theory that the power at which saturation effects occur decreases as the square of the pressure.

Helium Molecular Energy States as Detected by Collisions of the Second Kind in Helium

ROLAND MEYEROTT

Sloane Physics Laboratory, Yale University New Haven, Connecticut

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From a survey of the literature on spectra enhanced by collisions of the second kind, which take place in helium, evidence is presented for the existence in measurable concentrations of both the helium molecule-ion and the helium metastable molecule. From the intensity distribution of the enhanced spectra, the repulsive energy between two helium atoms at separations of 1.052A and 1.090A is derived to be 6.8 volts and 5.8 volts, respectively. The rates of formation of the molecular states are discussed in the special case of a steady-state discharge and the molecular states are shown to be very probable at high pressures. From this it is shown that the ion whose mobility is found to be 21.4 cm²/sec. volt is probably that of He_2^+ in helium and, hence, the discrepancy between the theoretical and experimental values of the mobilities can be removed by such an interpretation. The existence of neon molecules is also suggested.

INTRODUCTION

DIFFICULTY in interpreting certain types of experiments in electrical discharges in gases has led to the conclusion that processes which take place under such conditions are exceedingly complex and that little can be gained by their study. In helium, the simplest of all gases, we find numerous examples. The experimental value for the mobility of He^+ in He, 21.4 cm²/volt sec., as measured by Tyndall and Powell,[1] is almost double the theoretical value, 12 cm²/volt sec., calculated by Massey and Mohr.[2] The rate of decay of metastable helium atoms in pure helium is much larger than can be accounted for by the theory, or by comparison with the other noble gases.[3] Selective excitation of impurities in helium discharges is in disagreement

with theory. Duffendack and Smith,[4] Takahashi,[5] and others[6] have had difficulty in accounting for the enhanced spectra produced in helium. They assume the helium metastable atoms in the $1s2s^1S$ and $1s2s^3S$ states, and the helium ion, He^+, to be the carriers of the excitation energy. This requires in some cases an assumption of changes in kinetic energy in collisions of the second kind of 3 to 5 ev, which theory hardly permits. Experiments by Richardson[7] and others on the effect of helium on the hydrogen molecular spectra has led to the belief that, in the H_2 triplet spectrum, helium merely enhances the o,o bands with little or no effect on the states of higher vibrational energy. These results have led Smith[8]

[1] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. A134, 125 (1931).

[2] Massey and Mohr, Proc. Roy. Soc. A144, 188 (1934).

[3] See Mitchell and Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), pp. 236–250.

[4] O. S. Duffendack and H. L. Smith, Phys. Rev. 34, 68 (1929).

[5] Y. Takahashi, Ann. d. Physik 3, 49 (1929).

[6] For complete list consult Bibliography in references 4 and 5. See also L. S. Headrick and O. S. Duffendack, Phys. Rev. 37, 736 (1931).

[7] For summary, see Richardson, *Molecular Hydrogen and its Spectrum* (Yale University Press, New Haven, Connecticut, 1934), pp. 194–218.

[8] N. D. Smith, Phys. Rev. 49, 345 (1936).

to assume that the hydrogen continuum produced in a discharge containing an excess of helium would be caused by the molecules in the zero vibrational level in the upper state. His results on measurements of the intensity distribution of the continuous spectrum differs considerably both from theory and the later results of Coolidge,[9] indicating the presence of excitation in vibrational levels with $v' > 0$. In atomic spectra the excitation of a large number of levels of NI and H by means of a helium discharge is usually attributed to retardation of recombination by the relatively high helium pressure. However, since the atomic hydrogen or nitrogen is present only as a slight impurity, it seems evident that this interpretation also is incorrect.

It has been suggested by the author[10] that the molecule ion, He_2^+, might be the ion whose mobility was measured by Tyndall and Powell and, hence, the above disagreement in mobility could be expected. It now appears from an extensive but by no means exhaustive survey of the

Fig. 1. Morse curves for He_2^+ and He_2^*. Repulsion energy as calculated by Slater. The energies 6.8 ev and 5.8 ev are obtained for the points $r = 1.052A$ and $r = 1.090A$, respectively.

[9] A. S. Coolidge, Phys. Rev. 65, 236 (1944).
[10] R. Meyerott, Phys. Rev. 66, 242 (1944).

literature of spectra enhanced in helium that not only He_2^+ is present in larger concentrations than He^+ in certain types of discharges, but that the metastable molecule, He_2^*, is more abundant than the atomic metastables, He^*. By assuming the presence of the above molecular states in helium, not only can all the above mentioned difficulties be removed, but the best of these data can be used to measure the repulsive energy between two normal helium atoms in the neighborhood of 1A.

