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m_J Mixing in Oriented $4\,^2P_{3/2}$ Potassium Atoms Induced by Collisions with Inert Gases*

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The cross sections for the decay of circular and of linear polarization in oriented $4\,^2P_{3/2}$ potassium atoms, induced in collision with inert-gas atoms, were determined in a series of fluorescence experiments. A modified Zeeman scanning method was used to populate selectively the m_J sublevels of the $^2P_{3/2}$ potassium atoms mixed with inert gases and placed in a strong magnetic field. Measurements of depolarization of the fluorescence, in relation to gas pressures, yielded the following depolarization cross sections: σ_1 (disorientation): K-He, 86 Å^2; K-Ne, 86 Å^2; K-Ar, 164 Å^2; K-Kr, 248 Å^2; K-Xe, 251 Å. σ_2 (disalignment): K-He, 127 Å; K-Ne, 120 Å^2; K-Ar, 240 Å^2, K-Kr, 301 Å^2, K-Xe, 336 Å^2. The experimental values are in satisfactory agreement with the calculations of Nikitin and Ovchinnikova.

I. INTRODUCTION

The depolarization of alkali atoms in their $^2P_{1/2}$ and $^2P_{3/2}$ resonance states, induced in collisions with inert-gas atoms, has been the subject of several recent studies, both theoretical and experimental. The general theoretical problem of collisional relaxation of excited atoms has been treated by Dyakonov and Perel,[1] and by Omont.[2] Franz and Franz[3] proposed two models for the description of the depolarization in the particular case of alkali atoms, of which one involved a random reorientation of the total electronic angular momentum J, while the second assumed the existence of selection rules according to which $\Delta m_J = 0, \pm 2$. Elbel and Naumann[4] suggested that the mixing of the Zeeman sublevels is due to collisional phase shifts between the molecular σ and π substates, into which the atomic ^2P state is split during a collision, and obtained the selection rule $m_J \not\to -m_J$ for mixing within a J multiplet state. A similar result was derived by Franz, Leutert, and Shuey.[5] Mandelberg,[6] using an impact-parameter method, calculated the cross sections for m_J mixing in alkali atoms, induced in collisions with the inert gases. His results did not, however, indicate the existence of any restrictive selection rules, nor did the most recent calculations of Gordeev, Nikitin, and Ovchinnikova,[7] who assumed Coriolis mixing of adiabatic electronic molecular states, or of Grawert,[8] whose treatment did not assume any particular model but was based on general conservation laws.

The experimental investigations of these processes were carried out largely in optical pumping or Hanle experiments. Thus Elbel and Naumann[4] determined the total cross sections for the depolarization of the $^2P_{3/2}$ resonance state in sodium, the corresponding cross section for the $P_{1/2}$ state in rubidium was obtained by Marrus and Yellin[9] and for both the $^2P_{1/2}$ and $^2P_{3/2}$ states by Gallagher,[10] who also studied the $^2P_{1/2}$ state in cesium in which the $^2P_{3/2}$ state was investigated by Fricke, Haas, Lüscher, and Franz.[11]

In the present investigation, the modified Zeeman scanning method was used to study the collisional transitions between the Zeeman substates of the $4\,^2P_{3/2}$ state in potassium. The method, which was successfully employed to determine the m_J mixing cross section for the $4\,^2P_{1/2}$ state,[12] involves the selective excitation of one Zeeman substate ($m_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$, or $\frac{3}{2}$) by means of σ^- or σ^+ light of the appropriate frequency, and measurements of the degrees of linear and circular polarization of the fluorescence, which becomes depolarized as a result of collisions between the excited potassium atoms and the ground-state inert-gas atoms. It is thus possible to determine the decays of linear and circular polarizations which can be compared with theoretical predictions. An advantage of this simple and direct method is that it is not subject to errors arising from the broadening and self-reversal of the exciting line, which constitute an important source of uncertainty in the optical pumping measurements.[11] The shape of the resonance line remains constant at low inert-gas pressures, and the operating conditions of the source of exciting radiation are so chosen that there is no self-reversal and that the relative intensities of the Zeeman components are virtually in the theoretically predicted ratio.[13] The sensitivity of the method is such that measurements may be confined to inert-gas pressures below 1 Torr, at which $^2P_{1/2} \rightarrow {}^2P_{3/2}$ mixing effects are negligible.[12]

II. SELECTIVE EXCITATION OF $^2P_{3/2}$ ZEEMAN SUBLEVELS

The optical excitation of the Zeeman sublevels proceeds as follows. A potassium spectral lamp[13] is placed in a constant magnetic field of about 5 kG, and the σ^- component of the emitted resonance radiation of wavelength 7665 Å is made incident on potassium vapor at low pressure, placed in a parallel magnetic field which can be varied from 0 to 10 kG. Excitation takes place with the beam of exciting light directed perpendicularly to the field surrounding the potassium vapor, according to the selection rule $\Delta m_J = -1$. In the absence of depolarizing collisions, fluorescent light is emitted through the decay of only those Zeeman sublevels which have been excited optically. The fluorescence which, in general, consists of σ^-, σ^+, and π components, is appropriately polarized and it is possible to calculate the degrees of polarization corresponding to particular modes of excitation and observation.

