Inelastic collisions of excited atoms: sensitized fluorescence of sodium atoms mercury molecules.

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INELASTIC COLLISIONS OF EXCITED ATOMS; SENSITIZED
FLUORESCENCE OF SODIUM ATOMS AND
MERCURY MOLECULES

by

Michael Stupavsky

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1971
ABSTRACT

The total cross sections for $^2P_{1/2} - ^2P_{3/2}$ mixing in sodium, induced in collisions with CH$_4$, CD$_4$, C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$ molecules, have been determined using the method of sensitized fluorescence. The sodium vapour-molecular gas mixtures were irradiated with each Na$_D$ component in turn, and the cross sections were obtained from measurements of relative intensities of the two D components present in the fluorescent light.

The sodium vapour in the fluorescence cell was maintained at a pressure of $5 \times 10^{-7}$ mm Hg to avoid radiation trapping, and the molecular gas pressures were in the range 0 - 1 mm Hg.

The following cross sections were obtained:

For CH$_4$: $Q_{12} (^2P_{1/2} \rightarrow ^2P_{3/2}) = 148^2$, $Q_{21} (^2P_{1/2} \rightarrow ^2P_{3/2}) = 77^2$;

for CD$_4$: $Q_{12} = 151^2$, $Q_{21} = 81^2$;

for C$_2$H$_2$: $Q_{12} = 182^2$, $Q_{21} = 96^2$;

for C$_2$H$_4$: $Q_{12} = 178^2$, $Q_{21} = 94^2$;

for C$_2$H$_6$: $Q_{12} = 182^2$, $Q_{21} = 95^2$.

The cross sections $Q_{21}$ are in good agreement with the values calculated on the basis of the theory of Callaway and Bauer.

The 3350$\AA$ and 4850$\AA$ molecular fluorescence bands of mercury, produced when a mixture of mercury vapour and nitrogen gas at room temperature is excited with the 2537$\AA$ mercury resonance radiation, have been studied with a scanning spectrometer. The 4850$\AA$ band which had previously been regarded as continuous, was found to possess a sequence of intensity maxima which were interpreted as arising from the transitions between the vibrational levels of the $^3O_u^-$ state and the continuum states of the repulsive ground state. The analysis of the band yielded
\omega_e' = 212 \text{ cm}^{-1} \text{ and } D_e' = 2.4 \text{ eV for the } ^30_u^- \text{ state, and produced direct}
evidence for a rapid variation of the electronic transition moment
\mathcal{R}_e(r) \text{ for the } ^30_a^- \rightarrow ^1\Sigma^+_g \text{ transition. The variation in the integrated}
intensity of this band and of the 3350\AA\text{ continuous band was also}
investigated in order to clarify the mechanism by which the } ^30_u^- \text{ and } ^31_u^- \text{ mercury molecules are formed.}
ACKNOWLEDGEMENTS

I am most grateful to Dr. L. Krause for his supervision and support of this work and in particular for his tireless reading of this dissertation in manuscript. I should like to express my most sincere thanks to Dr. C. W. F. Drake who interpreted the structure observed in the $^3\Omega_u^- - ^1\Sigma^+_g$ band spectrum as arising from bound-continuum transitions and who performed all the detailed calculations and to the other members of the Atomic Physics Group for many profitable discussions.

Acknowledgements are due to Mr. W. Eberhart for his skill in constructing the fluorescence cell, to Mr. W. Grewe for his cooperation in the design and construction of the carriage-mounted filter holders and other pieces of apparatus and to Mr. A. Buzzo who prepared most of the diagrams found in this dissertation.

I am indebted to the National Research Council for financial support in the form of a graduate scholarship.
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I. INTRODUCTION

The physical behaviour of systems such as plasmas, stellar atmospheres, the upper atmosphere and others, where atoms and molecules are continuously being excited and de-excited by the absorption and emission of radiation and by collisions with other atoms, molecules and electrons, is determined by the reaction rates or cross sections for the various processes involved. Much effort has been directed recently towards the understanding of such processes of which inelastic collisions leading to the transfer of excitation energy in alkali and in mercury atoms have been receiving special attention in this laboratory. Collisions involving alkali atoms are of special interest because their relatively simple hydrogen-like structure makes possible a comparison between theory and experiment. Theoretical calculations have had considerable success in predicting cross sections for collision-induced excitation transfer between the lowest fine-structure states of sodium and potassium (Jordan 1964; Callaway and Bauer 1965; Dashevskaya and Nikitin 1967; Dashevskaya et al 1969; Reid and Dalgarno 1970; Massou-Seemu 1970) where the energy separations between the resonance doublet states are small and may be neglected. More recently agreement within order of magnitude between theory and experiment has been achieved for collisions involving atoms such as rubidium and cesium where the energy separations between the fine-structure states are large and cannot be neglected (Dashevskaya et al 1970; Hidalgo and Geltman 1970). Although a fair body of experimental and theoretical information for alkali-alkali and alkali-inert gas collisions is now
available (Krause 1971) only a small amount of experimental work has thus far been done on similar collisions between excited alkali atoms and molecules in their ground states (McGillis and Krause 1967, 1968; Stupavsky and Krause 1968; Hrycyshyn and Krause 1970) while attempts to develop a comprehensive theory which would permit the prediction of the cross sections for the atom-molecule mixing collisions have been confined to the case of alkali-nitrogen where the excitation transfer is thought to proceed through the formation of an intermediate ionic complex (Andreev and Voronin 1969).

There is also evidence of considerable interest in the various energy transfer processes occurring during inelastic collisions of excited mercury atoms with ground state atoms and molecules (Bigeon 1967; Karl, Kruus and Polanyi 1966). The most recent studies by Deech, Pitre and Krause (1971) who investigated the quenching of the mercury $6^3P_1$ state by the isotopes of nitrogen and by other gases, have yielded information regarding the importance of a close energy match between the downward electronic transition in the mercury atom and the upward vibrational transition in the quenching molecule. Czajkowski, Skardis and Krause (1971) have studied inelastic collisions leading to excitation transfer from the $6^3P_1$ state of mercury to various states in sodium with particular attention given to the dependence of the cross sections on the energy separation between the $6^3P_1$ mercury state and the collisionally excited sodium states.

When a mixture of mercury vapour and nitrogen is irradiated with $\text{Hg}^{253.7}\lambda$ resonance radiation, some of the mercury atoms excited to the $6^3P_1$ state, become quenched to the metastable state in collisions
with nitrogen molecules. In addition, interactions between the $^3P_0$ atoms and $^1S_0$ ground state atoms result in the formation of excited $^3_{1u}$ and $^3_{0u}$ mercury molecules. The molecular formation becomes an important collisional process at mercury densities corresponding to room temperature and at higher densities. The excited molecules decay spontaneously to the ground state, emitting the well-known molecular fluorescence bands at 3350Å and 4850Å. It was considered that a study of these bands would help in elucidating the mechanism of the molecular formation and the origin of the molecular fluorescence, and would provide quantitative information about the excited states. The most recent studies of Hg$_2$ band fluorescence employed only broad band-pass colour filters (McCoubrey 1954; Berberet and Clark 1954; McAlдуff, Drysdale and Le Roy 1967; Pенzes, Gunning and Strausz 1967) and there has been no systematic investigation of the fluorescent bands at higher resolution since the early studies of Rayleigh (1932) who produced these bands under conditions of high mercury density and temperature. Any new information about the Hg$_2$($^3O_u^-$) state would be of particular interest because of the possibility of obtaining laser action utilizing the $^3O_{u}^- \rightarrow 1\Sigma^+_g$ transition (Carbone and Litvak 1967).

The first part of this dissertation deals with the measurement of the total cross sections for the $^3P_{1/2} - ^3P_{3/2}$ mixing in sodium induced in collisions with various molecules. The second part concerns a study of the mercury fluorescence resulting from the $^3_{1u} \rightarrow 1\Sigma^+_g$ and $^3_{0u} \rightarrow 1\Sigma^+_g$ transitions. Each part is a study of sensitized fluorescence. When one of the resonance sub-states of a sodium atom is excited by the absorption of radiation of the appropriate wavelength, the excitation
energy may be collisionally transferred to the other state and the atom will then emit radiation of a wavelength different from that used for the excitation. In other words, fluorescence is sensitized through a collisional transfer of excitation between the resonance states.

Similarly, when the $^3P_1$ state of mercury is excited by the absorption of the 2537 Å resonance radiation, the excitation may first be collisionally transferred to $^3P_0$ metastable state and further collisions of mercury atoms in this state with atoms in the $^1S_0$ ground state may lead to the formation of mercury molecules in the $^3P_0$ and $^3P_1$ states which, in decaying to the ground state, emit band fluorescence.
II. SENSITIZED FLUORESCENCE OF SODIUM INDUCED IN COLLISIONS WITH MOLECULES

1. Rate Equations for the Sensitized Fluorescence and Quenching Processes

Collisional transfer of excitation between the fine-structure sub-states of the alkali resonance state can be detected by observations of sensitized fluorescence, and there is a long history of such measurements (Krause 1966). The standard sensitized fluorescence technique is to excite the alkali atom to one of the \( ^2P \) sub-states with one "\( D \) line" of the resonance doublet and observe the resulting fluorescence which includes the "\( D \) line" used for excitation (resonance fluorescence) as well as the other "\( D \) line" which arises as a result of collisional excitation transfer (sensitized fluorescence). The process of excitation transfer between the \( ^3P \) sub-states of sodium, induced by a collision with a molecule \( M \), may be described by the following equation:

\[
Na(^3P_{3/2}) + M \rightarrow Na(^3P_{1/2}) + M + \Delta \varepsilon_f
\]

(1)

where \( \Delta \varepsilon_f \), the energy difference between the fine structure components (17.2 cm\(^{-1}\)), is supplied or carried away by the various degrees of freedom of the colliding partners. Molecules are known to be also efficient in causing collisional deactivation of the \( ^3P \) sodium atoms to the ground state (Pringsheim 1949). This simultaneous quenching reaction proceeds according to the equation,

\[
Na(^3P_f) + M \rightarrow Na(^3S_{1/2}) + M^* \]

(2)

where \( M^* \) is a molecule which, having participated in an inelastic
collision, has become modified in its content of translational, vibrational and rotational energy.

The processes that take place when a mixture of sodium vapour and molecular gas is irradiated continuously with the $D_2$ component of the sodium resonance doublet are shown schematically in Fig. 1. The solid arrows indicate transitions giving rise to sensitized fluorescence and the broken arrows represent collisional deactivation of the $3^2P$ sodium atom to the ground state, which manifests itself by the quenching of the resonance radiation.

Fig. 1. Energy levels involved in sensitized fluorescence and in the quenching of sodium resonance radiation, induced in collisions with molecules.

The various interactions between a sodium atom and a diatomic molecule $M$ may be represented by the following equations:

$$Na(3^2S_{1/2}) + h\nu_2 \xrightarrow{S_2} Na(3^2P_{3/2}),$$ 

(3)
\[ \text{Na}(3^2P_{3/2}) + \text{M} \xrightarrow{Z_{21}} \text{Na}(3^2P_{1/2}) + \text{M}^* , \]  
(4)

\[ \text{Na}(3^2P_{1/2}) + \text{M} \xrightarrow{Z_{12}} \text{Na}(3^2P_{3/2}) + \text{M}^* , \]  
(5)

\[ \text{Na}(3^2P_{3/2}) + \text{M} \xrightarrow{Z_{20}} \text{Na}(3^2S_{1/2}) + \text{M}^* , \]  
(6)

\[ \text{Na}(3^2P_{1/2}) + \text{M} \xrightarrow{Z_{10}} \text{Na}(3^2S_{1/2}) + \text{M}^* , \]  
(7)

\[ \text{Na}(3^2P_{3/2}) \xrightarrow{(\tau_2)^{-1}} \text{Na}(3^2S_{1/2}) + h\nu_2, \]  
(8)

\[ \text{Na}(3^2P_{1/2}) \xrightarrow{(\tau_1)^{-1}} \text{Na}(3^2S_{1/2}) + h\nu_1, \]  
(9)

where \( S_2 \) is the density of sodium atoms excited per second from the \( 3^2S_{1/2} \) state to the \( 3^2P_{3/2} \) state, \( \tau_1 \) and \( \tau_2 \) are the mean lifetimes of the \( 2^2P_{1/2} \) and \( 2^2P_{3/2} \) states (\( \tau_1 = \tau_2 = 1.63 \times 10^{-8} \) sec. (Kibble, Copley and Krause, 1967a)) and \( Z_{21} \), \( Z_{12} \), \( Z_{20} \) and \( Z_{10} \) are the collision numbers for the processes designated in Fig. 1, defined as the number of collisions per excited sodium atom per second, leading to the appropriate process of excitation transfer. \( \text{M} \) is a ground-state diatomic molecule and \( \text{M}^* \) a molecule which, having participated in an inelastic collision, has become modified in its content of translational, vibrational and rotational energy.

