Some Remarks Concerning Luminescence.— We may usefully here record some notes regarding the behaviour under the ultra-violet lamp of the various individual specimens referred to above.

The three Chinese works of art of green fluorspar all showed a blue-violet glow of considerable intensity. The octahedron of a pale green hue showed a violet-coloured luminescence of much smaller intensity.

The purple and blue octahedra both exhibit a feeble luminescence of a violet colour, as also the massive specimens which allow light of a purplish light to filter through.

The two very clear pieces of fluorspar also exhibit luminescence, that of the smaller specimen being particularly brilliant. This suggests that the pale yellow colour exhibited by these specimens is due to the absorption at the violet end of the spectrum associated with luminescence.

The most remarkable case of all is the yellow fluorspar which exhibits a bright luminescence exhibiting a colour similar to that of the specimen itself.

FINE STRUCTURE ANALYSIS OF ^{63}Cu ^{127}I BANDS

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MANY molecules occur as mixtures of several isotopic species in nature. It is very difficult or impossible, especially if the molecule is heavy, to analyse the fine structure of the band spectra of such molecules even with the highest dispersions and resolutions now available. Obviously the analysis will become considerably easier if the spectrum of *only* one isotopic species could be investigated. Such investigations became possible in the last few years with the availability of separated isotopes and the development of sealed electrodeless discharge tubes[1] which require only milligram quantities of the substance.

Thus, for instance, the fine structure analysis of the band systems of CuCl, consisting of four isotopic species, was carried out by the author[2] using separated isotopes of copper and chlorine. In continuation of these investigations the fine structure of the bands of ^{63}Cu ^{127}I molecule [natural CuI consists of two isotopic species ^{63}Cu ^{127}I (69%) and ^{65}Cu ^{127}I (31%)] has been analysed and the results of the analysis are reported in this note.

^{63}CuI was prepared by directly reacting in vacuum at high temperature copper (^{63}Cu—99·8%) and iodine. Electrodeless discharge tubes containing milligram quantities of ^{63}CuI were prepared in the manner described in reference 1. The bands were obtained by exciting the electrodeless tube, heated by a furnace to a temperature of 600 to 800° C., by a microwave oscillator (2450 mc./sec.). The bands were photographed in the second order of the 6·6 meter, 1,200 lines per mm. concave grating spectrograph, at a dispersion of about 0·5 Å/mm.

Bands belonging to three systems *C*, *D* and *E*, out of the four known[3] band systems of the molecule, have been analysed. Bands, whose fine structure has been analysed, are listed in Table I. Figure 1 shows a typical spectrum.

TABLE I

Bands of ^{63}Cu ^{127}I molecule whose fine structure has been analysed

System	Bands analysed
C system ($C\,^1\Sigma - X\,^1\Sigma$)	4574·8 Å (0–0) ; 4630·7 Å (0–1); 4687·5 Å (0–2)
D „ ($D\,^1\Pi - X\,^1\Sigma$)	4359·6 Å (0–0) ; 4410·3 Å (0–1) ; 4461·9 Å (0–2) ; 4514·4 Å (0–3)
E „ ($E\,^1\Sigma - X\,^1\Sigma$)	4168·2 Å (0–0) ; 4214·5 Å (0–1) ; 4261·4 Å (0–2) ; 4309·4 Å (0–3) ; 4358·1 Å (0–4) ; 4174·4 Å (1–1) ; 4129·0 Å (1–0) ; 4090·9 Å (2–0) ; 4141·9 Å (3–2)

The rotational analysis indicates that the *C*, *D* and *E* band systems involve respectively $^1\Sigma$–$^1\Sigma$, $^1\Pi$–$^1\Sigma$ and $^1\Sigma$–$^1\Sigma$ transitions. The bands of the *C* and *E* systems are single-headed and their structure consists of either two series of lines, the *P* and *R* branches or one series of lines. In the bands showing only one series of lines, the *P* and *R* branches coalesce, as the analysis shows. The bands of the *D* system

are double-headed. The structure between the two heads, consisting of *R* lines, is not resolved; the resolved structure shows two series of lines, the Q and the P branches. The members of the *Q* branch are uniformly more intense than the members of the *P* branch. The returning *R* branch gets too weak already at the band origin and cannot be traced beyond it, therefore, only the lines of *Q* and *P* branches are measured.

