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Collisional excitation transfer from excited mercury to ground state sodium atoms.

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COLLISIONAL EXCITATION TRANSFER FROM EXCITED MERCURY TO GROUND STATE SODIUM ATOMS

by

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ABSTRACT

The method of sensitized fluorescence was used to determine the absolute cross-sections for excitation transfer from excited $Hg(6^3P_1)$ atoms to various S, P and D states of sodium. A vapour mixture of mercury and sodium atoms was irradiated with 2537Å Hg resonance radiation and the intensities of the sensitized sodium spectral components resulting from the decay of collisionally-populated levels were measured. The vapour pressure of the mercury was maintained below 10^{-5} torr to avoid imprisonment of resonance radiation. The observed cross-sections were corrected for cascade transitions from higher sodium levels. In all, twenty-two effective cross-sections were calculated ranging from $0.05Å^2$ to $40Å^2$. A pronounced resonance was observed between the $Hg(6^3P_1)$ state and near-lying sodium states. The results of this investigation for Hg-Na collisions were compared with previously obtained cross-section for K-Rb and Rb-Cs mixtures, and a similar dependence of the cross-sections on ΔE was indicated by the three systems.

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I INTRODUCTION

During the past fifty years much effort has been devoted to the study of inelastic collisions during which electronic excitation energy is transferred between collision partners. Sensitized fluorescence[(1)] resulting from collisional transfer of excitation provides quantitative information about the inelastic collisions in the form of collision cross-sections leading to better understanding of interatomic and intermolecular interactions.

The term sensitized fluorescence was originally applied to excitation transfer occurring during an inelastic collision between different atomic species[(2)], but has been extended to cover inelastic collisions between atoms of the same species, in which the transfer of excitation takes place between fine structure states[(3)]. Generally, sensitized fluorescence is observed when a vapour mixture of two kinds of atoms, A and B, is irradiated with resonance radiation appropriate to species A. When an excited atom A^* collides inelastically with a ground state atom B, the excitation energy is transferred to B, either as excitation energy, translational energy, or both. Provided the densities of A and B are relatively low and the time between collisions (A^*, B) exceeds the lifetime of B^*, the dominant process of energy loss for B^* is sensitized fluorescence.

If there are several levels of B close in energy to the optically excited level of the sensitizing species A, the most efficient non-radiative excitation transfer will be to those B^* levels differing by a small amount of energy, ΔE, from the excited state of A, because collisional transfer occurs with a higher probability when the least amount of excitation energy is converted into translational energy.

A cross section for an inelastic collision such as (A^*, B) represents the probability of collisional deactivation of A^* and excitation of electronic states B^*. According to Franck's empirical rule, cross sections for excitation transfer decrease with the increase of the resonance defect ΔE. Knowledge of the absolute cross-sections for energy transfer is of fundamental importance in understanding such diverse phenomena as flash photolysis, flames, discharges, shocks, auroras and stellar atmospheres.

As early as 1920-1930 sensitized fluorescence resulting from collisional transfer of excitation energy was being studied but without any attempt to calculate the absolute cross-sections. In 1922 Cario and Franck irradiated a mixture of mercury and thallium with 2537Å mercury resonance radiation and observed a large number of thallium spectral components in addition to the mercury resonance line[2]. Sensitized fluorescence was also observed by Cario and Franck in the vapours of cadmium and silver with Hg^* as the sensitizer[2,4]. Winans and his co-workers sensitized zinc, tin, iron and chromium using mercury as the primary excited species[5,6,7,8].

From about 1940 to 1955 there was little progress in the field of sensitized fluorescence. Then, the advent of new techniques and better developed equipment made possible a more quantitative study of energy transfer. Within the past decade or so, investigations of sensitized fluorescence have been carried out and absolute cross-sections have been calculated for mixtures of mercury and thallium [Kraulinya and Lezdin 1966; Hudson and Curnutte 1966][9,10]; mercury and zinc [Sosinskii and Morozov 1965][11]; and cadmium and cesium [Friedrich and Seiwert 1957][12]. Cross-sections for collisions between two alkali metals have been reported. Systems such as rubidium and cesium [Czajkowski, McGillis and Krause 1966][13], and potassium and rubidium [Hrycyshyn and Krause 1969;[14] Ornstein and Zare 1969; Stacey and Zare 1970][15,16,17] have been studied.

The measured cross-sections which, in most cases, were determined only over a small range of ΔE, did indicate a dependence of the cross-section on ΔE as predicted by Franck's rule. It should be emphasized that although collision cross-sections are velocity dependent, the various cross-sections[3] have been obtained for a variety of collision partners ($Na^* - Na$, $K^* - K$, $Rb^* - Rb$, $Cs^* - Cs$, K - Rb, Cs - Rb etc.) having different relative velocities. The velocity dependence of cross-sections has been shown to be critical [A. Gallagher][18] but its form has not been predicted theoretically. For this reason, no satisfactory general formulation concerning the dependence of the cross-sections on ΔE has been proposed.

The investigation of sensitized fluorescence in sodium with Hg* as the sensitizer lends itself ideally to the study of Franck's rule. Mercury excitation energy may be transferred from the $Hg(6^3P_1)$ state to more than 20 excited sodium levels which decay emitting radiation in the u.v. and visible spectral regions and have a large range of ΔE values. Several studies involving Hg - Na mixtures have been performed.

Beutler and Josephy (1929) originally observed the sensitized fluorescence of sodium vapour induced by inelastic collisions with excited mercury atoms[19]. The intensities of the sensitized lines were measured photographically, but no cross-sections were calculated. Beutler and Josephy did, however, observe the greater probability of excitation transfer to sodium levels lying close to the 6^3P_1 state of mercury.

More recent investigations of the mercury-sodium system have been carried out by Frisch and Kraulinya (1955)[20], Rautian and Sobelman (1960)[21], and Frisch and Bochkova (1961)[22]. The most extensive attempt to determine the absolute cross-sections for excitation transfer in (Hg*, Na) collisions has been conducted by E.K. Kraulinya (1964; 1968; 1969)[23,24,25]. She measured the absolute intensities of the sensitized lines photoelectrically by comparison with the continuous spectrum of a hydrogen lamp. Kraulinya determined the densities of ground-state Na atoms and of excited Hg atoms by reabsorption of the wavelength components $\lambda_{Na} = 3302$ Å and $\lambda_{Hg} = 4358$ Å, and corrected the collision cross-sections for cascade transitions. Her results did not indicate, however, very marked resonance in the cross-sections with respect to ΔE, but maintained relatively high values even for large energy defects of ~1 eV. Kraulinya interpreted these results on the basis of quasi-molecular formation and proposed a model which departed from the usual binary collision mechanism.

In this investigation the absolute cross-sections for collisional excitation transfer from excited mercury to ground-state sodium atoms have been determined under carefully controlled experimental conditions. The absolute intensities of the sensitized sodium lines were measured using a photomultiplier calibrated with respect to spectral sensitivity. The density of ground-state sodium was determined by a quasi-absorption method using 5890Å sodium resonance radiation. Calculation of the sodium transition probabilities was accomplished with the aid of the same sodium oscillator strengths [Anderson and Zilitis 1963][26] as were used by Kraulinya.

It was intended that the absolute cross-sections should maintain some basis of comparison with Kraulinya's results but should offer a greater degree of accuracy. Moreover, it was hoped to find evidence for or against Kraulinya's proposed mechanism for energy transfer involving quasi-molecular formation.

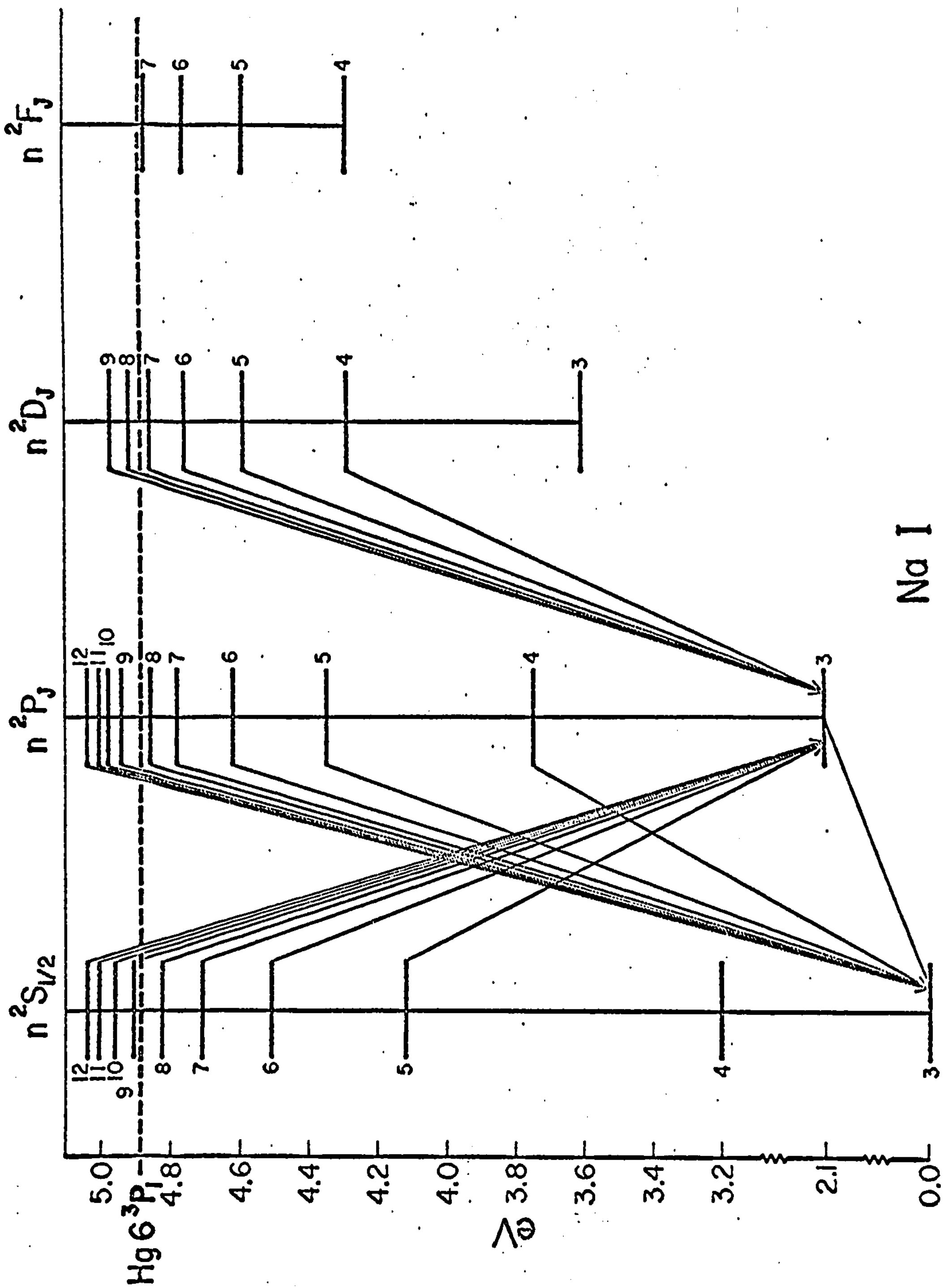

Fig. 1 The Hg and Na energy levels involved in sensitized fluorescence of sodium. Only those transitions are indicated which correspond to the components observed in the fluorescent spectrum.

TABLE I

Wavelength components of the Na spectrum in sensitized fluorescence

Transitions	λ (Å)	Transitions	λ (Å)
10S → 3P	4345, 4342	12P → 3S	2464
9S → 3P	4423, 4420	11P → 3S	2475
8S → 3P	4545, 4542	10P → 3S	2491
7S → 3P	4752, 4748	9P → 3S	2512
6S → 3P	5153, 5149	8P → 3S	2544
5S → 3P	6161, 6154	7P → 3S	2594
		6P → 3S	2680
		5P → 3S	2853
9D → 3P	4325, 4321	4P → 3S	3303
8D → 3P	4393, 4390		
7D → 3P	4498, 4494		
6D → 3P	4669, 4665		
5D → 3P	4983, 4979		
4D → 3P	5688, 5683		

II THEORETICAL

Consider a mercury-sodium vapour mixture which is continuously irradiated with 2537Å Hg resonance radiation, then

$$Hg(6^1S_o) + h\nu(2537Å) \rightarrow Hg(6^3P_1) \quad (1)$$

As a result of inelastic collisions between excited $Hg(6^3P_1)$ and ground-state $Na(3^2S_{1/2})$ atoms, part of the mercury excitation energy is transferred to the sodium in the following manner:

$$Hg(6^3P_1) + Na(3^2S_{1/2}) \rightarrow Hg(6^1S_o) + Na(n^2S_{1/2}) \quad (2)$$

$$Hg(6^3P_1) + Na(3^2S_{1/2}) \rightarrow Hg(6^1S_o) + Na(n^2P_J) \quad (3)$$

$$Hg(6^3P_1) + Na(3^2S_{1/2}) \rightarrow Hg(6^1S_o) + Na(n^2D_J) \quad (4)$$

If the experiment is performed at relatively low mercury and sodium vapour pressures, and if the time between collisions is greater than the lifetime of the excited state of sodium, the dominant deexcitation process is spontaneous emission. The allowed transitions belonging to the sodium series nS→3p, nP→3s, nD→3p are presented in Fig. 1. The various wavelengths corresponding to these sensitized spectral components of sodium are listed in Table I.