Collisional mixing of the \( 2^2P \) states due to Na-Na collisions has been neglected since the ratio of sensitized to resonance fluorescent intensities due to such collisions is of the order of \( 10^{-6} \) at the vapour pressure used in the experiment (5 \( \times \) 10\(^{-7} \) mm Hg) and does not contribute significantly to the observed sensitized fluorescence (Pitre and Krause, 1968).

Assuming that the vapour-gas mixture exists in a dynamic
equilibrium involving only continuous optical excitation of the $3^2P_{1/2}$ and $3^2P_{3/2}$ states in turn by means of the $D_1$ and $D_2$ resonance components, respectively, spontaneous decay and the various binary collisional processes, eqs. (3) - (9) may be combined to give two rate equations, each describing the population of the collisionally excited state.

\[
\frac{dn_2}{dt} = 0 = Z_{12}N_1 - \frac{n_2}{\tau} - Z_{21}n_2 - Z_{20}n_2,
\]

\[
\frac{dn_1}{dt} = 0 = Z_{21}N_2 - \frac{n_1}{\tau} - Z_{12}n_1 - Z_{10}n_1.
\]

\(N_1\) or \(N_2\) is the density of atoms in the state being optically excited, \(n_1\) or \(n_2\) is the density of atoms in the other, collisionally excited \(3^2P\) state and \(\tau\) is the average lifetime of the \(3^2P\) states.

Dividing (10) and (11) by \(N_1\) and \(N_2\), respectively, yields

\[
Z_{12} = \left(\frac{1}{\tau} + Z_{21} + Z_{20}\right)n_2,
\]

\[
Z_{21} = \left(\frac{1}{\tau} + Z_{12} + Z_{10}\right)n_1,
\]

where

\[
\eta_1 = \frac{I(D_1)}{I(D_2)} = \frac{n_1}{N_2},
\]

\[
\eta_2 = \frac{I(D_2)}{I(D_1)} = \frac{n_2}{N_1}.
\]

\(I(D_1)\) and \(I(D_2)\) are the intensities of the two fluorescent components and the wavelengths in the denominators are, in each case, the same as those used in the exciting light.
Eqs. (12) and (13) yield:

$$Z_{12} = \frac{\tau^{-1}(\eta_1 + \eta_1 \eta_2) + Z_10 \eta_1 \eta_2 + Z_{20} \eta_2}{1 - \eta_1 \eta_2},$$

and

$$Z_{21} = \frac{\tau^{-1}(\eta_1 + \eta_1 \eta_2) + Z_{20} \eta_1 \eta_2 + Z_{10} \eta_1}{1 - \eta_1 \eta_2}.$$

Because of the small energy difference between the $3^2P_{1/2}$ and $3^2P_{3/2}$ states of sodium, equal quenching cross sections for the two states are expected. Hence, taking $Z_{20} = Z_{10}$ (Kibble, Copley and Krause, 1967b), eqs. (16) and (17) become respectively:

$$Z_{12} = \frac{(\eta_2 + \eta_1 \eta_2)}{1 - \eta_1 \eta_2} (\tau^{-1} + Z_{10}),$$

and

$$Z_{21} = \frac{(\eta_1 + \eta_1 \eta_2)}{1 - \eta_1 \eta_2} (\tau^{-1} + Z_{10}).$$

The collision numbers $Z$ are functions of temperature:

$$Z(T) = N \int q(v) v f_T(v) dv$$

where $N$ is the density of ground state atoms, $q(v)$ is the differential cross section, $v$ is the velocity of relative motion and $f_T(v)$ is the Maxwell-Boltzmann probability that, at a temperature $T$, colliding partners will have a relative velocity between $v$ and $v + dv$.

By analogy with the gas-kinetic cross section an effective total cross section $Q$ may be defined,

$$Z_{12} = N \ Q_{12} \ v_T,$$

and

$$Z_{21} = N \ Q_{21} \ v_T.$$
where \( v_r \) is the mean relative velocity of the collision partners:

\[
v_r = \left( \frac{8kT}{\pi \mu} \right)^{1/2}
\]

(23)

\( k \) is the Boltzmann constant and \( \mu \) is the reduced mass of the colliding atoms.

According to the principle of detailed balancing the two cross sections should be in the ratio:

\[
\frac{Q_{12}}{Q_{21}} = \frac{g_2}{g_1} \exp \left( \frac{-\Delta E}{kT} \right)
\]

(24)

where \( g_1 = 2 \) and \( g_2 = 4 \) are the statistical weights of the \( ^2P_{1/2} \) and \( ^2P_{3/2} \) states, respectively, and the Boltzmann factor, \( \exp \left( \frac{-\Delta E}{kT} \right) \), is the probability that in a collision the kinetic energy of relative motion will be greater than \( \Delta E \) where \( \Delta E \) is the energy difference between the \( ^2P \) fine structure components.

It has been assumed in the above treatment that there is no imprisonment of radiation. If resonance radiation were trapped, the effective lifetime of the \( ^2P \) levels would no longer be equal to their mean lifetime and this would result in spurious values of the cross sections.

2. Description of the Apparatus

The arrangement of the apparatus is shown in Fig. 2. Sodium resonance radiation emitted from a sodium spectral lamp was passed through a rectangular slit, was collimated and resolved into the fine-structure components by interference filters. The resulting monochromatic beam was brought to a focus in the fluorescence cell containing a mixture
Fig. 2. Schematic diagram of apparatus:
A, sodium lamp; B, fluorescence tube and oven; C, greaseless stopcock; D, photomultiplier and cryostat; M, amplifier-discriminator; N, scaler; P, pinhole;
L, lenses; F, Type 'U' Spectrolab filters;
F₁, Type 'P' Spectrolab filter; F₂ Kodak 701 filter; F₃, neutral density filter.
of sodium vapour and the molecular gas. The fluorescent light emitted from the cell normally to the incident beam was collimated, resolved into its two D components by interference filters and brought to a focus on the S\textsubscript{20} photocathode of a liquid air-cooled photomultiplier, whose output pulses were amplified, passed through a discriminator and registered with a scaler. An electromechanical sequencing system integrated with the counting train operated motor driven filter holders in the incident and fluorescent beams and allowed for an automatically programmed sequence of operations (Pitre 1965). The complete apparatus was enclosed in a light-tight box to eliminate stray light.

A detailed description of the light source has been given elsewhere (Stupavsky 1968). The lamp, the inner discharge tube of a commercial Phillips sodium spectral lamp, was placed in the tank coil of an rf oscillator operating at 165 Mc/s. A small heater was employed at each end of the discharge tube. For maximum intensity, the cooler end of the discharge tube containing the liquid sodium was maintained at 210\textdegree C thus controlling the vapour pressure, while the other end was maintained at 230\textdegree C. The lamp showed no signs of discolouration or deterioration after weeks of operation. It was very stable and, during the experiments, the intensity of the resonance fluorescence was found to vary less than ± 2 per cent over a 12 hour period.

Spectrolab Type "U" interference filters were used for the separation of the sodium resonance doublet. These filters typically transmitted about 60 per cent of the wanted resonance component and about 1 per cent of the unwanted component. Two D\textsubscript{1} filters in series producing a spectral purity of about 5 parts in 10\textsuperscript{5} or three D\textsubscript{2} filters in series producing a spectral purity of about 5 parts in 10\textsuperscript{6} were used
in the exciting beam. The exciting light was also passed through a Spectrolab Type "P" interference filter which had a 60Å transmission band half-width centred at the Na-D wavelength, and through a Kodak "301" short wave pass filter, whose purpose was to remove all other alkali resonance radiation which would cause fluorescence in traces of alkali impurities that might be present in the sodium. The Na-D lines in the fluorescent spectrum were separated by two Type "U", D<sub>1</sub> filters which had an overall transmission of 31 per cent for the D<sub>1</sub> line and 5 x 10<sup>−3</sup> per cent for the D<sub>2</sub> line. The transmissions of Type "U" filters, which are sensitive to the changes in ambient temperature, were measured before each experimental run. A series of slits and stops ensured that, in both the exciting and fluorescent beams, the light passing through the interference filters was strictly parallel as it must be for optimal resolution. The stops also confined the light beams to the central regions of the filters since their edges appeared to reject less efficiently the unwanted spectral component than their central portions. The filters were mounted in holders which allowed them to be precisely oriented with respect to each other and to the light beam, and to be rotated about the light axis. These holders were mounted on motor-driven slides operated by an electromechanical sequencing system capable of automatic operation (Pitre 1965).

The design of the fluorescence cell, shown in Fig. 3, minimizes both unwanted absorption of the incident beam and trapping of resonance radiation. The exciting beam was focussed in the corner formed by the entrance and exit windows. To minimize imprisonment of radiation, the
Fig. 3. The Fluorescence Cell: A, entrance window; B, side window; S, side arm; C, copper tubing from the ultrathermostat which controls the side arm temperature; V, connection to vacuum system.
image of the slit, which was 2.7 mm wide, was positioned about 0.5 mm from the side window of the cell. With the image in this position, the scattered light which was further reduced by coating the cell with Aquadag (a colloidal dispersion of graphite), was found to be of negligible intensity.

The oven containing the fluorescent cell consisted of a double-walled copper box, thermally insulated by glass wool. The exciting and fluorescent beams passed through pyrex windows set in annular teflon plugs. The heater, a 56 ohm coil wound non-inductively on a ceramic tube, was mounted in one corner of the oven behind a copper shield coated with Aquadag, and heating took place by convection. The alternating current for the heater was controlled by a powerstat and a saturable core reactor. Control of the direct current for the latter was provided by a transistorized D.C. amplifier employing a suitably placed Veco 41A2 thermistor as a sensing element. The circuit for this heater control unit was described by Pitre (1965).

The temperature of the side-arm of the fluorescence cell, which contained the liquid sodium, was controlled by circulating, from a Jena Ultrathermostat, Dow Corning No. 200 fluid of 10 centistoke viscosity, through a closely fitting 3/16 inch copper coil surrounding the side arm. With this arrangement, the main oven temperature could be stabilized within ±0.1°C over a range extending from 100°C to 200°C, and the side arm temperature could be maintained with ±0.05°C over a range extending from 100°C to 200°C. All temperatures were measured by means of copper-constantan thermocouples and a Leeds and Northrup model 8662 potentiometer.
The glass vacuum and gas filling system, to which the cell was connected, was evacuated by an Edwards E02 diffusion pump which was equipped with an Edwards H5L2A baffle valve and a low-resistance liquid air trap and was backed by an Edwards ES 35, rotary pump. The diffusion pump was protected from cooling water failures by an FSM-1 Flowtrol unit. The lowest reproducible pressures obtained, using Dow Corning 704 Silicone fluid in the diffusion pump, was about $5 \times 10^{-8}$ mm Hg. Vacuum measurements were carried out with a GIG-110A CVC ionization gauge ($10^{-3} - 10^{-8}$ mm Hg) and with a 3294B LKB Autovac gauge ($10^{-2} - 10^{-3}$ mm Hg). Molecular gas pressures were measured approximately with the Autovac gauge and then, more accurately, with a liquid-air trapped CVC type CM 100A McLeod gauge ($10^{-3} - 10$ mm Hg).

The molecular gases were first dried by slow passage through a liquid air trap and then were gettered for two days in a storage bottle whose walls were coated with cesium. During the gettering period, the bottle was periodically heated. After gettering the bottle was immersed in liquid air overnight to remove the cesium vapour from the gas. Before being admitted to the fluorescence cell, the gas was again dried by slow passage through a liquid air trap, to keep out of the cell any water vapour coming out of unbaked glass surfaces.

The fluorescent light emerging from the cell was focussed on the photocathode of a 16 stage ITT FW 130 X photomultiplier tube mounted in a liquid air cryostat. The Sb-K-Na-Cs photocathode which had $S_{20}$ spectral response and a quantum efficiency of about 7.5 per cent for the Na D lines, had a diameter of 0.1 inch. The 1.3 kv operating voltage was supplied by a 412-B Fluke regulated power supply and was distributed at about 80 volts per stage by means of a resistive divider chain. Pulses from the photomultiplier were passed through
a PW 4270 Phillips amplifier-discriminator and were recorded on a PW 4230 scaler. The scaler readings were registered with a Victor printer used in conjunction with a PW 4200 printer control. The dark noise of the photomultiplier was 30 counts/min. (equivalent to a D.C. dark current of $2 \times 10^{-14}$ amp) and remained constant for many months. The tube had a gain of $3 \times 10^5$ for the 60 per cent of the pulses which were above the discriminator threshold level, and had an effective quantum efficiency* of 4.5 per cent.

