

Temperature Effect on the CH Stretching Spectrum of Gaseous -3H_1 Monohydrogenated Cyclopentene

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The CH stretching infrared spectra of the gaseous -3H_1 monohydrogenated cyclopentene have been recorded at room temperature (300 K) and low temperature (192 K) and compared. The “hot band” character of the central feature of the spectral triplet structure is pointed out and well reproduced by the theoretical model which takes into account the effect of the coupling between the CH stretching vibration and the ring-puckering internal motion.

Introduction

Cyclopentene is certainly one of the most thoroughly studied pseudo-four-membered-ring molecules.^{1–6} Different theoretical and experimental investigations have established a double minimum puckering potential function: $V(x) = V_2 x^2 + V_4 x^4$, x being the ring-puckering coordinate with a barrier to planarity of some 230 cm^{-1} .

A vibrational contribution to this potential barrier has been pointed out in some theoretical works^{7–9} and also in spectroscopic studies of several gaseous monodeuterated or monohydrogenated cyclopentenones.^{9–13} Indeed, the isotopic monosubstitution in the allylic position in cyclopentene induces an asymmetry not only in the kinetic energy function, but also in the potential energy function. This leads to an asymmetrical ring-puckering potential energy function of the gaseous monohydrogenated 1,2,3,4,4,5,5 d_7 -cyclopentene (-3H_1) $V(x) = V_2 x^2 + V_3 x^3 + V_4 x^4$. This asymmetry is shown to result primarily from the difference in the zero-point vibrational energies of the two isotopomers when the CH bond is in the axial position or in the equatorial position. In the excited vibrational states, the potential asymmetry of the effective ring-puckering potential increases with increasing energy.

Further theoretical and spectroscopic studies of cyclopentene and of several selectively deuterated derivatives have thoroughly analyzed the coupling between the ring-puckering motion and the higher energy vibrations, in particular the CH stretching ones and their overtones.^{14–16} These works have shown that the CH stretching fundamental and overtone spectra can be correctly reproduced with a model which takes into account, in the adiabatic approximation, the coupling between the puckering motion and the other vibrations and considers the rapid intramolecular vibrational redistribution between the CH stretching and the HCH and CCH bendings through Fermi resonance couplings. It has also been shown that a V_1 term is to be introduced in the polynomial form of the potential to a better reproduction of the spectra.^{9,14–16}

The analysis of the temperature dependence of the $\nu(\text{CH})$ spectrum is a new additional contribution to this study in the gas phase. The decrease of temperature yields a simplification in the spectrum by removing the bands issued from the excited

puckering levels or at least reducing their intensity. This allows the refinement of the potential parameter values and the confirmation of the hot band character of the central feature of the spectrum. It can be considered as a test of the quality of our model.

Experimental Section

The monohydrogenated 1,2,3,4,4,5,5 d_7 -cyclopentene (-3H_1) has been synthesized by organotin route according to the procedure described previously with an isotopic purity higher than 96%.^{9–16}

The room-temperature spectrum was recorded on a BRUKER 113V FTIR spectrometer with a resolution of 0.5 cm^{-1} . The gas cell with a path length of 10 cm was equipped with CaF_2 windows and the gaseous sample conditioned at room temperature with a pressure of 120 Torr.

The low-temperature spectrum was recorded on a BRUKER 120 FTIR spectrometer with a resolution of 0.1 cm^{-1} . The gaseous sample was conditioned in a White-type gas cell with a 36m path length equipped with (CaF_2) windows at a temperature of 192 K with a pressure of 0.1 Torr. The temperature was continuously monitored during the recording of the spectrum and its stability was better to 2 K.

