ELECTRODELESS DISCHARGE LAMPS AND SOME FEATURES OF SPECTRA EMITTED BY THEM

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ABSTRACT

Some salient features, such as self-absorption and selective excitation of elements, of microwave excited thorium iodide and other electrodeless discharge lamps are discussed. The importance of these features for classification and analysis of spectra and possibly for spectrochemical analysis is indicated. The use of the electrodeless lamp as a source for the excitation of molecular spectra is pointed out.

INTRODUCTION

FOR the last several years microwave excited electrodeless discharge lamps containing metallic halides have been recognized to be among the best sources for exciting atomic spectra (Tomkins and Fred, 1957). In fact, they are at present the most commonly employed sources in the investigation of the atomic spectra of heavy elements. The lines emitted by them are very intense and sharp. Several hundred atomic lines of thorium emitted by the thorium iodide lamps have been interferometrically measured (Giacchetti *et al.*, 1964 and earlier references mentioned in that article) and in many laboratories where precision spectroscopic work is carried out the thorium lamp is replacing the iron hollow cathode lamp as the source for providing standard wavelengths. Some special features of the spectra emitted by the metallic halide electrodeless discharge lamps, first observed by Tomkins and Fred (1957), have been recently exploited as aids in the analysis of complex atomic spectra for example in the case of gadolinium and curium by Worden *et al.* (1964) and in the case of erbium by Marquet and Davis (1965).

The electrodeless discharge lamp has also been found to be an intense source for the excitation of certain molecular spectra (Ramakoteswara Rao and Brody, 1961). It has been so employed, especially in this laboratory,

in the investigation of the spectra of several diatomic molecules (CuCl, CuBr, CuI, S_2 and AlI).

When the 6·6 metre concave grating spectrograph was set up in this laboratory (Apparao, Ramakoteswara Rao and Saksena, 1964) the need was felt for a spectral source providing suitable wavelength comparison spectra on the grating spectrograms. Thus the preparation of the thorium iodide electrodeless discharge lamps was undertaken and several successful lamps were prepared. A few uranium iodide lamps were also prepared for use by the interferometry group in this laboratory.* In this paper some salient features observed in the spectra emitted by such lamps are discussed and illustrated.

PREPARATION AND SPECIAL FEATURES

The method followed of preparation of the lamps was similar to that described in detail by Tomkins and Fred (1957), except that the thorium and uranium iodides were formed by directly reacting thorium or uranium with iodine (instead of thoria or uranium oxide with aluminium iodide) in vacuum at high temperature. The sealed electrodeless lamps were 1 cm. in diameter and 4 to 8 cm. long and contained a few milligrams of thorium or uranium tetraiodide and neon or argon to a pressure of about 2 mm. of Hg. The lamps were excited by a 2450 Mc./sec. diathermy microwave oscillator with a maximum power output of 120 watts. External heating was provided by a furnace consisting of a quartz tube on which were wound a few turns of nichrome wire.

A. Source of Standard Lines

The availability as standards of a sufficient number of sharp lines of precisely known wavelengths is a distinct advantage for the accurate determination of the wavelengths of the fine structure of bands. Compared to that of iron, the thorium spectrum for instance, contains a much larger number of lines in the entire optical region and thus serves as a much better wavelength reference spectrum. This is illustrated in Fig. 1, which shows the $\Delta v = 0$ sequence of the D system of ^{63}CuI molecule at 4359·6 Å photographed in the second order of the 6·6 metre grating spectrograph (dispersion 0·6 Å/mm.) with comparison spectra of a two-ampere iron arc at the top

* Electrodeless lamps of cupric chloride, bromide and iodide, of aluminium iodide and of sulphur have also been successfully prepared in this laboratory in connection with investigations of molecular spectra.

and of a thorium lamp at the bottom. In the region covered by the band sequence, there are only three iron lines as against more than twenty-five evenly spaced sharp thorium lines, six of which (marked in the figure) are interferometrically measured.