3. Experimental Procedure

At the start of each experiment, the system was baked at a pressure of $1 \times 10^{-7}$ mm Hg. During the experiments the temperature of the sodium in the side-arm of the fluorescence cell, which controlled the vapour pressure, was 115°C and corresponded to a vapour pressure of $5 \times 10^{-7}$ mm Hg. The main part of the cell was kept at 175°C to prevent condensation of the sodium on the windows. When a vacuum of $5 \times 10^{-8}$ mm Hg was reached, the appropriate gas was admitted to the cell from a pyrex bottle which had been previously connected to the system and which was opened under vacuum by a glass-enclosed magnetic breaker. CH$_4$ (99.99%), C$_2$H$_4$ (99.98%), C$_2$H$_6$ (99.9%) supplied by Matheson of Canada, Ltd., CD$_4$ (± 96.97%) supplied by Merck, Sharp and Dohme of Canada, Ltd., and commercial grade of C$_2$H$_2$ were used in the experiment. Chemically active impurities were removed from the gases by gettering.

*The effective quantum efficiency is the product of the photocathode efficiency (7.5 per cent at 5890Å for an S$_{20}$ surface) and a factor arising from the use of pulse discriminating techniques.
with hot cesium vapour.

The transmissions of the filters were measured in situ and were remeasured before each experimental run. The transmission of a Type "U" Spectrolab filter to the appropriate Na D component depends on the polarization of the incident light (Dobrowolski 1959). Thus the D₂ component in the fluorescent light could not be directly isolated by means of the appropriate filter because of its partial linear polarization which amounted to about 5 per cent in pure sodium vapour and which decreased rapidly with increasing gas pressure. Instead, the intensity of the D₂ component in the fluorescent light was obtained by subtracting the intensity of the D₁ component, measured with the D₁ filters in the fluorescent light beam, from the total fluorescent light intensity. This difficult measurement produced satisfactory results only for molecular gas pressures greater than 0.1 mm Hg at which the values η₂ were already relatively large.

At each gas pressure, the electromechanical sequencing system (Pitre, 1965) controlling the motor-driven slides which held the interference filters in the incident and fluorescent beams, was programmed for eight alternating measurements of η₁ and η₂ values. Each η value was determined from two alternating one-minute photon count accumulations carried out with and without the interference filters in the fluorescent light beam. The arithmetic mean of these results was accepted as the η₁ and η₂ value, respectively, corresponding to the particular gas pressure.

The dark noise of the photomultiplier, which amounted to 30 counts/minute, resulted, in the case of the sensitized fluorescence measurements, in a signal-to-noise ratio ranging from 100 to 1000. For the much more intense resonance fluorescence, the dark noise was negligible,
but corrections to the measured fluorescent intensities were made for reflected light in the cell which contributed 0.5 per cent to the observed signal.

The $D_2$ light in the incident beam was 83 per cent linearly polarized with the axis of polarization at an angle of $15^\circ$ to the plane defined by the incident and fluorescent beams. This polarization was due to the optical activity of the mica in the interference filters. The polarization of the $D_2$ resonance radiation in the fluorescent beam was 5.5 per cent for zero molecular gas pressure and decreased rapidly with increasing gas pressure (Mitchell and Zemansky 1961). A simple calculation (Feofilov 1961) showed that under these conditions the effects on the calculation of the $\eta$ values, arising from the anisotropy of the $D_2$ radiation, were negligible.

4. Results and Discussion

The experimental values of the fluorescent intensity ratios, $\eta_1$ and $\eta_2$, obtained in mixtures of sodium vapour with methane, deuterated methane, ethane, ethylene and acetylene are shown in Tables 1-5 respectively. Each Table represents values obtained in at least two experimental runs with increasing and decreasing molecular gas pressures. Figures 4 and 5 are the graphical representations of Tables 1 and 2 and Tables 3, 4 and 5, respectively, and show plots of the $\eta$-values against pressures of $\text{CH}_4$, $\text{CD}_4$, $\text{C}_2\text{H}_6$, $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$.

The experimental values of $\eta_1$ and $\eta_2$ were used in a computer program to obtain the collision numbers $Z_{12}$ and $Z_{21}$ from eqs. (18) and (19) and hence, from eqs. (21) and (22), the corresponding values for the cross sections $Q_{12}$ and $Q_{21}$ which were then averaged and yielded the final
TABLE 1

Fluorescent Intensity Ratios for Sodium-Methane Collisions

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<tr>
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\textbf{TABLE 4}

Fluorescent Intensity Ratios for Sodium-Ethylene Collisions

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TABLE 5

Fluorescent Intensity Ratios for Sodium-Acetylene Collisions

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<td>.190</td>
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</table>
Fig. 4. Plots of intensity ratios $\eta_1$ and $\eta_2$ against CH$_4$ and CD$_4$ pressures. (o) CH$_4$; (△) CD$_4$. 
Fig. 5. Plots of intensity ratios $\eta_1$ and $\eta_2$ against $C_2H_2$, $C_2H_4$, and $C_2H_6$ pressures. (o) $C_2H_2$; (Δ) $C_2H_4$; (o) $C_2H_6$. 
Fig. 6. Plots of collision numbers $Z_{12}$ and $Z_{21}$ against $C_2H_4$ pressure.
(O) Results corrected for quenching; (Q) results not corrected for quenching.
cross sections for the particular sodium-molecular gas collisions process. The differences between the individual values of \( Q_{12} \) and \( Q_{21} \) were, before averaging, less than 4 per cent for all the mixtures.

To solve eqs. (18) and (19), it is necessary to know the value \( Z_{10} \), corresponding to \( ^3P_\downarrow \rightarrow ^3S_{1/2} \) quenching. Figure 6 shows plots of the collision numbers \( Z_{12} \) and \( Z_{21} \) against ethylene pressure and includes points calculated assuming the total absence of quenching \( (Z_{10} = 0) \) as well as values of \( Z_{12} \) and \( Z_{21} \) corrected for quenching on the basis of the quenching cross section \( (138 \text{A}^2) \) determined by Norrish and Smith (1940). The latter points lie on straight lines whose slopes are proportional to the respective cross sections \( Q_{12} \) and \( Q_{21} \). At pressures below about 0.2 mm Hg or in cases of very low quenching cross sections, the plots \( Z_{12} \) and \( Z_{21} \) are linear even if no corrections for quenching are made (McGillis and Krause 1968; Stupavsky and Krause 1968). Thus the mixing cross sections for \( \text{CH}_4, \text{CD}_4 \) and \( \text{C}_2\text{H}_6 \) which exhibit quenching cross sections of less than \( 0.5 \text{A}^2 \), and for \( \text{C}_2\text{H}_2 \) which was used at pressures below 0.2 mm Hg, were derived from eqs. (18), (19), (20) and (21), putting \( Z_{10} = 0 \). In all four cases, the collision numbers \( Z_{12} \) and \( Z_{21} \) varied linearly with gas pressure.

Table 6 shows the cross sections \( Q_{12} \) and \( Q_{21} \) obtained in this experiment together with the previously determined values for \( \text{H}_2, \text{HD}, \text{D}_2 \) and \( \text{N}_2 \) (Stupavsky and Krause 1968) and with the cross sections calculated on the basis of the theory of Callaway and Bauer.

The statistical uncertainties in the mixing cross sections were negligible in all cases. Uncertainties in filter transmissions and in the lifetime of the sodium resonance state each added about 2 per cent to the error, and the pressures read off the McLeod gauge were estimated
<table>
<thead>
<tr>
<th>Collision Partners</th>
<th>$Q_{12}(^2P_{1/2} \rightarrow ^2P_{3/2})$ ($\AA^2$)</th>
<th>$Q_{21}(^2P_{1/2} \rightarrow ^2P_{3/2})$ ($\AA^2$)</th>
<th>$Q_{12}/Q_{21}$</th>
<th>$2\exp(-\Delta E/kt)$</th>
<th>$Q_{21}$ Theoretical ($\AA^2$)</th>
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<td>Na - H$_2$</td>
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<td>1.88</td>
<td>33.1</td>
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<td>1.88</td>
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<td>1.88</td>
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accurate to within 3 per cent. The combined errors should not exceed 
± 10 per cent.

All the ratios $Q_{12}/Q_{21}$ are in agreement with the principle 
of detailed balancing. The cross sections appear to increase with the 
polarizabilities of the molecules, from $H_2$ to $C_2H_6$ and, in the cases 
of the hydrocarbon molecules, are in excellent agreement with the cross 
sections calculated on the basis of Callaway and Bauer's (1965) theory 
which had been derived for the case of sodium-noble gas collisions 
and was applied without modification to the calculation of cross 
sections for sodium-molecule collisions.

Callaway and Bauer have developed a general approximate method 
for the theoretical study of inelastic collisions, which can be applied 
to the calculation of cross sections for the special case of non-
adiabatic mixing collisions between the excited alkali atoms and noble 
gas atoms in their ground states. Their procedure is founded on the 
possibility of obtaining, with the use of the impact parameter method, 
a complete solution to the equations of the time-dependent perturbation 
theory. The wave functions used were Slater determinants and the inter-
action was reduced to the one-electron case.

Their model requires the knowledge of the dominant (least 
negative) power of $R$, the internuclear separation between the alkali 
atom and the centre of mass of the molecule, in the diagonal and off 
diagonal matrix elements of the potential energy function for the inter-
action between the alkali atom and the molecule. The dominant term in 
the interaction function $V$, between an excited alkali atom and a molecule, 
deeps on whether the colliding partners possess permanent multipole 
 moments and on whether the transition in the alkali atom occurs between
states of the same or opposite parity. Table 7 shows the matrix elements $(3/2|V|1/2)$ appropriate to the $3^2P_{3/2} \rightarrow 3^2P_{1/2}$ electronic transition in sodium, induced by various interactions with a molecule together with the dependence of the theoretical cross section on the respective type of interaction. The quantity $<r^N>$ is a matrix element of the $n$th power of the electronic coordinate of the $3^2P_J$ states of sodium. All angular factors and vector or tensor indices have been omitted. $v$ is the relative velocity of the colliding partners. The theoretical cross section for a molecule possessing a permanent dipole moment $p$, a permanent quadrupole moment $D$, and a polarizability $\alpha$, is the sum of the individual cross sections derived for the alkali atom interacting with the dipole moment, the quadrupole moment and the polarizability of the molecule. Thus,

$$Q_{21} = k_\alpha \left( \frac{2 \langle r \rangle^2}{h\nu} \right)^{2/5} + k_D \left( \frac{6 \langle r^2 \rangle}{h\nu} \right)^{2/4} + k_p \left( \frac{8 \langle r^2 \rangle^2}{h\nu} \right)^{2/3} \tag{25}$$

The constants $k_\alpha$, $k_D$, and $k_p$ are determined from the solution of the collision problem. Callaway and Bauer (1965) solved the problem only for the case of the van der Waals interaction and obtained $k_\alpha = 0.468$.

Table 8 gives the values of the permanent dipole moments and of the polarizabilities obtained from a Handbook of Chemistry and Physics (1959) and of the permanent quadrupole moments (Krishnaji and Prakash 1966) for the various molecules.

