

## HIGH MULTIPLICITY ELECTRONIC TRANSITIONS IN THE SPECTRUM OF FeCl

THE spectrum of FeCl excited in a R.F. discharge from a 1/2 K.W. oscillator has disclosed the existence of a new system of red degraded bands designated as  $\alpha$  in the region  $\lambda$  3250- $\lambda$  3150. The bands appear to be double-headed when photographed in the first order of a 21 ft. concave grating spectrograph having a dispersion of 1.25 Å/mm. The vibrational analysis of the system suggests that it involves a  ${}^4\Pi-4\Sigma$  transition. The multiplet intervals between the corresponding heads in the sub-systems are unequal as in systems I and II of FeCl and found to be 12.7, 21.9, and 40.6 cm.<sup>-1</sup> The vibrational constants of the upper and lower states of the system given in Table I, do not correspond with any of the previously identified electronic states of the molecule.

The systems I and II of FeCl in the ultra-violet  $\lambda$  3350- $\lambda$  3650 were previously analysed by Meischer,<sup>1</sup> Mesnage,<sup>2</sup> and Muller<sup>3</sup> and attributed to  ${}^6\Pi-6\Sigma$  and  ${}^4\Pi-4\Sigma$  transitions respectively. The bands of these two systems have been reexamined in the first order with the object of giving a complete multiplet analysis of the two systems.

The bands of  $\Delta v = 0 \pm 1$  sequences of system I, revealed only P and Q heads. The absence of 'O' and 'N' heads indicates a tendency towards case 'c' in the upper  ${}^6\Pi$  state.

The bands of  $\Delta v = 0, -1$  sequence of system II revealed the presence of Q, P and 'O' heads. The presence of 'O' heads indicates that the coupling in the upper  ${}^4\Pi$  state is intermediate between Hund's case 'a' and 'b'.

The vibrational constants of the upper and lower states of systems I and II are summarised in Table I. The vibrational constants of system II differ from those of Muller. The vibrational analyses of systems I and II have been well confirmed from a detailed study of the chlorine isotope effect in the  $\Delta v \pm 1$  sequences.

TABLE I

|                   | $\alpha$ system          | System I                | System II               |
|-------------------|--------------------------|-------------------------|-------------------------|
| $\omega_0'$       | 415.6* cm. <sup>-1</sup> | 433.8 cm. <sup>-1</sup> | 428.0 cm. <sup>-1</sup> |
| $x_0'\omega_0'$   | ...                      | 1.70 "                  | 1.56 "                  |
| $\omega_0''$      | 427.3* cm. <sup>-1</sup> | 408.0 "                 | 407.8 "                 |
| $x_0''\omega_0''$ | ...                      | 1.58 "                  | 2.96 "                  |

\* These values refer to  $\omega_0 - 2X_0\omega_0$ .

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## A MODEL FOR THE REYNOLDS STRESS IN TURBULENT SHEAR FLOWS

It is now well known that a satisfactory prediction of turbulent shear flows cannot in general be made by any of the older theories relying on such local concepts as mixing length or eddy viscosity.<sup>1</sup> The rather elaborate methods that have been more recently devised are based either on further physical assumptions or on hypotheses on the turbulent energy balance.<sup>2,3</sup> The purpose of this note is to propose for the Reynolds stress a model equation which incorporates, in a phenomenological way, some of the essential characteristics of a turbulent shear flow. For simplicity we consider only two-dimensional flows in which the boundary layer approximations are valid; extension to more general flows will be relatively obvious.

Townsend and others<sup>4,5</sup> have emphasized the importance of the concepts of equilibrium and self-preservation to an understanding of the structure of turbulent shear flows. All experiments indicate that when the equations of motion admit a self-preserving solution, the actual turbulent flow ultimately corresponds to that solution. However, while real flows display a tendency towards such equilibrium whenever possible, the evolution takes place at a finite rate. This relaxation process is strikingly demonstrated in some experiments on turbulent wakes now being completed in our laboratory. These considerations suggest an equation for the stress  $\tau$  of the type

$$\frac{d\tau}{dt} = A (\bar{\tau} - \tau) \quad (1)$$

where  $d/dt$  is the time-derivative following the fluid,  $\bar{\tau}$  is the stress at equilibrium (assuming that for the given local external conditions a corresponding equilibrium flow can be uniquely defined), and  $A$  is the reciprocal of a relaxation time which in general could depend on velocity, position and possibly also on  $\tau$ . Equation (1) is the simplest model for relaxation; it can be considered as a first approximation for small departure from equilibrium,



and can be easily refined further if experiments warrant it.

