Assignment of Infrared-Active Vibrational Frequencies in Butatriene

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Infrared spectrum of butatriene in the NaCl region has been recorded. An assignment of nearly all infrared-active fundamentals is proposed. Also given are a set of symmetry coordinates, and the corresponding G-matrix elements for the appropriate molecule model (symmetry D_{2h}).

Comparatively little work has been done on the vibrational spectra of butatriene.[1] We have now found it possible to establish a nearly complete set of infrared-active fundamentals. In the present work we have performed a tentative assignment of the previously published infrared data in the LiF region,[1] along with previously not published data from the NaCl region. We have also evaluated a set of symmetry coordinates and the corresponding G matrix elements,[2] which will be useful for a complete normal-coordinate analysis.
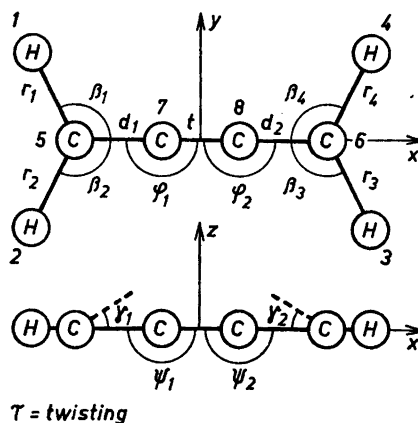

Fig. 1. Orientation of principal axes, numbering of atoms, and the valence coordinates used in butatriene.

T = twisting

SYMMETRY COORDINATES

The planar molecular model of symmetry D_{2h} (Fig. 1) is assumed. The set of eighteen symmetry coordinates should be distributed among the appropriate symmetry species according to

$$4a_g + 3b_{1g} + 2b_{2g} + a_u + 2b_{1u} + 3b_{2u} + 3b_{3u}$$

A suitable set has been obtained from the valence coordinates given below.

r: CH stretching.
d: CC stretching for the terminal bonds.
t: CC stretching of the middle bond.
β: HCC bending (in-plane).
φ: CCC in-plane linear bending.
γ: CH$_2$ out-of-plane bending.
ψ: CCC out-of-plane linear bending.
τ: Twisting.

The twisting coordinate has been defined as in ethylene[3] by

$$R\tau = (1/4 \sin A) (z_1 - z_2 + z_3 - z_4)$$

where R denotes the equilibrium CH distance, and the equilibrium HCH angle is $2A$. The other equilibrium parameters introduced are D and T, denoting the CC terminal bond and middle bond distances, respectively. The evaluated set of symmetry coordinates is given in the following.

$$
\begin{aligned}
&\textit{Species } a_g: & S_1 &= \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4) \\
& & S_2 &= 2^{-\frac{1}{2}}(d_1 + d_2) \\
& & S_3 &= t \\
& & S_4 &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1 + \beta_2 + \beta_3 + \beta_4) \\
&\textit{Species } b_{1g}: & S_5 &= \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4) \\
& & S_6 &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1 - \beta_2 + \beta_3 - \beta_4) \\
& & S_7 &= 2^{-\frac{1}{2}}(DT)^{\frac{1}{2}}(\varphi_1 - \varphi_2) \\
&\textit{Species } b_{2g}: & S_8 &= 2^{\frac{1}{2}-}(RD)^{\frac{1}{2}}(\gamma_1 - \gamma_2) \\
& & S_9 &= 2^{-\frac{1}{2}}(DT)^{\frac{1}{2}}(\psi_1 - \psi_2) \\
&\textit{Species } a_u: & S_{10} &= R\tau \\
&\textit{Species } b_{1u}: & S_{11} &= 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\gamma_1 + \gamma_2) \\
& & S_{12} &= 2^{-\frac{1}{2}}(DT)^{\frac{1}{2}}(\psi_1 + \psi_2) \\
&\textit{Species } b_{2u}: & S_{13} &= \tfrac{1}{2}(r_1 - r_2 - r_3 + r_4) \\
& & S_{14} &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1 - \beta_2 - \beta_3 + \beta_4) \\
& & S_{15} &= 2^{-\frac{1}{2}}(DT)^{\frac{1}{2}}(\varphi_1 + \varphi_2) \\
&\textit{Species } b_{3u}: & S_{16} &= \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4) \\
& & S_{17} &= 2^{-\frac{1}{2}}(d_1 - d_2) \\
& & S_{18} &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_1 + \beta_2 - \beta_3 - \beta_4)
\end{aligned}
$$

G MATRIX

The elements of the symmetrized **G** matrix[2] are specified in the following.

