INTERACTION OF ATOMIC ENERGY LEVELS—V

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Introduction and Summary

In a series of papers with the same title, T. S. Subbaraya, K. Seshadri and N. A. Narayana Rao[1] have investigated the influence that Hg, Zn, Cd and Sn have on each other when they are excited under the same conditions:—the spectra of the individual elements were compared with those of mixtures of the same two by two, and information was obtained regarding the strengthening of some lines and the weakening of others on account of the mutual influence of the two elements in various energy states. Mixtures have been often studied, but mostly in connection with problems of quantitative analysis. A discussion along these lines is given for example by F. H. Newman.[2] Our problem is on the other hand linked with investigations on sensitised fluorescence and impacts of the second kind. In such experiments one is usually limited to investigating the effect of the impact of an atom in the normal state with a quantum or another atom in an excited state, the dispersion employed being low on account of the low intensity of fluorescent light. The method of mixture, on the other hand, has the advantage that a large dispersion can be employed and the effect of the impacts of atoms already highly excited can be studied. From an experimental point of view the only difficulty is to excite various elements under similar conditions. An arc or spark in air is inadmissible since we are interested in seeing that atoms of one or two elements alone exist in a condition suitable for mutual impacts. An arc or discharge in vacuum is the only available method. On account, however, of the variation in the conductivity and boiling point of various elements, suitable modifications of the discharge tube are required. The design by one of us (T. S. S.) employed in the present has proved very successful and extremely easy of construction and operation. The object of the present investigation was to test whether the method of the investigation of metallic vapours could be extended to binary compounds. The halides and sulphides of Hg, Cd and Zn were available for immediate

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[1] *Curr. Sci.*, 1939, **8**, 508; 1940, **9**, 14; 1940, 9, 173; 1941, **10**, 71.
[2] *Phil. Mag.*, 1939, **28**, 584.

use and the investigation was conducted with the sulphides first. The present paper deals with the case of mercury sulphide (HgS). The other two sulphides will be dealt with later on.

Experimental

A very simple design of discharge tube was developed so as to require no knowledge of the glass-blower's art which is particularly difficult when silica tubes are concerned. The construction is evident from Fig 1. S is a

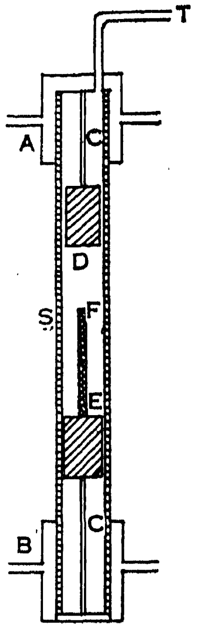

FIG. 1

transparent silica tube of about 1 cm. inner diameter and about 30 cm. long. Two cylindrical caps A and B, of copper or brass, provided with concentric cylindrical jackets having an inlet and outlet for water are fixed to the tube S by means of shellac. The upper cap A has a tube T of copper soldered to it, and this is connected to a Cenco Hyvac pump which is kept running throughout the operation of the tube. Since the power employed is large, these caps would get hot enough to melt the shellac in spite of the water-cooling. To prevent this, two stiff copper wires C and C are fixed to the caps and carbon cylinders D and E are fixed to the ends of these wires. The lower carbon cylinder E fits the tube like a piston while the upper is somewhat loose. When metals are to be excited they can be placed directly over the carbon E and the discharge started. But for non-conducting substances a slight modification is employed. A carbon rod F is fixed to the lower carbon cylinder E and the substance is placed all round this rod F. The heat of the discharge will usually vaporise the substance, but if necessary the silica tube can be heated by means of a Bunsen burner. Since we employed a high voltage source, the burner used for this purpose was provided with a long glass tube to serve as a handle, the rubber tube leading the gas to the burner passing through the glass tube. The two terminals of the secondary of a 4000 volt, 3 KVA transformer were connected to B and C. The primary was connected to 220 volt A.C. mains through a resistance which served to regulate the current. The discharge tube was fixed vertically before the spectrograph. It is well known that the intensities of spectral lines are modified considerably by the conditions of the discharge. Accordingly, the current, voltage pressure, etc., were kept constant as far as possible but even then, no attempt was made to compare the intensity of any particular line of the element with that of the same line in the spectrum of the compound. Instead, the relative intensities of various lines in one spectrum were compared with the relative intensities in the other. To eliminate the influence of accidental factors still further, two different spectrographs were used on many different days, the tube being cleaned and again filled with the substance in each case. Only those alterations of intensity which could be established without doubt in the spectra of both the spectrographs were taken into consideration. One of these spectrographs was a 10 ft. concave grating in a Rowland mounting, giving a dispersion of 5·5 Å per mm. in the first order. The other was a medium sized quartz spectrograph made by Hilger (E_2) giving the whole spectrum from 7000 Å to 2000 Å on a 10-inch plate. With the latter, spectra having different exposures ranging from 5 sec. to 6 min. were taken. The spectra of mercury, sulphur and mercury sulphide were taken with the grating while with the quartz spectrograph, only mercury and HgS spectra were taken. This was because sulphur gave only its band spectrum together with the band spectrum of CS and no lines were obtained. In one way the fact that the line spectrum of sulphur did not appear under the conditions employed was a disadvantage since modification in the intensities of sulphur lines cannot be brought forward in support of the interactions proposed to explain the observed changes in the intensities of mercury lines. More recently we (T. S. Subbaraya and Syed Yusuff) have been employing an electrodeless discharge to study the same problem but the enormous number of lines obtained (some 600 lines in sulphur with the E_2 spectrograph) has prevented us from being able to examine these results and report them in the present paper. We hope to present the latter results in a future communication.