In general, the absolute intensity of a spectral component arising from a transition from a higher energy level k to a lower energy level i is given by[27]:

$$I_{ki} = N_k A_{ki} h\nu_{ki} + N_k B_{ki} \rho(\nu_{ki}) h\nu_{ki} \quad (5)$$

where N_k is the density of atoms in the k^{th} state, A_{ki} and B_{ki} are the respective Einstein coefficients for spontaneous and induced transitions from level k to level i, h is Planck's constant, ν_{ki} is the spectral frequency corresponding to the transition $k \rightarrow i$, and $\rho(\nu_{ki})$ represents the density of the radiation with frequency ν_{ki} as shown in Fig. 2.

Stimulated or induced transitions can be neglected since the radiation density $\rho(\nu_{ki})$ is small. In this case, the absolute intensity of a spectral line can be written as:

$$I_{ki} = N_k A_{ki} h \nu_{ki} \tag{6}$$

The density of ground state $Na(3^2S_{1/2})$ atoms excited per sec. due to inelastic collisions with excited $Hg(6^3P_1)$ atoms is given by

$$\Delta N(Na^*) = N_o(Na)N(Hg^*)\ Q_{ok} \cdot v_r \tag{7}$$

where $N_o(Na)$ is the ground state density of sodium, $N(Hg^*)$ is the density of mercury atoms in the 6^3P_1 state, Q_{ok} is the effective cross-section for an inelastic collision causing excitation transfer to a particular sodium level k, and v_r is the relative velocity of the colliding partners given by

$$v_r = \sqrt{\frac{8kT}{\pi\mu}} \tag{8}$$

where k is Boltzmann's constant, T is the temperature of the vapour mixture in deg.K, and μ is the reduced mass of the colliding partners.

Since the profile of the Hg 2537Å component emitted by the rf oscillator is narrow and not self-reversed, the

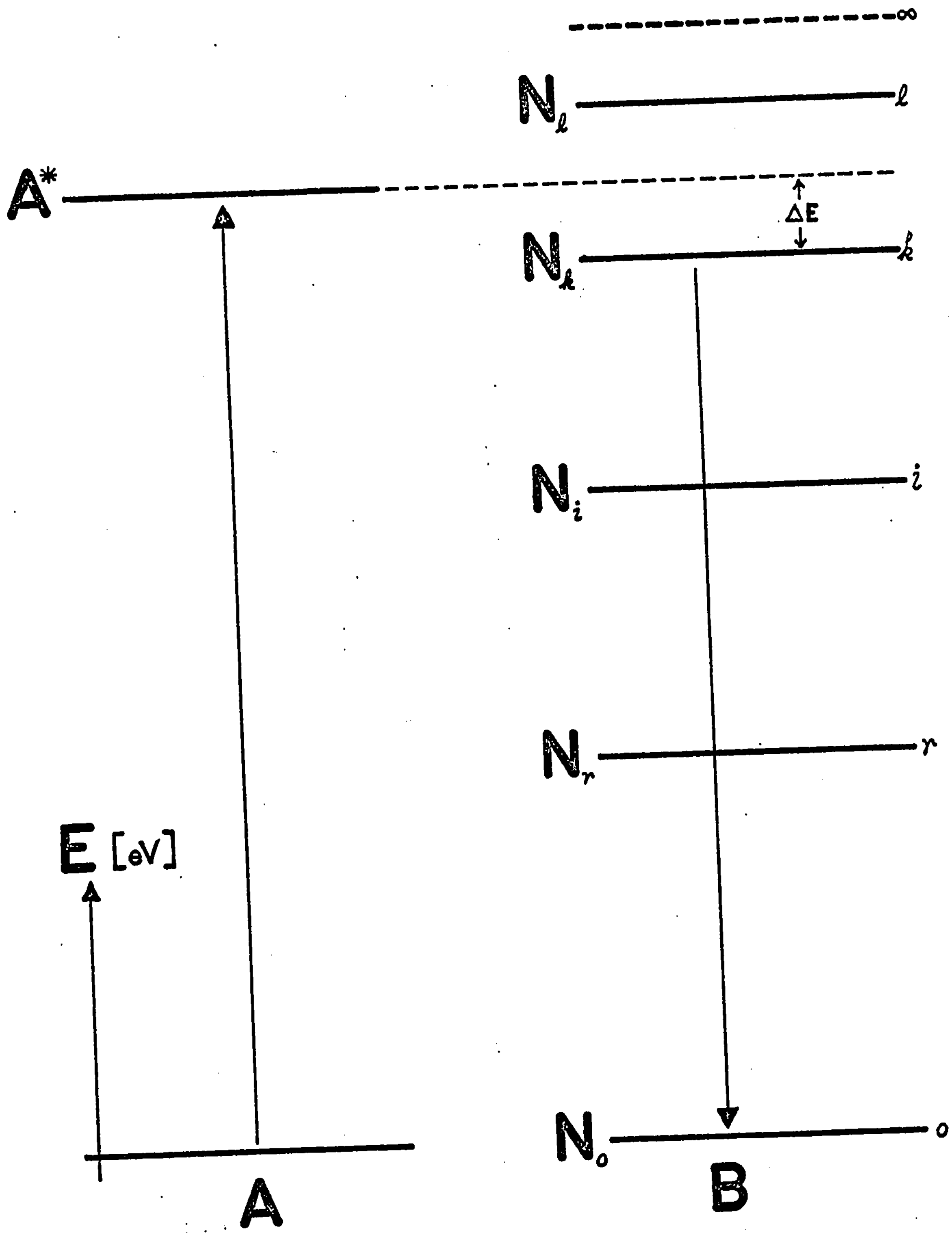

Fig. 2 Atomic energy level labelling scheme for excitation transfer
A* is the optically excited species;
B* states are excited by energy transfer during inelastic collisions (A*, B).

mercury 6^3P_1 atoms have a Maxwellian velocity distribution and the use of the relative velocity v_r is justified in relation to the colliding partners.

If the 6^3P_1 level of mercury is being excited continuously with monochromatic light, the equilibrium conditions for the k^{th} level of sodium may be written:

$$\Delta N_{ok} + \sum_{\ell=k+1}^{\infty} \Delta N_{\ell k} = \sum_{r=k-1}^{o} \Delta N_{kr} + \Delta N_{ko} \qquad (9)$$

In Eq. (9) ΔN_{ok} and ΔN_{ko} represent respectively the incremental increase in the population of the k^{th} sodium level due to inelastic collisions with $Hg(6^3P_1)$ atoms and the decrease in the population of the k^{th} sodium level due to quenching collisions with $Hg(6^1S_o)$ atoms. The summation on the left hand of Eq. (9) represents the contributions to the population of the k^{th} level by cascade transitions from higher-lying sodium levels, and the summation on the right hand of Eq. (9) indicates the depopulation of the k^{th} level due to spontaneous emission.

A further simplification of Eq. (9) yields:

$$\Delta N_{ok} + \sum_{\ell=k+1}^{\infty} N_\ell A_{\ell k} = N_k \sum_{r=k-1}^{o} A_{kr} + \Delta N_{ko} \qquad (10)$$

Substituting Eq. (7) into Eq. (10), an expression is obtained involving the effective cross-section Q_{ok}

$$N_o(Na)N(Hg^*)Q_{ok}v_r + \sum_{\ell=k+1}^{\infty} N_\ell(Na)A_{\ell k}$$
$$= N_k(Na) \sum_{r=k-1}^{o} A_{kr} + N_o(Hg)N_k(Na^*)Q_{ko}v_r \qquad (11)$$

where Q_{ko} is the cross-section for the reverse transfer of excitation from the k^{th} level of sodium to the 6^3P_1 state of mercury. The two cross sections Q_{ok} and Q_{ko} are related in the following way through the principle of detailed balancing[28]

$$g_m p^2 Q_{ok} = g_k p'^2 Q_{ko} \quad (12)$$

where g_m and g_k are the statistical weights and p and p' are the momenta of mercury atoms in the 6^3P_1 state and sodium in the k^{th} state respectively. It is possible to simplify Eq. (11) using Eq. (12), in order to obtain an expression for the collision cross sections.

$$Q_{ok} = \frac{N_k(Na^*) \sum_{r=k-1}^{o} A_{kr} - \sum_{\ell=k+1}^{\infty} N_\ell(Na^*)A_{\ell k}}{N_o(Na)N(Hg^*)v_r - N_o(Hg)N_k(Na^*)\left(\frac{g_m p^2}{g_k p'^2}\right) v_r} \quad (13)$$

Under the experimental conditions of this investigation the product $N_o(Hg)N_k(Na^*)$ is approximately five orders of magnitude smaller than the product $N_o(Na)N(Hg^*)$, and thus the second term in the denominator of Eq. (13) may be neglected.

The population of the k^{th} excited level of sodium N_k is related to the experimentally measured absolute intensity I_{ki} by Eq. (6). A rearrangement of Eq. (6) yields:

$$N_k = \frac{I_{ki}}{A_{ki} h\nu_{ki}} \quad (14)$$

Substituting Eq. (14) into Eq. (13), the form of the effective cross-section for collisional excitation transfer from $Hg(6^3P_1)$ atoms to the k^{th} excited level of sodium becomes:

$$Q_{ok} = \frac{1}{N_o(Na)N(Hg^*)v_r} \left[\frac{I_{ki} \sum_{r=k-1}^{o} A_{kr}}{A_{ki} h\nu_{ki}} - \sum_{\ell=k+1}^{\infty} N_\ell(Na) A_{\ell k} \right] \quad (15)$$

Equation (15) applies to collisional transfer to sodium states lying below the $Hg(6^3P_1)$ level. For collisional transfer to excited sodium states lying above 4.88 eV, some translational energy of the colliding partners is converted into excitation energy of the sodium. Assuming a Maxwell-Boltzmann energy distribution in the atomic vapour, only the fraction α of the inelastic collisions for which the relative energy of the colliding partners is greater than ΔE, participates in excitation transfer. The fraction of the inelastic collisions leading to excitation of sodium states lying above 4.88 eV is given by[29]

$$\alpha = \frac{2}{\sqrt{\pi}\,(kT)^{3/2}} \int_{\Delta E}^{\infty} e^{-\frac{E}{kT}} \sqrt{E}\, dE \quad (16)$$

where ΔE is the energy separation between the $Hg(6^3P_1)$ level and a particular sodium level. For excited sodium levels with excitation energy less than 4.88 eV, $\alpha = 1$.

The last term in Eq. (15) is a correction for cascade transitions. This correction term may be neglected when dealing with excited sodium states close to the 6^3P_1 level of mercury; however, cascade transitions play an important role in populating sodium S, P, and D levels removed by more than 0.15 eV from the $Hg(6^3P_1)$ state.

