Fourier Transform Infrared Emission Spectroscopy of SeH

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The infrared vibration–rotation bands of SeH have been measured in the $X^2\Pi$ ground state using a Fourier transform spectrometer. The bands were observed in a microwave discharge of a mixture of H_2 and Se in the presence of He. The rotational structure of the 1–0, 2–1, 3–2 bands of the $X^2\Pi_{3/2}$ spin component and the 1–0 band of $X^2\Pi_{1/2}$ spin component has been observed in the 1800–2600 cm^{-1} region. The principal ground state molecular constants obtained are $\omega_e = 2421.7153(234)$ cm^{-1}, $\omega_e x_e = 44.6012(110)$ cm^{-1}, $\omega_e y_e = 0.20697(236)$ cm^{-1}, $B_e = 7.899187(696)$ cm^{-1}, $\alpha_e = 0.220749(399)$ cm^{-1}, and $r_e = 1.464319(64)$ Å. This work is the first determination of the equilibrium molecular constants of the $X^2\Pi$ state of SeH. © 2000 Academic Press

INTRODUCTION

SeH is a free radical of considerable experimental and theoretical interest. This radical is in the same group as OH and SH, which have been extensively studied over the past decades and are species of astrophysical importance. OH has already been detected in the sun (*1*), stars (*2*), interstellar medium (*3, 4*), and comets (*5, 6*). SH has recently been detected in an S-type star (*7*), although it has not been seen yet in the interstellar medium (*8, 9*). SeH is also a molecule of potential astrophysical importance, but limited high-resolution data are available compared to OH and SH. Note that the Se atom has been detected in the interstellar medium (*10*). In recent years, considerable efforts have been devoted to the high-resolution spectroscopy of OH and SH. In addition to providing precise spectroscopic parameters, these studies also provide data for comparison with the results of *ab initio* calculations. Because of the presence of a heavy atom, *ab initio* calculations on molecules such as SeH are challenging, and relativistic and spin–orbit effects need to be included.

The SeH radical has been studied over the past decades from the infrared to the vacuum ultraviolet regions. SeH was first observed by Radford (*11*) in a gas-phase electron paramagnetic resonance (EPR) experiment. The EPR work was further extended and refined by Carrington and co-workers (*12, 13*). The ultraviolet spectra were recorded by Lindgren (*14*), who observed several diffuse bands in the 3000–3250 Å region from the flash photolysis of SeH$_2$. These bands were assigned to the $A^2\Sigma^+ - X^2\Pi_i$ transition but the diffuseness of the spectra limited the accuracy of the derived constants. The vacuum ultraviolet spectra of SeH have been studied by Donovan *et al.* (*15*) and Bollmark *et al.* (*16, 17*) and several Rydberg transitions

were observed. Again the spectra were diffuse due to predissociation and the spectroscopic constants were not well determined. The UV and vacuum UV spectra have also been observed for the SeD isotopomer (*14–17*).

The far- and mid-infrared spectra of SeH and SeD have been studied by several groups. The laser magnetic resonance (LMR) technique was applied by Davies *et al.* (*18*) to detect a pure rotational transition in the $X^2\Pi_{3/2}$ spin component, while Brown *et al.* (*19*) and Ashworth and Brown (*20*) have measured pure rotational transitions in the $X^2\Pi_{3/2}$ spin component as well as the forbidden $X^2\Pi_{1/2} - X^2\Pi_{3/2}$ transition between the two spin components (for the $v = 0$ vibrational level) of SeH in the mid-infrared. These studies provided spectroscopic constants as well as information on the nuclear hyperfine structure for the $v = 0$ vibrational level of the ground state of SeH. Similar LMR studies are also available for SeD (*21–23*).

