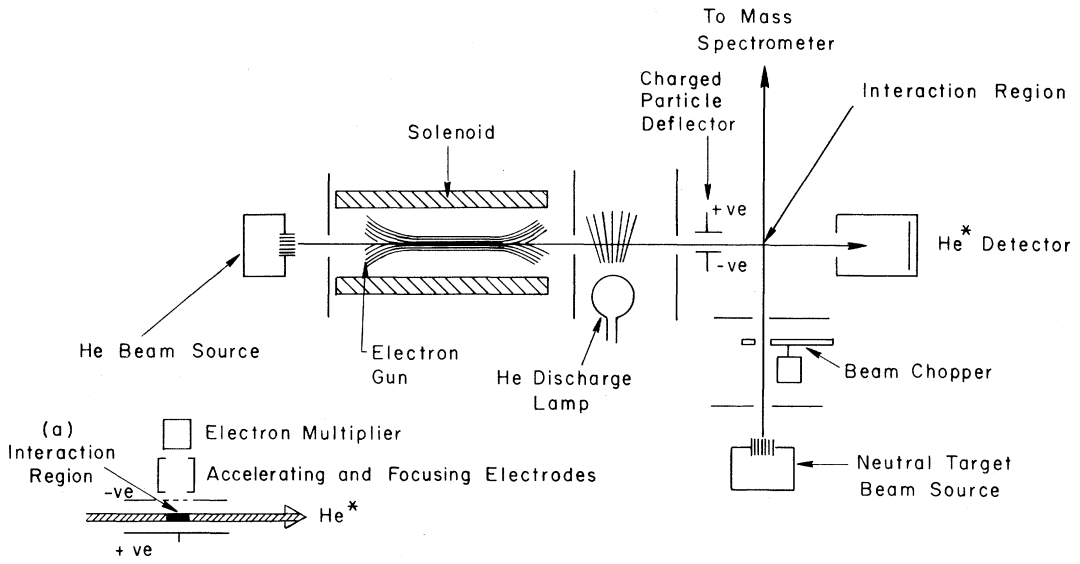

FIG. 1. Schematic diagram of the apparatus.

by electron impact is determined:

$$S' = Q_e I_e l_e \rho / ek, \tag{2}$$

where Q_e is the known electron impact ionization cross section,[8] I_e is the electron current, l_e is the effective path length of electrons, and e is the electronic charge. From Eqs. (1) and (2), k and ρ may be eliminated and the chemi-ionization cross section is then given by

$$Q = (SI_e l_e / S'Fel_m) Q_e. \tag{3}$$

It should be noted that l_e and l_m are not equal because of the finite target beam velocity, and that in Q_e proper account must be taken of multiple ionization.

In order to determine F, it is necessary to know the secondary electron ejection coefficient γ for both He(2^1S) and He(2^3S) metastables incident on the detector surface. Since these coefficients, for a gas-contaminated surface, are almost certainly apparatus dependent, they were measured *in situ* utilizing an extension of the gas-cell method developed originally by Stebbings[9] and later improved by Dunning and Smith.[10] Details of this method will be published elsewhere.[11] For the gas-contaminated stainless-steel detector surface it was determined that $\gamma(2^1S) = 0.49 \pm 0.06$ and $\gamma(2^3S) = 0.74 \pm 0.09$. It must be emphasized, however, that these results apply only to a particular surface in a particular apparatus, and values of γ even for apparently similar surfaces in similar apparatuses may well lie outside the range of these values.

Measurements using the gas-cell technique are also capable of yielding absolute cross sections for chemi-ionization of the gas used in the cell, which in the present experiment was Ar. Except for the value of γ, this method of cross-section measurement is completely independent of the crossed-beams method, and thus provides a useful verification of the results. The accuracy obtainable was not, however, as great as that using the crossed-beams method.

The present results for chemi-ionization cross sections are shown in Table I together with earlier published data. Because of the pronounced disagreements between various measurements, it is appropriate to discuss briefly the earlier work.

Sholette and Muschlitz[5] used a beam–gas-cell technique which required knowledge of γ. Nevertheless, they did not measure γ directly, but assumed that $\gamma(2^3S) = \gamma(2^1S) = 0.3$, which was the value obtained for $\gamma(2^3S)$ by Stebbings[9] for a gas-contaminated gold surface. However, the more recent work of Dunning and Smith and Stebbings,[10,12] and the present results, consistently obtain values of γ for various gas-contaminated surfaces within the range 0.5–1.0, implying that these higher values may be more typical. If Sholette and Muschlitz had assumed γ to be within this range, their results would no longer be in agreement with those derived from afterglow measurements, but could be brought into substantial agreement with the present results.

The stationary afterglow results of Benton *et al.*[2] for $Q(2^3S)$ are in good agreement with the

TABLE I. Experimental results for chemi-ionization of Ar by He(2^3S) and He(2^1S) metastable atoms.

