have radial asymmetry for effects such as these to be observed. Beenakker[4,5] and Gorelik[6] have shown that a variety of polyatomic gases exhibit the Senftleben effect. More recently, Korving *et al.*[7] have reported a transverse component in both the viscous flow and the heat flow of gases in a magnetic field. It has been shown by a number of theorists[8–10] that rotational-flow terms would result with external fields if the participating particles have internal degrees of freedom. However, detailed calculations have not yet been made to indicate whether or not the correct magnitude for this torque could be predicted.

ACKNOWLEDGMENTS

Since the explanation for these observations was not immediately apparent the data and equipment have been exposed to numerous physicists both in our own organizations and elsewhere over a period of a year and a half. The authors wish to acknowledge these many helpful discussions.

[5] J. Korving, H. Holsman, H. F. P. Knaap, and J. J. M. Beenakker, Phys. Letters **17**, 33 (1965).
[6] L. I. Gorelik, Yu. N. Redkoborody, and V. V. Sinitsyn, Zh. Eksperim. i Teor. Fiz. **48**, 761 (1965) [English transl.: Soviet Phys.—JETP **21**, 503L (1965).
[7] J. Korving, H. Hulsman, H. F. P. Knaap, and J. J. M. Beenakker, Phys. Letters **21**, 5 (1965).
[8] J. S. Dahler, in Proceedings of the International Seminar on the Transport Properties of Gases, Brown University, 1964 p. 85 (unpublished).
[9] L. Waldman, in Proceedings of the International Seminar on the Transport Properties of Gases, Brown University, 1964 p. 59 (unpublished).
[10] Yu. Kagan and L. Maksimov, Zh. Eksperim. i Teor. Fiz. **41**, 842 (1961) [English transl.: Soviet Phys.—JETP **14**, 604 (1962)].

PHYSICAL REVIEW VOLUME 158, NUMBER 1 5 JUNE 1967

Decay of Excited Species in a Pulsed Discharge in Krypton

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(Received 21 November 1966; revised manuscript received 30 January 1967)

The emission in the afterglow of a pulsed discharge in krypton has been investigated. Measurements of the decay times of the resonance radiation at λ1236 Å and a diffuse molecular radiation at λ1250 Å and longer wavelengths have been made as functions of pressure at 295 and 196°K. The measurements have been interpreted on the assumption of a simple two-time-constant model, leading to values of the collision frequencies for collision-induced transitions between the metastable level ($1s_5$) and the resonance level ($1s_4$) of 13×10^{-14} cm³/sec and 22×10^{-14} cm³/sec at 295 and 196°K, respectively, for de-exciting collisions ($1s_4-1s_5$), and 7.6×10^{-16} cm³/sec and 1.3×10^{-16} cm³/sec, respectively, for exciting collisions ($1s_5-1s_4$). The coefficients for the conversion of metastable atoms to molecules in two- and three-body collisions with normal atoms has also been determined. The two-body collision frequency for molecule formation was found to be 15×10^{-16} cm³/sec and 26×10^{-16} cm³/sec at 295 and 196°K, respectively, and the three-body collision frequency was found to be 4×10^{-32} cm⁶/sec and 6.9×10^{-32} cm⁶/sec at 295 and 196°K. The results are compared with existing measurements in other rare gases. The two-body part of the molecule formation is discussed in terms of an interatomic potential which has a hump similar to that proposed in the case of helium.

EXPERIMENTS on metastable lifetimes,[1] referred to as I, and the decay of resonance radiation[2] in krypton, referred to as II, have been reported earlier. The present paper describes an extension of the work to higher krypton pressures and also to lower temperatures.

The interpretation of the results of II was based on a three-level model having a ground state, metastable state (M) and resonance state (R). The decay of the excited atom populations was attributed to the effects of (a) diffusion of excited atoms, (b) escape of resonance radiation, and (c) collision-induced transitions between R and M.

In the present work, measurements of the decay of radiation emitted during the krypton afterglow have been made using a vacuum monochromater to isolate certain regions of the spectrum. It has been established that at higher pressures a considerable fraction of the afterglow energy is dissipated as molecular radiation. From the lifetime of radiation in isolated regions of the spectrum it is now possible to give a more complete picture of the decay of energy of the afterglow in terms of resonance and metastable atomic levels R and M and a molecular level. Coefficients for the collision-induced transitions have been determined. The conclusions reached in II regarding the diffusion of resonance radiation are still relevent and the differential equations for the decay of excited states are unchanged if the coefficient α_d in II is interpreted to include an extra term to allow for the conversion of metastable atoms into excited molecules.

[1] D. S. Smith and R. Turner, Can. J. Phys. **41**, 1949 (1963).
[2] R. Turner, Phys. Rev. **140**, A426 (1965).

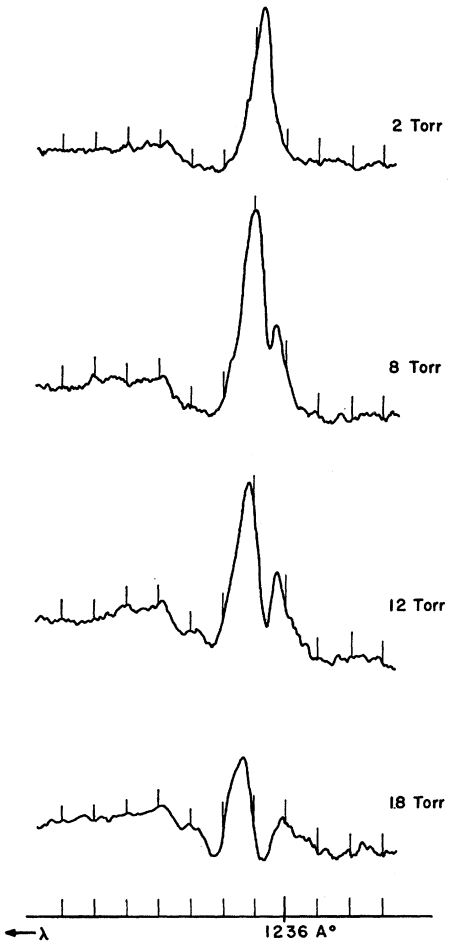

FIG. 1. Emission spectra of krypton afterglows at pressures of 2, 8, 12, and 18 Torr. Photomultiplier current i versus wavelength λ. Wavelength markers at 5 Å intervals.