Since none of the molecules has a permanent dipole moment, the theoretical cross section $Q_{21}$ in eq. (25) should be given by only the first two terms. For CH₄ and CD₄, which possess no permanent quadrupole moments, only the first term remains. The theoretical values
TABLE 7

Matrix Elements for the $^{3}P_{3/2} \rightarrow ^{3}P_{1/2}$ Electronic Transition in Sodium Induced by the Various Possible Interactions with a Molecule
(Callaway and Bauer 1965)

<table>
<thead>
<tr>
<th>Molecule possesses</th>
<th>Matrix element: $\Delta \ell = 0, 2$</th>
<th>Matrix element: $\Delta \ell = 1$</th>
<th>Cross Section $Q_{21}$ for $\Delta \ell = 0, 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanent dipole moment $p$</td>
<td>$\frac{e \rho \langle r^2 \rangle}{R^4}$</td>
<td>$\frac{e \rho \langle r \rangle}{R^3}$</td>
<td>$k \left( \frac{e \rho \langle r^2 \rangle}{h \nu} \right)^{2/3}$</td>
</tr>
<tr>
<td>Permanent quadrupole moment $D$</td>
<td>$\frac{eD \langle r^2 \rangle}{R^5}$</td>
<td>$\frac{eD \langle r \rangle}{R^4}$</td>
<td>$k \left( \frac{eD \langle r^2 \rangle}{h \nu} \right)^{2/4}$</td>
</tr>
<tr>
<td>Polarizability $\alpha$</td>
<td>$\frac{ae \langle r^2 \rangle}{R^3}$</td>
<td>$\frac{ae \langle r \rangle}{R^2}$</td>
<td>$k \left( \frac{ae \langle r^2 \rangle}{h \nu} \right)^{2/5}$</td>
</tr>
<tr>
<td>Molecule</td>
<td>Permanent dipole moment</td>
<td>Permanent quadrupole moment ($x 10^{-26}$ e.s.u. cm$^2$)</td>
<td>Polarizability ($x 10^{-24}$ cm$^3$)</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------</td>
<td>--------------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td></td>
<td>measured or calculated values</td>
<td>minimum</td>
<td>maximum</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>.38</td>
<td>1.0</td>
</tr>
<tr>
<td>HD</td>
<td>0</td>
<td>.82</td>
<td>3.25</td>
</tr>
<tr>
<td>D$_2$</td>
<td>0</td>
<td>1.02</td>
<td>3.25</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td>-2.55</td>
<td>2.75</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>0</td>
<td>3.0</td>
<td>13.06</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0</td>
<td>1.32</td>
<td>4.24</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0</td>
<td>.3</td>
<td>1.72</td>
</tr>
</tbody>
</table>
\(Q_{21}\) derived from Callaway and Bauer's (1965) theory, which are quoted in Table 6, were calculated from the first term of eq. (25). They are in very good agreement with experimental values for all the molecules, even for those having permanent quadrupole moments. This fact leads one to believe that the second term in eq. (25) contributes relatively little to the cross section. It also implies that the van der Waals interaction of an excited sodium atom with a molecule is much more effective in inducing transitions between the fine-structure states of sodium than the interaction involving the quadrupole moment of the molecule, even though the van der Waals interaction is of relatively short range \((V \sim R^{-6})\), as compared with the quadrupole interaction \((V \sim R^{-5})\). This is consistent with the adiabatic hypothesis. The short range van der Waals force gives rise to a non-adiabatic collision for which, according to the Massey criterion, (Massey and Burhop 1952), the probability of excitation transfer is large. On the other hand, the long range force involving the permanent quadrupole moment of the molecule results in a nearly adiabatic collision for which the probability of excitation transfer is small.
III. SENSITIZED FLUORESCENCE OF MERCURY MOLECULES

1. The 3350Å and 4850Å Fluorescence Bands

When mercury vapour at a high density corresponding to a temperature of about 200°C is excited by the 2537Å resonance radiation it emits, in addition to the imprisoned atomic resonance fluorescence, band spectra whose intensities depend strongly on the vapour density. The molecular fluorescence consists of two bands, one in the visible region centred at 4850Å and the other in the near ultraviolet, centred at about 3350Å. When the exciting radiation is extinguished, there is an afterglow arising from the fluorescence bands which persist for several milliseconds. Phillips (1913) who first discovered the afterglow and later Rayleigh (1927) were able to observe the band fluorescence in a stream of mercury vapour at some distance from the region of excitation. Rayleigh (1932) also found evidence for the simultaneous decay of the 3350Å and 4850Å bands and showed that the mercury vapour emitting the band fluorescence in the flowing afterglow, contained metastable $6^3P_0$ mercury atoms. In the presence of nitrogen which is known to produce metastable Hg($6^3P_0$) atoms by quenching the Hg($6^3P_1$) state, the band fluorescence can also be observed at the low mercury vapour pressures which prevail at room temperatures (Pringsheim 1949). Franck and Grotrian (1921) first associated these bands with excited levels of the mercury molecule.

Mrozowski (1937) suggested that the 4850Å band fluorescence arose from the spontaneous decay of the mercury $^3O^-_u$ metastable molecules. Because of its metastability the $^3O^-_u$ state was presumed to act as the
primary reservoir for both molecular emissions. The $^{3}350\AA$ band was ascribed to the decay of the $^{3}1_{u}$ state which is believed to have a lifetime of the order of $10^{-7}$ s (Mrozowski 1944). The persistence of the $3350\AA$ band was attributed to a continual repopulation of the $^{3}1_{u}$ state from the lower lying $^{3}0_{u}^{-}$ state as a result of inelastic collisions. Because of the short lifetime of the $^{3}1_{u}$ state, both bands should decay with the population of the $^{3}0_{u}^{-}$ state. In this way it is possible to explain the common persistence times of the $3350\AA$ and $4850\AA$ bands, as observed by Rayleigh (1927, 1932).

McCoumbrey (1954) studied a system containing pure mercury at $200^\circ$C, confirmed that the two bands had a common persistence time and found that the persistence time depended strongly on the mercury density. To account for these results, he postulated that the $3350\AA$ band arises by spontaneous decay of the $^{3}0_{u}^{-}$ state while the $4850\AA$ emission results from a three body collision involving a Hg$_{2}$$^{(3)0_{u}^{-}}$ molecule and two mercury atoms in their ground states. This explanation was a departure from the earlier interpretation of Mrozowski (1937).

Berberet and Clark (1955) investigated the $4850\AA$ band in the presence of nitrogen and postulated the formation of an electronically excited Hg$_{2}$ molecule in a three body collision of a Hg($^{6}3P_{0}$) atom, a Hg($^{6}1S_{0}$) atom and a nitrogen molecule. The excited Hg$_{2}$ molecule was then assumed to decay either by spontaneous emission or by diffusion to the walls.

McAlduff, Drysdale and Le Roy (1967) investigated the origin of the $4850\AA$ and $3350\AA$ bands. They suggested that in their system which consisted of a mixture of mercury vapour and nitrogen gas, the first stage
in the process leading to molecular fluorescence in mercury, should be the absorption of the mercury resonance radiation by ground state Hg\(^{6}\text{S}_0\) atoms:

\[\text{Hg}^{6}\text{S}_0 + h\nu(2537) \rightarrow \text{Hg}^{3}\text{P}_1\]  \hfill (26)

During the next step, the Hg\(^{3}\text{P}_1\) atoms should be transferred to the metastable 6\(^3\text{P}_0\) state by collisions with nitrogen molecules:

\[\text{Hg}^{3}\text{P}_1 + N_2 \rightarrow \text{Hg}^{3}\text{P}_0 + N_2\]  \hfill (27)

The presence of 6\(^3\text{P}_0\) atoms in mercury vapour emitting molecular fluorescence has been documented quite early (Rayleigh, 1932) and it has long been known that nitrogen is very effective in producing metastable atoms as a result of collisions with atoms in the 6\(^3\text{P}_1\) resonance state. The metastable atoms would next combine with ground state atoms to form diatomic molecules as the result of three body collisions:

\[\text{Hg}^{3}\text{P}_0 + \text{Hg}^{6}\text{S}_0 + N_2 \rightarrow \text{Hg}_2^{3}\text{L}_u + N_2\]  \hfill (28)

According to the authors' interpretation, the 3350\(\AA\) results from the spontaneous decay of the 3\(^3\text{L}_u\) state.

\[\text{Hg}_2^{3}\text{L}_u \rightarrow 2\text{Hg} + h\nu(3350\AA)\]  \hfill (29)

The \(\text{Hg}_2^{3}\text{O}^-\) molecules are formed in collisions of \(\text{Hg}_2^{3}\text{L}_u\) molecules with nitrogen:

\[\text{Hg}_2^{3}\text{L}_u + N_2 \rightarrow \text{Hg}_2^{3}\text{O}^- + N_2\]  \hfill (30)
and their spontaneous decay produces the $4850\AA$ band:

$$\text{Hg}_2(^3\text{O}_u^-) \rightarrow 2\text{Hg} + \text{hv}(4850\AA)$$

(31)

The exact origin of the $3350\AA$ and $4850\AA$ bands in mercury is still in doubt and, even the most recent proposals are in some cases radically different. It is hoped that the present study of the two bands at higher resolution than has been employed in the recent past, will contribute to a better understanding of the problem.

2. Potential Energy Curves for the Hg$_2$ Molecule

Apart from the weak polarization forces, only repulsive forces act between two unexcited mercury atoms approaching each other. The dissociation energy of the van der Waals molecule Hg$_2(^1\Sigma_g^+)$, bound by polarization forces, is about $0.08$ eV and the potential minimum occurs at a nuclear separation of about $3.2\AA$ (Kuhn 1937). Excited mercury atoms in the states $6^3\text{P}_0, 1, 2$, $6^1\text{P}_1$, $7^3\text{S}_1$, etc., are able to combine with unexcited $6^1\text{S}_0$ mercury atoms and form genuine stable molecules. The dissociation energies of these molecules in some cases exceed $1$ eV and their vibrational and rotational energies are completely quantized. Fig. 7 shows the potential energy curves for the Hg$_2$ molecule, as given by Finkelnburg (1964). Alternative potential energy curves which were proposed from time to time, differ only in the actual depths of the potential wells and in the equilibrium internuclear separations of the excited states (Pringsheim 1949; McCoubrey 1954). On the right-hand side, at large internuclear distances, the states of the separated atoms are specified. At intermediate internuclear distances, the molecular states are identified by the notation
appropriate to Hund's coupling case (c) 
(Herzberg, 1950) (the vectors L and S are 
coupled into a vector J which precesses 
about the molecular axis with a component \( \Omega \). 
At small nuclear separations the states are 
specified by Hund's case (a) (the inter-
action of the two atoms breaks the coupling 
of the vectors L and S and forces L and S 
to precess independently around the molecular 
axis).

The transition from the \( ^3O_u^- \) state 
to the \( ^1\Sigma^+_g \) ground state is forbidden for 
pure c coupling, but at small internuclear 
distances, the two states \( ^3O_u^- \) and \( ^3\Sigma_u^- \) combine into a \( ^3\Sigma^+_u \) state from which 
the probability of transition to the ground state can be as high as \( 10^7 \) 
sec\(^{-1} \). Vibrating metastable molecules trapped in the \( ^3O_u^- \) state are able 
to radiate only at the time of closest approach of the two atoms, and 
the 4850\( \text{Å} \) band is therefore emitted mostly by molecules with high vibrational 
energies. The observed lifetime of the order of \( 10^{-2} \) sec is an average 
which depends on the average vibrational energy, that is, on the temperature 
of the gas. For the \( ^3\Pi_u \) state, a constant transition probability over the 
whole range of internuclear distances is expected (Franck-Condon intensity 
distribution) (Mrozowski 1944).

Kuhn and Freudenberg (1932) obtained some quantitative information 
about the \( ^3\Pi_u \) state. They studied the molecular absorption, beginning at 
the 2537\( \text{Å} \) atomic line and extending their measurements to a long wavelength 
limit of 3300\( \text{Å} \). They found that the intensity of the absorption at the
long-wavelength limit increased with the square of the atomic vapour
density and with temperature, indicating that positive energy levels of the
molecular ground state were responsible for the absorption. They assumed
that these positive energy states were populated according to the Maxwell-
Boltzmann distribution and that the absorption at the long wavelength
limit involved transitions to the minimum of the $^3_1\text{u}_0$ potential energy
curve in accordance with the Franck-Condon principle. On this basis
they calculated the position of the potential minimum of the $^3_1\text{u}_0$ curve
and found it to be directly above the 0.27 eV point on the ground-state
curve. From the value of the long-wavelength limit of the absorption
and from the wavelength of the atomic line $2537\lambda (6^3\text{P}_1 \rightarrow 6^1\text{S})$ they found
the dissociation energy of the $^3_1\text{u}_0$ state to be 0.84 eV.

No quantitative information concerning the $^3_0\text{u}_0$ state has been
available thus far. This state is responsible for the band emission at
$4850\lambda$, but no corresponding absorption has been observed. The state
results from the combination of the metastable $6^3\text{P}_0$ atoms with the $6^1\text{S}_0$
ground state atoms. The $^3_0\text{u}_0$ state does not combine optically with the
$^1\Sigma^+_g$ ground state at large internuclear distances (absorption) but does
so at small internuclear distances (emission) at which different molecular
selection rules have to be used (Herzberg 1950).

Pringsheim (1949) divided the many molecular bands of mercury
into three groups:

(1) The narrow bands centred at $2540\lambda$ and at $2345\lambda$, which were
ascribed to transitions between van der Waals molecules in the ground
state and similar molecules in higher electronic states.