Theoretical Recall. The theoretical approach used to analyze the $\nu(\text{CH})$ profile has been extensively described in the previous papers.^{9–16} The basic idea of this theory is to suppose that two main types of couplings perturb the CH stretching vibrations of cyclopentene: the coupling with the puckering motion and the vibrational couplings between one CH stretching mode and the deformation modes. The ring-puckering motion being slower than the other considered motions, the total Hamiltonian can be solved in the adiabatic approximation and is the sum of two vibrational Hamiltonians

$$H_{\text{T}}(x, q) = H_{\text{v-r}}(x, q) + H_{\text{r}}(x) \quad (1)$$

$H_{\text{r}}(x)$ describing the ring-puckering motion can be written

$$-\frac{\hbar^2}{2} \left(\frac{\partial}{\partial x} \right) g(x) \left(\frac{\partial}{\partial x} \right) \Psi_n(x) + V_{\text{eff}}^{\nu}(x) \Psi_n(x) = E_n^{\nu} \Psi_n(x) \quad (2)$$

where x is the ring-puckering coordinate, $g(x)$ the inverse of

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the reduced mass of the motion, V_{eff}^{ν} the ring-puckering effective potential in the ν vibrational state. In the ground vibrational state, V_{eff}^0 is the sum of the ring-puckering potential and of the zero-point vibrational energy.^{9–16} In the ν excited CH stretching state, it is increased by the CH stretching vibrational energy variation. This energy variation is obtained by the resolution of the vibrational Schrödinger equation. The vibrational Hamiltonian $H_{\nu-r}(x,q)$, analogous to that extensively described in the previous papers,^{14–16} is written in curvilinear coordinates, which allows to use the same set of potential parameters for the different isotopic derivatives. The kinetic matrix is computed by a Taylor series expansion up to the third order. The potential matrix is developed in the same way. Owing to the size of the here considered molecule, only the most relevant internal coordinates are retained for the calculation, that is to say the CH (or CD) bond stretching, the HCH (or HCD) bending and HCC (or DCC) angle deformations. The anharmonic couplings governing the Fermi resonances are non zero only between the coordinates belonging to the same methylene group.^{14–16}

The reconstruction of the vibrational spectrum is achieved in two steps. First, the diagonalization of the vibrational Schrödinger equation is completed for different values of the ring-puckering coordinate x (between -0.3 and 0.3 Å by step of 0.01 Å) on basis functions that are the product of the seven wave functions of all the possible combinations of the seven coordinate vibrations corresponding to a given overtone. The so calculated vibrational energy variation $V_{\text{eff}}^{\nu}(x)$ is then introduced in the Schrödinger eq 2, which is diagonalized on a basis set of 80 harmonic oscillators. This gives the energy E_n^{ν} and the wave function $\Psi_n(x)$ corresponding to the state $|\nu, n\rangle$. In the present paper, we only consider the ground vibrational state and the first excited CH stretching state, thus $\nu = 0$ and 1. The fundamental CH stretching spectrum is the sum of all the transitions between the ring-puckering states in the ground vibrational state $|0, n\rangle$ and the $|1, n\rangle$ states in the first excited stretching state. The intensity of these transitions are given by

$$I_{|1,m\rangle \leftarrow |0,n\rangle} = \nu_{1m,0n} P \left(\int \Psi_{1m}^*(x) \langle 0 | \bar{\mu}(x) | 1 \rangle \Psi_{0n}(x) dx \right)^2 \quad (3)$$

where $\nu_{1m,0n}$ is the wavenumber of the transition $(E_m^1 - E_n^0)/hc$, P the Boltzman factor and $\langle 1 |$ and $| 0 \rangle$ the vibrational wave functions corresponding to the first excited and the ground vibrational states. $\bar{\mu}(x)$ is the molecular dipole moment developed as a Taylor series expansion in the CH stretching displacement coordinate around the equilibrium geometry. The effect of the rotation of the entire molecule is taken into account by convoluting each transition by the theoretical asymmetrical top vibration–rotation profile corresponding to the dipole moment variation along the molecular axes.^{10–16}

The set of parameters used in this model may not be unique. Some of them are calculated by ab initio methods, but the others are experimentally determined from the fit of six CH stretching overtone spectra of several isotopic species. Furthermore, owing to the size of the molecule, only the modes likely to mostly perturb the CH stretching spectra are explicitly introduced, which gives an effective character to the determined coupling parameters which implicitly take into account the effect of all the other non considered modes. However, as shown in the previous studies, this set of parameters leads to a correct reconstruction of all the overtone spectra of different isotopic species.

