

## Rare-Gas and Hydrogen Molecule Electronic States, Noncrossing Rule, and Recombination of Electrons with Rare-Gas and Hydrogen Ions\*

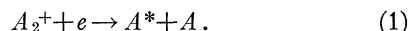
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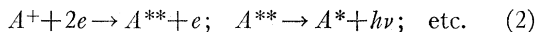
(Received 23 June 1964)

Recent experimental work on helium jets has indicated that excited atoms result usually from collisional-radiative electron capture by atom ions ( $A^+ + 2e \rightarrow A^* + e$ ; etc.) rather than by dissociative recombination by molecule ions ( $A_2^+ + e \rightarrow A^* + A$ ), while for the heavier rare gases, the latter process is apparently relatively important. It is shown in the present paper that the theoretically expected forms of the potential curves of excited  $\text{He}_2$  and other rare-gas molecules make dissociative recombination improbable for  $\text{He}_2^+$  but more probable for the other rare-gas diatomic ions. Available spectroscopic data and theoretical considerations make it fairly sure that many of the familiar excited states of  $\text{He}_2$  have high maxima in their potential curves, but that no pure repulsion curves, except the one for two normal He atoms, exist below the energy of  $\text{He}^+ + \text{He}$ . Besides the stable states with stable  $\text{He}_2^+$  core ( $1\sigma_g^2 1\sigma_u, {}^2\Sigma_u^+$ ) plus a Rydberg electron, there must be others with a core ( $1\sigma_g 1\sigma_u, {}^2\Sigma_g^+$ ) which *per se* is unstable but which on addition of an electron in a sufficiently strongly bound Rydberg orbital is stable; consideration of these states makes possible a reasonable explanation of the Hornbeck-Molnar effect in helium. Statements analogous to those about potential curves and electron recombination in helium are applicable also to a large extent for hydrogen.

**F**OLLOWING Bates,<sup>1,2</sup> it was rather generally accepted<sup>3</sup> that the relatively rapid recombination rate of electrons into excited states of atomic rare-gas ions in discharge afterglows can be explained only by assuming that the major responsible process is "dissociative recombination":



Recently, however, the general usefulness of this explanation has been seriously questioned, and a "collisional-radiative" mechanism,<sup>4</sup>



has been found to explain many results previously interpreted by Eq. (1). Experimental work on helium jets<sup>5</sup> indicates that mechanism (2) and not (1) is dominant in these for the recombination of electrons with helium ions.<sup>6</sup> For neon,<sup>3</sup> however, there seems to be good evidence for the importance of Eq. (1). As will now be shown, theoretical considerations on the forms of the potential curves of the excited states of  $\text{He}_2$  and of other rare-gas diatomic molecules indicate that these

curves are such as to make dissociative recombination of electrons [Eq. (1)] improbable for  $\text{He}_2^+$  except for higher vibrational states but, tentatively, entirely likely [though not to the exclusion of Eq. (2)] for the other rare-gas diatomic ions.

In 1932, I published a potential-curve diagram<sup>7</sup> for  $\text{He}_2$  which included many repulsive states such that electron capture into them by  $\text{He}_2^+$  would have resulted in dissociative electron recombination. However, the existence of such states contradicted the "noncrossing rule" for potential curves of any one electronic species. In 1932 confidence in the noncrossing rule was much less secure than now, and there was evidence which seemed to indicate its violation for certain states of  $\text{He}_2$ . Namely, near their minima the potential curves of the electronic states  $A3d\sigma$ ,  ${}^3\Sigma_u^+$ ,  $A3d\pi$ ,  ${}^3\Pi_u$  and  $A3d\delta$ ,  ${}^3\Delta_u$ , where the  $\text{He}_2^+$  core  $A$  has the normal-state configuration  $1\sigma_g^2 1\sigma_u$  and the excited electron is in a Rydberg MO (molecular orbital), all lie close together with energies which for  $v=0$  are above that of two normal He atoms by amounts  $I - D^+ - X$  eV, where  $X=1.574, 1.550, \text{ and } 1.491$  for  $3d\sigma, 3d\pi, \text{ and } 3d\delta$ , respectively. ( $I$ =ionization energy of He atom,  $v$ =vibrational quantum number,  $D^+$ =dissociation energy of  $\text{He}_2^+$  into  $\text{He}^+ + \text{He}$ .) Now if the  $3d\sigma, {}^3\Sigma_u^+$  and  $3d\pi, {}^3\Pi_u$  states dissociate in the manner expected from simple linear-combination-of-atomic-orbitals (LCAO) MO theory and the noncrossing rule, they would both dissociate to  $\text{He}(1s^2) + \text{He}(1s2p, {}^3P)$ , with energy  $I - 3.623$  eV,<sup>8</sup> but the  $A3d\delta, {}^3\Delta_u$  state necessarily goes to

