Synchrotron-Based Highest Resolution Terahertz Spectroscopy of the ν24 Band System of 1,2-Dithiine (C₄H₄S₂): A Candidate for Measuring the Parity Violating Energy Difference between Enantiomers of Chiral Molecules

Siegard Albert,*† Fabienne Arn,† Irina Bolotova,† Ziqiu Chen,† Csáva Fábi,† Guido Grassi,† Philippe Lerch,‡ Martin Quack,*† Georg Seyfang,† Alexander Wokaun,§ and Daniel Zindel†

†Physical Chemistry, ETH Zurich, CH 8093 Zurich, Switzerland
‡Swiss Light Source, PSI Villigen, CH 5232 Villigen, Switzerland
§Energy Department, PSI Villigen, CH 5232 Villigen, Switzerland

Supporting Information

ABSTRACT: The chiral C₂ symmetric molecule 1,2-dithiine (1,2-dithia-3,5-hexadiene, C₄H₄S₂) has been identified as a possible candidate for measuring the parity violating energy difference between enantiomers. We report here the observation and analysis of the low-frequency fundamental ν₂₄ using highest resolution synchrotron-based interferometric Fourier transform infrared (FTIR) spectroscopy in the terahertz range with a band center of ν₀ = 6.9537559 THz (ν₀ = 231.952319 (10) cm⁻¹) and two related hot bands, the ν₁₃ band at ν₀ = 6.97256882 THz (ν₀ = 232.579861 (33) cm⁻¹) and the 2ν₂₄ band at ν₀ = 7.01400434 THz (ν₀ = 233.962001 (14) cm⁻¹). This success in the difficult analyses of the THz spectrum of a complex chiral molecule of importance for fundamental tests on molecular parity violation is enabled by the ideal setup of an FTIR experiment of currently unique resolution with the very stable and bright synchrotron radiation at the Swiss Light Source (SLS).

Within the ordinary quantum theory of molecules retaining only the electromagnetic force,¹−⁶ the enantiomers of chiral molecules are energetically exactly equivalent by symmetry,⁴,⁵ and the ground state would be delocalized with a well-defined parity as part of a tunneling doublet separated by a small splitting ΔEₚ. This would result in a reaction enthalpy ΔₚH₀ = 0 exactly for the stereomutation reaction (eq 1) for localized enantiomers as superposition states of the tunneling doublet states. However, with the discovery of parity violation,⁹−¹¹ one predicts a small "parity violating" energy difference ΔₚE₀ between the ground states of the two enantiomers as localized eigenstates (provided that ΔₚE₀ ≫ ΔEₚ⁻¹), leading to the prediction of a nonzero parity violating reaction enthalpy ΔₚH₀

P ← M  ΔₚH₀ = N₀ΔₚE₀
(1)

where N₀ is the Avogadro constant and we use the P and M notation for "axially chiral" molecules.¹¹ For a discussion of the consequences for our understanding of the foundations of stereochemistry⁵ and possibly also of the evolution of biomolecular homochirality¹³−¹⁹ as well as a review of theory and the so far unsuccessful experimental attempts to detect molecular parity violation, we refer to the recent reviews²₀−²² and the literature cited therein. After early erroneous results²³,²⁴ (quantitatively incorrect by up to two orders of magnitude for benchmark molecules), theory now seems to converge on consensus.²⁵⁻³¹ However, experimental confirmation or rejection of theory remains a major challenge.²⁻⁴⁰ In this context, it is essential to identify suitable chiral molecules as candidates for experimental tests and to characterize them in preliminary spectroscopic investigations.

We have recently shown⁴¹ that 1,2-dithiine shown in Figure 1 is a potential candidate for measuring ΔₚE as proposed in refs 33, 39, 40, and 42. The barrier for inversion by ring puckering is ≈2500 cm⁻¹ (in wavenumbers), of appropriate magnitude. While the infrared spectra in the higher wave-number ranges can be partly analyzed on the basis of FTIR spectra using ordinary light sources,⁴¹ the important lowest frequency fundamentals fall in the terahertz range ν = 5 to 8 THz (ν = 165 to 284 cm⁻¹ as summarized in Figure 2), very difficult for traditional FTIR spectroscopy but accessible to highest resolution FTIR spectroscopy using synchrotron light sources as available at the Swiss Light Source (SLS).⁴³,⁴⁴ We
report here a first successful analysis of the spectra of 1,2-dithiine in this range. The FTIR spectra of 1,2-dithiine (C₇H₅S₂) as synthesized following ref 41 (and refs cited therein) were recorded with the ETHSLS-2009 Bruker prototype using synchrotron radiation in the range 200 to 340 cm⁻¹. This prototype spectrometer has a resolution corresponding to an unpolarized instrumental bandwidth of 0.00053 cm⁻¹ (16 MHz), which is currently the highest for a FTIR spectrometer worldwide. Apertures of 1.8 mm, which allow for an effective instrumental resolution of 0.0006 cm⁻¹, were applied. The sample pressure in a 3 m glass cell at 296 K was 0.8 mbar, excluding substantial pressure broadening. The Doppler width of 1,2-dithiine is 0.8 mbar, excluding substantial pressure broadening. The equilibrium structure of 1,2-dithiine has C₂ point-group symmetry and the molecular symmetry group MS₂ (and M₅₄ when including inversion tunneling). The nuclear spin statistical weights g of 1,2-dithiine arising from the 2² = 16 nuclear spin functions of the four protons combining with the rotational functions to Pauli allowed states correspond for K, K = eeeEOEEE to 10:10:6:6 (e for even and odd values of the quantum numbers K and K). 1,2-Dithiine has 24 vibrational modes with symmetry (ν₁) = A (13 modes) and (ν₁) = B (11 modes). According to the C₂ symmetry, the modes with A symmetry generate a-type transitions, and the modes with B symmetry generate b- and c-type transitions. In a more detailed description the modes with A symmetry can split into A₁ and A₂ symmetry and the modes with B symmetry into B₁ and B₂ symmetry, as derived for the C₂ point group of the planar transition state as reference. As a consequence, the fundamentals with B symmetry generate mainly c-type transitions and weak b-type transitions if they correspond to “out-of-plane modes” in the planar transition state (B₂) or stronger b-type transitions than c-type transitions if they correspond to “in-plane modes” (B₃).

