**Determination of the Ring-Inversion Barrier in γ-Thiobutyrolactone by Microwave Fourier Transform Spectroscopy**

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The microwave spectrum of γ-thiobutyrolactone has been reinvestigated using microwave Fourier transform spectroscopy. The μ, rotation inversion transitions have been found to be splitted for the first excited state of the vibration at ~ 250 cm⁻¹. An inversion splitting of 0.014 MHz has been measured directly from these transitions. These splittings indicate that the vibration is related to a double minimum potential function describing two ring-twisted conformations connected by inversion. A one-dimensional reduced potential function has been derived for this vibration and gives a barrier to ring inversion of 1380 ± 350 cm⁻¹.

The microwave spectrum of γ-thiobutyrolactone (tetrahydrothiophen-2-one), C₇H₆OS, (I) was studied previously by Alonso et al. [1, 2]. It was concluded that the ground-state ring conformation is non-planar on the basis of the observed value of the inertial defect Δ = -2Σmᵢcᵢ², where mᵢ is the mass of the i-th atom and cᵢ is the out-of-plane distance. In this way it could be expected for the potential energy surface arising from the out-of-plane ring vibrations to have two equivalent minima belonging to the twisted configurations as in other cyclopentanone derivatives [3–6].

A characteristic feature associated with potential energy surfaces with two equivalent minima is that vibrational energy levels lower than the barrier occur in closely spaced pairs. In the limit of infinite barrier to inversion the pairs become degenerate. The energy separations between these pairs of levels, the so called inversion splittings, are very sensitive to the barrier heights. Microwave spectroscopy offers the possibility of measuring inversion splittings directly when there is a non-zero inverting electric dipole component. For the related molecule γ-butyrolactone (II) [5] an inversion splitting of ΔE = 30.3 MHz and for tetrahydrothiophen-3-one (III) [6] a splitting of ΔE = 0.3 MHz of the first excited state approximately 200 cm⁻¹ above the ground state have been determined. These transitions occur at νᵢ ± ΔE, where νᵢ is the pure rotational frequency and ΔE is the inversion splitting. Barriers to ring inversion of 670 cm⁻¹ for γ-butyrolactone and 1050 cm⁻¹ for tetrahydrothiophen-3-one have been derived from a one-dimensional treatment.

For γ-thiobutyrolactone (I) no inversion splittings were observed using a computer-controlled Stark modulation spectrometer [7], which indicates a very high barrier to ring inversion with inversion splittings not resolvable with the Stark spectrometer (~0.2 MHz). The higher resolution combined with the high sensitivity of microwave Fourier transform (MWFT) spectroscopy makes this investigation feasible, so we decided to reexamine the microwave spectrum of γ-butyrolactone using this technique.

The sample of γ-thiobutyrolactone supplied by Pfaltz and Bauer was used without further purification, and measured in the pressure and temperature range from 1 to 3 mTorr and from −40° to −50 °C.

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The spectra were recorded in the 8–13 GHz frequency region using a microwave Fourier transform spectrometer with a single microwave source [8].

No doublets were observed for rotational transitions of the ground state. Splittings of ~0.03 MHz were recorded for rotational transitions of an excited state approximately 250 cm⁻¹ above the ground state. This provides evidence that this vibration is related to a double minimum potential function describing two twisted ring conformations connected by inversion. In this case the correct vibrational quantum number labelling for the ground and first excited state of this motion should be 0–1 and 2–3, respectively. This labelling is used in Table I, which collects the inversion splittings observed for several \( \mu \)-branch transitions. The frequencies of narrow splitted lines were determined by a fit procedure of the time domain signal [9].

As a way of determining the barrier to ring inversion it was decided to start with a one-dimensional Hamiltonian

\[
H(x) = \frac{p_x^2}{2\mu} + ax^2 - bx^4
\]  

with \( x \) a ring-puckering coordinate, \( p_x = \frac{h}{i} \frac{\partial}{\partial x} \) its conjugate linear momentum, \( \mu \) the reduced mass, \( a \) and \( b \) harmonic and quartic potential coefficients. By introduction of a reduced dimensionless coordinate \( X \) and momentum \( P_x \) according Chan and Stelman [10],

\[
X = \left( \frac{8\mu a}{h^2} \right)^{\frac{1}{6}} x,
\]

\[
P_x = \left( \frac{8}{\mu a h^2} \right)^{\frac{1}{6}} P_x
\]  

with the commutator \([P_x, X] = 2i \) a reduced Hamiltonian

\[H(X) = v_0 [P_x^2 + X^4 - \eta X^2]\]

is derived with

\[
v_0 = \left( \frac{a h^4}{64 \mu} \right)^{\frac{1}{3}},
\]

\[
\eta = \left( \frac{8 \mu b^3}{a^2 h^2} \right)^{\frac{1}{3}}.
\]

