was assigned to Eu^{154}. These energies were determined by spectrometer and by spectrograph. Two further high-energy gamma rays were found in the long-lived europium impurity; one of energy 0.980 Mev by absorption was associated with Eu^{152}, and one of energy 1.17 Mev by absorption was associated with Eu^{154}.

VIII. ACKNOWLEDGMENTS

The cooperation of the Union Carbide and Carbon Corporation, Oak Ridge, Tennessee, in making enriched samarium isotopes available and of the Argonne National Laboratories in bombarding these isotopes is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 93, NUMBER 1 JANUARY 1, 1954

Nuclear Spins and Band Spectra of the Selenium Isotopes

SUMNER P. DAVIS*
Department of Physics, University of California, Berkeley, California

(Received August 19, 1953)

An investigation of the rotational structure of the ${}^1\Sigma_u{}^+ - {}^1\Sigma_g{}^+$ band system of Se_2 in the region 3700–3815A, using separated isotopes of selenium, has made possible the assignment of $I=\frac{1}{2}$ to the nucleus Se^{77}, and the confirmation of $I=0$ for Se^{78} and Se^{80}. At the same time a number of new facts regarding the predissociation and the rotational constants of the Se_2 molecules are established.

I. INTRODUCTION

THE work described here was originally undertaken to resolve a discrepancy[1] that existed between the values of the nuclear spin of ${}_{34}Se^{77}$ indicated by optical hyperfine structure[2] and by microwave spectra.[3] The former method indicated $I=7/2\pm1$ and the latter $I=\frac{1}{2}$, although with certain reinterpretations[2,4] of the data either result could be reconciled with the other. Under these circumstances it was decided to try the band-spectroscopic method of nuclear-spin determination, since this was the one originally used[5] to establish the value $I=0$ for Se^{80} and is the only one that gives a direct, positive result for a nuclear spin of $I=\frac{1}{2}$ (or $I=0$).

Of the previous analyses of the band spectrum of selenium,[6–10] those of Rosen and of Olsson are the most important. It was clear from the work of Olsson that a separated isotope would be needed to study the rotational structure of the $(Se^{77})_2$ bands, since in the normal isotopic mixture Se^{77} is present to the extent of only 8 percent. [Olsson was able to detect only bands resulting from $(Se^{80})_2$ and $Se^{78}Se^{80}$.] Enriched samples[11] containing as much as 92 percent of this isotope were eventually required to obtain sufficiently accurate intensity measurements on the alternation ratio $(I+1)/I$ in the spectrum of $(Se^{77})_2$. Other samples enriched in Se^{78} and Se^{80} also gave greatly simplified spectra and permitted clarification of certain features of the structure of these bands.[12]

II. EXPERIMENTAL

The sources were electrodeless radio-frequency discharge tubes, this type being chosen principally because of its basic simplicity, freedom from contamination by electrodes, and adaptability to the use of milligram quantities of the elements to be excited. They were straight sealed quartz tubes from 2 to 5 mm in diameter and from 20 to 100 mm long, containing argon gas at several mm pressure and a small sample of metallic selenium, between 2 and 25 milligrams. With this arrangement the entire tube could easily be heated to the desired temperature, if necessary, in the neighborhood of 300°C. To provide better control of the selenium vapor pressure, some of the tubes had side arms which could be heated separately. The external electrodes were made by platinizing the ends of the tubes. Excitation was accomplished by a 60-Mc/sec rf power oscillator, this frequency being chosen because it was high enough to give a satisfactory discharge, but not so high as to require the use of special tubes and circuit components. During operation of the discharge tubes, the power drawn from the oscillator was very small, of the order of 5 or 10 watts.

A large part of the success of this work was due to the availability of enriched isotopes of selenium. In the natural mixture, the principal isotope Se^{80} constitutes

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[*] Now at Department of Physics, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

[1] J. E. Mack, Revs. Modern Phys. **22**, 64 (1950).

