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Collision-Induced Mixing in the 2^3P Levels of Helium

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The cross section for the transfer of excitation from the 2^3P_0 level of helium to the 2^3P_1 and 2^3P_2 levels as a result of collisions with the ground-state helium atom (1^1S_0) has been measured with a conventional resonance-fluorescence technique. A He^4 source excited the $2^3S_1-2^3P_0$ transition in a He^3 absorption cell. The scattered light was examined with a high-resolution grating spectrometer and the ratio of the $2^3P_0\rightarrow 2^3S_1$ to the $2^3P_{1,2}\rightarrow 2^3S_1$ intensitities was measured as a function of cell pressure from 0.05 to 10 Torr. The cross section for collision-induced transitions out of the 2^3P_0 level is found to be $(68\pm3)\times10^{-16}$ cm^2 at room temperature.

INTRODUCTION

THE effects of excitation transfer between excited states of an atom as a result of collisions are an important process in determining the equilibrium populations of many gaseous systems. These collisional mixing processes are of considerable interest in the analysis of optical pumping experiments and the behavior of gas lasers. The effects of collisional mixing processes in the $2S$ and $3S$ states of neon have recently been investigated[1,2] as has mixing caused by collisions between alkali atoms and foreign gas atoms.

The earliest observation of collisional mixing was made by Mohler and Wood[3] in sodium vapor. More recently, Jordan and Franken,[4] Krause and his colleagues,[5] and Beahn, Condell, and Mandelberg[6] have repeated work of this type for the alkali atoms.

The effect of collisions of the alkali atoms in their first excited states with noble gas atoms is particularly amenable to study. The usual procedure for observing the effects of mixing is to populate one of the ^2P levels in the alkali atom by irradiation with one of the components of the resonance radiation doublet and then examining the resonance fluorescence in which both components appear. In all of the alkalis except sodium the doublet is sufficiently well separated so that simple interference filters can be used to isolate either component. By varying the noble-gas buffer pressure the cross section for excitation transfer between the $^2P_{1/2}$ and $^2P_{3/2}$ of the alkali atom can be determined. For sodium the doublet separation is 7 Å; the lines cannot be isolated by the use of filters without a large sacrifice in intensity. Jordan and Franken,[4] however, were able to determine the cross section for sodium–noble-gas collisional mixing by exciting both resonance transitions and examining the fluorescence with a grating spectrometer.

In helium the resonance radiation connects the metastable 2^3S_1 level with the $2^3P_{0,1,2}$ levels and consists of three components near 1.08 μ separated by 1 and 0.08 Å, respectively. The components cannot be efficiently isolated because of the small separation between them. Fortunately, however, the isotope shift[7] of the spectral lines of He^3 and He^4 is such that the $2^3S_1-2^3P_{1,2}$ radiation line in He^4 coincides with the $2^3S_1-2^3P_0$ transition in He^3. Consequently, an intense source of radiation is available which will selectively populate one of the He excited fine-structure levels. Collisional mixing between the 2^3P_J levels as a result of collisions with the ground-state He atoms modifies the light-induced populations.

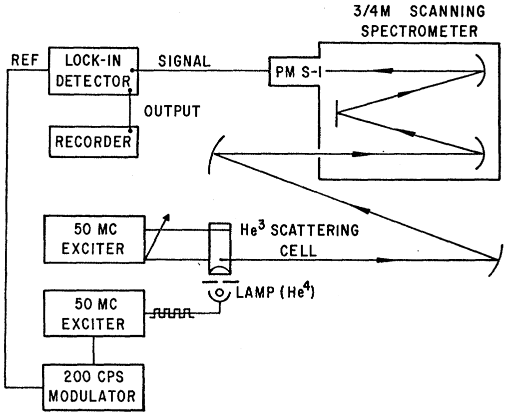

FIG. 1. Block diagram of the experimental apparatus.