I. APPARATUS

The basic apparatus used in the present work is the same as that described in II, with the exception that additional measurements were made using a $\frac{3}{4}$ metre vacuum monochromator. The krypton afterglows were excited in a spherical discharge tube of radius 9.5 cm the radiation in the region of 1200 Å being taken out through a lithium fluoride window which was mounted on a 12-mm bore tube extending radially from the side of the sphere a distance of 10.5 cm. The discharge tube was pulsed at frequencies from 1000 to 100 cps, the excitation pulse lasting for approximately 60 μsec. In order to avoid the effects of collisional de-excitation of excited krypton atoms by slow electrons, the electron density in the afterglow was kept at a minimum by using very low excitation currents (less than[3] 1 mA). Checks were frequently made at different discharge-tube currents to ascertain whether collisions with electrons were influencing the results. To achieve stability and reproducibility the discharge-tube load resistor was made large, 15–30 $M\Omega$, and the power supply was capable of providing a stabilized current at voltages of up to 60 kV.

The detector used with the monochromator was a salicylated IP21 photomultiplier, gated at the dynodes with pulses variable from $\frac{1}{10}$ to 5 μsec in length to achieve time resolution.

Measurements were also made at solid CO_2 temperature (nominally −78.5°C) by surrounding the discharge tube with crushed solid CO_2 contained in a thermally insulated box. Temperature stability was checked by monitoring the krypton pressure which was found to be constant to better than 1% during an experiment.

II. MEASUREMENTS

A. Spectra

In Fig. 1 are shown recordings of the photomultiplier output as the monochromator was scanned over the

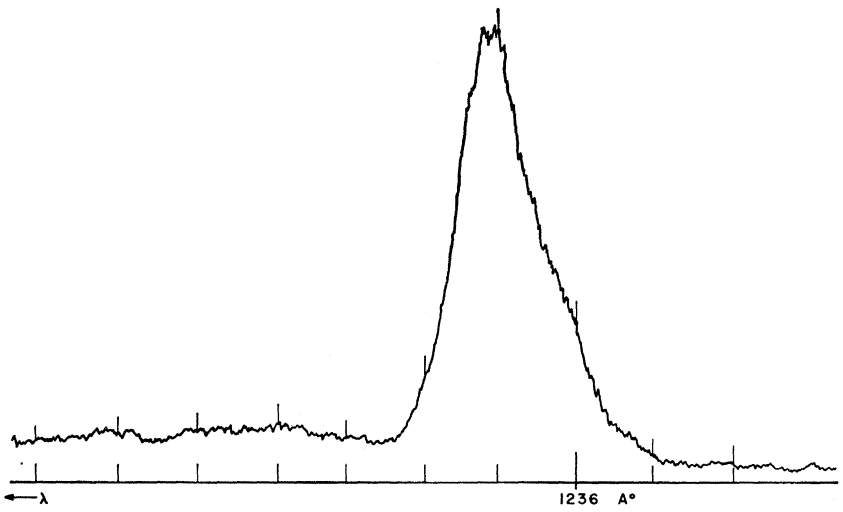

FIG. 2. Time-resolved spectrum of krypton afterglow. Photomultiplier current i versus wavelength λ. Pressure 9.24 Torr, $\frac{1}{10}$-μsec gate pulse 4 μsec after termination of excitation pulse. Monochromator slits are too wide to resolve the self-reversal effects in the resonance line.

[3] J. R. Dixon and F. A. Grant, Phys. Rev. 107, 118 (1957).

region of the resonance line λ1236. The signals for krypton pressures between 2 and 18 Torr are shown. The discharge tube was pulsed with 1-mA pulses approximately 60 μsec long and the photomultiplier was operated dc with a long time constant at the output. Thus the recordings represent a time integral of the discharge-tube emission. On the photomultiplier signal are superimposed wavelength markers at 5 Å intervals. The wavelength scale of the spectrometer was not calibrated absolutely; the resonance line at λ1236 is indicated on the wavelength axis. The two main features of interest in Fig. 1 are the resonance line itself and the band stretching from about λ1250 to longer wavelengths. This band is attributed to molecular emission. Similar bands have been observed previously in emission from pulsed discharges in krypton and other rare gases at somewhat higher pressures than those used here.[4–6] As will appear later, the molecular emission has a slow decay in the afterglow compared with the resonance radiation so that the recordings in Fig. 1, being time integrals, do not represent instantaneous relative intensities of the resonance and molecular radiation. The resonance line has a width of a few angstroms as has been observed in absorption by Wilkinson[7] and has an appearance characteristic of self-reversal at higher pressures. This self-reversal is probably exaggerated by the passage of the radiation through the tube on which the window is mounted. In order to ensure that no spurious effects were present it was confirmed experimentally that both parts of the self-reversed resonance line have the same decay time.