As the magnetic field surrounding the fluorescence cell is increased, various coincidences occur between the Zeeman components in emission from the lamp and in absorption by the fluorescing vapor, as is shown in Fig. 1. A scan of the magnetic field results in three σ-polarized fluorescent intensity peaks or two π-polarized peaks. The degrees of linear polarization P_0' and of circular polarization P_0 may be determined experimentally in each of the peaks by means of the usual relations:

$$P_0' = \frac{I_\pi - I_\sigma}{I_\pi + I_\sigma}\,, \quad P_0 = \frac{I_{\sigma^-} - I_{\sigma^+}}{I_{\sigma^-} + I_{\sigma^+}}\,, \tag{1}$$

where I_π and I_σ are the relative intensities of the π and σ fluorescent components, respectively, emitted perpendicularly to the field and I_{σ^-} and I_{σ^+} are the intensities of the σ^- and σ^+ components, respectively, emitted parallel to the field.

The values of P_0' and P_0 may also be calculated from first principles, using Van Vleck's equations[14] and bearing in mind that excitation is accomplished by means of the individual Zeeman components rather than with a broad line. When excitation takes place by means of σ components, the following expressions are obtained for the fluorescent intensities I_π and I_σ:

$$I_\pi = \tfrac{1}{2} C I' \left[A_\pi' A_\sigma' / (A_\pi' + A_\sigma')\right]\,, \tag{2}$$

$$I_\sigma = \tfrac{1}{4} C I' \left[A_\sigma'^2 / (A_\pi' + A_\sigma')\right] + \tfrac{1}{4} C I'' A_\sigma''\,, \tag{3}$$

where C is a constant, A_π' and A_σ' are the transition probabilities for the decays of the $m_J = \pm\frac{1}{2}$ substates of the $4\,^2P_{3/2}$ state, proceeding through the emission of π and σ radiation, respectively, and A_σ'' is the corresponding transition probability for the $m_J = \pm\frac{3}{2}$ substates. I' and I'' are the relative intensities of those σ components in the exciting light, which excite the $m_J = \pm\frac{1}{2}$ and $m_J = \pm\frac{3}{2}$ substates, respectively.

Assuming the intensities of the Zeeman components to be in the ratio $I'' : I' = 3:1$ and using Eqs. (2) and (3), it is possible to calculate the relative intensities of the σ and π fluorescent components, which are compared in Table I with the