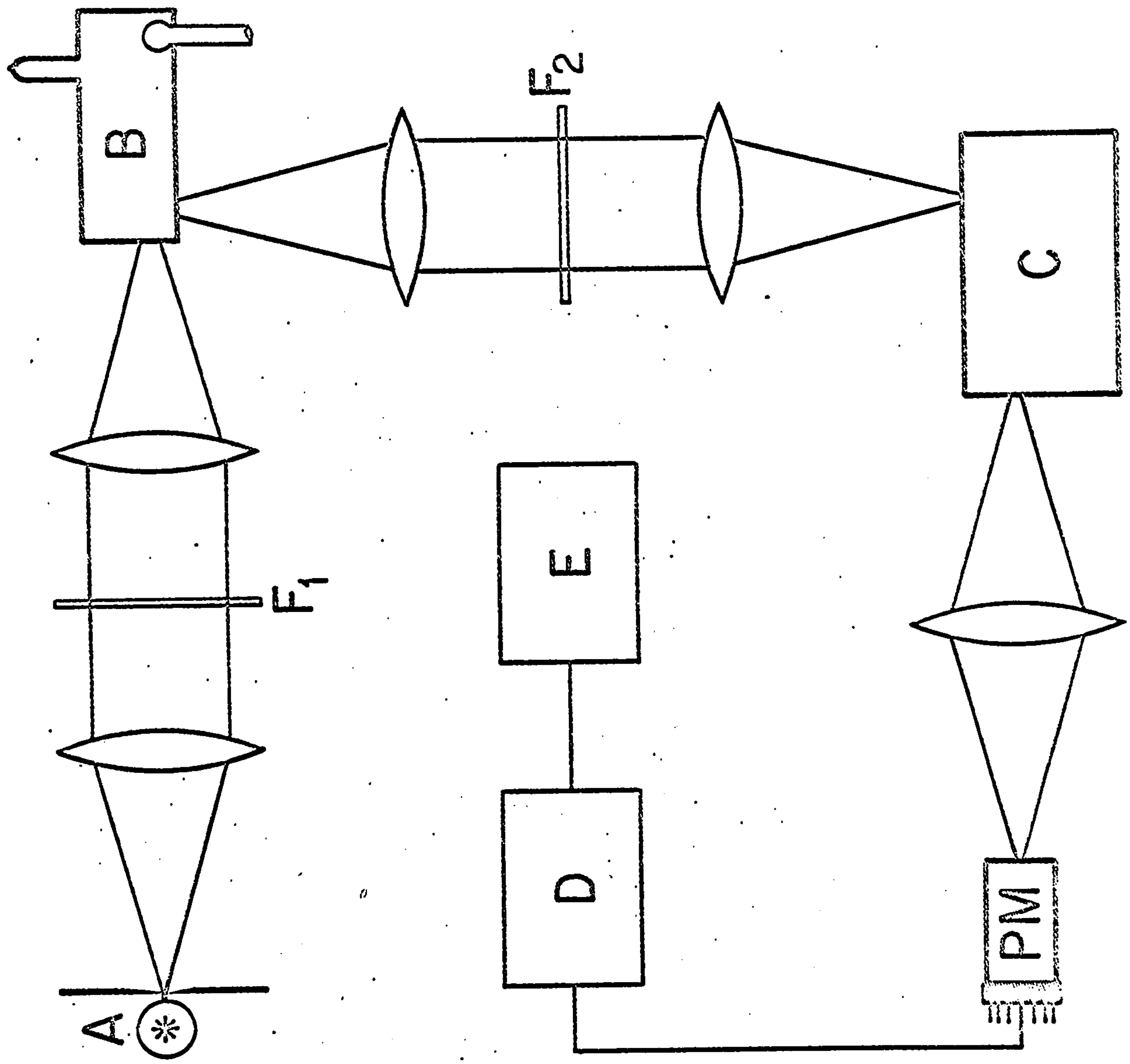

Fig. 3 Arrangement of the apparatus:

A, mercury rf lamp; B, fluorescence cell; C, spectrometer; D, picoammeter; E, strip chart recorder; PM, photomultiplier; F_1 and F_2, 2537Å transmission filter and neutral density filter, respectively.

III EXPERIMENTAL

A. Description of the Apparatus

A schematic diagram of the apparatus is shown in Fig. 3. The source of exciting light was a mercury rf lamp positioned in front of an adjustable slit. Light from the rf lamp was made parallel and was passed through an interference filter which had a peak transmission of 22% at 2537Å, rendering the beam monochromatic within one part in 10^3. The exciting beam was focused in the fluorescent cell containing a mixture of mercury and sodium vapours. The resulting fluorescence due to collisional excitation transfer was observed at right angles to the direction of the incident beam. The fluorescent light was resolved by means of a grating monochromator whose output was brought to a focus on the photocathode of a cooled photomultiplier. A picoammeter was used to amplify the P.M. signal and its output was recorded on a strip chart.

B. The rf Oscillator and Spectral Lamp

The radio-frequency oscillator used to excite the mercury discharge is shown in Fig. 4. This type of rf oscillator has been used previously by Stupavsky (1971)[30]. A Fluke model 407DR served as a power supply for the rf oscillator.

The mercury discharge bulbs were prepared on a separate vacuum station. The bulbs were made of quartz and cylindrically shaped, approximately 1.5 cm in diameter and 8 cm long, tapered at the bottom. A small amount of mercury was

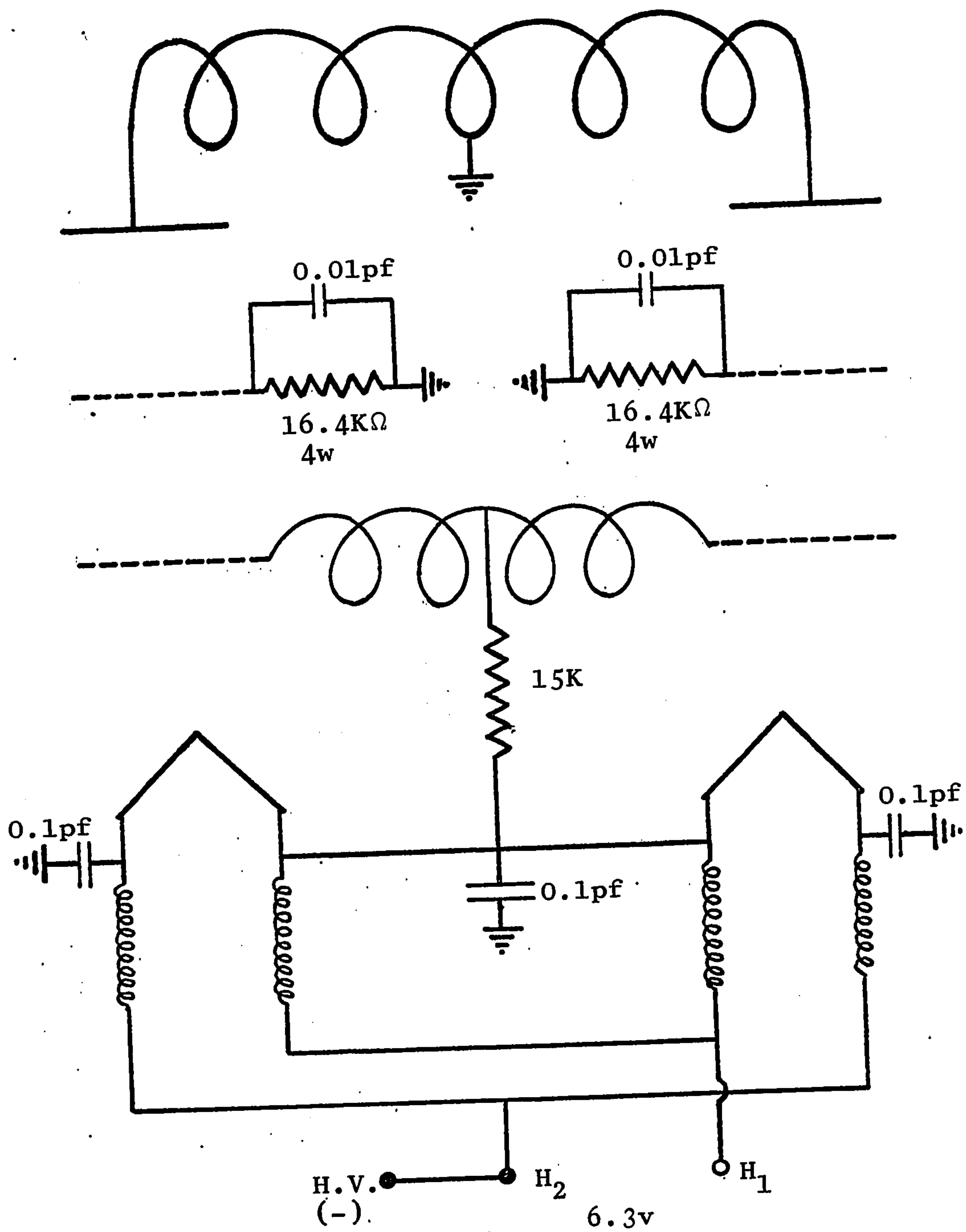

Fig. 4 RF oscillator employing two Philips 8165 power tubes

distilled into each bulb and argon was added to act as the carrier gas for the electrodeless discharge. An argon pressure of about 1 torr provided the best stability of the lamps and the best effectiveness for the excitation of mercury resonance radiation.

In actual operation, the mercury lamp was air-cooled and was maintained at an effective oscillator voltage and rate of cooling to provide optimal intensity and stability of the 2537Å mercury resonance radiation.

C. The Fluorescence Cell

The quartz fluorescence cell, shown in Fig. 5, was designed with the aim to keep reabsorption of resonance radiation to an absolute minimum, by limiting the distance which the exciting and the fluorescent light had to traverse through the absorbing vapour. In the experimental arrangement, the exciting beam was focused just inside the rectangular corner formed by the entrance and observation windows. As a result, the optical path through the cell was kept to less than 1 mm.

Ordinary quartz of optical quality, when irradiated with ultraviolet light, fluoresces very strongly in a band extending from 3500Å to 4800Å. Since this undesirable fluorescence would exceed at least ten-fold the intensity of the sodium sensitized fluorescence, special non-fluorescent quartz was used for the windows of the cell. The entire cell was painted externally with aquadag to reduce the amount of

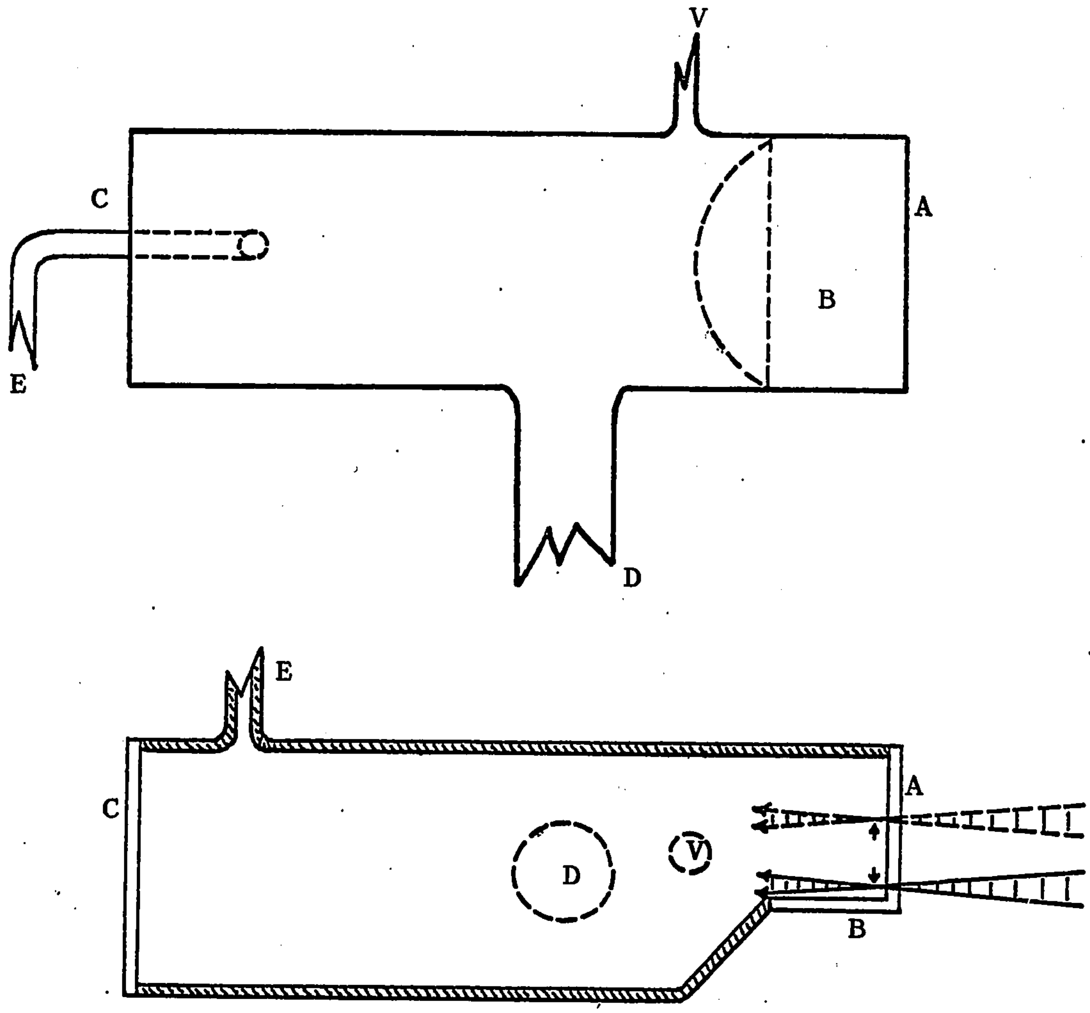

Fig. 5 The fluorescence cell.
A, entrance window; B, exit window for the fluorescent light; C, viewing window; D and E, connections to side-arms with sodium and mercury respectively; V, capillary to vacuum system. Two extreme positions of light beams during Na vapor-pressure calibration are also shown.

scattered light entering the spectrometer. During the painting procedure, the entrance and exit apertures were shaped in the form of slits to ensure a well-defined geometry which was required for absolute intensity measurements. A third window perpendicular to the longitudinal axis of the cell was provided to facilitate preparatory optical alignment with a He - Ne laser and to monitor the corrosive action of the sodium vapour on the quartz. After prolonged contact with sodium vapour at temperatures of 230°C, the quartz windows showed a discoloration coupled with a change in transmission characteristics in both visible and ultraviolet spectral regions. The discoloration was easily removed by rinsing the fluorescence cell from time to time.