SeH has also been the subject of several theoretical studies focused on the determination of the spectroscopic properties of the low-lying electronic states, including relativistic effects (*24–26*). The theoretical electric dipole moments and dissociation energies for the ground states of GaH, GeH, AsH, SeH, and BrH have been calculated by Pettersson and Langhoff (*24*). Balasubramanian *et al.* (*25*) have determined the spectroscopic properties of the low-lying $X^2\Pi_{3/2}$, $X^2\Pi_{1/2}$, $^2\Sigma^+_{1/2}$, 3/2(II), and 5/2 states, including relativistic and the spin–orbit effects, which have considerable effect on the spectroscopic properties. In a recent publication Pisani and Clementi (*26*) have studied relativistic effects on group six monohydrides, OH, SH, SeH, and PoH, and have calculated the ionization potentials and dissociation energies for these species. Ashworth and Brown (*27*) have recently discussed the electric-dipole moments for SeH and GeH as determined from the measurements of the relative intensity of electric and magnetic dipole transitions in their LMR spectra. The dipole moment of SeH was more reliably determined to be 0.483 D by Byfleet *et al.* (*13*).

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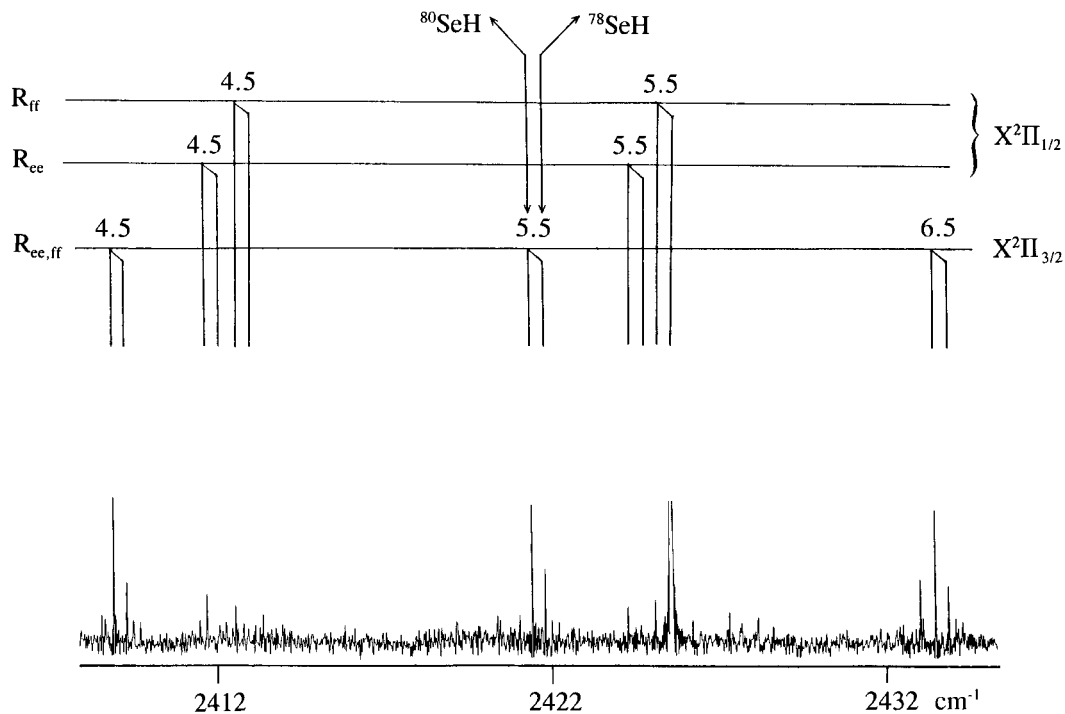
FIG. 1. A part of the spectrum showing R lines of the 1–0 vibration–rotation band of SeH.

A photoionization study of SeH and SeH_2 has been carried out by Gibson *et al.* (*28*) from which they have determined the adiabatic ionization potential of 9.985 ± 0.003 eV and a dissociation energy of 74.27 ± 0.23 kcal/mol for SeH. The electron affinity of SeH is 2.21 eV (*29*). The ionization energies and bond dissociation energies of GeH_n, AsH_n, and SeH_n have been calculated (*30*), and Binning and Curtis predict a ground state bond length of 1.458 Å, a ground state vibrational frequency of 2567 cm^{-1}, and a dissociation energy of 73.7 kcal/mol for SeH.

