The Ground State Rotational Constants of H_3SiD

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The J-dependent rotational constants up to sextic coefficients of $H_3{}^{28}SiD$ were determined by a fit ($\sigma = 3.5 \times 10^{-4}$ cm^{-1}) of 1505 ground state combination differences formed from transitions of the ν_3, ν_5, and ν_6 vibrational fundamentals which were measured with a resolution of 0.005 cm^{-1}. The K-dependent constants A_0 and D_K^0 were obtained from perturbation-allowed transitions observed within ν_6.

The ground state constants of the prolate symmetric top $H_3{}^{28}SiD$ have been determined from rovibrational transitions in the ν_1/ν_4 region near 2200 cm^{-1}, measured with a grating instrument with a resolution of 0.030 and an accuracy of ca. 0.004 cm^{-1}[1]. B_0, D_J^0 and D_{JK}^0 were determined by means of 417 ground state combination differences which were fitted with a standard deviation of 3.9×10^{-3} cm^{-1}, while the quantity $(A_0 - B_0 - 5\,D_K^0)$ was deduced from perturbation-allowed transitions [2]. Combination of these and allowed transitions provided combination differences between the $K = 1$ and $K = 2$ ground state levels. Since A_0 and D_K^0 could not be separated from these differences, D_K^0 was constrained to the value listed in Table 1.

In context with the rovibrational analysis of the $\nu_3/\nu_5/\nu_6$ bands spanning the 660 to 1070 cm^{-1} region, we have recorded high resolution spectra with the FT spectrometer at the University of Oulu. The resolution was 0.0045 cm^{-1}, which combines with the Doppler width (2×10^{-3} cm^{-1} at 1000 cm^{-1}) and the pressure broadening at 2.7 mbar to yield an experimental fwmh of ~ 0.005 cm^{-1}. Calibration was with CO_2 lines [3]; wavenumber accuracy $< 1 \times 10^{-4}$ cm^{-1}. About 3000 transitions belonging to ν_3 (912.9 cm^{-1}), ν_5 (951.4 cm^{-1}) and ν_6 (784.3 cm^{-1}) were assigned. A total of 1505 ground state combination differences were formed from pairs of normally allowed, unit-weighted lines with $\Delta J = +1$ and 0, $+1$ and -1 and 0 and -1 respectively, all reaching the same upper state. Lines which were either too broad or too strong and obviously composites of several components were not used in the refinement. Of these pairs, 292, 527 and 686 belonged to ν_3, ν_5 and ν_6 respectively with J_{max} and $K_{max} = 21$ and 16 respectively. The combination differences were fitted to yield the coefficients in the J-dependent terms of the rotational term value expression (1):

$$\begin{aligned} E_0(J,K) = {} & (A_0 - B_0)\,K^2 + B_0\,J(J+1) \\ & - D_J^0\,J^2(J+1)^2 - D_{JK}^0\,J(J+1)\,K^2 \\ & - D_K^0\,K^4 + H_J^0\,J^3(J+1)^3 \\ & + H_{JK}^0\,J^2(J+1)^2\,K^2 \\ & + H_{KJ}^0\,J(J+1)\,K^4 + H_K^0\,K^6 . \end{aligned} \qquad (1)$$

The results are listed in Table 1. It is obvious that the J-dependent sextic coefficients are required to

Table 1. Ground state constants of $H_3{}^{28}SiD$ (cm^{-1}).

	Ref. [1, 2]	This study	
A_0	2.863 34(45)	2.863 424(40)	
$D_K^0 \times 10^5$	−3.85[a]	−3.82(29)	
B_0	2.099 477(11)	2.099 483 7(19)	2.099 568 7(11)
$D_J^0 \times 10^5$	1.564 4(20)	1.564 5(3)	1.591 7(4)
$D_{JK}^0 \times 10^5$	5.237(9)	5.246 2(15)	5.379 5(19)
$H_J^0 \times 10^{10}$	–	–	2.10(5)
$H_{JK}^0 \times 10^9$	–	–	2.89(3)
$H_{KJ}^0 \times 10^9$	–	–	−1.45(7)
No. of differences	417	1505	1505
$\sigma \times 10^3$	3.9	1.08	0.35

[a] D_K^e from harmonic force field.

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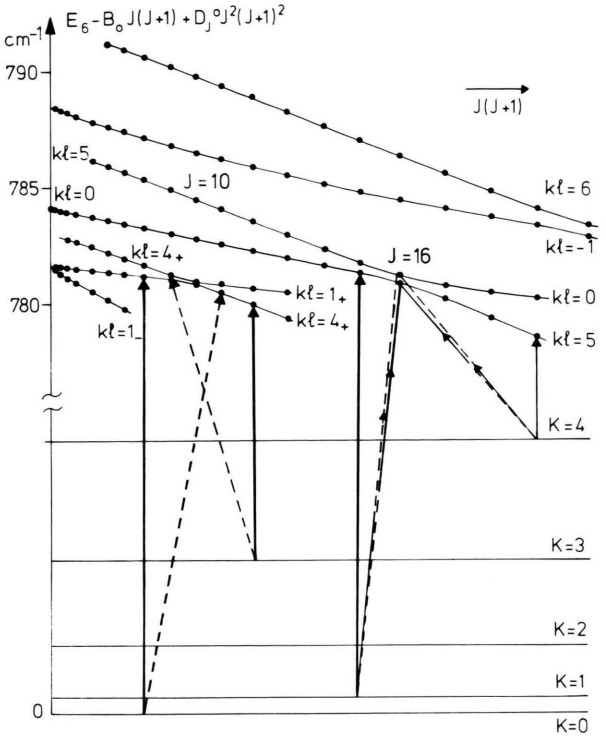

