Resolving a long-standing ambiguity:
The non-planarity of *gauche*-1,3-butadiene revealed by microwave spectroscopy

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1,3-butadiene (butadiene, C₄H₆) is the prototype molecule for the Diels-Alder reaction which requires a planar conjugated cis-diene.

\[\text{[4+2] cycloaddition}\]

\[\text{diene } \quad \text{dienophile } \quad \text{cyclohexene}\]
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\[
\text{[4+2] cycloaddition}
\]

Regioselective and stereoselective reaction  
→ **Concerted mechanism**
The structure of butadiene – the simplest conjugated polyene – remains elusive for its cis forms.

\[ \sim 3\% \text{ of the population at room temperature} \]

\[ \sim 3.5 \text{ kcal/mol} \]
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\[ \sim 3\% \text{ of the population at room temperature} \]

Competition between steric interactions and conjugation of the double bonds.
Need of unambiguous experimental and theoretical results to resolve the ambiguity on cis-butadiene structure

**Planar structure**
\[
\text{cis} \\
(C_{2v})
\]

**Twisted structure**
\[
\text{gauche} \\
(C_2)
\]

**Exp.**
- IR
- Raman
- IR matrix
- UV matrix

**Calc.**
- MCSCF
- SCF, CISD, MP2, CCSD(T)

Need of unambiguous experimental and theoretical results to resolve the ambiguity on cis-butadiene structure

**Planar structure**

* cis
  * (C\textsubscript{2v})

**Twisted structure**

* gauche
  * (C\textsubscript{2})

**Exp.**

- IR Raman
- IR matrix
- UV matrix

**Calc.**

- MCSCF
- SCF, CISD, MP2, CCSD(T)

We show that the second most stable conformer of butadiene possesses a gauche structure in the gas phase.
We show that the second most stable conformer of butadiene possesses a *gauche* structure in the gas phase.
The small calculated dipole moment requires sensitive microwave techniques

<table>
<thead>
<tr>
<th>Cavity FTMW</th>
<th>Buffer gas cell FTMW + CP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Range</strong></td>
<td>5–40 GHz</td>
</tr>
<tr>
<td><strong>Rot. temperature</strong></td>
<td>5–10 K</td>
</tr>
<tr>
<td>supersonic expansion</td>
<td></td>
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<tr>
<td>1 kV dc discharge</td>
<td></td>
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<tbody>
<tr>
<td>Range</td>
<td>5–40 GHz</td>
<td>12–18 GHz</td>
</tr>
<tr>
<td>Rot. temperature</td>
<td>5–10 K</td>
<td>5–10 K</td>
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<tr>
<td></td>
<td>supersonic expansion</td>
<td>buffer gas cooling</td>
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<tr>
<td></td>
<td>1 kV dc discharge</td>
<td>230 °C capillary</td>
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<tr>
<td>FWHM</td>
<td>∼ 40 kHz</td>
<td>∼ 100 kHz</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>0.1–5</td>
<td>∼ 1</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>6 Hz</td>
<td>50,000 Hz</td>
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Our measurements reveal the existence of two tunneling components for *gauche*-butadiene.

Chirped-pulse spectrum, buffer gas cell, 

\[ \sim 2 \text{ min integration time} \]
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Chirped-pulse spectrum, buffer gas cell, 
~ 2 min integration time

Initial prediction 
$1_{10} - 1_{01}$
Measurements reveals the different dynamics of the two experiments

Buffer gas cell

Cavity

\[ \frac{I(0^+)}{I(0^-)} \approx 1 \]

\[ \frac{I(0^+)}{I(0^-)} \approx 20 \]
The accurate molecular parameters derived confirm the non planarity of the molecule

<table>
<thead>
<tr>
<th></th>
<th>GS</th>
<th>0⁺</th>
<th>0⁻</th>
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<tr>
<td></td>
<td>Calc.ᵃ</td>
<td>Calc.ᵇ</td>
<td>Exp.</td>
</tr>
<tr>
<td>A₀</td>
<td>21244</td>
<td>21220</td>
<td>21223</td>
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<tr>
<td>B₀</td>
<td>5654</td>
<td>5678</td>
<td>5671</td>
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<tr>
<td>C₀</td>
<td>4576</td>
<td>4589</td>
<td>4577</td>
</tr>
</tbody>
</table>

Δ = −2.5

ᵃ Full dimensional VPT2 calculation: AE-CCSD(T)/PCVQZ (rₑ) + FC-(T)/CCSD(T)/ANO0 (α)
ᵇ 1D torsional calculation: FC-CCSD(T)/ANO1
ᶜ δ = Exp. / Calc.
Subsequent isotopic spectroscopy has highlighted the dipole moment variation between isotopologues.

\[ \frac{I}{I_0} = 0.6\% \]

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Dipole moments calculated at the ANO0 level, adjusted with \( \mu_{\text{ANO1}} \).
Subsequent isotopic spectroscopy has highlighted the dipole moment variation between isotopologues.

$I/I_0 = 0.6\%$

$NA$

$I/I_0 = 0.6\%$

$NA$

$0^{-}$, $0^{+}$

$13444$ $13446$ $13448$ $13450$ GHz

$Pure$

$I/I_0 = 80\%$

$Pure$

$I/I_0 = 1 - 10\%$
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Dipole moments calculated at the ANO0 level, adjusted with \( \mu_e \) ANO1.
Subsequent isotopic spectroscopy has highlighted the dipole moment variation between isotopologues.

Dipole moments calculated at the ANO0 level, adjusted with $\mu_e$ ANO1.
A partial geometry has been derived from the accurate molecular parameters determined

**Partial $r_{e}^{\text{SE}}$ structure:**

$0^+$ experimental rotational constants corrected for zero point vibration effects at the VPT2 level ($\alpha$: FC-(T)/CCSD(T)/ANO00)

*Bond lengths in Å*
Butadiene is a non-planar molecule and thus must adopt first a planar conformation for Diels-Alder reaction.