Species a_g:

$$G_{11} = \mu_H + 2\mu_C \cos^2 A$$
$$G_{22} = G_{33} = 2\mu_C$$
$$G_{44} = (D/R)(\mu_H + 2\mu_C \sin^2 A)$$
$$G_{12} = -2^{1/2}\,\mu_C \cos A$$
$$G_{23} = -2^{1/2}\,\mu_C$$
$$G_{34} = G_{13} = 0$$
$$G_{24} = -(D/R)^{1/2}2^{1/2}\,\mu_C \sin A$$
$$G_{14} = (D/R)^{1/2}\,\mu_C \sin 2A$$

Species b_{1g}:

$$G_{55} = \mu_H + 2\mu_C \sin^2 A$$
$$G_{66} = (D/R)(\mu_H + 2\mu_C \cos^2 A) + 4[(R/D) + \cos A]\mu_C$$
$$G_{77} = \{(2T/D) + 4[(D/T) + 1]\}\mu_C$$
$$G_{56} = -2(D/R)^{1/2}[(R/D) + \cos A]\mu_C \sin A$$
$$G_{67} = 2^{1/2}(T/R)^{1/2}[(2R/D) + (2R/T) + \cos A]\mu_C$$
$$G_{57} = -2^{1/2}(T/D)^{1/2}\mu_C \sin A$$

Species b_{2g}:

$$G_{88} = (D/R \cos^2 A)(\tfrac{1}{2}\mu_H + \mu_C) + 2[(R/D) + (1/\cos A)]\mu_C$$
$$G_{99} = \{(2T/D) + 4[(D/T) + 1]\}\mu_C$$
$$G_{89} = -(T/R)^{1/2}[(2R/D) + (2R/T) + (1/\cos A)]\mu_C$$

Species a_u:

$$G_{10\ 10} = (1/4 \sin^2 A)\mu_H$$

Species b_{1u}:

$$G_{11\ 11} = (D/R \cos^2 A)(\tfrac{1}{2}\mu_H + \mu_C) + 2[(R/D) + (1/\cos A)]\mu_C$$
$$G_{12\ 12} = (2T/D)\mu_C$$
$$G_{11\ 12} = -(T/R)^{1/2}[(2R/D) + (1/\cos A)]\mu_C$$

Species b_{2u}:

$$G_{13\ 13} = \mu_H + 2\mu_C \sin^2 A$$
$$G_{14\ 14} = (D/R)(\mu_H + 2\mu_C \cos^2 A) + 4[(R/D) + \cos A]\mu_C$$
$$G_{15\ 15} = (2T/D)\mu_C$$
$$G_{13\ 14} = -2(D/R)^{1/2}[(R/D) + \cos A]\mu_C \sin A$$
$$G_{14\ 15} = 2^{1/2}(T/R)^{1/2}[(2R/D) + \cos A]\mu_C$$
$$G_{13\ 15} = -2^{1/2}(T/D)^{1/2}\mu_C \sin A$$

Species b_{3u}:

$$G_{16\ 16} = \mu_H + 2\mu_C \cos^2 A$$
$$G_{17\ 17} = 2\mu_C$$
$$G_{18\ 18} = (D/R)(\mu_H + 2\mu_C \sin^2 A)$$
$$G_{16\ 17} = -2^{1/2}\mu_C \cos A$$
$$G_{17\ 18} = -2^{1/2}(D/R)^{1/2}\mu_C \sin A$$
$$G_{16\ 18} = (D/R)^{1/2}\mu_C \sin 2A$$

In the above expressions μ_H and μ_C denote as usual the inverse masses of the H and C atoms, respectively.

ASSIGNMENT OF FREQUENCIES

The selection rules for the fundamentals of butatriene are given in Table 1, and are based on the true planar molecule model. The designation of parallel and perpendicular bands refers to the molecule considered as a symmetric top, which is approximately correct. In fact the parallel and perpendicular bands are easily recognized in the gaseous spectra of this molecule, particularly because of the very low moment of inertia with respect to the x axis (cf. Fig. 1). We may also take the advantage of the fact that the molecule may approximately be considered as linear. Hence the in-plane and out-of-plane CCC bending vibrations (symmetric or antisymmetric) may be expected to have nearly the same frequencies.

Species b_{1u}: The very strong band with well-resolved fine structure and band centrum at 852 cm^{-1} (see Fig. 2) should evidently be assigned as the ν_{11}
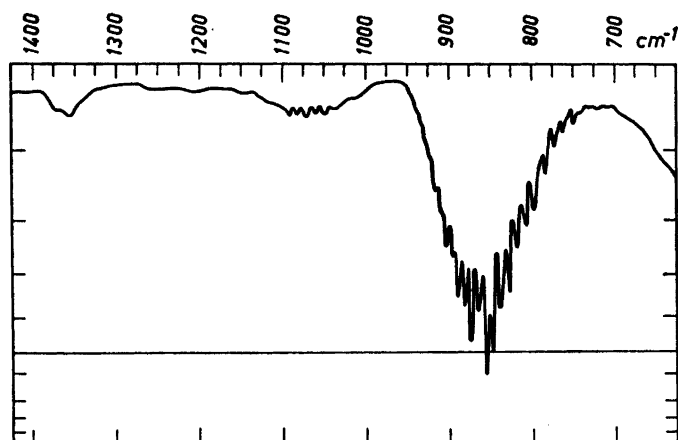

Fig. 2. I.R.-Spectrum of butatriene gas. Prism NaCl.

