JOURNAL OF MOLECULAR SPECTROSCOPY 58, 375–383 (1975)

The Ground State Rotational Spectrum of H_2Se: Weighted Microwave–Infrared Analysis[1]

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Ninety-four transitions of the five major species of hydrogen sulfide have been measured in the 100–600 GHz region of the microwave spectrum. These data have been combined with infrared data for the calculation of the energy levels and spectral constants of the several species. The data in both spectral regions can be fitted to within expected experimental error by means of Watson's reduced centrifugal distortion Hamiltonian. The rotational and P^4 distortion parameters are for $H_2{}^{80}Se$ (in MHz): $\mathcal{A} = 244\,099.89 \pm 0.29$, $\mathcal{B} = 232\,561.95 \pm 0.29$, $\mathcal{C} = 116\,874.93 \pm 1.76$, $\Delta_J = 34.950 \pm 0.03$, $\Delta_{JK} = -118.189 \pm 0.07$, $\Delta_K = 88.1873 \pm 0.13$, $\delta_J = -2.12091 \pm 0.012$, $\delta_K = 461.0394 \pm 1.0$.

I. INTRODUCTION

H_2Se has been studied in the infrared by a number of workers (*1*, *2*) and most recently by Hill and Edwards (*3*, *4*), who resolved for the first time the spectra of the several isotopic species. In the microwave region Jache, Moser, and Gordy (*5*) measured the three lines of each isotopic species that fall in the region below 175 GHz. In this work we report the measurement and assignment of 94 previously unobserved transitions in the 100–600 GHz region and the analysis of these data. The microwave data for $H_2{}^{80}Se$ and $H_2{}^{78}Se$ are analyzed with the infrared combination differences of Hill (*6*) to provide the most comprehensive analysis. For the less abundant species $H_2{}^{76}Se$, $H_2{}^{77}Se$, and $H_2{}^{82}Se$ no infrared combination differences are available. These species are analyzed primarily on the basis of the observed microwave transitions. These analyses are shown to be consistent with the more comprehensive analyses of $H_2{}^{78}Se$ and $H_2{}^{80}Se$.

Since there are five abundant isotopic species of H_2Se, these species present a unique opportunity to study the effects of isotopic substitution in light asymmetric rotors of the form H_2X. The abundance of these species also leads to a dense, complex spectrum in the microwave region because the isotopic multiplets are not well isolated from one another and in many cases overlap. In addition, the large rotational constants of these species result in low J transitions which are scattered throughout the millimeter and submillimeter region of the microwave spectrum. It has been shown previously (*7*, *8*) that a large number of these transitions must be measured to calculate adequately the rotation-distortion parameters which are necessary to characterize the observed spectrum to within the accuracy of microwave spectroscopy (<1 MHz).

[1] This work was supported by the National Science Foundation, Grant No. GP-34590.

We have previously discussed the use of Watson's (*9*, *10*, *11*) reduced centrifugal distortion Hamiltonian for the analysis of light asymmetric molecules (e.g., H_2O, NH_2D). It is well known that the transformation that leads to this Hamiltonian breaks down in the symmetric top limit and it has also been suggested (*12*, *13*) that different transformations are more advantageous under certain circumstances. Since H_2Se is substantially more symmetric ($\kappa \approx 0.82$) than any of the other light asymmetric species which we have analyzed, it is interesting to see what effects, if any, result.

II. EXPERIMENTAL PROCEDURE

The millimeter and submillimeter microwave spectrometer used for this work has been discussed previously (*14*, *15*). In brief, it consists of a klystron-driven crystal harmonic generator, a quasi-free-space absorption cell 1 m in length, and a 1.5 K InSb photodetector. The inside of the copper cell was coated with "Plasti-Kote"[2] to retard the decomposition of the molecules. The H_2Se was prepared by the reaction

$$Al_2Se_3 + 6H_2O \rightarrow 3H_2Se + 2Al(OH)_3. \tag{1}$$

Small quantities of H_2O remain in the sample, but were easily identified from the known spectrum of H_2O in the microwave region (*16*).