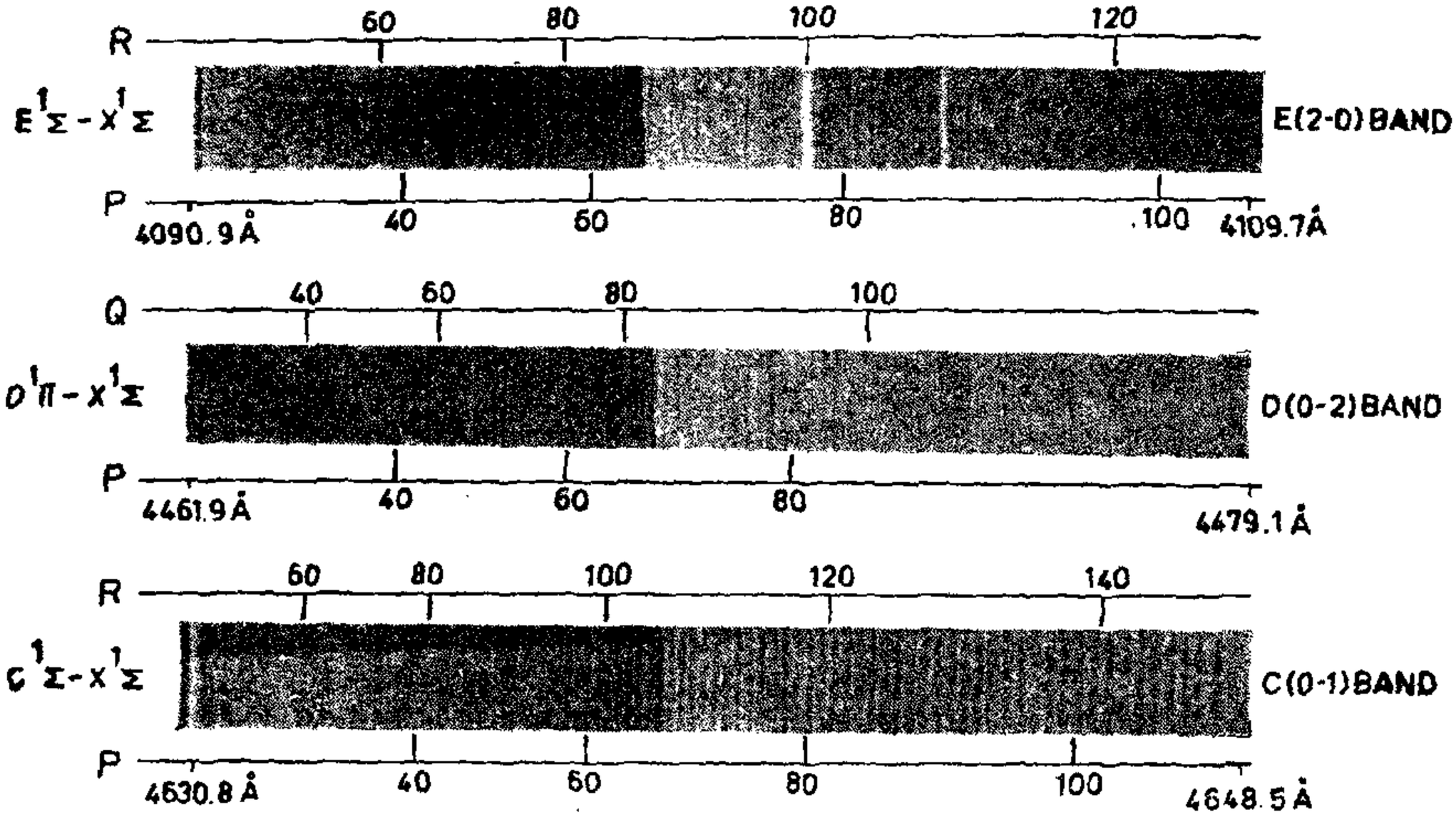

FIG. 1. Bands of ^{63}Cu ^{127}I.

Due to the high temperature of the emission source and the relatively small B_v values involved in the bands, members with low *J* values are not observed in the different branches and this necessitated a large extrapolation in arriving at the *J* numbering. To ensure that correct *J* numbering is obtained, the rotational constants *D'* and *D''* have also been included in the appropriate formulæ used to check the correctness of the numbering. Though only two branches could be measured for the D bands, since more than one band could be analysed, it was possible to obtain the *J* numbering from internal evidence only. The fine structure analysis also confirms that the three systems have a common lower state, the ground state of the molecule.

The Λ-doubling in the $D^1\Pi$ state is very small; the value of q being about −0·0001. This $^1\Pi$ state has a $^1\Sigma$ state on either side of it—the $C\ ^1\Sigma$ state 1080 cm.$^{-1}$ below it and the $E\ ^1\Sigma$ state 1050 cm.$^{-1}$ above it. The negative sign of the Λ-doubling constant q indicates that, compared to the $C\ ^1\Sigma$ state, the $E\ ^1\Sigma$ state plays a larger role in the Λ-doubling of the $D^1\Pi$ state. This is understandable because at the *J* values involved ($J = 50$ to $J = 80$) the energy levels of the $D\ ^1\Pi$ state are considerably closer to the $E\ ^1\Sigma$ state (800 cm.$^{-1}$ to 450 cm.$^{-1}$) than to the $C\ ^1\Sigma$ state (1300 cm.$^{-1}$ to 1700 cm.$^{-1}$).

The rotational constants obtained from the present analysis are shown in Table II. Details will be published elsewhere.

TABLE II

Rotational constants of ^{63}Cu ^{127}I molecule

State	B_0 (cm.$^{-1}$)	$\alpha \times 1000$ (cm.$^{-1}$)	$D_0 \times 10^{-7}$ (cm.$^{-1}$)	$q^{ap} \times 10^4$ (cm.$^{-1}$)	r_0 Å
$E\ ^1\Sigma$	0·0892	$0{\cdot}2_5$	≈0·9	.	2·117
$D\ ^1\Pi$	0·0911*	..	..	−1·0	2·096
$C\ ^1\Sigma$	0·0919	..	≈0·9	..	2·086
$X\ ^1\Sigma$	0·0969	$0{\cdot}3_2$	≈0·5	..	2·032

* B_0^d.

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1. Ramakoteswara Rao, P. and Brody, J. K., *J. Chem. Phys.*, 1961, **35**, 776.
2. —, — and Asundi, R. K., *Can. J. Phys.*, 1962, **40**, 1443 and other papers referred therein.
3. Ritschl, R., *Z. Phys.*, 1927, **42**, 172.