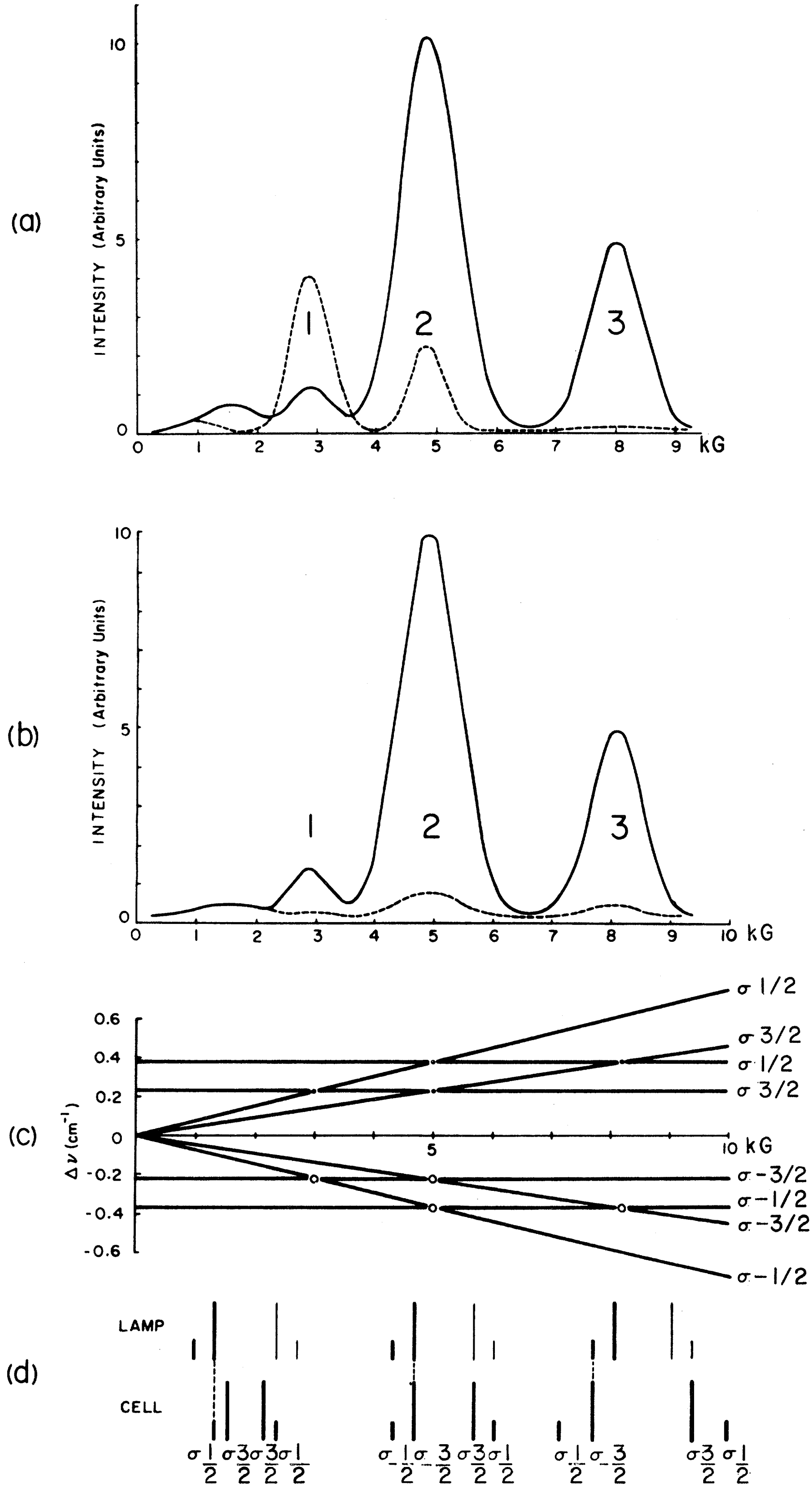

FIG. 1. Selective excitation by σ^- light of resonance fluorescence in the Zeeman components of the $4\,^2P_{3/2}$ level in potassium. (a) Experimental intensity profile of the fluorescence observed perpendicularly to the magnetic field (solid line, σ component; dashed line, π component). (b) Experimental profile with parallel observation (solid line, σ^- component; dashed line, σ^+ component). (c) Zeeman splitting of the 7665-Å line in the lamp (const at 5 kG) and in the cell (variable). The π components are not shown. (d) Resonances between the σ Zeeman components in the lamp and fluorescence cell.

corresponding experimentally determined values obtained at very low potassium vapor pressures which were maintained both in the lamp and fluorescence cell. The two sets of values are in good agreement with each other. The small difference between the calculated and experimental P_0' in the

TABLE I. Relative intensities of σ and π components and the polarization of fluorescence excited with the σ components of the 7665-Å resonance radiation.

Intensities and degree of polarization	1st peak (3 kG)		2nd peak (5 kG)		3rd peak (8 kG)	
	expt	calc	expt	calc	expt	calc
I_σ	3.22	3	28	28	9.24	9
I_π	11.34	12	4.20	4	0	0
$P'_0=(I_\pi-I_\sigma)/(I_\pi+I_\sigma)$	0.56	0.60	−0.74	−0.75	−0.99	−1.00

first peak is probably due to an admixture of the π component in the exciting light, whose presence is indicated by a low and broad intensity maximum in Fig. 1(a) and 1(b). It should also be considered that the Zeeman splitting is smallest at the lower magnetic field, giving rise to a possibility of overlap between the Zeeman components and, consequently, to a decrease in the degree of polarization. Finally, the assumed ratio of $I'':I'=3:1$ in the exciting light might be subject to a slight error because of some reabsorption taking place in the lamp. The degree of circular polarization P_0, which can be determined directly from the intensity profiles given in Fig. 1(a), amounts to 94–96% in all three peaks. The departure from the expected value of 100% is caused by two factors: the presence of a π impurity which could not be completely eliminated from the exciting σ^- light, and the difficulty of effecting a complete separation of the σ^- and σ^+ components in both the exciting and fluorescent light, because of the imperfections of the quarter-wave plates.

III. COLLISIONAL m_J MIXING PROCESSES

The addition of an inert gas to the fluorescence cell results in collisions between the excited potassium atoms in their Zeeman substates and the ground-state inert-gas atoms. The collisions tend to equalize the populations of the Zeeman sublevels and, thus, to depolarize the resonance fluorescence. The alkali-vapor–inert-gas mixture exists in a steady state which involves continuous optical excitation with σ^- (and σ^+) light of wavelength 7665 Å, spontaneous decay and inelastic collisions. The collisions induce transitions between the Zeeman sublevels, which proceed according to the equation

$$K(4\,^2P_{3/2,m_J})+X(^1S_0)+\Delta E \leftrightarrow K(4\,^2P_{3/2,m'_J})+X(^1S_0)\ , \tag{4}$$

where $K(4\,^2P_{3/2,m_J})$ and $K(4\,^2P_{3/2,m'_J})$ are $4\,^2P_{3/2}$ potassium atoms in m_J and m'_J Zeeman substates, respectively, $X(^1S_0)$ is an inert-gas atom in the ground state, and ΔE is the energy defect between the substates m_J and m'_J, which depends on the magnitude of the magnetic field but is much smaller than kT at the operating temperature.