THE RATE EQUATIONS

If resonance radiation from a He^4 lamp is incident on a He^3 gas cell containing atoms in the 2^3S_1 state, they will be excited to the 2^3P_0 level. Collisions between atoms in the 2^3P_0 level and ground-state 1^1S_0 atoms can result in a nonradiative transition to either the 2^3P_1 or 2^3P_2 levels. The resonance fluorescence will then contain components resulting from $2^3P_0\rightarrow 2^3S_1$ (D_0 component), $2^3P_1\rightarrow 2^3S_1$ (D_1 component), and $2^3P_2\rightarrow 2^3S_1$ (D_2 component). The D_1 and D_2 components remain unresolved since their separation is on

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the order of the doppler width, and we henceforth refer to the sum of the two components as D_3. A collisional transfer to another J level can occur if a collision between the 2^3P_J atom and the ground-state atom occurs before the P state atom reradiates. Consequently, the relative populations of the 2^3P levels depend upon the density of ground-state atoms.

The rate equations for the 2^3P_J levels can then be written as[8]

$$dn_0/dt=I\sigma_A N_m-n_0/\tau-(\sigma_{01}+\sigma_{02})Nvn_0+(n_1\sigma_{10}+n_2\sigma_{20})Nv, \quad (1a)$$

$$dn_1/dt=-n_1/\tau-(\sigma_{10}+\sigma_{12})Nvn_1+(n_0\sigma_{01}+n_2\sigma_{21})Nv, \quad (1b)$$

$$dn_2/dt=-n_2/\tau-(\sigma_{20}+\sigma_{21})Nvn_2+(n_0\sigma_{02}+n_1\sigma_{12})Nv. \quad (1c)$$

The density of atoms in the $2^3P_{0,1,2}$ levels are, respectively, n_0, n_1, and n_2. The σ_{ij} are defined as the cross sections for a collision-induced transition from the fine-structure level i to the level j. τ is the radiative decay time, N is the ground-state density, and v is the mean relative velocity of the colliding atoms. The intensity of the incident radiation is given by I, σ_A is the absorption cross section, and N_m is the metastable density.

The first term in Eq. (1a) describes the rate at which the 2^3P_0 level is populated by the exciting radiation. The second term is the loss rate due to radiative decay. The next two terms represent scattering rates out of and into the 2^3P_0 level as a result of mixing collisions. The terms in (1b) and (1c) are similarly defined.

The steady-state solutions for the populations yield the ratio

$$\frac{n_0}{n_1+n_2}=\frac{(Nv\tau)^2(\sigma_{10}\sigma_{20}+\sigma_{10}\sigma_{21}+\sigma_{12}\sigma_{20})+Nv\tau(\sigma_{20}+\sigma_{21}+\sigma_{10}+\sigma_{12})+1}{(Nv\tau)^2(\sigma_{01}\sigma_{12}+\sigma_{21}\sigma_{02}+\sigma_{10}\sigma_{02}+\sigma_{02}\sigma_{12}+\sigma_{01}\sigma_{20}+\sigma_{01}\sigma_{21})+Nv\tau(\sigma_{01}+\sigma_{02})}. \quad (2)$$

This equation can be used to determine the collision-induced mixing cross section for transitions out of the 2^3P_0 level. Implied in the derivations of Eq. (2) is the assumption that the radiative decay time is independent of pressure and is the same for both the D_1 and D_2 transitions. Thus, it is assumed that the metastable density is sufficiently low so that imprisonment of radiation does not occur. The ratios of the populations of the levels are then just the ratios of the emitted intensities.

EXPERIMENTAL DETAILS

The experimental apparatus is shown in Fig. 1. The 1-μ resonance radiation from a He^4 lamp is incident on a Pyrex cylinder containing He^3 gas. The light scattered at 90° was focused on the slits of a $\frac{3}{4}$-meter scanning spectrometer. The detector was a photomultiplier cooled to liquid-nitrogen temperature with an $S-1$ response.

The light source consisted of a He^4-gas-filled capillary excited with 8 W of rf power at 50 MHz. The excitation was modulated at 200 Hz and provided square-wave intensity modulation of the source. A lens was used to focus the exciting light at a point just inside the front surface of the absorption cell.