(2) Bands exhibiting long sequences of intensity fluctuations,
which can only correspond to transitions from excited molecular states to the nearly horizontal branch of the ground state potential curve. These bands occur in absorption as well as in emission. Even when excited with monochromatic light, the whole sequence of fluctuations is usually emitted, because the same average distribution over the various vibrational levels of the excited state is produced by collisions.

(3) Broad bands without any structure, which are due to transitions from excited stable molecules to a part of the ground-state potential curve where the slope is already steep. At moderate temperatures and vapour pressures these bands are missing in the absorption spectrum because the relative thermal energies of the unexcited atoms are practically never large enough for them to approach each other sufficiently closely. Pringsheim (1949) included in this group the bands centred at 3350 Å and 4850 Å.

3. Apparatus and Experimental Procedure

The arrangement of the apparatus is shown in Fig. 8. Mercury radiation emitted from a mercury spectral lamp was passed through a rectangular slit and was collimated by a fused silica lens. After passing through appropriate filters, the light was brought to a focus in a fluorescence cell which was made of fused silica and which contained a mixture of mercury vapour and nitrogen at room temperature. The fluorescent light emitted from the vapour at right angles to the incident beam, was focussed onto the entrance slit of a Perkin-Elmer scanning spectrometer and, after dispersion, was detected with a photomultiplier whose output current was amplified by an electrometer and recorded with a strip chart recorder.
The complete apparatus was enclosed in a light-tight box to eliminate stray light.

The lamp, which consisted of a fused silica tube 5 cm long and 1.5 cm in diameter, containing a drop of mercury and filled with 1 torr of argon, was placed in the coil of an rf oscillator operating at 165 Mc/s. About 60 watts of rf power was used by the lamp which was cooled by a small variable-speed fan; the amount of cooling was adjusted for maximal intensity of resonance fluorescence. It was found necessary to vent the light-tight box containing the lamp into a fume hood, as the lamp generated large quantities of ozone. During the course of the experiments, various filters were employed in the exciting beam. Initially a Corion interference filter was used, which transmitted about 15% of the 2537Å radiation in a band width of 150Å, and about 10⁻⁵% of the visible light. Although the molecular fluorescence could be observed with this filter in the exciting beam, the resulting intensity was too low and in all subsequent experiments a Corning CS 7-54 colour filter was employed as it had a transmission of 63% at 2537Å and transmitted a negligible quantity of the visible mercury radiation emitted from the lamp. In the fluorescent beam, a Corning CG 774 (Pyrex) filter was placed in series with the scanning spectrometer to eliminate the 2537Å stray light scattered in the spectrometer.

The model 112 Perkin-Elmer scanning spectrometer was equipped with a Jarrell Ash 980-30-20-18 grating which had 1180 grooves/mm and was blazed at 3000Å. The efficiency of the grating was specified as 70% at 2537Å and 62% at 4000Å. Only the first-pass images were detected; the mirrors responsible for the second pass were blocked off with black paper.
Fig. 8. Schematic diagram of the apparatus: A, mercury lamp; S, beam stop; F₁, CS 7-54 filter; C, fluorescence cell; M, spectrometer; F₂, CG 774 filter; E, electrometer; R, recorder.
It was found necessary to block off also about one inch of the right-hand side of the paraboloid mirror which was producing broad defocussed images at the exit slit for certain settings of wavelength drum. The wavelength scale of the spectrometer was calibrated in situ as both the first and second order of the 2537Å resonance line could be detected. Also, with nitrogen in the cell, the stepwise radiations connecting the $^3P_0$ state to higher excited states of mercury were present in the fluorescent light and were easily identified.

The fluorescence cell was constructed from a section of D-shaped G.E. type 151 non-fluorescing fused silica. The cell was 5 cm long and had fused silica (type 151) plane windows sealed onto the ends. The cell fluoresced only slightly when illuminated with 2537Å radiation, emitting a purple glow which, however, was too faint to be detected with the spectrometer. The temperature in the side-arm of the cell which contained a drop of mercury, could be controlled by circulating around it cold nitrogen gas boiled off from a liquid nitrogen container. A small heater was located inside the liquid nitrogen and YSI 44003 thermistor mounted on the side-arm served as the temperature-sensing element for a transistorized D.C. amplifier controlling the current in the heater. With this arrangement, the temperature of the side-arm could be varied from $-40^\circ C$ to $+25^\circ C$.

Although provisions were made for working at low mercury vapour pressures, all the experimental data were obtained with the side-arm at room temperature. The intensity of the molecular fluorescence depends on the square of the mercury vapour density and the fluorescence bands were only just of sufficient intensities to be detected at a mercury vapour pressure corresponding to room temperature. The cell was connected to a glass
vacuum system by means of a graded seal. The various components comprising
the vacuum system were similar to those described in an earlier part of
this thesis.

The fluorescent light emerging from the cell, was dispersed by
the spectrometer and was focussed on the photocathode of a 16 stage ITT
FW 4013 photomultiplier tube. No cooling was employed as the tube had a
sapphire window glued with epoxy cement to the pyrex envelope and there
was some risk of breakage as a result of strains developed in cooling the
tube. The Sb-K-Na-Cs photocathode had a spectral response, a quantum
efficiency of 0.215 at 2537 Å and 0.15 at 5500 Å. The effective photocathode
was in the form of a slit 0.05" wide and 0.15" long. The 1.8 kv operating
voltage was supplied by a 412-B Fluke power supply and was distributed
at about 90 volts per stage by means of a resistive divider chain. The
tube had a gain of 6.5 x 10^5 at 1800 volts. The anode current from the
photomultiplier was amplified by a Keithley Model 301 solid state electro-
meter. The output voltage of the electrometer was recorded with a Moseley
7101 B strip chart recorder equipped with a model 17501A input module.
The dark current of the photomultiplier at 1.8 kv was about 4 x 10^{-11}
amperes and remained constant during the experiment.

At the start of the experiment the system was baked at a pressure
of 1 x 10^{-7} mm Hg. Afterwards, when a pressure of 5 x 10^{-8} mm Hg was
reached, the appropriate gas was admitted to the cell from a pyrex bottle
connected to the system which was opened under vacuum by a glass-enclosed
magnetic breaker. Linde M.S.C. grade Ar, N_2 and H_2 (nominal purity 99.99%) and
Matheson research grade CO were used in the experiments. The nitrogen
gas was purified by gettering with hot rubidium for several days; the
other gases were used without further purification apart from being passed through a liquid nitrogen trap. Slow-scan recordings of the fluorescence were made with various gases in the cell, each recording requiring about 2 hours to complete. Such a slow scan speed was necessary to allow the electrometer, which was operated with a small amount of damping at a gain of 10^11, to respond to changes in the photomultiplier anode current. There was no noticeable decrease in the intensities of the fluorescent bands with time, even after the nitrogen gas had been in the cell for 24 hours. The 4850Å band was intense enough to be observed visually when nitrogen (> 10 torr) was present in the cell even with the room lights on. The green fluorescence could be seen along the path of the exciting light, being most intense where the exciting light entered the cell and gradually diminishing in intensity as the distance from the entrance window increased.

4. Results and Discussion

(a) The 4850Å band.

Fig. 9 shows a recorder trace of the Hg_2 fluorescent band in the visible region, emitted from a mixture of mercury vapour and nitrogen at 295°K and at a nitrogen pressure of 20 mm Hg. The band exhibits a sequence of intensity peaks which are most intense and best resolved at long wavelengths and gradually diminish in intensity and definition towards the short wavelengths. The first intensity maximum at the long wavelength edge rises steeply from the level of the photomultiplier dark noise. It is suggested that the peaks, which have not been observed before, are due to transitions from the various vibrational states of the excited 3P^0_u mercury molecules to the repulsive region of the 1S^0_g ground state.
Fig. 9. The $^3\Omega_u - ^1\Pi_g$ fluorescence band: a, experimental spectrum; b, calculated spectrum; $T = 250^\circ K$, $R_e(r) = e^{-22(r_0/r)}$. 
The intensity of an electronic transition from an upper vibrational state \( v' \) to a lower continuum state of energy \( E \) is given by:

\[
I_{v',E} = k N_v \omega_v^Q \int_0^\infty \psi_{v',E}(r) R_e(r) \psi_E(r) dr \]

(32)

where \( k \) is a constant which depends on units and geometry, \( N_v \) is the population of the upper vibrational state, \( \omega \) is the frequency of the transition, \( \psi_{v',E}(r) \) is the vibrational wave function, \( \psi_E(r) \) is the continuum wave function, and \( R_e(r) \) is the electronic transition moment.

Let us examine the behaviour of eq. (32) for transitions from the \( v'' = 0 \) upper vibrational state to lower continuum states of energy \( E \). The harmonic oscillator vibrational wave function for \( v' = 0 \) is

\[
\psi_o = A_o e^{-1/2a(r-r_e')^2}
\]

(33)

where \( A_o \) is a normalization constant, \( a = \mu \omega_o \), \( \mu \) is the reduced mass, \( \omega_o \) is the vibrational frequency and \( r_e' \) is the equilibrium internuclear separation for molecules in the \(^3\Sigma_u^-\) state. The continuum wave functions satisfy Schrödinger's equation:

\[
\frac{d^2}{dr^2} \psi_E(r) + 2\mu(E - V(r))\psi_E(r) = 0
\]

(34)

Since \( \psi_o(r) \) is a rapidly decreasing function of \( r \) about \( r = r_e' \), it is sufficient to know \( \psi_E(r) \) for only a small range of \( r \) about the classical turning point \( \bar{r} \). The potential \( \bar{V}(r) \) of the ground state can therefore be expanded about \( \bar{r} \):

\[
V(r) = V(\bar{r}) - \beta(r-\bar{r}) + ...
\]

(35)
where $\beta = \frac{d}{dr} V(r)|_{r=R}$ and $V(R) = E$.

The substitution of eq. (35) in eq. (34) yields

$$\frac{d^2}{dr^2} \psi_E + 2\mu \beta (r-R) \psi_E = 0$$

(36)

Putting $z = -(2\mu \beta)^{1/3} (r-R)$, eq. (36) becomes

$$\frac{d^2}{dr^2} \psi_E - z \psi_E = 0$$

(37)

Eq. (37) is Airy's equation and has an oscillating regular solution $Ai(z)$ for negative values of $z$ which is represented in Fig. 10.

![Fig. 10 Plot of Airy's function $Ai(z)$.](image)

Fig. 11 illustrates electronic transitions from $\nu' = 0$ vibrational state to lower continuum states. The first maximum of $Ai(z)$ at $z = -1$ corresponds to the primary intensity peak and the first minimum of $Ai(z)$ at $z = -3.2$ corresponds to the second peak. In general, an intensity peak occurs whenever the phase of the continuum wave function is shifted by $\pi$ with respect to the fixed point $r_e$ on the $r$ axis. On the left of Fig. 11 is a schematic diagram showing the intensity as a function of frequency for
Fig. 11. Schematic diagram illustrating the origin of the intensity peaks arising from transitions between the \( v' = 0 \) state and the ground continuum states. \( 0_1 \), primary maximum, \( \gamma_1 = (E' - E_1)/\hbar; \) \( 0_2 \), secondary maximum, \( \gamma_2 = (E' - E_2)/\hbar; \) \( 0_3 \), tertiary maximum, \( \gamma_3 = (E' - E_3)/\hbar. \)
these transitions. The first two intensity peaks are separated by
\[ \Delta E = E_2 - E_1 \] and their corresponding classical turning points are \( \bar{r}_1 \) and \( \bar{r}_2 \). From the properties of \( Ai(z) \)

\[
(2\mu\beta)^{1/3}(r'_e - \bar{r}_1) = 1
\]

\[
(2\mu\beta)^{1/3}(r'_e - \bar{r}_2) = 3.2
\]

and

\[
(2\mu\beta)^{1/3}(\bar{r}_1 - \bar{r}_2) = 2.2.
\]

(38)

It may be seen from Fig. 11 that

\[
\beta = \frac{dV(r)}{dr} \bigg|_{r_0} = \frac{\Delta E}{\bar{r}_1 - \bar{r}_2}
\]

(39)

Combining eqs. (38) and (39) yields

\[
(2\mu\beta)^{1/3} \frac{\Delta E}{B} = 2.2
\]

or

\[
\beta = (2\mu)^{1/2} \left( \frac{\Delta E}{2.2} \right)^{3/2}
\]

(40)

