

## Millimeter-Wave Transitions of H<sub>2</sub>Se

The H<sub>2</sub>Se molecule is so far the only asymmetric-top molecule in which the effect of fourfold clustering of rotational levels has been observed (1, 2). The clustering means that rotational levels in  $J$ -multiplets start to group in sets of four, counting down from the highest in energy. This effect begins with the critical value of total angular momentum  $J_{CR}$ , which for H<sub>2</sub>Se is 12. One particular consequence of clustering is a regular series of rotational transitions with  $\Delta J = 0$  within the clusters, decreasing in frequency with increase of  $J$  above  $J_{CR}$ . This frequency decrease of "intracluster" lines was traced in Ref. (1) up to  $J = 20$  in the region between 300 and 650 GHz. The rate of clustering, i.e., the ratio of the energy interval between the first fourfold cluster and the next-nearest energy level to the energy spread of the cluster itself, was equal to 5 at  $J = 20$ .

The general qualitative theory of clustering, or so-called "critical phenomenon" theory, can be found in Ref. (3) and references therein. The application of this theory to H<sub>2</sub>Se is considered in Ref. (1). To derive a quantitative theory of the effects and to find the best model of an effective rotational Hamiltonian for describing this effect, it is necessary to observe transitions with as high  $J$  as possible, where the clustering effect is most apparent. The goal of this work was the search for intracluster transitions with  $J$  higher than in Ref. (1), that is  $J > 20$ . This requires measurements in a lower frequency range than that explored in Refs. (1, 2).

The region of clustering of rotational levels with  $J$  higher than 20 corresponds to extremely high rotational energies. This leads first of all to strong centrifugal distortion effects in the molecule, which results in difficulties in predicting these level energies. Furthermore, in order to observe these transitions, it is necessary to heat the sample to increase the Boltzmann factor in the intensity of transition lines with such large  $J$ . However, very strong heating leads to rapid dissociation of H<sub>2</sub>Se. The optimum heating for our experiment was up to 250–350°C. At these temperatures the concentration of H<sub>2</sub>Se decreases by a factor of two during an hour.

The investigations were performed by means of a millimeter-wave spectrometer operating normally in the range 37–80 GHz, sensitive enough to detect an absorption line of intensity  $10^{-9}$  cm<sup>-1</sup>, and allowing Doppler resolution (4). In the present work we used a modification of this system with an upper limit of the operating range 180 GHz. The investigated gas was let into a quartz cell of 1 m length, placed in an electric furnace. The gas pressure in the cell was about 6–9 Pa (50–70 mTorr).

The rotational constants of Refs. (1, 2) easily permitted the identification and measurement of a series of weak transitions, which were then used as reference lines for monitoring the spectrometer sensitivity and gas heating. Table I lists both the lines known before (5), but measured here more accurately, and new measurements. The measured frequencies were added to the set of frequencies of Refs. (1, 2) and the same kind of fitting described there was performed.

The intracluster lines we sought are not seen in this range at room temperature. For example, the intensity of the strongest H<sub>2</sub> <sup>80</sup>Se line, the transition  $22_{22,1} \leftarrow 22_{21,2}$ , equals  $3 \times 10^{-10}$  cm<sup>-1</sup>. It is enhanced upon heating to  $5 \times 10^{-7}$  cm<sup>-1</sup> at  $T = 300^\circ\text{C}$  and decreases with time due to H<sub>2</sub>Se dissociation. The intensities of the observed lines were estimated relative to those of known lines of Table I. A reliable criterion for assignment is the distance between the doublet components  $J_{J,0} \leftarrow J_{J-1,1}$  and  $J_{J,1} \leftarrow J_{J-1,2}$ , which can be predicted much more accurately than the frequencies themselves.

