

## Submillimeter-Wave Spectrum of H<sub>2</sub>Se. Analysis of Rotational Spectra of All Selenium Isotopomers in the Ground State

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Submillimeter rotational spectra of all selenium modifications of H<sub>2</sub>Se in the ground vibrational state were investigated. The number of MW data increased three times and the H<sub>2</sub><sup>74</sup>Se rotational spectrum was measured for the first time. The data were analyzed using the modified Watson Hamiltonian, enabling us to reduce the number of parameters and to determine them more accurately compared to a conventional Hamiltonian. A combined analysis of MW frequencies and IR ground state combination differences yields rotational and centrifugal H<sub>2</sub>Se constants.

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### INTRODUCTION

The rotational spectrum of the H<sub>2</sub>Se molecule was investigated by numerous authors. Palik and Oetjen (1) studied the FIR spectrum. Yashe, Moser, and Gordy (2) measured the MW spectrum and were the first who resolved five isotopic H<sub>2</sub>Se components. Helminger and De Lucia (3) raised the upper boundary of MW measurements up to 600 GHz. The rotational and centrifugal distortion constants for the ground vibrational state were evaluated most accurately in Ref. (4), where MW data (2, 3) were fitted together with IR ground state combination differences (GSCD) from IR data (4, 5).

The critical phenomenon in the H<sub>2</sub>Se rotational spectrum was experimentally discovered in Ref. (6). This phenomenon results in a fourfold level clustering when  $J$  increases higher than a critical value of total angular momentum  $J_{CR} = 12$ . The investigation of effects caused by the critical phenomenon was the main reason of our interest to the H<sub>2</sub>Se rotational spectrum. Besides, the H<sub>2</sub>Se spectrum is very rich isotopically, since selenium has six isotopes. We believe that the frequencies presented here will be useful both for applied analytical purposes and for isotopical substitution analysis, although the main incentive for us to undertake this study is the necessity of detailed knowledge of the H<sub>2</sub>Se spectrum for further studies of the clustering phenomenon.

The present paper is the continuation of our earlier study (6). It reports on measurements of frequencies of four isotopic components which were not included in Ref. (6), the measurements of the MW rotational H<sub>2</sub><sup>74</sup>Se spectrum being presented for the first time. Due to small abundance of the H<sub>2</sub>Se isotopomers considered here, it was difficult to observe high- $J$  transitions and the number of measured frequencies was not so large as for H<sub>2</sub><sup>78</sup>Se and H<sub>2</sub><sup>80</sup>Se. Still some features of the critical phenomenon can also be observed in the present measurements. The newly measured frequencies were fitted together with all known MW data (2, 3) and IR GSCD (4, 5) and the most accurate rotational and centrifugal constants were obtained.

## EXPERIMENT AND DATA ANALYSIS

The measurements were carried out using RAD-2 (7) and RAD-3 (8) spectrometers. The pressure line shift was not controlled because the estimates show that it does not exceed the accuracy provided by the experiment. This is confirmed by the fit which showed absence of large deviations.

The MW data given in Tables I and II were analyzed together with IR GSCD (4, 5) using the modified Watson Hamiltonian (6)

$$\begin{aligned}
 H = & (B + C)/2J_+^2(A - (B + C)/2)J_z^2 - D_JJ^4 - D_{JK}J^2J_z^2 - D_KJ_z^4 + H_JJ^6 \\
 & + H_{JK}J^4J_z^2 + H_{KJ}J^2J_z^4 + H_KJ_z^6 + c_{40}(J^2 - J_z^2)^4 + c_{31}(J^2 - J_z^2)^3J_z^2 \\
 & + c_{22}(J^2 - J_z^2)^2J_z^4 + c_{13}(J^2 - J_z^2)J_z^6 + c_{04}J_z^8 + c_{50}(J^2 - J_z^2)^5 \\
 & + c_{32}(J^2 - J_z^2)^3J_z^4 + c_{05}J_z^{10} + c_{06}J_z^{12} + 1/2[\{(B - C)/4 - d_JJ^2 - d_KJ_z^2 \\
 & + h_JJ^4 + h_{JK}J^2J_z^2 + h_KJ_z^4 + b_{30}(J^2 - J_z^2)^3 + b_{21}(J^2 - J_z^2)^2J_z^2 + b_{03}J_z^6 \\
 & + b_{40}(J^2 - J_z^2)^4 + b_{13}(J^2 - J_z^2)J_z^6 + b_{04}J_z^8\}, \{J_+^2 + J_-^2\}]_+.
 \end{aligned}$$