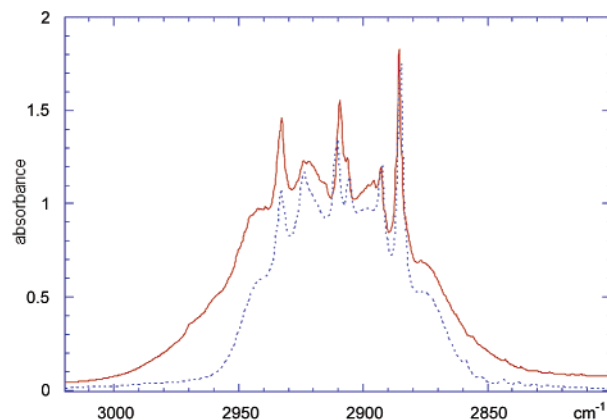


Figure 1. Infrared spectra of gaseous monohydrogenated 1,2,3,4,4,5,5-d₇-cyclopentene in the CH stretching region at 300 K (top solid line: experimental spectrum; bottom dotted line: calculated spectrum).

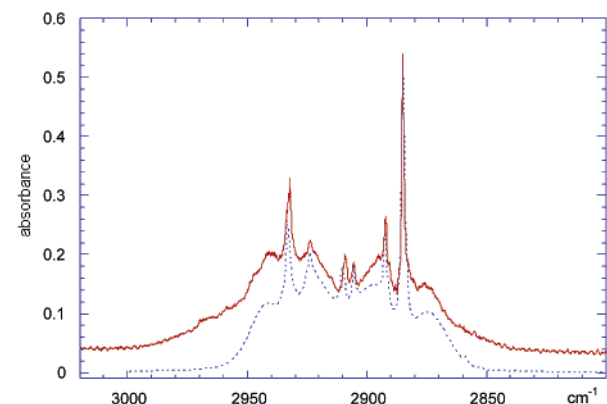


Figure 2. Infrared spectra of gaseous monohydrogenated 1,2,3,4,4,5,5-d₇-cyclopentene in the CH stretching region at 192 K (top solid line: experimental spectrum; bottom dotted line: calculated spectrum).

Results and Discussion

At room temperature, the infrared spectrum of the CH fundamental stretching vibration exhibits three intense Q branches at 2885.5, 2909.4, and 2932.8 cm^{-1} and three weaker ones at 2892.7, 2906.2, and 2924.0 cm^{-1} superimposed on a broad envelop due to the overlap of the P and R wings corresponding to each Q branches¹² (Figure 1). Contrary to what is observed in the case of the perhydrogenated compound,¹⁷ the low temperature spectrum presents the same spectral pattern but less embedded by P and R wings owing to the rotational levels depopulation with decreasing temperature. This shows the absence of additional features due to possibly other coupling terms not introduced in the model and not observed owing to the broadening of the room-temperature spectrum. The most striking difference between the two spectra is the considerable decrease of the relative intensity of the central features (Figure 2).

The spectra calculated from the above recalled model are in good agreement with the experimental ones (Figures 1 and 2). Their temperature dependence is well reproduced by only changing the Boltzman factor in the used model. The reproduction of the central spectral feature, which is more precisely defined at low temperature, allows a better determination of the potential parameters. In particular, the ring-puckering effective potential function has been expanded to the six order in the first excited CH stretching state (Figure 3).