THEORY

The theory of resonance collision and a discussion of the results can be found in Mott and Massey.[11] The characteristic feature of these processes is that the cross sections become very large, perhaps ten times the kinetic theory cross sections for collisions which require no change in kinetic energy of the particles. Changes in energy other than that which can arise through the polarizability or Van der Waals forces between the particles are very improbable. An estimation of the energy due to the polarizability of an atom or molecule in the field of an ion at closest distance of approach shows that this is not likely to exceed 0.5 ev or 4000 cm⁻¹. Thus the atomic ion, He^+, can become neutralized on collision with an impurity if the impurity has an energy level above its ground state (or in some cases above a metastable state) within ±4000 cm⁻¹ of the ionization energy of helium, 198,298 cm⁻¹. If this energy state is not the ground state of the impurity ion or a metastable state, we can expect to observe the spectra of very small quantities of the impurity. In the same way, the metastable helium atom in the $1s2s^3S$ state, which we shall call He^*, can excite energy levels on collision of 159,884±4000 cm⁻¹. We shall, for simplicity, neglect the singlet metastable $1s2s^1S$ state as being too short lived compared with the ^3S to have an appreciable effect on the enhanced spectra, although its effects have been observed.

The molecular states are slightly more complicated than the above atomic states. The ground state of the helium molecule is, of course, a repulsive state. In Fig. 1 are shown Morse curves
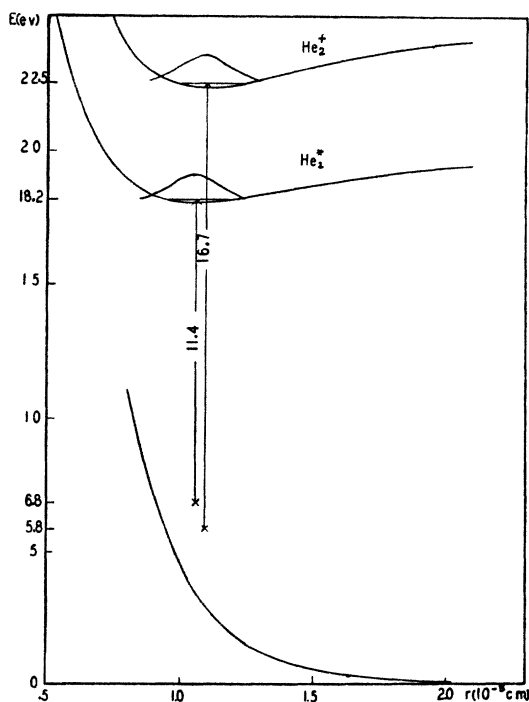
[11] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, New York, 1933), pp. 236–243.

TABLE I. Spectra enhanced by presence of helium.

1			2					3				4			5				6				7		
N₂⁺C—X²Σ		Energy above N₂	N₂⁺ neg. bands B—X²Σ			IN₂ R—— IHe	Energy above N₂	CO⁺ first neg. bands			Energy above CO	CO⁺ comet tail bands		Energy above CO	N₂ sec. pos. C³Πu—B³Πg			Energy above N₂	H. Lyman and Balmer			Energy above H	NI ns²P1/2, 3/2		Energy above NI (Aver. of ½ and ½ states)
v'	I	N₂	v'	IN₂	IHe	IHe	N₂	v'	ICO	IHe	CO	v'	I	CO	v	IN₂	IHe	N₂	n	L	B	H	n	I	
8	32	196,317	0	16	29	1.8	151,240	0	35	33	157,651	0	7	133,309	0	38	38	88,591	2	SS		82,286	3	20	86,150
9	25	198,303	1	13	22	1.7	153,616	1	51	23	159,423	1	12	134,845	1	38	37	90,585	3	SS	100	97,492	4	20	104,153
10	15	200,267	2	9	29	3.2	155,950	2	45	5	161,046	2	14	136,353	2	36	36	92,525	4	SS	31.8	102,822	5	10	110,054
11	8	202,232	3	3	18	6.0	158,242	3	38	3	162,620	3	9	137,832	3	28	17	94,214	5	S	6.8	105,291	6	4	112,731
12	1	204,134	4	1	24	24.0	160,493	4	27		164,146	4	7	139,284	4	21	6	96,249	6	5.0	1.03	106,631	7	4	114,093
13	1	206,036	5	1	3	3.0	162,700	5	16		165,623	5	5	140,707					7	4.3	0.184	107,439	8	3	114,924
												6	2	142,102					8	3.4		107,963	9	2	115,446
												7		143,469					9	3.0		108,324	10	1.5	115,865
												8		144,808					10	2.8		108,581	11	1	116,074
																			11	2.6		108,771	12	0.5	116,273
																			12	0.6		108,916	13	0.5	116,435

IN₂ denotes intensity in N₂, etc.

for the molecule ion, He₂⁺, and the metastable molecule, He₂*. The curve for the repulsive state shown was calculated from Slater's[12] formula

$$E = 4.8 \times 10^2 e^{-4.6r} \text{ ev},$$

r in A.

