Rotational constants and structure of para-difluorobenzene determined by femtosecond Raman coherence spectroscopy: A new transient type
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Rotational constants and structure of para-difluorobenzene determined by femtosecond Raman coherence spectroscopy: A new transient type

Takuya Den,1 Hans-Martin Frey,1 Peter M. Felker,2 and Samuel Leutwyler1,a)

1Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland
2Department of Chemistry and Biochemistry, University of California at Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095-1569, USA

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Femtosecond Raman rotational coherence spectroscopy (RCS) detected by degenerate four-wave mixing is a background-free method that allows to determine accurate gas-phase rotational constants of non-polar molecules. Raman RCS has so far mostly been applied to the regular coherence patterns of symmetric-top molecules, while its application to nonpolar asymmetric tops has been hampered by the large number of RCS transient types, the resulting variability of the RCS patterns, and the $10^3$–$10^4$ times larger computational effort to simulate and fit rotational Raman RCS transients. We present the rotational Raman RCS spectra of the nonpolar asymmetric top 1,4-difluorobenzene (para-difluorobenzene, p-DFB) measured in a pulsed Ar supersonic jet and in a gas cell over delay times up to $\sim$2.5 ns. p-DFB exhibits rotational Raman transitions with $\Delta J = 0, 1, 2$ and $\Delta K = 0, 2$, leading to the observation of $J^+$, $K^-$, $A^-$, and C-type transients, as well as a novel transient (S-type) that has not been characterized so far. The jet and gas cell RCS measurements were fully analyzed and yield the ground-state ($v = 0$) rotational constants $A_0 = 5637.68(20)$ MHz, $B_0 = 1428.23(37)$ MHz, and $C_0 = 1138.90(48)$ MHz (1σ uncertainties). Combining the $A_0, B_0,$ and $C_0$ constants with coupled-cluster with single-, double- and perturbatively corrected triple-excitation calculations using large basis sets allows to determine the semi-experimental equilibrium bond lengths $r_e(C\text{-}C_2) = 1.3849(4)$ Å, $r_e(C_2\text{-}C_3) = 1.3917(4)$ Å, $r_e(C\text{-}F) = 1.3422(3)$ Å, and $r_e(C_2\text{-}H_2) = 1.0791(5)$ Å. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4932602]

I. INTRODUCTION

Fluorinated compounds are rare in nature but are widely used in pharmaceuticals, medicine, and for agricultural applications. A major trend in pharmaceutical chemistry has been to introduce F atoms to change the chemical and physicochemical properties (such as the hydro/lipophilicity, H-bonding properties, and biodegradability) of previously known pharmaceutically active molecules.

In order to treat the effects of H/F substitution by quantum chemistry, highly correlated methods with very large basis sets must be used, since the high nuclear charge of the F atom increases the relative importance of electron correlation. Thus, the performance of both the computational methods and the basis sets must be benchmarked for fluorinated compounds; for this, accurate experimental data are needed. Demaison et al.1 have examined the experimentally available high-accuracy experimental structures and bond lengths of fluorobenzenes with one to six fluorene atoms, and compared these to the predictions of coupled-cluster with single-, double- and perturbatively corrected triple-excitation [CCSD(T)] calculations using systematically larger basis sets.1 The accurate structural data from microwave spectroscopy were only available for non-centrosymmetric (and hence polar) fluorobenzenes,1 while inversion-symmetric molecules are not accessible by microwave spectroscopy. Using femtosecond (fs) Raman rotational coherence spectroscopy (RCS), the Bern group has previously determined rotational and centrifugal distortion constants for the symmetric tops 1,3,5-trifluorobenzene (TFB) and hexafluorobenzene (HFB) by fitting the experimental RCS transients.2,3 Combining these results with CCSD(T) correlated calculations allowed to determine semieperimental C–F and C–C bond lengths.1–3

Para-difluorobenzene (p-DFB), shown in Figure 1, is also nonpolar. However, compared to the treatments of the symmetric top molecules TFB and HFB, the asymmetric-top Raman RCS simulations are significantly more involved: First, the asymmetric-top rotational eigenfunctions and energy eigenvalues $E(J, K_1, K_2)$ must be computed numerically, in contrast to symmetric tops whose rotational level energies can be expressed analytically. Second, the rotational Raman transition intensities of symmetric tops are given analytically by the Placzek-Teller factors,4,5 which involve only a few multiplication and division operations, while for asymmetric tops, the evaluation of the rotational Raman intensities involves $\sim J^3$ floating-point operations.4 Third, the three different diagonal (in some cases also off-diagonal) components of the molecular polarizability tensor of asymmetric-top molecules give rise to different rotational transient types.6–8 Thus, the computational time required to generate asymmetric-top Raman RCS transients is typically $10^3$–$10^4$ times larger than for symmetric-rotor RCS transients. The C–C and C–F bond lengths of gas-phase p-DFB have previously been determined by Domenicano et al. using the
The fs degenerate four-wave mixing setup at the University of Bern has been previously described. Briefly, three parallel laser beams from an amplified Ti:Sapphire laser system provide the ~75 fs pulses at 800 nm employed for the stimulated Raman pump, dump, and probe steps. The stimulated Raman polarization induced by the pump/dump steps at time zero is detected by the DFWM signal generated from the time-delayed probe pulse. The energy of the three laser pulses is ~100 µJ/pulse per beam. The three pulse trains are spatially overlapped and focused by an f = 1000 mm achromatic lens in a folded BOXCARs arrangement. For the supersonic jet experiments, in which intermolecular collisions that lead to decoherence of the rotational wave packet are strongly reduced, the p-difluorobenzene (Sigma Aldrich, ≥99% purity) is heated to 70 °C, mixed with Ar carrier gas to a total backing pressure of P0 = 400 mbar and sent through a pulsed valve (0.45 mm nozzle diameter) operating at a repetition rate of 333 Hz. The supersonic jet expands into a ~0.1 mbar vacuum. The DFWM mixing signal is generated in the overlap volume of the three laser beams within the core of the supersonic-jet expansion at a distance of ~2 mm from the nozzle. After the output window of the vacuum chamber, the intense pump, dump, and probe laser pulses are blocked by a mask, while the DFWM signal beam is recollimated, spatially filtered, and detected by a cooled GaAs photomultiplier. The transients are obtained by scanning the delay time in steps of ~20 fs, giving 7 data points on the instrument response function of 140 fs. Analogous measurements were performed in a static gas cell at room temperature (T = 293 K) and a p-DFB pressure of 15 mbar.