[2] J. E. Mack and O. H. Arroe, Phys. Rev. **76**, 173 (1949).

[3] Strandberg, Wentink, and Hill, Phys. Rev. **75**, 827 (1949); Geschwind, Minden, and Townes, Phys. Rev. **78**, 174 (1950).

[4] Townes, Foley, and Low, Phys. Rev. **76**, 1415 (1949).

[5] K. Wurm, Naturwiss. **20**, 85 (1932).

[6] J. Messerschmitt, Z. wiss. Phot. **5**, 249 (1907).

[7] B. Rosen, Z. Physik **43**, 69 (1927).

[8] B. Rosen, Physica **6**, 205 (1939).

[9] T. Nevin, Phil. Mag. **20**, 347 (1935).

[10] E. Olsson, Z. Physik **90**, 138 (1934); Dissertation, Stockholm, 1938 (unpublished).

[11] All enriched isotopes were supplied by the Stable Isotopes Research and Production Division, Y-12 Area, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[12] Preliminary accounts of this work have appeared in Phys. Rev. **83**, 891, 1269 (1951).

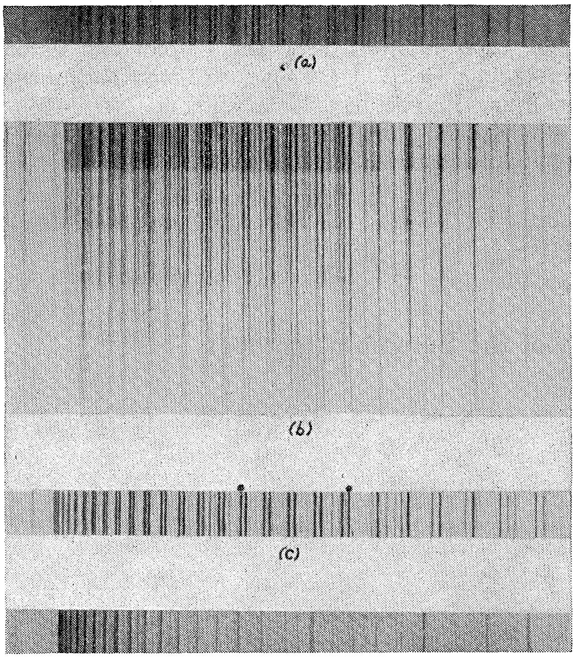

FIG. 1. (a) 10−5 band of Se_2 from the natural isotopic mixture. (b) 10−5 band of Se_2 from 92-percent Se^{77}, photographed through a step-weakener with transmissions at this wavelength of 100, 67.5, 51, 35, 22, and 9.5 percent. (c) 10−5 band of Se_2, from 83-percent Se^{78}. (d) 11−5 band of Se_2, from 92-percent Se^{77}.

48 percent, whereas in the enriched samples the amounts of the most abundant isotope were: Se^{77} sample I, 58 percent; Se^{77} sample II, 92 percent; Se^{78}, 83 percent; Se^{80}, 95 percent. Only in the natural mixture and in Se^{77} sample I were the intensities of mixed isotopic molecules objectionable. Sample II of this isotope was the result of a special separation kindly made at our request by the Oak Ridge National Laboratory.

Spectrograms were taken in the second order of a 21-foot concave grating, which has 30 000 lines per inch. In the region near λ3800 the plate factor was 0.67 A/mm. Exposure times were from one-half hour to eight hours, on Eastman IIa-O Spectroscopic Plates.

The intense ${}^1\Sigma_u{}^+ - {}^1\Sigma_g{}^+$ system of Se_2 covers a wide range of the spectrum between 3400 and 6000A, with the strongest bands in the visible near 4600A. Over the latter region there is so much overlapping of bands that an analysis of the rotational structure of the bands involving low vibrational quantum numbers seems impossible with the emission spectrum. Only a few bands of relatively high v at the ultraviolet end of the spectrum are clearly enough separated for this purpose, and it was with several of these that Olsson's analysis was concerned. In the present work, the high-dispersion spectrograms covered the region 3700–3800A. The optimum operating conditions for the source could be monitored by observing the intensity of the visible bands with a small spectroscope.

