Butadiene potentially exhibits many different modes of bonding to a surface, the aim of this work is to fully characterise how the spectrum of the s-cis conformer changes on coordination. A model complex, C$_4$H$_6$Fe(CO)$_3$, and its deuterated isotopomer, was studied with infrared, Raman and inelastic neutron scattering (INS) spectroscopies and has provided a definitive set of assignments for the ligand. These differ in many respects from previous work that was solely based on empirical correlations. The use of INS spectroscopy has allowed observation of several of the low energy modes for the first time, the most significant of which is the C1–C1′ torsion at 485 cm$^{-1}$. The comparison of observed and calculated infrared spectra for butadiene on silica confirms the surprising assignment that the molecule is adsorbed as the gauche form.

Introduction

Buta-1,3-diene (butadiene, C$_4$H$_6$) is a significant commodity chemical; global production was >12 million metric tonnes in 2013 [1]. Two-thirds of the output was used as a co-monomer to make synthetic elastomers including styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), poly-chloroprene (Neoprene) and nitrile rubber (NR). These are used in products as diverse as tyres, gloves, wetsuits and seals. It is largely manufactured by steam cracking of hydrocarbons [2].

As shown in Figure 1, butadiene exhibits conformational isomerism about the central C–C single bond. The lowest energy structure is the s-trans conformer, the (perhaps) obvious second conformation of a planar C$_{2v}$ structure (s-cis) is actually a transition state and the stable conformer has a C$_2$ gauche structure with a dihedral angle of ~30°. Both the s-cis and the gauche conformers are high energy states, ~15 kJ mol$^{-1}$ above the ground state and also well above the 2.5 kJ mol$^{-1}$ corresponding to 300 K. Thus the gauche conformer has only been detected in the gas phase [3] at high temperature or by matrix isolation of the high temperature vapour [4, 5]. However, it is possible to stabilise the s-cis conformer by complexation and the compound [6] C$_4$H$_6$Fe(CO)$_3$ (see Figure 2) is an example of this.

The vibrational spectroscopy of butadiene has been extensively studied both as the free molecule e.g. [4, 5, 7] and adsorbed on a variety of oxide [8, 9] and metal surfaces [10–16]. Butadiene potentially exhibits many different modes of bonding to a surface [17], the aim of this work is to fully characterise how the spectrum of the s-cis conformer changes on coordination. State-of-the-art computational methods enable transition...
energies as well as infrared, Raman and inelastic neutron scattering (INS) intensities to be computed with high accuracy [18–20]. To this end, we have also carried out a comprehensive assignment of the infrared, Raman and INS spectra of C₄H₆Fe(CO)₃, with the assignments supported by density functional theory (DFT) calculations. This has resulted in several re-assignments of the spectra. The comparison between observed and calculated spectra of the complex provides a stringent test of the reliability of the methods employed. We then use the same methods to calculate the infrared spectra of both s-trans and gauche butadiene and compare them to the surface species on silica [8]. This work provides an example of the parallel between coordinated molecules in metal complexes and adsorbed species – the Cluster-Surface analogy [21].

**Materials and methods**

**Computational studies**

DFT calculations were carried out with Gaussian 03 [22] and CASTEP [18]. Gaussian 03 was employed for the relaxed potential energy scan of butadiene about the central C–C bond shown in Figure 1, using the 6.311G(d,p) basis set with the B3LYP functional, with 1° steps between 0° (s-trans) and 180° (s-cis).

The plane wave pseudopotential based program CASTEP was used for the calculation of the vibrational transition energies and their intensities [19, 20]. For the initial structure of C₄H₆Fe(CO)₃, the most recent [23] crystal structure determined by X-ray diffraction was used. The crystal structure of butadiene is not known [24], thus a 10 × 10 × 10 Å cell was constructed with the s-trans, s-cis or the gauche conformer at the centre. The generalised gradient approximation Perdew–Burke–Ernzerhof functional was used in conjunction with optimised norm-conserving pseudopotentials. The plane-wave cut-off energy was 990 eV for the complex and 750 eV for the isolated butadiene calculations. For the complex a 4 × 4 × 6 (12 k-points) Monkhorst-Pack grid was used, the isolated molecule calculations were carried out at the Γ-point. All of the calculations were converged to better than |0.0035| eV Å⁻¹. After geometry optimisation, the vibrational spectra were calculated in the harmonic approximation using density-functional perturbation-theory [19, 20]. This procedure generates the vibrational eigenvalues and eigenvectors, which allows visualisation of the modes within Materials Studio [25] and is also the information needed to calculate the INS spectrum using the program ACLIMAX [26]. Transition energies for isotopic species were calculated from the dynamical matrix that is stored in the CASTEP checkpoint file using the PHONONS utility [27]. We emphasise that none of the transition energies have been scaled.

