TABLE VII. Conversion factors.[a]

System	μ/m_e	μ/m_μ
$H_2^+(\infty)$	1.0	...
T_2^+	0.999818	...
D_2^+	0.999728	...
H_2^+	0.999456	...
$t\mu t$	199.26_5	0.96375
$d\mu d$	195.73_4	0.94667
$p\mu p$	185.83_4	0.89879
$\mu\alpha\mu$	201.06	0.97243

[a] In the column headings μ = reduced mass and m_μ = mass of meson. In the row headings μ indicates a μ meson.

the energies by a factor μ/m_μ and distances by its reciprocal.[30]

[30] Note the two different meanings of the symbol μ.

The results of Tables II and III, while being specifically for systems with $Z=-1$ and $Z_3=2$, may easily be made to apply to systems with any value of Z and Z_3 such that their ratio $\sigma=Z_3/Z=-2$. As has been mentioned in Sec. II it is possible to work in charge-dependent units in which case the Eqs. (II.8) may be used to convert the results for one system with a given set of charges to those for a different one. Thus, for example, by dividing the energy of the system $\rho=10^8$ in Table II by 16 one obtains the energy of the system with the same mass ratio, but where the nuclei each have one-half of the charge of a proton, and the odd particle has the electronic charge. The energies reported in eV are based on the value

$$m_e e^4 \hbar^{-2} = 27.2097 \text{ eV}.$$

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Dissociative Recombination in Helium Afterglows

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Helium-afterglow experiments which have been interpreted in the literature in terms of dissociative recombination of He_2^+ cannot be so interpreted in light of recent experimental and theoretical developments. These include the quantitative theory of collisional-radiative recombination, estimates of He_2^+ vibrational relaxation times, considerations of He_2^* (excited-state) potential curves, and rather detailed experimental results from steady-state flowing afterglow systems.

INTRODUCTION

A CONSIDERABLE fraction of the research effort in gaseous electronics has been devoted to studies of helium discharges and helium afterglows. The reasons for this concentration on helium are varied and include such experimental factors as the relative ease in purification and handling of helium and such theoretical factors as the relative simplicity of atomic rare gases. Helium is preferred over other rare gases because of the simplicity of the electron-atom elastic-scattering cross section (He being a non-Ramsauer gas) and the strong *LS* coupling which simplifies the atomic energy-level structure. In spite of the rather considerable effort which has been extended to the study of helium afterglows, it is widely recognized that the detailed mechanisms controlling the afterglow behavior are far from understood.

In the past year, significant advance in the understanding of the properties of molecular helium ions and particularly their role in helium afterglows has taken place. The contributions to this advance are both experimental and theoretical, and have come from several laboratories. They are, to a considerable extent, uncorrelated in the literature, and in some cases unpublished, so that a correlation and discussion along with a presentation of some unpublished results from this laboratory seem to be justified.

The most interesting result concerns the process of electron recombination with molecular helium ions. In contrast to earlier (and very recent) belief, it now appears that dissociative recombination does not occur to a significant extent for molecular helium ions. He_2^+ is the *only* molecular ion which has clearly been shown not to have a relatively large dissociative recombination coefficient.

The quantitative development of a three-body (two-electron-plus-positive-ion) recombination theory appears to make possible an alternative interpretation of all helium-afterglow experiments reporting recombination coefficients larger than those of simple radiative recombination.

DISSOCIATIVE RECOMBINATION

It has been apparent for some time that the recombination coefficient for He_2^+ was at least anomalously low, Kerr[1] finding $\alpha<1.5\times10^{-9}$ cm^3 sec^{-1}, and Oskam and Mittelstadt[2] reporting $\alpha<4\times10^{-9}$ cm^3 sec^{-1}. Col-

[1] D. E. Kerr, Johns Hopkins University, 1960 (unpublished report).
[2] H. J. Oskam and V. R. Mittelstadt, Phys. Rev. 132, 1445 (1963).

