Diode Laser Spectrum of the ν_8 Band of CH_3SH

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Synopsis. The Stark effect was used to assign four series of the transitions in the heavily perturbed spectrum of methanethiol in the 14 μm region: K=0 and two K=1 series of A torsional symmetry and K=0 series of E symmetry. Effective parameters were determined for each series. The K=0 levels of A symmetry in the ν_8 state were found to be perturbed by a Fermi-type resonance.

Studies on the torsion-rotation energy levels in the excited states of the vibrations other than the torsion provide detailed information on hindered internal rotation. Most of the studies reported so far[1-4] are on methanol in the 9—10 μm region. In the present work, the torsion-rotation levels in the first excited ν_8 state of methanethiol (C-S stretching, 710 cm^{-1})[5] are studied.

The diode laser spectrometer described previously[6] was used in the present work. The frequency-modulated laser beam was passed through a cell of 55 cm in length equipped with parallel Stark plates separated by about 3 mm. A commercially available sample of methanethiol was used without further purification. The sample pressure was in the region of 0.3—2 Torr (1 Torr=133.322 Pa). About one thousand absorption lines were observed with four laser diodes in the range of 703.3—718.2 cm^{-1}. The absorption line frequencies were measured by interpolating the CO_2 ν_2 band lines[7,8] using etalon fringes. The absolute accuracy in the frequencies is estimated to be better than 0.003 cm^{-1} for unoverlapped lines.

At a medium resolution, the ν_8 band looked like a parallel band of a symmetric top, but once the P- and R-branches were resolved at a high resolution, their structures were much more complicated than those expected for a parallel band. Several series of lines were found in the complicated structures with the help of a Loomis-Wood diagram. Each of the series is composed of transitions with different J, the total angular momentum quantum number, and with the same quantum numbers, n, σ, and K,[9] where n is the torsional quantum number, σ specifies the torsional symmetry (σ=0 for A- and 1 for E-species), and K is the quantum number of the component of the total angular momentum along the internal rotation axis.[10] It was found, however, impossible to explain the spectrum on the basis of the conventional internal axis method (IAM)[10,11] by choosing appropriate torsional and rotational parameters for the excited vibrational state, because the ν_8 state was seriously perturbed by the torsionally excited states in the ground vibrational state. Accordingly, no assignment could readily be made for any of the series without further information, except that a pair of the $A(\sigma=0)$, K=1 series were identified unambiguously by their characteristic K-doubling pattern. The pair series are listed in the latter half of Table 1.

The Stark effect of the spectral lines provided another clue. The observed Stark-modulated spectrum was congested with Stark components and was very complicated. In contrast, a source-modulated spectrum with a DC field was found to be much simpler and readily gave a rough estimate of the magnitude of the Stark effect of each line. As the DC field was increased, most of the absorption lines were broadened and their peak intensities were decreased. Only the lines with a small Stark effect were left relatively unaffected in the spectrum even by a field as strong as 670 V/cm. An example is shown in Fig. 1. Since the transitions involving the K=0 levels do not show the first-order effect, they must be assigned to