The wave functions for the lowest vibrational states of the stable molecules are also indicated. If we apply the Franck-Condon principle, we see that the most probable value of the energy, E_p, will be that corresponding to a transition when r is near r_e. Transitions for r greater or less than r_e will be less probable but will occur, hence, we have available a continuous range of energies. Judging from Fig. 1, this range will extend approximately 25,000 cm⁻¹ on either side of E_p. This, of course, neglects the ±4000 cm⁻¹ which can arise due to polarizability or Van der Waals forces mentioned previously. For a transfer of excitation to be probable, we must have an impurity having energy levels in the range $E_p \pm 25,000$ cm⁻¹.

The intensity distribution in these energy levels of the impurity will depend on the transition probabilities of the impurities as well as those for helium. For simplicity, it will be assumed here that the maximum intensity will occur in those levels in the impurity which have energy in closest resonance with E_p, corresponding to the equilibrium distance, r_e, of the helium molecules in question. This, we shall see, is not in variance with the present experimental evidence.

In the above discussion we have neglected

[12] J. C. Slater, Phys. Rev. 32, 349 (1928).

possible excitation of the helium molecules in vibrational states above the ground state. This is justified to some extent by the fact that very little intensity is ever observed in the higher vibrational states of He₂, in fact, so little that the dissociation energies of helium molecules are not easily derived from the data. While this may cause some error in the repulsive energy, we can at least set a lower limit to this energy from the data to be considered.

Thus far, no assumption has been made about selection rules for energy transfer other than that the states are nearly in resonance. Some restriction must be placed on this. It is obvious that a collision between a helium ion and an impurity must result in ionization of the impurity, if energy transfer is to take place. For collisions with either of the metastable states considered here, the metastables make a triplet to singlet transition, hence, in order to preserve the total spin, the impurity must suffer a change in spin. If the impurity has doublet states, no difficulties will be encountered. If it has only singlets and triplets, then transitions which occur on collision must be triplet to singlet, or vice versa. In the case of ionization by collision with a metastable state, the spin can be preserved by ejecting an electron with the proper spin.

EXCITATION BY THE ATOMIC STATES, He⁺ AND He*

In Table I is shown a number of spectra enhanced in helium discharges. From the considerable mass of data that has come to the author's attention, this list was selected as

representative of the processes taking place. Data from enhanced molecular spectra have been used whenever available, since transitions to various vibrational levels of a given electronic state are more likely to depend only on the energy, E_p, than transitions to different states in atoms. Also, the energy separation between vibrational levels in molecules is likely to be less than between different energy states in atoms, and hence, we obtain a more nearly continuous measure of the energy states in helium.

Evidence for the atomic ion, He^+, and the allowable range of excitation is shown in column 1. Here is shown the sum of the intensities in all the upper, v', levels of N_2^+, $C - X^2\Sigma$ system enhanced in helium, as measured by Watson and Koontz.[13] The greatest intensity occurs in the $v' = 8$ and 9 levels having energies, respectively, 1981 cm^{-1} smaller and 5 cm^{-1} larger than the ionization energy of He^+. It can be seen that there is still considerable intensity in the $v' = 11$ state, 3929 cm^{-1} greater than this ionization energy. Probable transitions having $v' < 8$, unfortunately, are confused by the tail of the $v' = 8$ band and, hence, are not observed. This may account for the greater intensity in the $v' = 8$ level than the $v' = 9$, which is more nearly resonant with the helium ion.

The metastable atom, He^*, is responsible for most of the enhancement of the N_2^+ negative bands shown in the second column of Table I. These data of Merton and Pilley[14] were obtained with a Tesla coil discharge through helium containing N_2 impurity. For comparison is shown the excitation of this system in pure N_2 under identical conditions. The intensity in the $He - N_2$ mixture cuts off sharply at 160,493 cm^{-1}, 609 cm^{-1} above the excitation energy, 159,884 cm^{-1}, of He^* and can be identified as caused by He^*. The considerable intensity present in the lower levels may be caused by several effects. The process involves ionization and the electron may carry away the excess energy, almost 1 ev in this case, the N_2 concentration may be large enough to contribute to the excitation by electron impact, or perhaps the transition probabilities are

such to give this, more or less, uniform distribution of intensity. In connection with the last two suggestions, it may be significant that the ratio of the intensity in He to that in pure N_2 rises to a sharp maximum at the correct energy as shown in Table 1, Some intensity in the $v' = 0$ level can also be caused by He_2^+, as we shall see later.