lins and Robertson[3] have recently pushed this limit down to $\alpha<2\times10^{-11}$ cm^3 sec^{-1} at 1800°K electron temperature. By contrast, dissociative recombination coefficients for Ne_2^+, Ar_2^+, Kr_2^+, Xe_2^+, Ne_2^+, O_2^+, and NO^+ exceed 10^{-7} cm^3 sec^{-1} and in some cases exceed 10^{-6} cm^3 sec^{-1}. Persson and Brown,[4] and Gray and Kerr[5] have shown that the failure to take into account the effect of electron removal by higher order diffusion modes in measurements of the time dependence of electron density in pulsed-cavity afterglows has led to erroneous deduction of recombination coefficients. The Gray and Kerr[5] criteria for a valid determination of α for helium has not often been met in past experiments. Rogers and Biondi[6] state that Chen, Leiby, and Goldstein[7] are the only investigators who have achieved recombination control in their afterglow.

VIBRATIONAL RELAXATION

Dissociative recombination requires a curve crossing between the stable molecular-ion potential curve and a repulsive neutral-molecular curve, the point of intersection corresponding to the internuclear configuration at which a radiationless electron capture can occur. It is obvious that the vibrational state of the molecular ion involved is critical and that adjacent vibrational states might have drastically different dissociative recombination coefficients. Therefore a knowledge of the vibrational population of the relevant molecular ion is essential for a detailed analysis of its recombination rate. The experiments which have been interpreted as evidence for dissociative recombination of He_2^+ depend on the He_2^+ existing largely in vibrationally excited states, as will be discussed below.

It seems likely that most helium-afterglow experiments, in particular those in which dissociative recombination has been inferred, involve largely ground vibrational state He_2^+. These experiments can be characterized as involving times greater than a millisecond in the afterglow and pressures greater than 1 Torr.

Takayanagi[8] has recently estimated the mean vibration lifetime of the vth vibrational level of $He_2^+(v)$ to be about $10^{-2}/v$ msec at 1 Torr pressure of helium.

It is known that the helium molecular afterglow spectra involve largely transitions originating in $v'=0$ bound states, those originating from higher vibrational states being orders of magnitude weaker in intensity.[3] This supports the conclusion that vibrational relaxation of He_2^+ in helium is relatively fast, since the three-body formation of He_2^+ as well as the Hornbeck-Molnar process very likely result in quite highly vibrationally excited He_2^+.[9] However, it is not unlikely that vibrational relaxation might occur more rapidly by ion-atom interchange reaction, $He_2^+(v)+He\rightarrow He_2^+(v'<v)+He$, than by ordinary collisional deactivation.

COLLISIONAL-RADIATIVE RECOMBINATION

The development of a quantitative theory of collisional-radiative recombination[10] plays an essential role in the understanding of recombination in laboratory afterglows. Collisional-radiative recombination involves the coupled processes: radiative recombination

$$X^+ + e \rightarrow X^* + h\nu \qquad (1)$$

and collisional recombination

$$X^+ + e + e \rightarrow X^* + e, \qquad (2)$$

in which a third-body electron carries off energy. The excited (atomic or molecular) states X^* may then be transferred to higher or lower energy levels, or reionized by electron collisions, or they may radiate to lower levels. The fraction of X^* ending up in the ground state then constitutes the recombination. The recombination rate is expected to be relatively insensitive to the nature of the positive ion involved since the critical collisional processes involved occur in high principal quantum-number levels of the neutral which tend to be hydrogenic. Bates and Kingston[11] have recently made quantitative comparisons of their theory with some low-pressure Stellerator afterglow experiments where the helium ions are atomic. It is clear from the nature of the theory that no gross differences will occur for molecular ions.

Incidentally, Bayet[12] suggested some time ago that the rate of recombination to He^+ is of the same order of magnitude as that to He_2^+!

DISCUSSION OF EXPERIMENTAL RESULTS

Only two published experimental results which have been interpreted as supporting dissociative recombination of He_2^+ appear to merit consideration. The first of these is the experiment of Chen, Leiby, and Goldstein[7] in which the recombination coefficient was measured in helium afterglows which were recombination-controlled and in which the dominant positive ion was undoubtedly He_2^+.