The relative intensity decrease of the central feature can be readily explained. Because of the potential asymmetry, the wave functions corresponding to the first ring-puckering levels are

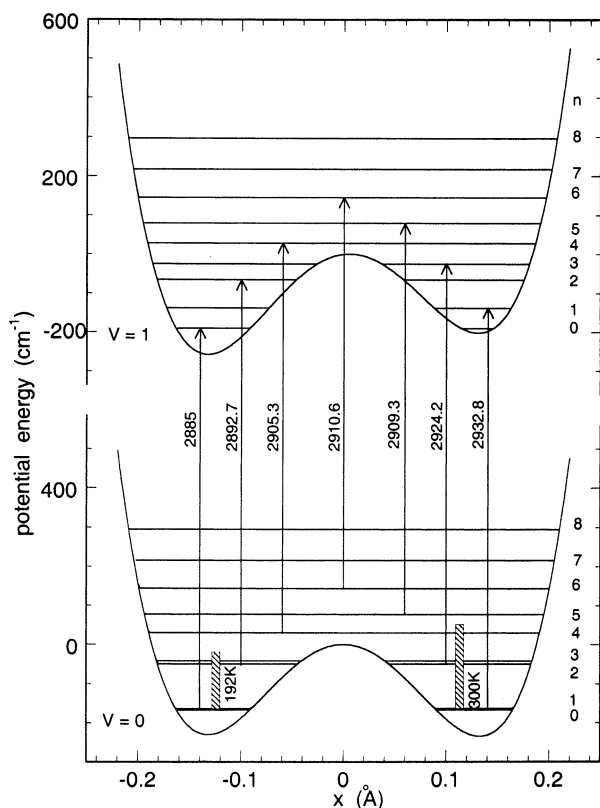


Figure 3. Calculated effective potentials of the ring-puckering motion in the ground vibrational state ($V=0$) and in the first excited state of CH stretching of the monohydrogenated 1,2,3,4,4,5,5d₇-cyclopentene. ($V^0(x) = -26452x^2 + 952.8x^3 + 754\,020x^4 \text{ cm}^{-1}$; $V^1(x) = 278x - 26274x^2 - 3690.2x^3 + 748131x^4 + 4369x^5 + 111\,150x^6 \text{ cm}^{-1}$).

strongly localized in each potential well.^{9–13} The transition $|1,0\rangle \leftarrow |0,0\rangle$ gives rise to the lower frequency intense band at 2885 cm^{-1} which is assigned to the axial CH stretching. In the same manner, the transition $|1,1\rangle \leftarrow |0,1\rangle$ corresponds to the higher frequency intense band at 2932.8 cm^{-1} which is related to the equatorial CH stretching. The central clump of bands is due to several transitions $|1,n\rangle \leftarrow |0,n\rangle$ with $n > 1$. The bands at 2924 and 2892.7 cm^{-1} correspond to transitions between ring-puckering levels situated very near the top of the potential barrier ($n = 2$ and 3 respectively) (Figure 3). The features around 2909 cm^{-1} correspond to transitions between ring-puckering levels higher than the top of the potential barrier ($n \geq 4$) corresponding

to an energy $(E_n^0 - E_0^0) \geq 197 \text{ cm}^{-1}$. They are the most depopulated levels when temperature decreases from 300 K ($\approx 209 \text{ cm}^{-1}$) to 192 K ($\approx 133.5 \text{ cm}^{-1}$) (Figure 3), leading to a strong decrease of the intensity of the band involved in the corresponding transitions.

Conclusion

The analysis of the temperature dependence of the infrared spectrum of the fundamental CH stretching vibration of gaseous -3H_1 monohydrogenated cyclopentenes has allowed us to improve the potential parameter and to test the validity of the model used to reproduce this spectrum. The assignment of the observed spectral structure is confirmed, in particular, the hot band character of the central features due to transitions arising from ring-puckering levels whose energy is higher than the top of the ring-puckering barrier. The presence of such a central feature in the spectrum is the signature of an asymmetric ring-puckering potential.

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