It was shown in Ref. (6) that this modification of the traditional  $A$ -reduced Hamiltonian enables one to decrease the number of fitted parameters. There are two reasons for that: 1) the fitted data have high- $J$  frequencies with  $K_a \sim J$  and  $K_a \sim 0$  only, 2) the modification decreases essentially the absolute values of the high power centrifugal constants (see Ref. (6)). Thus some Hamiltonian parameters can be set equal to zero. A number of parameters (similarly to Ref. (4)) were fixed equal to the constants of more abundant isotopomers which have the closest atomic weights. As a result, we managed to reduce the number of the parameters when fitting the data on  $\text{H}_2^{76}\text{Se}$ ,  $\text{H}_2^{77}\text{Se}$ , and  $\text{H}_2^{82}\text{Se}$  by 2, 2, and 1 respectively, as compared to Ref. (4), in spite of the fact that we included all the data fitted in Ref. (4) (MW frequencies and IR GSCD) and the newly measured frequencies with high  $J$  in the fitting procedure.

Helminger and De Lucia (3) found that the frequency of  $1(1,0) \leftarrow 1(0,1)$  transition of  $\text{H}_2^{78}\text{Se}$  reported in Ref. (2) is in error by 5 MHz. We have found that frequencies of the same transition of  $\text{H}_2^{77}\text{Se}$  and  $\text{H}_2^{76}\text{Se}$  are also in error. Our analysis has shown that these frequencies are off about 1.5 MHz. So frequencies of  $1(1,0) \leftarrow 1(0,1)$  transition of  $\text{H}_2^{77}\text{Se}$  and  $\text{H}_2^{76}\text{Se}$  were not included in the final fit.

The rotational  $\text{H}_2\text{Se}$  spectrum is quite dense. It was identified at several stages on the basis of the  $\text{H}_2^{80}\text{Se}$  spectrum, which is known to be the most intense. Strong effects of nonrigidity in the molecule caused the main difficulty. Since there are six selenium isotopes, it is very useful to find characteristic isotopic groups of rotational lines when identifying the  $\text{H}_2\text{Se}$  spectrum and, in particular, the  $\text{H}_2^{74}\text{Se}$  one. However, for large  $J$ , the width of the line groups increases drastically. In this case we used the predictions of line intensities relative to the lines which have already been identified.

Similarly to the results of Ref. (6) dealing with the  $\text{H}_2^{80}\text{Se}$  and  $\text{H}_2^{78}\text{Se}$  spectra in rotational spectra of less abundant isotopomers, the nonrigidity results in a critical phenomenon and the effects associated with it. The masses of isotopomers being close enough, the critical value of the total angular momentum  $J_{\text{CR}}$  is nearly the same for all isotopomers and equals 12. The  $J(J,0) \leftarrow J(J-1,1)$  and  $J(J,1) \leftarrow J(J-1,2)$  branch frequencies increase with increasing  $J$  before  $J_{\text{CR}}$ . When the critical phenomenon

TABLE I  
Observed MW Frequencies of H<sub>2</sub><sup>82</sup>Se, H<sub>2</sub><sup>77</sup>Se, and H<sub>2</sub><sup>76</sup>Se