B. Decay Times

In Fig. 2 a recording is shown of the photomultiplier signal obtained under time-resolved conditions. The multiplier was gated on for a $\frac{1}{10}$-μsec interval at a time 4 μsec after the end of the discharge pulse. The krypton pressure was 9.24 Torr. The low intensity of all radiation except the resonance emission shows that the molecular band has a long decay time relative to the resonance radiation. Similar results in the case of helium have previously been reported.[8]

Time-resolved studies were made of both the resonance radiation and the molecular emission using the monochromator to study each feature separately and also using the electron-multiplier detector and no monochromator to examine the decay of the total radiation output. Krypton pressures of up to 26 Torr were used. Typical results for the decay of resonance and molecular radiation are shown in Figs. 3(a) and 3(b), respectively, where the detector output is plotted as a function of time on a log scale. The departure from linearity of the resonance radiation decay at longer times [Fig. 3(a)] may be due to a small amount of molecular radiation incident on the detector. It is impractical from signal-to-noise considerations to close the monochromator slits to a point where all molecular

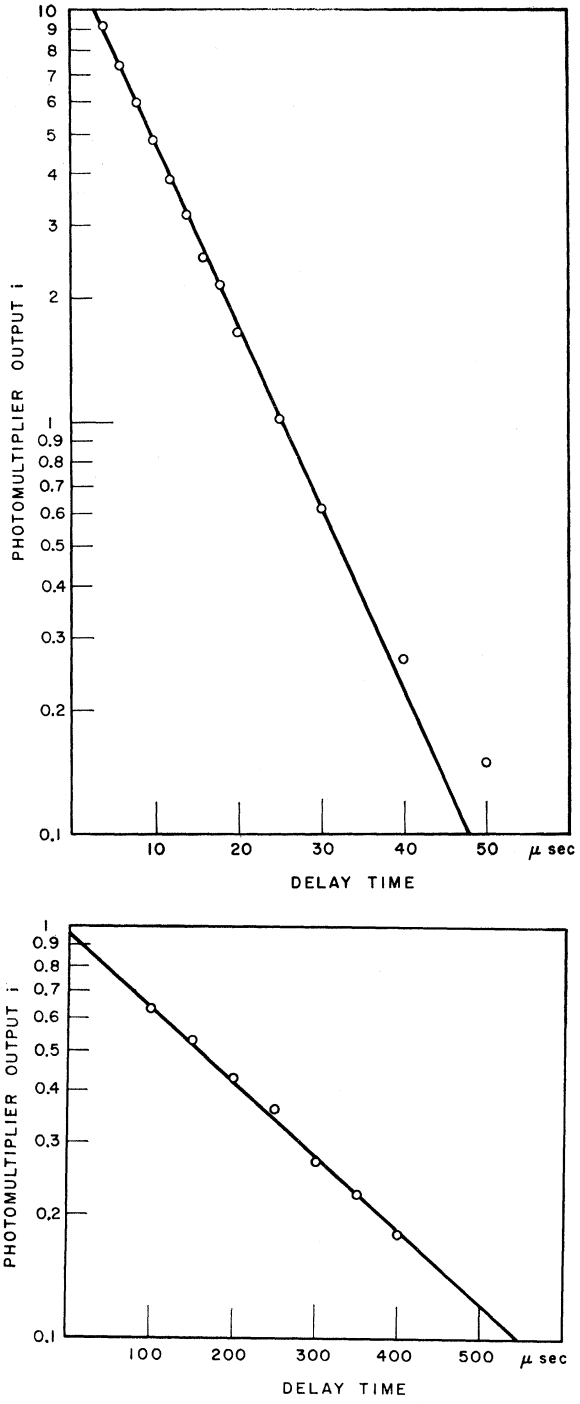

FIG. 3. Typical decay of resonance radiation (a) and molecular radiation (b) as functions of time. Photomultiplier current in units of 10^{-10} A.

[4] Y. Tanaka, Opt. Soc. Am. 45, 710 (1955).
[5] Y. Tanaka, Opt. Soc. Am. 48, 304 (1958).
[6] R. E. Huffman, Y. Tanaka, and J. C. Larrabee, Opt. Soc. Am. 52, 851 (1962).
[7] P. G. Wilkinson, J. Quant. Spectry. Radiative Transfer 5, 503 (1965).
[8] R. E. Huffman, J. C. Larrabee, and Y. Tanaka, Opt. Soc. Am. 55, 101 (1965).

radiation is excluded, since a small correction for the presence of a weak and slowly decaying component is easily made. Even with very wide monochromator slits, the results are inferior to those obtained with the non-dispersed radiation on the electron multiplier (see II) because of the lower signal-to-noise ratio of the monochromator-IP21 combination. From measurements such as those shown in Fig. 3 are obtained values for (a) the decay constant for the resonance radiation at short decay times and (b) the decay constant for the molecular radiation at later times.

The measurements for the two regions of the spectrum agree well with those made by taking the total radiation, as was done when the electron multiplier detector was used.

III. INTERPRETATION OF THE RESULTS

A. Theoretical Model

We now consider the decay of energy in the afterglow using a model involving the metastable state M, resonance state R and the ground state of the atom, and also let us assume for simplicity only one excited molecular state P: see Fig. 4. The various destruction processes as discussed in II still apply. They are indicated in Fig. 4 as follows: β is the decay constant for the escape of trapped resonance radiation; ρ is the decay constant for spontaneous radiation by the excited molecules; α_{MR}, α_{RM}, α_{MP}, α_{PM} are coefficients for the collision-induced transitions M to R, R to M, M to P, and P to M, respectively. The following symbols are also used: d_M indicates the measured metastable decay constant at late t; d_{Mol} indicates the measured molecular radiation decay constant at late t; d_R indicates the measured resonance radiation decay constant at early t; d_f indicates the larger decay constant for two-time constant model; and d_s indicates the smaller decay constant for two-time constant model.