The scattering cell is a Pyrex cylinder 3 in. in length with a diameter of 1.2 in. The cells were filled with He^3 over a range of pressures from 0.05 to 10 mm Hg. The He^3 gas was obtained from Monsanto Mound Laboratory and was purified by flowing it through a liquid-helium trap. The partial pressure of impurities[9] was much less than 10^{-4} mm Hg after the cell was sealed off. The pressure of the sample cell was measured with a Pirani gauge that had been calibrated against a precision McLeod gauge. The gas in the cell was weakly excited by a 50 MHz source of rf power to provide a small fraction of atoms in the absorbing 2^3S_1 metastable level. The density of absorbing 2^3S_1 atoms[9] was varied between approximately 10^{10} and 4×10^{11} cm^{-3}.

The light scattered by the excited He^3 gas at 90° was focused on the slits of a Spex $\frac{3}{4}$-m scanning spectrometer by means of two off-axis parabolic reflectors. The magnification ratio was unity; consequently, the scattered light entering the slits came from a very small volume of the scattering cell. The resolution of the spectrometer provided good separation of the D_0 and D_3 lines. A photomultiplier cooled to liquid-nitrogen temperature was used as a detector, and its output was fed to a lock-in detector. An 0.3-sec time constant was more than adequate to provide a useful signal-to-noise ratio. Specular reflection from the glass walls of the cells was always negligible, as could easily be verified by monitoring the intensity component of the He^4 light reaching the detector which was not absorbed by the He^3 gas (see Fig. 2).

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[8] An additional term representing the rate at which the population of the ^3P_j level changes due to electron-atom collisions in the discharge should also be included in Eq. (1). This excitation rate is effectively eliminated, however, by intensity modulating the exciting resonance radiation and then detecting the change in the fluorescence at the modulation frequency. The n_j in Eqs. (1) are then to be interpreted as the changes in the ^3P state densities due to the exciting light. Detection at the modulation frequency discriminates against the constant background light due to the discharge excitation.

[9] The impurity concentration and the metastable density can inferred from optical pumping experiments. See, for example, F. D. Colegrove, L. D. Schearer, and G. K. Walters, Phys. Rev. **132**, 2561 (1963).

[10] J. Lifsitz and R. H. Sands, Bull. Am. Phys. Soc. **10**, 1214 (1965).

[11] The Boltzmann factor for the three ^3P levels is the same since the separation between all the levels is MkT.

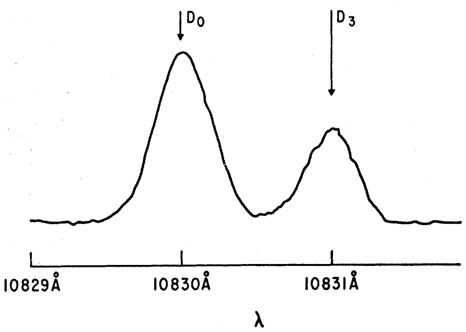

FIG. 2. Lock-in output versus wavelength scan for the light scattered by the He^3 absorption cell at 0.013 mm Hg. The He^4 excitation is shown below. The He^4 component at 10 829 Å is not absorbed by the He^3 gas but it serves as a monitor for any stray light which might be scattered by reflecting surfaces.

At each pressure the ratio of the two scattered components was measured as a function of the metastable density. This was done to avoid the effects of resonance trapping of the scattered light which would cause the effective radiative decay rates for the different excited-state levels to be different. The measured ratio of the D_0 to D_3 components as the metastable density is varied is shown in Fig. 3. The ratios were determined by measuring the area under the curves corresponding to the two components although the ratio of peak intensities was always within 10% of the area measurements. A typical recorded scan of the spectrometer is shown in Fig. 2. All the measurements were made at room temperature. The largest uncertainty in the measurement is the determination of the pressure in the sealed-off cells which is on the order of 5%. In Fig. 4 is plotted the ratio of the D_0 to D_3 intensities in the limit of zero metastable density as a function of reciprocal He^3 gas pressure. The slope of this curve is then used to obtain the mixing cross section.