The radiative and collisional processes which contribute to the steady state and which are depicted in Fig. 2 may be represented by the following rate equations:

$$\frac{dn_{-3/2}}{dt}=\frac{-1}{\tau}n_{-3/2}-Z_1n_{-3/2}-Z_2n_{-3/2}-Z_3n_{-3/2}$$
$$+Z_1n_{-1/2}+Z_2n_{1/2}+Z_3n_{3/2}+s_{-3/2}=0\ , \tag{5}$$

$$\frac{dn_{-1/2}}{dt}=\frac{-1}{\tau}n_{-1/2}-Z_1n_{-1/2}-Z_0n_{-1/2}-Z_2n_{-1/2}$$
$$+Z_1n_{-3/2}+Z_0n_{1/2}+Z_2n_{3/2}+s_{-1/2}=0\ , \tag{6}$$

$$\frac{dn_{1/2}}{dt}=\frac{-1}{\tau}n_{1/2}-Z_1n_{1/2}-Z_0n_{1/2}-Z_2n_{1/2}$$
$$+Z_1n_{3/2}+Z_0n_{-1/2}+Z_2n_{-3/2}+s_{1/2}=0\ , \tag{7}$$

$$\frac{dn_{3/2}}{dt}=-\frac{1}{\tau}n_{3/2}-Z_1n_{3/2}-Z_2n_{3/2}-Z_3n_{3/2}$$
$$+Z_1n_{1/2}+Z_2n_{-1/2}+Z_3n_{3/2}+s_{3/2}=0\ , \tag{8}$$

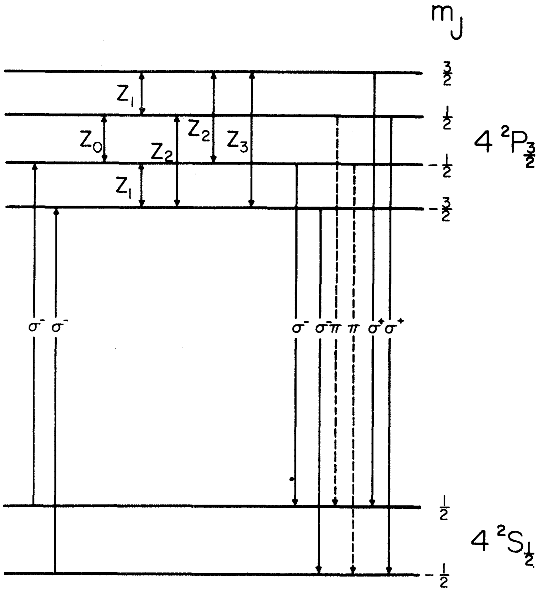

FIG. 2. Transitions between the Zeeman sublevels of the ground and resonance states.

where $\tau = 2.77\times10^{-8}$ sec is the average lifetime of the $4\,^2P$ states,[15] $n_{-3/2}$, $n_{-1/2}$, $n_{1/2}$, and $n_{3/2}$ are the densities of $4\,^2P_{3/2}$ potassium atoms in the $m_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$, and $\frac{3}{2}$ substates, respectively, and Z_0, Z_1, Z_2, and Z_3 are the respective collision numbers (frequencies of collisions per excited atom) corresponding to the following transitions between Zeeman substates of the $4\,^2P_{3/2}$ state: $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$, $\mp\frac{3}{2} \leftrightarrow \mp\frac{1}{2}$, $\mp\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$, and $-\frac{3}{2} \leftrightarrow +\frac{3}{2}$. $s_{-3/2}$, $s_{-1/2}$, $s_{1/2}$, and $s_{3/2}$ are the densities of atoms excited optically per second to the $m_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$, and $\frac{3}{2}$ substates, respectively.

The depolarization of the resonance radiation is caused not only by collisional mixing between the m_J substates within the $4\,^2P_{3/2}$ state, but also by collision-induced transitions to the $4\,^2P_{1/2}$ state. However, at inert-gas pressures below 1 Torr, the latter effect may be considered negligible to a good approximation,[12] bearing in mind that the sensitized fluorescence emitted from the $^2P_{1/2}$ level is rejected by the interference filters and that, therefore, the only observable result of any collisional transfer to the $^2P_{1/2}$ state would be an effective decrease of about 1% in the lifetime of the $^2P_{3/2}$ state. It may also be safely assumed that, at potassium vapor pressures below 10^{-6} Torr, which were employed in the experiments, effects due to multiple scattering are absent.[15,16] The addition and subtraction of the above equations in pairs [(6) ± (7)] and [(5) ± (8)], yield the expressions:

$$\alpha d - yb = s_{-1/2} + s_{1/2}\,, \tag{9}$$

$$(2Z_0+\alpha)c - xa = s_{-1/2} - s_{1/2}\,, \tag{10}$$

$$\alpha b - yd = s_{-3/2} + s_{3/2}\,, \tag{11}$$

$$(2Z_3+\alpha)a - xc = s_{-3/2} - s_{3/2}\,, \tag{12}$$

where

$$a = n_{-3/2} - n_{3/2},\quad b = n_{-3/2} + n_{3/2}\,,$$

$$c = n_{-1/2} - n_{1/2},\quad d = n_{-1/2} + n_{1/2}\,,$$

$$x = Z_1 - Z_2,\quad y = Z_1 + Z_2,\quad \alpha = y + 1/\tau\ .$$

If it is assumed that $A'_\pi : A''_\sigma : A'_\sigma = 4:6:2$ and, considering that only one-half of the total intensity of circularly polarized light is observed when the fluorescence is monitored perpendicularly to the magnetic field, it is possible to express the degrees of linear polarization P' and of circular polarization P by means of the following relations:

$$P' = \frac{I_\pi - I_\sigma}{I_\pi + I_\sigma} = \frac{4(n_{-1/2}+n_{1/2}) - (n_{-1/2}+n_{1/2}) - 3(n_{-3/2}+n_{3/2})}{4(n_{-1/2}+n_{1/2}) + (n_{-1/2}+n_{1/2}) + 3(n_{-3/2}+n_{3/2})} = \frac{3d-3b}{5d+3b}\,, \tag{13}$$

$$P = \frac{I_{\sigma^-} - I_{\sigma^+}}{I_{\sigma^-} + I_{\sigma^+}} = \frac{n_{-1/2} + 3n_{-3/2} - n_{1/2} - 3n_{3/2}}{n_{-1/2} + 3n_{-3/2} + n_{1/2} + 3n_{3/2}} = \frac{3a+c}{3b+d}\ . \tag{14}$$

Equations (9) and (12) may be solved to yield a, b, c, and d, which, on substitution in Eqs. (13) and (14), give

$$P' = \frac{P'_0}{1 + 2\tau y - \frac{2}{3}\tau y P'_0}\,, \tag{15}$$

$$P = \frac{(\alpha^2 - y^2)\left[(3U+x)(s_{-3/2} - s_{3/2}) + (W+3x)(s_{-1/2} - s_{1/2})\right]}{(UW - x^2)\left[(3\alpha+y)(s_{-3/2} + s_{3/2}) + (\alpha+3y)(s_{-1/2} + s_{1/2})\right]}\,, \tag{16}$$

where $U = 2Z_0 + \alpha$ and $W = 2Z_3 + \alpha$. Equation (15), which represents the degree of linear polarization of fluorescence observed perpendicularly to the magnetic field, is a modification of the Stern-Volmer formula,[17] which may be derived by means of an identical argument for a system of three Zeeman sublevels such as arises in the case of the $6\,^1S_0 - 6\,^3P_1$ transition in mercury. The ordinary Stern-Volmer expression is not applicable to the case of the $4\,^2P_{3/2}$ potassium atoms where it is necessary to take into consideration the fact that the $m_J = \pm\frac{1}{2}$ levels decay by means of both π and σ transitions, with their appropriate transition probabilities. Equation (16) gives the degree of circular polarization of fluorescence observed parallel to the magnetic field.

Equations (15) and (16) apply in the most general case, when all the m_J sublevels of the $^2P_{3/2}$ state are being optically excited. In particular, in cases of selective excitation, which correspond to the fluorescent peaks in Figs. 1(a) and 1(b), the appropriate values of P'_0 must be used in Eq. (15), and Eq. (16) is reduced to the following forms, corresponding to the first and third fluorescent peaks, respectively:

$$P_1 = P_0\,\delta(W+3x)/(UW - x^2)\,, \tag{17}$$

$$P_3 = P_0\,\beta(3U+x)/(UW - x^2)\,, \tag{18}$$

where

$$\beta=(\alpha^2-y^2)/(3\alpha+y)$$

and

$$\delta=(\alpha^2-y^2)/(\alpha+3y) \ .$$

The measurement of P' in any one of the three fluorescent peaks in relation to inert-gas pressure and substitution in Eq. (15) leads to a value of $y=Z_1+Z_2$, and thus to $\alpha=Y+1/\tau$. Similar determinations of P in the first and third peaks of Fig. 1(b) reduce Eqs. (17) and (18) to a system of two equations with three unknowns: $x=Z_1-Z_2$, $U=2Z_0+\alpha$, and $W=2Z_3+\alpha_0$.

Even though the experiment as described will not yield the individual m_J mixing rates Z_1, Z_2, Z_3, and Z_4, it does permit the determination of the decay rates of circular and linear polarization which, according to the notation of Dyakonov and Perel,[1] are denoted by γ_1 and γ_2, respectively, and are related to the collision numbers Z as follows:

$$\gamma_1=\tfrac{1}{5}Z_0+\tfrac{2}{5}Z_1+\tfrac{8}{5}Z_2+\tfrac{9}{5}Z_3 \ , \tag{19}$$

$$\gamma_2=2Z_1+2Z_2 \ . \tag{20}$$

The remaining decay rates are given by

$$\gamma_3=\tfrac{9}{5}Z_0+\tfrac{8}{5}Z_1+\tfrac{2}{5}Z_2+\tfrac{1}{5}Z_3 \ , \tag{21}$$

$$\gamma_4=-\tfrac{3}{5}Z_0+\tfrac{4}{5}Z_1-\tfrac{4}{5}Z_2+\tfrac{3}{5}Z_3 \ . \tag{22}$$