<sup>7</sup> R. S. Mulliken, Rev. Mod. Phys. 4, 1 (1932), Fig. 49, p. 61. In this figure,  $D^+=2.6$  eV was assumed for  $\text{He}_2^+$ .

<sup>8</sup> This ignores a minor complication which does not alter the essential conclusions reached here. Namely, the potential curve of the  $A3s, {}^3\Sigma_u^+$  state, in order to dissociate to  $1s^2 + 1s3s, {}^3S$  as it tends to do, would have to cross that of the  $A3d\sigma, {}^3\Sigma_u^+$  state (see Fig. 1). But the interaction matrix element is probably large enough near the prospective crossing point so that the  $A3s, {}^3\Sigma_u^+$  shortcuts and actually dissociates into  $1s^2 + 1s2p\sigma, {}^3P$ , leaving the  $A3d\sigma, {}^3\Sigma_u^+$  to dissociate into  $1s^2 + 1s3s, {}^3S$ . Analogous statements hold for  $4p\sigma, {}^3\Sigma_g^+$  and  $4f\sigma, {}^3\Sigma_g^+$ , whose curves are shown in Fig. 1.

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<sup>1</sup> D. R. Bates, Phys. Rev. 77, 718 (1950).

<sup>2</sup> D. R. Bates, Phys. Rev. 78, 492 (1950).

<sup>3</sup> For example, W. A. Rogers and M. A. Biondi, Phys. Rev. 134, A1215 (1964), on helium; T. R. Connor and M. Biondi, Bull. Am. Phys. Soc. 9, 184 (1964), on neon.

<sup>4</sup> D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) A267, 297 (1962); A270, 155 (1962); N. D'Angelo, Phys. Rev. 121, 505 (1961); S. Byron, R. C. Stabler, and P. I. Bortz, Phys. Rev. Letters 8, 376 (1962).

<sup>5</sup> C. B. Collins and W. W. Robertson, J. Chem. Phys. 40, 2202, 2208 (1964); F. E. Niles and W. W. Robertson, *ibid.* 40, 2909 (1964).

<sup>6</sup> Further, experimental results obtained by E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf at the National Bureau of Standards in Boulder show that the molecular and atomic emissions in helium afterglows have the same dependence on electron temperature in the millimeter pressure range, which has led them to believe that dissociative recombination is not a significant process under the conditions where it has generally been thought to occur (private communication from Dr. Ferguson).

He( $1s^2$ )+He( $1s3d$ ,  $^3D$ ), at an energy  $I-1.513$  eV. Now if, for example,  $D^+=2.1$  eV,<sup>9</sup> the energies of the  $v=0$  level of the  $A3d\sigma$ ,  $^3\Sigma^+_u$  and  $A3d\pi$ ,  $^3\Pi_u$  states would be almost equal to that of the separate atoms He( $1s^2$ )+He( $1s2p$ ,  $^3P$ ): see Fig. 1. This expectation seemed in 1932 (Ref. 7, footnote 147) to be inconsistent with the close similarity of the potential curves of the two Rydberg states mentioned to that of the  $A3d\delta$ ,  $^3\Delta_u$  state, which pointed to the conclusion that all three states dissociate alike to He( $1s^2$ )+He( $1s3d$ ,  $^3D$ ). The  $^3\Sigma^+_u$  and  $^3\Pi_u$  curves would then have to violate the noncrossing rule and cross other repulsion curves of the same species (see Fig. 49 of Ref. 7). Electron capture into such repulsion curves could give rise to dissociative recombination.