They found $\alpha=8.9\pm0.5\times10^{-9}$ cm^3 sec^{-1} at $T_e=300$°K and $n_e=1.6\times10^{11}$ cm^{-3} by optical and microwave measurements. The calculated collisional-radiative recombination coefficient for these conditions is 1.8×10^{-8} cm^3 sec^{-1}, using the universal curve of Bates and

[3] C. B. Collins and W. W. Robertson, J. Chem. Phys. (to be published).
[4] K. B. Persson and S. C. Brown, Phys. Rev. **100**, 729 (1955).
[5] E. P. Gray and D. E. Kerr, Ann. Phys. (N. Y.), **17**, 276 (1962).
[6] W. A. Rogers and M. A. Biondi, Phys. Rev. **134**, A1215 (1964).
[7] C. L. Chen, C. C. Leiby, and L. Goldstein, Phys. Rev. **121**, 1391 (1961).
[8] K. Takayanagi, University of Colorado, 1962, JILA report No. 17 (unpublished).
[9] A detailed argument along this line has been presented in Ref. 21.
[10] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297; **270**, 155 (1962).
[11] D. R. Bates and A. E. Kingston, Proc. Roy. Soc. (London) **279**, 10 (1964).
[12] M. Bayet, Compt. Rend. **232**, 612 (1961).

Kingston.[13] It is clear then that collisional-radiative recombination is sufficient to account for the magnitude of the experimental results at 300°K. The feature which requires explanation is their observation, based on spectral intensities observed with filters, that the recombination coefficient had a temperature dependence $\alpha(T)=\alpha_0(T_e/T_0)^{-3/2}$. Collisional-radiative recombination has a very much larger temperature coefficient. The coefficient is a function of T_e and n_e, but under their experimental conditions, is approximately given by $\alpha=\alpha(300)(T_e/300)^{-9/2}$. Contrary to the statement of Chen *et al.*, the temperature dependence of dissociative recombination is not expected to be $T_e^{-3/2}$. Neither the magnitude nor the temperature dependence of dissociative-recombination coefficients are calculable, since both depend on details of potential curves which are not available. Bates has discussed this point in some detail.[14]

Using a spectrometer, we have found the electron-temperature dependence of the intensity of most of the strong atomic-helium lines including λ5876 Å in an afterglow, to be greater than $T_e^{-7/2}$ in the range $T_e \sim 300$°K, $n_e \sim 10^{10}$ cc^{-1}, p(He)~ 1 Torr, and $\tau > 1$ msec. The theory of collisional-radiative recombination predicts a recombination coefficient dependence close to $T_e^{-9/2}$ under these conditions. The intensity of λ5876, which reflects the population of the 3^3D state, is closely a measure of the recombination rate under these circumstances.[15]

Niles and Robertson[16] have shown very graphically that the afterglow emission converts rapidly from atomic to molecular emission and that the light transmitted by a 5876 Å filter will be predominantly molecular at less than a millisecond at 5 Torr so that the identity of the emission observed optically in the experiment of Chen *et al.* is questionable.

Vibrational population considerations also weigh against interpretation of the recombination as dissociative in their experiment. The upper states of both the 3889- and 5876-Å lines lie sufficiently high in energy that they would have to arise from at least the third vibrationally excited level of He_2^+. The observations were made as late as 3.5 msec in the afterglow with a helium pressure of 30.3 Torr. A significant fraction of vibrationally excited He_2^+ ions would not likely have existed under these conditions.

The only remaining evidence of any weight which seems to support dissociative recombination in He_2^+, is the observed line broadening of λ5876 Å in the afterglow reported recently by Rogers and Biondi.[6] The λ5876 Å line becomes wider with time, which they interpret as being due to a few hundredths of a volt kinetic energy obtained from dissociative recombination.

