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Vibrational Overtone Spectroscopy of Cycloheptatriene-d_6 at the Third and Fourth Overtone Regions

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In a previous report[1] the vibrational overtone spectrum of gaseous cycloheptatriene (CHT) was presented. The main absorption features at the third and fourth overtones were assigned to the CH olefinic oscillators of CHT using a direct correlation method. Assignments were also suggested for the methylenic CH absorptions; however, further confirmation of these spectral assignments was required. In CHT-d_6 the CH olefinic transitions are eliminated, and only features due to the methylenic group of the CHT ring will remain in the spectrum.

The CHT-d_6 was synthesized by refluxing 12 mL of C_6D_6 (99.6 atom % d, Aldrich) in the presence of CuBr for 3.5 h with dropwise addition of 40 mL of diazomethane (CH_2N_2) solution in C_6D_6 as was described by Muler et al.[2] The diazomethane solution was generated from nitrosomethylurea according to the procedure proposed by Arndt.[3] Nitrosomethylurea was prepared from acetamide and bromine as was recommended by Amstutz and Myers.[4] The resulting reaction mixture contained about 2.4% CHT-d_6 dissolved in the deuterated benzene. The ^{1}H NMR of the mixture displayed the single broad peak around 2.1 ppm corresponding to the CH_2 group of the CHT-d_6. The amount of solvent was reduced using rotatory evaporation to bring the CHT-d_6 content to 43%. Then the CHT-d_6 sample (91%) was collected using preparative gas chromatography.

The third and fourth overtone spectra of CHT-d_6 were obtained using the photoacoustic spectrometer described previously.[1] The sample pressure was 14 Torr, and 300 Torr of argon was added to increase the photoacoustic signal.

The spectra of CHT-d_6 and CHT at the third and fourth overtone regions are shown in Figures 1 and 2, respectively. Peak positions and vibrational assignments are tabulated in Table 1. At the third overtone the absence of the olefinic CH bond stretch absorptions in the CHT-d_6 spectrum around 11 300−11 400 cm^{-1} leaves only two well-resolved peaks associated with the methylenic CH bonds of the CHT-d_6 ring (Figure 1). Based on the general pattern reported for the CH methylenic bond in cyclic hydrocarbons[5] ($r\mathrm{CH}_{ax} > r\mathrm{CH}_{eq}$) and ab initio geometry optimization for CHT,[1] the lower energy peak at 11 096 cm^{-1} can be assigned to the CH_{ax} of CHT-d_6, while the higher energy transition, located at 11 215 cm^{-1}, belongs to the CH_{eq}. Similar arguments can be made for the two peaks recorded in the next overtone region (Figure 2), where the CH_{ax} peak appeared at 13 643 cm^{-1} and the CH_{eq} transition appeared at 13 785 cm^{-1}. Thus, the spectral results for CHT-d_6 confirmed the assignments suggested for the CHT third and fourth overtone methylenic peaks.

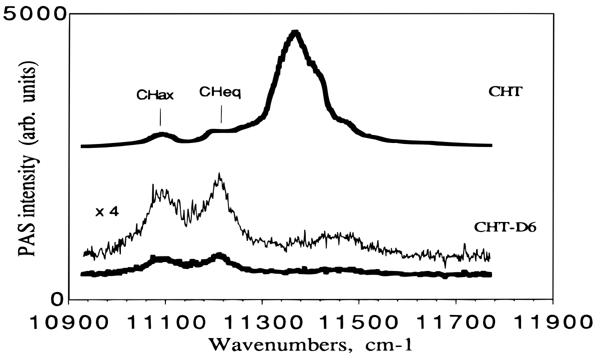

Figure 1. Vibrational spectra of CHT (upper line) and CHT-d_6 (lower lines) at the third overtone region. Spectra were recorded for gaseous samples at room temperature.

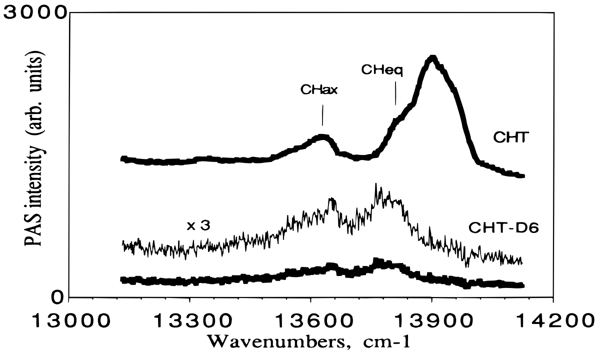

Figure 2. Vibrational spectra of CHT (upper line) and CHT-d_6 (lower lines) at the fourth overtone region. Spectra were recorded for gaseous samples at room temperature.

TABLE 1: Peak Positions (in cm^{-1}) and Vibrational Assignments for CHT and CHT-d_6 Molecules

quantum no. (v)	CHT	CHT-d_6	assign
4	11 094	11 096	4v CH^{ax}
	11 216	11 215	4v CH^{eq}
	11 313		combination
	11 366		4v $\mathrm{CH}^{ol}_{2,3,4,5}$
	11 437		4v $\mathrm{CH}^{ol}_{1,6}$
5	13 622	13 643	5v CH^{ax}
	13 864	13 785	5v CH^{eq}
	13 915		4v $\mathrm{CH}^{ol}_{2,3,4,5}$
	13 981		4v $\mathrm{CH}^{ol}_{1,6}$

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References and Notes

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