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FINAL TECHNICAL REPORT

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ON

ATOMIC EMISSION SPECTROSCOPY

Covering the period 2-1-69 through 1-31-75

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ATOMIC EMISSION SPECTROSCOPY

I. Summary of Research Activity

1. Research Aims

We have investigated both theoretically and experimentally relatively simple spectra chosen to shed the most light on the relationship between the Slater-Condon theory and the conditions within the atom as revealed by experimental data. The importance of the Slater-Condon theory is that it is the most readily applicable and hence the most widely used theory for the interpretation of experimental atomic spectra and structure. It plays a particularly significant role in that it must be very heavily leaned upon in the interpretation of the more complex spectra such as rare earth spectra which comprise a large share of present day efforts in atomic spectroscopy. It was consequently important to choose carefully and to investigate thoroughly simpler spectra where various individual facets of the theory can be checked with more assurance and where departures between theory and reality could be more easily isolated and studied. One important consequence of such reinforcements and discrepancies was to give us a guide to what extent we could rely on the Slater-Condon theory and where we must develop new approaches to the application of theory.

We chose for our investigations those spectra which had not been adequately analyzed, or whose analyses showed fundamental discrepancies with the theory, or with the analyses of closely related spectra. We provided for each a relatively complete wavelength and wave number description, and an atomic energy-level array with intermediate coupling wave functions that gave the most nearly appropriate configuration and angular momentum composition labels. These carefully prepared experimental data and subsequently derived level arrays and wave functions were provided to accomplish in varying degrees the following objectives:

To provide sufficiently accurate intermediate-coupling wave functions for the reliable calculation of oscillator strengths, transition probabilities, g values, relative Stark shifts and other fundamental atomic properties.

To determine the range and pattern of coupling conditions which prevail in these spectra.

To provide laboratory data which will aid in the identification of unknown lines encountered in the solar and stellar spectra being obtained by astronomers and in the current spectroscopic programs with rockets and orbiting satellite observatories.

To establish, particularly in the vacuum ultraviolet, wavelength standards needed by modern higher dispersion blazed-grating spectrographs.

To obtain better values of the series limits and ionization potentials.

To learn more about the types of shifts that are encountered or can be expected in the laboratory sources used.

At the same time we expended considerable effort in developing electronic digital computer methods that are applicable to the general problems of data reduction and to theoretical interpretation of atomic spectra.

2. Spectra Investigated and Work Completed Under this Grant

a. Silicon

The principal contribution to the previous knowledge of the spectrum of Si I and its analysis was made by Kiess (1938). Work in our laboratory under this grant has included the use of low pressure arcs, electrodeless discharge tubes and hollow cathode sources for silicon. With these sources, approximately 400 lines of Si I were measured by grating spectrograph and more than one-third of these determined interferometrically. Through the cooperation of Mrs. Charlotte Sitterly who made available the revised solar ledger prior to publication we were able to identify as Si I more than 100 previously unidentified lines of the solar spectrum. Cooperating with Kaufman at NBS and Litzén at the University of Lund, Sweden, knowledge of the Si I spectrum now extends from 1540 to 25000 Å. A paper (Ref. 31) on the vuv was published giving a complete list of low-pressure source levels and Ritz standards of Si I. Ab initio calculations of oscillator strengths have been made for some of the Si I transitions which appear in solar spectra (Ref. 44).

b. As II

The first analysis of the As II spectrum was carried out by Gartlein (1928) with the classification of 75 lines. The analysis was extended by Rao (1932) who classified 187 lines with wavelengths between 802 and 6528 Å. The most recent and most extensive investigation of the spark spectra of arsenic was carried out by Bedford and Crooker (1954-1958). Bedford observed the region between 530 and 9301 Å and was able to classify 495 of these lines as transitions between 47 even and 57 odd levels of As II. Zeeman effect measurements of the arsenic spectra were made by Green and Barrows (1935).