Careful reconsideration has convinced me that the reason for the close proximity and similarity of the potential curves of the three Rydberg states mentioned is that at the equilibrium distance  $R_e$  the Rydberg MO is still nearly a united-atom  $3d$  atomic orbital (AO). This conviction has been in fact a key clue to a better understanding of diatomic Rydberg states in general.<sup>10</sup>

The anomaly discussed above is resolved if the  $3d\pi$ ,  $^3\Pi_u$  and  $3d\sigma$ ,  $^3\Sigma^+_u$  curves at first nearly follow the  $3d\delta$ ,  $^3\Delta_u$  curve (which is very similar to the  $A$  curve of He $_2^+$ ), but as  $R$  increases, fall below the latter, reach a maximum or hump of as much as 0.5 eV or possibly even 1 eV height, and from there<sup>8</sup> go down to their dissociation asymptotes as  $R$  increases. As a matter of fact, there are indications pointing toward such behavior. Namely,  $R_e$  increases slightly and the vibration frequency  $\omega_e$  and the energy fall slightly as one proceeds from  $3d\delta$  to  $3d\pi$  to  $3d\sigma$ . These deviations are just in the direction expected if there is already a *small* tendency away from the united-atom AO toward the respective LCAO forms  $\delta_a3d$ ,  $\pi_a2p$ , and  $\sigma_a2p$  (that is,  $3d\delta_a+3d\delta_b$ ,  $2p\pi_a-2p\pi_b$ , and  $2p\sigma_a+2p\sigma_b$ ) which the MO's should tend to assume as  $R$  increases, on the way toward respective dissociation<sup>8</sup> to  $1s^2+1s3d\delta$ ,  $^3D$  or  $1s2p\pi$ ,  $^3P$  or  $1s2p\sigma$ ,  $^3P$ .

In general, any Rydberg state which at  $R_e$  is well described as  $1\sigma_g^2 1\sigma_u x$  must undergo two kinds of changes as  $R \rightarrow \infty$ ; (1) the  $x$  MO goes over to an LCAO form  $y+y$  or  $y-y$ ; (2) the wave function goes over toward  $1\sigma_g^2 1\sigma_u(y\pm y)+\lambda 1\sigma_g 1\sigma_u^2(y\mp y)$ , with  $\lambda \rightarrow 1$  as  $R \rightarrow \infty$ . The  $1\sigma_g$  and  $1\sigma_u$  MO's have the respective forms  $\sigma_g 1s$  and  $\sigma_u 1s$ , that is,  $1s+1s$  and  $1s-1s$ . For  $\lambda=1$  we attain the covalent Heitler-London state He+He\*( $1s y$ ), while for  $\lambda=-1$  we have the ion-pair state He $^++$ He $^-(1s^2 y)$  or, since He $^-(1s^2 y)$  is unstable, just He $^++$ He $+e$ . All states except those with unpro-

<sup>9</sup> A thoroughly reliable value of  $D^+$  is not yet available (Ref. 12); however, experimental data of E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 29, 361 (1958), are in good agreement with  $D^+=2.16$  eV, while the best available theoretical calculation, by P. C. Reagan, J. C. Browne, and F. A. Matsen, J. Am. Chem. Soc. 84, 2650 (1962), after subtracting 0.1 eV for zero-point energy, gives  $D^+ \geq 2.04$  eV.

<sup>10</sup> See R. S. Mulliken, J. Am. Chem. Soc. 86, 3183 (1964) for parts I-V; parts VI and VII to be published later.