III. RESULTS

The simple structure of single P and R branches found by Olsson was confirmed, as was the correctness of the assignment of the rotational quantum numbers[13] N in the 10−4 and 10−5 bands of $(Se^{80})_2$ and $Se^{78}Se^{80}$. The greater simplicity is of the structure resulting from higher isotopic purity may be seen by comparing Fig. 1(a) with 1(b) and 1(c). It made possible the complete measurement of the 9−4 and 9−5 bands, in addition to those studied by Olsson, for the three molecules $(Se^{77})_2$, $(Se^{78})_2$, and $(Se^{80})_2$ on different plates taken with these three isotopes as the major constituents in the source.

For the measurement of the nuclear spin of Se^{77}, exposures were taken with a calibrated step-weakener in front of the plate [see Fig. 1(b)]. The last five lines of the P branch in the 10−5 band were traced with the Zeiss microphotometer and yielded values of the alternation ratio between 2.65 and 3.30, with an average of 3.02. Hence, it is concluded without question that $I=\frac{1}{2}$ for Se^{77}. As expected for an odd number of nucleons, the lines of odd N'' were stronger. The bands resulting from $(Se^{78})_2$ and $(Se^{80})_2$ showed lines of even N'' only, corresponding to zero nuclear spin for these isotopes. The very simple appearance of the $(Se^{80})_2$ bands was similar to that of the $(Se^{78})_2$ band shown in Fig. 1(c).

It is worth noting that the observed isotope shifts do not agree well with those calculated from

$$\Delta G^i = (\rho-1)\omega_e(v+\tfrac{1}{2}) - (\rho^2-1)x_e\omega_e(v+\tfrac{1}{2})^2,$$

using Olsson's values of the vibrational constants and v numbering. A somewhat better agreement, although far from a satisfactory one, was obtained by increasing v in the upper state by two units. The difficulty appears to arise from the presence of rather strong vibrational perturbations. It does not invalidate the adopted assignment of rotational quantum numbers, however, since the isotope shifts for the different molecules bore ratios in very close agreement with those predicted from the relative values of $\rho=\mu/\mu^i$.

This agreement is shown in Table I, where the molecular constants for the three molecules are compared. The rotational constants were calculated by applying least squares to the average combination differences $\Delta_2F(N)$. The table shows satisfactory agreement of the ratios of B with ρ^2 and agreement within the probable error of the ratios of α with ρ^3.

Predissociation effects in the upper state are very clear on the plates. The breaking-off of the rotational lines at $N'=49$, 45, and 44 in the state $v'=10$ for the

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[13] The notation N in place of the customary K for the rotational quantum number in Hund's case b is in accordance with the recommendations of the Joint Commission for Spectroscopy at its Rome meeting in September, 1952. [See J. Opt. Soc. Am. **43**, 410 (1953).] Other recommended modifications employed here are the use of a dash between the designations of the upper and lower states in a transition, of σ for wave number, and of K (kaysers) for cm^{-1}.

TABLE I. Molecular constants of Se_2.