We have investigated the second spectrum of arsenic over the spectral region 701-11064 Å by means of high-resolution grating spectrographs and the Fabry-Perot interferometer. The light sources were electrodeless discharge tubes. Wavelengths of As II lines were measured relative to thorium or iron standards in the region above 2000 Å and relative to silicon and germanium standards or persistent well-known impurity lines of C, N, O, etc., in the region below 2000 Å which was done with the aid of V. Kaufman at NBS. For interferometric measurements, the ^{198}Hg lines 2537 and 5462 Å were used as standards.

The total number of measured As II lines is 1034, of which 391 are newly found and 987 are now classified. This includes 540 newly classified lines that either extablish new levels or fill gaps in the previcusly known level array. We extended the analysis of As II by the addition of 44 new even levels and 37 new odd levels. Reassignment has been made of three even and three odd previously found levels. The total number of classified levels is 76 even and 90 odd. The series limit of As II identified with $^2P_{1/2}$ As III was calculated from 12 Rydberg series to be 149932 $\pm$ 8 cm^{-1}, corresponding to an ionization potential of 18.588 $\pm$ 0.01 V for the As^+, ion. (Ref. 50)

We followed this investigation with a Zeeman study in which we operated As electrodeless discharge tubes in a field of 24025 G. We obtained Zeeman patterns for 232 As II spectral lines from 2361 to 10556 Å and their measurement yielded 80 Landé g factors, of which more than half are new. There is agreement between these and the g values calculated by least-squares fitting for single configurations or for multiconfigurations where configuration interaction is noticeable. However a surprising and important result for the multiconfiguration group $4s4p^3$-4p4d-4p5d-4p6d-4p7s was obtained and is discussed in Refs. 54, 55, and 57.

c. Rb I

We developed an atomic-beam light source for the optical study of alkali emission spectra. This source was used to study the hyperfine structure of the resonance lines of Rb isotopes 85 and 87. The small Doppler width of this source, .0015 cm^{-1}, permitted the first optical measurements on individual transitions that make up these two resonance lines, 7802 Å and 7949 Å. The relative intensities and separations of the twenty individual components were measured by means of a pressure-scanned Fabry-Perot spectrometer with digitized output. The absolute wavelength of one hfs component in each resonance line was then measured interferometrically with respect to the international standard of length, Kr 6057.802105 Å and this was combined with the former results to obtain the following centers of gravity for the two lines of natural rubidium 7802.41319 Å and 7949.7897 Å. (Ref. 52)

d. Cu II

The spectrum of singly ionized copper has been investigated photographically from 1979 to 11227 Å using plane and concave grating spectrographs and Fabry-Perot interferometers. The light source employed was a water-cooled hollow-cathode discharge tube operated with helium or neon. We have measured 1966 lines, 1125 of which were newly observed, 1011 of which were measured interferometrically, and 1834 have been classified. Our analysis has added 97 new energy levels and 11 doubly degenerate levels were resolved, bringing the total of known levels to 173 even and 178 odd. As a consequence of the analysis we have been able to compute the wavelengths of 509 vuv lines using the Ritz combination principle. Of these 436 are recommended as wavelength standards with estimated uncertainties less than 0.0005 Å. The lines of Cu II are not suitable for the most precise standards because of the presence of hyperfine structure, however the density and accuracy of these calculated lines provide a system of wavelengths in the vacuum ultraviolet down to 675 Å superior to that of any other single spectrum. A slightly improved value of the series limit has been calculated to give 163669.2 $\pm$ .5 cm^{-1} or 20.29529 $\pm$ .00007 eV. (Refs. 46,49)

e. P II

The most recent previous work on the analysis of P II was that of W. C. Martin in 1956. As a result of problems he pointed out in his analysis, we investigated the Zeeman effect of P II. Electrodeless-discharge tubes operated in a field of 32215 G have given Zeeman patterns for 223 P II spectral lines from 2285 to 7846 Å and yielded 76 Landé g factors. There is good agreement between these g values and those calculated from wave functions obtained by least-squares fitting of energy levels for the single configurations, 3p4p, 3p5p, 3p4f, 3p4s, 3p5s, and 3p6s. However, even when configuration interaction is introduced in the multiconfiguration case, 3s3p -3p3d-3p4d-3p5d, experimental energy levels will not give good agreement with the corresponding calculated values unless LS-dependent parameters are used in the least-squares fitting. The newly obtained g factors, combined with the predictions of the least-squares energy-level fitting process, have forced a rejection of one even and two odd previously found levels, established nine new levels, reclassified three even and ten odd levels. The new levels belong to the now completed configurations 3p5p and 3p5d. A careful search for transitions to support poorly established levels yielded 44 new lines that confirm newly found levels and fill gaps in the previously known level array. (Ref. 58).