The differential equations governing the excited-state populations are

$$dR/dt=-(\beta+\alpha_{RM})R+\alpha_{MR}M\,, \tag{1}$$

$$dM/dt=\alpha_{RM}R+\alpha_{PM}P-(\alpha_{MR}+\alpha_{MP})M\,, \tag{2}$$

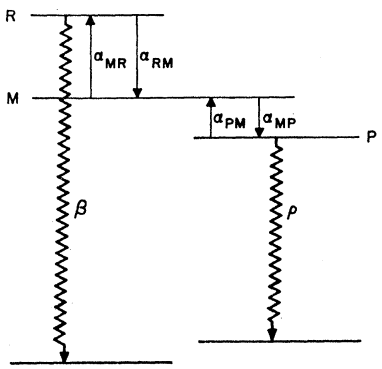

FIG. 4. Proposed model showing transitions between levels.

and

$$dP/dt=-(\rho+\alpha_{PM})P+\alpha_{MP}M\,. \tag{3}$$

In solving the Eqs. (1) to (3) we make the assumption that the molecular excited-state decays by radiation with a lifetime of 10^{-6} sec or less. A short lifetime would be expected for a radiative transition of such a high energy as that involved here. This assumption is supported by the findings of Colli and Facchini[9] in the case of argon although the possibility of a metastable molecule cannot be ruled out completely.[10] The assumption also implies that the molecular radiation process is fast compared with the collision processes by which the molecules are formed. Under these circumstances the population of excited molecules must be small and we can ignore the transitions P to M. Equation (2) then becomes

$$dM/dt=\alpha_{RM}R-(\alpha_{MR}+\alpha_{MP})M\,. \tag{4}$$

Equations (1) and (4) can be solved exactly giving

$$R=Ae^{-d_f t}+Be^{-d_s t}\,, \tag{5}$$

where A and B are constants and d_f, d_s are given in terms of α_{RM}, α_{MR}, α_{MP} and β (see Appendix).

Equation (5) represents the decay of resonance radiation as an initial fast decay d_f followed by a slow decay d_s. The fast decay may logically be interpreted as resulting from the escape of resonance radiation so that $d_f=d_R$.

It also follows that the slow decay d_s at late times is determined by the decay constant for the metastable atoms, as is the molecular radiation decay, thus $d_s=d_M=d_{\mathrm{Mol}}$.

In order to obtain values for the collision coefficients above from measurements of d_s, d_f one uses

(a) a relation between α_{RM}, α_{MR} from detailed balancing considerations:

$$\alpha_{RM}=K\alpha_{MR}\,,$$

$$K=\frac{2J_M+1}{2J_R+1}e^{\Delta E/kT}\,,$$

where J_M, J_R are the J values of the metastable and resonance levels, respectively, k is Boltzmann's constant, and ΔE is the energy difference between the resonance and metastable states;

(b) a value of β giving the best fit to the analysis of present data and agreeing within experimental error with the value obtained in II using different discharge tubes and lower pressure.

Thus, using (a) and (b) the number of unknowns is reduced to two, so that measurements of the two quantities d_f, d_s are sufficient to yield a solution.

[9] L. Colli and U. Facchini, Phys. Rev. **88**, 987 (1952); **96**, 1 (1954).
[10] A. V. Phelps, Phys. Rev. **99**, 1307 (1955).

A discussion of the reliability of the value of β is given later. In the present measurements, the decay constant d_f of the isolated resonance line was measured at any given pressure but the decay constant d_s could not be determined accurately from resonance-radiation measurements because of the very small emission of resonance-radiation at later times. A much more reliable value for d_s is obtained from the decay of the molecular radiation d_{Mol}, since as noted above, for the two-time constant model, $d_{\text{Mol}}=d_s$.

The pertinent measurements are then the fast-decay constant of resonance-radiation and the decay constant d_{Mol} of the molecular radiation measured at long times after the end of the discharge tube pulse.

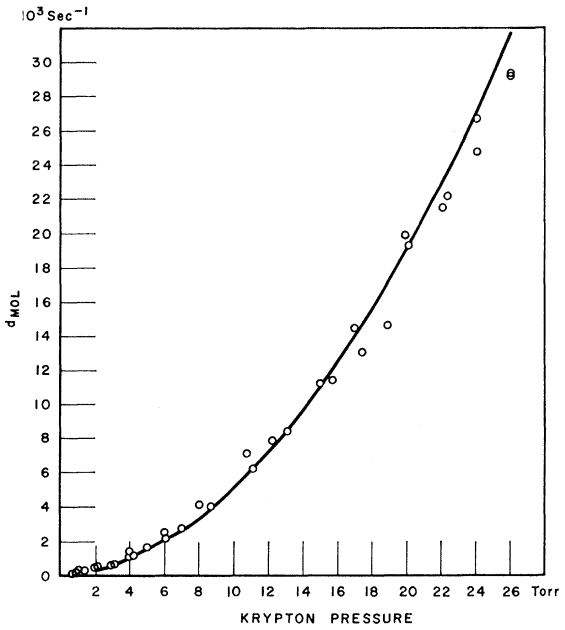

FIG. 5. The slow decay d_{Mol} of the molecular radiation versus krypton pressure. The solid line represents the equation $d_s=75p+44p^2$. Measurements made at 295°K.

B. Analysis of Results of Room-Temperature Measurements

The measured molecular decay constant d_{Mol} is the same, within experimental error, as the decay d_M of the metastables as measured in I. Justification of this statement is demonstrated in Fig. 5 where the measured room-temperature values of the molecular decay constant are plotted versus krypton pressure. The solid line represents the equation $d_M=75p+44p^2$ (pressure p) as obtained in I. (The diffusion term proportional to $1/p$ is omitted since it becomes insignificantly small at the pressures of Fig. 5.) These results therefore fit the two-time constant model.

