Lawrence Berkeley National Laboratory
Recent Work

Title
THE ABSORPTION SPECTRUM OF ASTATINE

Permalink
https://escholarship.org/uc/item/3j83k4hx

Author
McLaughlin, Ralph.

Publication Date
1964-02-01

eScholarship.org Powered by the California Digital Library
University of California

UCRL-11253

University of California

Ernest O. Lawrence Radiation Laboratory

THE ABSORPTION SPECTRUM OF ASTATINE

Ralph McLaughlin

February 1964

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted for publication in
J. Am. Optical Soc.

UCRL-11253

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE ABSORPTION SPECTRUM OF ASTATINE

Ralph McLaughlin

February 1954

THE ABSORPTION SPECTRUM OF ASTATINE *

Ralph McLaughlin

Lawrence Radiation Laboratory
University of California
Berkeley, California

February 1964

ABSTRACT

A highly sensitive method of spectrographic detection of gases was developed. This method was used to detect the absorption of atomic astatine. Two lines were recorded whose wavelengths were 2244.01 Å and 2162.25 Å. These lines were tentatively assigned to transitions $^2P_{3/2}{}^0 - {}^4P_{5/2}$ and $^2P_{3/2}{}^0 - {}^4P_{3/2}$. The assignment of two resonance lines of polonium was confirmed.

INTRODUCTION

Astatine was first identified in 1940.[1] The optical spectrum of this element has not yet been reported. The reason for this delay is that the most stable At isotope has a half life of only 8.2 h. Because of this, the largest quantity of At that has been accumulated thus far is of the order of 1 microgram. Further, the handling of this quantity of At involves the problem of protecting personnel from fairly high levels of radioactivity.

These difficulties have been overcome by the development of a highly sensitive method of spectroscopic detection. The method is an adaptation of capillary-absorption-cell spectroscopy[2,3] in which gaseous rather than liquid samples may be used. It appears that atomic vapors are more easily detected by this method than are ions in solution. Craig, Bartel, and Kirk report detection of 2 nanograms of Cr ions in solution.[3] In this experiment as little as 0.2 nanograms of At were detected. This difference in sensitivity is undoubted related to the differences in oscillator strengths of ions in solutions and atomic vapors. The method should be applicable to any atom that has an appreciable vapor pressure below the melting point of quartz.

EXPERIMENT

The astatine was produced in the 88-inch Cyclotron at the Lawrence Radiation Laboratory, Berkeley. The reaction is Bi^{209} (α,xn) At^{211}, At^{210}, and At^{209}. A total of 11 microampere-hours of 50-MeV α particles was used. Calculations using known excitation functions[4] indicate that roughly 2×10^{14} atoms of At were produced. This corresponds to 70 nanograms. Survey-meter readings were consistent with this calculation.

Metallic Bi was used as the target material. The At was distilled from the Bi target onto a 1-mil Pt disk.[5] The disk was folded and dropped into a 8-mm-o.d. quartz tube, having a 14/35 standard taper on one end and the quartz capillary absorption cell on the other. The tube was evacuated to roughly 30 microns and sealed off. The sealed-off portion contained the Pt disk and the capillary cell. This was placed in a furnace and heated to 700°C in order to decompose any organic material that may have followed the At chemistry. The tube was next partially placed in a furnance such that the Pt disk was in the hot zone and the capillary cell was in a bath of liquid nitrogen. The furnace was heated to about 700°C. This caused most of the At to be condensed into the capillary cell. The tube was allowed to cool and again sealed off such that the Pt disk was in one section and most of the At in the other. The section containing the At was kept immersed in the liquid-nitrogen bath during this operation. The result was that most of the At was now contained in a capillary T-tube whose total volumne was about 50 micro-liters. No attempt was made to determine accurate yields for this procedure, but survey-meter readings indicated that better than 50% of the calculated amount of the At ended up in the T-tube.