In the present paper we report on the observation of the $\Delta v = 1$ infrared vibration–rotation bands of SeH in the 2000–2600 cm^{-1} region at high resolution. We have measured the rotational structure of the 1–0, 2–1, and 3–2 bands of the $X^2\Pi_{3/2}$ spin component, which is lowest in energy. For the $X^2\Pi_{1/2}$ spin component, which lies at 1760 cm^{-1} above the $X^2\Pi_{3/2}$ spin component, we have observed the vibration–rotation structure for only the 1–0 band. The present infrared data provide improved spectroscopic constants for the ground state of SeH.

SeH is the last of the nonradioactive main-group monohydrides for which an equilibrium vibrational and rotational structure needs to be determined. An equilibrium bond length and vibrational frequency are known, however, for SeD (*23*).

EXPERIMENTAL

The vibration–rotation bands of SeH were recorded between 1800–2600 cm^{-1} region with the 1-m Fourier transform spectrometer associated with the McMath–Pierce telescope of the National Solar Observatory at Kitt Peak. SeH was produced in an electrodeless discharge lamp operated with 80 W power from a 2450 MHz microwave oscillator. The lamp was a quartz tube with an outer diameter of 12 mm. In this experiment we reused a lamp which was previously used to record the spectra of the Se atom. A thin film of reddish Se was already deposited on the inner wall of the discharge tube and no additional Se powder was added. A mixture of 60 mTorr of H_2 and 2.2 Torr of He flowed slowly through the lamp to make SeH. Helium served simply as a carrier gas.

The emission from the lamp was sent directly into the entrance aperture of the Fourier transform spectrometer. The spectrometer was equipped with a CaF_2 beam splitter and liquid-nitrogen-cooled InSb detectors. The use of an InAs optical filter limited the observation of the spectra to the 1800–3000 cm^{-1} spectral region. A total of 14 scans were coadded in about 35 min at a resolution of 0.02 cm^{-1}.

In addition to SeH bands, this spectrum also contained Se and H atomic lines and H_2O molecular absorption lines. The spectra were calibrated by use of measurements of Se atomic lines by Engleman (*31*). The precision of measurements of strong and unblended lines of SeH, which appear with a typical signal-to-noise ratio of ~10:1, is expected to be better than ± 0.002 cm^{-1}.

RESULTS AND DISCUSSION

The line positions of SeH were extracted from the spectra using a data reduction program called PC-DECOMP developed

TABLE 1

Line Positions (in cm^{-1}) for the Vibration–Rotation Bands of ^{80}SeH and ^{78}SeH