DISCUSSION OF RESULTS

A plot of the intensity ratio D_0/D_3 as a function of reciprocal pressure p yields a straight line, implying that Eq. (2) reduces to an expression of the form

$$D_0/D_3 = ap^{-1}+b.$$

An expansion of Eq. (2) as a sum of partial fractions gives

$$a^{-1} = (\sigma_{01}+\sigma_{02})vA\tau,$$

where $A=N/p$ and

$$b=\frac{\sigma_{10}\sigma_{20}+\sigma_{10}\sigma_{21}+\sigma_{12}\sigma_{20}}{\sigma_{01}\sigma_{12}+\sigma_{21}\sigma_{02}+\sigma_{10}\sigma_{02}+\sigma_{02}\sigma_{12}+\sigma_{01}\sigma_{20}+\sigma_{01}\sigma_{21}}.$$

For He^3 the mean relative velocity at 300°K is $v=2.06\times10^5$ cm sec^{-1}. The constant A is 3.22×10^{16} cm^{-3} mm^{-1} Hg at 300°K. The radiative decay time has been measured previously[10] and found to be $\tau=1.05\times10^{-7}$ sec. The cross section for scattering out of the 2^3P_0 level and into the 2^3P_1 and 2^3P_2 levels is then $\sigma_{01}+\sigma_{02}=(68\pm3)\times10^{-16}$ at 300°K.

If one makes the additional assumption that the cross sections for transitions from the fine-structure level i to the level j is related to the inverse process by the statistical weights of the levels,[11] i.e.,

$$\sigma_{ij}/\sigma_{ji}=g_j/g_i,$$

then the expression for the intercept b reduces to $\frac{1}{8}$. The experimental value for the intercept from the straight-line plot in Fig. 4 also yields $\frac{1}{8}$, implying the validity of this assumption. That the cross sections and their inverses are related by their statistical weights strongly suggests that there are no selection rules on Δm_J for the mixing transitions.[12] In addition one can also show that the reduction of Eq. (2) to the equation of a straight line which is required to fit the form of the experimental data implies that

$$\sigma_{ij}/\sigma_{ki}=g_j/g_i.$$

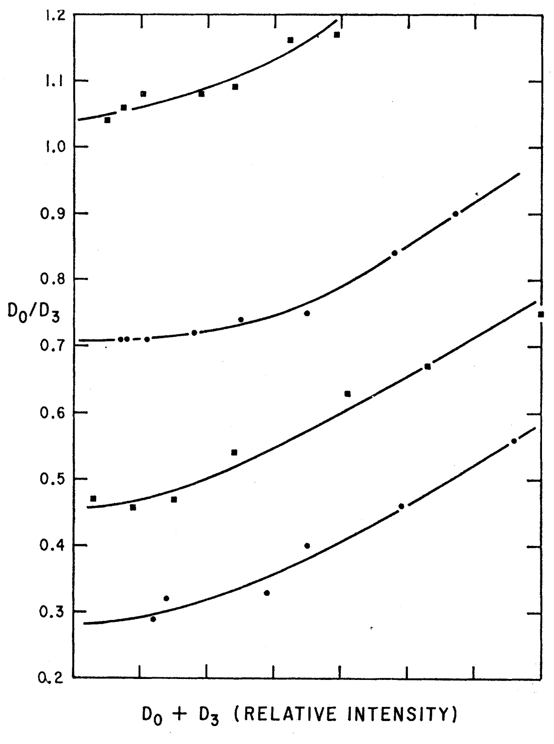

FIG. 3. The intensity ratio D_0/D_3 plotted against the total scattered light for various pressures. The effects of resonance trapping appear as the number of metastable absorbing atoms increases. From bottom to top the He^3 cell pressures are 1.5, 0.58, 0.37, and 0.21 mm Hg, respectively, for the curves shown.

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[12] J. A. Jordan *et al.* (Ref. 4) assume implicitly that the cross sections for mixing out of the $m_j=\pm\frac{3}{2}$ and $m_j=\pm\frac{1}{2}$ sublevels of the $^2P_{3/2}$ level of sodium are the same. Their experimental findings support this assumption. Jordan's theoretical treatment of the interaction (Ref. 13) also implies at best only a very weak dependence on Δm_j.