It should be noted that γ_3 cannot be determined under the conditions of this experiment and that $\gamma_4=0$.[1,18] Equations (15), (17), and (18) can be expressed in terms of γ_1 and γ_2:

$$P'=P'_0/(1+\tau\gamma_2-\tfrac{1}{3}\tau\gamma_2P'_0) \ , \tag{23}$$

$$P_1=P_0\,(1+\tau\gamma_2)/(1+\tau\gamma_1)(1+2\tau\gamma_2) \ , \tag{24}$$

$$P_3=P_0\,3(1+\tau\gamma_2)/(1+\tau\gamma_1)\,(3+2\tau\gamma_2) \ . \tag{25}$$

In this way, measurements of P' directly yield γ_2 and determinations of P_1 or P_3 lead to γ_1. The cross sections σ_1 and σ_2 for the collisional decay of circular and linear polarization, respectively, may be defined analogously with the gas-kinetic cross section:

$$\gamma_i=N\sigma_i v_r \ , \tag{26}$$

where N is the density of the inert-gas atoms and v_r is the average relative velocity of the colliding partners. The quantities σ_1 and σ_2 are also known as the cross sections for collisional disorientation and disalignment, respectively. The cross sections for the individual m_J mixing processes are similarly defined:

$$Z_i=NQ_iv_r \tag{27}$$

and are connected as follows with the quantities σ_i :

$$Q_0=\tfrac{1}{20}\sigma_1-\tfrac{1}{4}\sigma_2+\tfrac{9}{20}\sigma_3-\tfrac{3}{10}\sigma_4 \ , \tag{28}$$

$$Q_1=-\tfrac{3}{20}\sigma_1+\tfrac{1}{4}\sigma_2+\tfrac{3}{20}\sigma_3+\tfrac{2}{5}\sigma_4 \ , \tag{29}$$

$$Q_2=\tfrac{3}{20}\sigma_1+\tfrac{1}{4}\sigma_2-\tfrac{3}{20}\sigma_3-\tfrac{2}{5}\sigma_4 \ , \tag{30}$$

$$Q_3=\tfrac{9}{20}\sigma_1-\tfrac{1}{4}\sigma_2+\tfrac{1}{20}\sigma_3+\tfrac{3}{10}\sigma_4 \ , \tag{31}$$

where $\sigma_4=0$.

IV. EXPERIMENTAL

The apparatus used in the present investigation has been described previously.[12] The σ^- Zeeman components of the 7665-Å potassium resonance line, emitted by an rf lamp[13] placed in a magnetic field of 5 kG, were made incident on the vapor-gas mixture contained in a fluorescence tube which was mounted in a constant-temperature oven and located in a parallel (or antiparallel) magnetic field, continuously variable in the range 0–10 kG. The fluorescent light was observed along two directions perpendicular to the exciting light beam and to each other, and was registered with refrigerated ITT FW118 photomultipliers, whose outputs, after amplification, were applied to the y axes of xy plotters, the x axes of which were connected to the output of a magnetometer. The 7665-Å component of the resonance doublet was isolated in the exciting and fluorescent light with a spectral purity better than 1 ppm, by means of Spectrolab interference filters. The inclusion of appropriate circular and linear polarizers in the exciting and fluorescent light beams permitted the observation of the σ^-, σ^+, σ, and π fluorescent components and the direct recording of their intensities in relation to the strength of the variable magnetic field.

The fluorescence tube was of cylindrical shape and had in its front end three plane windows set

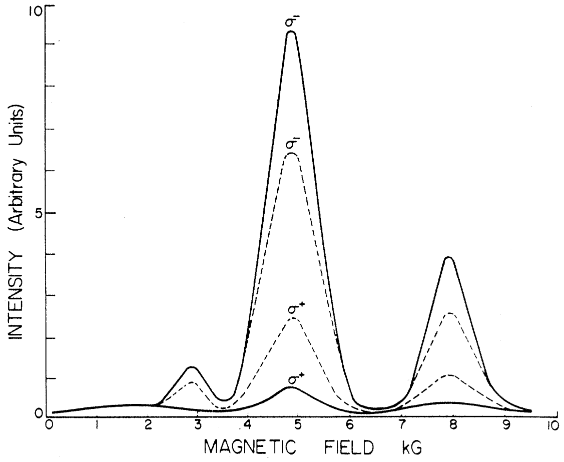

FIG. 3. Fluorescence from the $4\,^2P_{3/2}$ level in potassium atoms in mixture with helium, excited with σ^- light (solid line, pure K; dashed line, 1.1 Torr He).