J'	J''	Obs.	O-C	J'	J''	Obs.	O-C
		^{80}SeH X$^2\Pi_{1/2}$ 1-0				^{80}SeH X$^2\Pi_{3/2}$ 2-1	
2.5 f	1.5 f	2371.9250	-0.0001	9.5	8.5	2366.3000	-0.0031
3.5 f	2.5 f	2385.9291	-0.0097	10.5	9.5	2376.4142	0.0004
4.5 f	3.5 f	2399.4728	-0.0006	11.5	10.5	2386.0092	-0.0010
5.5 f	4.5 f	2412.5235	0.0021	1.5	2.5	2207.5285	-0.0014
6.5 f	5.5 f	2425.0768	0.0021	2.5	3.5	2191.4088	0.0011
7.5 f	6.5 f	2437.1309	0.0049	3.5	4.5	2174.8774	0.0003
8.5 f	7.5 f	2448.6662	-0.0018	5.5	6.5	2140.6256	0.0031
9.5 f	8.5 f	2459.6907	-0.0022	6.5	7.5	2122.9145	-0.0005
1.5 f	2.5 f	2293.7256	-0.0014	7.5	8.5	2104.8321	0.0007
2.5 f	3.5 f	2276.9679	-0.0015	8.5	9.5	2086.3890	0.0089
3.5 f	4.5 f	2259.7907	-0.0007			^{80}SeH X$^2\Pi_{3/2}$ 3-2	
4.5 f	5.5 f	2242.2031	0.0013	2.5	1.5	2194.5578	0.0016
5.5 f	6.5 f	2224.2062	-0.0027	3.5	2.5	2207.6202	-0.0028
6.5 f	7.5 f	2205.8206	-0.0010	4.5	3.5	2220.2274	0.0014
7.5 f	8.5 f	2187.0523	0.0035	5.5	4.5	2232.3567	-0.0014
3.5 e	2.5 e	2384.9808	0.0034	6.5	5.5	2244.0142	0.0022
4.5 e	3.5 e	2398.5631	0.0026	7.5	6.5	2255.1795	-0.0012
5.5 e	4.5 e	2411.6582	0.0001	8.5	7.5	2265.8571	0.0002
6.5 e	5.5 e	2424.2613	-0.0010			^{78}SeH X$^2\Pi_{3/2}$ 1-0	
7.5 e	6.5 e	2436.3627	-0.0028	2.5	1.5	2368.8100	-0.0015
8.5 e	7.5 e	2447.9605	0.0003	3.5	2.5	2382.7593	0.0021
0.5 e	1.5 e	2311.2365	-0.0016	4.5	3.5	2396.2403	0.0007
1.5 e	2.5 e	2294.9489	0.0001	5.5	4.5	2409.2556	0.0043
2.5 e	3.5 e	2278.2281	-0.0006	6.5	5.5	2421.7859	0.0008
3.5 e	4.5 e	2261.0868	0.0004	7.5	6.5	2433.8331	-0.0002
4.5 e	5.5 e	2243.5273	-0.0030	8.5	7.5	2445.3866	-0.0024
5.5 e	6.5 e	2225.5694	0.0004	9.5	8.5	2456.4445	-0.0005
6.5 e	7.5 e	2207.2138	0.0025	10.5	9.5	2466.9955	0.0013
7.5 e	8.5 e	2188.4754	0.0097	1.5	2.5	2292.3998	-0.0022
8.5 e	9.5 e	2169.3411	0.0000	3.5	4.5	2258.8662	-0.0006
		^{80}SeH X$^2\Pi_{3/2}$ 1-0		4.5	5.5	2241.4943	-0.0002
2.5	1.5	2368.4433	-0.0003	5.5	6.5	2223.7307	0.0006
3.5	2.5	2382.3842	-0.0016	6.5	7.5	2205.5857	0.0037
4.5	3.5	2395.8672	0.0023	7.5	8.5	2187.0543	-0.0042
5.5	4.5	2408.8720	-0.0012	8.5	9.5	2168.1684	0.0003
6.5	5.5	2421.4013	-0.0021			^{78}SeH X$^2\Pi_{3/2}$ 2-1	
7.5	6.5	2433.4469	-0.0009	2.5	1.5	2282.0773	-0.0021
8.5	7.5	2444.9985	-0.0008	3.5	2.5	2295.5909	0.0007
9.5	8.5	2456.0508	0.0006	4.5	3.5	2308.6369	-0.0015
10.5	9.5	2466.5933	-0.0004	6.5	5.5	2333.3160	-0.0002
1.5	2.5	2292.0537	-0.0020	1.5	2.5	2207.8528	0.0022
2.5	3.5	2275.5002	0.0028	2.5	3.5	2191.7253	0.0010
3.5	4.5	2258.5316	0.0007	3.5	4.5	2175.1894	0.0002
4.5	5.5	2241.1654	0.0012	4.5	5.5	2158.2476	-0.0061
5.5	6.5	2223.4074	0.0019	5.5	6.5	2140.9262	0.0006
6.5	7.5	2205.2646	0.0016			^{78}SeH X$^2\Pi_{3/2}$ 3-2	
7.5	8.5	2186.7438	-0.0012	3.5	2.5	2207.9407	-0.0011
8.5	9.5	2167.8829	0.0230	4.5	3.5	2220.5472	0.0013
		^{80}SeH X$^2\Pi_{3/2}$ 2-1		5.5	4.5	2232.6799	0.0004
2.5	1.5	2281.7388	0.0010	6.5	5.5	2244.3431	0.0073
3.5	2.5	2295.2432	-0.0013	7.5	6.5	2255.5072	-0.0012
4.5	3.5	2308.2857	-0.0026	8.5	7.5	2266.1916	0.0006
5.5	4.5	2320.8635	0.0018				
6.5	5.5	2332.9579	0.0007				