Two side-arms were attached to the cell. One side-arm containing the metallic sodium was approximately 22 cm. long and 16 mm. in diameter to ensure efficient transport of the sodium vapour to the fluorescence cell [Hoffmann 1962][31]. The side-arm extended down through a metal sleeve between the inner and outer box sections of the main oven into a connecting side-oven. The side-oven consisted of a brass cylinder wound with copper tubing and several layers of insulating asbestos tape on the exterior. A Neslab ultra-thermostatic bath circulated Dow Corning 200 fluid through the copper tube and provided accurate temperature control of the sodium side-arm to within ± 0.2°C. In this manner, the temperature of the side-arm effectively controlled the sodium vapour pressure in the main body of the cell. To prevent the condensation of sodium on the cell windows, the side-arm was kept at 20°C below the temperature of the cell at all times.

The second side-arm, containing mercury, was connected to the fluorescence cell at a separate position by a capillary tube 40 cm. in length and 0.7 mm. in diameter to prevent the migration of sodium to the mercury reservoir. A close-fitting heater made of chromel wire and insulating tape capped the end of the side-arm. Current to the heater wire was delivered through a variac in series with a step-down transformer.

D. <u>The Main Oven</u>

The fluorescence cell was mounted inside an aluminum box which served as a main oven. Twelve G.E. strip heaters were secured to the external surface of this aluminum box. The heaters were connected in parallel through a variac transformer to a regulated power supply. The entire oven was positioned centrally in a transite box equipped with a water-cooled jacket. The apertures where the two side-arms passed through the inner or outer box were packed with asbestos pulp to improve the thermal insulation. It was possible to maintain the main oven temperature within $\pm$ 1.0°C, in a range 100-250°C. The temperatures were measured by copper constantum thermocouples placed at various positions on the fluorescence cell and the side-arms.

Non-fluorescent quartz plates were mounted in appropriately placed apertures in the inner and outer boxes and served as the entrance and observation windows.

E. The Vacuum System

The fluorescence cell was connected to a vacuum station by means of a capillary approximately 40 cm. long and 0.5 mm. in diameter which effectively prevented the migration of atomic vapours from the cell, over a period of several weeks of operation at temperatures of 230°C. The system was evacuated continuously by an Edwards E02 diffusion pump, backed with a rotary pump. A CVC ionization gauge Type GIC-110B and an Edwards Pirani gauge Model 8/1 monitored the vacuum. The station was capable of maintaining a vacuum of the order of 5×10^{-8} torr.

F. The Absorption Cell

The fluorescent light emerging from the cell was passed either through a mercury absorption cell or through a neutral density filter. The quartz absorption cell, containing a trace of mercury, was heated by several turns of electrical heating tape until the 2537Å mercury line was almost completely absorbed. This absorption cell made possible the measurement of the weak components in the nP → 3s series of sodium in the ultraviolet spectral region, which were close to the relatively intense 2537Å mercury resonance line. During the measurements on the nS → 3p and nD → 3p fluorescent series in the visible region, the mercury absorption cell was replaced by a neutral density filter to attenuate the Hg 2537Å line which would otherwise produce unwanted background noise during scanning of the visible components of sodium.

G. The Monochromator and Photomultiplier Tube

The fluorescent light was resolved by a Jarrell-Ash model 82-000 spectrometer. This particular monochromator was equipped with a 1180 grove/mm. diffraction grating blazed at 3000Å in the first order and had an aperture of f/8.6, a focal length of 500 mm. and a reciprocal dispersion of 16Å/mm. in the first order.

The output of the monchromator was focused on the photocathode of a 16 stage ITT F-4085 photomultiplier tube mounted in a cryostat cooled with liquid nitrogen. The photomultiplier had an S-20 photocathode with peak sensitivity around 4000Å. A Fluke model 412B power supply provided 1.7 KV to the resistor chain. In operation, the photomultiplier had a dark current of the order 10^{-14} amperes which enabled it to detect even extremely weak sensitized sodium components.

H. Calibration of the Spectrometer and Photomultiplier

In order to calculate the excitation transfer cross-sections Q_{ok}, it was necessary to measure the absolute intensities of the sensitized spectral components resulting from mercury-sodium collisions. This required an accurate knowledge of the light losses in the spectrometer and of the absolute spectral response of the photomultiplier over the entire spectral region covered by the experiment.

The transmission characteristics of the spectrometer were obtained using two Jarrell-Ash spectrometers in tandem, with slit widths of 0.5 mm. and employing an air-cooled Osram Hg-3 spectral lamp as a light source. A vacuum photodiode with an effective photocathode area 4 cm. in diameter detected all the light entering and leaving the Jarrell-Ash spectrometer. Numerous scans of the frequency components of the Hg-3 lamp were made to establish the reproducibility of the transmission curve shown in Fig. 6.

Since the photomultiplier had been provided with a spectral response curve for room temperature by the manufacturer, it was not anticipated initially that any additional calibration of the absolute spectral response would be necessary. However, after preliminary calculations of the excitation transfer cross-sections Q_{ok}, it was suspected that cooling of the photomultiplier to liquid nitrogen temperatures (about $-196^{o}C$) was not only suppressing its dark current, as was intended, but also markedly changing its spectral sensitivity.

Recalibration of the photomultiplier was performed by allowing the same light energy to be incident on it and on a calibrated RBL-500 thermopile manufactured by C.M. Reeder. The thermopile had a flat spectral response throughout the spectral region and a sensitivity of 12.8 $\frac{\mu V}{\mu W}$.

The arrangement of the apparatus which was used is illustrated in Fig. 7. The light source was an air-cooled Osram Hg-3 lamp focused on the open entrance slit of the Jarrell-Ash spectrometer. A two-stop position holder was

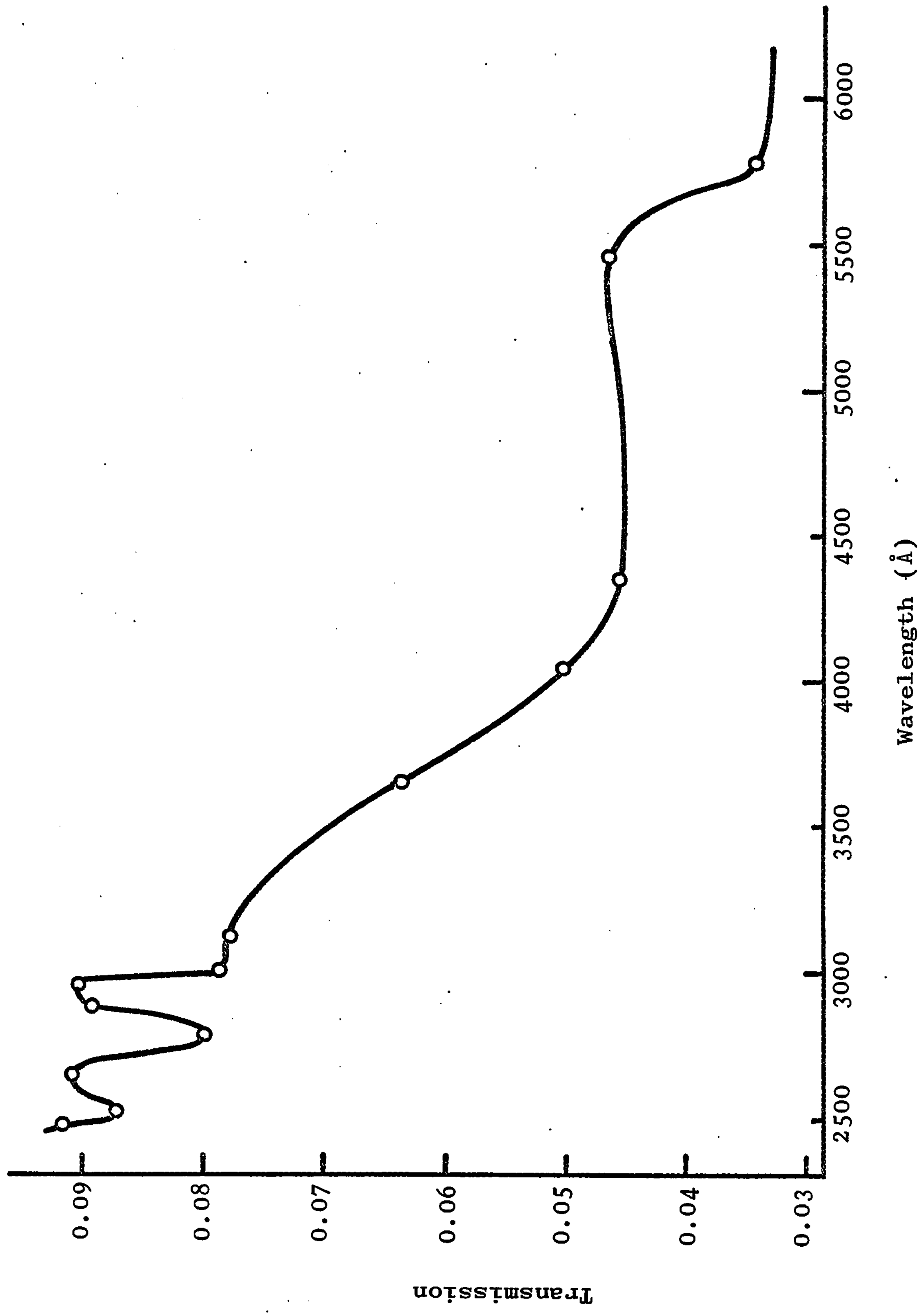

Fig. 6 Transmission of Jarrell-Ash Monochromator

placed in the path of the output light beam from the monochromator. On the holder were mounted an RBL-500 thermopile equipped with a quartz eye having an effective rectangular area 2 mm. by 0.5 mm., and a light baffle with a rectangular window 2 mm. by 0.5 mm. The baffle window corresponded precisely to the dimensions and orientation of the effective rectangular area of the thermopile. At the first stop, the thermopile sampled the beam, and a Keithley model 149 milli-microvoltmeter recorded the resulting millivolt signal. When the holder was positioned at the second stop, a window permitted exactly the same portion of the beam to be focused by a lens within the effective cathode area of the photomultiplier. In this way the photomultiplier signal corresponded to a definite flux of light energy and the absolute spectral response of the photomultiplier at both room temperature and liquid nitrogen temperature was determined throughout the spectral range covered by the experiment. The spectral response at liquid nitrogen temperatures was similar as at room temperature in the ultraviolet region, but not in the visible region as may be seen in Fig. 8.

I. Determination of the Density of Ground-State Sodium Atoms

It was essential to determine accurately the density of ground-state sodium atoms, $N_o(Na)$, in the Hg-Na mixture in order to obtain the cross-sections Q_{ok}. Since mercury and sodium form an amalgam, the sodium vapour pressure in the two-component system differed considerably from the vapour pressure

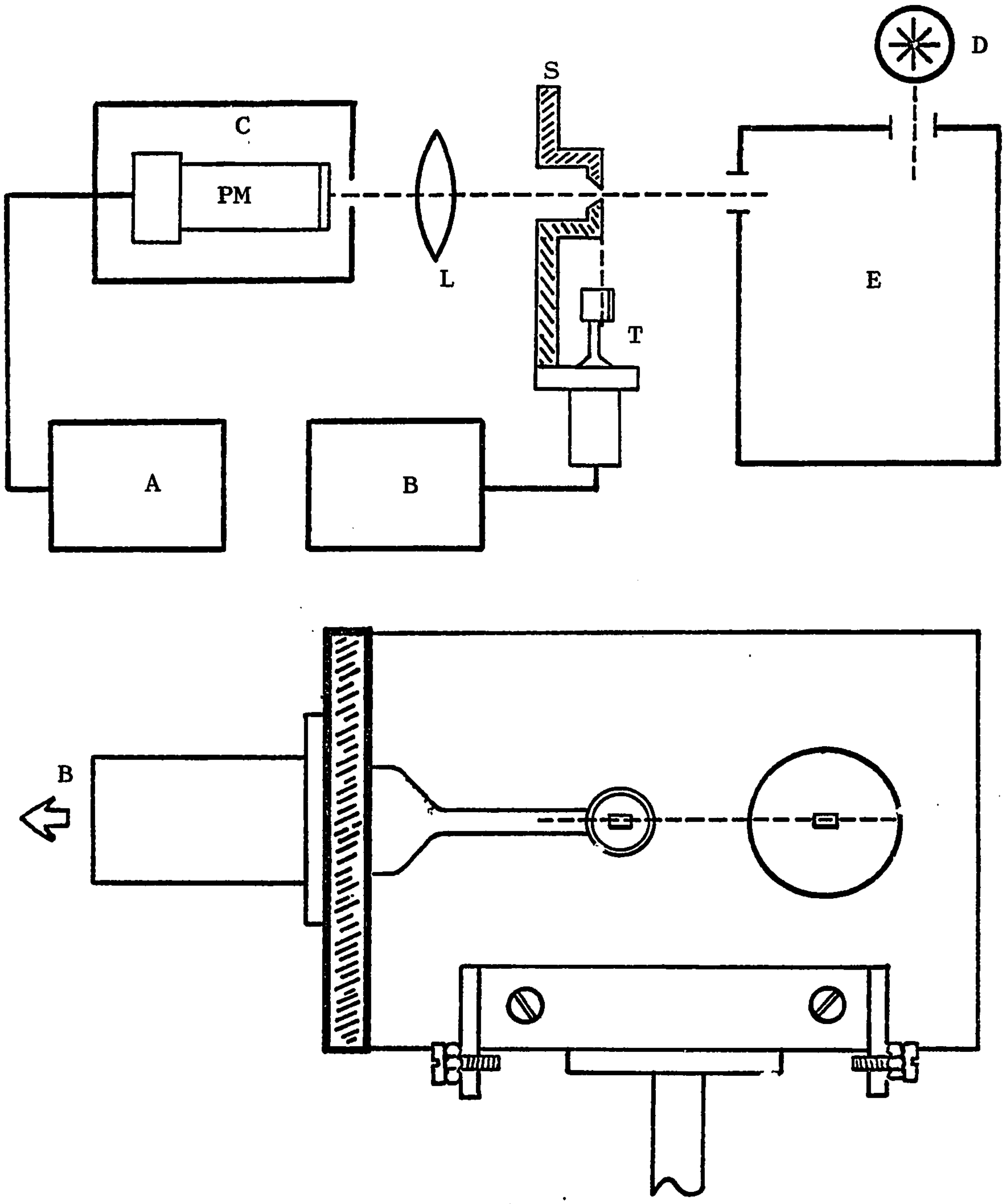

Fig. 7 Apparatus for measuring spectral response of photomultiplier showing fron view of slide-holder. A, picoammeter; B, millimicrovoltmeter; C, cryostat with PM tube; D, Osram lamp; L, lens; S, slide-holder; T, thermopile.

of pure sodium at the same temperature. For this reason, the usual semi-empirical temperature-vapour pressure relations [Nesmeyanov 1963][32] could not be used. The effective vapour pressure of sodium was difficult to determine since the relative concentrations of the two components in the mixture varied in time [Poindexter 1926][33].