f. Cl I, Br I, and I I; 1.8-4.0 μm Region

By use of liquid-nitrogen-cooled lead sulfide detectors Humphreys has extended observations of the first spectra of the halogens in the infrared region as far as 4.0 μm. Descriptions, comprising wavelengths, wave numbers, intensities, and classifications, are presented that serve to close the gap between the upper wavelength limit of the detailed published analyses of these spectra at about 2.5 μm and the groups of recently classified lines near 4 μm, and also to report newly observed lines in the 1.8-2.5-μm region made accessible by detectors of improved response characteristics. Listed wavelengths of observed and identified lines are calculated from established values of the energy levels. The descriptions should facilitate the identification of halogen lines in mixed spectra excited in electrodeless tubes containing halogen compounds. (Ref. 56)

g. Ne I, Ar I, and ^{136}Xe I; 1.2-4.0 μm Region

Humphreys has prepared descriptions of the first spectra of neon, argon, and xenon 136, comprising calculated wavelengths, calculated wave numbers, relative intensities, and classifications. The calculated values are derived from currently best established energy levels, obtained mostly from interferometric observations and adopted as standards by the International Astronomical Union. All listed lines have actually been observed. This paper makes available a compilation of all results previously presented in fragmentary or relatively inaccessible reports with intensities normalized to as nearly a uniform scale as the various observations permit. (Ref. 59)

h. Stability of Fringe Counting Interferometers

In order to check the linearity of the stage drive of our large Grant Wavelength Comparator against the wavelength of a He-Ne Lamb-stabilized laser, we constructed several configurations of a corner cube interferometer on the comparator. In this article, two configurations of an automatic bidirectional, fringe-counting corner-cube interferometer are compared. They differ only in the method of quadrature phase introduction. The one using polarization coding has excellent phase stability at optical path differences as large as 955 mm, whereas the one using adjacent beams has such poor phase stability as to render it useless at path differences greater than 700 mm. A useful, well-defined alignment procedure is given for the corner-cube interferometer. (Ref. 60)

i. An Autoranging Scanning System and Compatible Methods of Noise Reduction

We have designed and constructed an autoranging scanning system to digitize the output of an infrared spectrometer and record it on magnetic tape. This system combines in a unique way four different known methods of removing noise; a different method being used for each of four different but overlapping frequency ranges in which the noise is encountered. The input signal, whose amplitude may range over ratios of 2000 to 1, is automatically scaled to give a signal between 0.25 and 0.90 multiplied by an appropriate factor. The four noise reduction techniques are compatible with the autoranging feature. Two are a part of the electronic system itself and two utilize the computer in data processing. In particular, smoothing of data by least squares convoluting numbers and co-addition (addition of corresponding points) of spectral scans over the same region give definite advantages when compared to narrow band amplifier methods in distinguishing and measuring real features with intensities of the order of the noise background of the system. The methods described have general applicability to scanning systems in which the profile of the curve generated is the important measurement. (Ref. 61).

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This project was started in 1958 under support of NSF and since October 1963 has been jointly supported by NSF and NASA. The NASA support started with Grant NSG 301-63 and on February 1, 1969 was changed to NGL 15-005-003, which is the grant covered by this final technical report. Much of the background for this work is contained in the publications which appeared during this earlier support period. The following list of publications and papers concerns work relevant to these grants that was done by members of the Purdue spectroscopy section or by cooperating individuals from other laboratories. Those numbered from 42 to 63 appeared during the period covered by this final technical report.

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