by J. Brault. The peak positions were determined by fitting a Voigt lineshape function to each spectral feature. The branches in the different subbands were sorted using a color Loomis–Wood program run on a PC computer.

The observed spectrum consists of three vibration–rotation bands including 1–0, 2–1, and 3–2 for the $X^2\Pi_{3/2}$ spin component and only the 1–0 band of the $X^2\Pi_{1/2}$ spin component. The intensity of higher vibrational bands decreases rapidly with increasing vibration and bands with $v \geq 4$ in the $X^2\Pi_{3/2}$ spin component and $v \geq 2$ in the $X^2\Pi_{1/2}$ spin component were

too weak to be observed. Because the $X^2\Pi_{1/2}$ spin component lies about 1760 cm^{-1} above the $X^2\Pi_{3/2}$ spin component, the lines of the $X^2\Pi_{1/2}$ spin component are much weaker in intensity than those in the $X^2\Pi_{3/2}$ spin component.

The SeH molecular lines were easily identified from their characteristic narrow linewidths and isotopic patterns. A part of the high-resolution spectrum of the R-branch region of the 1–0 band is provided in Fig. 1. Se has five major isotopes (^{76}Se (10%), ^{77}Se (9%), ^{78}Se (23%), ^{80}Se (50%) and ^{82}Se (10%)), of which ^{78}Se (23%) and ^{80}Se (50%) are the most abundant. The

	v	T_v	B_v	$10^4 \times D_v$	p_v[a]	$10^4 \times p_{Dv}$
^{80}SeH $X^2\Pi_{1/2}$	0	0.0[b]	7.8253261(818)	3.43384(731)	-1.14147(128)	2.730(101)
	1	2334.28643(95)	7.6001572(766)	3.40058(692)	-1.09852(132)	2.537(105)
^{80}SeH $X^2\Pi_{3/2}$	0	0.0	7.7517622(884)	3.26683(917)	--	--
	1	2331.61206(106)	7.5337384(651)	3.24405(556)	--	--
	2	4577.60803(145)	7.3157582(643)	3.22221(437)	--	--
	3	6737.52080(584)	7.097060(242)	3.1796(222)	--	--
^{78}SeH $X^2\Pi_{3/2}$	0	0.0	7.7541204(831)	3.27456(690)	--	--
	1	2331.97039(117)	7.5359099(705)	3.23854(510)	--	--
	2	4578.29784(262)	7.317899(239)	3.2146(405)	--	--
	3	6738.51920(527)	7.098737(304)	3.1343(353)	--	--

[a] Notice that the sign of p_v in the empirical fit is negative compared to the positive sign in the Hund's case (a), Table 4. This is because of the different definition of the Λ-doubling parameters.

[b] The T_0 values have been fixed to zero in the empirical fit.

lines of the ^{78}SeH and ^{80}SeH are expected to be observed with an approximate intensity ratio of 1:2 as can be clearly seen in our spectra (Fig. 1). Lines of the vibration–rotation bands of the $X^2\Pi_{3/2}$ spin component consist of single R and single P branches with no noticeable Λ-splitting. On the other hand, the lines in the 1–0 band of the $X^2\Pi_{1/2}$ spin component are observed to have a relatively large Λ-doubling starting from very low J values. The lines of the minor isotopomer ^{78}SeH are very weak in the 1–0 band of the $X^2\Pi_{1/2}$ spin component.