With regard to the interpretation of the experiment of Rogers and Biondi[6] several comments can be made. (1) In view of the He_2^+ vibrational relaxation efficiency, it is unlikely that the $v=3$ molecular vibrational level, necessary to lead to the 5876 Å ($3^3D \rightarrow 2^2P$) atomic transition by dissociative recombination is significantly populated. Without regard to the actual vibrational de-excitation efficiencies, it would be rather surprising if a substantial fraction of the He_2^+ vibrational population were in any one excited state, such as $v=3$. Moreover, for the populations of states $v=3$ and some states with $v>3$ to stay essentially constant over 2 msec, as implied by the close parallelism between the intensities and the electron density, would be remarkable indeed. (If a dissociative recombination mechanism were operative, λ5876 Å would arise from $v=3$ presumably, and λ4472 Å probably from $v>6$, see Fig. 10, Ref. 6.) Kerr[1] finds that below 3 Torr, every line which he could measure, including 4472, 5876, and 3889 Å had the same rate of decay for times as long as 5 msec. (2) At the 77° temperature of some of the Rogers and Biondi experiments and with their electron densities of $\sim 10^9$, the collisional-radiative recombination coefficient[10] is $\sim 10^{-8}$ cm^3 sec^{-1}, so that electron recombination would be dominated by this process. (3) The very low ratio of He_2^+/He^+ reported by Rogers and Biondi in their Fig. 4, $\sim 10^{-3}$, greatly aggravates the problem of explaining observable atomic emission as arising from molecular ions, which must compete with the faster collisional-radiative recombination of the much more abundant atomic ions. This latter process leads to λ5876-Å emission with greater than 10% efficiency (5876-Å photons per recombination) according to measurements in our laboratory.

On the other hand, considerable evidence for the collisional-radiative recombination mechanism in helium afterglows exists. In high-pressure (Torr range) afterglows of the kind discussed in this paper, a series of important investigations[3,16,17] showed that the visible atomic lines originate from atomic ions, while the recombination to molecular ions leads to molecular bands. These observations have been substantiated in this laboratory in the following way. Neon has been added to a flowing helium afterglow in small quantities while the intensities of a number of atomic helium lines were monitored including 3889 and 5876 Å. The He_2^+ ions are destroyed by the very rapid reaction,[18] $He_2^+ + Ne \rightarrow Ne^+ + 2He$. At a time when the molecular-ion concentration is observed with a mass spectrometer to have decreased by more than an order of magnitude (and the molecular-band emission to have similarly diminished), the atomic-line intensities had dropped

[13] D. R. Bates and A. E. Kingston, Proc. Phys. Soc. (London) **83**, 43 (1964).

[14] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 264.

[15] We are indebted to Dr. R. W. P. McWhirter for supplying us with collisional-radiative calculations of excited-state populations appropriate for these conditions.

[16] F. E. Niles and W. W. Robertson, J. Chem. Phys. **40**, 2909 (1964).

[17] C. B. Collins and W. W. Robertson, J. Chem. Phys. **40**, 701, 2202, 2208 (1964).

[18] E. E. Ferguson and F. C. Fehsenfeld (to be published).

only a few percent. The helium pressure in this case was 0.4 Torr and the time from the discharge ~ 5 msec. An upper limit of $\sim 10^{-11}$ cm^3 sec^{-1} can be assigned to any dissociative recombination leading to visible atomic-light emission at 300°K electron temperature from this experiment.

OTHER RECOMBINATION MECHANISMS

While it is not evident from experimental results so far obtained that collisional-radiative recombinaton is inadequate to account satisfactorily for electron recombination in helium afterglows, several additional mechanisms are possible besides dissociative recombination. Ordinary radiative recombination is extremely slow since the radiation process requires in excess of 10^{-8} sec. The merit of dissociative recombination is that the energy is converted to electronic energy and atomic kinetic energy on a vibrational period time scale, $\sim 10^{-14}$ sec for He_2^+. Collisional-radiative recombination, on the other hand, invokes a third-body electron to carry off excess kinetic energy, the escaping electron being rather effectively coupled to the captured one through the long-range Coulomb interaction.