Results.

As previously stated sulphur gave only its band spectrum together with the band spectrum of CS. In the mercury sulphide spectrum the bands of CS were stronger than when sulphur was employed, while the sulphur bands were weaker than in pure sulphur. The relative intensities of the mercury lines in the spectrum of Hg were compared with the relative intensities of the same lines in the HgS spectrum. Both grating and prism spectra were examined and each helped to decide points which were doubtful in the other. The following alterations in intensity have been established as the result of such a comparison. Some of these alterations can be easily noticed in the portions of spectra reproduced in the plates appearing herewith, but where the lines are rather faint in the negatives, the reproductions do not show the results clearly and hence these portions have been omitted. But the negatives allow definite conclusions to be reached even though the reproductions fail to show up properly. We have not been able to avail ourselves of a microphotometer and the results are based on visual estimates of a qualitative nature only. Lines enclosed in square brackets show an effect which is small and somewhat ambiguous.

Mercury Lines

Strengthened	*Weakened*
	2284 (6^3P_0) — 11^3S_1)
2534 ($6^3P_0 - 7^3D_1$)	2302 ($6^3P_0 - 9^3D_1$)
2652 ($6^3P_1 - 7^3D_2$)	2323 ($6^3P_2 - 11^3D_2$)
2654 ($6^3P_1 - 7^3D_1$)	2345 ($6^3P_0 - 10^3S_1$)
2655 ($6^3P_1 - 7^1D_2$)	2352 ($6^3P_2 - 10^3D_2$)
2753 ($6^3P_0 - 8^3S_1$)	2400 ($6^3P_1 - 9^3D_{1,2}$)
[2967 ($6^3P_0 - 6^3D_1$)]	[2447 ($6^3P_1 - 10^3S_1$)]
3125 ($6^3P_1 - 6^3D_2$)	[2482 ($6^3P_1 - 8^3D_{1,2}$)]
3131 ($6^3P_1 - 6^3D_1$)	2536 ($6^1S_0 - 6^3P_1$)
4916 ($6^1P_1 - 8^1S_0$)	2564 ($6^3P_1 - 9^1S_0$)
6072 ($7^3S_1 - 8^1P_1$)	2593 ($6^3P_2 - 13^3S_1$)
6716 ($7^1S_0 - 8^1P_1$)	2603 ($6^3P_2 - 11^3D_1$)
[6908 ($7^3S_1 - 8^3P_2$)]	2625 ($6^3P_2 - 12^3S_1$)
3984 Hg II	2640 ($6^3P_2 - 10^3D_1$)
	2675 ($6^3P_2 - 11^3S_1$)
	2699 ($6^3P_2 - 9^3D_{2,3}$)
	2760 ($6^3P_2 - 10^3S_1$)
	{ 2803 ($6^3P_2 - 8^3D_3$)
	{ 2804 ($6^3P_2 - 8^3D_2$)
	{ 2805 ($6^3P_2 - 8^3D_1$)
	3902 ($6^1P_1 - 8^3D_2$)
	3906 ($6^1P_1 - 8^1D_2$)

Discussion

The theory of the interaction of atoms in different energy states is not developed in sufficient detail to understand each case of alteration of intensity in entirety. The chief theoretical result is that an exchange of excitation energy is most probable when the energy levels are sufficiently close. From the curves given in Mott and Massey's *Theory of Atomic Collisions*, pp. 235-46, it appears that the probability of transfer is a maximum when the "Resonanz-Unschärfe" is zero for collisions which result in transitions both of which are allowed by the selection rules. If one of the transitions is allowed and the other is associated with only a quadrupole moment, the probability is a maximum for zero 'resonanz-unschärfe' for heavy and large atoms only, while the maximum for small and light atoms occurs when the change in energy as a result of the interaction is a gain of atomic energy from the kinetic energy of the interacting atoms. When the interaction between the two atoms is large there are two possibilities according as a certain function $k^2 - k_n{}^2 - \frac{8\pi^2 M}{h^2}(V_{00} - V_{nn})$ has a positive zero R or not. If a zero R exists, the maximum shifts towards positive ΔE (ΔE being the energy difference between initial and final states) while if R does not exist the maximum occurs at $\Delta E = 0$ but the resonance is still not sharp. We shall try to interpret our results in the light of these general considerations.