Rotational lines of both ^{78}SeH and ^{80}SeH isotopomers have been measured and used in the determination of molecular constants. For the major isotopomer ^{80}SeH, two kinds of fits were carried out. In the first fit, lines of the two spin components were fit separately with the a simple empirical energy level expression and, in the second fit, lines of both spin components were fit together as Hund's case (a) state. For the minor isotopomer ^{78}SeH, for which the lines in the $X^2\Pi_{1/2}$ spin component are very weak, only the empirical fit was obtained. The line positions for the ^{80}SeH and ^{78}SeH isotopomers are provided in Table 1 and the observed − calculated (O − C) values were obtained with the empirical constants for both ^{78}SeH and ^{80}SeH.

(a) Empirical Fits of ^{78}SeH and ^{80}SeH

In this fit the lines of the ^{78}SeH and ^{80}SeH isotopomer were fit to the following simple energy expression,

$$E(J) = T_v + B_v J(J+1) - D_v[J(J+1)]^2$$
$$\pm 1/2[p_v(J+1/2) + p_{Dv}(J+1/2)^3] \qquad [1]$$

for $^2\Pi_{1/2}$. The expression for $^2\Pi_{3/2}$ lacks the Λ-doubling terms containing p_v and p_{Dv}. The lines of both spin components were fit separately. For the ^{78}SeH isotopomer, the empirical constants were obtained only for the $X^2\Pi_{3/2}$ spin component because the minor isotopomer was too weak to be measured in the $X^2\Pi_{1/2}$ spin component. The empirical constants for the ^{80}SeH and ^{78}SeH are provided in Table 2. The empirical constants are helpful in quickly predicting the transition wavenumbers by simple calculations using Eq. [1]. Effective vibrational constants for the $^2\Pi_{3/2}$ spin component of ^{80}SeH are $\omega_e = 2416.7805(120)$ cm^{-1}, $\omega_e x_e = 42.45772(506)$ cm^{-1}, $\omega_e y_e = -0.07785(110)$ cm^{-1}.

(b) Case (a) Fit of the $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ Spin Components of ^{80}SeH

Initially, the rotational lines of both spin components of the 1–0 band of ^{80}SeH were fit using the effective N^2 Hamiltonian for a $^2\Pi$ state. In this fit, the spin–orbit parameter A_0 for the $v = 0$ vibrational level was fixed to the value obtained by Ashworth and Brown (*20*). Their $v = 0$ constants were determined using the same N^2 Hamiltonian (see below) that we used. An explicit listing of the matrix elements of this Hamiltonian is provided by Amiot *et al.* (*32*). Because we were

TABLE 3
Zero Field Line Positions of SeH

J'	F_1/F_2	J''	F_1/F_2	Predicted [a]	P-C [b]
1.5 f	F_2	1.5 e	F_2	0.00048	0
2.5 f	F_2	2.5 e	F_2	0.00192	0
1.5 e	F_1	1.5 e	F_2	1778.68610	12
1.5 f	F_1	1.5 f	F_2	1780.95556	-103
1.5 e	F_1	1.5 f	F_2	1778.68561	11
1.5 f	F_1	2.5 e	F_2	1742.21879	0

[a] These values have been predicted using the constants of Brown et al. (19).
[b] P − C are predicted minus calculated values in units of 10^{-5} cm^{-1}, using the constants of Table 4.

unable to resolve the Λ-doubling in the $^2\Pi_{3/2}$ spin component, we had problems fitting the high J transitions and the Λ-doubling constant q had a peculiar value. Unfortunately, the constants presented by Ashworth and Brown (20) were derived from the usual Hamiltonian modified to contain two vibrational perturbation terms in order to account for the interaction of $v = 1$ $^2\Pi_{3/2}$ with $v = 0$ $^2\Pi_{1/2}$. This interaction is very strong for SeD but is much smaller for SeH. The constants presented by Ashworth and Brown (20) are not compatible with our constants because they result from slightly different effective Hamiltonians. Even when we tried to use their constants to predict transitions to include in our fits, the results were not completely satisfactory.