The prediction of intracluster transition frequencies should be described in detail separately. Initially the lines observed were assigned on the basis of predictions using the rotational constants of Ref. (1). But recently the FIR rotational spectrum of H<sub>2</sub>Se has been measured (6). The use of these data enabled us to make more reliable predictions of the intracluster transition in the MMW range and to increase the accuracy of the predictions. Even in this latter case the bad convergence of the effective rotational Hamiltonian does not allow predictions of intracluster transitions better than 10 MHz. Table II shows the measurements and assignment of the intracluster transition frequencies for the most abundant H<sub>2</sub> <sup>80</sup>Se isotopomer. Besides the frequencies, the predictions or the differences between the observed and calculated values obtained by fitting are shown. Several fits were performed using the same Hamiltonian, with the maximum power of an angular momentum term  $J_z^4$ , but with different frequency sets. The data set included more than 100 FIR frequencies of the rotational spectrum up to  $J = 20$  (6), SubMMW data (1), and MMW data of the present work. In the column with the subtitle "Fit 1" the results of the fitting with maximum  $J = 18$  is given, in the "Fit 2"

TABLE I  
Measured Frequencies of H<sub>2</sub>Se in the Millimeter-wave Region

Transition	Frequency /MHz/	O.-C. /kHz/	Unc. /kHz/	Selenium isot.weight
7 <sub>1 6</sub> ←6 <sub>4 3</sub>	75652.09	-40.	100.	82
7 <sub>1 6</sub> ←6 <sub>4 3</sub>	75706.329	2.	50.	80
7 <sub>1 6</sub> ←6 <sub>4 3</sub>	75763.22	-16.	100.	78
4 <sub>1 4</sub> ←3 <sub>2 1</sub>	125902.02	-13.	100.	80
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	127860.534 <sup>a</sup>	0.	20.	82
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	127973.567 <sup>a</sup>	14.	20.	80
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	128092.366 <sup>a</sup>	-5.	20.	78
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	128153.961 <sup>a</sup>	23.	20.	77
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	128217.371 <sup>a</sup>	13.	20.	76
1 <sub>1 0</sub> ←1 <sub>0 1</sub>	128349.070	2.	20.	74
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	141889.232 <sup>a</sup>	7.	20.	82
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	142172.116 <sup>a</sup>	27.	20.	80
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	142469.597 <sup>a</sup>	-2.	20.	78
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	142623.848 <sup>a</sup>	52.	20.	77
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	142782.956 <sup>a</sup>	42.	20.	76
2 <sub>2 0</sub> ←2 <sub>1 1</sub>	143113.324	27.	20.	74
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	164663.309 <sup>a</sup>	23.	20.	82
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	165240.407 <sup>a</sup>	2.	20.	80
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	165847.969 <sup>a</sup>	22.	20.	78
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	166163.316 <sup>a</sup>	57.	20.	77
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	166488.342 <sup>a</sup>	48.	20.	76
3 <sub>3 0</sub> ←3 <sub>2 1</sub>	167164.160	5.	20.	74

<sup>a</sup> lines were previously observed in Ref. (5).

column the maximum  $J$  retained was 19, in the "Fit 3" column  $J_{\max} = 20$ , and in the last  $J_{\max} = 22$ . To increase the prediction accuracy we included only the frequencies of transitions with  $(J - K_a) \leq 2$ . It is seen from Table II that: (i) the doublet splitting is independent of the selection of frequencies with high  $J$ , and (ii) the prediction error strongly depends on adding frequencies with high  $J$ . Note that the prediction usually, but not always, gives a lower value than the experimental frequency. The negative prediction error in Fit 2 and the lack of improvement in the prediction from Fit 2 to Fit 3 are both due to the polynomial form and bad convergence of the Hamiltonian. We can conclude from the Table II, however, by looking at all four fits, that the assignments of these intracluster transitions are reliable. The estimations of the intensities of these lines support the assignment.

A search for an analogous intracluster doublet with  $J = 22$  for the isotopomer H<sub>2</sub><sup>78</sup>Se, which has 25% abundance, was also performed. Two lines were detected, but due to the fact that the weaker doublet component (due to spin statistics) has not been observed, we were unable to unambiguously identify the transition 22<sub>22 1</sub> ← 22<sub>21 2</sub>. We present here the frequencies of the two candidates: 174 232.90(20) MHz and 174 244.49(20) MHz. The frequencies of intracluster transitions with  $J = 24$  should be near of 70 GHz but could not be observed. Only the reference lines (see Table I) could be measured in this region.