III. ANALYSIS

We have previously discussed the use of Watson's reduced centrifugal distortion Hamiltonian for the analysis of the microwave spectra of light asymmetric rotors (*7*). For $H_2{}^{80}Se$ this Hamiltonian takes the form

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d^{(4)} + \mathcal{H}_d^{(6)} + \mathcal{H}_d^{(8)} + \mathcal{H}_d^{(10)}, \tag{1a}$$

$$\mathcal{H}_r = \tfrac{1}{2}(\mathcal{A} + \mathcal{B})P^2 + [\mathcal{C} - \tfrac{1}{2}(\mathcal{A} + \mathcal{B})][P_z^2 - b_0 P_-^2], \tag{1b}$$

$$\mathcal{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K [P_z^2 P_-^2 + P_-^2 P_z^2], \tag{1c}$$

$$\mathcal{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2 + h_{JK} P^2 [P_z^2 P_-^2 + P_-^2 P_z^2] + h_K [P_z^4 P_-^2 + P_-^2 P_z^4], \tag{1d}$$

$$\mathcal{H}_d^{(8)} = L_{JJK} P^6 P_z^2 + L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P_z^8 + l_{JK} P^4 [P_z^2 P_-^2 - P_-^2 P_z^2] + l_K [P_z^6 P_-^2 + P_-^2 P_z^6], \tag{1e}$$

$$\mathcal{H}_d^{(10)} = P_{JK} P^6 P_z^4 + P_{KJ} P^4 P_z^6 + P_{KKJ} P^2 P_z^8 + P_K P_z^{10}, \tag{1f}$$

where $P^2 = (P_x^2 + P_y^2 + P_z^2)$ is the total angular momentum, $P_-^2 = (P_x^2 - P_y^2)$, and $b_0 = (\mathcal{A} - \mathcal{B})/(2\mathcal{C} - \mathcal{A} - \mathcal{B})$ is Wang's asymmetry parameter for a near-oblate top.

Table I shows the 25 microwave lines of $H_2{}^{80}Se$ that are included in the analysis along with the 84 distinct combination differences obtained by Hill (*6*) from his analysis of the near-infrared spectrum. Since the microwave data are approximately 3000 times more accurate than the combination differences, each microwave transition was assigned a weight of 9×10^6 for transitions between levels for which $J \leq 2$. In order to allow for

[2] A product of Plasti-Kote Corporation, Medina, Ohio.

Table I. Observed Microwave Transitions of H_2Se (MHz).

	$H_2{}^{76}Se$	$H_2{}^{77}Se$	$H_2{}^{78}Se$	$H_2{}^{80}Se$	$H_2{}^{82}Se$
$1_{01} \to 1_{10}$	128 219.10[a]	128 155.40[a]	b	127 973.40[a]	127 860.35[a]
$0_{00} \to 1_{11}$	362 268.84	362 167.63	362 069.14	361 879.28	361 698.54
$2_{11} \to 2_{20}$	142 783.02[a]	142 623.48[a]	142 469.58[a]	142 171.86[a]	141 889.02[a]
$2_{12} \to 2_{21}$	384 193.75	384 003.88	383 819.46	383 463.65	383 125.26
$2_{02} \to 2_{11}$	344 787.62	344 830.49	344 872.29	344 953.15	345 030.44
$1_{11} \to 2_{02}$			581 180.62	581 098.89	
$1_{01} \to 2_{12}$	596 336.52	596 197.06	596 061.86	595 800.97	595 552.80
$3_{21} \to 3_{30}$	166 488.14[a]	166 163.20[a]	165 847.57[a]	165 240.46[a]	164 663.10[a]
$3_{22} \to 3_{31}$	403 783.97	403 463.92	403 153.22	402 553.93	401 983.80
$3_{12} \to 3_{21}$	329 590.51	329 694.48	329 795.90	329 992.71	330 181.47
$4_{31} \to 4_{40}$	201 000.01	200 420.65	199 858.66	198 776.38	197 748.81
$4_{32} \to 4_{41}$	429 195.99	428 701.45	428 221.28	427 295.16	426 414.26
$4_{22} \to 4_{31}$	315 684.32	315 807.45	315 928.10	316 164.20	316 392.66
$5_{41} \to 5_{50}$	247 308.71	246 382.75	245 484.52	243 754.69	242 112.28
$5_{42} \to 5_{51}$	459 562.13	458 850.63	458 160.01	456 827.96	455 560.94
$5_{32} \to 5_{41}$	307 626.96	307 690.68	307 754.78	307 884.72	308 016.04
$6_{51} \to 6_{60}$	304 643.20	303 301.44	301 999.28	299 490.16	297 106.08
$6_{52} \to 6_{61}$				489 861.69	
$6_{42} \to 6_{51}$	309 760.43	309 661.16	309 568.45	309 399.66	309 251.68
$7_{61} \to 7_{70}$	369 837.86	368 058.70	366 331.05	362 998.90	359 829.07
$7_{52} \to 7_{61}$	325 677.38	325 299.72	324 938.27	324 255.52	323 624.01
$8_{71} \to 8_{80}$				429 235.84	
$8_{62} \to 8_{71}$	358 010.12	357 239.79	356 498.41	355 087.30	353 768.27
$9_{81} \to 9_{90}$				492 152.55	
$9_{72} \to 9_{81}$	408 036.27	406 781.99	405 571.85	403 259.55	401 087.63