Thus, the slope of the continuum curve near \( r'_e \), can be calculated from the energy separations of the intensity peaks. It may be seen from Fig. 9 that the separation between peaks \( 0_1 \) and \( 0_2 \), which corresponds to \( \Delta E \), is about 90 cm\(^{-1}\) or \( 4.01 \times 10^{-4} \) a.u. Also, \( \mu = 100.3 \times 1836 = 1.8415 \times 10^5 \) a.

and \( \beta = 0.00156 \text{ a.u.} / a_0 = 0.08 \text{ eV/A.} \) This suggests that the slope of the ground state potential energy curve in the vicinity of \( r'_e \) is quite small, as would be expected from the presence of the relatively sharp peaks in the band. A detailed spectrum was calculated for transitions from the
first 12 vibrational states using harmonic oscillator wave functions for
the upper states and Airy functions for the continuum states near the
turning point. The quantity

\[ I(\omega) = \sum_{\nu' = 0}^{\nu' = 12} \omega_{\nu}' \sum_{\nu} N_{\nu} \int_{0}^{\infty} \psi_{\nu'}(r) R_{e}(r) \psi_{e}(r) dr^2 \]  

(41)

is plotted as a function of wavelength in Fig. 12. The input data
\[ \omega_{\nu}' = 220 \text{ cm}^{-1}, \beta = 0.08 \text{ eV/A, } N_{\nu}' = 0.647 \text{ cm}^{-1}\]  
and \[ R_{e}(r) = e^{22(r_e - r)} \]
was used. The band origin was assumed to occur at 5639 Å. The electronic
transition moment \( R_{e}(r) \) in eq. (41) was varied until the intensity dis-
tribution in the calculated spectrum was in general agreement with that
in Fig. 16 \((N_2 + A)\) which was obtained under conditions in which the
population of the various vibrational states of the \( ^3 \Omega_u \) state approach
that given by the Maxwell-Boltzmann distribution. It should be noted
that according to molecular theory (Herzberg 1950) the electronic transition
probability and thus the electronic transition moment for the \( ^3 \Omega_u \rightarrow ^1 \Sigma_g \)
varies extremely rapidly with internuclear separation. It has been
suggested that at large internuclear separations the transition probability
may be as small as \( 10^{-2} \text{ sec}^{-1} \) and increase to \( 10^{7} \text{ sec}^{-1} \) at very small inter-
nuclear separation (Mrozowski 1944). The final expression \( R_{e}(r) = e^{22(r_e - r)} \)
is consistent with this suggestion and, in fact, constitutes direct
evidence for such a strongly varying transition probability. The gross
features of the calculated spectrum are almost identical to the experi-
mental spectrum shown in Fig. 9, although the calculated spectrum shows
somewhat more structure. This should be expected since it corresponds to
conditions of much higher resolution than that employed in the experiment.
Fig. 13 shows the calculated spectrum averaged over a normalized triangular slit function with a 80 cm$^{-1}$ base. The slit function modifies the calculated spectrum in such a way as to make it correspond to the actual resolution of the spectrometer. In eq. (41) the population $N_v$ of the various vibrational states was assumed to be given by a Maxwell-Boltzmann distribution corresponding to a temperature of 300$^\circ$K. This assumption will be shown later to be incorrect and Fig. 9 shows the calculated spectrum for transitions from the first 12 vibrational states when a non-equilibrium vibrational population distribution was used in eq. (41). The vibrational temperature of $T = 250^\circ$K was found to produce a calculated spectrum in virtually exact agreement with the experimentally observed spectrum also shown in Fig. 9. The overall shape of the band as well as the relative intensities, the positions and the width of the peaks are almost identical, except for the first three peaks corresponding to $v' = 0,1,2$ transitions where a slight mismatch occurs. This excellent agreement as to the shape and width of individual peaks is significant as their width and to a smaller extent their shape are determined by the slope $\beta$ of the ground state curve. For $\beta = 0.2$ eV/A which is only 2.5 times the value $\beta = 0.08$ eV/A used in the calculation of eq. (41), the widths of the maxima in the calculated spectrum are more than 2 times the observed width even without averaging over the slit function. These various considerations support the correctness of the interpretation of the observed fluorescent band, on the basis of transitions between bound and continuum states.

The calculation represented in Fig. 12, 13 and 9 is valid only if the continuum potential energy curve remains nearly linear over the
Fig. 12. Calculated spectrum for the $^3\Sigma_u^- \rightarrow {}^1\Sigma_g^+$ fluorescence band. $T = 300^\circ K$; $R_e(r) = e^{22(r_e - r)}$. 
Fig. 13. Calculated spectrum for the $^3\Pi_u \rightarrow \Sigma^+ \Lambda$ fluorescence band averaged over a normalized triangular slit function. $T = 300^\circ K$; $g_e(r) = e^{22(r - r_e)}$. 
range of internuclear separations involved in transitions from all the vibrational states. This requires the $\frac{1}{g}$ ground state curve to have a small and almost constant slope for a range of internuclear distances $r_e - 4\lambda < r < r_e$. The Airy function approximation to the continuum wave function is exact for an exactly linear potential energy curve. For non-linear curves, it is equivalent to the WKB approximation near the classical turning point. It can be seen from Fig. 9, that each transition from the upper vibrational state $v'$ to the lower continuum energy states gives rise to a primary intensity maximum along with a number of secondary peaks. The position of the calculated primary intensity peak for the $v' = 0$ transition occurs at a slightly longer wavelength than 5639Å which was assumed to be the calculated band origin. The reason for this may be seen in Fig. 11. The primary peak results from the maximum overlap of the $v' = 0$ vibrational wavefunction of the upper state with the first maximum of the Airy function of the lower state, and this overlap corresponds to a transition of slightly smaller energy than the transition to the actual repulsive potential curve which gives rise to the band origin.

The various intensity peaks in Fig. 9 are identified according to the values $v'$ of the vibrational states from which transitions take place to the ground state. Only the primary peaks are labelled. The first peak at the long wavelength edge of the band is ascribed to the transition from the $v' = 0$ state. This assignment is consistent with the fact that for heavy molecules which have many closely spaced vibrational levels, a sharp emission band-edge occurs only for transitions from the lowest vibrational state, since the intensity of the emission arising from the higher vibrational states decreases gradually with the decrease in
their population (Herzberg 1950). The maximum at \( v' = 3 \) is particularly intense because of the presence in this position of the Hg 5461 Å line which results from the excitation by a small quantity of Hg 4047 Å radiation passing through the CS 7-54 colour filter in the incident beam of the Hg(6^3P_0) metastable atoms to the Hg(7^3S_1) state, followed by their decay to the Hg(6^3P_2) metastable state. The intensity peak labelled Hg 2537 Å is due to the small amount of the second-order diffraction of the mercury resonance line which passes through the CG 774 filter placed in series with the spectrometer.

Table 9 lists the quantum numbers \( v' \) for the various vibrational states of the \( ^3O_u^- \) molecules which give rise to the appropriate peaks in the band together with the frequencies of the peaks and the energy spacing between them. The observed frequencies should be accurate to about 6 cm\(^{-1}\) and the spacing between the consecutive peaks should be somewhat more accurate. This spacing is nearly constant for all the peaks except those corresponding the \( v' = 0, v' = 1 \) and \( v' = 2 \) for which the spacing is somewhat smaller. The mean spacing of 212 cm\(^{-1}\) should be approximately equivalent to the spacing \( \omega_e' \) between the vibrational levels of the \( ^3O_u^- \) state because, at the internuclear separation corresponding to its potential minimum, the potential energy curve of the ground state has a relatively small slope (\( \approx 0.08 \text{ eV/Å} \)). The true value of \( \omega_e' \) should be somewhat larger and the value \( \omega_e' = 220 \text{ cm}^{-1} \), when substituted in eq. (41), produces a calculated spectrum in which the positions of the maxima agree very well with those of the experimental peaks except for \( v' = 0,1,2 \). This partial mismatch is not particularly surprising if it is considered that a constant value of \( \beta \), the slope of the ground state curve, was assumed in eq. (41),
TABLE 9

The Designation and Spacing between the Primary Peaks of the Hg$_2$($^{3}O_u$ $\rightarrow$ $^1\Sigma_g^+$) Fluorescence Band

<table>
<thead>
<tr>
<th>Vibrational Quantum Number ($v'$)</th>
<th>Frequencies of the peaks (cm$^{-1}$)</th>
<th>Peak Separations (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17734</td>
<td>$E(1) - E(0) = 182$</td>
</tr>
<tr>
<td>1</td>
<td>17916</td>
<td>$E(2) - E(1) = 191$</td>
</tr>
<tr>
<td>2</td>
<td>18107</td>
<td>$E(3) - E(2) = 206$</td>
</tr>
<tr>
<td>3</td>
<td>18312</td>
<td>$E(4) - E(3) = 202$</td>
</tr>
<tr>
<td>4</td>
<td>18514</td>
<td>$E(5) - E(4) = 218$</td>
</tr>
<tr>
<td>5</td>
<td>18732</td>
<td>$E(6) - E(5) = 209$</td>
</tr>
<tr>
<td>6</td>
<td>18941</td>
<td>$E(7) - E(6) = 208$</td>
</tr>
<tr>
<td>7</td>
<td>19149</td>
<td>$E(8) - E(7) = 212$</td>
</tr>
<tr>
<td>8</td>
<td>19361</td>
<td>$E(9) - E(8) = 226$</td>
</tr>
<tr>
<td>9</td>
<td>19587</td>
<td>$E(10) - E(9) = 207$</td>
</tr>
<tr>
<td>10</td>
<td>19794</td>
<td>$E(11) - E(10) = 218$</td>
</tr>
<tr>
<td>11</td>
<td>20012</td>
<td>$E(12) - E(11) = 206$</td>
</tr>
<tr>
<td>12</td>
<td>20218</td>
<td>$E(13) - E(12) = 227$</td>
</tr>
<tr>
<td>13</td>
<td>20445</td>
<td></td>
</tr>
</tbody>
</table>
whereas the actual slope probably varies somewhat over the range of the internuclear separations involved in the transitions.

(b) The $3350\AA$ Band.

Fig. 14 shows the recorder trace of the $^{3}1_u \rightarrow ^{1}\Sigma^+_8$ fluorescence band emitted from a mixture of mercury vapour, nitrogen and argon at room temperature. The nitrogen and argon were at pressures of 12 torr and 350 torr, respectively. The band appears continuous even with the narrowest setting of the spectrometer slit and has a broad maximum centred at 3360\AA.

The two lines labelled Hg 3131 and Hg 3660 result from the excitation by the 2967\AA radiation in the incident beam of the Hg$(6^3P_0)$ metastable atoms to the $6^3D_1$ state, followed by their decay to the $6^3P_1$ and $6^3P_2$ states. It should be noted that at low nitrogen pressures the Hg $3341\AA$ atomic line deforms the shape of the band but at higher pressures the line becomes faint and has a negligible effect on the shape of the band. The shape and position of the band agree with previous observations (Pringsheim 1949).

The $3350\AA$ band is continuous unlike the $4850\AA$ band which exhibits a well defined structure. This totally different appearance of the two bands must be due to the fact that transitions from the $^{3}1_u$ state take place to a more repulsive and steeper part of the $^{1}\Sigma^+_8$ ground state curve than the transitions from the $^{3}0_u$ state.

(c) The effect of $N_2$ and Ar pressure on the intensities and shapes of the $4850\AA$ and $3350\AA$ bands.

McAluff, Drysdale and Le Roy (1967) studied the effect of nitrogen pressure on the intensities of the $3350\AA$ and $4850\AA$ bands. They examined the $4850\AA$ band using 5 broad-band pass colour filters in turn
Fig. 14. The $^3_{1u} \rightarrow {1t^+}_8$ fluorescence band.
and concluded from their measurements of the relative intensities at various nitrogen pressures, that the shape of the band was independent of the gas pressure. In the present investigation the effects of nitrogen and argon pressures were studied using a scanning spectrometer which revealed much more information about the shape and structure of the band.

Fig. 15 shows scale drawings of the recorder traces of the 4850Å band for various nitrogen pressures and Fig. 16 similarly depicts the effect of the combined nitrogen and argon pressure on the band. It should be noted that Figs. 9 and 15 were obtained using a narrow spectrometer slit and show more details of the structure than Fig. 16 which, because of intensity considerations, was obtained with a wide slit. It may be seen that the shape and the integrated intensity of the 4850Å band changes with the pressure of both pure nitrogen and nitrogen-argon mixture. The long wavelength region of the band is more intense at low nitrogen pressures than the short wavelength region. The intensity of the latter, however, increases rapidly with nitrogen pressure, so that at the highest nitrogen pressure employed (150 mm Hg), the band exhibits a broad maximum centred at about 5200Å. The shape of the 3350Å band is not affected by gas pressure and only its integrated intensity increases with the pressure of pure nitrogen or nitrogen-argon mixture.