In column 3 is shown the intensity of CO^+ first negative bands $B^2\Sigma \rightarrow X^2\Sigma$ enhanced in He as compared with those in pure CO. The intensities in He are my own estimate as Johnson[15] apparently estimates the intensities in He from the head of the band, which is usually overexposed. The energies in this case were calculated, using $I(CO) = 14.0$ ev. The agreement between the energy of $v' = 1$, 159,423 cm^{-1}, is taken as a measure of the correctness of this value for $I(CO)$. The limits of error are not likely to be greater than ± 0.1 ev. This is in agreement with the value, 14.1 ± 0.2 ev, as given by Sponer,[16] but in disagreement with the recent value of 14.55 ev of Amand, quoted by Gaydon and Penney.[17] In any case, we have a measure of $I(CO)$ to be used in connection with He_2^+ and it is not likely to be in error by more than 0.5 ev.

EXCITATION BY THE MOLECULAR STATES IN HELIUM, He_2^+ AND He_2^*

The best example of enhancement by the molecule ion, He_2^+, is found in the comet tail bands of CO^+, the $A^2\Pi \rightarrow X^2\Sigma$ system. The work by Duffendack and Smith[4] in remeasuring the intensities of these bands gives us an excellent measure of the energy of the repulsive ground state of He_2 and a check on our earlier predictions. Column 4 of Table I shows the intensity distribution in the upper state of the comet tail system and the corresponding energies above the ground state of CO, using the value for $I(CO) = 14.0$ ev as discussed previously. The increase in intensity up to the level $v' = 2$ and subsequent decrease with higher energies well illustrates what we anticipated. We take the corresponding energy 136,000 cm^{-1} to be E_p, the energy obtained in a transition between He_2^+ and He_2 repulsive state

[13] W. W. Watson and P. G. Koontz, Phys. Rev. **46**, 32 (1934).
[14] T. R. Merton and J. G. Pilley, Phil. Mag. **50**, 195 (1925).

[15] R. C. Johnson, Proc. Roy. Soc. **A108**, 343 (1925).
[16] H. Sponer, *Molekulspectren* (Verlagsbuchhandlung, Julius Springer, Berlin, 1935).
[17] A. G. Gaydon and W. G. Penney, Proc. Roy. Soc. **A183**, 374 (1944).

with electron capture, at the equilibrium distance, 1.090A, for He_2^+. The limits of excitation by He_2^+ are by no means restricted to the values given in the table. With longer exposures, Johnson[15] obtains excitation to $v' = 9$. The $v' = 0$ level of N_2^+ negative bands, having energy 151,000 cm^{-1}, can also be excited by He_2^+.

The N_2 second positive band system enhanced in helium would be an excellent example for resonance with He_2^* since the excitation potential is nearly correct, but the bands break off at $v' = 4$ and, hence, we cannot follow the intensities as we did in the case of the comet tail bands. In column 5 of Table I are shown the intensities of this system in pure N_2 and in He. The intensities in He are my own eye estimates. It would be difficult to tell, without very careful measurement, whether the decrease in intensity indicated in the column is real or only apparent. To supplement this information we have shown the intensities of excitation in helium of the Lyman and Balmer series of atomic hydrogen in column 6 and the principal series of NI in column 7. The Lyman series up to $n = 6$ is usually strongly over exposed. Estimates of intensities from $n = 6$ to $n = 12$ are from Rao and Badami[18] and indicate merely the range of excitation to be expected. The Balmer series has been measured carefully by Merton and Nicholson[19] and the intensities listed are absolute. This distribution may be affected somewhat by transition from higher levels and, hence, the sharp decrease with increasing n is not too significant. The lowest observed line at 97,492 cm^{-1} is much stronger than the rest.

In NI, column 7, the result is similar. These data taken from Kamiyama[20] show the lines having excitation energies 86,150 cm^{-1} as much stronger (although probably overexposed) than the remaining lines. The range of excitation is almost the same as that in hydrogen. It is perhaps significant that the only members of the $sp^4\ ^4P$ series which appear have excitation energy 88,000 cm^{-1} and appear with maximum intensity 10. (The intensity 20, as indicated in the table, is a result of two transitions.) It might be noted, parenthetically, that Duffendack, Henshaw, and

Goyer[21] have measured strong excitation of Mg^+ in He at an energy 12.02 volts $\sim$96,000 cm^{-1} above the ground state of Mg, but only the strong lines are given so that we cannot observe the trend.