From this it follows that there are no selection rules on ΔJ.

It is perhaps of some interest to compare the results obtained here with the mixing cross sections for Na-He and K-He measured by Jordan and Franken.[4] In the case of Na-He they measured a cross section of $41.1\pm 2.9\times 10^{-16}$ cm^2 for the transition $^2P_{1/2}\rightarrow {}^2P_{3/2}$ and for K-He they obtained $52.8\pm 5.8\times 10^{-16}$ cm^2. No evidence of any selection rule for Δm_J was found. Estimates of these collision-induced cross sections have been made by Jordan[13] by assuming that the interaction between the colliding atom pairs was electrostatic and essentially of the van der Waals type. In K-K collisions the large reported mixing cross section[14] is presumably due to the existence of long-range exchange forces between colliding alkali atoms. The similarity in the measured cross sections for He($2\,^3P$)-He($1\,^1S_0$), Na-He, and K-He suggests that the interaction in the He-He case is also primarily of the van der Waals type.

It is important to note that while the increase in the P-state populations due to the absorbed light is thermalized when $\sigma vN \gg \tau^{-1}$ the total populations of the P-state levels approach thermal equilibrium only when atom–atom collisions also dominate the rate for P-state excitation by electron-atom collisions. The pressure required to overcome the effects of electron–atom collisions can be estimated crudely from the condition

$$\gamma \ll \sigma vN,$$

where γ is the electron-atom excitation rate. Since $\gamma = \sigma_e n_e v_e$, where n_e is the electron density, σ_e is the excitation cross section, and v_e is the relative velocity, and taking $\sigma_e \simeq 10^{-19}$ cm^2 and $n_e \simeq 10^9$ cm^{-3}, we find that the pressure must exceed several tens of mm Hg.

EFFECTS OF MIXING ON OPTICAL PUMPING IN He^3 AND He^4

The effect of P-state mixing on the efficiency of the optical pumping process in He^4 and He^3 has been described earlier by the author and his colleagues.[9,15] In both cases the polarization obtainable is limited by the mixing process as pressures of several mm Hg are approached. An analysis of the rate equations for the pumping process indicates that the D_3 component produces a polarization in the sample which reverses when the effects of excited-state mixing become important. It has been suggested[16,17] that this radical change in the sample polarization would provide a large "signal" from which it would be possible to extract the mixing cross sections.

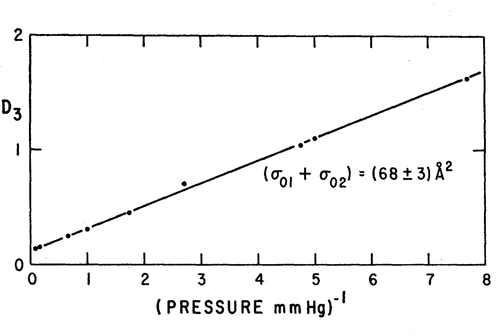

FIG. 4. The intensity ratio D_0/D_3 in the limit of no resonance trapping plotted against the reciprocal pressure. Experimental points at lower pressures were also obtained but are not shown. They also fall along the straight line.

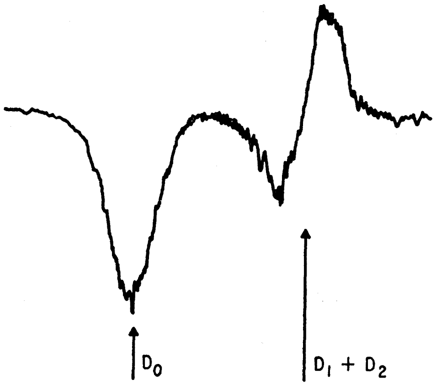

FIG. 5. The optical pumping signal from a He^4 cell using He^4 excitation. The area under the $D_3(D_1+D_2)$ signal is nearly zero. The optical signal is then due solely to the D_0 component. The absence of a signal inversion as the mixing condition is changed as discussed in the text implies that the sample polarization is due to the D_0 component alone, the D_3 component having little effect.