Using the equations derived in the Appendix together with the measured values of d_{Mol}, d_f (Fig. 6) and the

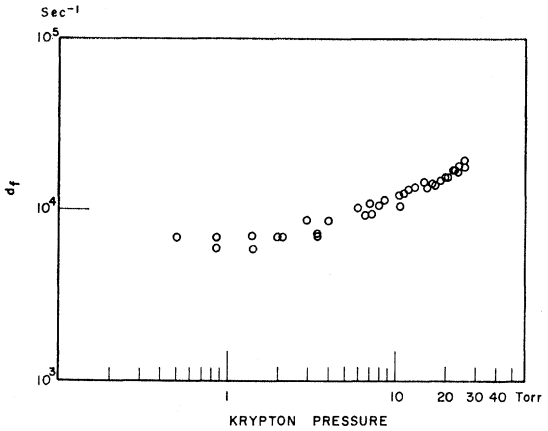

FIG. 6. The fast decay d_f of the resonance radiation versus krypton pressure. Measurements made at 295°K.

values of β from II, the values of α_{MR}, α_{RM}, α_{MP} have been obtained as functions of pressure. The results are plotted in Figs. 7 and 8. In the case of α_{RM}, α_{MR}, the results are plotted as $(K+1)\alpha_{MR}$. We observe that to a good approximation the experimental points fit a straight line which has a slope of 44.4×10^2p. The line should pass through the origin from theoretical considerations since α_{RM}, α_{MR} depend on collision processes which do not exist at zero pressure. The value of β used in calculating $(K+1)_{MR}$ was taken as 6.9×10^4, giving the best line fit for the present results and being within experimental error of II. Using the value of $K=178$ gives the values of

$$\alpha_{RM}=44.1\times10^2p \text{ sec}^{-1}, \quad (p \text{ in Torr}),$$
$$\alpha_{MR}=24.8p \text{ sec}^{-1}.$$

The results for α_{MP} are plotted on a log-log scale in Fig. 8. At higher pressures α_{MP} approaches asymptotically the value $44p^2$ as shown by the straight line drawn on the graph. At lower pressures the scatter in the results is too large to determine the form of α_{MP}

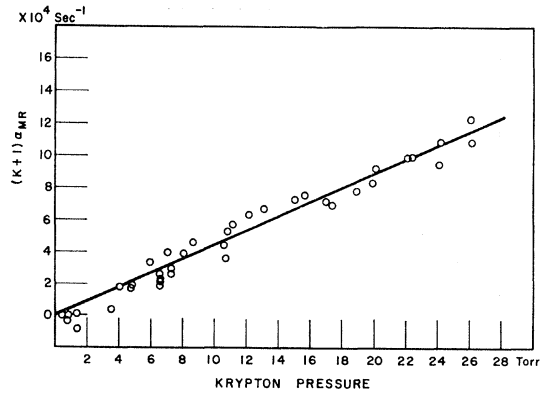

FIG. 7. Plot of $(K+1)\alpha_{MR}$ versus pressure at 295°K. The straight line represents the equation $(K+1)\alpha_{MR}=44.4\times10^2p$.

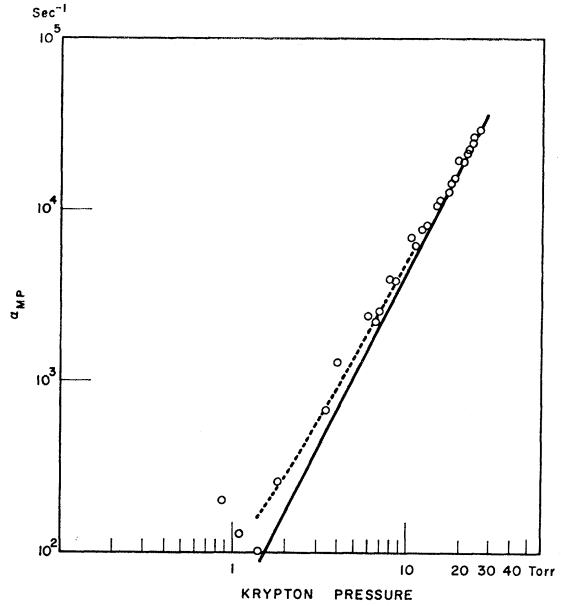

FIG. 8. Plot of α_{MP} versus pressure at 295°K. The dotted line represents the equation $\alpha_{MP}=50.2p+44p^2$. The full line is $\alpha_{MP}=44p^2$.

versus pressure to good accuracy. However, one can assume that α_{MP} is of the form $\alpha_{MP}=Xp+Yp^2$ where X and Y represent the coefficients for molecule formation in 2- and 3-body collisions with normal atoms as described by the reactions

$$Kr_M+Kr\rightarrow Kr_2^*,$$
$$Kr_M+2Kr\rightarrow Kr_2^*+Kr+\text{kinetic energy}.$$

Thus the deviation of the experimental points from the straight line $44p^2$ on the log-log plot gives a measure of the two-body coefficient X, while the value of the three-body coefficient is given by $Y=44$. The value of X is best obtained from the results of I (i.e., $d_M=75p+44p^2$) and using the fact that the metastables decay by two

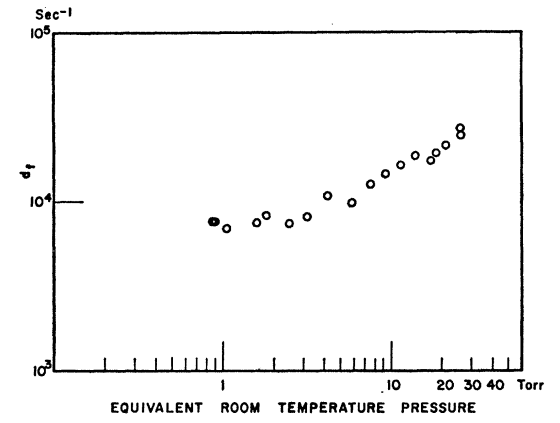

FIG. 9. The fast decay d_f of the resonance radiation versus equivalent room-temperature pressure. Measurements made at 196°K.