The integrated intensities of the 3350Å and 4850Å bands for various nitrogen pressures are listed in Table 10 and plotted in Fig. 17.

Penzes, Cunning and Strausz (1967) and McAlduff, Drysdale and Le Roy (1967) observed a similar increase of the intensities of the bands with nitrogen pressure and suggested on the basis of their results that Hg₂(3₁ᵤ) molecules are formed first and the Hg₂(3₀⁻) molecules result from collisions of the 3₁ᵤ molecules with nitrogen. This is possible because
Fig. 15. The $^3\text{O}_u - ^1\text{P}_g$ fluorescence band at various nitrogen pressures: a, 30 mm Hg; b, 54 mm Hg; c, 94 mm Hg; d, 150 mm Hg.
Fig. 16. The $^3O_u - ^1I_g$ fluorescence band with pure $N_2$ and $N_2 - Ar$ mixture.
<table>
<thead>
<tr>
<th>$N_2$ Pressure (mm Hg)</th>
<th>$I_{3350}$ (arbitrary units)</th>
<th>$I_{4850}$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>3.4</td>
<td>very low</td>
</tr>
<tr>
<td>30</td>
<td>8.5</td>
<td>17</td>
</tr>
<tr>
<td>54</td>
<td>12</td>
<td>31</td>
</tr>
<tr>
<td>94</td>
<td>13</td>
<td>55</td>
</tr>
<tr>
<td>150</td>
<td>14</td>
<td>87</td>
</tr>
</tbody>
</table>
Fig. 17. The variation of the integrated intensities of the $^3 \Sigma_u^- \rightarrow 1 \Pi_g^+$ and $^3 \Pi_u \rightarrow 1 \Sigma_g^+$ fluorescence bands with nitrogen pressure. (o) $^3 \Sigma_u^- \rightarrow 1 \Pi_g^+$ and (e) $^3 \Pi_u \rightarrow 1 \Sigma_g^+$.
the $3^1_u$ state which results from the combination Hg($6^3P_1$) + Hg($6^1S_0$) atoms, and the $3^0_0$ state which results from the combination Hg($6^3P_0$) + Hg($6^1S_0$) atoms, merge into a single $3^3\Sigma^+_u$ state at small internuclear distances. The intersection of the two potential energy curves lies below the dissociation limit of the $3^0_0$ state and therefore the combination of Hg($6^3P_0$) + Hg($6^1S_0$) atoms, will populate both states with equal probability. Since no dissociation is possible along the $3^1_u$ potential curve, collisional stabilization may favour this state (Mrozowski, 1937). On this basis it is possible to explain the variation of the band intensities with gas pressure.

As can be seen in Fig. 17, the intensity of the 3350Å band increases almost linearly with nitrogen pressure up to about 50 mm Hg, above which a levelling-off occurs with only a very slight further increase. A similar curve is obtained when the population of the Hg($6^3P_0$) metastable atoms which are formed by collisional quenching of Hg($6^3P_1$) atoms by nitrogen, is plotted against nitrogen pressure, (Kimbell and Le Roy 1960). Since the $3^1_u$ state results directly from the combination of Hg($6^3P_0$) + Hg($6^1S_0$) atoms, the population of this state and thus the intensity of the 3350Å band should vary with nitrogen pressure similarly as the density of the $6^3P_0$ metastable atoms. Collisions of the Hg$_2$($3^1_u$) molecules with nitrogen result in their transfer to the $3^0_0$ state. Since the population of the $3^1_u$ state remains almost constant at nitrogen pressures greater than 50 mm Hg, the density of the $3^0_0$ molecules and thus the intensity of the 4850Å band would be expected to vary linearly with nitrogen pressure as appears, in fact, to be the case.

It is apparent from Fig. 16 that the integrated intensity of the 4850Å band increases also with argon pressure in a nitrogen-argon mixture,
as does the integrated intensity of the 3350Å band (not shown). Since argon is very ineffective in causing collisional transfer of the Hg(6^3P_1) atoms to the 6^3P_0 metastable state (Pringsheim 1949), the observed increase must be due in part to a less efficient destruction of the Hg(6^3P_0) metastable atoms at the walls of the cell resulting from the decrease in the mean free path with increasing pressure; it is well known that at low nitrogen pressures, large numbers of the 6^3P_0 metastable atoms diffuse to the walls of the cell where they are quenched to the ground state (Bigeon 1967). A further increase in the band intensities with argon pressure should result from the increase with pressure of the number of three body collisions involving 6^3P_0 and 6^1S_0 mercury and ground-state argon atoms, resulting in the formation of stabilized mercury molecules.

The change in the shape of the 4850Å band caused by the addition to the cell of pure nitrogen or argon in a nitrogen-argon mixture may be explained by considering the variation in the population of the various vibrational states of the 3^0_u molecules with pressure of the foreign gas. Collisions of the Hg_2(3^1_u) molecules with nitrogen result in their transfer to the 3^0_u state and in the formation of Hg_2(3^0_u) molecules, of which those formed in high vibrational states relax rapidly to a Maxwellian distribution through further collisions with nitrogen molecules. Vibrational relaxation times depend strongly on the vibrational frequency of the molecule. For heavy molecules (such as I_2) colliding with molecules of the same species, such relaxation times have been shown to be of the order of 10^-7 s; foreign gases have been found to be even more effective in causing vibrational relaxation (Cottrell and McCoubrey 1961). The lifetime of the
The $0^+_u$ state, which was quoted by McCoubrey (1954) as $10^{-2}a^2$, represents an average value which depends on the average vibrational energy, and is about $10^5$ times longer than the vibrational relaxation time. Table 11 shows the thermal distribution of vibrational states in the $0^+_u$ molecules.

Since the radiative lifetime of the $0^+_u$ molecules in low vibrational states is very much longer than in the higher states, spontaneous emission should take place preferentially from the higher states which are continuously being repopulated collisionally from the lower states that serve as a reservoir of excited molecules (Mrozowski 1944). At low pressures of nitrogen there is an insufficient number of such collisions to restore the Maxwellian distribution and the populations in the higher vibrational states become depleted. As the nitrogen pressure is increased, the depletion resulting from spontaneous decay is prevented to a progressively larger extent by the increasing number of inelastic collisions.

This causes a shift in the position of the emission maximum to shorter wavelengths. The same argument is applicable to the case of a nitrogen-argon mixture except that there it is the inelastic collisions with argon that are important in transferring $0^+_u$ molecules from lower to higher states.

The collisional transfer of a $0^+_u$ molecule from a low to a high vibrational state requires $220 \text{ cm}^{-1}$ of energy per vibrational quantum. This energy is drawn either from the translational energy of the colliding partners or from the rotational energy in the case of collisions with nitrogen. The process is much less efficient than the reverse process, the collisional transfer of $0^+_u$ molecules from high to low vibrational state by collisions with nitrogen, in which vibrational energy can be exchanged between the two molecules. It should be borne in mind that in nitrogen the vibrational spacing equals $2330 \text{ cm}^{-1}$ and such vibrational exchange can only take place
TABLE 11

The Thermal Distribution of Vibrational States in the $^3\text{O}_u$ Molecules at 300 K

<table>
<thead>
<tr>
<th>Vibrational State $v$</th>
<th>Fraction of Molecules $\Delta N(v)/N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.647</td>
</tr>
<tr>
<td>1</td>
<td>.228</td>
</tr>
<tr>
<td>2</td>
<td>.081</td>
</tr>
<tr>
<td>3</td>
<td>.028</td>
</tr>
<tr>
<td>4</td>
<td>.010</td>
</tr>
<tr>
<td>5</td>
<td>.003</td>
</tr>
<tr>
<td>&gt; 6</td>
<td>.01</td>
</tr>
</tbody>
</table>
when the Hg₂ molecules change their vibrational energy by several quanta. However, even without vibrational exchange, when the change in the vibrational energy of the \( ^3\text{O}_u \) molecules is relatively small, the downward transfer proceeds more efficiently than the upward process which requires energy to be supplied from the kinetic energy continuum. This interpretation of the change in the band shape, which is based on a shift with increasing gas pressure of the vibrational distribution towards higher states is consistent with eq. (41). Figs. (18) and (19) show the calculated spectrum when it is assumed in eq. (41) that the first 27 vibrational states of the \( ^3\text{O}_u \) electronic state are populated according to the Maxwell-Boltzmann distribution corresponding to temperatures of 115°C and 200°C respectively. It may be seen that the position of the fluorescent band peak is progressively shifted towards shorter wavelengths as the temperature is increased reaching the wavelength of 4840Å at 200°C, in very good agreement with the value 4850Å which had been observed at this temperature (Pringsheim 1949).

It should be noted that the position of the band peak at a given temperature for the calculated spectrum depends very strongly on the variation of the electronic transition moment \( R_e(r) \) with internuclear separation. The actual variation \( R_e(r) = e^{23(r_e-r)} \) used in eq. (41) is probably too fast and \( R_e(r) = e^{22.5(r_e-r)} \) may be more realistic. The correct variation of the electronic transition moment may in fact be obtained by requiring the spectrum calculated according to eq. (41) to correspond to the observed spectrum for a range of temperatures. To do this precisely the shape of the band should be observed experimentally at various temperatures and at the same high pressure of a buffer gas to maintain a Maxwell-Boltzmann distribution of the \( ^3\text{O}_u \) vibrational states.
Fig. 18. Calculated spectrum for the $^{3}O_{u}^{+} \rightarrow L_{g}^{+}$ fluorescence band at $T = 115^\circ C$ and using $R_{e}(r) = e^{23(r_{e} - r)}$. 
Fig. 19. Calculated spectrum for the $^3\text{O}_u - ^1\Sigma_g^+$ fluorescence band at $T = 200^\circ$C and using $R_g(r) = \alpha R_0^{-23}(r - R_0)$. 
The dependence of the shape of the 4850Å band on nitrogen pressure observed in this experiment does not agree with the observations of McAlduff, Drysdale and Le Roy (1967) who found the shape of the band to be independent of nitrogen pressure. This disagreement may be due to the fact that the authors employed a set of 5 broad-band pass colour filters to observe various parts of the band but failed to observe a part of the band between 5300Å and 5700Å where the change in shape with pressure is most pronounced.

It may be interesting to speculate why the structure of the \( ^3\text{O}_{u} - {}^1\text{Σ}^+ \) fluorescent band was not observed previously. In the most recent studies, broad-band pass filters or at best small direct-vision spectrometers were used to observe the band (Berberet and Clark 1955; McCoubrey 1954; McAlduff, Drysdale and Le Roy 1967) and it is not surprising that, under these conditions, the band appeared continuous. Most of the early studies were carried out in pure mercury at temperatures of about 200°C, and in some of these investigations high resolution spectrographs were used (Rayleigh 1928). Under conditions of high temperature and high mercury density, the \( ^3\text{O}_{u} - {}^1\text{Σ}^+ \) band was continuous, showing no intensity fluctuations. Wood and Voss (1928) observed that, when the fluorescing mercury vapour was strongly heated at constant mercury density, the 4850Å band disappeared but the 3350Å band was enormously enhanced. They observed the peak of the green band at 4850Å while in the present study at room temperature and with a nitrogen pressure of 150 torr, the band exhibits a peak at 5200Å; at lower nitrogen pressures the peak appears at even longer wavelengths. Kenty and Larson (1953) studied the 4850Å band emitted from a low-current discharge in a mixture of mercury vapour and argon and found that at 115°C the peak emission occurred at 5130Å and was shifted progressively towards
shorter wavelengths as the temperature was increased.

These results indicate that at high temperatures the fluorescence results from the spontaneous decay of $^3O_u$ molecules in very high vibrational states which are continuously formed collisionally from the longer-lived molecules in lower states. The band is continuous because the excited molecules decay to a part of the ground state potential energy curve where the slope is already relatively steep.

(d) Sensitivity of the 4850 Å Band to Quenching by Impurities.

In some early investigations of molecular fluorescence in mercury, the 4850 Å band failed to appear under experimental conditions which should have been favourable for its observation. The reason for this was attributed to the great sensitivity of the band to quenching by impurities. Wood and Voss (1928) found the band to be extremely susceptible to quenching by water vapour. They reported that even extremely small amounts of water vapour were capable of extinguishing the fluorescence and found that, after a few hours of operating the fused silica cell at 250°C, sufficient water vapour was outgassed from the cell walls to destroy the band in spite of long preliminary baking at much higher temperatures. Pringsheim and Terenin (1928) found that the green fluorescence was completely quenched by hydrogen at a pressure of few thousandths of a torr.