**Vibrational spectroscopy**

The samples of C₄H₆Fe(CO)₃ were kindly provided by Durham University, UK. The samples were sealed in quartz “lollipops” which enabled FT-Raman and INS spectra to be recorded without exposure to air, a picture of the lollipop is shown in the inset to Figure 3. FT-Raman spectra were recorded with a Bruker MultiRam spectrometer using 1064 nm excitation, 4 cm⁻¹ resolution, 200 mW laser power and either 128 or 1024 scans. The compound is a liquid at room temperature; spectra were recorded from both the liquid and the solid after quenching in liquid nitrogen. It was confirmed that the compound was still solid after the scan was complete. The INS spectrum was recorded at 20 K with TOSCA [28] at
ISIS (Didcot, UK). The infrared spectrum was recorded in air from the liquid (after removal from a second lollipop) at room temperature using a Bruker Vertex70 FTIR spectrometer, over the range 50 to 4000 cm\(^{-1}\) at 1 cm\(^{-1}\) resolution with a DLaTGS detector using 64 scans and the Bruker Diamond ATR. The solid was recorded by dropping the liquid onto the pre-cooled ATR crystal. The use of the ultra-wide range beamsplitter enabled the entire spectral range to be recorded without the need to change beamsplitters. Successive spectra did not change over the course of the measurement, suggesting that the material is not adversely affected on this timescale.

**Results**

The INS spectrum of the solid phase is shown in Figure 3 and the infrared and Raman spectra of C\(_4\)H\(_6\)Fe(CO)\(_3\) in the liquid and solid phases are shown in Figures 4 and 5 respectively. The liquid phase spectra are in good agreement with previous work [29–32], to our knowledge the solid state spectra have not previously been reported.

C\(_4\)H\(_6\)Fe(CO)\(_3\) crystallises in the orthorhombic space group \(\text{Pnma}\) (no. 62) with four molecules in the unit cell and each molecule occupying a site with \(\text{C}_s\) symmetry [23]. Factor group splitting would be expected on the basis of four molecules per cell, however, comparison of the liquid and solid state infrared and Raman spectra shows that this is very small.

Periodic-DFT calculations of the complete cell reproduce the experimental solid state geometry very well, the only significant differences are with the C–H bond distances which are underestimated in the X-ray structure, as is the usual case. Table 1 compares selected bond distances and angles as found experimentally and computationally. Both theory and experiment find that
the C₄ skeleton is planar, this is a consequence of the C₃ symmetry, (the symmetry plane bisects the C₁–C₁′ bond and includes the Fe atom and carbonyl C₃O₃). The symmetry is not crystallographically imposed; as it is also present in the gas phase species, as shown by microwave spectroscopy [33]. The bonding present in the complex has been discussed previously [34].

Figures 3–5 also show the calculated spectra and it can be seen that for all three forms of spectroscopy the agreement is essentially quantitative below 1800 cm⁻¹, for both the transition energies and their intensities. The C=O and the C–H stretch modes are underestimated and overestimated respectively. The reason for the discrepancy in the C–H modes energies is that the calculation assumes a harmonic potential, whereas the real system is anharmonic. Thus the third overtones of the C–H stretch modes occur [35] around 11500 cm⁻¹, whereas they would be expected at ~12200 cm⁻¹ for a harmonic system. Making the naive assumption that the C–H stretch modes can be treated as a diatomic molecule and using the expression for an anharmonic oscillator [36], gives an anharmonicity correction of \( x \omega^2 = 67 \text{ cm}^{-1} \) from the overtone spectroscopy [35], while assuming that the difference between the observed and calculated values for the fundamental is solely due to anharmonicity gives \( x \omega^2 = 35 \text{ cm}^{-1} \), which is of the same order of magnitude. For the C=O stretch modes, the transition energy is extremely sensitive to the bond length, in the present case the 0.01 Å lengthening results in an error of ~120 cm⁻¹, other work using atom centered basis sets [37] on M(CO)₆ (M=Cr, Mo, W), for similar bond length errors overestimate the transition energy by ~65 cm⁻¹.