In all cases the maximum enhancement seems to occur from 85,000 cm^{-1} to 100,000 cm^{-1}, hence we shall take the decrease in intensity of the N_2 second positive system at $v' = 3$ as representing a decrease in excitation probability, and $v' = 2$ with an energy of 92,000 cm^{-1} as corresponding to E_p, the transition energy between He_2^* and He_2 at $r_e = 1.052A$. This is not likely to be in error by more than the energy, 2000 cm^{-1}, corresponding to one vibrational jump in N_2 or there would be a slightly different distribution of intensities relative to the $v' = 0$ and $v' = 1$ states. This error is not serious when we consider that the Van der Waals energies can be at least that large.

REPULSIVE ENERGY BETWEEN TWO NORMAL HELIUM ATOMS

In order to determine the repulsive energy of the ground state of the helium molecule we need to know, in addition to the above energy differences, the energy of the stable molecules above that of two unexcited helium atoms at infinite distance of separation. A knowledge of the dissociation products, their excitation potentials, and the dissociation energy is sufficient for this purpose. From spectroscopic data we know that He_2^* dissociates into $He^*(^3S)$, the atomic metastable (excitation energy of 159,884 cm^{-1} = 19.81 ev) and He, the normal helium atom. Similarly, He_2^+ dissociates into the normal ion He^+ (ionization potential 198,298 cm^{-1} = 24.58 ev) and a normal helium atom. Also, from the Rydberg series in He_2, we know the ionization potential of He_2^*, relative to He_2^+ to be 34,302 cm^{-1} = 4.25 ev. Hence, the dissociation energy of He_2^* or He_2^+ is all that is required. Unfortunately, the experimental values of these are very inaccurate because $v' = 2$ is the highest vibrational state observed in any of the molecules. From this Weizel[22] estimates the dissociation energies of the helium molecules to be around 2.5 ev. We shall take the recent theoretical value for $D_e = 2.22$ ev for He_2^+

[18] Rao and Badami, Proc. Roy. Soc. **A138**, 540 (1932).
[19] T. R. Merton and J. W. Nicholson, Proc. Roy. Soc. **A96**, 112 (1919).
[20] M. Kamiyama, Sci. Pap., I.P.C.R. **36**, 375 (1939).

[21] O. S. Duffendack, C. L. Henshaw, and M. Goyer, Phys. Rev. **34**, 132 (1929).
[22] W. Weizel, *Bandenspektren* (Akad. Verlagsges, m.b.z., Leipzig, 1931), pp. 255, 270.

obtained by Weinbaum[23] as being more nearly correct, since his values of the total energy and internuclear distance compare favorably with experimental values. Using this value and the cycle

$$D_e(\text{He}_2{}^*) + I(\text{He}^{*3}S) = I(\text{He}_2{}^*) + D_e(\text{He}_2{}^+),$$

we obtain $D_e(\text{He}_2{}^*) = 4.25 + 2.22 - 4.77 = 1.70$ ev. Errors in these values greater than 0.2 ev are very unlikely.

These values for D_e were used to construct the Morse curves for $\text{He}_2{}^*$ and $\text{He}_2{}^+$ in Fig. 1. The molecule ion is seen to have an energy of 22.4 ev electronic energy plus 0.1 ev vibrational energy or 22.5 ev in its lowest vibrational state. Subtracting the previously determined value for the most probable energy, $E_p = 136,000$ cm$^{-1} = 16.7$ ev, 5.8 ev is obtained for the repulsive energy at $r = 1.090$A. Likewise, $\text{He}_2{}^*$ is found to have 18.2 ev energy. Subtracting the value 92,000 cm^{-1} $= 11.4$ ev, the repulsive energy at $r = 1.052$A is found to be 6.8 ev. If our assumptions for determining the most probable value of the energy, E_p, are correct, these values are probably accurate to better than ± 0.5 ev. These points have been indicated in Fig. 1.

These results are in disagreement with the theoretical values and with other experiments. Slater's potential, which he indicates should represent the repulsive energy for distances greater than 1A, is only about half as large as those obtained here. Rosen[24] obtains values still lower. Amdur and Pearlman[25] from scattering experiments suggest still a softer potential. However, in their experiments they measure scattering of neutralized ions in helium, which, even if extreme purity conditions are satisfied, are confused by the presence of the molecule ion $\text{He}_2{}^+$.