B. Classification and Analysis of Complex Spectra of Heavy Atoms

Some of the spectral lines of atoms emitted by the lamps operating at high temperatures exhibit self-absorption. Such lines must obviously involve either the ground state or some very low-lying states in the atom. Similarly it is possible to distinguish between the first and second spectra of atoms, by recording the spectrum of the electrodeless lamp excited at different powers of the microwave oscillator. These features of the spectra emitted by electrodeless lamps, first noticed by Tomkins and Fred, have recently been exploited as aids in the classification and analysis of complex spectra. Thus for instance the ground term and a few other low-lying terms were identified by means of self-absorption, in the case of the curium spectrum by Worden *et al.* (1964) and in the case of the erbium spectrum by Marquet and Davis (1965). Similarly the former authors could separate out the spectra of the neutral atom and of the singly ionized ion in the case of Gd and Cm by studying the changes in the electrodeless lamp spectrum excited at different microwave powers.

The phenomenon of self-absorption is illustrated below in the spectra of the thorium and uranium lamps. Figure 2 is the spectrum of the thorium lamp excited by the microwave oscillator operating at 100 watts, recorded in the second order of the 6·6 metre grating. The lamp was also heated externally, the temperature of the lamp being around 600° C. The thorium lines which show self-absorption are marked in the figure. All these lines are shown to involve transitions to the ground state, $a\ ^3F_2$, of the thorium atom (Zalubas, 1959). Figure 3 reproduces the line contour of the 5027·398 Å line of uranium involving its ground state $a^5L_6^0$, recorded on a photoelectric recording type Fabry-Perot spectrometer.† This line, emitted by the uranium lamp operating at high temperature, provides another illustration of self-absorption. The above examples show that by enabling one to identify transitions involving the ground state (and possibly some other low-lying states), the electrodeless lamp spectra provide valuable clues in the analysis of an unknown spectrum. In this regard the information one obtains from

† This has been recently built in our laboratory. A report on the instrument is under preparation.

the spectra emitted by these lamps is similar to what one gets from absorption spectra in King's furnace.

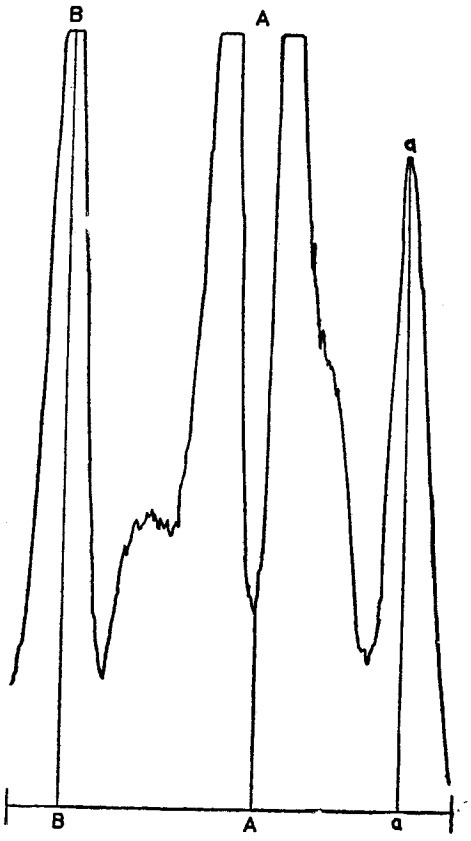

FIG. 3. 5027 Å lines of uranium, emitted by a microwave excited uranium iodide lamp operating at high temperatures, recorded on a Fabry-Perot spectrometer.

A—5027·398 Å line of ^{238}U, transition 19985·5 cm.$^{-1}$–$^{5}L°_{6}$ (ground state).

a—5027·294 Å line of ^{235}U, transition same as above.

B—5027·523 Å line of ^{238}U.