A technique, based on measurements of quasi-reabsorption in pure sodium vapour used successfully with a Rb-Cs mixture [Czajkowski, McGillis and Krause 1966][13], was employed to obtain the partial pressure of sodium in the Hg-Na vapour mixture. The fluorescence cell containing pure sodium vapour was irradiated with 5890Å sodium resonance radiation emitted from an Osram lamp in stable operation at 1.4 amperes. The exciting beam was passed through a narrow slit about 0.1 mm. wide and was focused by means of a movable lens just inside the cell and at d_o, a distance of about 0.5 mm. from the observation window. This limited the optical path through the vapour to less than 1 mm. A calibrated micrometric device shifted the slit image along the axis of observation to a second position d_1, as indicated in Fig. 5, increasing the optical path through the sodium vapour to 6 mm. Two fluorescent intensities were measured, I_o corresponding to d_o and I corresponding to d_1. The intensity ratio I_o/I for the sodium resonance line was determined throughout the temperature range 150°C - 215°C, with a reproducibility of ± 5%. A typical calibration curve with I_o/I plotted against temperature is shown in Fig. 9.

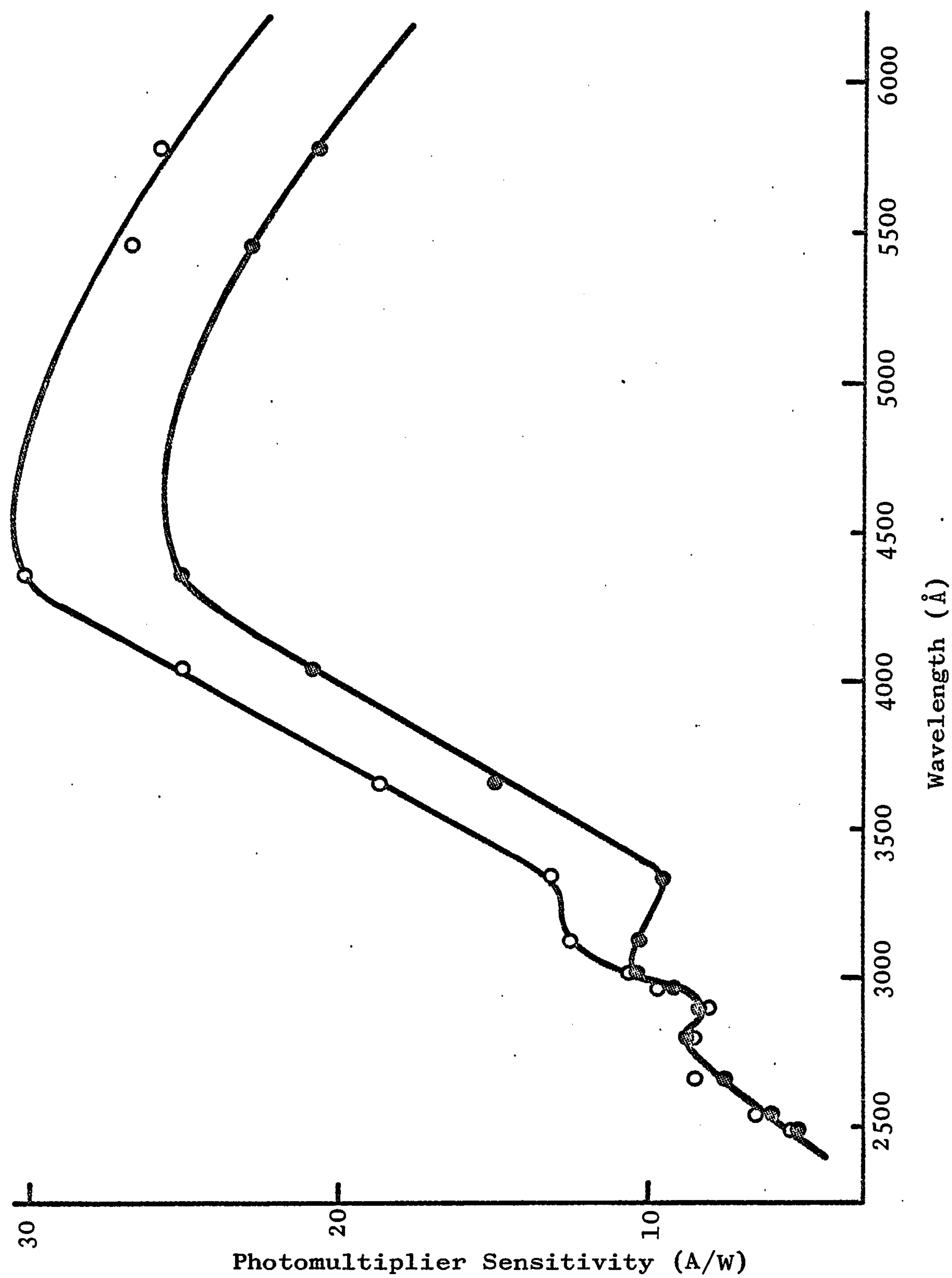

Fig. 8 ●, Spectral response of photomultiplier at room temperature, and at -196°C, O.

To obtain the ground-state sodium density in the Hg-Na mixture, the ratio I_o/I for sodium resonance fluorescence was measured in the binary mixture. From the previously determined calibration curve, the temperature corresponding to that particular ratio corresponded to the sodium vapour pressure in pure sodium vapour and thus to the partial pressure of sodium vapour in the binary mixture.

This method of calibration provided rapid and sufficiently precise information about the ground-state sodium as long as the geometry of the cell and optical alignment were undisturbed. The calibration had to be repeated whenever the cell was cleaned or refilled with new sodium and mercury. During optical alignment, the inspection window was used to monitor and centre the exciting light beam, in order to prevent masking of the beam at either of the two stop positions by the edges of the cell entrance window.

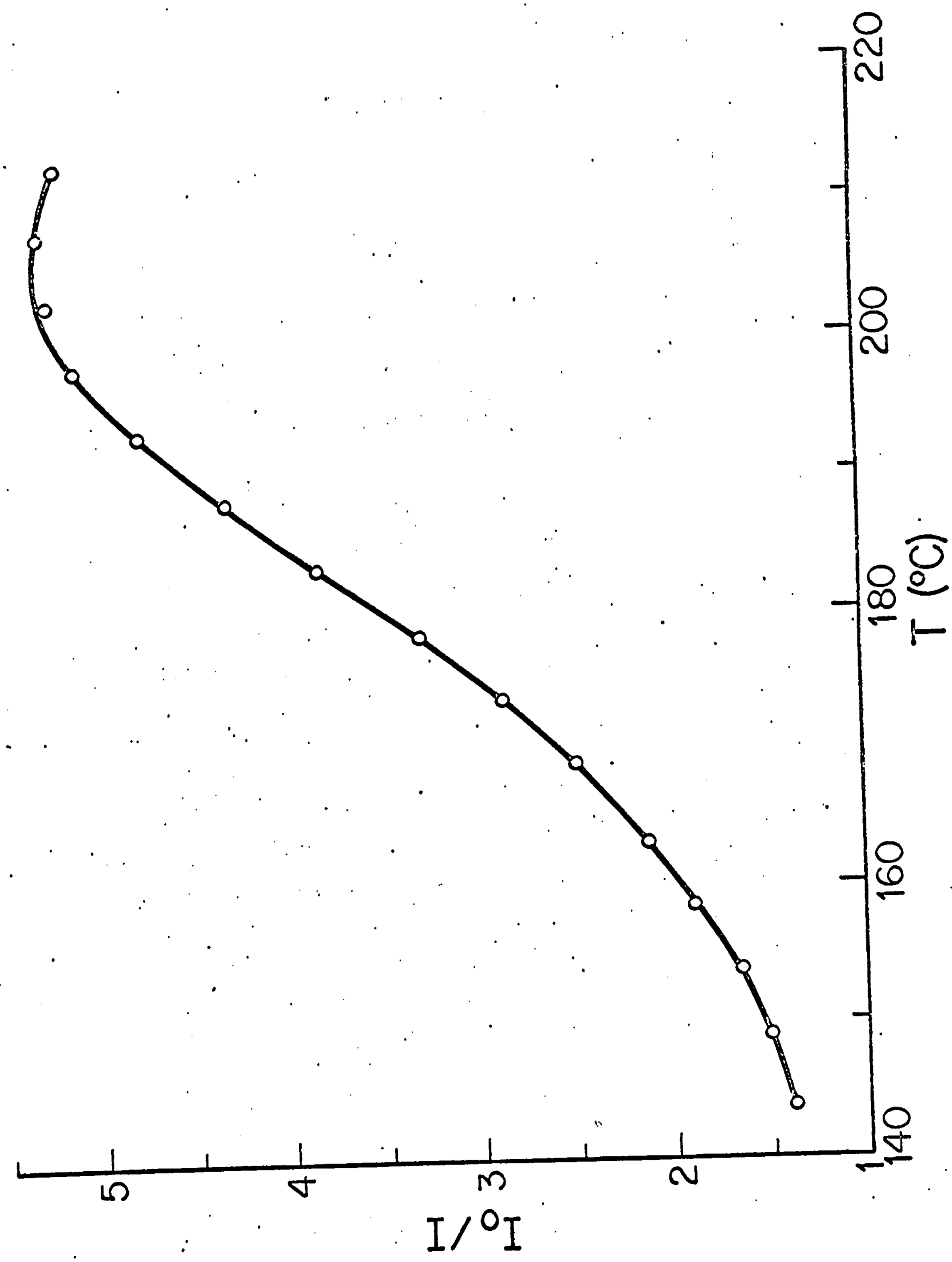

Fig. 9 A Plot of the ratio Io/I for Na resonance radiation against temperature, used to determine the partial pressure of sodium vapor.

IV EXPERIMENTAL PROCEDURE

The fluorescence cell was cleaned with a dichromate solution and rinsed thoroughly with distilled water. A pyrex ampoule containing 2 gm. of 99.95% pure sodium, supplied by A.D. McKay Co., was placed in the appropriate side-arm and about 1 gm. of triply-distilled mercury was sealed into the other side-arm. The cell was painted with aquadag, positioned inside the oven and fixed securely. Several thermocouples were placed in the main oven and on the side-arms of the cell. The main oven temperature was stabilized at approximately 230°C and the cell was baked until a vacuum of the order 10^{-8} torr was attained. The sodium capsule was then broken and most of the metal was distilled into the side-arm after which the extension containing the empty capsule was removed. The temperature of the sodium side-arm was maintained at about 15°C by means of the ultra thermostat for several days to remove any traces of sodium from the main body of the cell to the side-arm. In this way, the sodium vapour pressure in the fluorescence cell could be controlled by adjusting the temperature of the side-arm. The density of the ground-state sodium atoms was next determined as described above.

The mercury reservoir was opened and a small amount of mercury was admitted to the fluorescence cell. The side-oven containing the mercury side-arm was operated at a temperature of 50°C-60°C at which there was negligible trapping of mercury resonance fluorescence.

The exciting mercury radiation was made incident on the mercury-sodium mixture and the sensitized fluorescent spectrum of sodium was scanned automatically at a rate of 10Å/min. Since a typical run lasted six hours, the intensity ratio I_o/I and the intensity of the mercury resonance fluorescence were monitored repeatedly. All intensities were recorded with a Moseley 7100B strip chart recorder.