It seems unlikely that this disagreement is caused by the methods employed in this paper since none of the other results are capable of the accuracy quoted here. If transitions from $\text{He}_2{}^*$ and $\text{He}_2{}^+$ in higher vibrational levels occur, then E_p would be measured down from some higher point on the curves. This would make a positive

correction to the repulsive energy and, hence, increase the discrepancy. (The values quoted here correspond to the lower limit of the energy.) The perturbation methods employed by Slater, Rosen, and others in determining the repulsive energy are likely to be inferior to the variation method employed by Weinbaum in calculating the binding energy of $\text{He}_2{}^+$. The employment of two variation parameters instead of one as used by Pauling[26] only changed D_e by 0.2 ev. On the other hand, Rosen[24] and Slater,[12] using slightly different charge distributions, obtain results which agree only in the neighborhood of 3A but diverge at smaller distances. At $r = 1.43$A, the smallest distance given by Rosen, Slater obtains 0.67 ev compared with 0.39 ev obtained by Rosen. A final check on this curve would be the measurement of the intensity distribution of the helium continuum in the spectral region of 600A to 1200A. To date this has not been done.

The present method is not limited to the determination of the repulsive energy at two points as was done here, but can be extended to include most of the interesting range if careful intensity measurements are made in helium mixtures under controlled conditions. It should be possible to evaluate the energy from a molecular combination as simple as $\text{He}_2{}^*$ and H. It may even be possible to treat $\text{He}_2{}^+$ and CO which produce the comet tail bands. More will be said about the experimental conditions in the next section.

FORMATION OF THE MOLECULAR STATES OF HELIUM

Since helium is a monatomic gas, the question arises as to the mechanism responsible for the molecular states. Some clue to this is suggested by the work of Ebbinghaus discussed by Mitchell and Zemansky[3] on the rate of decay of metastable atoms, He*. The differential equation for the number, n, of He* per cc

$$dn/dt = -\beta n, \qquad (1)$$

where β is an experimentally determined constant. Metastable atoms are removed from the gas by diffusion to the walls and by collisions with other atoms. The first process varies inversely with the pressure, the second proportional to the pressure.

[23] S. Weinbaum, J. Chem. Phys. **3**, 547 (1935).
[24] N. Rosen, Phys. Rev. **38**, 255 (1931).
[25] Amdur and Pearlman, J. Chem. Phys. **9**, 503 (1941).
[26] L. Pauling, J. Chem. Phys. **1**, 56 (1933).

(It may be some higher power of p.) Mitchell and Zemansky give the following value for β,

$$\beta = 1350/p + 107p, \qquad (2)$$

where p is expressed in mm of Hg. From the first term, the cross section for diffusion of He* in He is found to be 11.1×10^{-16} cm², while from the second, the cross section for decay by collisions with helium atoms is found to be 0.000059×10^{-16} cm².

The assumption is made that this cross section, 0.000059×10^{-16} cm², is that of the following reaction,

$$\mathrm{He}(^3S) + \mathrm{He} + 0.78 \text{ volt} = \mathrm{He}(^1S) + \mathrm{He},$$
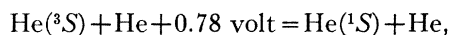
where the 0.78-volt energy is supposed to arise from the thermal energy of the gas. Not only is this a very large cross section for a process which requires this amount of energy, as is stated by Mitchell and Zemansky, but it requires a change in spin on collision, which is very improbable.

In line with the other evidence presented in this paper, it is suggested that this might be the cross section for the formation of the helium metastable molecule, He_2*. Comparing this cross section with that for diffusion, one can say roughly that one collision in 10^5 effective in diffusion produces a molecule He_2*. This hypothesis is susceptible to verification by measuring simultaneously the rates of decay of the atom, He*, and the molecule, He_2*.

EXPERIMENTAL CONDITIONS FOR OBSERVING MOLECULAR STATES

The optimum experimental conditions for the production of any spectra enhanced in helium are determined by the formation of He_2*. If the helium pressure is too high, enhancement of spectra of an impurity by He* may not take place because of molecule formation, while if it is too low the concentration of He* is diminished by diffusion to the walls of the vessel. On the other hand, if the spectra are enhanced by He_2*, at too low pressure, He_2* will not be formed, or if the impurity destroys He*,[†] too high a partial pres-

sure of the impurity will also hinder the production of He_2*.