2. Computational methods

The structure optimizations of para-difluorobenzene were first performed using the second-order Möller Plesset (MP2) method with the cc-pVTZ basis set. Subsequently, the structures were re-optimized using the coupled-cluster CCSD(T) method and the correlation-consistent weighted core-valence polarized cc-pwCVTZ and cc-pwCVTZ basis sets. All electrons were correlated and D2h symmetry was enforced throughout. At the CCSD(T)/pwCVTZ equilibrium geometry, the anharmonic vibrational frequencies and the vibration-dependent rotational constants A, B, and C were calculated with an anharmonic cubic force fields derived using analytical second-derivative techniques. All calculations were carried out with the CFOUR program.

II. ROTATIONAL RAMAN COHERENCE SPECTROSCOPY OF ASYMMETRIC-TOP MOLECULES

A. Modeling the degenerate four-wave mixing signal:

Rotational Raman RCS spectroscopy is a time-dependent variant of DFWM that can be applied to polar and non-polar molecules. In off-resonant four-wave mixing — which is appropriate here, since p-DFB is com-
completely transparent at the 800 nm laser wavelength — the DFWM signal of the gas sample is proportional to the square modulus of its time-dependent third-order susceptibility, \( \chi^{(3)}(t) \), which can be written as

\[
I(t) = \int_{-\infty}^{\infty} G(\tau) |\chi^{(3)}(t - \tau)|^2 d\tau,
\]

where \( G(\tau) \) is the experimental apparatus function, which is determined by the triple temporal convolution of the fs Raman pump/dump and probe pulses. \( G(\tau) \) was measured prior to each RCS experiment using the electronic zero-time Kerr-effect signal of the Ar carrier gas in the supersonic jet and is closely represented by a Gaussian of 140–150 fs full width at half maximum. The \( \chi^{(3)}(t) \) associated with fs DFWM induced coherences between asymmetric-top rotational states is given by

\[
\chi^{(3)}(t) \sim C + \sum_{\Gamma<\Gamma'} b_{\Gamma,\Gamma'} \sin[(E_{\Gamma'} - E_{\Gamma})\tau/\hbar],
\]

where \( \Gamma \equiv J_\tau \) and \( \Gamma' \equiv J'_\tau \) denote asymmetric-top energy levels, \( E_{\Gamma} \) and \( E_{\Gamma'} \) are their respective energies, \( b_{\Gamma,\Gamma'} \) are the modulation amplitudes, and the summation is over all those pairs of levels for which \( E_{\Gamma'} < E_{\Gamma} \). In general, we work at experimental conditions where the background parameter \( C \) is zero, as in Figs. 3(a)-3(g), and so \( C \) is not a fit parameter.

The dynamic range of the current measurements corresponds to a signal/noise ratio \( S/N \sim 1000:1 \) for the strongest recurrences. The weakest recurrences that are used in the RCS fit have \( S/N \sim 8:1 \). The main factors determining the signal intensity \( I(t) \) (and limiting the significant digits of the derived rotational constants) have been discussed in Ref. 20; very briefly these are (1) the anisotropy of the molecular polarizability tensor \( \Delta \alpha \), which is given in the last line of Table III. The signal is proportional to the fourth power of \( \Delta \alpha \). (2) The gas-phase density of \( p \)-DFB at 70 °C, which is the maximum operating temperature of our 333 Hz pulsed valve. For the cell measurement, the current limit is the vapor pressure of the substance at room temperature. The signal \( I(t) \) depends on the square of the gas-phase density.

In order to model the degenerate four-wave mixing signal, one first has to calculate the rotational energy levels of an asymmetric top \( E_{\Gamma} \) and the corresponding rotational eigenfunctions. From these, the rotational Raman transition intensities need to be calculated for all pairs of levels that contribute to the rotational beating. These procedures are detailed in Subsections II B and II C.

B. Energy levels of asymmetric-top molecules

The asymmetric-top energy levels are determined by diagonalization of the asymmetric-top Hamiltonian in a symmetric-top basis, as described in detail in, e.g., Gordy and Cook.\(^{39}\) By the spectral theorem, the asymmetric-top eigenfunctions \( |\Gamma M \rangle \) can be expressed as a linear combination of symmetric-top eigenfunctions \( |JKM \rangle \),

\[
|\Gamma M \rangle = |J\tau M\rangle = \sum_{K=-J}^{J} a(\Gamma, K)|JKM\rangle,
\]

where \( \tau = K_{-1} - K_{1} \) is the difference of the corresponding prolate and oblate symmetric-top state \( K \) quantum numbers.

![FIG. 2. Center: Schematic rotational energy level scheme for an asymmetric top molecule, as a function of \( \kappa \) = -1.0 to +1.0, corresponding to prolate (left) and oblate (right) symmetric-top limits, see the text. The \( \kappa = -0.87 \) for \( para \)-difluorobenzene is marked as a vertical dashed line. Symmetric-top levels with the same \( |K| \) values are degenerate, as indicated at the extreme left and right; this degeneracy is lifted in asymmetric tops. The rotational quantum numbers are \( J, K_{11}, K_{-1}, \tau = K_{-1} - K_{11} \), see the text. Examples of allowed rotational transitions are drawn as arrows, together with the RCS transient types (K-type, J-type, etc.) to which they contribute.](image-url)
The relationship of the irreducible spherical polarizability components $\alpha_k^{(j)}$ to their molecular polarizability Cartesian counterparts $\alpha_{\mu\nu}^{(j)}$ is discussed below.

The subscripts $-1$ and $+1$ refer to Ray’s asymmetry parameter $\kappa = (2B_0 - A_0 - C_0)/(A_0 - C_0)$, where the prolate symmetric-top limit corresponds to $\kappa = -1$ and the oblate symmetric-top limit to $\kappa = +1$. As usual, $K = J, J - 1, \ldots, -J$ denotes the projection of the total angular momentum $J$ on the major molecule-fixed principal axis, which for $p$-DFB is the $a$-axis, as indicated in Figure 1.