The earlier constants of Brown et al. (19) are much more compatible with our data (no perturbation terms were included) and we used these constants to predict the zero field lines listed in Table 3. These lines were then added to our fit in order to determine the spin–orbit coupling constant A_0 and the lambda-doubling constant q_0. We also fitted the unsplit, but slightly broadened, higher J lines of the $^2\Pi_{3/2}$ spin component as two

lines holding the width fixed at about 0.024 cm^{-1}, as observed for the lower J transitions. This somewhat dubious deconvolution procedure improved our fits. In the end, the Hund's case (a) constants of Table 4 were obtained by fitting the lines of 1–0, 2–1, and 3–2 bands together. The constant q_D for $v = 0$ was not determined in the initial free fit, and therefore its value was held fixed at 9.9×10^{-7} cm^{-1}, a value used by Brown et al. (19). The constants, A_0, B_0, D_0, γ_0, q_0, p_0, p_{D0} for $v = 0$ and T_1, A_1, B_1, D_1, γ_1, q_1, p_1, and p_{D1} for $v = 1$ were varied in the final fit. The values of $A_0 = -1763.27345(798)$ cm^{-1} and $A_1 = -1766.74871(738)$ cm^{-1} were determined for the $v = 0$ and 1 vibrational levels. For the $v = 2$ and 3 vibrational levels, where rotational lines were observed only in the $X^2\Pi_{3/2}$ spin component, only the constants T_v, B_v, and D_v were varied and the rest of the constants were held fixed to the approximate values for the $v = 1$ vibrational level. The strong vibrational dependence of A implied by $A_0 = -1763.27345(798)$ cm^{-1} and $A_1 = -1766.74871(738)$ cm^{-1} is caused by the interaction between the spin components. Without a complete deperturbation, "true" values of A_v cannot be derived. In the final fit, approximate weights for the individual rotational lines were chosen on the basis of signal-to-noise ratio and freedom from blending.

It is interesting to compare the case (a) constants obtained in this work to the values available previously. The present constants for $v = 0$ vibrational level are slightly different than the constants of Ashworth and Brown (20) because our data set includes higher J lines. In addition, Ashworth and Brown (20) included two perturbation terms to account for the interaction between $v = 1$ $^2\Pi_{3/2}$ with $v = 0$ $^2\Pi_{1/2}$, but the SeH data can be fitted without them. Our $v = 0$ constants of $B_0 = 7.7892244(836)$ cm^{-1}, $D_0 = 3.37581(830) \times 10^{-4}$ cm^{-1}, $\gamma_0 = -0.75022(769)$ cm^{-1}, $q_0 = -0.0059451(240)$ cm^{-1}, $p_0 = 1.148479(271)$ cm^{-1}, and $p_{D0} = -1.634(115) \times$

TABLE 4
Hund's Case (a) Constants (in cm^{-1}) for the $X^2\Pi$ State of ^{80}SeH

constants [a]	$v = 0$	$v = 1$	$v = 2$	$v = 3$
T_v	0.00	2333.18547(224)	4579.03121(428)	6738.7790(114)
A_v	-1763.27345(798)	-1766.74871(738)	-1766.7745 [b]	-1766.7745 [b]
B_v	7.7892244(836)	7.5675360(688)	7.3476333(782)	7.127191(462)
$10^4 \times D_v$	3.37581(830)	3.33426(605)	3.30125(549)	3.2514(434)
γ_v	-0.75022(769)	-0.39072(703)	-0.3907 [b]	-0.3907 [b]
$10^3 \times q_v$	-5.9451(240)	-5.421(208)	-5.3724 [b]	-5.3724 [b]
p_v	1.148479(271)	1.104648(704)	1.1046 [b]	1.1046 [b]
$10^4 \times p_{Dv}$	-1.634(115)	-1.545(111)	-1.5486 [b]	-1.5486 [b]

[a] Numbers in parentheses are one standard deviation in units of the last digit.