processes, namely (i) to the resonance state and (ii) to the molecular state. The coefficient for transfer to the resonance state as obtained above is $\alpha_{MR}=24.8p$. Therefore the two-body coefficient X is given by subtraction as $50.2p$. Thus we have

$$\alpha_{MP}=50.2p+44p^2 \text{ sec}^{-1},$$
$$\alpha_{RM}=44.1\times10^2p \text{ sec}^{-1},$$
$$\alpha_{MR}=24.8p \text{ sec}^{-1}.$$

Referring again to Fig. 8, the dotted line represents the equation $\alpha_{MP}=50.2p+44p^2$, showing reasonable agreement between the measured points and the line.

C. Analysis of Results of Measurements Made at 196°K

In the case of the low-temperature measurements it was not experimentally convenient to measure both fast and slow decays for the same gas filling. The analysis

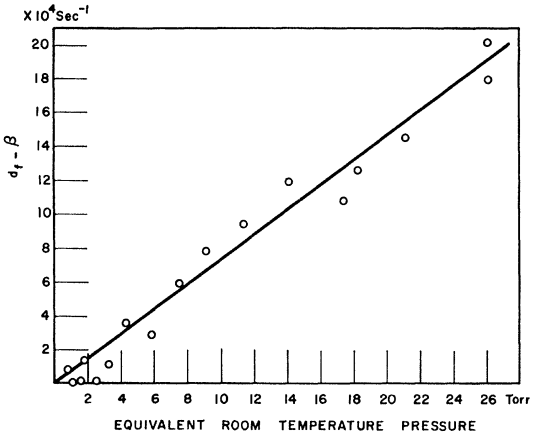

FIG. 10. Plot of $d_f-\beta$ versus equivalent room-temperature pressure. Measurements made at 196°K. The straight line represents the equation $\alpha_{RM}=7.4\times10^3p$.

of the results was carried out for a value of the detailed balancing factor $K=1.67\times10^3$. With this large value of K one can approximate

$$d_f=\alpha_{RM}+\beta$$

to better than 1%. Also,

$$d_s=\alpha_{MP}+\alpha_{MR}.$$

Thus using a value of $\beta=6.9\times10^4$ and the measured values of d_f (Fig. 9) one obtains α_{RM} as a function of pressure (Fig. 10). Drawing a straight line through the points gives $\alpha_{RM}=7.4\times10^3p$; so that $\alpha_{MR}=4.4p$. Since the accuracy of the value of β is good, the main source of uncertainty in the above values arises from the scatter in the measured values of d_f.

To obtain a value for α_{MP}, using the approximation $\alpha_{MP}=d_s-\alpha_{MR}$, we note that since α_{MP}, α_{MR} are polynomial functions of pressure, so also d_s is a polynomial

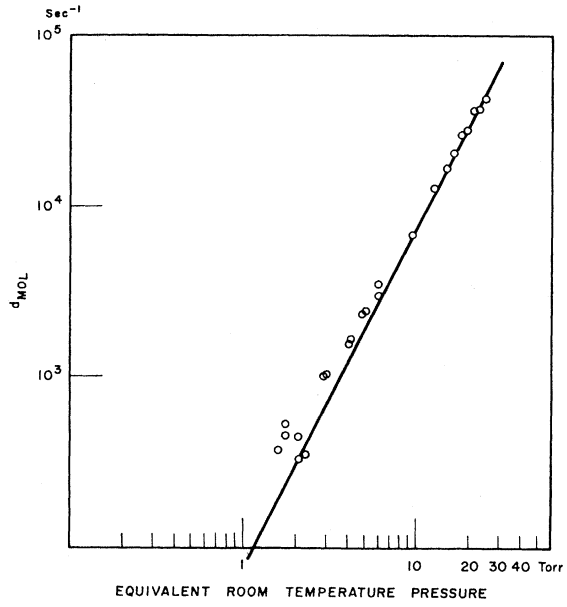

FIG. 11. The slow decay d_{Mol} of the molecular radiation versus equivalent room-temperature pressure. Measurements made at 196°K. The straight line is drawn at $d_{\text{Mol}}=75p^2$.

function of pressure. We write

$$d_s=Cp+Dp^2.$$

(We have neglected the small influence of diffusion of metastables to the walls, which would involve a term in $1/p$.)

The coefficient D can be obtained graphically by plotting $d_{\text{Mol}}=d_s$ as a function of p on log-log scale, as in Fig. 11. The measured points approach asymptotically the line $75p^2$ giving $D=75$. The value of C is now obtained by plotting d_s-75p^2 as a function of pressure (Fig. 12). In this figure the uncertainties on the points are indicated by error bars. At low pressure the largest uncertainty arises from the scatter of d_{Mol} values caused by low signal-to-noise ratio. At higher pressures the uncertainty in the value $D=75$ is the most significant cause of error. The result of drawing a straight line

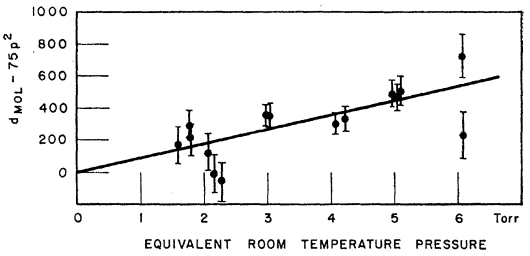

FIG. 12. Plot of $d_{\text{Mol}}-75p^2$ versus equivalent room-temperature pressure. The straight line represents the equation $d_{\text{Mol}}-75p^2=90p$.

through the points of Fig. 12 gives a value $C=90$, thus,

$$\alpha_{MP}=86p+75p^2.$$

IV. ACCURACY OF THE RESULTS

The accuracy of the results has been estimated from the scatter of the measured points and the uncertainty in fitting the lines to the points on the graphs. The collected results are presented in Table I where p is the equivalent room temperature pressure in Torr.