The rotational energy levels of an asymmetric-top molecule lie between the prolate and oblate limits, as shown in Figure 2. In contrast to symmetric-top states, which are degenerate for $J$-states with the same absolute $K$ value, no such degeneracy exists in asymmetric tops. In fact, $K$ is not a good quantum number for asymmetric-tops, instead states are specified by $J$ and $\tau$. However, for molecules that are only slightly asymmetric, $K_1$ and $K_{-1}$ are still approximately good quantum numbers. The rotational Raman selection rules that are discussed below are those for a prolate asymmetric top with $K \sim K_{-1}$.

### Table I

<table>
<thead>
<tr>
<th>$\Delta J$</th>
<th>$\Delta K$</th>
<th>$\alpha_k^{(j)}$</th>
<th>$\alpha_{\mu\nu}^{(j)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\alpha_2^{(2)}$</td>
<td>$\frac{1}{2}(\alpha_{xx} - \alpha_{yy}) + i(\alpha_{xy} + \alpha_{yx})$</td>
<td></td>
</tr>
<tr>
<td>±2</td>
<td>$\alpha_1^{(2)}$</td>
<td>$\frac{1}{2}(\alpha_{zz} + i(\alpha_{xz} + \alpha_{zy}))$</td>
<td></td>
</tr>
<tr>
<td>±1</td>
<td>0</td>
<td>$\alpha_0^{(2)}$</td>
<td>$\frac{1}{2}(2\alpha_{zz} - (\alpha_{xx} + \alpha_{yy}))$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{-1}^{(2)}$</td>
<td>$\frac{1}{2}(\alpha_{zz} + i(\alpha_{xz} - \alpha_{zy}))$</td>
<td></td>
</tr>
<tr>
<td>±2</td>
<td>$\alpha_2^{(2)}$</td>
<td>$\frac{1}{2}(\alpha_{xx} - \alpha_{yy} - i(\alpha_{xy} + \alpha_{yx}))$</td>
<td></td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Transient type</th>
<th>Position $\tau$</th>
<th>Contributing rotational transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric top transients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J$-type</td>
<td>$n/(2B + C)$</td>
<td>$</td>
</tr>
<tr>
<td>$K$-type</td>
<td>$n/(4A - 2B - 2C)$</td>
<td>$</td>
</tr>
<tr>
<td>Asymmetry transients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$-type</td>
<td>$n/4A$</td>
<td>$</td>
</tr>
<tr>
<td>$C$-type</td>
<td>$n/4C$</td>
<td>$</td>
</tr>
<tr>
<td>$S$-type</td>
<td>$n/(B + C)$</td>
<td>$</td>
</tr>
</tbody>
</table>

### Table III

<table>
<thead>
<tr>
<th>Rotational constants/MHz</th>
<th>MP2/ cc-pVDZ</th>
<th>MP2/ cc-pVTZ</th>
<th>CCSD(T)/ cc-pwCVDZ</th>
<th>CCSD(T)/ cc-pwCVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_e$</td>
<td>5606.3773</td>
<td>5729.6911</td>
<td>5583.1890</td>
<td>5682.0176</td>
</tr>
<tr>
<td>$B_e$</td>
<td>1404.4182</td>
<td>1436.6530</td>
<td>1401.2265</td>
<td>1429.6374</td>
</tr>
<tr>
<td>$C_e$</td>
<td>1123.0820</td>
<td>1148.6440</td>
<td>1120.1098</td>
<td>1142.2412</td>
</tr>
<tr>
<td>$A_0$</td>
<td>5559.1102</td>
<td>5683.4993</td>
<td>5533.7189</td>
<td>5583.1890</td>
</tr>
<tr>
<td>$B_0$</td>
<td>1398.3884</td>
<td>1429.8832</td>
<td>1395.1471</td>
<td>1429.6374</td>
</tr>
<tr>
<td>$C_0$</td>
<td>1117.2885</td>
<td>1142.4076</td>
<td>1114.1976</td>
<td>1142.2412</td>
</tr>
<tr>
<td>$\Delta A = A_e - A_0$</td>
<td>47.2671</td>
<td>46.1917</td>
<td>49.4701</td>
<td>50.1403</td>
</tr>
<tr>
<td>$\Delta B = B_e - B_0$</td>
<td>6.0298</td>
<td>6.7697</td>
<td>6.0795</td>
<td>6.2366</td>
</tr>
<tr>
<td>$\Delta C = C_e - C_0$</td>
<td>5.7935</td>
<td>6.2366</td>
<td>5.9122</td>
<td>5.9122</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Centrifugal distortion constants/kHz</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>$\delta f$</td>
<td>0.0352</td>
</tr>
<tr>
<td>$\delta k$</td>
<td>1.0060</td>
</tr>
<tr>
<td>$\delta_{jk}$</td>
<td>0.0448</td>
</tr>
<tr>
<td>$\delta_{jk}$</td>
<td>0.0082</td>
</tr>
<tr>
<td>$\delta_{jk}$</td>
<td>0.1403</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polarizability tensor elements/bohr$^3$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{aa}$</td>
<td>71.7</td>
</tr>
<tr>
<td>$\alpha_{bb}$</td>
<td>71.8</td>
</tr>
<tr>
<td>$\alpha_{cc}$</td>
<td>25.1</td>
</tr>
<tr>
<td>$\alpha_{off}$</td>
<td>0.9957</td>
</tr>
</tbody>
</table>

### C. Rotational Raman selection rules and Raman intensities for asymmetric tops

The rotational Raman selection rules pertaining to the pairs of levels $(\Gamma M')$ and $(\Gamma'M')$ that contribute to Eq. (2) are established by finding non-zero values of the rotational Raman transition moment $(\Gamma'M'|\tilde{a}|\Gamma M')$, where $\tilde{a}$ is the $3 \times 3$ molecular polarization tensor, defined in a molecule-fixed Cartesian axis system. For a detailed derivation for symmetric tops, see Ref. 41. With our choice of the molecule-fixed coordinate system for $p$-DFB, $\alpha_{zz} = \alpha_{aa}$, $\alpha_{yy} = \alpha_{bb}$, and $\alpha_{xx} = \alpha_{cc}$.