The optical pumping signal[18] consists of the three components, D_0, D_1, and D_2. The D_1 and D_2 components have opposite polarity and nearly equal intensity so that their contribution to the total signal is almost negligible. This can be seen more clearly from Fig. 5, which is a high-resolution tracing of the optical pumping signal in He^4. If the D_3 intensity dominates the pumping process, the polarization should reverse as the mixing rate increases with respect to the radiative decay rate. This polarization reversal is accompanied by a change in the polarity of the optical signal. However, no signal reversal was observed over a cell pressure range from 0.05 to 5 mm Hg although the measured mixing cross section would imply that a signal reversal should occur near 0.2 mm Hg, the point at which $\sigma vN = \tau^{-1}$ (radiation). The absence of this signal reversal suggests that the optical pumping process is dominated by the D_0 component. In this case a change

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[17] G. K. Walters (private communication).

[18] The optical pumping signal is defined as the change in the transmitted light that occurs when the sample goes from the pumped to the unpumped condition. In the limit of no mixing the transmitted intensities of the D_0 and D_1 components increase when the gas is polarized while the D_2 intensity decreases.

in the "degree of mixing" does not change the polarity of optical signal.[19]

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The author would like to thank Dr. G. K. Walters for several interesting discussions regarding this work. The technical skill of F. D. Sinclair in the preparation of the sample cells is also appreciated.

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[19] The use of a He^3 lamp to optically orient the He^4 sample provides a strong source of D_3 only light because of the isotope shift of the spectral lines. In this case a signal reversal has been observed as expected by N. D. Stockwell and G. K. Walters (private communication).

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Electron-Detachment in Slow Collisions between Atoms and Negative Ions

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The collision of a negative ion A^- and neutral atom B at a very low kinetic energy (a few eV or less) may lead to the release of an electron through the reaction $A^-+B\rightarrow(AB)+e$, known as "associative detachment." At higher energies, $A^-+B\rightarrow A+B+e$ also becomes possible. A theory of these processes is formulated by assuming that the electronic state is stable at large separations R of A^- and B, and changes adiabatically as R decreases; at very small R, of the order of 10^{-8} cm, the electronic state turns into an unstable compound state able to emit an electron. Expressions are derived for the total cross section for electron detachment, and for the cross sections for detachment leaving the nuclei in a single discrete final state. At thermal energies, the total cross section can become very large because of Langevin spiralling, arising from the long-range polarization between A^- and B. For example, in the reaction $H^-+H\rightarrow H_2+e$, the cross section is estimated to be of the order of 10^{-14} cm^2 at a relative kinetic energy of $k\times400°$K.

I. INTRODUCTION

UNSTABLE compound states of negative molecular ions which decay to neutral molecules by the emission of an electron are well known.[1–8] So far these states have usually been generated by the bombardment of neutral molecules with electrons, where they give rise to characteristic peaks in the cross sections as a function of energy. The existing theory[4–7] has been tailored for this case, and reasonable agreement with experiment has been obtained in those cases which have been treated in detail.[5,6]

In recent experiments,[9–11] similar unstable compound states have been generated by another method, the bombardment of neutral atoms or molecules by negative ions with kinetic energies up to a few electron volts. The object of this paper is to formulate a theory of this process, and to give expressions and estimates for the cross sections for the formation of different final states of the nuclei. We shall confine ourselves to the simplest case of a collision between a neutral atom and a negative atomic ion.

It might seem at first sight that no new theory is needed, because electron-molecule and ion-atom collisions are merely two different channels through which the same unstable compound states are formed; therefore it might seem that the expressions for the cross sections should differ only in the entry width which has

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[11] J. W. Ekin, J. L. Moruzzi, J. L. Pack, and A. V. Phelps, Gaseous Electronics Conference, Atlanta, 1966 (unpublished). This paper reports the observation of the free electrons produced by associative detachment involving O^- in H_2, whereas Refs. 9 and 10 report the destruction of the negative ions.