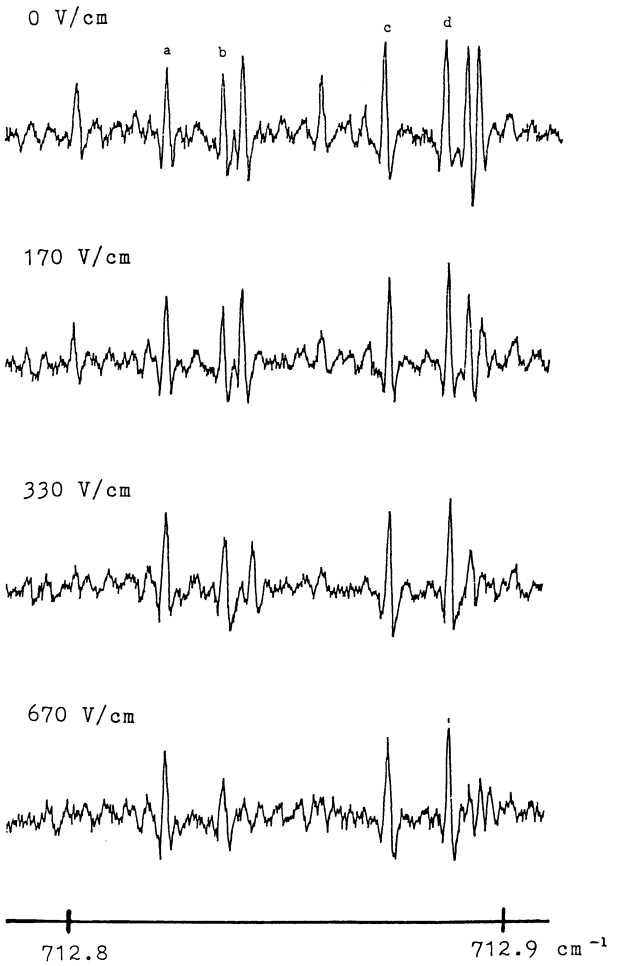

Fig. 1. Source modulated spectra of the CH_3SH ν_8 R(2) transitions with various DC Stark fields applied. At the Stark field of 670 V/cm, four lines, a—d, with relatively small Stark effect remain. a) 712.821, A, K=1, b) 712.835, unassigned, c) 712.874, A, K=1, d) 712.887 cm^{-1}, E, K=0.

Table 1. Assigned ν_8 Band Transitions and Fitting of the ν_8 Energy Levels of CH_3SH[a)]

Transition		Energy level[c)]			
	Obsd[b)]		Obsd[b,d)]	Calcd[e)]	(O-C)×10³
$A(\sigma=0)$, $K=0$ Series					
P (8)	703.957 (1)	7_{07}	734.309 (2) *	734.310	−1
P (7)	704.843 (3)	6_{06}	728.454 (3) *	728.454	0
P (6)	705.724 (3)	5_{05}	723.434 (3) *	723.435	−1
P (5)	706.600 (2)	4_{04}	719.251 (2)	719.251	0
P (4)	707.469 (3)	3_{03}	715.904 (3)	715.903	1
P (3)	708.331 (2)	2_{02}	713.392 (2)	713.392	0
R (3)	714.187 (5)	4_{04}	719.248 (5)	719.251	−3
R (4)	715.001 (3)	5_{05}	723.436 (3)	723.435	1
R (6)	716.602 (4)	7_{07}	734.312 (4) *	734.310	2
Obtained parameters[f)]					
$w_{A0}=710.8809\,(12)$, $b_{A0}=0.41857\,(10)$, $d_{A0}=3.5\,(15)\times10^{-6}$					
$E(\sigma=1)$, $K=0$ Series					
P (8)	703.476 (3)	7_0	733.828 (3)	733.825	3
P (7)	704.358 (2)	6_0	727.968 (2)	727.970	−2
P (6)	705.239 (2)	5_0	722.949 (2)	722.950	−1
P (5)	706.114 (2)	4_0	718.765 (2)	718.765	0
P (4)	706.981 (3)	3_0	715.416 (3)	715.417	−1
P (3)	707.846 (4)	2_0	712.907 (4)	712.906	1
P (2)	708.702 (5)	1_0	711.233 (5)	711.232	1
R (2)	712.887 (3)	3_0	715.418 (3)	715.417	1
R (3)	713.705 (3)	4_0	718.766 (3)	718.765	1
R (4)	714.518 (5)	5_0	722.953 (5)	722.950	3
R (5)	715.320 (3)	6_0	727.971 (3)	727.970	1
R (6)	716.117 (3)	7_0	733.827 (3)	733.825	2
R (7)	716.905 (3)	8_0	740.515 (3)	740.515	0
R (8)	717.687 (2)	9_0	748.039 (2)	748.039	0
Obtained parameters[f)]					
$w_{E0}=710.3943\,(12)$, $b_{E0}=0.41863\,(6)$, $d_{E0}=4.0\,(6)\times10^{-6}$					
$A(\sigma=0)$, $K=1$ Series					
P (8)	703.500 (1)	7_{17}	737.076 (3) *	737.078	−2
P (7)	704.377 (2)	6_{16}	731.277 (3) *	731.280	−3
P (6)	705.250 (2)	5_{15}	726.308 (2) *	726.310	−2
P (5)	706.117 (3)	4_{14}	722.166 (3) *	722.167	−1
P (4)	706.978 (2)	3_{13}	718.854 (2)	718.854	0
P (3)	707.831 (3)	2_{12}	716.367 (3)	716.368	−1
P (2)	708.680 (4)	1_{11}	714.712 (4)	714.711	1
R (2)	712.821 (2)	3_{13}	718.853 (2)	718.854	−1
R (3)	713.632 (1)	4_{14}	722.168 (1)	722.167	1
R (4)	714.435 (2)	5_{15}	726.311 (2)	726.310	1
R (5)	715.231 (2)	6_{16}	731.280 (2) *	731.280	0
R (6)	716.022 (3)	7_{17}	737.080 (3) *	737.078	2
R (7)	716.804 (3)	8_{18}	743.704 (3) *	743.704	0
Obtained parameters[f)]					
$w_{A1}=713.8828\,(13)$, $b_{A1L}=0.41426\,(8)$, $d_{A1L}=1.1\,(11)\times10^{-6}$					
$A(\sigma=0)$, $K=1$ Series					
P (8)	703.358 (1)	7_{16}	737.562 (2) *	737.562	0
P (7)	704.254 (1)	6_{15}	731.642 (1) *	731.642	0
P (5)	706.029 (2)	4_{13}	722.340 (2) *	722.340	0
P (4)	706.907 (2)	3_{12}	718.957 (2)	718.957	0
P (3)	707.778 (3)	2_{11}	716.419 (3)	716.420	−1
P (2)	708.644 (4)	1_{10}	714.728 (4)	714.728	0
R (2)	712.874 (3)	3_{12}	718.958 (3)	718.957	1
R (3)	713.700 (3)	4_{13}	722.341 (3)	722.340	1
R (4)	714.518 (5)	5_{14}	726.568 (5)	726.569	−1