The analogous procedure can be applied to asymmetric-top states, as these can be written as a superposition of symmetric-top states, see Eq. (3). An elegant way to deal with the
rotational Raman transition moment integrals is to decompose \( \alpha \) into irreducible spherical polarizability tensor components, \( \alpha^{(j)}_k \), and then use angular momentum coupling rules. The \( \alpha^{(j)}_k \) can be regarded as angular momentum states \( |J = j, K = k\rangle \), where \( k \) runs from \(-j\) to \(+j\). Detailed analysis shows that for \( p\)-DFB, only the tensor components \( \alpha^{(2)}_k \) contributes to the RCS signal. Each element in \( \alpha^{(2)}_k \) can be constructed as a linear combination of the molecular Cartesian polarizability tensor components in the way shown in Table I. In principle the detailed shape of the RCS transient allows to fit the relative ratio of the different \( \alpha^{(2)}_k \) contributions. Also, the dependence of the allowed changes in \( K \) quantum number on the molecular polarizability tensor components allows deeper insight into the simulated RCS transient: For example, if one is interested only in coherences with \( \Delta J = 1, 2 \) and \( \Delta K = 0 \), the molecular polarizability is set to values such that \( \alpha_{xx} = \alpha_{yy} \neq \alpha_{zz} \) and \( \alpha_{\text{off-diagonal}} = 0 \).

D. Rotational Raman transient types

For rotational quantum beats to be produced according to Eq. (2), the rotational transition frequencies must be correlated in a specific way, otherwise the individual sine terms interfere destructively and no time dependence on \( \chi^{(3)} \) is observed. Constructive interference is possible if two conditions hold: (1) The individual terms have to be phase locked. This is imposed by the experimental conditions as the coherent rotational wavepacket is explicitly created by the stimulated Raman pump and dump pulses. (2) The transition frequencies \( (E(\Gamma') - E(\Gamma))/\hbar \) must be correlated. Regular frequency spacing can be shown to occur for (rigid) symmetric-top rotors, e.g., \( E(J, K) = BJ(J + 1) + (A - B)K^2 \) for a prolate symmetric top. In asymmetric tops, for which the frequency regularities of symmetric-tops do not apply, one might expect that the time-dependent part of \( \chi^{(3)} \) does not survive thermal averaging. However, Felker and co-workers have shown that even for

![Experimental and simulated femtosecond rotational Raman RCS spectrum of \( p\)-DFB in a supersonic-jet for delay time \( t = 50-1400 \) ps (\( T_{rot} = 130 \) K). The two top panels show the complete RCS spectrum; (a)-(i) show magnified subsections of \( \sim 100 \) ps length.](image-url)
TABLE IV. CCSD(T)/cc-pwCVDZ calculated vibrational frequencies (in cm$^{-1}$) up to $\nu_{15}$, vibrational populations (in %) at 130 K and 293 K, and the three calculated rotation-vibration constants $\alpha^A$,$B$,C (in MHz).

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Wavenumber</th>
<th>Population (130 K)</th>
<th>Population* (293 K)</th>
<th>$\alpha^A$</th>
<th>$\alpha^B$</th>
<th>$\alpha^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>0</td>
<td>77.5</td>
<td>25.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>159.5</td>
<td>13.3</td>
<td>11.7</td>
<td>26.15</td>
<td>-0.64</td>
<td>-1.06</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>342.4</td>
<td>1.8</td>
<td>4.9</td>
<td>-24.23</td>
<td>0.08</td>
<td>0.47</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>377.4</td>
<td>1.2</td>
<td>4.1</td>
<td>65.06</td>
<td>-0.88</td>
<td>-0.82</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>422.1</td>
<td>0.7</td>
<td>3.3</td>
<td>5.06</td>
<td>-0.19</td>
<td>-0.56</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>437.3</td>
<td>0.6</td>
<td>3.1</td>
<td>-62.61</td>
<td>-0.19</td>
<td>1.15</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>448.5</td>
<td>0.5</td>
<td>2.9</td>
<td>-0.81</td>
<td>-0.11</td>
<td>-0.65</td>
</tr>
<tr>
<td>$\nu_{13}$</td>
<td>522.0</td>
<td>0.2</td>
<td>2.1</td>
<td>-0.48</td>
<td>0.17</td>
<td>-0.46</td>
</tr>
<tr>
<td>$\nu_{14}$</td>
<td>637.6</td>
<td>0.1</td>
<td>1.2</td>
<td>6.89</td>
<td>-0.02</td>
<td>0.34</td>
</tr>
<tr>
<td>$\nu_{15}$</td>
<td>656.6</td>
<td>0.1</td>
<td>1.1</td>
<td>-5.38</td>
<td>-0.22</td>
<td>-0.45</td>
</tr>
</tbody>
</table>

*Vibrational partition function truncated at 1000 cm$^{-1}$.

very asymmetric molecules, significant subsets of the rotational levels retain sufficiently regular frequency spacings.$^{6,8,42}$ These subsets produce transients that are characterized by their recurrence time and polarity. Transients are named either by their main contributing coherences ($J$-type and $K$-type) or by the rotational constants about which they convey information ($A$-type and $C$-type). Relevant transient types are listed in Table II and shown in Figure 2.$^{8,39}$ Note that a coherence

para-Difluorobenzene sub-transient analysis

![Detailed assignment of the supersonic-jet rotational RCS transient of p-DFB for time delays $t = 40–470$ ps: (a) complete experimental transient, (b) complete simulated transient, (c)-(g) simulated sub-transients generated by restricting the coherences to specific $\Delta J$, $\Delta K$ changes.](image-url)
TABLE V. Ground state rotational constants (in MHz) of \( p \)-difluorobenzene determined by different methods.

<table>
<thead>
<tr>
<th>Constant</th>
<th>CCSD(T)/cc-pwCVTZ(^a)</th>
<th>fs-DFWMB</th>
<th>( S_0/S_1 ) state model(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>5682.02</td>
<td>5637.68(19)</td>
<td>5639.1</td>
</tr>
<tr>
<td>( B_0 )</td>
<td>1429.64</td>
<td>1428.23(37)</td>
<td>1428.2</td>
</tr>
<tr>
<td>( C_0 )</td>
<td>1142.24</td>
<td>1138.90(48)</td>
<td>1139.5</td>
</tr>
</tbody>
</table>

\(^a\)CCSD(T)/cc-pwCVTZ calculated \( A_e, B_e \) and \( C_e \) corrected by CCSD(T)/cc-pwCVDZ calculated \( \Delta A, \Delta B \) and \( \Delta C \) from Table III.

\(^b\)±1σ uncertainties in parentheses.