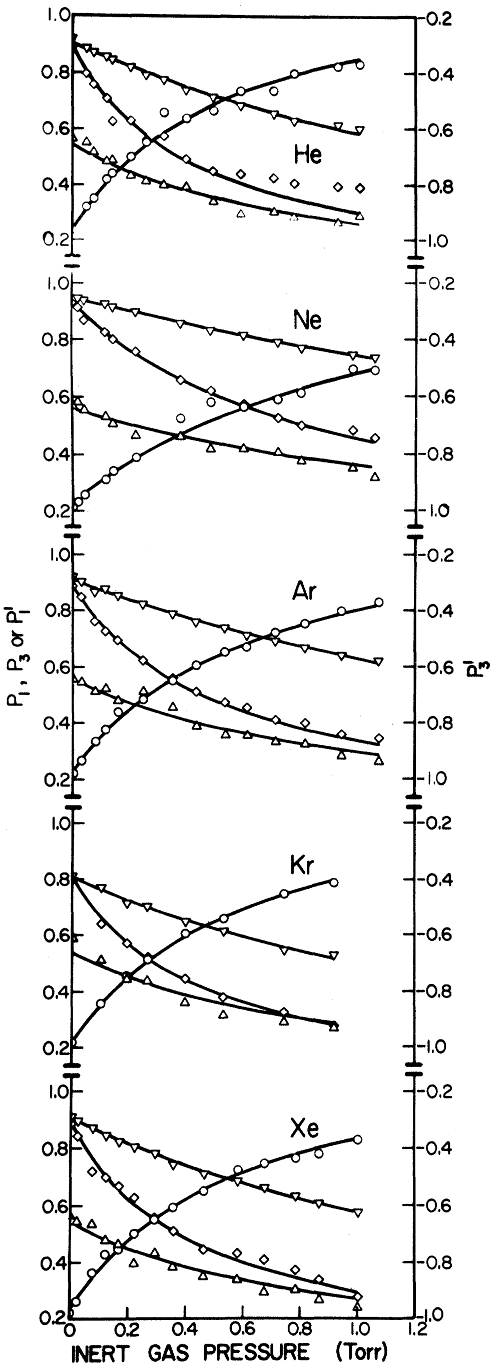

FIG. 4. Variation of the degrees of circular and linear polarization in the first and third fluorescent peaks, with inert-gas pressure. ◇, P_1; ▽, P_3; △, P_1'; ○, P_3'.

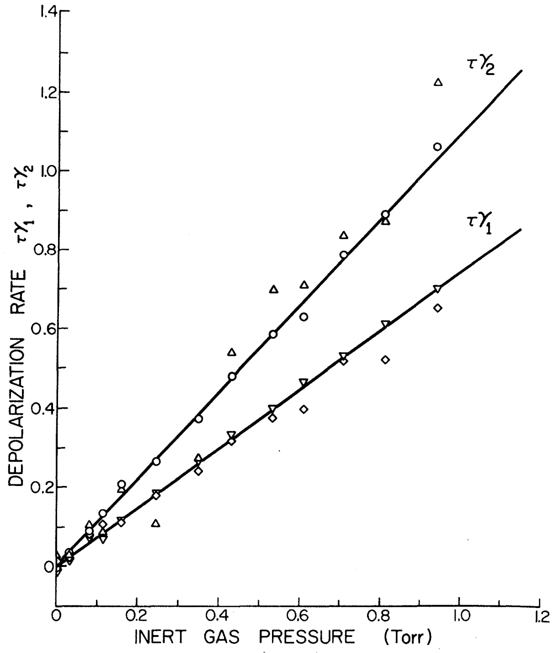

FIG. 5. Variation of decay rates γ_1 and γ_2 with argon pressure. ◇, $\tau\gamma_1$ from P_1; ▽, $\tau\gamma_1$ from P_3; △, $\tau\gamma_2$ from P_1'; ○, $\tau\gamma_2$ from P_3'.

perpendicularly to each other to permit the excitation and observation of fluorescence at small optical depths. It was mounted, together with its side arm which contained the liquid potassium metal, in a small oven which maintained the fluorescence tube at a constant temperature of 95° C, and the side arm at 64° C. The cell was connected by means of a 2-mm capillary to a vacuum and gas-filling system from which inert gases were admitted to the cell as required. Gas pressures were measured on a CVC-type GM-100A McLeod gauge.

V. RESULTS AND DISCUSSION

The depolarization of the fluorescence was studied by irradiating the vapor-gas mixture with σ^- light of wavelength 7665 Å, emitted in a direction antiparallel to the magnetic field surrounding the lamp, and incident perpendicularly to the variable field surrounding the fluorescence cell. In the course of repeated magnetic field scans carried

TABLE II. Cross sections for depolarization of excited potassium atoms, induced in collisions with inert gases. The theoretical values of σ_1 (disorientation) and σ_2 (disalignment) were calculated by Nikitin and Ovchinnikova (Ref. 18).

	This investigation			Theoretical		
Collision partners	σ_1 (Å^2)	σ_2 (Å^2)	$\frac{\sigma_2}{\sigma_1}$	σ_1 (Å^2)	σ_2 (Å^2)	$\frac{\sigma_2}{\sigma_1}$
K-He	86 ± 14	127 ± 37	1.5	38	65	1.72
K-Ne	86 ± 9	120 ± 31	1.4	84	144	1.72
K-Ar	164 ± 20	240 ± 34	1.5	147	253	1.72
K-Kr	248 ± 34	301 ± 30	1.2	243	402	1.72
K-Xe	251 ± 25	336 ± 61	1.3	283	536	1.72

out at each inert-gas pressure, the intensities of the σ^- and σ^+ fluorescent components were monitored in directions parallel and antiparallel to the field while, at the same time, the σ and π intensities were monitored in the perpendicular direction. All the inert gases were used in turn at pressures ranging from 0 to 1.5 Torr, and typical profiles resulting from such scans are shown in Fig. 3. A significant degree of depolarization was observed already at a pressure of 0.5 Torr.