a. Ref. 5.

b. Analysis indicates that frequency reported in Ref. 5 is in error by approximately 5 MHz.

possible contributions from model errors at higher J, the remaining microwave lines were assigned a weight of 10^6. The spectral constants which result from this analysis are shown in Table II. Also shown in Table II are the results of an analysis based entirely upon the microwave data of Table I. The apparent small differences (≈ 5 MHz) between the rotational constants of the two analyses are discussed in the following section. For both of these analyses the standard deviations for both the microwave and infrared lines are shown. It should be pointed out that the values for σ_{mw} are strongly dependent upon the relative weighting between the microwave and infrared data. Since both the standard deviations for the microwave and infrared data are consistent with expected experimental uncertainty, it can be concluded that model errors are of minimal significance.

The energy levels calculated from the constants of the combined analysis are shown in Table III. They are in good agreement with those of Hill at low τ (e.g., 9_{09}) but differ substantially at high τ (e.g., 9_{90}). This is not an unexpected result and demonstrates the manner in which the microwave and infrared data are complementary. At low J the microwave lines connect most of the energy levels, and as a result, these levels are known to approximately microwave accuracy. Although the infrared combination differences

Table II. Spectral Constants of Hydrogen Selenide (MHz).[a]

	$H_2{}^{78}Se$[b]		$H_2{}^{80}Se$[b]		$H_2{}^{80}Se$[c]	
	Constant	σ	Constant	σ	Constant	σ
$\mathcal{A}$	244 244.14	1.15	244 099.39	0.29	244 086.55	0.31
$\mathcal{B}$	232 588.27	1.10	232 561.96	0.25	232 543.124	0.31
$\mathcal{C}$	116 910.11	5.14	116 874.93	1.76	116 874.615	1.16
A	245 123.14		244 967.32		244 957.29	
B	231 548.37		231 523.31		231 503.63	
C	117 012.00		116 976.14		116 976.34	
$\Delta_J \cdot 10^{-2}$	0.35042	0.0010	0.34950	0.0003	0.349216	0.0007
$\Delta_{JK} \cdot 10^{-3}$	-0.113184	0.00015	-0.113139	0.00007	-0.1132033	0.00003
$\Delta_K \cdot 10^{-3}$	0.37903	0.005	0.381873	0.0013	0.389652	0.003
$\delta_J \cdot 10^{-1}$	-0.211471	0.0014	-0.212091	0.0012	-0.2073302	0.0004
$\delta_K \cdot 10^{-3}$	0.458372	0.002	0.510584	0.0010	0.465221	0.0007