\(^c\)Reference 10.

specified by a specific \( \Delta J , \Delta K \) cannot always be assigned to a single transition type. Thus, \( p \)-DFB coherences with \( \Delta J = 2, \Delta K_{-1} = 0 \) contribute intensity to both \( J \)-type as well as \( C \)-type transients.

E. Fitting procedure and data analysis

The asymmetric-top rotational coherence transients are generated and fitted to the experimental RCS signals using an IDL (Interactive Data Language) program (RSI, Inc.) that employs a Levenberg-Marquardt nonlinear least-squares fit. The program for calculating the asymmetric-top states and the rotational Raman transition amplitudes is written in FORTRAN. The evaluation of the transients is parallelized and distributed over 12 processors with a shared library written in C under the OPENMP protocol.

For the rotational constant fit, the initial values \( A_0, B_0, \) and \( C_0 \) were taken from the CCSD(T)/cc-pwCVDZ calculations, see Table III. The highest rotational level considered in the simulations was \( J_{max} = 150 \), corresponding to a cumulative rotational population of \( \sim 99\% \) at \( T = 130 \) K, which is the rotational temperature in the supersonic jet, see below. The measured apparatus function was \( G(t) = 140 \) fs. The \( A \)-reduced centrifugal distortion constants and the \( \alpha_{aa} \) and \( \alpha_{cc} \) components of the molecular polarizability tensor were taken from the CCSD(T)/cc-pwCVDZ calculation and were fixed to these values throughout the fit. The parameters that were varied to fit the computed RCS transient to experiment were the rotational constants \( A_0, B_0, \) and \( C_0 \), and the rotational temperature \( T_{rot} \). The ratio of the polarizability tensor component

![Image of gas-cell RCS transient](image_url)

FIG. 5. Top panel: Gas-cell RCS transient \( (T = 293 \) K) of \( para \)-difluorobenzene: (a) Comparison of RCS simulation and measurement from \( t = 50-1000 \) ps, (b) from \( t = 1000-2000 \) ps. The rich fine structure is well reproduced by the simulation upon including signal contributions from the low-lying vibrational levels \( \nu_7, 2\nu_7, \nu_8, \) and \( \nu_9 \), see Figure 6 for details.
\( \alpha_{bb} \) relative to \( \alpha_{aa} \) and \( \alpha_{cc} \) influences the relative intensity of \( \Delta K = 0 \) and \( \Delta K = 2 \) transitions, see the last line of Table I. This ratio was fitted in a final fitting round, holding the rotational constants fixed.

### III. RESULTS AND DISCUSSION

#### A. Supersonic jet measurements and assignments

The Raman RCS transient of \( p \)-DFB in a pulsed Ar supersonic jet was measured over the \( t = 0 \)–1400 ps time range and is shown in Figure 3. From the widths of the recurrences, the effective rotational temperature was determined to be \( T_{rot} \approx 130 \pm 5 \) K. This value agrees well with the translational temperature \( T_{trans} = 130 \) K calculated at \( x = 2.0 \) mm from the nozzle exit. Upstream molecules (closer to the nozzle) are at higher temperature than downstream molecules. The calculated translational temperature change along the jet axis between the upstream and downstream edges of the four-wave mixing overlap area is 3.5 K, i.e., the upstream edge is at 132 K, the downstream edge at 128.5 K. The stated \( \pm 5 \) K uncertainty should be understood to include such spatial averaging effects.

Based on the CCSD(T) harmonic vibrational frequencies given in Table IV (see Table S1 of the supplementary material for a full list),\(^{16}\) about \( \sim 78\% \) of the \( p \)-DFB population is in the \( v = 0 \) vibrational ground state at this temperature. Due to the quadratic dependence of \( \chi^{(3)} \) on the population of a given level (Eqs. (1) and (2)), the \( v = 0 \) population accounts for \( \sim 97\% \) of the DFWM signal. As mentioned above, we varied \( \alpha_{bb} \) to fit the observed ratio of the \( \Delta K = 0/\Delta K = 2 \) transitions, which is given by \( (2\alpha_{aa} - \alpha_{bb} - \alpha_{cc})/(\alpha_{bb} - \alpha_{cc}) \). The fitted ratio is \( 1.04 \pm 0.06 \), which is in good agreement with the CCSD(T) calculated ratios of 0.996–1.051 given in Table III.

There is practically no collisional dephasing in the supersonic jet, as we have shown experimentally for the symmetric-top molecules cyclohexane, trifluorobenzene, and hexafluorobenzene.\(^{1,3,4}\) Due to the irregular spacing of the transition frequencies in asymmetric-top molecules, their RCS transients decays more rapidly with time than compared to symmetric-top molecules; this is already quite marked given the sizable asymmetry of \( p \)-DFB with \( \kappa = -0.87 \). Thus, the RCS transient of hexafluorobenzene shows observable recurrences up to \( t \approx 5000 \) ps delay,\(^3\) but the last observable recurrences of \( p \)-DFB lie at \( t \approx 1375 \) ps, see Figure 3(i).

The asymmetric-top character and the polarizability tensor of \( p \)-DFB permits transitions with \( \Delta J = 0, 1, 2 \) and \( \Delta K = 0, 2 \). We thus expect \( J \)-, \( K \)-, \( A \)-, and \( C \)-type transients, as shown in Table II. Many features in the RCS transient of \( p \)-DFB can be straightforwardly assigned based on the expected recurrence times listed in Table II. For a more detailed analysis, we decomposed the RCS transient into sub-transients corresponding to coherences for specific \( \Delta J \) and \( \Delta K \). This procedure captures interferences between different coherences and allows to assign even small RCS signals to specific transient types. Since asymmetric-top states are eigenfunctions of the total angular momentum \( J \), see Eq. (3), one can restrict \( \Delta J \) to select for a subset of transitions. As outlined above, the coherences for specific \( \Delta K \) transitions are selected by setting specific values for the polarizability tensor elements. Combining \( \Delta J \) and \( \Delta K \) restrictions allows to simulate five different sub-transients, i.e., with \( \Delta J = 0/\Delta K = 2 \), \( \Delta J = 1/\Delta K = 0 \), \( \Delta J = 2/\Delta K = 0 \), \( \Delta J = 2/\Delta K = 2 \), and \( \Delta J = 1/\Delta K = 2 \). Note that changes of the \( K_{-1} \) or \( K_1 \) quantum numbers cannot be selected.