Table 1. (Continued)

Transition		Energy level[c]			
	Obsd[b]		Obsd[b,d]	Calcd[e]	(O-C)×10³
R (5)	715.333 (4)	6_{15}	731.644 (4)*	731.642	2
R (6)	716.140 (4)	7_{16}	737.564 (4)*	737.562	2
R (7)	716.938 (5)	8_{17}	744.326 (5)*	744.326	0
R (8)	717.730 (2)	9_{18}	751.934 (3)*	751.934	0
Obtained parameters[f]					
$w_{A1}=713.8822\,(6)$, $b_{A1U}=0.42292\,(3)$, $d_{A1U}=1.3\,(4)\times10^{-6}$					

a) All values in cm^{-1}. b) Values in parentheses are estimated errors in units of $10^{-3}\,cm^{-1}$. c) Energy level notation for A species follows that for asymmetric rotors, $J_{Ka,\,Kc}$. d) Energy is given relative to the $J=K=0$ level of each species in the ground state. The energies without an asterisk are obtained from the observed infrared frequencies in the left column and the observed microwave frequencies.[12,13] For the asterisked levels, the ground state energy levels were calculated from the constants[12] and their estimated errors include the uncertainties in the calculation. e) Calculated by Eq. 1 from the parameters given below. f) Parameters in Eq. 1 determined by weighted least-squares. The numbers in parentheses are standard errors in units of the last digit of the parameter.

some of these lines least affected by Stark effects. Two series involving the $K=0$ levels were thus identified. The one at higher-frequency was assigned to the A-species and the other one at lower frequency to the E-species, as shown in the former half of Table 1, on the basis of the following consideration. In the Loomis-Wood diagram, the lower series is in a cluster of several series, whereas the higher one is separated from the cluster by about $0.5\,cm^{-1}$. The shift can be explained by a resonance of the $n=0$, A, $K=0$ stack of the ν_8 state with the $n=4$, A, $K=0$ stack in the ground vibrational state, which is located at about $40\,cm^{-1}$ below the former stack. On the other hand, there are no nearby perturbing levels around the ν_8, $n=0$, E, $K=0$ stack.

The assigned transitions are combined with the ground state torsion-rotation energy levels[12,13] to give the vibration-torsion-rotation levels in the ν_8 state. The levels in the ν_8 state are fitted to

$$E(\sigma,\,J,\,K) = w_{\sigma K} + b_{\sigma K}J(J+1) - d_{\sigma K}\{J(J+1)\}^2, \quad (1)$$

by the weighted least-squares method; the results are shwon in Table 1. The fact that the values of b_{A0} and d_{A0} are close to those of b_{E0} and d_{E0} suggests that the resonance is of the Fermi type. The further analysis requires information on the perturbing $n=3$ and 4 levels in the ground vibrational state.

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9) As long as the levels with $n=0$ are discussed, the quantum number n is often dropped in the present note. Only the $\Delta K=0$ selection rule is considered because methanethiol is a near-symmetric top molecule and the ν_8 band is nearly a parallel band. The quantum number σ is the same as μ in Ref. 10.
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