C. *Trace Impurity of Zirconium in Thorium*

A freshly made thorium lamp showed only the spectrum of the rare gas when excited by a 2450 Mc./sec. microwave oscillator at low power, 20-30 watts. On increasing the power to between 40 and 60 watts, the spectrum of the rare gas was suppressed and the spectrum of zirconium‡ appeared. At

‡ Spectrochemical analysis of the thorium sample used revealed zirconium and a few other impurities in trace quantities.

still higher powers and in some cases with external heating in addition, the spectrum of thorium appeared and gained in intensity. At this stage it was the spectrum of thorium which was the most predominant, though lines due to zirconium and iodine were also present weakly. After the lamp was run a few times free iodine formed due to the decomposition of ThI_4, got accumulated and on starting, the lamp showed the spectrum of iodine instead of that of the rare gas. Some of these features are illustrated in Fig. 4.

D. Possible Applications to Spectrochemical Analysis

The behaviour of the zirconium impurity in thorium described above points to the possibility of employing the electrodeless lamp in spectrochemical analysis. Preliminary results obtained by working with uranium lamps also lend strength to this possibility. However more detailed work has to be carried out before the use of the microwave excited electrodeless discharge lamp in spectrochemical analysis can be exploited advantageously. The small amount of the sample required for analysis, its containment and its recoverability if need be, are some very favourable features of the electrodeless lamp for spectrochemical analysis of scarce and/or radioactive samples.

E. Excitation of Molecular Spectra

A brief reference here to the electrodeless lamp as a source of molecular spectra is probably not out of place. The possibility of excitation of the molecular spectrum in an electrodeless tube depends upon the stability of the molecule. The spectra of the constituent atoms also appear along with the molecular spectrum and gain in relative intensity with increasing excitation. The most important feature of the lamp in this context is the small amount of the substance required—a lamp containing even a milligram of the substance works for several hours. This permits the use of separated isotopes, which results in considerable simplification in the spectra of molecules consisting of more than one isotopic species. Thus, for instance, the fine structure analyses of some band systems in the copper halide molecules, known for a very long time, have only recently been made using electrodeless lamps containing milligram quantities of separated isotopes of copper and the halogens (*see* Ramakoteswara Rao, Brody and Asundi, 1962, for $^{63}Cu\ ^{35}Cl$. Fine structure analysis of the ^{63}CuI spectra is currently being carried out by the author).

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EXPLANATION OF PLATES

PLATE VI

FIG. 1. $\Delta v = 0$ sequence of the D system of ^{63}CuI molecule photographed in the second order of the 6·6 metre grating spectrograph at a dispersion of 0·6° Å per mm. The comparison spectrum at the top is that of a two-ampere iron arc, while the one at the bottom of a thorium iodide lamp. Lines marked with asterisks are interferometrically measured.

FIG. 2. Spectrum of the thorium iodide lamp operating at a high temperature photographed in the second order of the 6·6 metre grating spectrograph. Lines showing self-absorption are marked.

PLATE VII

FIG. 4. Spectrum of the thorium iodide lamp photographed in the first order of the 6·6 metre grating spectrograph. Spectra A, B, C and D correspond to 30, 40, 50 and 60 watts of power of the microwave oscillator exciting the lamp. Enlarged sections are shown in the bottom.

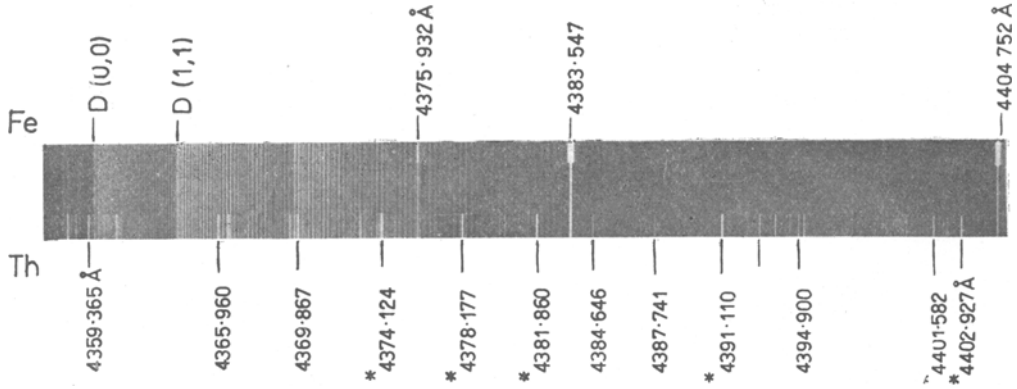
Fe
D (0,0)
D (1,1)
4375·932 Å
4383·547
4404 752 Å
Th
4359·365 Å
4365·960
4369·867
*4374·124
*4378·177
*4381·860
4384·646
4387·741
*4391·110
4394·900
4401·582
*4402·927 Å