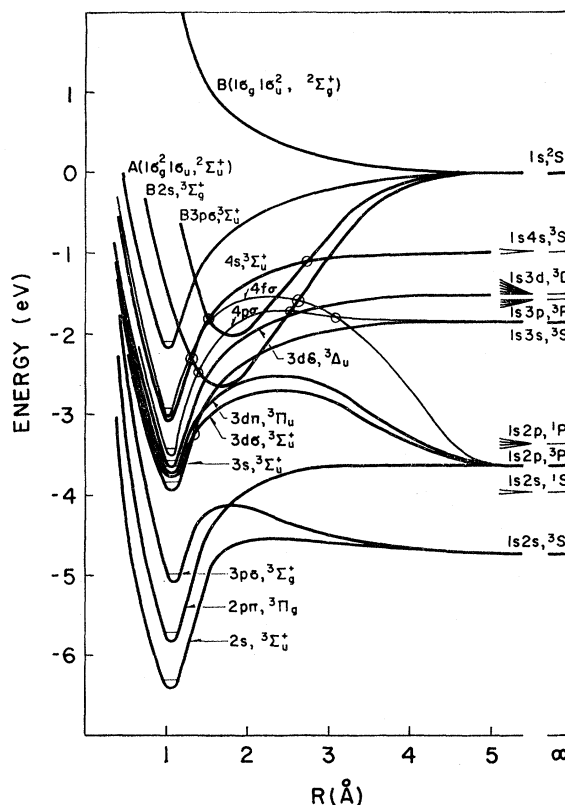


Fig. 1. Potential curves of He $_2^+$  and of some triplet states of He $_2$ . For the ten lower states shown, which have  $A$  core, the curve shapes near their minima and their depths relative to the  $A$  curve of He $_2^+$  are based on experimental data, except for  $4p\sigma$  and  $4f\sigma$ . The absolute depths of all these curves are based on an assumed value (Ref. 9) of 2.1 eV for the dissociation energy  $D^+$  of the  $v=0$  level of He $_2^+$ . The forms of the  $B$ -core curves, and of the  $A$ -core curves at larger  $R$  values, have no more than qualitative justification. Circles, for example where  $A3s$  intersects  $A3d\sigma$ , and where  $A4s$  intersects  $B3p\sigma$  (twice), indicate crossings which, although not so shown, *should* be avoided according to the noncrossing rule (see Ref. 8, and text). For every triplet state of He $_2$  a corresponding singlet state exists, but to avoid confusion these are omitted in Fig. 1.

moted  $x$  MO's (that is,  $y=x$  and  $x \rightarrow x+x$ ) probably have obligatory humps,<sup>11</sup> unless it turns out that  $D^+$  is much larger than 2.1 eV.<sup>9,12,13</sup> All the foregoing state-

<sup>11</sup> Meaning a hump which is necessary if a potential curve which is He $_2^+$ -like near  $R_e$  because the Rydberg MO is united-atom-like is to connect smoothly with the proper dissociation products indicated by LCAO theory and the noncrossing rule. The occurrence of small *nonobligatory* humps is also possible, as is suggested by theoretical calculations on the  $A2s$ ,  $^3\Sigma^+_u$  and  $^1\Sigma^+_u$  states by R. A. Buckingham and A. Dalgarno [Proc. Roy. Soc. (London) A213, 327 (1952)], and by G. H. Brigman, S. J. Brient, and F. A. Matsen [Phys. Rev. 132, 307 (1963)] for the  $^3\Sigma^+_u$  state, and supported by some experimental indications for the  $^3\Sigma^+_u$  state, and by apparently conclusive spectroscopic evidence [J. L. Nickerson, Phys. Rev. 47, 707 (1935); Y. Tanaka and K. Yoshino, J. Chem. Phys. 39, 3081 (1963)] for the  $^1\Sigma^+_u$  state.

<sup>12</sup> Intensive new studies of the He $_2$  spectrum by M. L. Ginter in this laboratory may throw light on this question; papers on the  $A2s$  and  $A3p\sigma$  singlet and triplet states will be published soon.

<sup>13</sup> An inspection of the data on the Rydberg states of He $_2$ , where  $D^+=2.648$  eV, makes it fairly certain that the  $3d\sigma$  and  $3d\pi$  states of He $_2$  have obligatory humps (perhaps 1 eV in height); but the  $3p\sigma$ ,  $^1\Sigma_u^+$  state probably has no hump. Further, He $_2$  should have Rydberg states with  $B$  core (i.e.,  $1\sigma_u$ ,  $^2\Sigma_u^+$  core) with character-

ments apply equally well to excited singlet as to corresponding triplet states.

