

High-resolution infrared spectra of the two nonpolar isomers of 1,4-difluorobutadiene

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ABSTRACT

High-resolution (0.0013 cm^{-1}) infrared spectra have been recorded for *trans,trans*-1,4-difluorobutadiene (ttDFBD) and *cis,cis*-1,4-difluorobutadiene (ccDFBD). The rotational structure in two C-type bands (ν_{10} and ν_{12}) and one A-type band (ν_{22}) for ttDFBD and in two C-type bands (ν_{11} and ν_{12}) for ccDFBD has been analyzed. Ground state and upper state rotational constants, except for ν_{10} of ttDFBD, have been fitted. Band centers are 934.1 cm^{-1} (ν_{10}), 227.985 cm^{-1} (ν_{12}), and 1087.919 cm^{-1} (ν_{22}) for ttDFBD. Band centers are 762.891 cm^{-1} (ν_{11}) and 327.497 cm^{-1} (ν_{12}) for ccDFBD. The small inertial defects in the ground state confirm that both isomers are planar. Obtaining the ground state rotational constants for the two isomers of DFBD is a first step toward determining their semi-experimental equilibrium structures.

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1. Introduction

Viehe and Franchimont were the first to prepare the three isomers of 1,4-difluorobutadiene (DFBD) and report the unusual energy relationship among them [1,2]. The *cis,cis* isomer, which has the closest approach of the fluorine atoms to the neighboring electron-rich double bonds, has the lowest energy, and the *trans,trans* isomer, which has the fluorine atoms most distant from the double bonds, has the highest energy. Using simpler chemistry to make DFBD, Craig et al. recorded the infrared and Raman spectra and assigned all the vibrational fundamentals of the three isomers [3].

To gain insight into the unusual energy relationships in the isomers of DFBD and to examine the influence of fluorine substitution on the π -electron distribution in butadiene, we have launched a program with the goal of fitting semi-experimental equilibrium structures to the three isomers of DFBD. A preliminary semi-experimental equilibrium structure of the polar *cis,trans* isomer was determined from a combination of ground state rotational constants obtained in a microwave investigation and quantum chemical calculations [4,5]. The nonpolar *trans,trans* and *cis,cis* isomers are microwave silent and must be investigated by high-resolution infrared spectroscopy. An equilibrium structure of butadiene itself, which shows the structural effects of π -electron delocalization, has recently been published [6].

This paper presents the first results of investigating the *trans,trans* and *cis,cis* isomers of DFBD by high-resolution (0.0013 cm^{-1}) infrared spectroscopy. Ground state rotational constants are reported from the analysis of the rotational structure in two C-type bands and one A-type band of the *trans,trans* isomer and in two C-type bands of the *cis,cis* isomer.

2. Experimental

Samples were synthesized by reaction of *cis*-3,4-dichlorocyclobutene (Fluka) with silver difluoride (Aldrich) to give mostly *trans*-3,4-difluorocyclobutene, which was isomerized at $100\text{ }^\circ\text{C}$ with iodine catalysis to give a mixture of the three isomers of 1,4-difluorobutadiene [3]. Individual isomers were isolated by preparative gas chromatography [3]. For shipping, samples were inhibited with hydroquinone and sealed in glass ampoules.

High-resolution spectra were recorded on a Bruker IFS 125 FS spectrometer at PNNL. Samples were contained in a multi-pass White cell. Table 1 summarizes the conditions used in recording the spectra. Initial spectra of the first C-type bands of the *trans,trans* and *cis,cis* isomers were recorded with 0.0018 and 0.0021 cm^{-1} resolution, respectively, by Dr. Michael Lock on the Bruker 120 instrument at Justus Liebig Universität in Giessen, Germany.

Finding and working with subband series was greatly aided by use of Loomis–Wood pattern-recognition software [9]. A number of locally written Fortran programs also assisted in handling the

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Table 1
Experimental conditions for spectra.

| Region/cm ⁻¹ | Resolution/cm ⁻¹ | Beam-splitter | Detector | No. of scans | Pathlength/m | Press./Torr | Calibrant gas |
|-------------------------|-----------------------------|---------------|---------------------|--------------|--------------|-------------|-------------------------------|
| <i>ttDFBD</i> | | | | | | | |
| 600–1000 | 0.0015 | KBr | HgCdTe ^a | 704 | 12.8 | 0.178 | CO ₂ ^b |
| 600–1100 | 0.0013 | KBr | HgCdTe ^a | 768 | 3.2 | 0.077 | CO ₂ ^b |
| 600–1100 | 0.0013 | KBr | HgCdTe ^a | 256 | 3.2 | 0.032 | CO ₂ ^b |
| 190–500 | 0.0013 | Mylar | Si ^c | 128 | 12.8 | 0.46 | H ₂ O ^d |
| <i>ccDFBD</i> | | | | | | | |
| 600–1070 | 0.0014 | KBr | HgCdTe ^a | 256 | 3.2 | 0.26 | CO ₂ ^b |
| 600–1000 | 0.0013 | KBr | HgCdTe ^a | 384 | 3.2 | 0.12 | CO ₂ ^b |
| 200–650 | 0.0013 | Mylar | Si ^c | 96 | 19.2 | 0.33 | H ₂ O ^d |
| 150–700 | 0.0013 | Mylar | Si ^c | 96 | 3.2 | ~0.5 | H ₂ O ^d |

^a Liquid nitrogen temperature.