A thermocouple was placed at the center of the T-tube. Each arm of the T was placed in a small tube furnance made of nichrome wire. Asbestos string was wrapped around the center section of the T which was not covered by the furnance. The thermocouple thus registered the lowest temperature in the T-tube. The arms were at a higher temperature. The absorption cell was next aligned with the optical path of the spectrograph. To accomplish this a light source was placed at the collimating mirror of the spectrograph. A lens was used to focus the image of this source on the inside of the entrance slit. The absorption cell was placed about 1/2 in. in front of the slit. Alignment was accomplished by moving the cell until the image of the slit was visible through the capillary. It was necessary to hold the eye within a few inches of the capillary in order to see the slit image. This alignment was accomplished as quickly as possible, since at this time 10 R of gamma radiation was coming from the cell. A 1000-W Hanovia hydrogen-discharge tube was used to produce the continuum. This tube lends itself to easy alignment, since it is possible to sight through the discharge region. Alignment was accomplished by adjusting the discharge tube until a bright spot of light could be seen coming through the capillary while sighting through the discharge tube. The cell was then heated such that the thermocouple registered a temperature of 600°C. This was done in order to thermally decompose molecules that might have contained At. Survey exposures were taken on Eastman Kodak 103a-O photographic plates. Ten-minute exposure times were adequate. The spectral region between 3000 and 2100 Å was recorded.

When it was found that At lines appeared on the plates, further exposures were taken using Eastman Kodak IV-O plates. These were exposed for 1h and developed for 9 min in D-19 developer. The ion-arc spectrum was recorded on

these plates for wavelength calibration by the use of a Hartmann diaphragm. Further exposures were taken to verify that the change in line intensity with time was consistent with the radioactive decay of At (see Fig. 1). Wavelengths were measured with a comparator produced by Grant Instruments, Inc. The spectrograph used was a 21-ft Wadsworth mount produced by the Jarell-Ash Co. It contained a 30,000-lines-per-inch grating which was blazed for 3000 Å. The capillary absorption cells were made by Harry S. Powell and Dane H. Anderberg at this laboratory. These were made of 1-mm-i.d. and 8-mm.-o.d. quartz capillary tubing. The absorption cell was 5-cm long. The T seal was made by drilling a 1-mm-diam hole perpendicular to the long axis of the tube. The side arm was also made of capillary tubing to minimize the volume that finally contained the At. To reduce stray light, both ends of the absorption cell were masked such that light could not pass through the walls of the tube. This was accomplished by painting both end windows with Liquid Bright Platinum produced by the Hanovia Chemical and Mfg. Co.

RESULTS

The most striking feature of these plates was an intense absorption band at 2537 Å which was 5-Å wide. If the cell was allowed to cool, this band narrowed down to a sharp line. It was concluded that this feature is due to Hg that had followed the At chemistry. The amount of Hg could be estimated from the known dependence of band width upon concentration.[6] These calculations indicated that a few micrograms of Hg were present. Mercury contamination of the Pt disk of the order of a few ppm seems the most likely source. Aside from the Hg band, the most intense features on the plate were two lines of Po and one line of At; Po^{210} is the decay product of At^{210}. Faint absorption lines of Cd (λ 2288) and Bi (λ 2228 and 2230) were also recorded. Light of shorter wavelength than 2100 Å was not transmitted. Broad diffuse absorption was detected which showed some structure. Absorption maxima were measured at λ 2246, 2238, 2216, 2206, 2174, and 2165 Å (See Fig. 2). The species causing this absorption is not known; Po_2 or HgPo seem like reasonable possibilities. It is believed that the same species is responsible for the more intense absorption of light of shorter wavelength. The second At line was more difficult to detect, since it was located in this region of diffuse absorption. High-contrast plates and long development times were resorted to in order to better define this line for wavelength measurement. The recording of Po lines 2558 and 2450 in absorption confirm the assignment of these lines to reasonant transitions.[7]

A comparison of different plates revealed a shift in the ion-arc spectrum with respect to the absorption spectrum. This resulted because it was not feasible to use the same optical path for light from the ion arc as was used for light passed through the absorption cell. The amount of shift was determined by comparing the

ion spectrum with the Cd and Bi lines. Four Si emission lines from the hydrogen-discharge tube were also used. After these corrections, measurements of the At lines from two different plates agree within 0.02 Å units. The values are 2244.01 and 2162.25 Å. Because of the appearance of the At lines in a region of diffuse absorption, it is difficult to make meaningful statements about line intensities. The indication was that the λ 2244 line was the more intense. However, as the At decayed the intensity of the two lines approached each other. When both lines were very weak, it was hard to detect a difference in intensity. The At lines were still visible 72 h after bombardment. This represents nine half lives of the At^{210} isotope. It follows that if 70 nanograms were initially produced, the final absorption was caused by 0.2 nanograms.