		Isotope	
Constant	80	78	77
B_5''	0.089 163±0.000 023K	0.091 422±0.000 025K	0.092 661±0.000 020K
B_4''	0.089 457±0.000 031K	0.091 809±0.000 036K	0.093 016±0.000 046K
B_e''	0.090 78 ±0.000 20 K	0.093 55 ±0.000 23 K	0.094 61 ±0.000 27 K
B_{10}'	0.068 141±0.000 037K	0.069 885±0.000 042K	0.070 787±0.000 042K
B_9'	0.068 443±0.000 028K	0.070 214±0.000 025K	0.071 112±0.000 022K
B_e'	0.071 32 ±0.000 46 K	0.073 34 ±0.000 48 K	0.074 20 ±0.000 46 K
$B_e''^i/B_e''$	···	1.0305±0.0034	1.0422±0.0038
$B_e'^i/B_e'$	···	1.0283±0.0094	1.0404±0.0093
ρ^2	···	1.0257	1.0390
α''	−0.000 294±0.000 038K	−0.000 387±0.000 044K	−0.000 355±0.000 055K
α'	−0.000 303±0.000 046K	−0.000 329±0.000 049K	−0.000 325±0.000 047K
α''^i/α''	···	1.32±0.23	1.21±0.24
α'^i/α'	···	1.09±0.23	1.07±0.23
ρ^3	···	1.04	1.06
D''	-2.1×10^{-8}K	-2.2×10^{-8}K	-2.2×10^{-8}K
D'	-2.7×10^{-8}K	-2.8×10^{-8}K	-2.9×10^{-8}K
r_e''	2.1555±0.0024A	2.1504±0.0026A	2.1523±0.0031A
r_e'	2.4319±0.0078A	2.4287±0.0080A	2.4303±0.0074A
ω_e'' [a]	391.9 K	···	···
$x_e''\omega_e''$	1.04K	···	···
ω_e'	271.1 K	···	···
$x_e'\omega_e'$	2.19K	···	···

[a] See reference 10.

isotopes 80, 78, and 77 may be observed in Figs. 1(a), 1(c), and 1(b) respectively. The result for Se^{80} agrees with Olsson's observation. For the adjacent vibrational states, however, his results are not confirmed. He found that $v'=9$ does not predissociate, but has a perturbation at $N'=65$. The present work shows a breakoff at this point for Se^{80}, with no further lines beyond the perturbation, which therefore had every appearance of a predissociation limit. Since its energy is considerably below the genuine limit in $v'=10$, however, it seems probable that it is actually a perturbation.

For the level $v'=11$, Rosen[8] found bands to be present, whereas Olsson was unable to detect any. A search was therefore made for the $11-4$ and $11-5$ bands, since they should have been present in a region relatively free from overlapping. On one of the most heavily exposed plates for $(Se^{77})_2$ both of the bands were found, although they were quite weak. After the lines of the $11-5$ band were measured, the combination differences were formed and compared with those from $10-5$ and $9-5$. The comparison is given in Table II. The good agreement is ample proof that the level $v'=11$ is in evidence. As a check, a rough calculation for B' yielded 0.07043K as compared to 0.07046K predicted from the data on the other two bands. The fact that Olsson did not find this band could easily be because of its weakness, since his exposure times were of the order of 30 hours. What is peculiar, however, is that $v'=11$ does appear above the predissociation energy in $v'=10$ and furthermore does not appear to predissociate within the observed range of rotational levels, as can be seen from Fig. 1(d).

A search was then made for the $12-4$ and $12-5$ bands, since Rosen found that the level $v'=12$ was strong in emission. On none of the plates was either of these two bands visible. Unfortunately Rosen did not make a rotational analysis of the bands that he found with $v'=12$, so that it is not possible to compare his work and definitely to determine the cause of this discrepancy. The most effective way to pursue the problem further would be to observe these bands in absorption under high dispersion.

Another interesting phenomenon that could be profitably studied in absorption is the exceptional weakness, with no sign of splitting, of the lines from the levels $N'=41$, 37, and 38 in the state $v'=10$ for the isotopes 80, 78, and 77. The two weakened lines for Se^{78} are marked on Fig. 1(c). This may possibly represent a perturbation, but the absence of any splitting or shift would seem to indicate a case of accidental predissociation.[14] A study of the line width in absorption might yield a confirmation of this interpretation.

IV. CONCLUSIONS

In regard to the nuclear spins, the values $I=0$, 0, and $\frac{1}{2}$ for Se^{80}, Se^{78}, and Se^{77} are in accord with the

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[14] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950), Vol. 1.

TABLE II. Combination differences for the 11−5, 10−5, and 9−5 bands of $(\mathrm{Se}^{77})_2$.