The relative intensities of the σ^-, σ^+, σ, and π fluorescent components were substituted in Eqs. (1) to obtain the degrees of polarization P' and P, which are plotted against the inert-gas pressures in Fig. 4. It may be seen that, in the absence of inert gas, the degrees of polarization P_0' and P_0 are nearly but not exactly equal to the theoretically predicted values. Equations (2) and (3) indicate that the degree of linear polarization P' obtained from the first or third peak is independent of the ratio I''/I' in the exciting light, whereas this ratio does influence the results obtained from the second peak and accounts for the small changes in P_0' which were observed when the side-arm temperature in the lamp was changed. This temperature was always chosen so as to obtain P_0' most nearly equal to the calculated values shown in Table I, while the lamp would still emit light of sufficient intensity for efficient excitation. P_0 also differs somewhat from the calculated value and has almost the same value in all three fluorescent peaks. Its magnitude, which depends on the resolution of the Zeeman components in the emission from the lamp and on the efficiences of the circular polarizers, indicates the degree of success with which the various Zeeman components have been resolved with respect to frequency and polarization. It was found that departures in P_0 from the expected value were caused mainly by stray scattered light in the lamp. The circular polarizers were adequate, and their slight imperfections had very little influence on the value of P_0, as did depolarizing collisions with cell walls.

The experimental values P' and P were substituted into Eqs. (23)–(25) which yielded the decay rates γ_1 and γ_2 and their variations with the inert-gas pressures, from which the corresponding cross sections σ_1 and σ_2 were calculated on the basis of Eq. (26). Figure 5 shows plots of $\tau\gamma_1$ and $\tau\gamma_2$ vs argon pressure which are linear and are representative of all potassium–inert-gas mixtures. Their slopes yield the cross sections σ_1 and σ_2 which are compared in Table II with theoretical values calculated by Nikitin and Ovchinnikova.[18] The agreement between theory and experiment is better than was apparent from a previous calculation by Wang and Tomlinson,[19] who obtained $\sigma_2/\sigma_1 = 2$ as compared with Nikitin and Ovchinnikova's value of 1.72 and experimental ratios obtained in this study, ranging from 1.2 to 1.5.

Measurements of γ_3 are now in progress, and it is hoped that the availability of this result will make possible the unambiguous determination of all the individual m_J-mixing cross sections and will provide further insight into the matter of selection rules for m_J mixing.

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Multiphoton Ionization of Molecules[*†]

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This work reports the first attempt at multiphoton ionization of molecules of iodine, heavy water, and carbon tetrachloride. Despite the occurrence of many different ions, only I^+, D^+, and CCl_3^+, respectively, were observed quantitatively using the technique of multiphoton ionization of atoms. "Saturation" was observed.

I. INTRODUCTION

Multiphoton ionization of atoms has been reported by many workers, both theoretically and experimentally.[1-6] But so far, to the best of our knowledge no work has been done on the multiphoton ionization of molecules, although there has been some work on multiphoton dissociation.[7,8] This work presents a first attempt experimentally to investigate multiphoton ionization of molecules.

It is generally agreed that the probability per unit time P of ionizing an atom by "simultaneously" absorbing k optical photons in an intense laser radiation (flux F cm^{-2} sec^{-1}) is proportional to F^k,

$$P = W_k F^k , \tag{1.1}$$

where W_k is the kth-order cross section. Usually, however, experimental verifications involve the ionization of atomic gases.[2,4-6] This creates a side effect, namely, substantial depletion of the neutral atoms.[3] The result[2] is that the experimental plot of $\log_{10} P$ vs $\log_{10} F$ will have a slope less than k. This depletion ("saturation") was also observed in the present work for molecules.

II. EXPERIMENT

The experimental method was the same as that employed in multiphoton ionization of atomic gases.[2,9] A 100-MW ruby laser was focused into a vacuum system into which different molecular gases were leaked. The ions created were analyzed by a time-of-flight mass spectrometer.

The following molecular vapors were used: I_2, D_2O, and CCl_4. The quantitative measurements were carried out in the same way as those customarily employed in atomic gases; i.e., the number of ions created was plotted against the laser flux in log-log plot.[2,4-6,9]

III. RESULTS AND DISCUSSIONS

A. I_2 Vapor

Only I^+ ions were observed when the ruby laser was focused into an I_2 vapor of ~10^{-5} torr. Figure 1 shows the log-log plot of N/τ vs F_0, where N is the number of ions created in the focal region, τ, the width of the laser pulse of half-maximum, and F_0 the peak laser flux. The saturation is evident in the plot.

The fact that only I^+ ions were observed would mean that I_2 could have been broken up through one or more of the following ways[10]:

$$I_2 + k_1 h\nu \rightarrow I_2^+ + e \tag{3.1}$$

followed by

$$I_2^+ + k_2 h\nu \rightarrow I^+ + I ,$$

or

$$I_2 + k_3 h\nu \rightarrow I + I \tag{3.2}$$

followed by

$$I + k_4 h\nu \rightarrow I^+ + e ,$$

or

$$I_2 + k_5 h\nu \rightarrow I^+ + I^- . \tag{3.3}$$

All the k's are integers and $h\nu$ is the ruby photon energy. The partial slope (~6) of Fig. 1 suggests that the formation of I^+ from any of the above three processes requires the absoprtion of six ruby-laser photons.

The ionization potential of an iodine atom is 10.6 eV, which lies between five and six ruby-laser photons. It thus suggests to us that I^+ would prob-