Figure 4 shows the assigned and decomposed transient for \( t = 0 \)–450 ps. The signal at early \( t \) is dominated by \( K \)-type transients spaced by \( t = 57 \) ps, but these rapidly decay and disappear after for \( t = 400 \) ps. Small \( A \)-type transients are observed from 40–200 ps at intervals of \( \Delta t = 44 \) ps. Two \( J \)-type transients at multiples of \( \Delta t = 93 \) ps are also readily identified. \( C \)-type transients are expected at multiples of \( \Delta t = 220 \) ps, but there are several signals that qualify as possible candidates around \( t = 220 \) ps. The assignment is most easily done by comparing to the sub-transient generated by coherences with \( \Delta J = 2/\Delta K = 0 \), shown in Figure 4(f), which are known to contribute to \( C \)-type transients. The transient decomposition leads to an unambiguous assignment, but also reveals that the most intense peak at \( t = 220 \) ps is produced by \( \Delta J = 2/\Delta K = 2 \) coherences, see Figure 4(d). The latter cannot be assigned to a specific transient type. In fact, many features cannot be assigned to a specific transient type listed in Table II, but one can assign the features to the coherences that produce them.

Interestingly, the strong feature at \( t = 400 \) ps in Figure 3(d) could not be assigned to any of the transient types defined so far.\(^{7,8}\) Transient decomposition reveals that this feature is produced mainly by \( \Delta J = 1/\Delta K = 2 \) coherences, as can be seen in Figure 4(g). In Figure S2\(^{16}\) of the supplementary material, we show a close-up of this feature and the related recurrences at \( t = 800 \) ps and \( t = 1200 \) ps. Coherences with \( \Delta J = 2/\Delta K = 2 \) also contribute weakly to the signal. However, they are slightly shifted to earlier delay times compared to the coherences with \( \Delta J = 1/\Delta K = 2 \). To investigate the origin of these transients, we computed the beat amplitude spectrum for \( p \)-DFB, while restricting the coherences to \( \Delta J = \pm 1, \Delta K = \pm 2 \). The spectrum shows a significant number of prominent beat peaks spaced by intervals close to 2.5 GHz. These beats seem to originate from \((J,K)/(J+1,K+2),(J+1,K)/(J+2,K+2),(J+2,K)/(J+3,K+2),\) etc., coherences for \( K \) values in the vicinity of \( J/2 \). Such a series of coherences have approximate beat frequencies equal to

\[
\begin{align*}
(J+1)(B+C)+(2A-B-C)(2K+2) & = A(4K+4)+(B+C)(J+1-2K-2), \\
(J+2)(B+C)+(2A-B-C)(2K+2) & = A(4K+4)+(B+C)(J+2-2K-2), \\
\vdots & \vdots \vdots \vdots \vdots \\
\end{align*}
\]
When $K$ is in the vicinity of $J/2$, this describes a set of beat peaks spaced by intervals of approximately $(B + C)$ about a central frequency of $A(4K + 4)$. Since $(B + C)$ is close to 2.5 GHz, these beats produce a time-domain feature near $t = 400$ ps. One can attribute the slight shift of this transient from the $J$-type recurrence time to asymmetric-rotor effects.

We denote the transients produced by $\Delta J = 1/\Delta K = 2$ coherences $S$-type, reflecting the “one-ahead and two to the side” movement of a “Springer” (=knight) in chess. There are other small features produced by coherences with $\Delta J = 1/\Delta K = 2$. The small peak at $\sim 440$ ps, for example, may contribute intensity $C$-type transients. The $S$-type transients are accompanied by small features produced by $\Delta J = 2/\Delta K = 2$ coherences. These features are due to coincidences between $A$-type transients with $n/2(B + C)$ transients. The large amplitude features in the RCS signal at $\sim 576$ ps and $975$ ps, see Figures 3(e) and 3(g), are caused by the same coincidences.

### B. Determination of rotational constants

The experimental and simulated RCS transients are shown in Figure 3. For the first 450 ps, segments of $\sim 100$ ps were fitted in a sliding window fashion with overlaps of $\sim 50$ ps. Segments of the transient measured at later delay times were fitted individually. By averaging over 11 individual fit windows, we determined the rotational constants $A_0 = 5637.68(19)$ MHz, $B_0 = 1428.23(36)$ MHz, and $C_0 = 1138.90(47)$ MHz, with the $\pm 1\sigma$ uncertainty given in parentheses. For all fit windows, the rotational temperature remained at around $130 \pm 5$ K.

The rotational constants of $p$-DFB determined here and previously are compared in Table V. Our experimental $B_0$ and $C_0$ values are very close to $B = 1428.2$ and $C = 1139.5$ MHz estimated by Cvitas et al. in 1970. However, our experimental $A_0$ constant is significantly smaller than their estimated value of $A = 5639.1$ MHz. This is not surprising, as their model

![FIG. 6. RCS simulations of the room-temperature gas cell transient measured from $t = 40–450$ ps time delay. Panels ((a)-(d)) show the contributions of the vibrational states to the third-order susceptibility $\chi^{(3)}(t)$, from (a) $\nu = 0$ (thermal population 26.2%), (b) $\nu_7 + 2\nu_7$ (total thermal population 17.5%), (c) $\nu_8$ (population 4.9%), and (d) $\nu_9$ (population 4.1%). Panel (e) shows the coherent addition of the ((a)-(d)) vibrational contributions. Panel (f) shows $|\chi^{(3)}(t)|^2$, which is compared to the experimental RCS trace in panel (g). The peaks marked by red asterisks are from a small contamination of the sample, see the text.](image-url)
did not include changes in C–C or C–H bond lengths upon fluorination.

The rotational constant $A_0 = 1135.3(6)$ MHz of the $p$-DFB·Ar van der Waals complex is smaller than the $C_0 = 1138.9(5)$ MHz of $p$-DFB determined here. Since the equilibrium geometry of the Ar atom in $p$-DFB·Ar is on the $c$ inertial axis of $p$-DFB, these rotational constants should be equal for rigid $p$-DFB·Ar. The small difference probably arises from the contribution of the vibrational zero-point motion of the Ar atom perpendicular to the $p$-DFB $c$ axis. Based on the rotational constants of $p$-DFB·Ar, we simulated its Raman RCS transient; no peaks were found that could be assigned to $p$-DFB·Ar.