Strengthened Lines.—The upper states of these strengthened lines fall into four groups, each of approximately equal energy. Thus λ 3131, 3125 and 2967 have upper levels which are 71333, 71394 and 71333 cm.$^{-1}$ respectively above the ground state of mercury. Sulphur has a level having the energy 71347 cm.$^{-1}$ which can be in resonance with these mercury levels and thus cause the observed increase in intensity. In this case the transition in the mercury atom is associated with a quadrupole moment while that in the sulphur atom is allowed. The next group consists of the lines 4916 and 2753 having upper levels with energies 74402 and 73959 cm.$^{-1}$ respectively. Transitions from these to the ground state are associated with a quadrupole moment. Sulphur has states of energy 73905, 73909 and 73915 cm.$^{-1}$ which can provide the necessary energy. We then have the lines 6908, 2655, 2654, 2652 and 2534 with upper states of energy 76821, 77061, 77082, 77105 and 77082 cm.$^{-1}$ respectively. The sulphur levels which probably provide the necessary energy are 76458 and 76721 cm.$^{-1}$ respectively. The remaining lines 6072 and 6716 with upper states at 78810 cm.$^{-1}$ can be strengthened by taking the energy of the sulphur level at 78264 cm.$^{-1}$ Confirmation of these explanations is not possible since we have not obtained any lines of sulphur and so cannot find if any of them have altered in intensity.

The strengthening of the spark line 3984 shows that mercury atoms are ionised in greater numbers than in the case of the discharge in pure mercury. This is probably because the ionisation energy of the sulphur atom (83554 cm.$^{-1}$) is very nearly equal to that of the mercury atom (84179 cm.$^{-1}$) and a resonant exchange of ionisation energy occurs.

As regards the strengthening of the CS bands as compared with the S_2 bands which appear weaker than in sulphur, the upper state of the CS bands having an energy $=38800$ cm.$^{-1}$ we see that it can take energy from the upper state of 2536, *viz.*, 39410 cm.$^{-1}$ The corresponding weakening of 2536 supports this view. The upper level of the S_2 bands, being at 32000 cm.$^{-1}$ is not in resonance with any mercury level and is thus not strengthened.

Weakened Lines.—The upper levels of the weakened lines also fall into four groups. Of these the upper states of 2564, 3906, 3902, 2806, 2804, 2803 and 2482 have energies equal to 78401, 79658, 79688, 79678, 79700 and 79688 respectively. The corresponding level of sulphur which can be excited at their expense is most probably that at 79986 cm.$^{-1}$ Then there are the lines 2345, 2447 and 2760 with an upper level at 80268 cm.$^{-1}$ This level probably gives its energy to excite the sulphur level at 80443 cm.$^{-1}$ Next we have the group 2302, 2400, 2699, 2675 and 2284 with upper levels of energies 81082, 81082, 81082, 81414 and 81414 cm.$^{-1}$ respectively. These are near the sulphur levels at 81275 and 81622 respectively and thus produce resonance. The upper level of 2352 ($=81909$) probably gives its erergy to the sulphur level at 82047. Lastly the lines 2625, 2603, 2323 and 2593 with upper states of energies 82121, 82444, 82444 and 82588 possibly weaken on account of the energy of their upper levels being used to excite the sulphur level at 82347.

Thus we see that corresponding to every line of mercury which shows an increase or decrease of intensity there is a sulphur level with which the upper state of the line in question is in resonance. Some other levels which are also of nearly the same energy in sulphur and in mercury involve lines which are outside our observations which extend from about 7000 Å to 2200 Å. Our observations therefore correspond to the theory though some further details cannot be checked owing to the non-appearance of sulphur lines. The experiments are further of interest in showing that the lines of an element do not occur with the same relative intensity in the spectrum of the element and in that of one of its compounds. There are many lines which remain unaffected and these must be the ones that should be resorted to in problems of spectrochemical quantitative analysis.

In conclusion, it is a pleasure to record our thanks to Professor A. Venkat Rao Telang for the facilities given to us during the prosecution of this work.