J''	K''	K'	J'	K'	K'	H <sub>2</sub> <sup>82</sup> Se	H <sub>2</sub> <sup>77</sup> Se	H <sub>2</sub> <sup>76</sup> Se
1	1	0	1	0	1	127860.35(10)a		
2	2	0	2	1	1	141889.02(10)a	142623.48(10)a	142783.02(10)a
3	3	0	3	2	1	154563.10(10)a	155163.20(10)a	155488.14(10)a
4	4	0	4	3	1	197748.81(10)b	200420.65(10)b	201000.01(10)b
5	5	0	5	4	1	242112.28(10)b	245382.75(10)b	247308.71(10)b
6	6	0	6	5	1	297106.08(10)b	303301.44(10)b	304643.20(10)b
6	1	5	5	4	2	306060.36(10)	305795.71(10)	
5	4	1	5	3	2	308016.04(10)b	307690.68(10)b	307626.96(10)b
6	5	1	6	4	2	309251.68(10)b	309661.16(10)b	309760.43(10)b
4	3	1	4	2	2	316392.66(10)b	315807.45(10)b	315684.32(10)b
7	6	1	7	5	2	323624.01(10)b	325299.72(10)b	325677.38(10)b
3	2	1	3	1	2	330181.47(10)b	329694.48(10)b	329590.51(10)b
3	1	3	2	2	0	336140.09(70)	336287.47(70)	
2	1	1	2	0	2	345030.44(10)b	344830.49(10)b	344787.62(10)b
8	7	1	8	6	2	353768.27(10)b	357239.79(10)b	358010.12(10)b
1	1	1	0	0	0	361698.54(10)b	362167.63(10)b	362268.84(10)b
7	7	0	7	6	1	359829.07(10)b	368058.70(10)b	369837.86(10)b
2	2	1	2	1	2	383125.26(10)b	384003.88(10)b	384193.75(10)b
3	3	1	3	2	2	401983.80(10)b	403463.92(10)b	403783.97(10)b
9	8	1	9	7	2	401087.63(10)b	406781.99(10)b	408036.27(10)b
4	4	1	4	3	2	426414.26(10)b	428701.45(10)b	429195.99(10)b
8	8	0	8	7	1	425333.67(10)	435453.13(10)	437636.00(10)
5	5	1	5	4	2	455560.94(10)b	458850.63(10)b	459562.13(10)b
10	9	1	10	8	2	464983.43(10)	473067.68(10)	474838.20(10)
10	8	2	10	7	3		474185.63(10)	474215.28(10)
9	7	2	9	6	3	479976.95(10)	478547.43(10)	478254.49(10)
11	9	2	11	8	3	486867.69(10)		489713.76(10)
6	6	1	6	5	2	488142.58(10)	492605.91(10)	493570.94(10)
9	9	0	9	8	1		499324.00(10)	501838.23(10)
8	6	2	8	5	3	498982.29(10)	496945.36(10)	496512.60(10)
7	5	2	7	4	3	524859.13(10)	522918.73(10)	522500.73(10)
12	10	2	12	9	3	521517.17(10)	526829.20(10)	528015.37(10)
7	7	1	7	6	2	522435.40(10)	528204.29(10)	
11	10	1	11	9	2	542178.51(10)	552417.28(10)	554648.71(10)
6	4	2	6	3	3	551473.50(10)	550075.30(10)	549771.13(10)
10	10	0	10	9	1	541153.95(10)	554026.09(10)	556792.65(10)
8	8	1	8	7	2	556334.60(10)	563492.42(10)	565038.88(10)
16	16	1	16	15	2			575282.43(10)
5	3	2	5	2	3		573421.20(10)	573264.96(10)
2	0	2	1	1	1	581020.83(10)	581222.61(10)	581265.94(10)
13	11	2	13	10	3	578757.00(10)	587464.52(10)	589382.81(10)
4	2	2	4	1	3	590414.37(10)	590292.36(10)	590264.22(10)
11	11	0	11	10	1	581755.52(10)		598500.46(10)
9	9	1	9	8	2	587487.57(10)		597920.04(10)
2	1	2	1	0	1	595552.80(10)b	596197.06(10)b	596336.52(10)b
3	1	2	3	0	3	600224.92(10)	600478.11(10)	600532.04(10)
3	2	2	3	1	3	606764.55(10)	607314.84(10)	607433.97(10)
4	3	2	4	2	3	609090.40(10)	609792.68(10)	609945.17(10)
5	4	2	5	3	3	614594.48(10)	615580.88(10)	615795.68(10)
12	12	0	12	11	1	607145.30(10)	621693.33(10)	624818.35(10)
10	10	1	10	9	2	613469.01(10)	623458.87(10)	625615.11(10)
14	14	0	14	13	1	609512.36(10)	625442.86(30)	628870.13(10)
6	5	2	6	4	3	624423.14(10)	625858.39(10)	626171.57(10)
13	13	0	13	12	1	616420.88(10)	631675.37(10)	
13	10	3	13	9	4	636533.31(10)	634554.66(10)	634164.52(10)
14	11	3	14	10	4	634764.83(10)	635548.34(10)	635770.78(10)
14	14	1	14	13	2	623883.90(10)	638809.93(10)	642029.65(10)
12	11	1	12	10	2	627012.67(10)	638773.82(10)	641326.15(10)
11	11	1	11	10	2	631960.74(10)	643314.18(10)	645764.35(10)
7	6	2	7	5	3	639480.40(10)	641544.69(10)	641995.58(10)
13	13	1	13	12	2	638617.51(10)	652461.62(10)	655447.46(10)
12	12	1	12	11	2	640904.46(10)	653549.61(10)	656277.03(10)
12	9	3	12	8	4			655082.37(20)