$H_J \cdot 10^{+1}$	0.193	0.01	0.217	0.014		
$H_{JK} \cdot 10^{-1}$	-0.113753	0.003	-0.120133	0.0015	-0.117154	0.0010
$H_{KJ} \cdot 10^{-1}$	0.24586	0.02	0.27426	0.004	0.2554505	0.010
$H_K \cdot 10^{-1}$	-0.03331	0.02	-0.11047	0.006		
$h_J \cdot 10^{+3}$	-0.59630	0.02	-0.626116	0.012	-0.581423	0.007
$h_{JK} \cdot 10^{0}$	0.20761	0.010	0.20217	0.007	0.223384	0.003
$h_K \cdot 10^{-1}$	0.345150	0.04	0.327653	0.012	0.3511358	0.009
$L_{JJK} \cdot 10^{+2}$	0.13122	0.017	0.17130	0.004	0.171333	0.003
$L_{JK} \cdot 10^{0}$	0.135773	0.003	0.136185	0.002	0.1364713	0.0015
$L_{KKJ} \cdot 10^{0}$	-0.335455	0.017	-0.366535	0.005	-0.357223	0.012
$L_K \cdot 10^{0}$	0.213034	0.009	0.221555	0.002		
$\ell_{JK} \cdot 10^{+3}$	0.37789	0.2	0.39213	0.04	0.396468	0.05
$\ell_K \cdot 10^{+2}$	0.2155	0.17	0.6340	0.12		
$P_{JK} \cdot 10^{+4}$	-0.2252	0.27	-0.43455	0.07		
$P_{KJ} \cdot 10^{+2}$	-0.243166	0.02	-0.226300	0.010	-0.232046	0.004
$P_{KKJ} \cdot 10^{+2}$	0.647601	0.06	0.604765	0.02	0.720281	0.07
$P_K \cdot 10^{+2}$	-0.396057	0.04	-0.373530	0.013		
σ_{MW}	0.07		0.14		0.01	
σ_{IR}	337.59		354.78			

a. The number of places retained are necessary if the spectral constants are to be used to calculate the spectrum to within experimental uncertainty. Because of the correlations among many of the constants, several additional places beyond that dictated by the uncertainties are required.

b. Weighted microwave-infrared analysis.

c. Microwave data only.

connect many more levels, they do not connect those at high τ, and as a result, previous energy levels which have been based primarily on these combination differences fail to predict accurately the high J, high τ microwave lines reported here. For example, the 9_{81}–9_{90} transition at 492 152.55 MHz is predicted to be at 502 242 MHz. Inclusion of the microwave data in the fit substantially improves the accuracy of these energy levels. On the other hand, the high J, low τ energy levels are primarily determined by the infrared combination differences although the inclusion of the high-precision microwave data in a good theoretical model should improve the accuracy of these levels. It is felt that at low J, the energy levels are good to approximately microwave accuracy and that now

Table III. Energy Levels of $H_2{}^{80}Se$ (cm^{-1}).[a]