Stabler[19] has discussed the capture of electrons by molecular ions, in a process where rotational excitation of the ion occurs to dispose of the electron's kinetic energy and bind it. He finds the rate of such a process to be large ($\sim 10^{-8}-10^{-7}$ cm^3 sec^{-1}). However, this will rarely lead to a recombination, since the autoionization rate will generally be many orders of magnitude greater than the stabilization rate, by either radiation or collision. Stabler concludes that rotational capture will not effect recombination rates when dissociative recombination occurs (i.e., when $\alpha \approx 10^{-8}$ cm^3 sec^{-1}). It is just possible that this phenomenon might be observable in helium where dissociative recombination is small, under conditions of very low n_e (to reduce collisional-radiative recombination) and high gas pressure (to facilitate collisional stabilization). Vibrational excitational capture is excluded from a decaying helium afterglow because the vibrational energy ~ 0.2 eV far exceeds the amount which most electrons possess.

Collins and Robertson[20] have recently proposed the possibility of a process of collisional-dissociative recombination of electrons and molecular ions. This is an extension of collisional-radiative or three-body recombination to the case of molecular ions where the possibility of collisional recombination into dissociating molecular states (repulsive potential curves) exists. The third-body electron can carry off energy so that the curve crossings required for dissociative recombination are not necessary. In collisional-radiative recombination by atomic ions, the electron is captured predominantly in very highly excited levels close to the electron continuum and in most cases the excited atom is reionized by electron collision. The small fraction of cases in which the excited atom is collisionally or radiationally stabilized (or both) constitutes the effective recombination. It is clear that in the case of molecular ions some irreversible process in these highly excited states, such as molecular dissociation, could enhance the rate of collisional radiative recombination. The process would also lead to excited atoms with kinetic energy if it occurred.

In addition, Collins and Robertson suggest that the possibility of superelastic electron collisions which would convert excited molecules from stable to unstable potential states should be considered.[20] These processes obviously merit detailed theoretical consideration. The possible consequences of the existence of such processes for many laboratory experiments is obvious and particularly the extrapolation of laboratory results at high electron densities ($n_e \sim 10^9-10^{11}$) where such dissociative processes might occur to ionospheric conditions ($n_e \sim 10^4-10^6$) where they surely do not, should be critically re-examined.

THEORETICAL CONSIDERATIONS

In view of the experimental evidence for very slow (at best) dissociative recombination in He_2^+, Mulliken[21] has considered the theoretical problem from the point of view of the molecular potential curve crossings required for dissociative recombination. New knowledge acquired theoretically[22] and supported by new experimental observations,[23] lead to drastically revised He_2^* potential curves. Mulliken's conclusion is "that the curves are such as to make dissociative recombination of electrons improbable for He_2^+ except for higher vibrational states, but tentatively, entirely likely for the other rare-gas diatomic ions." Essentially, the necessary repulsive He_2 potential-curve crossings for lower vibration states of He_2^+ do not occur. The option to the curve crossings is the existence of large potential humps (~ 1 eV) in stable potential curves. This preserves the rule that potential curves of the same symmetry should not cross, which was violated by potential curves drawn earlier.[24]

It is necessary to assume that dissociative recombination can occur for higher vibrational levels of He_2^+, since the process inverse to dissociative recombination, the Hornbeck-Molnar process

$$He + He^* \rightarrow He_2^+ + e,$$

is known to occur. Curran[25] finds from the appearance potential of He_2^+, that He* must lie above the $3p$ and $3s$ levels. This is consistent with Mulliken's potential curves.

It is likely[21] that the same theoretical conclusion can be drawn for H_2^+. On the other hand, when one con-

[19] R. C. Stabler, Phys. Rev. **131**, 1578 (1963).
[20] C. B. Collins and W. W. Robertson, paper presented at Seventeenth Annual Gaseous Electronics Conference, Atlantic City, New Jersey, October 1964 (unpublished).
[21] R. S. Mulliken, Phys. Rev. **136**, A962 (1964).
[22] R. S. Mulliken, J. Am. Chem. Soc. **86**, 3183 (1964).
[23] M. L. Ginter, J. Chem. Phys. **42**, 561 (1965).
[24] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).
[25] R. K. Curran, J. Chem. Phys. **38**, 2974 (1963).

siders homonuclear diatomic molecules formed from atoms containing ground state p electrons (e.g., Ne_2), the manifold of molecular states becomes so great that the necessary curve crossings for dissociative recombination can be expected to occur.