Some insight into the optimum pressures for a given process can be had from the data of Ebbinghaus. He used a rectangular gas absorption tube, length 5.2 cm and thickness 1.65 cm. These dimensions are not much different than those of discharge tubes, hence his coefficients will at least be of the correct order of magnitude. We shall take the term $1350n'/p$ to represent the diffusion of He_2*, while the term $107pn$ to represent the rate of increase of He_2* due to collisions, where $n' =$ number of He_2* per cc. Other processes for production of He_2* involving higher excited states are very likely operating, so that the term here only corresponds to a lower limit. The equation for the rate of change of He_2* in time is then,

$$dn'/dt = 107pn - 1350n'/p. \qquad (3)$$

In a steady-state discharge, as an uncondensed or Corona discharge, n and n' do not change with time. For this case we can equate $dn'/dt = 0$ and obtain the following relation between the concentrations of He_2* and He*

$$\frac{n'}{n} = \frac{107p^2}{1350} = 10^{-1}p^2.$$

For $p = 0.1$ mm, $n'/n = 10^{-3}$ while for $p = 100$ mm, $n'/n = 10^3$.

These results are in qualitative agreement with experiment. Helium molecular spectra are produced best in wide bore tubes at pressures above one cm. The measurements of N I and N_2 second positive spectrum enhanced by He_2* given in Table I, are for helium pressures of 4 cm and 30 cm, respectively. The helium pressure for enhancement by both He_2 and He in the same discharge (where pressure is given) seems to average several millimeters.

In the light of the present discussion, perhaps this theory, while not completely correct, may serve as a guide to the selection of the proper conditions under which to observe a given spectrum.

HELIUM IONS IN HELIUM

In attempting to decide which ion, He^+ or He_2^+, is most likely to be present at high helium

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† In N_2-He mixtures this is likely to occur. R. Bernard, Ann. de Physique **13**, 1 (1940), using controlled electron impact in mixtures containing 5 to 20 percent N_2 did not observe any unusual enhancement of the N_2 second positive system and hence states that the enhancement of N_2 in He is limited to the production of N_2^+ first negative system due to He. A partial pressure of N_2 of say one

part per 10^3 will likely hinder the production of He_2 molecules due to the formation of N_2^+ first negative system.

pressures, we have in addition to the above results, the following information. First: in the mass spectrograph, at pressures from 10^{-4} cm to 4×10^{-4} cm, Arnot and M'Ewen[27] find He_2^+ present and that its concentration increases relative to that of He^+ with pressure. Second: the Comet tail bands of CO^+ produced by He_2^+ appear readily at helium pressures of about one cm. Johnson[15] obtained these bands in an uncondensed discharge while Duffendack and Smith[4] used controlled electron impact in helium. This indicates the presence of measureable concentrations of He_2^+ at higher pressures. On the other hand, Watson and Koontz[13] and more recently Takamine, Suga, and Tanka[28] found a strongly condensed discharge at helium pressures from 0.01 cm to 1.8 cm and relatively long exposures necessary to bring out the $C - X^2\Sigma$ system of N_2^+, which indicates the presence of He^+. Third: Tyndall and Powell using a corona discharge at helium pressures of 30 cm find only *one* ion present (they can detect the presence of several ions with their method). Thus we know that He_2^+ is present at very low pressures and that the concentration increases with pressure relative to that of He^+. He_2^+ appears more easily than He^+ at high pressures as evidenced by collisions of the second kind.

These experiments at least demonstrate that He_2^+ should be produced by the ion source used by Tyndall and Powell. The fact that only one ion is found using this source would lead us to believe that the He^+ ion was present in insufficient concentration to be detected. If the previous calculations on the ratio of the concentrations of He_2^* to He^* are correct, this result is to be expected. Ionization in such a discharge is likely to be a step process with metastables first produced and then ionized. Production of He_2^+ from He_2^* is favored over that of He^+ from He^* by electron impact in the same gas, both by having a lower ionization potential and, probably, a larger cross section. The ionization potential of He_2^* is 4.25 ev as compared with 4.77 ev for He^*. Since He_2^* is a molecule consisting of two atoms separated by 1A, in a state analogous to He^*, geometrical considerations alone would predict a

larger cross section. Thus, the presence of He_2^+ to the exclusion of He^+ in the corona discharge at high pressures seems accounted for.