1_{01}	11.[illegible]	5_{05}	137.1[illegible]	7_{07}	[illegible]	9_{09}	[illegible]
1_{11}	12.0710	5_{15}	137.1[illegible]	7_{17}	[illegible]	9_{19}	[illegible]
1_{10}	15.[illegible]	5_{14}	178.[illegible]	7_{16}	[illegible]	9_{18}	455.[illegible]
		5_{24}	178.[illegible]	7_{26}	[illegible].3036	9_{28}	455.[illegible]
2_{02}	31.[illegible]	5_{23}	201.[illegible]	7_{25}	[illegible]	9_{27}	515.07[illegible]
2_{12}	31.5001	5_{33}	201.[illegible]	7_{35}	[illegible]	9_{37}	515.0795
2_{11}	42.[illegible]	5_{32}	220.[illegible]	7_{34}	[illegible]	9_{36}	566.7153
2_{21}	[illegible]	5_{42}	222.0171	7_{44}	[illegible]	9_{46}	566.71[illegible]
2_{20}	47.7051	5_{41}	230.[illegible]	7_{43}	403.[illegible]	9_{45}	610.092[illegible]
		5_{51}	237.2[illegible]	7_{53}	403.[illegible]	9_{55}	610.122[illegible]
3_{03}	53.3132	5_{50}	238.[illegible]	7_{52}	425.[illegible]	9_{54}	645.1234
3_{13}	53.[illegible]172			7_{62}	427.9993	9_{64}	645.5324
3_{12}	73.[illegible]	6_{06}	187.[illegible]	7_{61}	434.2133	9_{63}	670.3005
3_{22}	73.1[illegible]	6_{16}	187.[illegible]	7_{71}	[illegible].5001	9_{73}	673.7[illegible]
3_{21}	[illegible]	6_{15}	252.221[illegible]	7_{70}	[illegible].3217	9_{72}	686.9208
3_{31}	[illegible]	6_{25}	252.2217			9_{82}	[illegible].72[illegible]2
3_{30}	95.457[illegible]	6_{24}	[illegible]	8_{08}	312.[illegible]	9_{81}	700.3721
		6_{34}	[illegible]	8_{18}	312.[illegible]	9_{91}	716.[illegible]
4_{04}	94.1442	6_{33}	[illegible]	8_{17}	373.1544	9_{90}	716.7336
4_{14}	94.144[illegible]	6_{43}	[illegible]	8_{27}	373.15[illegible]		
4_{13}	122.32[illegible]	6_{42}	[illegible]	8_{26}	425.0[illegible]		
4_{23}	122.3533	6_{52}	317.1[illegible]	8_{36}	425.0[illegible]10		
4_{22}	1[illegible]2.0201	6_{51}	[illegible]	8_{35}	[illegible].3370		
4_{32}	1[illegible]2.[illegible]	6_{61}	[illegible]	8_{45}	[illegible].3457		
4_{31}	152.[illegible]	6_{60}	[illegible]	8_{44}	504.3231		
4_{41}	15[illegible].[illegible]			8_{54}	504.[illegible]		
4_{40}	15[illegible].1[illegible]			8_{53}	530.[illegible]		
				8_{63}	532.4[illegible]		
				8_{62}	547.5331		
				8_{72}	554.[illegible]		
				8_{71}	558.4275		
				8_{81}	573.1957		
				8_{80}	573.7452		

a. c = [illegible] km/sec.

both low and high τ levels at high J are good to approximately infrared accuracy (≈ 0.01 cm^{-1}, 300 MHz). At high τ the microwave lines in the analysis result in differences between the energy levels which are substantially more accurate than this.

Hill has reported 48 distinct combination differences for $H_2{}^{78}Se$. These have been combined with the 21 microwave lines shown in Table I in an analysis similar to the one described above for $H_2{}^{80}Se$. The spectral constants which result are shown in Table II.

For the less abundant species $H_2{}^{76}Se$, $H_2{}^{77}Se$, and $H_2{}^{82}Se$, no combination differences have been published. An analysis procedure similar to that discussed previously for $H_2{}^{17}O$ (*17*) has been adopted. Inspection of the results for $H_2{}^{80}Se$ and $H_2{}^{78}Se$ shows, to within experimental uncertainty, that the P^8 and P^{10} constants are identical. Therefore, for the analyses of the three less abundant species, their values of the P^8 and P^{10} constants were fixed at the $H_2{}^{80}Se$ values. In addition, it can be shown that the 21 microwave lines observed for each of these three species do not determine the value of H_J or H_K. These constants were also fixed to the $H_2{}^{80}Se$ values. The spectral constants which result from these analyses are shown in Table IV for all five species. Both the good fit of the experimental data and the excellent agreement between the $H_2{}^{78}Se$ constants calculated by this procedure and those shown in Table II indicate the general validity of this procedure. Since the uncertainties in the variables depend upon the uncertainties in the fixed constants that were obtained from the full $H_2{}^{80}Se$ analyses, the uncertainties of the constants in Table IV should be taken to be approximately the same as those of $H_2{}^{80}Se$.

