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

H. Harder, A. G. Lesarri†, J. L. Alonso†*, H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel,
Kiel, F. R. Germany

J. C. López

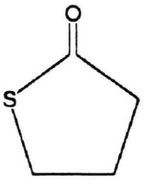
Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain.

Z. Naturforsch. **47 a,** 588–590 (1992); received January 20, 1992

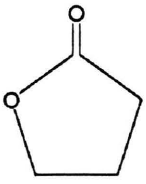
The microwave spectrum of γ-thiobutyrolactone has been reinvestigated using microwave Fourier transform spectroscopy. The μ_c rotation inversion transitions have been found to be splitted for the first excited state of the vibration at $\sim 250\ \mathrm{cm}^{-1}$. An inversion splitting of 0.014 MHz 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 $1380 \pm 350\ \mathrm{cm}^{-1}$.

The microwave spectrum of γ-thiobutyrolactone (tetrahydrothiophen-2-one), C_4H_6OS, (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 $\Delta = -2\sum m_i c_i^2$, where m_i is the mass of the i-th atom and c_i is the out-of-plane distance. In this way it could be expectd 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].

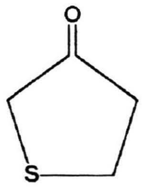
A characteristic feature associated with potential energy surfaces with two equivalent minima is that vibrational energy levels lower than the barrier occur in closely spaced pairs. In the limit of infinite barrier to inversion the pairs become degenerate. The energy separations between these pairs of 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 $\Delta E = 30.3$ MHz and for tetrahydrothiophen-3-one (III) [6] a splitting of $\Delta E = 0.3$ MHz of the first excited state approximately $200\ \mathrm{cm}^{-1}$ above the ground state have been determined. These transitions occur at $\nu_r \pm \Delta E$, where ν_r is the pure rotational frequency and ΔE is the inversion splitting. Barriers to ring inversion of $670\ \mathrm{cm}^{-1}$ for γ-butyrolactone and $1050\ \mathrm{cm}^{-1}$ for tetrahydrothiophen-3-one have been derived from a one-dimensional treatment.



(I)



(II)



(III)

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.

---

† Permanent address: Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain.

* Alexander Von Humboldt-Stiftung fellow 1990.

0932-0784 / 92 / 0400-0588 $ 01.30/0. – Please order a reprint rather than making your own copy.

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 ^{c}Q-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

$$H(x) = \frac{P_x^2}{2\mu} + a\,x^2 - b\,x^4 \tag{1}$$

with x a ring-puckering coordinate, $P_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$ its conjugate linear momentum, μ 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],

$$X = \left(\frac{8\,\mu\,a}{\hbar^2}\right)^{\frac{1}{6}} x, \tag{2a}$$

$$P_X = \left(\frac{8}{\mu\,a\,\hbar^4}\right)^{\frac{1}{6}} P_x \tag{2b}$$

with the commutator $[P_X, X] = 2\,i$, a reduced Hamiltonian

$$H(X) = \nu_0\,[P_X^2 + X^4 - \eta\,X^2] \tag{3}$$

is derived with

$$\nu_0 = \left(\frac{a\,\hbar^4}{64\,\mu}\right)^{\frac{1}{3}}, \tag{4a}$$

$$\eta = \left(\frac{8\,\mu\,b^3}{\alpha^2\,\hbar^2}\right)^{\frac{1}{3}}. \tag{4b}$$

The eigenvalues of (3), the dimensionless reduced vibrational energies, ε_v are calculated for a given value of η by diagonalization of the term between brackets in the Hamiltonian of (1) using a basis set of 100 factorized harmonic oscillator wave functions. The ν_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.

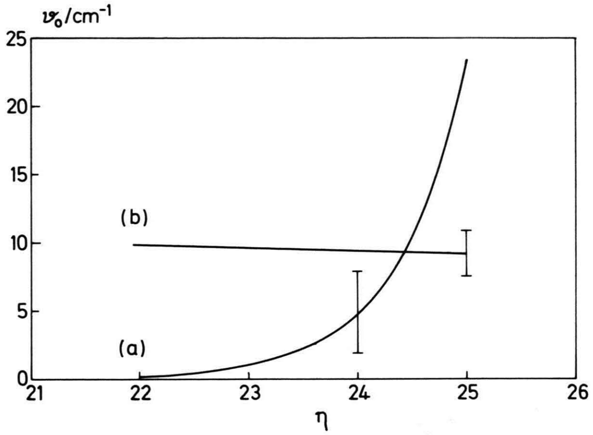


Fig. 1. Determination of the reduced potential function of γ-thiobutyrolactone. Representation of: (a) $\nu_0 = \frac{\Delta_{2-3}}{\varepsilon_3 - \varepsilon_2}$ and (b) $\nu_0 = \frac{\Delta_{01-23}}{\frac{1}{2}(\varepsilon_3 + \varepsilon_2 - \varepsilon_1 - \varepsilon_0)}$ as functions of η.

Table I. μ_c rotation-inversion transition frequencies in MHz measured for γ-thiobutyrolactone.