		$\Delta_2F''(N)$	
N	9−5	10−5	11−5
8	3.19K	3.15K	3.10K
9	...	...	...
10	3.89	3.88	3.87
11	...	4.31	4.27
12	4.63	4.69	4.63
13	...	5.04	5.00
14	5.39	5.32	5.34
15	...	5.72	5.73
16	6.10	6.16	6.08
17	...	6.51	6.52
18	6.84	6.86	6.83
19	7.19	7.20	7.23
20	7.56	7.57	7.58
21	7.86	7.95	7.97
22	8.31	8.35	8.35
23	8.70	8.71	8.69
24	9.04	9.06	9.06
25	9.50	9.43	9.46
26	9.78	9.88	9.82
27	10.18	10.22	10.15
28	10.55	10.56	10.58
29	10.95	10.92	10.88
30	11.30	11.26	11.33
31	11.69	11.68	11.69
32	12.04	12.02	12.04
33	12.48	12.52	12.50
34	12.76	12.75	12.76

and so forth

expectations of the shell model,[15] although the possibility that in Se^{77} the odd neutron was in a spin-9/2 state was not excluded. The only experimental evidence for a high value of the spin is that of hyperfine structure.[2] From the present result, it must be concluded that the structure observed by Mack and Arroe is due to isotope shifts, and the Se^{77} must have an exceptionally large shift. The other evidence for a spin of $\frac{1}{2}$, that of the lack of splitting of the microwave lines[3] of OCSe, and the β decay[16] of As^{77} are confirmed by the result reported here.

Conclusions concerning the structure of the band spectrum are as follows: the vibrational levels are so badly perturbed that accurate extrapolations of the vibrational constants to equilibrium values cannot be made. Further, the vibrational numbering of Olsson, which is used here, may be in error in the upper state by as much as two units. There is a definite predissociation which occurs at 28871K above the ground state in the state $v'=10$ for all isotopes. The apparent predissociation in $v'=9$ may be only a perturbation. It is certain, however, that the predissociation is weak, since it does not affect the rotational levels of $v'=11$. Further experiments on the absorption spectrum will be required to clarify the apparent absence of bands with $v'=12$ and the anomalous weakness of lines from a single rotational level in the state $v'=10$.

Thanks are due Dr. F. A. Jenkins, under whose direction this work was done, and Dr. Perlman, of the Chemistry Department, who kindly arranged the procurement of Se^{77} sample I.

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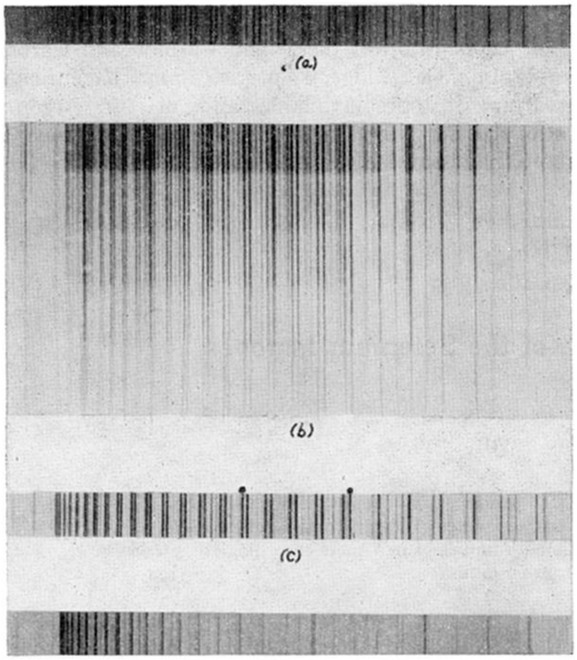
[15] M. G. Mayer, Phys. Rev. **78**, 16 (1950).

[16] R. Canada and A. C. G. Mitchell, Phys. Rev. **81**, 485 (1951).



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