Values in parentheses are uncertainties in last digits of frequency: a—Ref. (2); b—Ref. (3).

TABLE II  
Observed MW Frequencies of  $\text{H}_2^{74}\text{Se}$

$J''$	$K''$	$K''$	$J'$	$K'$	$K'$	FREQ.	$Q.-O.$	UNC.
6	6	0	6	5	1	307432.76	0.22	0.30
5	4	1	5	3	2	307502.39	0.16	0.30
6	5	1	6	4	2	309979.65	0.77	0.30
3	2	1	3	1	2	329375.38	-0.66	0.30
2	1	1	2	0	2	344698.82	0.04	0.30
8	7	1	8	6	2	359633.52	0.89	0.50
1	1	1	0	0	0	362479.35	0.25	0.20
7	7	0	7	6	1	373532.32	-0.09	0.10
2	2	1	2	1	2	384588.34	0.17	0.10
3	3	1	3	2	2	404448.62	0.12	0.10
9	8	1	9	7	2	410666.74	-0.10	0.10
4	4	1	4	3	2	430223.22	-0.02	0.10
8	8	0	8	7	1	442163.27	-0.02	0.10
5	5	1	5	4	2	461039.64	-0.08	0.10
10	8	2	10	7	3	474305.58	0.15	0.10
9	7	2	9	6	3	477664.70	0.05	0.10
9	9	0	9	8	1	507046.82	0.02	0.10
8	6	2	8	5	3	495622.85	0.05	0.10
7	5	2	7	4	3	521634.01	-0.02	0.10
7	7	1	7	6	2	532040.43	0.14	0.10
6	4	2	6	3	3	549137.52	-0.08	0.10
2	0	2	1	1	1	581355.61	-0.05	0.10
13	11	2	13	10	3	593406.63	0.04	0.10
4	2	2	4	1	3	590203.82	-0.02	0.10
9	9	1	9	8	2	601765.30	0.27	0.10
2	1	2	1	0	1	596625.51	0.09	0.20
3	1	2	3	0	3	600643.08	0.04	0.10
3	2	2	3	1	3	607681.57	0.16	0.10
4	3	2	4	2	3	610262.60	0.05	0.10
5	4	2	5	3	3	616243.53	-0.11	0.10
10	10	1	10	9	2	630088.93	-0.18	0.10
6	5	2	6	4	3	626825.15	-0.20	0.10
7	6	2	7	5	3	642937.11	-0.28	0.10

occurs these frequencies begin to decrease, since the levels involved in these transitions cluster with an increase of  $J$  beginning with  $J_{\text{CR}}$ . These  $Q$  subbranches for  $\text{H}_2^{80}\text{Se}$  and  $\text{H}_2^{78}\text{Se}$  are traced in Ref. (6) up to  $J = 20$ . We have also managed to measure several transitions of less abundant isotopomers in the region of clustering (see Table I).