DISCUSSION

Two facts support the contention that the lines observed were At lines. There are no other resonant lines reported at these wavelengths, and the decay of line intensity is consistent with the radioactive decay of At.

It has been difficult to establish the chemical properties of At.[5] This gives special ramifications to similarities or differences of the At spectrum compared to spectra of Cl, Br, and I. For example, if p^4d were the lowest excited configuration rather than p^4s, one might expect atypical chemical properties. An effort was made to shed some light on this issue from the meager data available. In effect, the question asked was "Is the recorded spectrum consistent with transitions to the lowest J-levels of configurations p^4s?" It was noted that if the energy of J-levels of p^4s are plotted against constant steps for Cl, Br, and I, the points lie nearly on a straight line. Knowing two absorption lines for At, we can define the energies of two J-levels. Now it was reasoned that if a straight line could be drawn which would lie close to levels for Cl, Br, I and At, then the statement could be made that the At spectrum is similar. The results are shown in Fig. 3. To test the effect of a closed shell of f electrons on this straight-line relationship, similar plots were made of A, Kr, Xe, and Rn as well as S, Se, Te, and Po. In both series no effect of the 4f shell was noticed. It is concluded that there is no spectral evidence indicating nontypical halogen behavior.

If L-S coupling were a good approximation, the lower three levels in Fig. 3 would be designated $^4P_{5/2}$, $^4P_{3/2}$, and $^4P_{1/2}$ and the upper two, $^2P_{3/2}$ and $^2P_{1/2}$. That this approximation has already broken down in Br has recently been demonstrated by Jack L. Tech.[8] However, for lack of an alternative, this notation will continue to be used. Figure 3 strongly suggests that the two absorption lines be assigned to

transitions $^2P_{3/2}{}^0 - {}^4P_{5/2}$ for the 2244-Å line and $^2P_{3/2}{}^0 - {}^4P_{3/2}$ for the 2162-Å line. Here we assume that $^2P_{3/2}{}^0$ level results from the Hund's-rule ground state of configuration p^5. The plot also indicates that the next resonant line of At will be found in the region of 1850 Å. It is recognized that this is a naive approach to the problem, but the conclusions reached seem worth-while and the best that can be done with the limited data.

Some consideration was given to the ultimate sensitivity of this type of absorption cell. Formulas governing light intensity as a function of absorption coefficients were consulated.[9] It was determined that with a constant amount of sample, the sensitivity increases as the square of the radius decreases. The sensitivity is independent of the length of the cell. The possibility exists of obtaining a ten-fold increase in sensitivity by going to 0.3-mm i.d. cells.

ACKNOWLEDGMENTS

It is, of course, not possible to carry out this type of experiment without the cooperation of many people. This approach to the problem was suggested by Professor Burris B. Cunningham, and his encouragement was invaluable. The contribution of the glass-blowing skills of Dane H. Anderberg and Harry S. Powell has already been mentioned. The production of the At was carried out by the 88-Inch Cyclotron crew, with Robert J. Cox making the major contribution. Thanks go to Ruth Mary Larimer, Harry J. Harrington, and the rest of the Health Chemistry Group for advice and assistance in dealing with the radioactive hazards associated with this work.