An extremely important result is the observation of Collins and Robertson[3,20] that the 10 830 Å (2^3P-2^3S) line does have a component which originates from He_2^+ in the afterglow, whereas all of the strong visible atomic lines originate from He^+, as demonstrated by the correlation of the intensities with molecular and atomic-ion distributions in flowing steady-state afterglow systems. Collins and Robertson calculate however that the contribution of dissociative (or collisional-dissociative) recombination which results in the 10 830 Å emission does not exceed $\alpha=2\times10^{-11}$ cm^3 sec^{-1} at 1800°K electron temperature. No reasonable extrapolation to 300°K can make this a significant contribution to the total electron recombination under ordinary laboratory conditions. Assuming $\alpha\approx T^{-3/2}$ leads to $\alpha(300°\text{K})<3\times10^{-10}$ cc sec^{-1} for example. The importance of the result lies in the fact that the mechanism for populating the 2^3P atomic state by electron recombination to the molecular ion is not apparent in the potential curves so far postulated.[21] An understanding of this experimental result thus offers promise of leading to new information concerning helium molecular potential states. In view of its importance, the experimental result should be carefully verified.

It might be pointed out that the observation of very complete molecular spectra of He_2 (in contrast to other rare gases for which molecular spectra are not observed) is presumably due in part to the fact that He_2^+ recombination is not dissociative, but rather leads to stable radiating He_2^* states. Members of the $n^3\Pi_g\rightarrow 2^2\Sigma_u^+$ Rydberg series with n as high as 15, have been observed in this laboratory, for example.

CONCLUSIONS

It seems reasonable to conclude that: (1) No convincing experimental evidence for dissociative recombination in He_2^+ which leads to visible light has as yet been reported. (2) No evidence for a large dissociative recombination coefficient exists and it appears that $\alpha_{DR}<3\times10^{-10}$ cm^3 sec^{-1}. (3) Theoretical explanations appear to exist. Recombination rates which have been measured in helium afterglows appear to be satisfactorily interpreted in terms of collisional-radiative recombination.

The combination of the new theoretical developments with the recently developed experimental technique of flowing afterglow systems can be expected to lead to substantial continued progress in understanding of the detailed mechanisms of helium and other afterglow systems.

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Elastic Resonances in Electron Scattering from He, Ne, Ar, Kr, Xe, and Hg†

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The transmission of electrons through the rare gases and mercury vapor has been examined as a function of electron energy, with energy resolution of about 0.04 eV. Many anomalies (resonances) localized in energy have been observed, totaling 11 in helium, six in neon, two each in argon and krypton, five in xenon, and 13 in mercury. The interpretation of these resonances in terms of compound negative ion formation is discussed, and in several cases electron configurations are assigned to the negative ions. In helium, neon, xenon, and mercury, sharp decreases in transmission are observed which are attributed to the onset of inelastic processes. Definite identification of the inelastic processes in the case of helium permits calibration of the absolute electron energy scale to within ±0.03 eV.

INTRODUCTION

RECENT observations of sharp anomalies (resonances) in the electron total-scattering cross section and in the differential elastic-scattering cross section of atoms and molecules have shown the existence of highly excited states of the negative ions of these atoms and molecules. Schulz[1] observed the first such

† This research was supported in part by Project DEFENDER, sponsored by the Advanced Research Projects Agency, Department of Defense.

[1] G. J. Schulz, Phys. Rev. Letters **10**, 104 (1963). Schulz has also observed elastic resonances for electrons of about 1.5 to 3 eV in N_2: *Proceedings of the Sixth International Conference of Ionization Phenomena in Gases* (Paris, 1963), p. 41. These resonances are also ascribed to the formation of short-lived negative ion states, although the states appear to be of a somewhat different nature than the negative ion states to be discussed in this paper.