In the present experiment, it was found that the addition of about $10^{-3}$ torr of CO to a mixture of mercury and nitrogen destroyed the green fluorescence completely. The addition of trace amounts of $H_2$ enhanced the band slightly but the further addition destroyed the fluorescence completely. Three different bottles of research-grade nitrogen were used in the course of this experiment. It was found that ungettered gas from two
of the bottles produced intense green fluorescence while gas from the third bottle gave rise to only weak fluorescent emission.

It is not surprising that the 4850Å band is so sensitive to quenching by impurities in view of the long lifetimes of the \( \text{Hg}_2(3^0_{u}) \) molecules, the spontaneous decay of which gives rise to the fluorescence, and of the \( \text{Hg}(6^3P_0) \) atoms which are necessary for the formation of the \( \text{Hg}_2(3^0_{u}) \) molecules. It is well known that \( \text{H}_2, \text{H}_2\text{O}, \) and \( \text{CO} \) are very efficient in quenching the \( 6^3P_0 \) mercury metastable atoms to the ground state (Pringsheim 1949). These same gases probably also quench the \( 3^0_{u} \) state to the \( 1^+_{e_g} \) ground state, and even trace amounts should be sufficient to quench totally this band fluorescence because of the very long radiative lifetime of the \( 3^0_{u} \) state.

(e) Construction of Potential Energy Curves for \( \text{Hg}_2 \) Molecules.

Any set of potential energy curves which may be proposed for the \( 3^1_{u}, 3^0_{u} \) and \( 1^+_{e_g} \) states must satisfy a number of requirements in order to be in accord with experimental observations. The potential minimum of the \( 3^1_{u} \) curve, corresponding to an internuclear separation \( r_e^* \) should be located vertically above the \( V(r_e^*) = 0.27 \text{ eV} \) point of the \( 1^+_{e_g} \) ground state curve and the dissociation energy \( D_e^* \) of the \( 3^1_{u} \) state should be 0.84 eV to be in agreement with the \( 1^+_{e_g} \rightarrow 3^1_{u} \) absorption measurements carried out by Kuhn and Freudenberg (1932). The slope of the \( 1^+_{e_g} \) curve near \( r_e^* \) must be steep so that the shape of the fluorescent band resulting from the \( 3^1_{u} \rightarrow 1^+_{e_g} \) transitions should agree with the observed continuous band. The potential minimum of the \( 3^0_{u} \) curve, corresponding to the internuclear separation \( r_e^* \), should be located vertically above a repulsive part of the \( 1^+_{e_g} \) ground state curve with a shallow \( (\approx 0.08 \text{ eV}/\text{A}) \) and approximately
constant slope for a range of internuclear separations \( r, r_e' < 4 < r_e' \), so that the \( ^3\!\_0 \rightarrow ^1\Sigma_u^+ \) bound-continuum transitions might give rise to a fluorescence band with a well-resolved structure. The transitions of \(^3\!\_0\) molecules in \( v' = 0 \) vibrational states to the continuum energy states of the \(^1\Sigma_u^+ \) curve should give rise to the band-edge at 5639Å and thus fix the potential minimum of the \(^3\!\_0\) curve at 2.19 eV above the \( V(r_e') \) point of the \(^1\Sigma_u^+ \) curve. From the 4.67 eV energy of the atomic transition \( 6^3\!\_P \rightarrow 6^1\!\_S \), the dissociation energy \( D_e' \) of the \(^3\!\_0\) state can be calculated as 4.67 - 2.19 - \( V(r_e') \) eV. The value of \( V(r_e') \) is still not known but it is expected to be much smaller than \( V(r_e') = 0.27 \) eV because near \( r_e' \) the slope of the ground state curve must be much smaller than the slope near \( r_e'' \). If \( V(r_e') << 0.27 \) eV, the dissociation energy \( D_e' \) of the \(^3\!\_0\) state would be about 2.4 eV.

Fig. 20 shows a semi-quantitative diagram of the \(^3\!\_1, ^3\!\_0\) and \(^1\Sigma_u^+ \) potential energy curves. The potential energy curve for the \(^3\!\_0\) state is consistent with the following interpretation of the experimental results obtained in the present investigation. The decay of the \( v' = 0 \) state gives rise to the long-wavelength edge of the fluorescent band at 5639Å and the decay of the higher vibrational states produce peaks at progressively shorter wavelengths. The large width of the \(^3\!\_0 \rightarrow ^1\Sigma_u^+ \) fluorescence band results from transitions from a large number of vibrational states of the \(^3\!\_0\) state to a nearly horizontal part of the \(^1\Sigma_u^+ \) curve where the slope is small. At small internuclear distances the \(^3\!\_0\) curve merges with the \(^3\!\_1\) curve into a \(^3\Sigma_u^+ \) curve. This occurs in a region which lies slightly below the dissociation energy of the \(^3\!\_0\) state, as it should to account for the formation of molecules in the \(^3\!\_1\) state from the combination \( \text{Hg}(6^3\!\_P) + \text{Hg}(6^1\!\_S) \).
Fig. 20. Potential energy diagram for the $^3\Sigma_u^-$ and $^3\Sigma_u^+$ mercury molecules.
The shape of the $^3O^-_u$ curve obtained from the present study generally agrees with that proposed by Krozowski (1937) which was based on a combination of theoretical and experimental arguments. The two curves are in agreement as to the large depth of the potential well but disagree as to the relative values of $r_e'$ appropriate to the $^3O^-_u$ and $^3I^-_u$ curves. In Fig. 20, $r_e^e' < r_e'$ whereas Krozowski places the potential minimum of the $^3I^-_u$ curve at a larger internuclear separation than the potential minimum of the $^3O^-_u$ curve. Nevertheless, the position of the crossing point between the $^3O^-_u$ and $^3I^-_u$ curves is the same in both cases.

The curve shown in Fig. 20 is significantly different from the forms proposed by McCoubrey (1954) and Finkelnburg (1964), both of which exhibit shallow potential wells. The fact that the $^3O^-_u \rightarrow ^1\Sigma^+_e$ band possesses a sharp edge at 5639Å and a sequence of intensity maxima, indicates conclusively that the band originates from spontaneous decay of molecules in the $^3O^-_u$ state which has a deep potential well. No structure would be present if the band resulted from a collision-induced emission by molecules in a $^3O^-_u$ state having a shallow well, as was suggested by McCoubrey (1954). In the latter process the collision partner would be expected to remove an indeterminate amount of excitation energy from the Hg$_2$ molecule and the resulting emission would extend continuously over the wavelength region of the band.

It should be noted that in Fig. 20 the potential minimum of the $^3I^-_u$ curve lies about 1.8 eV above the potential minimum of the $^3O^-_u$ curve. This large energy separation effectively prevents the collisional transfer of molecules from the $^3O^-_u$ state to the $^3I^-_u$ state by inelastic collisions and makes the explanation of the common persistence time of the $^3I^-_u$ and
$^3O_u$ bands, which is based on an effective collisional transfer of the molecules in the $^3O_u$ state to the $^3l_u$ state, somewhat improbable. An alternative interpretation of the common persistence time which is consistent with the results of this investigation, may be obtained by considering further the mechanism of formation of the mercury molecules in the $^3l_u$ and $^3O_u$ states. In pure mercury vapour at relatively high vapour pressure of about 17 mm Hg, the first step in the molecular formation process involves the excitation of the Hg($^6S_o$) to the $^6P_1$ resonance state by 2537Å resonance radiation. Inelastic collisions of atoms in the $^6P_1$ state with $^6S_o$ ground state atoms result in the quenching of the $^6P_1$ atoms to the $^6P_o$ metastable state. The combination of the $^6P_o$ atoms with two $^6S_o$ ground state atoms results in the formation of stabilized mercury molecules in the $^3l_u$ or in the $^3O_u$ states (Mrozowski 1937). The $^3O_u$ molecules are likely formed in highly excited vibrational states which have short radiative lifetimes compared with the $^6P_o$ metastable atomic state, and which do not rapidly become thermalised at this mercury vapour pressure. Thus in the afterglow the populations of the $^3l_u$ and $^3O_u$ states should decay with the population of the $^6P_o$ metastable state. The population of the $^6P_o$ state decays as the square of the mercury density and consequently the persistence times of the two bands should decrease with the square of the mercury density, as has in fact been observed by McCoubrey (1954).
IV. CONCLUSIONS

The sodium-molecule $^2P$ mixing cross sections $Q_{12}$ and $Q_{21}$ were found to be of the same order of magnitude as the corresponding sodium-noble gas cross sections (Krause 1966). A similar relationship has been found for the potassium-molecule collisions (McGillis and Krause 1968). This suggests that the interaction which causes spin-orbit decoupling in an excited alkali atom is not appreciably stronger for nonpolar diatomic molecules than for noble gas atoms. In fact, the dominant interaction responsible for excitation transfer between the $^2P$ states in sodium appears to be the van der Waals interaction which also operates in the case of sodium-noble gas collisions. The longer-range interaction involving the permanent quadrupole moment of the molecule, appears not to be effective in inducing transitions between the $^2P_J$ states.

The role of the internal molecular structure in determining the transfer of excitation energy in alkali-molecule collisions is still not clear, but it appears not to be of great importance for the case of sodium-molecule and potassium-molecule collisions where the energy defect between the $^2P$ states is small and is easily supplied from or converted to translational energy as in the case of sodium-noble gas and potassium noble-gas collisions. The cross sections for mixing collisions between rubidium (Hrycyszyn and Krause 1970) or cesium (McGillis and Krause 1968) and various isotopes of hydrogen, indicate that the excitation transfer process is greatly enhanced if the splitting between the molecular levels corresponds closely to the energy separation of the alkali $^2P_J$ states. No evidence was found, however, to suggest the possibility of a resonance effect. McGillis and Krause (1969) and later Walentynowicz, Phaneuf and
Krause (1971) have been able to relate the mixing cross sections observed for cesium in collisions with polyatomic molecules, to the molecular vibrational frequencies. Although the energy involved is too small to directly excite the molecular vibrations, the molecules generally vibrate several times during the collision time ($\sim 10^{-13}$ sec). This vibration may be instrumental in inducing the mixing. Further experiments which are now in progress should provide additional insight into the mechanism of excitation transfer.

The molecules responsible for the $3350\AA$ and $4850\AA$ band fluorescence in mercury appear to be formed according to the mechanism in which mercury atoms in the $6^3P_1$ state are first converted to metastable $6^3P_0$ atoms by quenching collisions with nitrogen. Some of the metastable atoms are then converted to the $Hg_2(^31_u)$ molecules by three-body collisions involving a ground state mercury atom and a nitrogen molecule. Finally, some of the $Hg_2(^31_u)$ molecules are transferred to the $3_0^-$ metastable state by collisions with nitrogen. The spontaneous decay of the $Hg_2(^31_u)$ and $Hg_2(^30_u)$ molecules to the $1\Sigma^+_g$ ground state gives rise to the $3350\AA$ and $4850\AA$ band fluorescence respectively.

Electronic transitions from the various vibrational states of the $3_0^-$ electronic state to the continuous region of the $1\Sigma^+_g$ ground state, where the slope is small ($\approx 0.08$ eV/A) give rise to a sequence of intensity peaks. Transitions from each vibrational state result in a primary peak accompanied by a number of secondary peaks. The distribution of the $3_0^-$ molecules among the various vibrational states determines the shape of the band and the position of its intensity peak. The addition of more nitrogen or argon results in a more effective repopulation of the high
vibrational states of the $^{3}O_{u}^{-}$ molecules, which become depleted at low pressures as a result of spontaneous decay from the long lived low vibrational states, thus effecting a change in the shape of the band and in the position of its intensity peak. The change in the shape of the band with temperature and gas pressure is being investigated further in order to provide additional information about the effectiveness of collisional transfer of vibrational energy.
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VITA AUCTORIS

I was born on April 4, 1944 in Glozang, Yugoslavia and came to Canada with my parents in 1953. I attended the Kingsville District High School and upon graduation in 1963 I enrolled at the University of Windsor with an Ontario Scholarship and an entrance scholarship; the latter I maintained until my graduation in Honours Physics in 1967. I then entered the Faculty of Graduate Studies and received a Master Degree in Physics in 1968 and shortly after proceeded to work towards a Ph.D. degree in Physics. Throughout my years as a graduate student, I was aided by a National Research Council Bursary.