Only 25 weak lines of  $\text{H}_2^{74}\text{Se}$  of the  $\nu_2$  band were assigned in Ref. (4). The authors could not derive the rotational constants directly because of the limited number of lines. They carried out a simultaneous fit of all ground state data of all the  $\text{H}_2\text{Se}$  isotopomers using isotopic mass correction terms (4). One can readily estimate the rotational constants of  $\text{H}_2^{74}\text{Se}$  employing the formulas and the constants from Ref. (4):  $A - (B + C)/2 = 71\,050.6$  MHz,  $(B + C)/2 = 174\,357.5$  MHz, and  $(B - C)/2 = 57\,287.8$  MHz. These constants were a good starting point for the line identification and were in excellent agreement with the rotational constants obtained experimentally (see Table III). The major part of the Hamiltonian parameters of  $\text{H}_2^{74}\text{Se}$  was fixed to the corresponding  $\text{H}_2^{76}\text{Se}$  parameters during data fit and only eight parameters were varied. The measured MW transitions for  $\text{H}_2^{74}\text{Se}$  are given in Table II.

TABLE III

Rotational and Centrifugal Distortion Constants of all Six H<sub>2</sub>Se Isotopomers

	H <sub>2</sub> <sup>82</sup> Se	H <sub>2</sub> <sup>80</sup> Se	H <sub>2</sub> <sup>78</sup> Se	H <sub>2</sub> <sup>77</sup> Se	H <sub>2</sub> <sup>76</sup> Se	H <sub>2</sub> <sup>74</sup> Se
(B+C)/2	174289.166(24)	174306.123(22)	174324.017(28)	174333.249(22)	174342.724(45)	174362.468(23)
A (B+D)/2	704907.271(12)	70620.170(18)	70756.666(20)	70827.421(13)	70900.293(12)	71051.604(15)
(B-D)/2	57356.490(11)	57339.680(15)	57322.047(16)	57312.898(11)	57303.498(11)	57283.954(11)
D <sub>J</sub>	15.8425(20)	15.8381(10)	15.8417(29)	15.8419(16)	15.8311(57)	15.8311
D <sub>JK</sub>	-55.4229(27)	-55.4309(39)	-55.4429(47)	-55.4481(28)	-55.4494(27)	-55.4577(28)
D <sub>K</sub>	78.9883(18)	79.0432(24)	79.1035(30)	79.1338(19)	79.1621(18)	79.2256(19)
d <sub>J</sub>	7.27044(48)	7.27025(82)	7.27044(95)	7.27014(50)	7.27053(49)	7.27039(47)
d <sub>K</sub>	-5.5097(11)	-5.4957(14)	-5.4809(16)	-5.4728(11)	-5.4658(11)	-5.4510(11)
H <sub>J</sub> · 10 <sup>+3</sup>	6.591(28)	6.519(26)	6.613(63)	6.618(23)	6.538(33)	6.538
H <sub>JK</sub> · 10 <sup>+3</sup>	-37.13(11)	-37.19(13)	-37.73(24)	-37.733(95)	-37.707(98)	-37.707
H <sub>KJ</sub> · 10 <sup>+3</sup>	38.27(19)	38.35(23)	39.12(36)	39.12(16)	39.06(16)	39.06
H <sub>K</sub> · 10 <sup>+3</sup>	13.473(93)	13.48(13)	13.18(18)	13.208(82)	13.265(83)	13.3083(15)
h <sub>J</sub> · 10 <sup>+3</sup>	3.2389(96)	3.234(17)	3.196(28)	3.1947(84)	3.1965(83)	3.1965
h <sub>JK</sub> · 10 <sup>+3</sup>	-12.235(49)	-12.200(51)	-11.995(93)	-11.989(42)	-11.996(44)	-11.996
h <sub>K</sub> · 10 <sup>+3</sup>	23.587(53)	23.571(63)	23.425(90)	23.433(46)	23.460(48)	23.460