Thus if the Rydberg MO is unpromoted (for example,  $2s$ , which tends to take on the LCAO form  $\sigma_g 2s$  as  $R$  increases, so that dissociation is to  $1s^2$  plus  $1s2s$ ; or  $2p\pi$ , which tends toward  $\pi_u 2p$  and dissociates to  $1s^2+1s2p$ ; or  $3d\delta$ , as discussed above), a potential curve with *no* obligatory hump is expected. But if it is promoted (e.g.,  $3p\sigma$ , which tends to  $\sigma_u 2s$ , so that a  $A3p\sigma$ ,  $^3\Sigma^+_g$  and  $^1\Sigma^+_g$  should dissociate to  $1s^2+1s2s$ ,  $^3S$  and  $^1S$ , respectively; or  $3d\sigma$  or  $3d\pi$ , as discussed above), a hump is expected if  $D^+$  is near 2.1 eV. However, for Rydberg MO's with  $n > 3$  in united-atom description, except  $4f\sigma$ , atomic dissociation products with  $n \geq 3$  for the excited atoms are required, and no more than *small* obligatory humps are expected. (For  $A4f\sigma$ ,  $^3\Sigma^+_g$  and  $^1\Sigma^+_g$ , larger obligatory humps may be expected.<sup>8</sup>) Figure 1 shows schematically how some of the lower triplet-state potential curves might look, with humps drawn in a plausible way including a small nonobligatory hump<sup>11</sup> in the  $A2s$ ,  $^3\Sigma^+_u$  state. [Note added in proof. Recent theoretical calculations by Browne<sup>13a</sup> confirm the conclusions reached here on the existence of obligatory humps in the  $A3d\pi$ ,  $^3\Pi_g$  and  $^1\Pi_g$  states of  $\text{He}_2$ , and also on those predicted<sup>13</sup> for the analogous  $1\sigma_g 3d\pi$ ,  $^3\Pi_u$  and  $^1\Pi_u$  states of  $\text{H}_2$ . Browne has made variational calculations using mixed  $1s2p\pi$  and  $1s3d\pi$ , plus  $1s^2$ , Heitler-London states for  $\text{He}_2$ , and mixed  $2p\pi$  and  $3d\pi$ , plus  $1s$ , for  $\text{H}_2$ , and obtains humps of heights from 0.4 to 0.6 eV. Calculations<sup>13a</sup> by Browne, on the  $2s$ ,  $^1\Sigma^+_u$  and  $3d\sigma$ ,  $^3\Sigma^+_g$  and  $^1\Sigma^+_g$  states of  $\text{He}_2$  also agree with the conclusions reached here.]

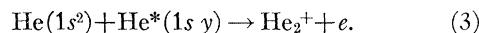
On the basis of the preceding considerations, there seems to be no reasonable doubt that, on the one hand, *all* excited states of  $\text{He}_2$  of the type  $A x$ ,  $^3X$  or  $^1X$ , where  $x$  is an excited (here Rydberg) MO, have potential curves with stable minima supporting at least several vibrational levels, and that, on the other hand, if we consider the potential curves for the approach of a normal atom  $1s^2$  and an excited atom  $1s y$ ,  $^3Y$  or  $^1Y$ , *all* of these correlate, probably very often over a hump, with stable excited molecular states of the type  $A x$ ,  $^3X$  or  $^1X$ .

One should now consider Rydberg states of the type  $B x$ ,  $^3X$  and  $^1X$ , where the B core is  $1\sigma_g 1\sigma_u^2$ ,  $^2\Sigma^+_g$ , corresponding to the repulsive potential curve of  $\text{He}_2^+$  (see Fig. 1). Assuming the term values for any Rydberg MO  $x$  in a  $B x$  state to be roughly the same at *small R values* as for a corresponding  $A x$  state, one concludes unavoidably that the potential curves of the lowest  $B x$  states, at least for  $2s$ ,  $2p\pi$ , and  $3p\sigma$ , must have stable minima which lie well below the energy of normal  $\text{He}^+$  plus  $\text{He}$  in spite of the repulsive character of the

core. Further, the  $B x$  states should all tend to dissociate to (virtual) excited  $\text{He}^-$  plus  $\text{He}^+$ , hence actually, since excited  $\text{He}^-$  is unstable, to  $\text{He}$  plus electron plus  $\text{He}^+$ . Plausible guesses for the forms of two such curves (for the triplet states with  $x=2s$  and  $3p\sigma$ ) are shown in Fig. 1.