FOOTNOTE AND REFERENCES

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

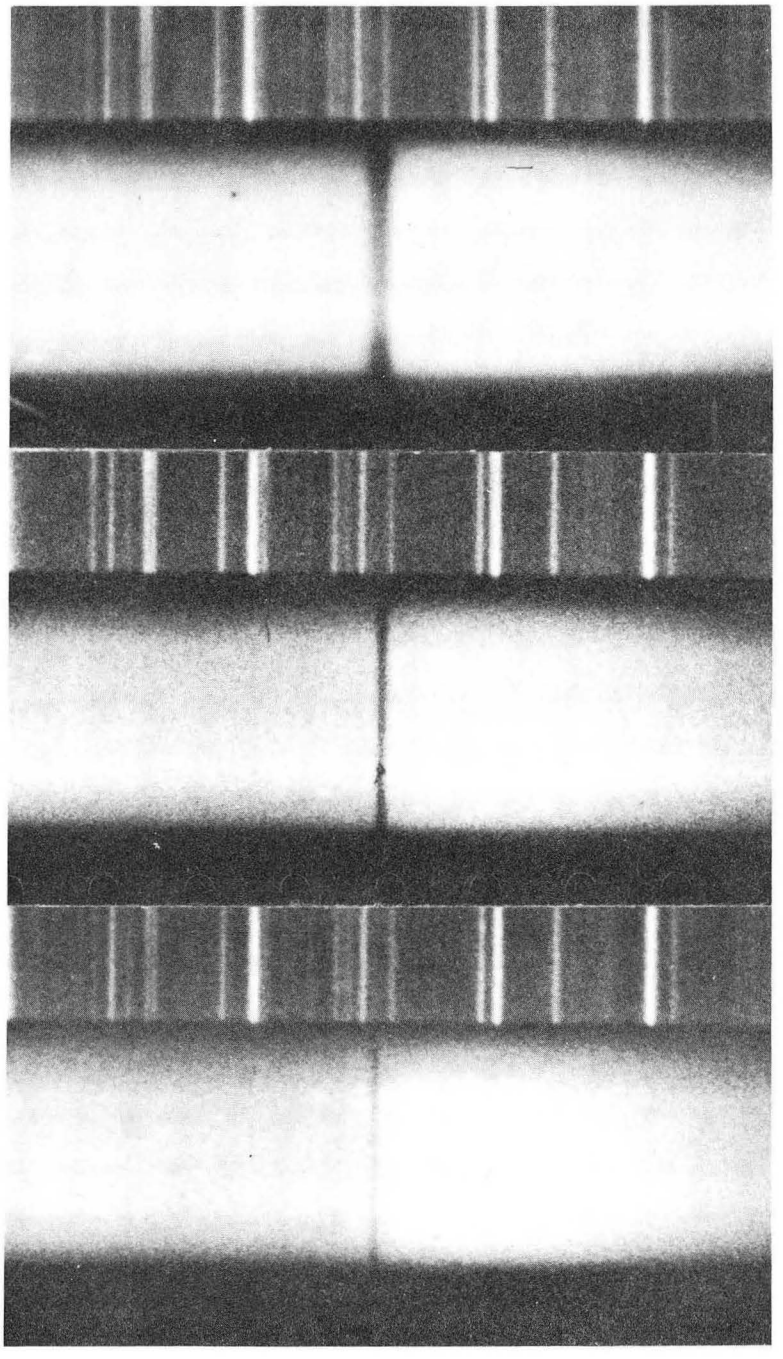
1. D. Carson, K. MacKenzie, and E. Segre, Phys. Rev. 8, 672 (1940).
2. B. B. Cunningham, Lawrence Radiation Laboratory Report UCRL-8518, October 1958.
3. R. Craig, A. Bartel, and Paul L. Kirk, Rev. Sci. Instr. 24, 49 (1953).
4. W. J. Ramler, J. Wing, D. J. Henderson, and J. R. Huizenga, Phys. Rev. 114, 154 (1959).
5. See procedure 1 from The Radiochemistry of Astatine, NAS-NS-3012, by Evan H. Appelman.
6. Lord Rayleigh, Proc. Roy. Soc. (London) 116, 702 (1927), ibid 119, 349 (1928).
7. G. W. Charles, D. J. Hunt, G. Pish, and D. L. Timma, J. Opt. Soc. Am. 45, 869 (1955).
8. Jack L. Tech, J. Res. Nat. Bur. Std. 67A, 505 (1963).
9. See, for example, A. C. G. Mitchell and M. W. Zemansky Resonance Radiation and Excited Atoms (University Press, Cambridge, 1961) p. 92, Eq. (20), and p. 100, Eq. (35).