The eigenvalues of (3), the dimensionless reduced vibrational energies, \( \varepsilon_n \), are calculated for a given value of \( \eta \) by diagonalization of the term between brackets in the Hamiltonian of (1) using a basis set of 100 factorized harmonic oscillator wave functions. The \( v_0 \) parameter, which has dimensions of energy, can be determined from experimentally observed vibrational spacings. In this way, if one deals with only vibrational energies, it is not necessary to know the reduced mass for the ring-puckering vibration.

This two-parameter Hamiltonian was used to fit the vibrational energy separations \( \Delta_2 - 3 \) of 0.014 MHz measured directly from the \( \mu \)-rotation-inversion transitions and \( \Delta_1 - 23 = 250 \text{ cm}^{-1} \) obtained from relative intensity measurements [2]. These energies and the

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![Fig. 1. Determination of the reduced potential function of \( \gamma \)-thiobutyrolactone. Representation of: (a) \( v_0 = \Delta_2 - 3 \) and (b) \( v_0 = \frac{\Delta_{01 - 23}}{2(\varepsilon_3 - \varepsilon_2)} \) as functions of \( \eta \).](image-url)
reduced energies are related by

\[
\begin{align*}
\nu &= \frac{\Delta_{2-3}}{(\varepsilon_3 - \varepsilon_2)} \\
\nu &= \frac{\Delta_{01-23}}{\frac{1}{2}(\varepsilon_3 + \varepsilon_2 - \varepsilon_1 - \varepsilon_0)}
\end{align*}
\]

The reduced energies have been calculated for values of \(\eta\) between 21 and 25. Figure 1 shows the representation of \(\nu\) versus \(\eta\) for (5) and (6). The error bars for these curves have been calculated using the same procedure considering the values for \(\Delta_{2-3}\) and \(\Delta_{01-23}\) within three times the quoted standard errors. At the intersection point we obtain values of \(\eta = 24.4 \pm 0.6\) and \(\nu = 9.3 \pm 1.7 \text{ cm}^{-1}\) which give a barrier height \((\frac{\eta^2}{4})\) of \(1380 \pm 350 \text{ cm}^{-1}\).

Following the same procedure as in \(\gamma\)-butyrolactone [5] and tetrahydrothiophen-3-one [6], and using the same definition for the ring twisting vibration, a value for the angle \(\tau_e = 27 \pm 7^\circ\) corresponding to the minimum of the potential function has been calculated. It can be compared with the value \(\tau = 24^\circ\) obtained from the ground-state rotational constants [11]. These angles are also of the same order as those calculated for \(\gamma\)-butyrolactone (\(\tau_e = 25^\circ\)) [5] and tetrahydrothiophen-3-one (\(\tau_e = 26^\circ\)) [6].

It is usual to consider the potential energy for the ring-puckering vibration to arise from contributions from deformation of the ring angles and from the torsional motion about the ring bonds [12–14]. Substitution of an endocyclic CH\(_2\) group by O or S atoms reduces the torsional strain and is thus a factor which favours a lowering of the inversion barrier. The angle strain is essentially the same for O atoms and CH\(_2\) groups. However, ring-angle strain is reduced for S atoms relative to CH\(_2\) groups and O atoms, so the torsional forces predominate in this case, and an increase in the inversion barrier for \(\gamma\)-thiobutyrolactone (1380 cm\(^{-1}\)) relative to cyclopentanone [3] (750 cm\(^{-1}\)) and \(\gamma\)-butyrolactone [5] (670 cm\(^{-1}\)) can be expected. On the other hand, the torsional strain in \(\gamma\)-thiobutyrolactone must be higher than for tetrahydrothiophen-3-one [6] due to the number of adjacent methylene groups. Hence an increase in the inversion barrier for \(\gamma\)-thiobutyrolactone relative to tetrahydrothiophen-3-one [6] (1050 cm\(^{-1}\)) is also reasonable.

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