It is seen from Fig. 1 that a curve like that of  $A4s$ ,  $^3\Sigma^+_u$  (as well as higher and perhaps also some lower  $^3\Sigma^+_u$  curves<sup>14</sup>) tends to intersect the  $B3p\sigma$  curve at two points. Validity of the noncrossing rule would require that these intersections should be avoided, and new curves should result. However, if two atoms are moving fast enough toward each other on a potential curve which crosses another curve of the same electronic species, the atoms may with high probability remain on the first curve if the electronic interaction matrix element is small enough. The required conditions may well be fulfilled at the outer of the two intersections of the  $A4s$  with the  $B3p\sigma$  curve in Fig. 1, but then at the inner intersection, the much larger matrix element may suffice to produce an avoided crossing, hence for the approaching atoms a change-over from the  $A4s$  to the  $B3p\sigma$ ,  $^3\Sigma^+_u$  curve. Then when the latter crosses curve  $A$  of the normal state of the ion (see Fig. 1), a radiationless transition  $B3p\sigma$ ,  $^3\Sigma^+_u \rightarrow A^*+e$  is not unlikely. Here  $A^*$  means a *vibrating* state of the  $\text{He}_2^+$  ion.

The foregoing discussion, although speculative as to quantitative aspects, should be qualitatively correct. It furnishes a reasonable explanation of the Hornbeck-Molnar (HM) effect,<sup>15,16</sup> whereby  $\text{He}_2^+$  ions are formed by reactions of the type



The HM effect occurs only for  $\text{He}^*$  states within 1 or 2 eV of ionization; that is, it does not occur except when  $y$  is a Rydberg AO with  $n \geq 3$  or perhaps (there is considerable experimental uncertainty<sup>15</sup> as to the exact limit) with  $n \geq 4$ . The experimental evidence suggests that the effect becomes increasingly strong for higher  $n$ . That it should not begin before  $n=3$  or 4 is in harmony with the discussion of  $B x$  potential curves given above.<sup>16a</sup> Although the HM mechanism for the formation of  $\text{He}_2^+$  is important at low pressures (perhaps under 0.1 mm Hg), three-body mechanisms become dominant at higher pressures.<sup>16</sup>

In view of the existence of the HM effect, its inverse, which would be a dissociative recombination, should also occur. However, according to the preceding discussion the HM effect should lead only to *vibrating*  $\text{He}_2^+$  molecules, with more vibration the higher  $n$  is for the

<sup>14</sup> Depending on the actual form of the  $B 3p\sigma$  curves, which can be estimated only roughly, and depending also on what is the true value of  $D^+$ .

<sup>15</sup> J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).

<sup>16</sup> J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, J. Chem. Phys. 36, 3332 (1962).

<sup>16a</sup> Note added in proof. R. K. Curran, J. Chem. Phys. 38, 2974 (1963), has shown that the effect occurs very weakly at  $n=3$  with  $l \geq 1$ , much more strongly at  $n=4$ , and still more strongly at  $n=5$ .

istics similar to those of  $\text{He}_2$ . Also, the formation of excited atoms by collisional-radiative electron capture by  $\text{H}^+$  should predominate over dissociative recombination by  $\text{H}_2^+$  in much the same way as for helium.

<sup>13a</sup> J. C. Browne (private communication).

y AO in Eq. (3). Hence, only vibrating  $\text{He}_2^+$  molecules should be capable of dissociative recombination by inverse HM processes. It is not evident whether or not these would occur at a rate which (for vibrating  $\text{He}_2^+$ ) would compete seriously with collisional-radiative electron capture. There exists also another possibility of dissociative recombination, but again only for vibrating  $\text{He}_2^+$  ions. Namely, for ions with high vibrational amplitude, electron capture into the vibrational continuum at or above the top of the hump of an  $A \ x$  state having an obligatory hump in its potential curve could occur with considerable probability.

Thus it appears that dissociative recombination to give  $\text{He}^*$  may be able to compete seriously with collisional-radiative  $\text{He}_2^*$  formation under conditions where  $\text{He}_2^+$  ions in high vibrational levels are abundant, but that for  $\text{He}_2^+$  ions which are in their low or lowest states of vibration, electron recombination should be almost entirely nondissociative. In this connection it is of interest that the observed band spectra of  $\text{He}_2$  hitherto reported in the literature, obtained usually in a mildly condensed discharge at 20 mm pressure, more or less, involve mainly  $v=0$ . Bands with  $v=1$  are in general much weaker, and in only one case was a  $v=2$  level seen. However, Ginter by a very thorough search for weaker bands has recently found states with  $v$  as high as 5.<sup>12</sup> Since the main process by which band-emitting  $\text{He}_2^*$  molecules are formed is probably<sup>5</sup> from  $\text{He}_2^+$  ions in a manner analogous to Eq. (2), and since in view of the Franck-Condon principle (taken in connection with the fact that all the  $A \ x$  potential curves have  $R_e$  values very similar to that of  $\text{He}_2^+$ )  $v$  should in most cases remain unchanged during electron capture, the strong predominance of  $v=0$  states in the observed spectra suggests that most  $\text{He}_2^+$  ions under the usual conditions where  $\text{He}_2$  bands are observed are also in the level  $v=0$ .<sup>17</sup>