o <sub>40</sub> · 10 <sup>+6</sup>	-4.62	-4.62(17)	-5.16(36)	-5.16	-5.16	-5.16
o <sub>31</sub> · 10 <sup>+6</sup>	14.97	14.97(35)	16.5(15)	16.5	16.5	16.5
o <sub>22</sub> · 10 <sup>+6</sup>	-14.3	-14.3(14)	-13.0(24)	-13.0	-13.0	-13.0
o <sub>13</sub> · 10 <sup>+6</sup>	19.64(15)	19.6(11)	20.0(17)	19.97(16)	19.98(14)	19.98
o <sub>04</sub> · 10 <sup>+6</sup>	-17.7892(88)	-17.82(21)	-17.66(36)	-17.673(10)	-17.6830(84)	-17.6830
b <sub>30</sub> · 10 <sup>+6</sup>	-2.105	-2.105(92)	-1.82(18)	-1.82	-1.82	-1.82
b <sub>21</sub> · 10 <sup>+6</sup>	4.83	4.83(37)	4.18(60)	4.18	4.18	4.18
b <sub>12</sub>						
b <sub>03</sub> · 10 <sup>+6</sup>	-24.165(72)	-24.13(23)	-24.16(30)	-24.159(71)	-24.204(66)	-24.204
o <sub>50</sub> · 10 <sup>+9</sup>	3.85	3.85(26)	4.91(61)	4.91	4.91	4.91
o <sub>41</sub>						
o <sub>32</sub> · 10 <sup>+9</sup>	19.5	19.5(34)	19.5	19.5	19.5	19.5
o <sub>23</sub>						
o <sub>14</sub>						
o <sub>05</sub> · 10 <sup>+9</sup>	16.88	16.88(17)	16.58(16)	16.58	16.58	16.58
b <sub>40</sub> · 10 <sup>+9</sup>	1.45	1.45(12)	0.94(30)	0.94	0.94	0.94
b <sub>31</sub>						
b <sub>22</sub>						
b <sub>13</sub> · 10 <sup>+9</sup>	20.51	20.51(95)	17.6(21)	17.6	17.6	17.6
b <sub>04</sub> · 10 <sup>+9</sup>	21.90	21.90(37)	21.96(50)	21.96	21.96	21.96
o <sub>06</sub> · 10 <sup>+12</sup>	-7.78	-7.78(12)	-7.63(12)	-7.63	-7.63	-7.63
Num. of fitted parameters	18	30	29	18	18	8
Num. of MW	58	77	70	56	59	33
MW Std.Dev	0.95	0.99	0.90	0.83	1.09	1.31
Num. of IR QSCD	153	510	355	143	160	4
IR Std.Dev.	1.0	0.96	1.12	0.62	0.86	0.14
Total Std.Dev.	0.99	0.96	1.09	0.69	0.93	1.24

Values in parentheses are one standard deviation in last digits of parameters. A blank entry means that the parameter was fixed to zero. The parameters without the standard deviation were fixed to the values of the corresponding parameters with standard deviation.

The ground state rotational and centrifugal distortion constants of all six H<sub>2</sub>Se isotopomers are presented in Table III. A blank entry means that the constant was fixed to zero.

## CONCLUSION

Our investigation has lead to a threefold increase of the experimentally observed rotational transitions of  $\text{H}_2\text{Se}$  in the MW region. The rotational spectrum of  $\text{H}_2^{74}\text{Se}$  was measured for the first time. The combined fit of MW data and IR GSCD using the modified Watson Hamiltonian allowed us to obtain the sets of rotational and centrifugal constants for all  $\text{H}_2\text{Se}$  isotopomers in the ground vibrational state. The parameters of these sets are determined most accurately due to the modification of a traditional Hamiltonian and the extended experimental data being treated.

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