	$Q(2^3S)$ (10^{-16} cm^2)	$Q(2^1S)$ (10^{-16} cm^2)	$\frac{Q(2^1S)}{Q(2^3S)}$
Present results: crossed beams	17.5 (±20%)	23.5 (±20%)	1.35 (±10%)
Present results: gas cell	23 (±35%)	27 (±35%)	1.2
Benton *et al.* (Ref. 2)	6.6 (±50%)	55 (±50%)	8.3
Bolden *et al.* (Ref. 3)	7 (±20%)	•••	•••
Schmeltekopf and Fehsenfeld (Ref. 4)	5.3 (±30%)	16.4 (±30%)	3.1
Sholette and Muschlitz (Ref. 5)	7.6 (±25%)	7.6 (±25%)	1
Dunning and Smith (Ref. 6)	•••	•••	1.1 (±25%)

flowing afterglow measurements of Bolden *et al.*[3] and Schmeltekopf and Fehsenfeld.[4] We feel, however, that in the analysis of the afterglow measurements a potential source of error may have been overlooked. In the case of a typical flowing afterglow, the He^+ ions will recombine most probably through collisional radiative recombination,

$$He^+ + 2e \rightarrow He^+ + e, \quad (4)$$

and this process may be expected to lead to a metastable helium atom in a substantial number of such collisions. When reactant gas is added, the electron density is increased due to chemi-ionization reactions, and thus Reaction (4) provides a source of metastable He atoms whose magnitude is dependent on the amount of reactant introduced. Neglect of this effect leads to an underestimate of the chemi-ionization cross section. An order-of-magnitude calculation, using the collisional radiative recombination coefficients of Bates, Kingston, and McWhirter,[13] indicates that Reaction (4) may affect the apparent chemi-ionization cross section significantly whenever the ion and electron densities in the afterglow are greater than about 10^{10} cm^{-3}. Such a process might therefore account for the discrepancy in $Q(2^3S)$ between the present results and those in Refs. 2, 3, and 4.

It is noteworthy that the ratio $Q(2^1S)/Q(2^3S)$ is observed to be fairly close to 1, both in the present work and also in the earlier beam studies of Sholette and Muschlitz[5] and Dunning and Smith.[6] This observation is in marked disagreement with the afterglow results which yield much larger ratios. In the case of the stationary afterglow results of Benton *et al.*,[2] $Q(2^1S)$ may conceivably be in error because of the effect of superelastic collisions of electrons with He(2^1S) metastables. If this effect were not properly taken into account, the data could have yielded too large a cross section. The conditions of the experiment make it unlikely, however, that these collisions would affect the measured $Q(2^3S)$.

The only flowing afterglow measurement[4] of $Q(2^1S)$ was done under conditions of extremely low electron density, in order to avoid the problem of singlet-to-triplet conversion by electrons. As a consequence, effects due to Reaction (4) are unlikely to have been important, and it is interesting to note that in this case the result for $Q(2^1S)$ agrees quite well with the present results.

In summary, therefore, we feel that previous experiments involving chemi-ionization in collisions of He metastable atoms and Ar are in error for a variety of causes. The agreement between earlier results for $Q(2^3S)$ would appear to be fortuitous. It is to be anticipated that for similar reasons the published data[2-5] for targets other than Ar are also in error.

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Linear Stark Effect Due to Resonant Interactions of Static and Dynamic Fields

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We investigated the line shape of the Lyman-α transition of a hydrogen atom simultaneously subjected to a static and a perpendicular high-frequency electric field. It was found that resonance effects occur, producing a profile substantially different from the Stark spectrum of the fields acting independently. This result shows that the interpretation of turbulent hydrogen plasma spectra by the Blokhintsev (dynamic field only) theory is not generally valid.

In turbulent plasmas the radiating atoms are subjected to an oscillating high-frequency electric field originating from electronic plasma oscillations. It appears to be generally believed that in hydrogen plasmas the radiation spectrum in this situation is well described by the theory of the dynamical linear Stark effect developed by Blokhintsev.[1] However, the atoms are radiating also under the simultaneous influence of a quasistatic field due to slowly moving ions or to low-frequency ion-acoustic turbulence. The present paper points out that the Blokhintsev theory is not adequate, as the resonant interactions between the Stark separation induced by the quasistatic field and the oscillations of the dynamic field produce a spectrum quite different from what could be explained as the combination of the independent effects of these fields.

The problem thus posed is that of radiation of an atom with degenerate states under the combined effects of static and dynamic electric fields. For a pure high-frequency dynamical field, the Blokhintsev theory predicts the appearance of a series of satellites at the harmonics of the frequency of the applied field. An addition of a static field parallel to the high-frequency field is still readily described by a simple extension of this theory and merely produces a symmetric splitting of each satellite with shifts proportional to the static field. However, when the static field has a component perpendicular to the dynamical field, then new results, essentially different from the Blokhintsev theory, emerge. In another sense this situation can be viewed as the formation of static Stark-split states which are connected by the off-diagonal matrix elements of the perpendicular dynamic field. For typical magnitudes of the plasma quasistatic field the energy separation due to the component perpendicular to the dynamic field can be of the same order of magnitude as the plasma frequency and resonance effects will occur. In plasmas of atoms which are not subject to the linear Stark effect, the theories[2-5] that only consider the dynamic field work well, because the atomic levels are naturally well separated and are only negligibly shifted by the usual magnitude of the quasistatic field in the plasma.

As the important physical effects are related to the perpendicular component of the static field, for simplicity we will ignore the parallel component. The more general case will be discussed elsewhere. We will concentrate on the structure of the hydrogenic Lyman-α line, which possesses