Table S1 lists all the calculated modes for the solid state, with their infrared and Raman intensities. The calculations confirm the deduction from the spectra that the factor group splitting is small: in only one instance does it exceed 10 cm⁻¹ ((CO)₃Fe–C₄H₆ torsion) and is generally only a few wavenumbers. Table 2 lists the observed transition energies of the internal modes (i.e. excluding translations and librations) and the average of the factor group split quartet from the solid state calculation and their assignments.

The infrared and Raman spectra of C₄D₆Fe(CO)₃ have been reported previously [31] and their assignments are also included in Table 2.

Figure 6 shows how the transition energies, as calculated by CASTEP, of the internal modes (excluding the C–H stretches) of butadiene are modified on going from the stable gauche form to the s-cis transition state to the s-cis conformer coordinated to iron, (Table S2 lists the

### Table 1. Comparison of selected observed [23] and calculated bond distances and angles in C₄H₆Fe(CO)₃ (C₃ symmetry, prime indicates mirror image).

| Bond distance Å | Gas phase [33] | Observed [23] | Calculated |
|-----------------|----------------|---------------|------------|
| C₁–C₂           | 1.385          | 1.419         | 1.430      |
| C₁–C₁′          | 1.410          | 1.414         | 1.419      |
| C₂–H₂A          | 1.096          | 0.974         | 1.089      |
| C₂–H₂B          | 1.089          | 0.955         | 1.089      |
| C₁–H₁           | 1.088          | 0.913         | 1.088      |
| C₁–Fe           | 2.127          | 2.068         | 2.050      |
| C₂–Fe           | 2.087          | 2.112         | 2.096      |
| C₃–O₃           | 1.351          | 1.142         | 1.154      |
| C₄–O₄           | 1.150          | 1.142         | 1.155      |
| C₃–Fe           | 1.770          | 1.789         | 1.733      |
| C₄–Fe           | 1.783          | 1.796         | 1.739      |

| Bond angle °   | Gas phase [33] | Observed [23] | Calculated |
|----------------|----------------|---------------|------------|
| C₂–C₁–C₁′      | 118.3          | 117.6         | 116.9      |
| H₂A–C₂–H₂B     | 120.8          | 116.4         | 114.3      |
| H₁–C₁–C₁′      | 121.6          | 122.6         | 122.0      |
| H₁–C₁–C₁′      | 120.1          | 118.8         | 120.5      |
| Fe–C₃–O₃       | 179.9          | 177.3         | 178.3      |
| Fe–C₄–O₄       | 179.8          | 178.3         | 178.3      |
| C₃–Fe–C₄       | 103.0          | 101.5         | 102.1      |

| Dihedral angle ° | Gas phase [33] | Observed [23] | Calculated |
|-----------------|----------------|---------------|------------|
| C₂–C₁–C₁′–C₂′  | 0.0            | 0.0           | 0.0        |
| H₂A–C₂–C₁–H₁   | 136.9          | 148.2         | 144.2      |

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**Figure 5.** Observed and calculated Raman spectra of C₄H₆Fe(CO)₃, (a) Liquid state at room temperature, (b) solid state at ~100 K and (c) calculated by CASTEP.

Note: For all three spectra, the range 400 – 1600 cm⁻¹ is also shown with a x 4 ordinate expansion.
Observed and calculated transition energies of the internal modes (i.e. omitting translations and librations) of C₄H₆Fe(CO)₃ and C₄D₆Fe(CO)₃.