^b Ref. [7].

^c Bolometer; liquid helium temperature.

^d Ref. [8].

large datasets. For fitting ground state combination differences (GSCDs) to the ground state (GS) rotational constants in a Watson-type Hamiltonian [10], a modification of Dr. Arthur Maki's ASYM program was employed. The asymmetric reduction and the I^r representation were used. Redundant use of lines from subband series with asymmetry splitting was avoided in computing GSCDs. Upper state (US) rotational constants were fitted to similar Hamiltonians with the GS constants held fixed. As needed, some quartic centrifugal distortion constants were supplied from calculations using a B3LYP/aug-cc-pVTZ model with Gaussian 03 (G03) software [11]. Cartesian coordinates were transformed into the principal axis system before use in the vibration–rotation module of G03 [12,13].

3. Results and discussion

3.1. General considerations

As shown schematically in Fig. 1, both *trans,trans*- and *cis,cis*-DFBD are near-prolate symmetric tops with C_{2h} symmetry. Twelve of their 24 normal modes are infrared active. The a principal rotation axis passes through the center of inversion and roughly bisects the C–F bonds. The b -axis also lies in the plane of the molecule. The c rotation axis is perpendicular to the molecular plane. Consequently, the normal modes of the b_u symmetry species, which have displacements in the molecular plane, give hybrid A/B-type band shapes in gas phase infrared spectra. Normal modes of the a_u symmetry species with displacements perpendicular to the molecular plane give C-type band shapes. Only A-type and C-type bands were investigated in this study. Selection rules for rotational transitions in A-type bands are $\Delta J = 0, \pm 1$; $\Delta K_a = 0$; and $\Delta K_c = \pm 1$. Selection

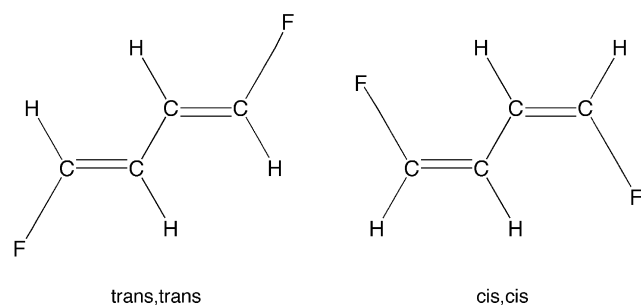


Fig. 1. Schematic structures for *trans,trans*-1,4-difluorobutadiene and *cis,cis*-1,4-difluorobutadiene.

rules for rotational transitions in C-type bands are $\Delta J = 0, \pm 1$; $\Delta K_a = \pm 1$; and $\Delta K_c = 0, \pm 2$.

3.2. Revised assignments of fundamentals

A reconsideration of the two lowest vibrational frequencies for the *trans,trans* isomer has led to an exchange of their assignments. Our previous assignment gave $\nu_{13}(a_u)$ the higher frequency and $\nu_{24}(b_u)$ the lower frequency, despite the predictions from quantum chemical calculations available at that time [3]. The problem in making these two assignments is the complex band shape of the gas phase infrared spectrum in the region from 170 to 130 cm⁻¹ [3]. Our high-resolution infrared scan in the low frequency region did not go low enough to provide new information. In the previous assignment, the apparent Q branch at 154 cm⁻¹ was decisive in making the assignments. We now prefer to assign the depression at 147 cm⁻¹ as the center of a B-type band for ν_{24} and regard the structure with added intensity near 133 cm⁻¹ as the overlap of the P branch of the band for ν_{24} and the Q branch for ν_{13} . Taking a frequency in the lower part of the overlapped band gives an approximate frequency for ν_{13} of 127 cm⁻¹. Not only does this revised interpretation conform to the band shapes, but it also agrees with the new predictions from the DFT calculations, which give, without any scaling, 145 cm⁻¹ for ν_{24} and 124 cm⁻¹ for ν_{13} . These predictions are very close to the previous Adiabatic Connection Method calculations, which gave 146 and 127 cm⁻¹, respectively [3]. The normal coordinate for ν_{24} has a substantial contribution from CF in-plane bending, and the normal coordinate for ν_{13} has a substantial amount of out-of-plane CF bending. The nearly perpendicular CF motions in these two modes are favorable for Coriolis coupling, and the direct product of these two modes has the correct symmetry species for Coriolis coupling. Such coupling could cause large perturbations in the rotational states and the intensities of the two bands, as was seen for *trans*-1,2-difluoroethylene, which is a similar case [14].

We also note a typographical error in one fundamental frequency reported for the *cis,cis* isomer of DFBD [3]. The frequency for ν_{16} observed in the liquid-phase Raman spectrum should be 560 cm⁻¹ instead of 580 cm⁻¹. We discovered this error by its effect on the interpretation of a Fermi resonance. Two similar bands of the same intensity occur at 644 and 620 cm⁻¹ in the gas phase infrared spectrum of *ccDFBD*. The fundamental for $\nu_{23}(b_u)$ is expected in this region. The correction for ν_{16} gives 638 cm⁻¹ for the estimate of the $\nu_{13} + \nu_{16}$ combination tone, as was correctly reported [3] and as would be reasonable for Fermi resonance between the combination state of B_u symmetry and the $\nu_{23}(b_u)$ fundamental. The absence of any Q-branch features in either band in the high-resolution infrared spectrum confirms that both bands

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