[*Note added in proof.* A new paper by Collins and Robertson<sup>17a</sup> reports that in a helium afterglow at sufficiently high pressures collisional-radiative formation of  $1s2p, \ ^3P$  helium atoms from  $\text{He}^+$  ions is increasingly supplemented by a process which they conclude is one of "collisional-radiative recombination of  $\text{He}_2^+$  into one or more molecular states dissociating into one of the  $2p$  atomic states," yet is not direct dissociative recombination in the usual sense. The authors suggest that the

observed phenomena may be explained by some sort of dissociation of the  $4p\sigma, \ ^3\Sigma_g^+$  state into  $\text{He}(1s^2) + \text{He}^*(1s, 2p, \ ^3P)$ .<sup>8</sup> This may be energetically possible for  $4p\sigma, \ ^3\Sigma_g^+$ , still more so for  $4f\sigma, \ ^3\Sigma_g^+$  and other states (see Fig. 1), and perhaps could occur through (collision-induced?) predissociation. Direct dissociation via a repulsive curve seems to be ruled out by Fig. 1. A need for further work is indicated.]

The theoretical reasoning on potential curves which leads to the conclusion that dissociative recombination of electrons should, as is observed, be unimportant in helium gas if the vibrational excitation of  $\text{He}_2^+$  ions is low, is not applicable to the other rare gases, because of the more complicated outer shells and excited states of their atoms. In fact, plausible tentative potential curves drawn some time ago for the  $\text{Xe}_2$  molecule but not yet published<sup>18</sup> indicate that Eq. (1) may well compete with or under suitable conditions predominate over Eq. (2) in the rare gases other than helium. Instead of just one attractive  $^2\Sigma_u^+$  and one repulsive  $^2\Sigma_g^+$  as in  $\text{He}_2^+$ , there are for all the other rare-gas molecule ions four states  $^2\Sigma_u^+, \ ^2\Pi_g, \ ^2\Pi_u,$  and  $^2\Sigma_g^+$  (or six if one counts substates  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  separately) derived from the normal state of the atomic ion ( $^2P$ , with substates  $^2P_{3/2}$  and  $^2P_{1/2}$ ) plus the neutral atom. Of these states, probably only the lowest, the  $^2\Sigma_u^+$  (analogous to the  $^2\Sigma_u^+$  of  $\text{He}_2^+$ ) is attractive. By the attachment of an electron in a Rydberg MO to any of these states of the molecule ion, various molecular Rydberg states are obtained. The resulting potential curve diagram is extremely complicated. Many curves tend to cross but the non-crossing rule, here especially potent because of strong spin-orbit couplings, should often or usually prevent this for states of any one  $J, j$ -like or case  $c$  species. It is fairly sure that many of the resulting potential curves are repulsive, thus permitting dissociative capture of electrons by molecule-ions.

Further details on the Rydberg states of  $\text{He}_2$  will be given in Parts VI-VII of Ref. 10, and, it is hoped, on those of heavier rare gases in a later paper. My interest in the electron recombination problem was stimulated by discussion with Dr. E. E. Ferguson of some of the latter's experimental results on helium jets, and I am, further, much indebted to Dr. Ferguson for valuable criticisms and suggestions.

<sup>17</sup> But possibly dissociative recombination could be wholly responsible for the observed scarcity of molecules with  $v>0$  in the band spectra. In my opinion, this seems unlikely.

<sup>17a</sup> C. B. Collins and M. M. Robertson, J. Chem. Phys. (to be published).

<sup>18</sup> Referred to by O. Schnepf and K. Dressler, J. Chem. Phys. 33, 49 (1960), and by other writers. I hope that an understanding of the nature of potential curves of diatomic molecular Rydberg states gained in recent studies (Ref. 10) will reduce the uncertainties involved so that better estimated curves for  $\text{Xe}_2$  can be drawn.