FIGURE LEGENDS

Figure 1. Astatine 2244.01 Å. Upper: Photograph taken 11.75 h after bombardment. This corresponds to 30 ng or 8×10^{13} atoms of At. Middle: Photograph taken 35.42 h after bombardment. This corresponds to 4 ng or 1×10^{13} atoms of At. Lower: Photograph taken 54.05 h after bombardment. This corresponds to 0.8 ng or 2×10^{12} atoms of At.

Figure 2. Densitometer tracing taken of exposure made 35.42 h after bombardment. The broad absorption features are of unknown origin. The Si emission lines are produced in the hydrogen discharge which was the source of the continuum.

Figure 3. Energies of the five lowest levels of configuration p^4s plotted against equal intervals for Cl, Br, and I. In LS coupling these levels would be designated $^2P_{1/2}$, $^2P_{3/2}$, $^4P_{1/2}$, $^4P_{3/2}$, and $^4P_{5/2}$. Straight lines were drawn such that they lie as close as possible to levels of the same J. In drawing the lowest two lines, At points were given equal weight.



ZN-4153

Fig. 1

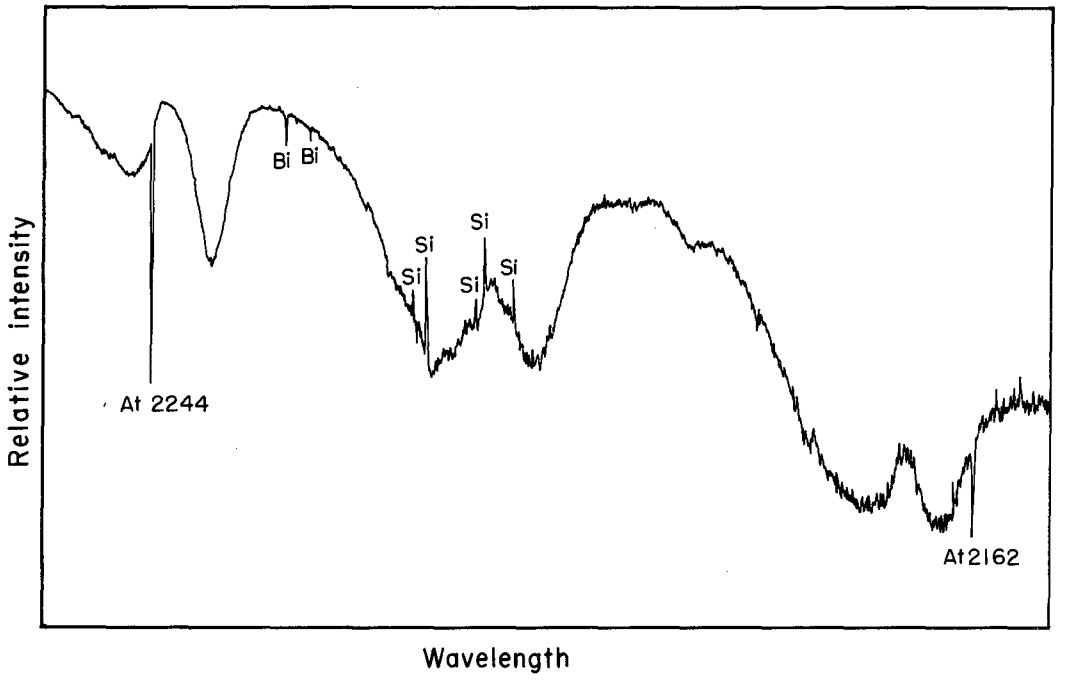

Relative intensity
Bi
Bi
Si
Si
Si
Si
Si
At 2244
At2162
Wavelength
MU-33291

Fig. 2

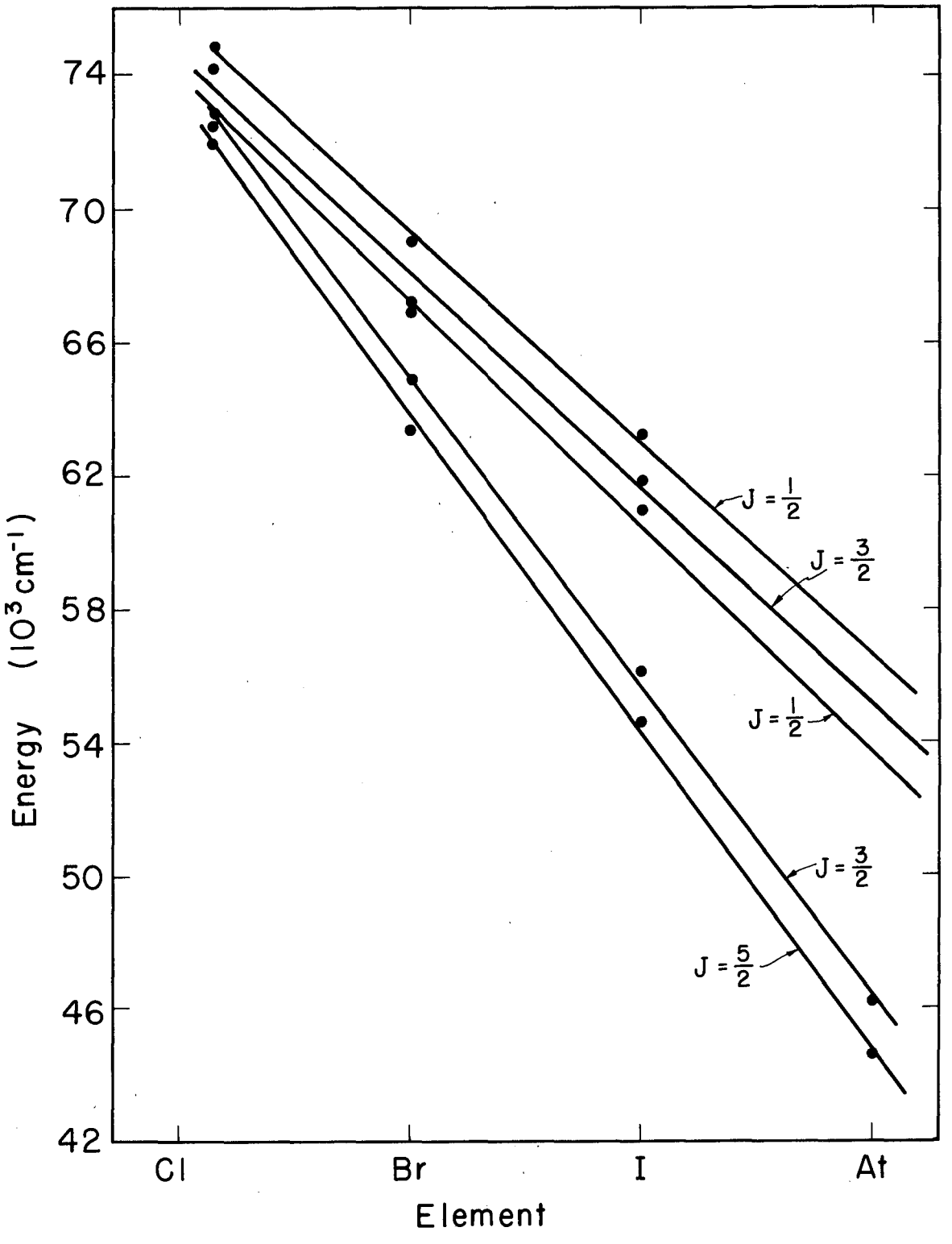

74
70
66
62
58
54
50
46
42
Energy (10³cm⁻¹)
Cl
Br
I
At
Element
J = 1/2
J = 3/2
J = 1/2
J = 3/2
J = 5/2
MUB-2382

Fig. 3

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.