| INS/cm⁻¹     | Raman/cm⁻¹  | Infrared/cm⁻¹ | CASTEP/cm⁻¹ | Sym  | Description                              | CASTEP/cm⁻¹ | Expt./cm⁻¹ |
|--------------|-------------|---------------|-------------|------|------------------------------------------|-------------|------------|
| Solid        | Liquid      | Solid         | Liquid      |      |                                          |             |            |
| 68w,91 m#    | 73sh        | 72sh          | 68,86,89,96 | A"  | (CO)⁻Fe–C_H₆ torsion                    | 76          |            |
| 101s         | 102s        | 104           | A'          | OC–Fe–CO bend (E)                      | 103         | 97         |
|              | 116sh       | 113           | A"          | OC–Fe–CO bend (E)                      | 112         | 107        |
| 137s         | 138sh       | 140           | A"          | OC–Fe–CO bend (A₁)                     | 125         | 128        |
| 143s         | 352m        | 146           | A"          | (CO)₆–Fe–C_H₆ deformation               | 141         |            |
| 351s         | 352 m       | 361           | A"          | C₂–C₁–C₁' + C₂'–C₁–C₁ in-phase bend    | 303         | 309        |
| 387 m        | 377 m       | 382           | A"          | C_H₆ tilt symmetric wrt mirror plane    | 365         |            |
| 419w         | 418w        | 417 m         | A"          | Fe–C≡O bend (A₂)                       | 441         |            |
| 455 m        | 452w,465w   | 462 m         | A"          | C_H₆ tilt symmetric wrt mirror plane    | 426         | 421        |
| 485s         | 494 m       | 492 m         | A"          | C₁–C₁' torsion                         | 400         |            |
| 514 m        | 513w        | 507 m         | A'          | Fe–CO stretch (E)                      | 489         | 479        |
| 540w         | 540         | 546           | A"          | Fe–CO stretch (A₂)                     | 509         | 509        |
| 571w         | 574w        | 563           | A"          | Fe–CO stretch (E)                      | 529         |            |
| 619w         | 612w        | 607s          | A"          | Fe–CO stretch (E)                      | 543         |            |
| 671 m        | 671 m       | 669w          | A"          | C₂–C₁–C₁' + C₂'–C₁–C₁ out-of-phase bend| 558         |            |
| 786s         | 796w        | 793w          | A"          | =CH₂ in-phase twist                    | 586         | 566        |
| 800 m        | 801         | 818           | A"          | =CH₂ out-of-phase twist                | 600         | 601        |
| 913s         | 899w        | 915           | A"          | C₁–H₁ + C₁'H₁ out-of-plane bend (wag)  | 700         | 683        |
| 925s         | 925w        | 925w          | A"          | =CH₂ out-of-phase wag                  | 711         |            |
| 958s         | 954w        | 953w          | A"          | =CH₂ in-phase rock                     | 715         | 714        |
| 972s         | 973s        | 962w          | A"          | C₁–H₁ + C₁'H₁ out-of-phase out-of-plane bend | 751         | 751        |
|              |             | 969w          | A"          | (twist)                               | 784         | 782        |
| 1056s        | 1046sh      | 1049w         | A"          | =CH₂ out-of-phase rock                 | 833         |            |
| 1167 m       | 1174w       | 1173w         | A"          | C₁–H₁ + C₁'H₁ out-of-plane in-plane bend (scissors) | 836         | 842        |
| 1200 m       | 1201w       | 1201w         | A"          | C₁–H₁ + C₁'H₁ out-of-plane in-plane bend (rock) | 948         |            |
| 1365 m       | 1371w       | 1370w         | A"          | C₁–C₁' stretch                         | 1166        | 1173       |
| 1444w        | 1442w       | 1442w         | A"          | =CH₆ out-of-phase scissors             | 961         | 973        |
| 1466 m       | 1475w       | 1478w         | A"          | =CH₆ in-phase scissors                 | 1033        | 1047       |
| 1952s        | 1968s       | 1943w         | A"          | C₁=C₂ + C₁'C₂ out-of-phase stretch     | 1306        | 1320       |
| 1972s/1982 m | 1990s/sh    | 1945vs        | A"          | C₁=C₂ + C₁'C₂ out-of-phase in-phase stretch | 1402        | 1413       |
| 2041s        | 2047s       | 2046s         | A"          | C>O stretch (E)                        | 1830        | 1978       |
| 3009s        | 3011s       | 3007w         | A"          | C>O stretch (A₁)                       | 1860        | 1988       |
|              |             | 3009w         | A"          | =CH₂ symmetric stretch, in-phase       | 2221        | 2203       |
| 3051sh       | 3062w       | 3059w         | A"          | =CH₂ symmetric stretch, out-of-phase   | 2223        |            |
| 3068 m       | 3079sh      | 3069sh        | A"          | CH stretch, out-of-phase               | 2305        | 2276       |
|              |             |               | A"          | CH stretch, in-phase                   | 2319        | 2300       |