Fig. 1. Reduced upper state and schematic ground state energies of $H_3{}^{28}SiD$. Normally allowed transitions are marked by full lines, perturbation-allowed transitions (only schematically) by broken lines. Note that for the transitions reaching the $J'=16$ doublet normally and perturbation-allowed transitions cannot be distinguished.

reproduce the experimental data to an accuracy corresponding to that of the measurement.

After the J-dependent coefficients had been calculated, the K-dependent constants A_0 and D_K^0 were determined in an independent second step. The $kl>0$ and $kl<0$ subsystems of ν_6 undergo $\Delta l=\pm 2$, $\Delta k=\pm 2$ and $\Delta l=\pm 2$, $\Delta k=\mp 1$ interactions. These provoke level crossings of (kl), $kl<0$ and $(kl)+5$, $kl>0$ levels at $J=10$, 16 and 20 for $|k-l|=0, 1$ and 2, respectively. Close to these crossings, $\Delta l=\pm 2$, $\Delta k=\pm 5$ interactions which are allowed by the Amat rule lead to perturbation-allowed transitions with $\Delta k=-2$ and $\Delta k=\pm 4$. These were observed near to the level crossings at $J'=10$ and 16 respectively while the respective transitions near to the crossing at $J'=20$ were too weak to be measured.

Of the (split) $kl=4$ (A_1A_2) level, only the A_+ component interacts with the attached A_+ component of the $kl=1$ sublevel. The $J=16$, ($k=0$, $l=-1$) and ($k=5$, $l=+1$) states are so close that the normally allowed $\Delta k=\pm 1$ and perturbation-allowed $\Delta k=-2$ and $\Delta k=+4$ transitions occur with apparently equal intensity as a doublet with a splitting of 0.2484(7) cm^{-1}.

Reduced upper state energies of relevant sublevels and transitions are illustrated in Figure 1. The observed perturbation-allowed transitions and representative, normally-allowed transitions which were employed to form $\Delta K''=3$ ground state combination differences are listed in Table 2. From these differences, the relations $9(A_0-9D_K^0)$ and $15(A_0-17D_K^0)$ were obtained by means of the coefficients of the J-dependent terms, and these allowed A_0 and D_K^0 to be determined. The present ground state constants, if calculated to the same order, agree with the previously reported data [1, 2] to

Table 2. Perturbation-allowed and attached normally allowed transitions of ν_6 of $H_3{}^{28}SiD$ [cm^{-1}].

Perturbation-allowed transitions J'; kl J''; K''					Normally allowed transitions J'; kl J''; K''				
8;	4_+	7;	0	815.32363	8;	4_+	8;	3	774.92014
8;	4_+	8;	0	781.76313					
10;	1_+	9;	3	816.10701	10;	1_+	10;	0	781.01351
10;	1_+	10;	3	774.18862					
10;	1_+	11;	3	728.09326					
11;	1_+	10;	3	820.10952	11;	1_+	11;	0	780.82870
11;	1_+	11;	3	774.01400					
11;	1_+	12;	3	723.74557					
17;	5	16;	1	850.62304	17;	5	17;	4	768.32704
17;	5	17;	1	779.55049					
17;	5	18;	1	704.33681					
18;	5	17;	1	853.92185	18;	5	18;	4	767.51311
18;	5	18;	1	778.71033					
18;	5	19;	1	699.36346					

Transitions J';	kl	J'';	K''		Upper state energies
16;	5/0	15;	4	836.16447/ 835.91607	1351.21211/ 1350.96371
16;	5/0	16;	4	769.26436/ 769.01607	1351.21193/ 1350.96364
16;	5/0	17;	4	698.21837/ 697.97044	1351.21189/ 1350.96396
16;	5/0	15;	1	847.44121/ 847.19347	1351.21208/ 1350.96426
16;	5/0	16;	1	780.51419[a]/ 780.26855	1351.21011/ 1350.96439
16;	5/0	17;	1	709.44508[a]/ 709.19562	1351.21355/ 1350.96401

[a] Weakly blended.

within three of their standard deviations. Due to the correlation with the H's, B_0 and the D's change when allowance is made in the fit for sextic coefficients.

In conclusion, due to the accuracy of the measurements, which has been improved by at least an order of magnitude, and the larger number of combination differences determined, the precision of the ground state constants has been enhanced in the present study by one order of magnitude. The sextic constants and D_K^0 have been determined experimentally for the first time. Finally, no indication for ground state perturbations was found.

Acknowledgements

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