Table IV. Spectral Constants of Hydrogen Selenide from Microwave Data and Fixed Higher Order Constants (MHz).[a]

	$H_2{}^{76}Se$	$H_2{}^{77}Se$	$H_2{}^{78}Se$	$H_2{}^{80}Se$	$H_2{}^{82}Se$
$\mathcal{A}$	244 434.51	244 348.74	244 262.14	244 099.68	243 945.73
$\mathcal{B}$	232 546.40	232 549.75	232 554.68	232 561.95	232 568.92
$\mathcal{C}$	116 945.72	116 927.29	116 909.32	116 874.98	116 841.45
$\Delta_J \cdot 10^{-2}$	0.35146	0.35122	0.34998	0.34948	0.34906
$\Delta_{JK} \cdot 10^{-3}$	-0.118341	-0.118408	-0.118142	-0.118186	-0.118264
$\Delta_K \cdot 10^{-2}$	0.865614	0.870799	0.873952	0.881802	0.889171
$\delta_J \cdot 10^{-1}$	-0.215431	-0.214838	-0.213477	-0.212053	-0.210903
$\delta_K \cdot 10^{-3}$	0.4524139	0.4541929	0.4572277	0.4610641	0.4645726
$H_{JK} \cdot 10^{-1}$	-0.114809	-0.115993	-0.116696	-0.120142	-0.123863
$H_{KJ} \cdot 10^{-1}$	0.25035	0.25778	0.262162	0.275212	0.288624
$h_J \cdot 10^{+2}$	-0.610582	-0.617029	-0.616165	-0.625713	-0.636121
$h_{JK} \cdot 10^{0}$	0.20083	0.19372	0.20383	0.20231	0.19916
$h_K \cdot 10^{-1}$	0.314709	0.312839	0.326500	0.327930	0.327415
σ_{MW}	0.390	0.438	0.196	0.129	0.141

a. The distortion constants omitted from this table are fixed at their $H_2{}^{80}Se$ values.

IV. REMARKS

H_2Se is the most symmetric ($\kappa \approx 0.82$) light asymmetric rotor that has been analyzed by means of the Hamiltonian of Eq. (1). For an oblate top the $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ of Watson are related to the A, B, C of Kivelson and Wilson (*18*) by

$$\mathcal{A} = A + 16R_6(C - B)/(B - A), \quad (2a)$$

$$\mathcal{B} = B - 16R_6(C - A)/(B - A), \quad (2b)$$

$$\mathcal{C} = C + 16R_6. \quad (2c)$$

In the limit of an oblate symmetric top these relations break down, and for near-symmetric tops these corrections can be large. This is one manifestation of the breakdown

Table V. Rotational Constants of Hydrogen Selenide (MHz).

	$H_2{}^{76}Se$	$H_2{}^{77}Se$	$H_2{}^{78}Se$	$H_2{}^{80}Se$	$H_2{}^{82}Se$
A[a]	[illegible]	245 202.36	245 121.50	244 967.31	244 820.43
B	[illegible]	231 541.71	[illegible]	[illegible]	[illegible]
C	117 047.30	117 025.68	117 011.52	116 976.1[illegible]	116 942.58
A[b]	245 250	245 175	245 101	[illegible]	244 737
B	231 662	231 662	231 668	[illegible]	231 650
C	117 033	117 015	116 994	116 958	116 919
A[c]	245 342	245 259	245 190	245 021	244 874
B	231 728	231 728	231 741	231 723	231 722
C	117 117	117 098	117 085	117 042	117 008

a. From the analysis of Table IV and Eq. (2).
b. From the infrared results of Ref. 4.
c. From data of Jache, Moser, and Gordy (Ref. 5) as analyzed by Oka and Morino (Refs. 19, 20).

in the symmetric top limit of the transformation which results in the reduced Hamiltonian of Eq. (1).

Since this breakdown occurs whenever $A - B$ is of the same order of magnitude as the P^4 distortion parameters (1500 and 500 MHz, respectively, for H_2Se), it is of interest to test for evidence of this breakdown in the results presented here. For the weighted microwave–infrared and the pure microwave $H_2{}^{80}Se$ analyses shown in Table II, $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ differ by approximately 5 MHz, while the A, B, C agree to about 0.2 MHz. Changes in the $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ for $H_2{}^{80}Se$ can also result from different choices of the higher-order distortion constants. Although these changes can be as large as 100 MHz, the A, B, C which result via Eq. (2) are in good agreement with the analyses presented here.