V RESULTS AND DISCUSSION

A. Calculation of Q_{ok}

The measured absolute intensities of the sensitized sodium components were used to calculate the cross-sections for excitation transfer to the various sodium states. The values Q_{ok} represent averages over all experimental runs for each particular transfer process listed in Table I. Corrections to the cross-sections were made for light losses in the quartz optics and for the small amount of reabsorption of the Hg2537Å resonance radiation. In the case of excitation transfer from the $Hg6^3P_1$ state to sodium states with small energy defect ΔE, the individually determined values Q_{ok} lay within 20-30% of the averages. In the cases of excitation transfer to sodium levels far removed from the $Hg(6^3P_1)$ level, the scatter increased to 60% because of the considerable effect of the cascade transitions which could not be accurately estimated.

B. Corrections for Cascade Transitions

The intensities I_{ki}, in Eq. (15), arise due to direct excitation transfer and, in some instances, cascade transitions to the k^{th} sodium level. Since the cross-section values, Q_{ok}, must reflect the probability of direct excitation transfer to the k^{th} level, contributions to the intensities I_{ki} by cascade transitions cause an unwanted increase in the values Q_{ok}. The magnitude of the cascade contributions to each of the sodium spectral components has to be determined and removed.

High-lying sodium levels are populated primarily by

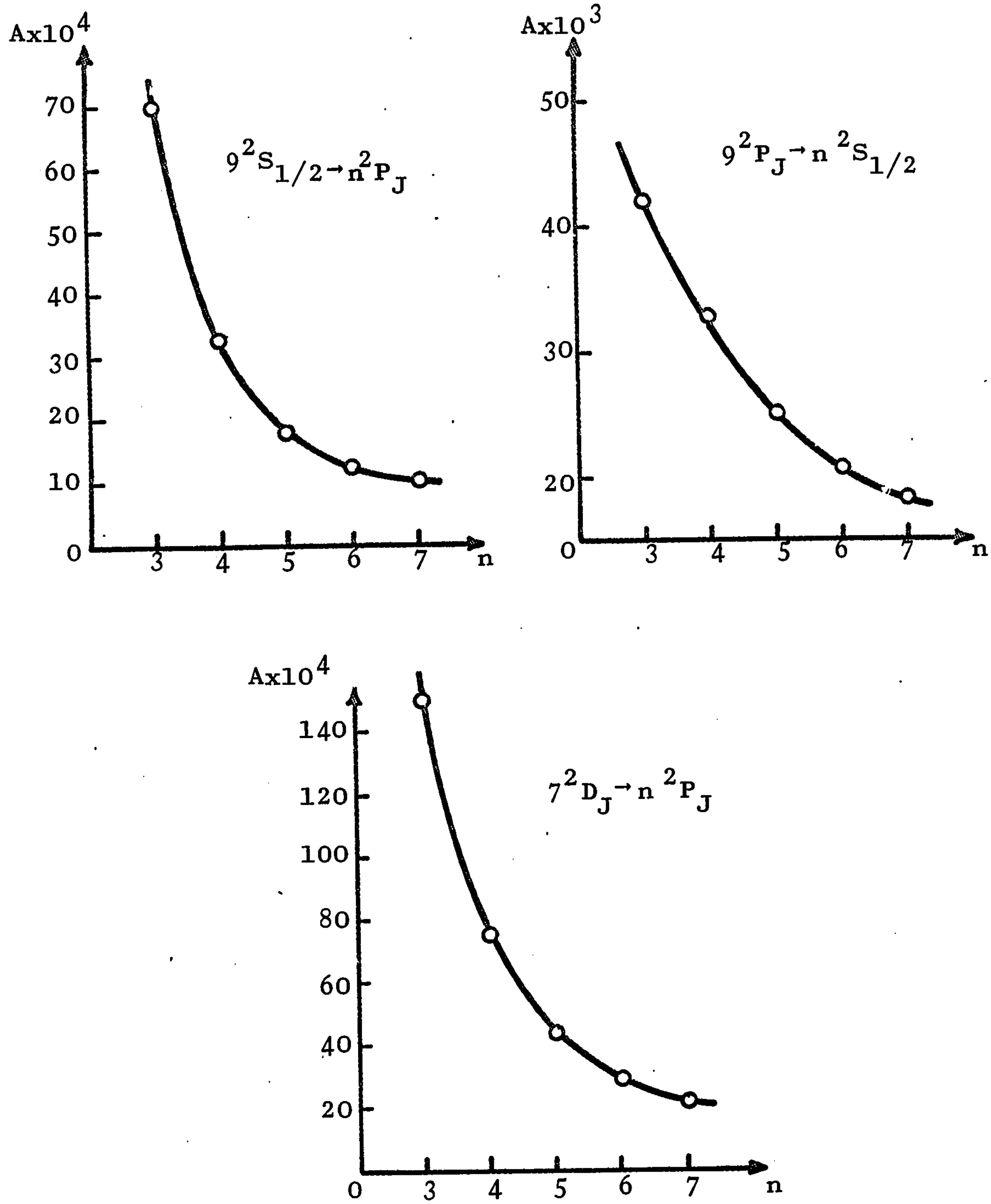

Fig. 10 Plots of A_{ki} against n for the transitions $9^2S_{1/2}\to n^2P_J$, $9^2P_J\to n^2S_{1/2}$, and $7^2D_J\to n^2P_J$

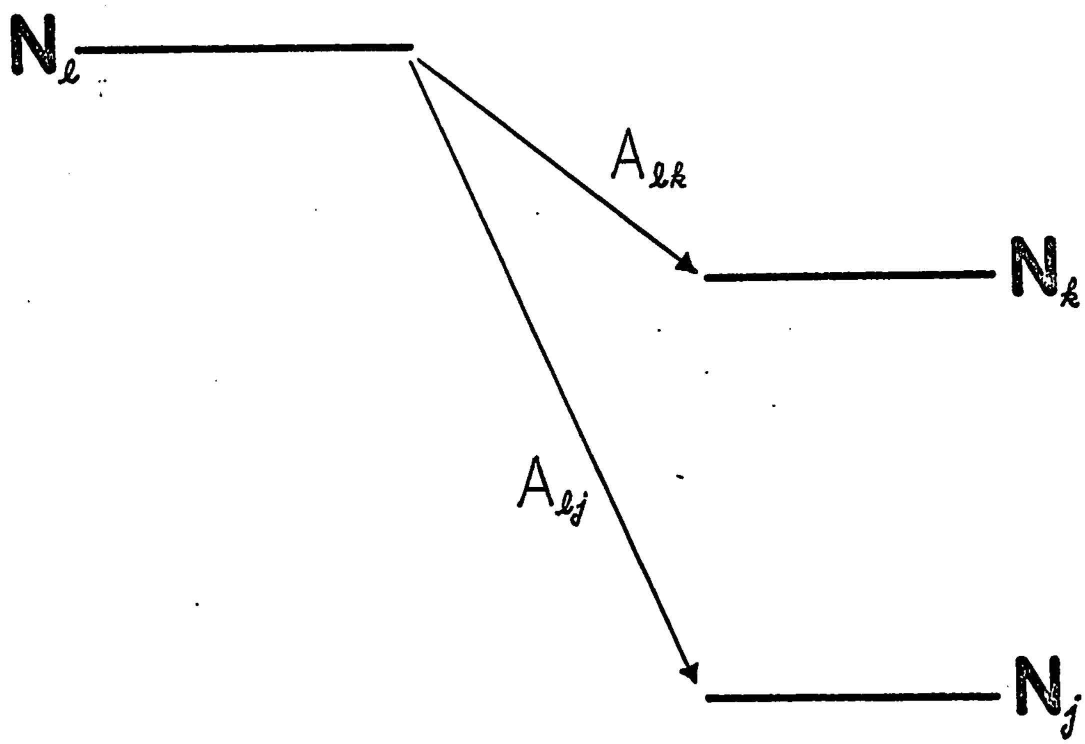

Fig. 11 Atomic energy level labelling diagram in the correction of Q_{ok} for cascade transitions.

direct collisional excitation transfer from $Hg(6^3P_1)$ atoms. Thus, in determining the cross-sections for collisional excitation of sodium levels close to the $Hg(6^3P_1)$ state, the role of cascade transitions may be neglected

$$Q_{ok} \sim \frac{1}{N_o(Na)N(Hg^*)\bar{v}_r} \left(\frac{I_{ki} \sum_{r=k-1}^{o} A_{kr}}{A_{ki}\, h\nu_{ki}} \right) \quad (17)$$

For energy levels with $n \leq 6$, where n is the principal quantum number, the probability of population by spontaneous transitions from more highly excited sodium levels increases rapidly. The importance of cascade transitions in the cases of the lower states is reflected by plots of A_{ki} against n for the transitions $9^2S_{1/2} \rightarrow n^2P_J$, $9^2P_J \rightarrow n^2S_{1/2}$, and $7^2D_J \rightarrow n^2P_J$, which are shown in Fig. 10. As a result, sodium S, P and D levels, removed by more than 0.15 eV from the $Hg(6^3P_1)$ state, are populated not only by direct collisional excitation transfer but by cascade transitions. In practice, these collision cross-sections are corrected for cascade transitions by considering the second term of Eq. (15).

$$\left\{ \begin{array}{l} \text{Contributions} \\ \text{to } Q_{ok} \text{ by Cascade} \\ \text{Transitions} \end{array} \right\} = \frac{\sum_{\ell=k+1}^{\infty} N_\ell(Na) A_{\ell k}}{N_o(Na)N(Hg^*)\bar{v}_r} \quad (18)$$

The numerator in Eq. (18) accounts for all contributions to the population of the k^{th} sodium state by spontaneous transitions from higher sodium energy levels. By subtracting the factor (18) from the first term of Eq. (15), the effective increase in the value Q_{ok} due to cascade transitions is removed and the corrected Q_{ok} results from only direct excitation transfer.

The simple term diagram shown in Fig. 11 indicates the method of correction. Populations of the j, k, and ℓ levels are given respectively by N_j, N_k, and N_ℓ, where $(k + 1) \leq \ell \leq \infty$. Spontaneous transition probabilities are $A_{\ell k}$ for the cascade transition $\ell \rightarrow k$ and $A_{\ell j}$ for the transitions $\ell \rightarrow j$. In order to calculate expression (18), the quantity $N_\ell(Na)$ must be determined. The intensities $I_{\ell k}$ corresponding to cascade transitions $\ell \rightarrow k$ need not be measured since it is more convenient to express $N_\ell(Na)$ in terms of previously measured intensities of the sodium spectral components listed in Table I. Expressing $I_{\ell j}$ with the aid of Eq. (6).

$$I_{\ell j} = N_\ell(Na)\, A_{\ell j}\, h\nu_{\ell j} \tag{19}$$

Rearrangement of Eq. (19) yields the population of the ℓ^{th} level

$$N_\ell(Na) = \frac{I_{\ell j}}{A_{\ell j} h\nu_{\ell j}} \tag{20}$$

Although the summation in the numerator of Eq. (18) extends to an infinite number of contributing levels, contributions from sodium levels lying above 4.89 eV can be neglected because the initial excitation of these levels by means of collisional energy transfer is unlikely.