[b] Constrained to the approximate values for v = 1 (see text for details).

TABLE 5
Equilibrium Constants (in cm^{-1}) for the $X^2\Pi$ State of ^{80}SeH

ω_e	2421.7153(234)	B_e	7.899187(696)	$10^4 \times D_e$	3.39210(391)
$\omega_e x_e$	44.6012(110)	α_e	0.220749(399)	$10^7 \times \beta_e$	-0.03687(204)
$\omega_e y_e$	0.20697(236)	$r_e(\text{Å})$	1.464319(64)	--	--

[a] Values in parentheses are one standard deviation in the last digits.

10^{-4} cm^{-1} can be compared with the constants of $B_0 = 7.7893423(85)$ cm^{-1}, $D_0 = 3.3503(14) \times 10^{-4}$ cm^{-1}, $\gamma_0 = -0.8271(15)$ cm^{-1}, $q_0 = -0.005934(25)$ cm^{-1}, $p_0 = 1.14755(11)$ cm^{-1}, and $p_{D0} = -9.70 \times 10^{-5}$ cm^{-1} obtained by Ashworth and Brown (*20*). Our constants are much more accurate than the constants obtained by Donovan *et al.* (*15*) and Bollmark *et al.* (*16, 17*) from their studies of UV and vacuum UV transitions.

Prior to the present work, no high-resolution data were available for vibrational levels with $v > 0$ for SeH. Although the UV region has spectra for several transitions involving the ground state, bands with $v'' > 0$ could not be identified because all of the excited states were predissociated and the spectra were recorded in absorption. The constants for the $v'' = 0$ vibrational level obtained from these studies were not very reliable because the rotational lines were broad. The recent far- and mid-infrared studies of the ground state has provided much improved constants for the $v = 0$ vibrational level of the $X^2\Pi$ state, but data for vibrational levels with $v'' > 0$ vibrational level were still lacking. In fact, the best vibrational constants for SeH were those calculated from SeD using isotope relations. The observation of bands with vibrational levels up to 3 has provided spectroscopic constants for the $v'' = 1, 2,$ and 3 vibrational levels for the first time.

The Hund's case (a) constants of Table 4 have been used to determine the equilibrium molecular constants for the ground state of ^{80}SeH, which are provided in Table 5. The ground state term values of $T_1 = 2333.18547(224)$ cm^{-1}, $T_2 = 4579.03121(428)$ cm^{-1}, and $T_3 = 6738.7790(114)$ cm^{-1} have been obtained with T_0 held fixed to zero. These vibrational intervals provide the vibrational constants of $\omega_e = 2421.7153(234)$ cm^{-1}, $\omega_e x_e = 44.6012(110)$ cm^{-1}, and $\omega_e y_e = 0.20697(236)$ cm^{-1} for ^{80}SeH from an exact fit. The rotational constants for the individual vibrational levels provide the equilibrium constants of $B_e = 7.899187(696)$ cm^{-1} and $\alpha_e = 0.220749(399)$ cm^{-1}. The equilibrium rotational constant results in the ground state equilibrium bond length of 1.464319(64) Å, which can be compared with the equilibrium bond length of 1.4640708(20) Å for the ground state of ^{80}SeD (*23*). Note that the interaction between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin components compromises the mechanical reliability of r_e and particularly the vibrational constants.

CONCLUSION

The infrared vibration–rotation spectra of 1–0, 2–1, and 3–2 bands of $X^2\Pi_{3/2}$ spin component and 1–0 band of $X^2\Pi_{1/2}$ spin component has been observed at high resolution using a Fourier transform spectrometer. SeH was made in a microwave discharge lamp from the reaction of Se with H_2. The analysis of observed bands provides an improved set of molecular constants for the ground state of SeH. This work provides the first independent determination of the equilibrium vibrational constants for the SeH molecule.

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