Table V shows the A, B, C which result from the analyses of Table IV via Eq. (2). Since an on-axis substitution should not affect the moment of inertion about that axis, B should remain unchanged for isotopic selenium substitutions. For these analyses the difference between $\mathcal{B}$ for $H_2{}^{76}Se$ and $\mathcal{B}$ for $H_2{}^{82}Se$ is 22 MHz, while the same difference for B is only 1.5 MHz. Also included in Table V are the rotational constants calculated by Oka and Morino (*19*, *20*) from the microwave measurements of Ref. (*5*) and distortion constants calculated from infrared vibrational data via the force field relations as well as the infrared results of Hill and Edwards (*4*).

Since $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ are fitting parameters and have no direct physical meaning, no inconsistency results from any of the above. Furthermore, it can be demonstrated that, like the A, B, C, the energy levels which result from the various analyses are in good agreement. The consistency of the results presented here may in large part depend upon the accuracy of the numerical methods employed. All calculations reported in this work were performed in double-precision arithmetic on an IBM 370/165.

It is interesting to note that although the asymmetry of CH_2DF is substantially less ($\kappa = -0.978$) than that of H_2Se, the $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ of CH_2DF are extremely stable (*21*). But unlike H_2Se, for CH_2DF the P^4 constants are small compared to $\mathcal{B} - \mathcal{C}$ and it is this ratio which is a measure of the breakdown of Watson's transformation (*10*).

V. THE RESULTS OF DISTORTION ANALYSES OF LIGHT ASYMMETRIC MOLECULES

The combination of the millimeter and submillimeter microwave techniques described in Ref. (*14*) and Watson's Hamiltonian have made it possible to characterize the rotational spectra of the lighest asymmetric molecules over a wide range of J_τ states. These molecules can be divided into classes: First, the bent triatomic species of water and hydrogen sulfide, all of which are rather asymmetric; second, hydrogen selenide, which is considerably more symmetric than the first group; third, prymidal XY_2Z molecules such as NH_2D and ND_2H; and finally, slightly asymmetric species with large A rotational constants like CH_2O and CH_2DF.

Table VI summarizes the results of these analyses and shows both a number of similarities as well as several important differences. In all cases the experimental data can be fit to within experimental uncertainty and transitions within the general J_τ range of the data set, but not included in the analyses, can be predicted with good accuracy. But only for NH_2D/ND_2H and CH_2DF has it been demonstrated that transitions well beyond the J_τ range of the rest of the data can be predicted accurately. This is not the

Table VI. Comparison of the Results of Analyses of Light Asymmetric Rotors

Molecular type	Accurate fit of experimental data	Accurate prediction of transitions for J_τ similar	Typical number of distortion constants	Accurate prediction of transition for higher J_τ	Evidence for transformation break down
Water, hydrogen sulfide and isotopic species	Yes	Yes	15^+	No	No
Hydrogen Selenide	Yes	Yes	15^+	No	Some
Asymmetric Ammonia	Yes	Yes	6	Yes	No
Slightly Asymmetric	Yes	Yes	6	Yes	No

case for the first two classes of molecules. This result is directly related to the number of distortion parameters required to characterize the spectrum of each specie. Since the higher-order constants are often highly correlated for the available data set, substantial errors can result in the predictions of the frequencies of transitions beyond the general J_τ range of the data set.

It is also important that the constants which result from any spectroscopic study be characteristic of the molecular species and not the details of the data set or choice of Hamiltonian. This has been demonstrated for all of the species represented in Table VI if, as discussed above for H_2Se, it is remembered that it is A, B, C which relate to molecular geometry rather than $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$. In particular, for the species of water and hydrogen sulfide it has been demonstrated both that accurate structural parameters can be calculated from the rotational constants and that the molecular force fields calculated from the P^4 distortion constants are consistent with those calculated directly from vibrational data (*22*, *23*).

ACKNOWLEDGMENTS

The authors thank Professor Walter Gordy for his support and encouragement during this work. One of us (P.H.) acknowledges support from a grant to the Department of Physics, Duke University, by the Shell Companies Foundation.

RECEIVED: June 2, 1975

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