Table 2. Observed and calculated transition energies of the internal modes (i.e. omitting translations and librations) of C₄H₆Fe(CO)₃ and C₄D₆Fe(CO)₃.
It can be seen that apart from the C1–C1′ torsional mode, the transition energies of the gauche and the s-cis conformers are almost identical. Coordination to iron results in a significant perturbation and all of the modes are shifted. The largest shift is for the C1–C1′ torsion (+611 cm⁻¹) but several modes undergo shifts greater than ±100 cm⁻¹. The most significant of these are the C=C and C–C stretch modes, which reflects

Figure 6. How the transition energies of the internal modes of butadiene are modified on going from the stable gauche form to the s-cis transition state to the s-cis coordinated to iron.

Note: the modes that undergo shifts > 100 cm⁻¹ are named and shown in colour.

Figure 7. Comparison of infrared spectra: (a) the experimental spectrum of butadiene on silica (reproduced from ref. [8] with permission of Elsevier) with calculated spectra of (b) the gauche and (c) the s-trans forms with (d) that of the iron complex. (b) and (c) are plotted on the same ordinate scale so the intensities are directly comparable.

Table 2. (Continued).

| C4H6Fe(CO)3 | C4D6Fe(CO)3 |
|-------------|-------------|
| INS/cm⁻¹    | Raman/cm⁻¹  | Infrared/cm⁻¹ | CASTEP*/cm⁻¹ | Sym$ | Description                       | CASTEP*/cm⁻¹ | Expt/£/cm⁻¹ |
| Solid       | Solid       | Liquid        | Solid       | Liquid       |     |                                    |              |             |
| 3078s       | 3145        | A′            | =CH₂ asymmetric stretch, in-phase | 2341 | 2343 | 2320 |
|             | 3147        | A″            | =CH₂ asymmetric stretch, out-of-phase | | | |

*Calculated values are the average of the factor group split quartet from the solid state calculation; $Symmetry class for the isolated molecule with C₃ symmetry.

w = weak, m = medium, s = strong, v = very, sh = shoulder.
The asymmetric tilt is generated by the combination of Fe–C stretches: (Fe–C2 + Fe–C1) out-of-phase with (Fe–C2' + Fe–C1').
The symmetric tilt is generated by the combination of Fe–C stretches (Fe–C2 + Fe–C2') out-of-phase with (Fe–C1 + Fe–C1').

Note: The model that undergoes shifts > 100 cm⁻¹ are named and shown in colour.
the decreased and increased, respectively, sp² character of the bonds.

Discussion

The spectra in Figures 3–5 emphasises the need for infrared, Raman and INS spectroscopies in order to observe all of the modes and illustrates their complementarity. INS highlights the modes involving hydrogen motion and readily accesses the low energy region, whereas the infrared and Raman spectra are generally sensitive to the carbonyl related modes. They also include the C–H stretch region, where INS spectroscopy with this type of spectrometer gives no useful information [38].

The assignments in Tables 2 and S1 differ significantly from those in the literature [29−32] (see Tables S3 and S4), particularly regarding the Fe–CO stretch and the Fe–C≡O deformation modes and the out-of-plane modes of butadiene that occur below 1000 cm⁻¹. The reason for this is that the literature assignments are based on empirical correlations and incomplete data. The INS spectra enable several of the modes to be clearly observed for the first time, the most significant of which is the C1–C1’ torsion at 485 cm⁻¹.

The adsorption of butadiene on alumina [8, 9] and silica [8] surfaces has been studied by infrared spectroscopy. On alumina, the molecule adsorbs as the s-trans conformer, but on silica the spectra were assigned to the s-cis conformer. Figure 7 compares the experimental infrared spectra of butadiene on silica with that of the iron complex and also with the calculated infrared spectra of the s-trans and gauche conformers. Although the spectral range is limited (because of the silica lattice absorption at >1400 cm⁻¹), it can be seen that the gauche conformer is easily the best match to the experimental spectrum. The question arises as to the reliability of the calculated spectra: Table 3 compares experimental infrared data [4] and that calculated here for the gauche conformer. It can be seen that both the transition energies and relative intensities are accurately reproduced, this is consistent with what was found for the iron complex, see Figures 3–5.