Transition $J''_{K''_{-1}\,K''_{+1}} \leftarrow J'_{K'_{-1}\,K'_{+1}}$	Frequencies	Splitting
$15_{8,8}\,(2) \leftarrow 15_{7,8}\,(3)$[a]	10 343.304	
$15_{8,8}\,(3) \leftarrow 15_{7,8}\,(2)$	10 343.335	0.031
$35_{17,19}\,(2) \leftarrow 35_{16,19}\,(3)$	9 177.797	
$35_{17,19}\,(3) \leftarrow 35_{16,19}\,(2)$	9 177.826	0.029
$39_{19,21}\,(2) \leftarrow 39_{18,21}\,(3)$	10 932.781	
$39_{19,21}\,(3) \leftarrow 39_{18,21}\,(2)$	10 932.801	0.020
$41_{20,22}\,(2) \leftarrow 41_{19,22}\,(3)$	11 865.545	
$41_{20,22}\,(3) \leftarrow 41_{19,22}\,(2)$	11 865.580	0.035
$43_{21,23}\,(2) \leftarrow 43_{20,23}\,(3)$	12 835.607	
$43_{21,23}\,(3) \leftarrow 43_{20,23}\,(2)$	12 835.633	0.026
$48_{23,26}\,(2) \leftarrow 48_{22,26}\,(3)$	8 124.250	
$48_{23,26}\,(3) \leftarrow 48_{22,26}\,(2)$	8 124.278	0.028
	$2\,\Delta_{2-3} = 0.028 \pm 0.005$ MHz	

[a] Numbers in parenthesis refer to the vibrational quantum number labelling.

This two-parameter Hamiltonian was used to fit the vibrational energy separations Δ_{2-3} of 0.014 MHz measured directly from the μ_c rotation-inversion transitions and $\Delta_{1-23} = 250$ cm^{-1} obtained from relative intensity measurements [2]. These energies and the reduced energies are related by

$$\nu_0 = \frac{\Delta_{2-3}}{(\varepsilon_3 - \varepsilon_2)} \tag{5}$$

$$\nu_0 = \frac{\Delta_{01-23}}{\frac{1}{2}(\varepsilon_3 + \varepsilon_2 - \varepsilon_1 - \varepsilon_0)}. \tag{6}$$

The reduced energies have been calculated for values of η between 21 and 25. Figure 1 shows the representation of ν_0 versus η for (5) and (6). The error bars for these curves have been calculated using the same procedure considering the values for Δ_{2-3} and Δ_{01-23} within three times the quoted standard errors. At the intersection point we obtain values of $\eta = 24.4 \pm 0.6$ and $\nu_0 = 9.3 \pm 1.7\ \mathrm{cm}^{-1}$ which give a barrier height $\left(\nu_0 \frac{\eta^2}{4}\right)$ of $1380 \pm 350\ \mathrm{cm}^{-1}$.

Following the same procedure as in γ-butyrolactone [5] and tetrahydrothiophen-3-one [6], and using the same definition for the ring twisting vibration, a value for the angle $\tau_e = 27 \pm 7°$ corresponding to the minimum of the potential function has been calculated. It can be compared with the value $\tau = 24°$ obtained from the ground-state rotational constants [11]. These angles are also of the same order as those calculated for γ-butyrolactone ($\tau_e = 25°$) [5] and tetrahydrothiophen-3-one ($\tau_e = 26°$) [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 γ-thiobutyrolactone ($1380\ \mathrm{cm}^{-1}$) relative to cyclopentanone [3] ($750\ \mathrm{cm}^{-1}$) and γ-butyrolactone [5] ($670\ \mathrm{cm}^{-1}$) can be expected. On the other hand, the torsional strain in γ-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 γ-thiobutyrolactone relative to tetrahydrothiophen-3-one [6] ($1050\ \mathrm{cm}^{-1}$) is also reasonable.

Acknowledgements

Funds were provided by the Deutsche Forschungsgemeinschaft, the Fonds der Chemie and the Land Schleswig-Holstein. J. L. A. thanks the von Humboldt Foundation for financial support.

[1] J. L. Alonso, J. Chem. Soc., Chem. Comm. **1981,** 577.

[2] J. L. Alonso, J. C. López and F. Mata, Z. Naturforsch., **37a,** 129 (1981).

[3] H. Kim and W. Gwinn, J. Chem. Phys. **51,** 1815 (1969).

[4] J. L. Alonso, R. Cervellati, A. Degli Esposti, D. G. Lister, and P. Palmieri, J. Chem. Soc. Faraday Trans. (2) **82,** 837 (1986).

[5] J. C. López, J. L. Alonso, R. Cervellati, A. Degli Esposti, D. G. Lister, and P. Palmieri, J. Chem. Soc. Faraday Trans. **86,** 453 (1990).

[6] J. C. López, R. M. Villamañán, J. L. Alonso, and J. M. Muñoz, J. Chem. Soc. Faraday Trans. **86,** 5 (1990).

[7] J. C. López, J. L. Alonso, and F. J. Peláez, J. Mol. Spectrosc. **131,** 9 (1988).

[8] M. Krüger and H. Dreizler, Z. Naturforsch., **45a,** 724 (1990).

[9] J. Haekel and H. Mäder, Z. Naturforsch., **43a,** 203 (1988).

[10] S. I. Chan and D. Stelman, J. Mol. Spectrosc. **10,** 278 (1963).

[11] J. C. López, Tésis Doctoral, Universidad de Valladolid (1982).

[12] A. C. Legon, Chem. Rev. **80,** 770 (1969).

[13] S. I. Chan, J. Zinn, and W. D. Gwinn, J. Chem. Phys. **34,** 1319 (1961).

[14] J. Laane, J. Chem. Phys. **50,** 770 (1969).