FIG. 1

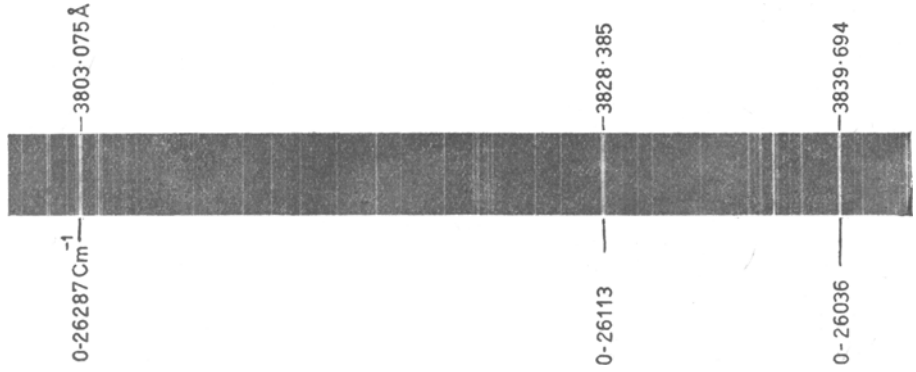
3803·075 Å
3828·385
3839·694
0-26287 Cm⁻¹
0-26113
0-26036

FIG. 2

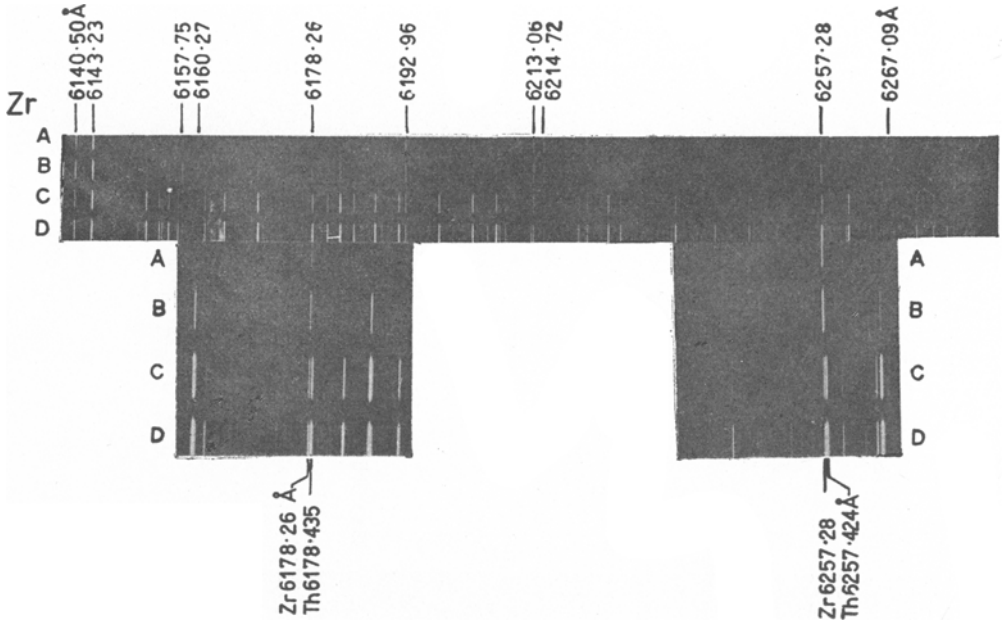
Zr
6140·50Å
6143·23
6157·75
6160·27
6178·26
6192·96
6213·06
6214·72
6257·28
6267·09Å
A
B
C
D
Zr6178·26 Å
Th6178·435
Zr6257·28
Th6257·424Å

FIG. 4