We do not present here the rotational constants obtained as a result of the final fit, as we intend to make a joint fit of all the data after we finish the FIR analysis (6). The present data allowed more accurate predictions of higher  $J$  transitions, where an even stronger display of the clustering effect can be expected. Already, it is evident from the frequencies of Table II that the energy spread of the cluster decreases by a factor of 3 from  $J = 20$  to  $J = 23$ . Taking into account that the intercluster interval increases with  $J$ , we can calculate that the experimentally observed rate of clustering (see above) is 20 at  $J = 23$ .

TABLE II  
Measured "Intracuster" Frequencies of H<sub>2</sub> <sup>80</sup>Se and Predictions Using Different Frequency Sets

Transition	Exp.Freq. /MHz/	Unc. /MHz/	Obs.-Calc. Fit 1	Obs.-Calc. Fit 2	Obs.-Calc. Fit 3	Obs.-Calc. Fit 4
18 <sub>18 0</sub> ←18 <sub>17 1</sub>	443219.07 <sup>a</sup>	0.10	<u>0.09</u>	<u>0.05</u>	<u>0.03</u>	<u>-0.03</u>
18 <sub>18 1</sub> ←18 <sub>17 2</sub>	445382.77 <sup>a</sup>	0.10	<u>-0.07</u>	<u>-0.11</u>	<u>-0.11</u>	<u>0.11</u>
19 <sub>19 0</sub> ←19 <sub>18 1</sub>	373816.77 <sup>a</sup>	0.10	2.50	<u>0.02</u>	<u>0.03</u>	<u>0.16</u>
19 <sub>19 1</sub> ←19 <sub>18 2</sub>	375107.10 <sup>a</sup>	1.00	2.18	<u>-0.31</u>	<u>-0.28</u>	<u>-0.08</u>
20 <sub>20 0</sub> ←20 <sub>19 1</sub>	0.0 <sup>b</sup>		-301565.48	-301578.27	-301577.85	-301578.00
20 <sub>20 1</sub> ←20 <sub>19 2</sub>	302316.34 <sup>a</sup>	0.10	12.37	-0.44	<u>0.00</u>	<u>0.06</u>
21 <sub>21 0</sub> ←21 <sub>20 1</sub>	0.0 <sup>b</sup>		-231849.91	-231890.59	-231888.63	-231892.12
21 <sub>21 1</sub> ←21 <sub>20 2</sub>	0.0 <sup>b</sup>		-232249.25	-232289.96	-232287.98	-232291.39
22 <sub>22 0</sub> ←22 <sub>21 1</sub>	169753.59	0.10	106.87	9.35	15.12	<u>0.05</u>
22 <sub>22 1</sub> ←22 <sub>21 2</sub>	169955.083	0.05	106.89	9.31	15.09	<u>0.01</u>
23 <sub>23 0</sub> ←23 <sub>22 1</sub>	118514.97	0.10	224.14	33.98	46.85	5.50
23 <sub>23 1</sub> ←23 <sub>22 2</sub>	118609.05	0.20	224.06	33.82	46.70	5.42
Total MW Std. Dev.			1.03	1.04	1.03	1.08
Total IR Std. Dev.			0.47	0.47	0.47	0.46

<sup>a</sup> - frequencies from Ref. (1). <sup>b</sup> - no data available. The underline means that this frequency was included in fit, otherwise it was predicted. For other comments see text.

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#### REFERENCES

1. I. N. KOZIN, S. P. BELOV, O. L. POLYANSKY, AND M. YU. TRETYAKOV, *J. Mol. Spectrosc.* **152**, 13-28 (1992).
2. M. YU. TRETYAKOV, S. P. BELOV, I. N. KOZIN, AND O. L. POLYANSKY, *J. Mol. Spectrosc.* **154**, 163-168 (1992).
3. I. M. PAVLICHENKOV AND B. I. ZHILINSKII, *Ann. Phys. (N.Y.)* **184**, 1-32 (1988).
4. L. I. GERSHTEIN, V. L. VAKS, AND S. I. PRIPOLZIN, *Opt. Spectrosc. (USSR)* **64**, 1-2 (1988).
5. A. W. JACHE, P. W. MOSER, AND W. GORDY, *J. Chem. Phys.* **25**, 209-210 (1956).
6. I. N. KOZIN, S. KLEE, P. JENSEN, O. L. POLYANSKY, AND I. M. PAVLICHENKOV, *J. Mol. Spectrosc.*, submitted for publication.

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