C. Gas cell measurements

The gas-cell RCS transient of $p$-DFB was measured at $p = 15$ mbar and $T = 293$ K over the time range $t = 0–2000$ ps and is shown in Figure 5. This transient exhibits a rich fine structure that cannot be reproduced by a $v = 0$ simulation at $T = 293$ K, because of the low-lying excited ($v > 0$) vibrational levels that are populated at room temperature, which also contribute to the RCS transient. The $v$-dependent rotational constants $A_v$, $B_v$, and $C_v$ differ significantly from the $v = 0$ rotational constants, as expressed by the rotation-vibration coupling constants $\alpha_v^A$, $\alpha_v^B$, and $\alpha_v^C$. The CCSD(T) calculated values are given in Table IV.

The thermally most strongly populated vibrations are $\nu_7$, $\nu_8$, and $\nu_9$, as shown in Table IV. This Table also shows that the $\alpha_v^A$ values are large, being $+26.15$, $-24.24$, and $65.06$ MHz, respectively. The $\alpha_v^B$ and $\alpha_v^C$ values are comparatively small, see Table IV. Thus, the contributions from vibrationally excited $v > 0$ levels to transient types that depend strongly on $A$ (such as $K^-$ and $A$-type) decrease more rapidly with increasing delay time $t$ than transients that depend on $B$ and $C$ ($J^-$, $C^-$, and $J^+$-type).

The fine structure of the room temperature RCS transient is well reproduced by including the vibrationally excited levels up to $\nu_9$, as shown in Figure 6. Note that the contributions from the levels $v = 0, \nu_7, 2\nu_7, \nu_9$, and $\nu_9$ to $J_9^{(3)}$, shown individually in Figures 6(a)-6(d), must be added coherently as in Figure 6(e), i.e., the different contributions interfere with one another. The modulus-square of the sum of all contributions in Figure 6(f) can then be compared to the experimental RCS signal in Figure 6(g). The agreement with the experimental RCS trace is very good, except for three weak peaks marked with red asterisks in Figure 6. These are due to an unidentified contaminant in the sample (possibly 1,2- or 1,3-difluorobenzene), since the same peaks also occur in the supersonic jet spectra.

It is difficult to fit the intensities of the later part of the RCS transient, due to the influence of the $J$, $K$-specific collisional dephasing rate constants, which increases with time. These rates are larger for states with small $J$, $K$ because their energies are smaller (exponential energy gap law). While the determination of the $J$, $K$-specific rate constants is of great interest, this is extremely difficult because of (1) the enormous number of $J''$, $K'' \rightarrow J'$, $K'$ microscopic rates involved and (2) the very long fitting times, due to the complexity of the asymmetric-top level structure.

D. Semiexperimental structure determination

Since F has a single stable isotope and since deuterated derivatives were not available in sufficient amounts, it was not possible to solve analytically for the molecular structure based on the rotational constants. However, experimental rotational constants can be combined with those calculated by high-level
**ab initio** methods to determine a semiexperimental structure by linear basis-set extrapolation, as has been described earlier for symmetric-top molecules for which only one rotational constant is experimentally accessible.1–3,17,19,20,48 In short, a structural parameter \( r \) (bond length, bond angle) is calculated using highly correlated **ab initio** calculations, e.g., the CCSD(T) method using a systematic series of basis sets, e.g. the Dunning correlation-consistent weighted core-valence polarized basis set series cc-pwCVXZ, where \( X \) = 2, 3, . . . , corresponds to the double-zeta, triple-zeta, etc., basis sets. The calculated \( r \) structure parameter is expected to asymptotically approach the experimental \( r \) value as \( X \to \infty \). Assuming linearity \( r \) is expressed as \( r = r_0 + m(B) \cdot \Delta r \), where the offset \( r_0 \) is given by \( r_{\text{calc}} \) calculated with a smaller basis-set (e.g., cc-pwCVDZ) and the slope \( \Delta r \) is the difference between \( r_{\text{calc}} \) calculated with a larger (e.g., cc-pwCVTZ) basis set respectively. The parameter \( m(B) \) is determined by intersecting the extrapolation vector with the experimental \( B \)-value, \( B_{sb} + m + \Delta B = B_{exp} \), where \( B_{sb} \) is the rotational constant \( B_{calc} \) calculated at the small basis and \( \Delta B \) is the difference between \( B_{calc} \) calculated at the large and small basis respectively.

For asymmetric-rotor molecules for which all three rotational constants are experimentally accessible, the equation for \( m \) is over-determined. The standard method to find the “best” value for \( m \) (denoted \( \bar{m} \)) is to employ linear least squares; a more robust estimate of \( \bar{m} \) is obtained by employing a weighted version of least squares which accounts for the differences in uncertainty of the experimentally determined rotational constants.1,48 Geometrically, the least-squares approach corresponds to projecting the set of experimental rotational constants onto the extrapolation vector where one can solve analytically for \( \bar{m} \).

Figure 7 shows an orthographic projection of this procedure using the fs-DFWM rotational constants and the corresponding CCSD(T) calculated rotational constants given in Table V. The CCSD(T)/cc-pwCVTZ calculated vibrational ground-state rotational constants \( A_0, B_0, \) and \( C_0 \) were obtained from the equilibrium rotational constants \( A_e, B_e, \) and \( C_e \) and the corresponding rotation-vibration coupling constants \( \Delta A, \Delta B, \Delta C \) given in Table III. As Figure 7 shows the calculated extrapolation parameter \( m = 1.055(27) \) lies not far beyond the CCSD(T)/cc-pwCVTZ value. The basis-set extrapolated semiexperimental bond lengths and angles determined in this way are listed in Table VI.

These semiexperimental bond lengths are smaller than the GED values.9 This is expected, since GED gives vibrationally averaged structure \( r_g \) parameters at the experimental temperature (\( T = 298 \) K). To compare the spectroscopic \( r_e \) to the GED \( r_g \) structure parameters,9 we calculated the small differences between the \( r_g \) and \( r_e \) parameters induced by the thermal vibrational averaging, using the second-order perturbation-theory method for calculating \( r_g \) structures implemented in the DALTON program.49,50 Since DALTON employs coupled-pair Hartree-Fock equations for this type of calculation, we calculated the \( (r_e - r_g) \) values at the Hartree-Fock level, using the 6-311G(d,p) basis set, and combined these with the above-mentioned semiexperimental \( r_e \) values, yielding the fs-DFWM semiexperimental \( r_g \) values listed in Table VI.