The equilibrium flow however does not represent a static situation as in thermodynamics; even when  $\tau = \bar{\tau}$ ,  $d\bar{\tau}/dt \neq 0$ . In fact, examination of some simple flows suggests that the equilibrium flow is essentially a diffusive process. Thus, in the equilibrium wake, the stress  $\bar{\tau}$  is given approximately by

$$\bar{\tau} \sim yx^{-3.2} \exp\left(\frac{-y^2}{4k'x}\right)$$

(where  $x$  and  $y$  are co-ordinates along and normal to the main flow), which is just the dipole solution to the diffusion equation

$$\frac{\partial \bar{\tau}}{\partial x} = k' \frac{\partial^2 \bar{\tau}}{\partial y^2}, \quad (2)$$

with a constant diffusion coefficient  $k'$ .

The simplest model which describes both relaxation and diffusion is

$$\frac{d\tau}{dt} = A(\bar{\tau} - \tau) + \frac{\partial}{\partial y} \left( k \frac{\partial \tau}{\partial y} \right), \quad (3)$$

where we now allow for a diffusivity which in general may not be a constant.

Together with equations of conservation of mass and momentum, (3) provides a closed system. To a first approximation, the parameters  $k$  and  $A$  in (3) can be determined from data on the equilibrium flow and a relaxation experiment.

A rigorously exact equation for  $\tau$  can of course be derived from the equations of motion, but it contains higher order correlations. Term-by-term modelling of this equation (along the lines adopted by Bradshaw et al.<sup>3</sup> for the energy equation) is of course possible, but this involves detailed assumptions which may be questionable in themselves, and are only valid to the extent that the general solutions are properly behaved. The present proposal has the advantage that it models the overall behaviour of the terms taken together rather than individually; the essential behaviour of shear flows is directly incorporated into the equations, without making specific assumptions about relations between the stresses and other mean quantities. Furthermore, at least for the simpler shear flows, the present system seems amenable to general analysis; a detailed application to non-equilibrium wake flows is now being made.

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### REACTION BETWEEN SULPHUR TETRAFLUORIDE AND HYDROGEN IODIDE

THE chemistry of sulphur tetrafluoride has been the subject of intensive study ever since it was isolated and identified<sup>1,2</sup> in 1954. It was of interest to study its reaction towards hydrogen iodide as the latter has been employed in this laboratory to characterise a variety of sulphur compounds.<sup>3,4</sup> Preliminary studies indicated that the gas would readily get reduced to hydrogen sulphide and a corresponding amount of iodine liberated.

Pure sulphur tetrafluoride was prepared by the fluorination of sulphur dichloride with sodium fluoride in acetonitrile medium.<sup>5</sup> Traces of impurities such as chlorine, sulphur chlorofluoride and sulphur chloride were removed by shaking with mercury. The purified gas was collected over mercury and metered from a gas measuring burette.

A known volume of sulphur tetrafluoride (8-10 ml.) was allowed to react with a large excess (10-15 times) of anhydrous hydrogen iodide in a reaction vessel. A series of colour changes (orange-yellowish brown-violet) appeared immediately after the gases were allowed to come in contact with each other. The intensity of the colour deepened and finally the violet colour of iodine was prominent. When the reaction was complete (20-30 minutes), the products were analyzed in the following way. A stream of nitrogen was passed (30 mts.) through the vessel to sweep off the products through traps containing chilled carbon-tetrachloride ( $-16^\circ \text{C}$ .) followed by sodium hydroxide (4N.) holding a cadmium hydroxide suspension. The carbon tetrachloride dissolved and retained iodine vapours present in the gaseous stream while hydrogen sulphide and hydrogen fluoride were absorbed by the alkali. Cadmium sulphide