V. VALIDITY OF THE ASSUMPTION OF A CONSTANT β

First, let us consider the validity of the assumption that the decay constant β for the resonance radiation is a constant over the range of pressures of this experiment. In the above theory we have assumed that the decrease in the lifetime of the resonance radiation emission is caused by collisional de-excitation of the resonance atoms. However, it is possible that modification of the resonance-radiation-trapping mechanism takes place at higher pressures. The factors in support of the assumption of a constant value of β are as follows:

(i) *Consistency of present measurements:* Holstein's theory of resonance radiation trapping[11,12] shows that, when conditions of impact pressure broadening of the resonance line exist, the value of β is independent of both pressure and temperature. The present experi-

TABLE I. Collected results of measurements at two temperatures, 295 and 196°K. At each temperature the various collision coefficients α for two-body collisions are given in units of sec^{-1} at pressure p in Torr, in units of cm^3/sec for the collision frequency per atom and in units of cm^2 for the corresponding cross-section. For three-body collisions the coefficients are given in units of sec^{-1} at pressure p in Torr and also in units of cm^6/sec for the collision frequency per atom.

	295°K			196°K		
	sec^{-1}	cm^3/sec	Cross section (cm^2)	sec^{-1}	cm^3/sec	Cross section (cm^2)
α_{RM}	$(44\pm3)\times10^2p$	$(13\pm2)\times10^{-14}$	$(4.8\pm3)\times10^{-18}$	$(74\pm4)\times10^2p$	$(22\pm1)\times10^{-14}$	$(10\pm0.5)\times10^{-18}$
α_{MR}	$(25\pm2)p$	$(7.6\pm0.6)\times10^{-16}$	$(2.8\pm0.3)\times10^{-20}$	$(4.4\pm0.3)p$	$(1.3\pm0.1)\times10^{-16}$	$(0.6\pm0.05)\times10^{-18}$
α_{MP} (two-body)	$(50\pm6)p$	$(15\pm2)\times10^{-16}$	$(5.6\pm0.8)\times10^{-20}$	$(86\pm20)p$	$(26\pm7)\times10^{-16}$	$(12\pm4)\times10^{-20}$
		cm^6/sec			cm^6/sec	
α_{MP} (three-body)	$(44\pm2)p^2$	$(4.0\pm0.2)\times10^{-32}$		$(75\pm4)p^2$	$(6.9\pm0.4)\times10^{-32}$	

[11] T. Holstein, Phys. Rev. **83**, 1159 (1951).
[12] T. Holstein, Phys. Rev. **72**, 1212 (1947).

ments are consistent with the assumption that the measured decay constant d_f has the form $a+bp$, where a and b are constants and p is the pressure, in support of the theory proposed earlier. Moreover, the low-pressure measurements at the two temperatures indicate that β is independent of temperature.

(ii) *Theoretical considerations:* The theory of Holstein is based on the assumption of a Lorentzian shape for the resonance line. Change of line shape from a simple Lorentzian would be expected to produce a change in the value of β. However, at the pressures of the present experiment the resonance-line profile for krypton has been measured by Kuhn and Vaughan (private communication) and found to be Lorentzian. Their technique is the same as that used in their work on helium and neon.[13] Furthermore, Kuhn and Vaughan have also shown that the line broadening is linear with pressure, from which it also follows by Holstein's theory that β is independent of pressure over the range of the present measurements.

A factor which is not in favor of the use of Holstein's theory is asymmetry and shift of the resonance line as shown in Figs. 1 and 2. This may be due to the particular geometry of discharge tube employed in these experiments. It is proposed to investigate these effects further using discharge tubes specifically designed for this type of experiment (e.g., the use of a "gas window" would eliminate the long path which the resonance radiation must take between the discharge and the lithium fluoride window).

VI. DISCUSSION

A. De-excitation of Resonance Atoms to the Metastable Level

From the measured coefficient α_{RM} the calculated cross sections for the $1s_4$-$1s_5$ collision induced transition, at 295 and 196°K are 4.8×10^{-18} and 10×10^{-18} cm^2, respectively. These values can be compared with those for the corresponding transition in neon[14] which are 5.2×10^{-19} cm^2 at 300°K, falling to about 2.5×10^{-19} cm^2 at 200°K. Thus we observe that the krypton cross section is larger by an order of magnitude than the neon cross section and increases with decreasing gas temperature by a factor 2 while the neon cross section decreases by about the same factor. Theory uses the parameters $(\Delta E/h)(d/v)\gg1$ as a criterion that the probability of excitation transfer be small[15] and also for a measure of the applicability of the sudden approximation,[16] where v is the average atomic velocity of krypton, ΔE is the difference in energy of the atomic states, h is Planck's constant, and d is the range of the interaction. Using for d the collision radius obtained from the measured cross section one finds $(\Delta E/h)(d/v)\sim2$ i.e. not large compared with one. One would therefore expect a relatively large transition probability for krypton. However, the same theory predicts a smaller transition probability at lower temperatures, which is opposite to what is observed. This is not surprising since for the small values of $(\Delta E/h)(d/v)$ found for krypton one would not expect the theory to yield consistent results. There is an obvious need for theoretical calculations similar to those recently made for alkali-metal–rare-gas collisions.[17] The assumption which was made in this latter calculation that the speed of the colliding particles would not be altered by the collision would hardly be expected to apply in the present case, however.