Figs. (12), (13) and (14) represent semi-logarithmic plots of the cross sections Q_{ok} against the energy defect, ΔE, obtained from measurements of absolute intensities of the components in the $nS \rightarrow 3P$, $nP \rightarrow 3s$ and $nD \rightarrow 3P$ series in sodium,

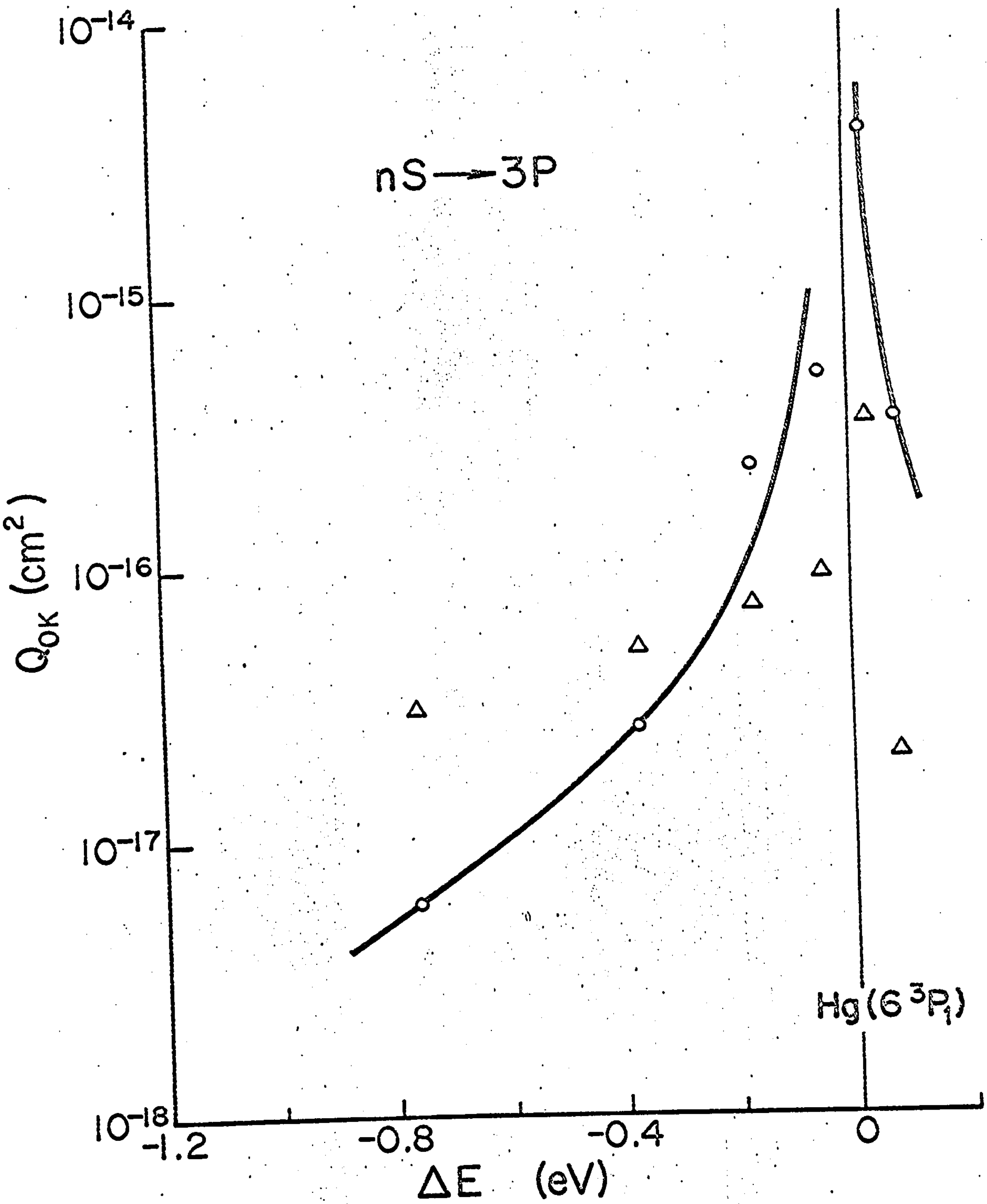

Fig. 12 A plot against ΔE of the cross sections for excitation transfer to the nS states in sodium, obtained from measurements on the nS→3P spectral series. O, this investigation; Δ, Kraulinya (1964).

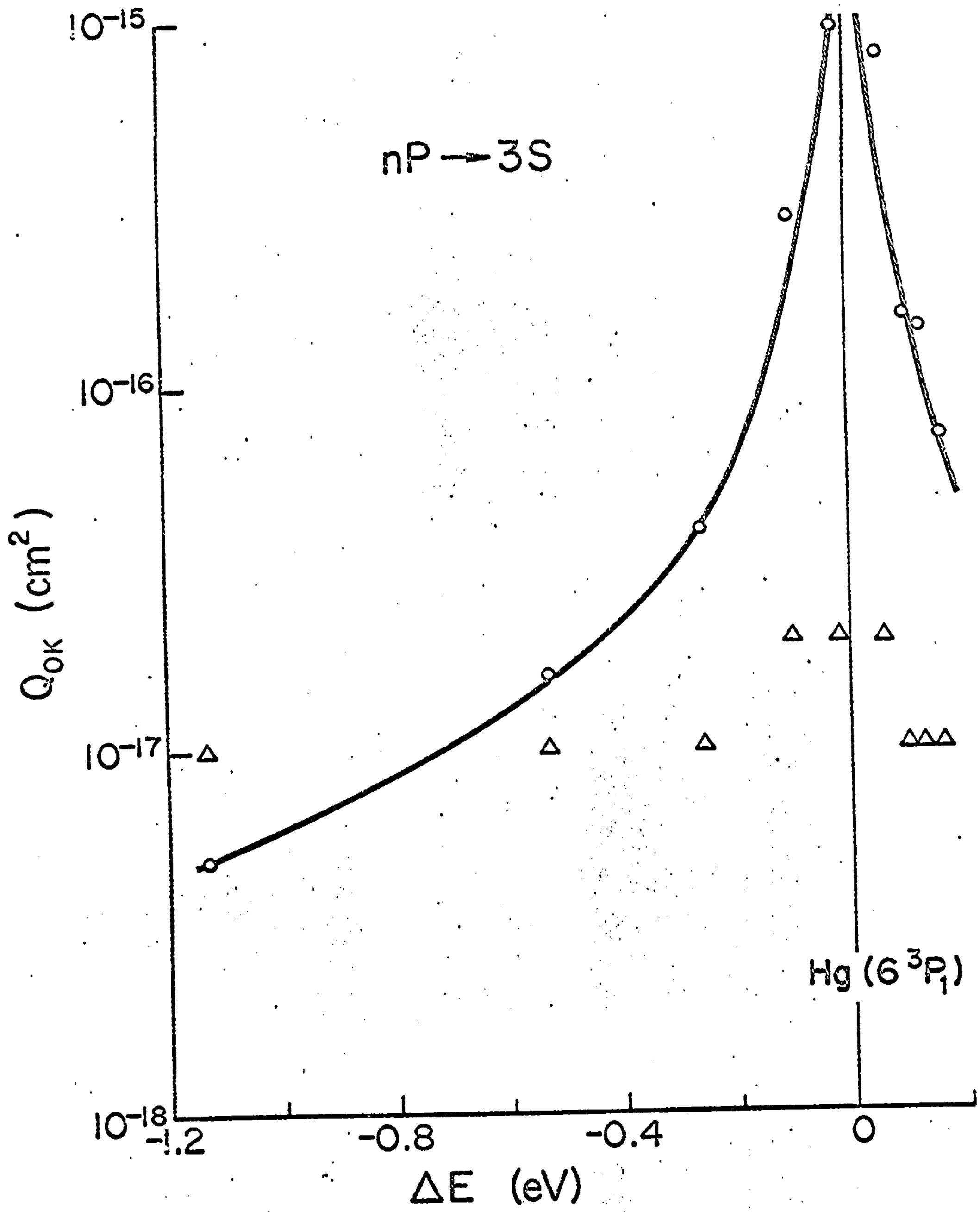

Fig. 13 A plot against ΔE of the cross sections for excitation transfer to the nP states in sodium, obtained from measurements on the nP→3S spectral series. O, this investigation; Δ, Kraulinya (1964).

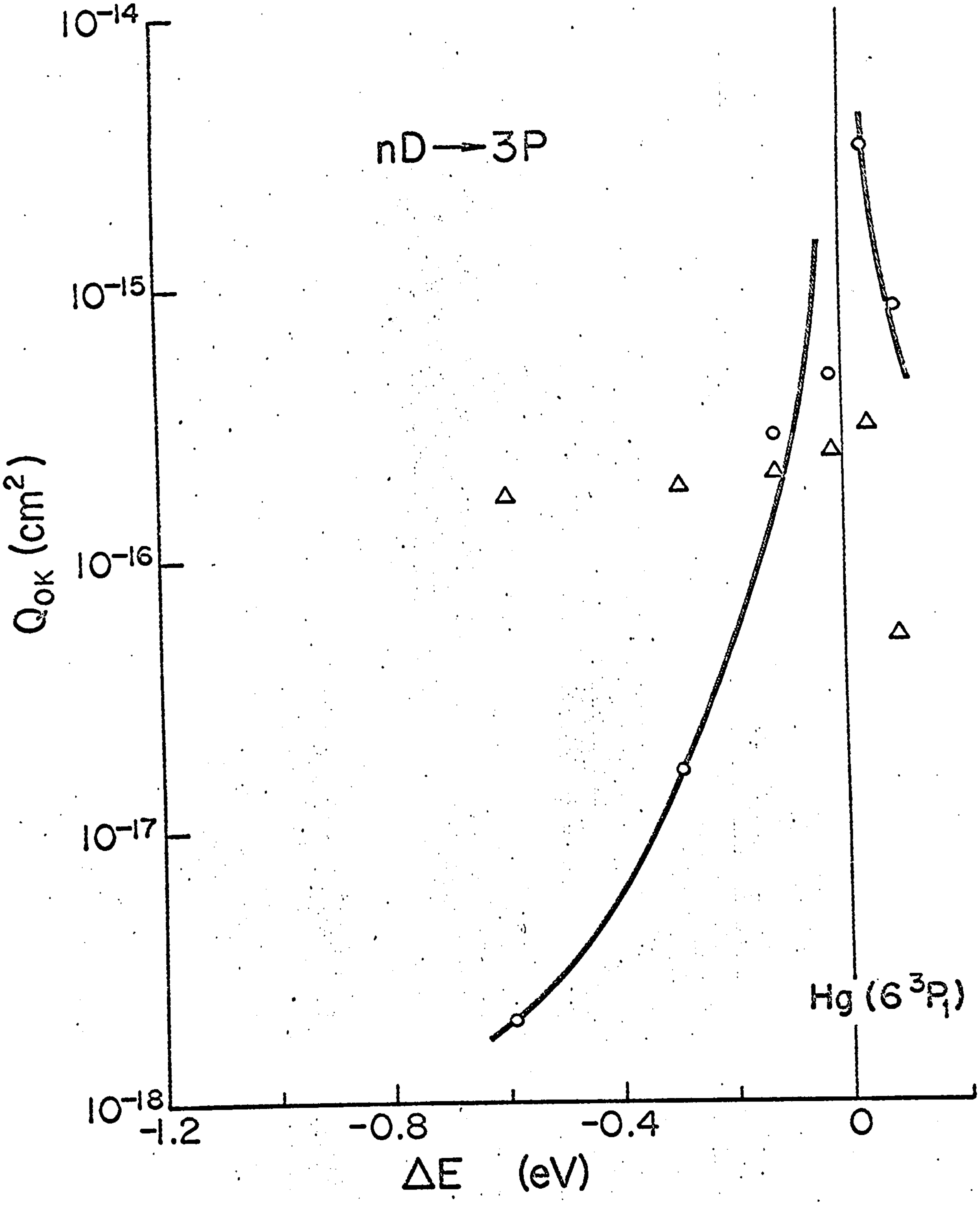

Fig. 14 A plot against ΔE of the cross section for excitation transfer to the nD states in sodium, obtained from measurements on the nD→3P spectral series. O, this investigation; Δ, Kraulinya (1964).

respectively. In Fig. (12), the cross sections have been corrected for cascading from higher-lying P levels; in Fig. (13), the cross-sections have been corrected for cascading from both S and D levels; and in Fig. (14) the cross-sections have been corrected for cascading from P and F levels with the assumption that the population of the D and F states are approximately equal. This approximation is reasonable because the F and D states with corresponding quantum number, n, have comparable excitation energies, and was necessary because the spectral components due to the transitions from the F levels could not be observed.

In Figs. (12), (13), (14) and Table II, the cross-sections for excitation transfer to sodium states lying above the Hg(6^3P_1) level have been divided by the Boltzmann factor [Kraulinya 1968][24]. This correction was essential since only the fraction α of the inelastic collisions for which the relative energy of the colliding partners is greater than ΔE, participates in excitation transfer.