fundamental, taking into account its shape and position. The other fundamental is expected in a low spectral region, and has not been observed with CsBr optics. Assignment:

$$\nu_{11} = 852 \text{ cm}^{-1}$$
$$\nu_{12} < 300 \text{ cm}^{-1}$$

Species b_{2u}: There is no difficulty in assigning the observed frequency[1] of 3059 cm^{-1} as the ν_{13} fundamental. Next we have assigned the 1070 cm^{-1} frequency (see Fig. 2) as the ν_{14} fundamental since it exhibits a definite fine structure. The ν_{15} frequency remains unobserved, but is expected to be close to ν_{12} (see above). Assignment:

$$\nu_{13} = 3059 \text{ cm}^{-1}$$
$$\nu_{14} = 1070 \text{ cm}^{-1}$$
$$\nu_{15} < 300 \text{ cm}^{-1}$$

Table 1. Activity and designation of the fundamentals in butatriene

		Approximate mode	Activity *	Type**
a_g	ν_1	sym. CH stretching		
	ν_2	sym. C=C terminal-bond stretching	R	p
	ν_3	C=C middle-bond stretching		
	ν_4	sym. CH_2 bending		
b_{1g}	ν_5	*trans*-type CH stretching		
	ν_6	antisym. CH_2 rocking	R	dp
	ν_7	antisym. CCC in-plane bending		
b_{2g}	ν_8	antisym. CH_2 out-of-plane bending	R	dp
	ν_9	antisym. CCC out-of-plane bending		
a_u	ν_{10}	twisting	ia	
b_{1u}	ν_{11}	sym. CH_2 out-of-plane bending	IR	$\perp$
	ν_{12}	sym. CCC out-of-plane bending		
b_{2u}	ν_{13}	*cis*-type CH stretching		
	ν_{14}	sym. CH_2 rocking	IR	$\perp$
	ν_{15}	sym. CCC in-plane bending		
b_{3u}	ν_{16}	asym. CH stretching		
	ν_{17}	antisym. C=C terminal-bond stretching	IR	$\parallel$
	ν_{18}	antisym. CH_2 scissoring		

* R = Raman-active, IR = infrared-active, ia = inactive.
** p = polarized, dp = depolarized, $\perp$ = perpendicular, $\parallel$ = parallel.

Species b_{3u}: There is no difficulty in assigning the observed parallel band at 3001 cm^{-1} with the peak separation of 13.5 cm^{-1} to the ν_{16} fundamental. For ν_{17} we have chosen the very strong band at 1607 cm^{-1}. There remains a very strong parallel band[1] at 1711 cm^{-1} with the proper peak separation (16 cm^{-1}). We hesitate to assign this frequency to ν_{18} because a CH_2 scissoring

Table 2. Symmetry of infrared-active binary combination frequencies in butatriene

Species	Type
$a_g \times b_{1u} = B_{1u}$	$\perp$
$a_g \times b_{2u} = B_{2u}$	$\perp$
$a_g \times b_{3u} = B_{3u}$	$\parallel$
$b_{1g} \times a_u = B_{1u}$	$\perp$
$b_{1g} \times b_{3u} = B_{2u}$	$\perp$
$b_{1g} \times b_{2u} = B_{3u}$	$\parallel$
$b_{2g} \times b_{3u} = B_{1u}$	$\perp$
$b_{2g} \times a_u = B_{2u}$	$\perp$
$b_{2g} \times b_{1u} = B_{3u}$	$\parallel$

by experience usually appears as a very characteristic band at about 1400—1450 cm^{-1}. There has in fact been observed a weak band at 1364 cm^{-1} (see Fig. 2) with a peak separation of 16 cm^{-1}. Assignment:

$$\nu_{16} = 3001 \text{ cm}^{-1}$$
$$\nu_{17} = 1607 \text{ cm}^{-1}$$
$$\nu_{18} = 1364 \text{ cm}^{-1}$$

Combinations. Because of the large number of unobserved frequencies (one inactive, two infrared-active, and all the Raman-active) it is not possible to explain any of the combination bands with great confidence. A survey of the infrared-active binary combinations is given in Table 2. It is clear, however, that an explanation of the parallel band at 1711 cm^{-1} (see above) as a combination must be possible, if our assignment in species b_{3u} is correct. In this case the high intensity of the combination band in question strongly suggests Fermi resonance with ν_{17}. In addition we have two weaker bands with uncertain contours at 1687 and 1736 cm^{-1}, which probably are combinations. Here we give a tentative suggestion of an assignment of these combinations as

$$\nu_9 + \nu_{18} = 1687 \qquad B_{1u} \perp$$
$$\nu_8 + \nu_{11} = 1711 \qquad B_{3u} \;||$$
$$\nu_7 + \nu_{18} = 1736 \qquad B_{2u} \perp$$

From this assignment one obtains $\nu_9 = 323$, $\nu_8 = 859$, and $\nu_7 = 372$ cm^{-1}. Because of the mentioned Fermi resonance the probable value of ν_8 should be slightly higher (perhaps 870 cm^{-1}).

Conclusion. It is not possible to construct a reliable force field for butatriene only by means of the presently assigned frequencies. This problem, however, may possibly be solved with the additional aid of a comparative study of the force constants in the series ethylene-allene-butatriene.

REFERENCES

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