B. Collisional Excitation of Metastable Atoms to the Resonance Level

The energy necessary to effect this transition being relatively large, one would expect from energy considerations alone that the probability for excitation of metastable atoms to the resonance level would be smaller at lower temperatures.

The measured values of collision frequency per atom for α_{MR} are 7.6×10^{-16} cm^3/sec and 1.3×10^{-16} cm^3/sec at 295 and 196°K, respectively. At 196°K the number of normal atoms having sufficient energy to effect the transition is less by a factor of about 10 than the corresponding number of 295°K. Since the collision frequency falls by a factor of approximately 3 only one must conclude that the excitation process is relatively more efficient at lower temperatures, as was observed for the corresponding de-excitation frequency discussed in Sec. VI A above. Again, no theory is available which would be applicable in the present case.

C. Molecule Formation

1. Two-Body Collisions

The physical processes occurring when a metastable and a normal atom collide to cause the emission of a molecular radiation have been discussed from two points of view. In the case of helium Tanaka and Yoshino[18] have proposed that the presence of a hump[19] in the interatomic potential function makes possible the existence of molecular levels having energies equivalent to the sum of kinetic-plus-potential energies of the colliding atoms: A temporary molecule may then be formed in the excited state by a process involving tunnelling through the hump. Alternatively, and also for helium,

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two-body de-excitation has been ascribed to collision-induced radiation. Earlier theoretical estimates by Burhop and Marriott[20] were different from the measured values of the two-body collision coefficient made by Phelps[10] by two orders of magnitude. However, Allison, Browne, and Dalgarno[21] have recently made a calculation using wave functions which are modified to allow for the polarizing effects of one atom on the other. Their results give a value for the height of the potential hump of about 0.084 eV, which is lower than the previous estimate by Scott *et al.*[22] Moreover, the cross section for collision-induced transitions was calculated to be 2×10^{-20} cm^2, which is in good agreement with the experimental value of Phelps.

The two-body destruction of krypton metastables observed in the present work can therefore be explained on the assumption of a hump in the interatomic potential as in the case of helium. The good agreement between theory and experiment for the collision-induced radiation hypothesis in the case of helium appears to favor this interpretation also for the case of krypton. However, the calculations of Allison *et al.* show an increase in cross section with increasing temperature whereas the present results show the opposite effect.

Limited comparison only is possible between the present work and that for other rare gases. The two-body cross sections measured for helium and argon are 3×10^{-20} cm^2 and 4×10^{-20} cm^2 at room temperature. The value of 5.6×10^{-20} cm^2 found in this experiment is thus of the same order of magnitude. No measurements have been made in other rare gases to show the variation of the cross section with temperature.

2. *Three-Body Collisions*

The three-body coefficient for molecule formation in krypton shows an increase with decreasing temperature. This is in contrast to the case of neon where the three-body coefficient decreases with decreasing temperature.[14] The krypton collision frequency of 40×10^{-33} cm^6/sec is larger than the collision frequencies for argon[23] and neon[14] which are 9.8×10^{-33} and 0.5×10^{-33} cm^6/sec, respectively.

The mechanism of molecule formation by collisions of metastables with ground-state atoms with the subsequent emission of molecular radiation has been proposed to explain the production of delayed current pulses in a coaxial discharge tube in the case of argon[9] and also in krypton.[24]

ACKNOWLEDGMENTS

The author is grateful to Dr. W. H. King for assistance during part of the work, to Dr. A. V. Phelps for helpful advice and comments, to R. Bouciqué for communicating his results and their interpretation, and to Dr. H. G. Kuhn and Dr. J. M. Vaughan for their preliminary values of resonance-line broadening in krypton. He also wishes to thank Dr. W. R. Hindmarsh for his advice and for reading the manuscript.

APPENDIX

To solve

$$\frac{dR}{dt}=-(\beta+\alpha_{RM})R+\alpha_{MR}M\,, \tag{1}$$

$$\frac{dM}{dt}=\alpha_{RM}R-(\alpha_{MR}+\alpha_{MP})M\,, \tag{4}$$

write

$$\alpha_{MP}+\alpha_{MR}=\alpha\,,\quad \alpha_{RM}+\beta=\gamma\,,$$

$$DM=-\alpha M+\alpha_{RM}R\,, \tag{1'}$$

$$DR=-\gamma R+\alpha_{MR}M\,. \tag{2'}$$

The two simultaneous equations (1′) and (2′) give

$$R=Ae^{-d_f t}+Be^{-d_s t}\,, \tag{5}$$

where

$$d_f,\,d_s=-\frac{1}{2}\left[-(\alpha+\gamma)\pm(\alpha-\gamma)\left(1+\frac{4\alpha_{MR}\alpha_{RM}}{(\alpha-\gamma)^2}\right)^{1/2}\right]. \tag{6}$$

Simplification is achieved by using

$$d_f+d_s=\theta_+=\alpha+\gamma\,, \tag{7}$$

$$d_f d_s=\theta_x=\alpha\gamma-\alpha_{MR}\alpha_{RM}\,, \tag{8}$$

and, from detailed balancing,

$$\alpha_{RM}=K\alpha_{MR}\,. \tag{9}$$

Solving for α_{MP},

$$\alpha_{MP}=\tfrac{1}{2}[\theta_+-\sqrt{F}]\,, \tag{10}$$

where

$$F=\theta_+^2-\frac{4}{K}[\theta_x(K+1)-(\theta_+-\beta)] \tag{11}$$

also

$$\alpha_{MR}=\frac{\theta_+-\alpha_{MP}-\beta}{K+1}\,. \tag{12}$$

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