C. Trapping of Hg and Na Resonance Radiation

The effect of the imprisonment of mercury resonance radiation on the cross-sections was found to be negligible. The intensity ratio $\frac{I(4393\text{Å})}{I(2537\text{Å})}$ was measured over a wide range of mercury side-arm temperatures while keeping the sodium side-arm temperature constant. The fluorescent component Na 4393Å is unaffected by cascade transitions, and thus $\frac{I(4393\text{Å})}{I(2537\text{Å})}$ should be directly proportional to the excitation

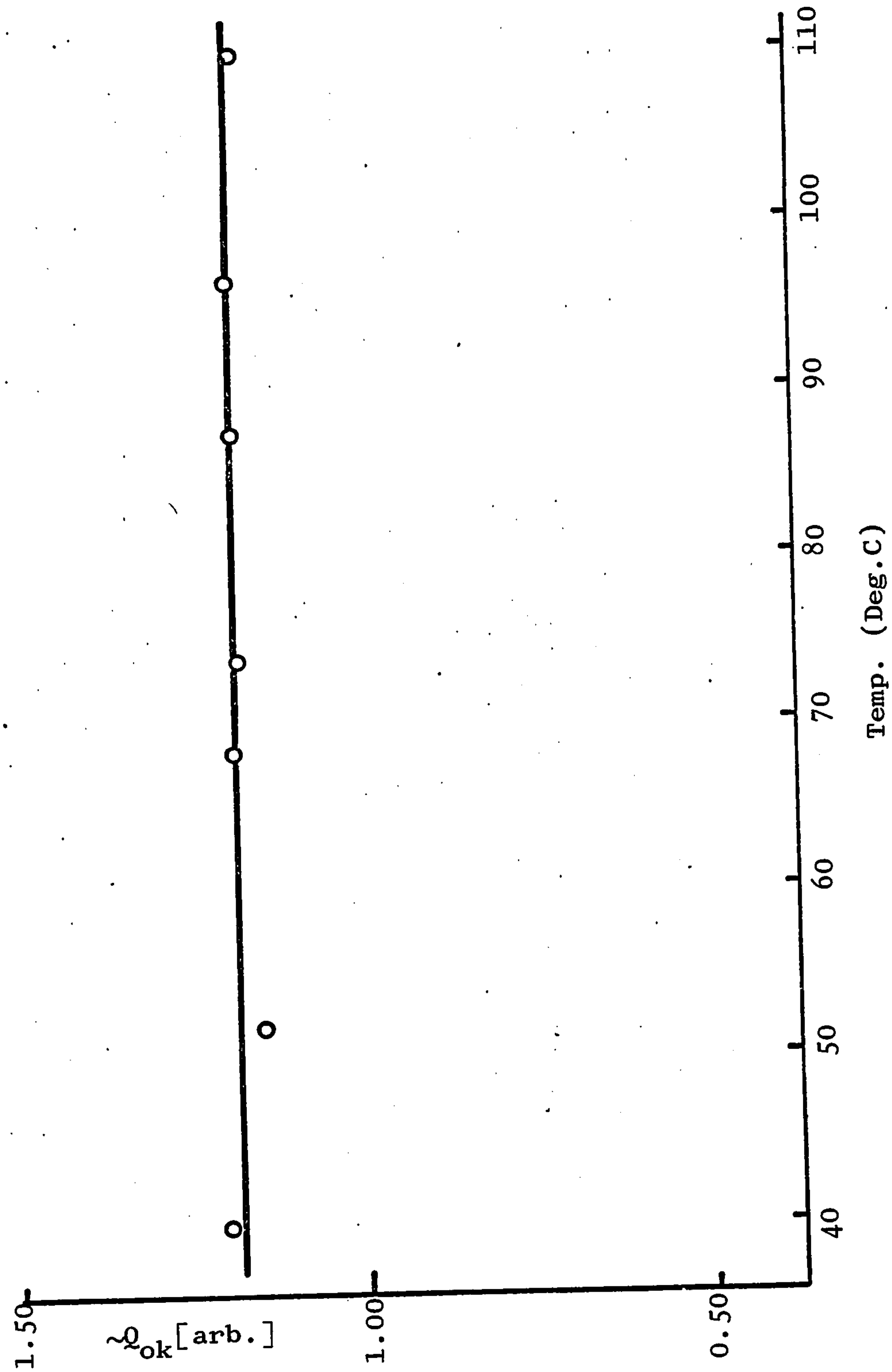

Fig. 15 Variation of excitation transfer cross-section Q_{ok} versus Hg side-arm temperature.

transfer cross-section Q_{ok}. Consequently, any significant reabsorption of the mercury resonance radiation should be reflected by an increase in the intensity ratio. As indicated by the horizontal straight line in Fig. 15, the reabsorption of Hg resonance radiation is unimportant and does not affect the value of the excitation transfer cross-section.

The absorption of fluorescent radiation by 3s atoms, which might result in the excitation of the sodium atoms to nP states where $n \geq 3$ was considered. Reabsorption of Na 5890Å resonance radiation is insignificant since the vapour pressure of sodium is relatively low[34], and the optical path through the absorbing vapour is less than 1 mm. Since the probability of absorption of fluorescent radiation resulting in the excitation of sodium nP states with $n > 3$ is several orders of magnitude smaller, the reabsorption of sodium fluorescent radiation by the $3s \rightarrow nP$ series is quite negligible.

D. Discussion

As seen in Figs. (12), (13) and (14), the excitation transfer cross-sections Q_{ok} show a marked resonance effect with respect to the energy of the $Hg(6^3P_1)$ state which corresponds to $\Delta E = 0$. The collision cross-sections for the $nP \rightarrow 3S$, $nS \rightarrow 3P$, $nD \rightarrow 3P$ series can also be plotted in one common diagram of Q_{ok} against ΔE, as shown in Fig. (16). The values of the cross-sections range over three orders of magnitude and fit the common plot well, but are slightly asymmetric about $\Delta E = 0$ even though one might expect the cross-sections to depend mainly on ΔE and to exhibit a symmetry in the positive and negative ΔE branches. However, the values of Q_{ok} corresponding to negative ΔE are influenced by cascade transitions and are subject to errors which give rise to the asymmetry. Even with the corrections, the rather large values of Q_{ok} at large $-\Delta E$ should be viewed as upper limits of the cross-sections. Values of Q_{ok} for $+\Delta E$ are not influenced by cascade transitions and, consequently, are more accurate.

Kraulinya (1969)[25] obtained cross sections for Hg* - Na collisional excitation transfer which, however, did not exhibit the pronounced resonance near $\Delta E = 0$, were inexplicably large at large ΔE and did not show a uniform dependence on ΔE in the different spectral series (nS, nP and nD). Kraulinya concluded that different mechanisms of excitation transfer were operative in the three series and that the mechanism probably involved the formation of quasi-molecules of the type HgNa.

In this investigation, it has been shown that all the cross-sections for the three series can exhibit a common type of behaviour with ΔE which may be regarded as an indication of a single mechanism for excitation transfer in Hg - Na collisions. The recent findings of Sosinskii, Morozov and Selyavskii (1971)[35], who considered the case

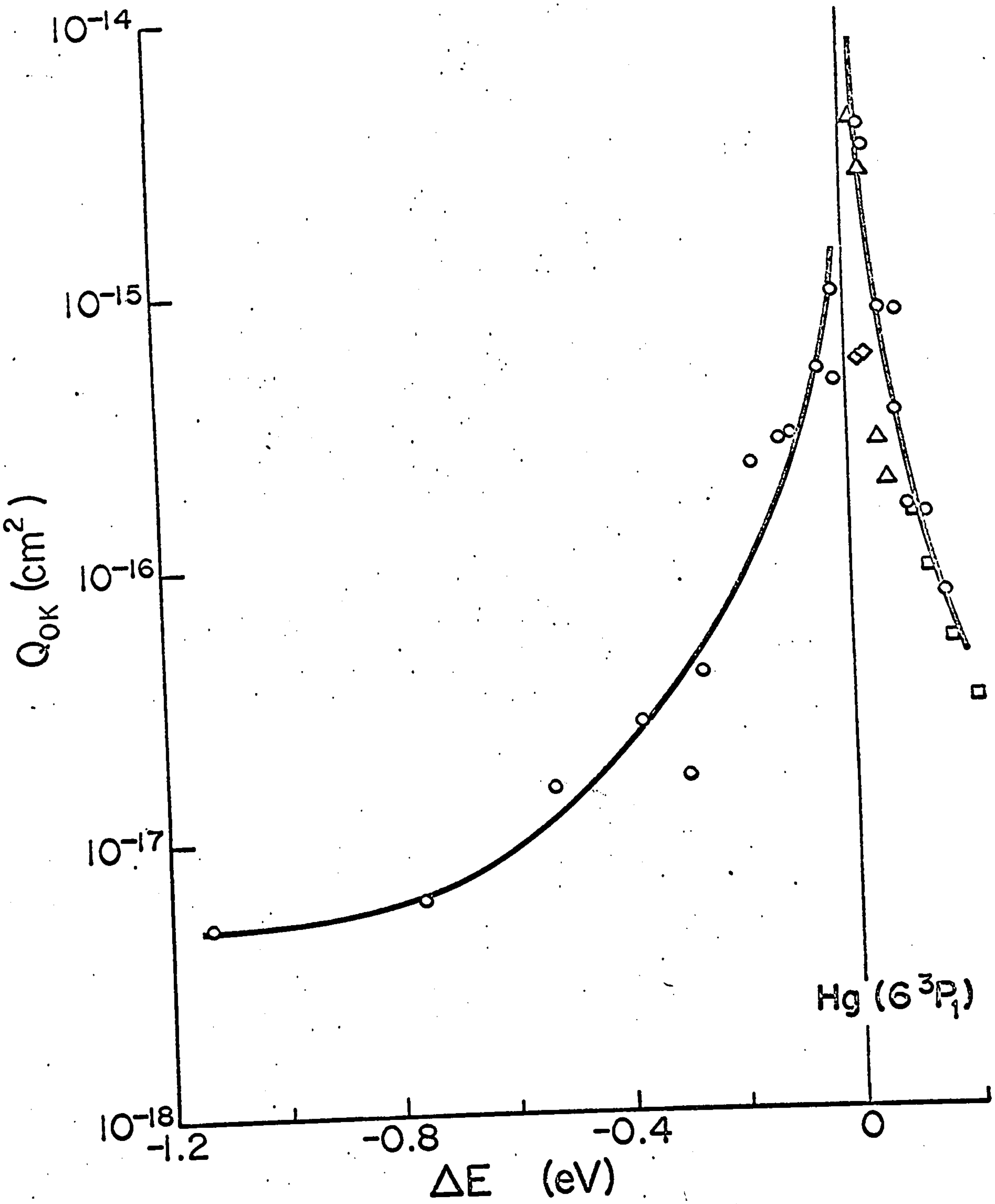

Fig. 16 A plot against ΔE of the cross-sections for excitation transfer to S, P and D states in sodium. O, this investigation; □, Rb→Cs transfer (Czajkowski, McGillis and Krause, 1966); Δ, K→Rb transfer (Hrycyshyn and Krause, 1969); ◊, Stacey and Zare (1970).

TABLE II

Cross sections for Hg → Na excitation transfer

Collisional Process	ΔE (eV)	ΔE (cm^{-1})	Collision cross section ($Å^2$) This investigation	Collision cross section ($Å^2$) Kraulinya (1964)
$Hg(6^3P_1)$→Na(10S)	+0.069	556	3.42	0.2
→Na(9S)	+0.019	153	38.50	2.7
→Na(8S)	-0.057	460	4.92	0.9
→Na(7S)	-.0175	1411	2.30	0.7
→Na(6S)	-.0378	3049	0.26	0.5
→Na(5S)	-0.771	6219	0.06	0.3
→Na(9D)	+0.083	669	8.06	0.5
→Na(8D)	+0.038	306	31.36	3.0
→Na(7D)	-0.028	226	4.50	2.4
→Na(6D)	-0.129	1040	2.87	2.0
→Na(5D)	-0.296	2387	0.17	1.8
→Na(4D)	-0.604	4872	~0.02	1.7
→Na(12P)	+0.142	1145	0.74	0.1
→Na(11P)	+0.119	960	1.47	0.1
→Na(10P)	+0.088	710	1.56	0.1
→Na(9P)	+0.046	371	8.06	0.2
→Na(8P)	-0.015	121	9.35	0.2
→Na(7P)	-0.10	806	2.90	0.2
→Na(6P)	-0.263	2121	0.40	0.1
→Na(5P)	-0.54	4355	0.16	0.1
→Na(4P)	-1.13	9114	≤0.05	0.1

of collisions between excited mercury and ground state cadmium atoms, confirm the view that transfer of excitation occurs by way of binary collisions.

In Fig. (16) the results of the present investigation are compared with previously obtained cross-sections for excitation transfer in K-Rb and Rb-Cs mixtures [Hrycyshyn and Krause 1969; Czajkowski, McGillis and Krause 1966][15,13]. The average relative velocities of the colliding partners in the three cases are in the following ratio,

$$v_r(\text{K-Rb}) : v_r(\text{Rb-Cs}) : v_r(\text{Hg-Na}) = 1 : 1.4 : 1.8$$

Since these relative velocities are of the same order of magnitude, a comparison of the respective cross-sections would not be unjustified. In fact, the excitation transfer cross-sections for K-Rb and Rb-Cs fit remarkably well on the cascade-free, positive branch of the curve.

Fig. (16) also includes four cross-sections determined by Stacey and Zare (1970)[17] for the system K-Rb. Two of these cross-sections corresponding to $\Delta E = 0.05$ and 0.06 eV respectively, agree with the results obtained by Hrycyshyn and Krause (1969) and follow the same dependence of cross-sections in relation to ΔE as do the Hg-Na cross-sections. The other two cross-sections for $\Delta E = 0.02$ and 0.03 eV are in disagreement; that is, the value of Q_{ok} for $\Delta E = 0.03$ eV is larger than the cross-section for $\Delta E = 0.02$ eV. According to Franck's rule, cross-sections for excitation transfer decrease with the increase of the resonance defect ΔE. It appears that the cross-section for $\Delta E = 0.03$ eV should be smaller than the cross-section for $\Delta E = 0.02$ eV.

The findings of this study indicate a general dependence of the excitation transfer cross-section on ΔE, in accordance with Franck's rule, and should assist the formulation of a more precise quantitative theory for the relation of Q_{ok} on ΔE.

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In 1966, I registered at the University of Windsor and graduated in 1970 with a B.Sc. Degree from the Honours Physics program. While working toward a Masters Degree, I have held a National Research Council Scholarship (1970-71).