The experimental data [8] of butadiene on silica show a pronounced downshift of ~250 cm⁻¹ of the O–H stretch of the surface silanols when butadiene is adsorbed. To test how hydrogen-bonding of the C=C bond(s) to silanols modified the spectra of the conformers, the calculations were repeated with a water molecule present. This resulted in a weak hydrogen bond of 2.5 Å, a downshift of the O–H stretch of ~120 cm⁻¹ and negligible changes in the butadiene spectra.

Busca [8] noted that since the barrier between the s-trans and gauche conformers is less than the adsorption enthalpy of hydrocarbons on silica, stabilisation of

| Table 3. Observed and calculated transition energies and relative infrared intensities of the internal modes of gauche-C₄H₆. |
|---|---|---|---|---|---|
| CASTEP | Experimental [4] | Description |
| Transition energy/cm⁻¹ | Infrared intensity/ km mol⁻¹ | Relative infrared intensity | Transition energy/cm⁻¹ | Relative infrared intensity |
| 154 | 0.37 | 0.01 | 0.35 | C1–C’ torsion |
| 263 | 0.00 | 0.00 | 0.16 | C2–C1–C’ + C2’–C1–C1 in-plane bend |
| 459 | 15.94 | 0.27 | 472 | =CH₂ in-phase twist |
| 597 | 9.22 | 0.15 | 600 | C2–C1–C’ + C2’–C1–C1 out-of-plane bend |
| 730 | 2.97 | 0.05 | =CH₂ out-of-plane twist |
| 863 | 1.06 | 0.02 | =CH₂ in-plane rock |
| 901 | 21.83 | 0.37 | =CH₂ out-of-plane wag |
| 902 | 59.73 | 1.00 | 913 | =CH₂ in-plane wag |
| 938 | 1.89 | 0.03 | | |
| 993 | 29.90 | 0.50 | 995 | C1–H1 + C1’–H1 in-plane out-of-plane bend (wag) |
| 1035 | 0.06 | 0.00 | 1089 | C1–C1’ stretch |
| 1073 | 5.61 | 0.09 | 1089 | =CH₂ out-of-plane rock |
| 1269 | 0.25 | 0.00 | =CH₂ in-plane rock |
| 1301 | 0.11 | 0.00 | 1612 | C1=C2 + C1’–C2’ in-plane stretch |
| 1392 | 2.78 | 0.05 | 1632 | C1=C2 + C1’–C2’ out-of-plane stretch |
| 1417 | 11.02 | 0.18 | 1425 | CH stretch, out-of-phase |
| 1602 | 3.28 | 0.05 | 1612 | =CH₂ symmetric stretch, in-plane |
| 1627 | 7.40 | 0.12 | 3020 | =CH₂ symmetric stretch, out-of-plane |
| 3041 | 8.58 | 0.14 | 3142 | CH stretch, in-phase |
| 3050 | 27.44 | 0.46 | 3143 | =CH₂ asymmetric stretch, out-of-plane |
| 3052 | 4.71 | 0.08 | 3143 | =CH₂ asymmetric stretch, in-plane |
| 3058 | 2.76 | 0.05 | |
| 3142 | 15.39 | 0.26 | 3020 | 0.24 | |
| 3143 | 5.25 | 0.09 | 3143 | 0.09 | |
the gauche conformer was not surprising. Our calculations, Figure 1, show that the barrier to conversion is ~30 kJ mol\(^{-1}\), while the difference in energy of the two stable conformers is ~15 kJ mol\(^{-1}\). An empirical correlation [39] between the shift of the O–H stretch mode and the heat of adsorption, indicates that the latter is ~17 kJ mol\(^{-1}\), however, this is only half the barrier height so it suggests that there is an additional stabilisation that is specific to alumina.

**Conclusions**

This work has provided a definitive set of assignments for C\(_4\)H\(_6\)Fe(CO)\(_3\) and C\(_4\)D\(_6\)Fe(CO)\(_3\). These differ in many respects from previous work that was solely based on empirical correlations. In particular, the modes of a strongly coordinated s-cis butadiene are clearly defined. The use of INS spectroscopy has allowed observation of several of the low energy modes for the first time, the most significant of which is the C1–C1′ torsion at 485 cm\(^{-1}\).

The comparison of observed and calculated infrared spectra for butadiene on silica confirms the surprising assignment that the molecule is adsorbed as the *gauche* form.

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