These \( r_g \) values differ from those reported by Domenicano et al.9 by \(-0.003 \) to \(-0.004 \) Å for the C–C bond lengths and by \(-0.010 \) Å for the C–F bond length. Also, the \( C_6–C_1–C_2 \) angle is 122.3° or 1.2° smaller than the GED value. These differences can be partly attributed to the fact that Domenicano et al. restricted the \( C_1–C_2 \) and \( C_2–C_3 \) bond lengths to be equal,9 whereas we find that \( C_2–C_3 \) bond is 0.007 Å longer than the \( C_1–C_2 \) bond, in agreement with the prediction of Demaison et al.1 We estimate that the semiexperimental fs-DFWM values are 5–10 times more accurate than the GED values.

### IV. CONCLUSIONS

Femtosecond rotational Raman coherence transients detected by four-wave mixing have been measured for para-difluorobenzene in a 130 K Ar supersonic jet expansion over time delays up to \( t = 1400 \) ps. Analogs measurements were also performed in a room temperature gas-cell at \( T = 293 \) K up to \( t = 2000 \) ps. The rotational and vibrational cooling of \( p \)-DFB in the supersonic jet allowed to determine the \( v = 0 \) ground-state rotational constants \( A_0 = 5637.68(19), B_0 = 1428.23(37), \) and \( C_0 = 1138.90(48) \) MHz \((\pm 1 \sigma)\). While the experimental \( B_0 \) and \( C_0 \) rotational constants agree with the values predicted by a model approach of Cvitas et al.,10 their estimate of \( A = 5639.1 \) MHz differs from our \( A_0 \) by 1.4 MHz or 0.1%.

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**Table VI.** Calculated and semi-experimental equilibrium bond lengths \( r_e \), thermally averaged \( r_g \) bond lengths (both in Å), and equilibrium bond angles (in degrees) for para-difluorobenzene.

<table>
<thead>
<tr>
<th>( r_e ) (C–C)</th>
<th>( r_g ) (C–C)</th>
<th>( r_g ) (C–F)</th>
<th>( r_g ) (C–H)</th>
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<tr>
<td>cc-pwCVDZ</td>
<td>cc-pwCVTZ</td>
<td>pCVTZ</td>
<td>Extrapolation (^{ab} )</td>
</tr>
<tr>
<td>( r_e ) (C–C)</td>
<td>( r_g ) (C–C)</td>
<td>( r_g ) (C–F)</td>
<td>( r_g ) (C–H)</td>
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</tr>
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<td>122.10</td>
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<tr>
<td>( \angle C_1–C_2–H )</td>
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<td>118.96</td>
<td>118.95</td>
</tr>
<tr>
<td>( \bar{m} ) (144306-11)</td>
<td>118.87</td>
<td>118.94(1)</td>
<td>119.01(1)</td>
</tr>
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</table>

\(^{ab} \)From Ref. 1. \(^{cc-pwCVTZ} \) values extrapolated for TZ→ QZ basis set extension by adding the MP2/cc-pwCVQZ-MP2/cc-pwCVTZ geometry differences, from Table 11 in Ref. 1. \(^{fs-DFWM} \) are also performed in a room temperature gas-cell at \( T = 293 \) K. To compare the spectroscopic \( r_e \) to the GED \( r_g \) structure parameters, we calculated the small differences between the \( r_g \) and \( r_e \) parameters induced by the thermal vibrational averaging, using the second-order perturbation-theory method for calculating \( r_g \) structures implemented in the DALTON program. Since DALTON employs coupled-pair Hartree-Fock equations for this type of calculation, we calculated the \( (r_e - r_g) \) values at the Hartree-Fock level, using the 6-311G(d,p) basis set, and combined these with the above-mentioned semiexperimental \( r_e \) values, yielding the fs-DFWM semiexperimental \( r_g \) values listed in Table VI.

These \( r_g \) values differ from those reported by Domenicano et al.9 by \(-0.003 \) to \(-0.004 \) Å for the C–C bond lengths and by \(-0.010 \) Å for the C–F bond length. Also, the \( C_6–C_1–C_2 \) ring angle is 122.3° or 1.2° smaller than the GED value. These differences can be partly attributed to the fact that Domenicano et al. restricted the \( C_1–C_2 \) and \( C_2–C_3 \) bond lengths to be equal, whereas we find that \( C_2–C_3 \) bond is 0.007 Å longer than the \( C_1–C_2 \) bond, in agreement with the prediction of Demaison et al.1 We estimate that the semiexperimental fs-DFWM values are 5–10 times more accurate than the GED values.

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**Note:** The table and text may require further formatting or citation for full context and accuracy. The provided data should be validated against the original source for complete understanding.
In order to assign RCS features that are associated with different types of rotational coherences, we decomposed the RCS transient into five sub-transients corresponding to coherences with specific rotational quantum number changes ($\Delta J = 0, 1, 2$ combined with $\Delta K = 0, 2$). This decomposition also captures cross-coherence interferences, giving deeper insight than heuristics-based assignments. The sub-transient analysis allowed to characterize a new transient, which we denote $S$-type. It is mainly produced by coherences with $\Delta J = 1/\Delta K = 2$ that occur at delay times $t \sim n/(B + C)$.

Combining the experimental results with CCSD(T)/cc-pwCVXZ $(X = 2, 3)$ calculations also allowed to determine accurate semiexperimental bond lengths and angles. Demaison et al.\(^1\) have previously performed CCSD(T) calculations and analyzed the microwave spectroscopic constants of polar fluorobenzenes, and predicted that the two $C–C$ bond lengths of $p$-DFB differ by 0.007 Å. We have obtained the semi-experimental values $r_2(C_1–C_2) = 1.3849(4)$ Å and $r_2(C_2–C_3) = 1.3917(4)$ Å, thereby confirming their predictions.\(^1\) The $C–F$ bond length is $r_2(C–F) = 1.3422(3)$ Å, which differs by only 0.001 Å from that predicted in Ref. 1.

The ability to simulate Raman RCS transients of asymmetric tops will allow to accurately determine the gas-phase structures of strongly asymmetric nonpolar molecules.

ACKNOWLEDGMENTS

Financial support from the Schweiz. Nationalfonds through Grant No. 200020-130376 is gratefully acknowledged.

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\(^24\) D. A. Long, The Raman Effect (John Wiley & Sons Ltd., 2002).