THE MOBILITY OF He_2^+ AND He^+ IN HELIUM

The interpretation of the data presented in this paper gives strong support to the earlier suggestion by the author[10] that the value 21.4 cm²/sec. volt for the mobility of helium ions produced by a positive corona source refer to that of the molecule ion He_2^+. The theoretical value of the mobility of He^+ in helium calculated by Massey and Mohr,[2] 12 cm²/sec. volt, and perhaps confirmed by earlier measurements by Tyndall and Powell[29] using an α-particle ion source, is much smaller than that of He_2^+. We have here what on first sight appears to be a paradoxical situation in which a "clustered" ion, He_2^+, has a larger mobility and, hence, a smaller cross section for diffusion than the unclustered one. This paradox results from the fact that the possibility of charge exchange exists in collision of He^+ with a helium atom which is absent in the case of He_2^+. This charge exchange can be interpreted as a large angle scattering and, hence, a large cross section. Massey and Mohr[2] have shown that without taking charge exchange into account, the theoretical mobility of He^+ in He would be 24 cm²/sec. volt while taking it into account, the value of the mobility is reduced to 12 cm²/sec. volt. When these exchange forces are small, the mobility is determined by the polarizability of the helium atom in the field of the ion. If this is assumed to be the case for He_2^+ in helium, and the value 24 cm²/sec. volt is corrected for the fact that He_2^+ has a mass 8 instead of 4, to which the above value would refer, we obtain 22 cm²/sec. volt as an approximate theoretical value of the mobility of He_2^+ in He. The agreement between this value and the experimental value 21.4 cm²/sec. volt is the best yet reported in this field.

H_2 SPECTRA EXCITED IN HELIUM

The H_2 spectrum excited in helium discharges has been subjected to extensive investigation and the results have been summarized by Richardson.[7] In the triplet spectrum, the excitation is practically confined to the low vibrational levels of H_2.

[27] F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. A171, 106 (1939).

[28] Takamine, Suga, and Tanka, Sci. Pap. I.P.C.R. 36, 437 (1939).

[29] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. A129, 162 (1930).

The action of the helium in this case is usually interpreted as quenching the higher vibrational levels of the excited molecules before they radiate. This is feasible, since the masses of the H_2 molecule and the He atom in this case are nearly equal. This is not the complete explanation, however. The observations have all been made on the transitions where the initial levels are all about 112,000 cm^{-1} above the ground state of H_2. Reference to column 7, Table I, will show that this is about the limit of the excitation of He_2^*. Since the vibrational levels are separated by about 2000 cm^{-1}, the excitation of the various electronic states in the range of 112,000 cm^{-1} is more probable than excitation of higher vibrational levels of a low-lying electronic state.

The level $1s\sigma 2s\sigma^3\Sigma_g^+$, 95,226 cm^{-1} above the ground state of H_2, which is responsible for the hydrogen continuum, may have many vibrational levels excited. This coupled with the "quenching" action of helium may account for discrepancy between Smith's[8] measurements of the intensity distribution of the hydrogen continuum produced in helium and hydrogen mixtures, and those of Coolidge[9] produced in pure hydrogen by controlled electron impact.

NEON MOLECULES

In most of the references listed in this paper, data of enhanced spectra in neon mixtures are also given. Enhancement appears at energies slightly higher than that caused by He_2^* and possibly over a longer range of energies. This is probably caused by neon metastable molecules. However, discussion of these effects must be deferred until more information is available, about either the attractive or the repulsive state in neon.

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The Determination of X-Ray Diffraction Line Widths

C. G. SHULL*
Beacon Research Laboratory, The Texas Company, Beacon, New York
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The methods which have been suggested for correcting x-ray diffraction line widths for geometrical effects are reviewed. Experimental data are presented for two samples of finely-divided NiO and MgO which show that neither the Warren nor the Jones correction method is valid for *these particular specimens*. A direct Fourier transform procedure is given which permits calculation of the corrected diffraction line width for all experimental cases.

INTRODUCTION

IT is well known in x-ray diffraction studies that the size of the diffracting crystals determines to a certain extent the sharpness or diffuseness of the observed diffraction line. With the usual type of diffraction cameras, the diffraction broadening is noticeable with crystal sizes in the range of 400–500Å and becomes more pronounced as the crystal size is reduced. Numerous applications of this broadening have been made in the past in determining the crystal sizes present in experimental systems.

It has been shown[1-3] that the angular breadth β of a diffraction line should be given by

$$\beta = C\lambda/L \cos \theta, \qquad (1)$$

where C is a constant, λ the x-ray wave-length, L the size of the crystal, and θ the Bragg angle corresponding to the diffraction line under study. In this expression, either the "half-width" (total width at half maximum) or the "integral width"

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[1] P. Scherrer, *Kolloidchemie* (Zsigmondy, 1920), third edition, p. 387.
[2] W. H. and W. L. Bragg, *Crystalline State* (The Macmillan Company, New York, 1933), p. 189.
[3] A. L. Patterson, Phys. Rev. 56, 972–982 (1939).