Harmonic frequencies, integrated absorption coefficients (corresponding to the double harmonic approximation), and anharmonic energy levels were calculated by the Gaussian 09 program package at the MP2/cc-pVTZ and B3LYP/cc-pVTZ levels of theory and are listed in the Supporting Information. The B3LYP results agree better with experiment than the MP2 results for the four by now known fundamentals, but in any case the results from the two methods indicate the general uncertainties of theories at these levels. We have also calculated the electric dipole transition moment components μ∥, μ⊥, and μ, for the vibrational fundamentals in order to assist the assignments. The ν₂₄ mode has been predicted to have a relatively high integrated absorption coefficient of ~1.20 km mol⁻¹. The anharmonic constants defined by the matrix elements (Xₖ) were used to estimate some selected hot band transitions and their shifts from the ν₂₄ fundamental transition.

The infrared spectral region between 200 and 300 cm⁻¹ illustrated in Figure 3 shows three major strong absorption features associated with the Q branches of the ν₂₄ fundamental, of the hot band 2ν₂₄ ← ν₂₄, and of a third band which we assign as (ν₁₃ + ν₂₄) ← ν₁₃. Figure 2 illustrates the vibrational level diagram of the lower energy region. Transitions in this energy range include 25 vibrational fundamental, combination, and overtone states (see Figure 2). The strong sharp lines visible in Figure 3 are due to water absorption lines. In the following description the term “subband” or “series” describes the transitions belonging to one Kₗ or Kₗ value. The assignment of the observed rovibrational transitions belonging to a particular subband consisting of P and R branches has been carried out with an interactive Loomis—Wood (LW) assignment program.

The ν₂₄ band of 1,2-dithiine centered at 231.95 cm⁻¹ (Figure 3) consists of c- and b-type transitions. The c- and b-type transitions are not split for Kₗ ≤ 7. The c- and b-type series were

Figure 1. Two enantiomers of 1,2-dithiine (C₇H₅S₂, left P, right M enantiomer, following ref 12 for the conventions).

Figure 2. Energy level diagram of 1,2-dithiine (C₇H₅S₂) up to 750 cm⁻¹. The solid transitions are experimentally detected; the dashed transitions are calculated.
identified as P, R, and Q branches with ee ↔ oe/oe ↔ oo transitions and ee ↔ oo/oe ↔ oe transitions, respectively (e and o indicating whether \(K_a\) and \(K_c\) are even or odd). The lines have been assigned for \(J \leq 70\), \(K_a \leq 70\), and \(K_c \leq 35\) for the \(c\)-type transitions and for \(J \leq 70\), \(K_a \leq 70\), and \(K_c \leq 57\) for the \(b\)-type transitions. In the gigahertz spectra the \(b\)-type rotational transitions in the \(\nu_{24}\) vibrational state have been assigned for \(J = 21\) to 29 and \(K_a = 0\) to 12 and \(K_c = 10\) to 28. The hot band \(2\nu_{24} \leftrightarrow \nu_{24}\) is centered at 233.96 cm\(^{-1}\) and consists mainly of \(c\)-type transitions that have been assigned for \(J \leq 68\), \(K_a \leq 68\), and \(K_c \leq 26\). The \(b\)-type transitions have not yet been detected for this band. The third band assigned as \((\nu_{13} + \nu_{24}) \leftrightarrow \nu_{13}\) is centered at 232.96 cm\(^{-1}\) and consists of \(b\)-type transitions for \(J = 21\) to 27, \(K_a = 0\) to 10, and \(K_c = 10\) to 27. This band is interesting because it provides information about the puckering mode \(\nu_{13}\). A more detailed look at the Q branch region shows that there are three additional weak Q branches that can be assigned in a preliminary way without detailed rotational analysis but with

![Figure 3](image-url)

**Figure 3.** FIR spectrum of 1,2-dithiine (C\(_4\)H\(_4\)S\(_2\)) between 200 and 300 cm\(^{-1}\) using the Swiss Light Source (decadic absorbance \(\log(I/I_0)\) is shown, conditions as given in the text). The numerous Q branches resulting from the fundamental and hot bands are visible in the experimental spectrum (see notation in the spectrum).

| Table 1. Spectroscopic Constants in cm\(^{-1}\) of the Ground State of 1,2-Dithiine and the Other Bands in the A Reduction\(^a\) |
|---|---|---|---|---|
| ground state\(^b\)| \(\nu_{24}\)| \(2\nu_{24}\)| \(\nu_{13}\)| \(\nu_{13} + \nu_{24}\) |
| \(A_\nu/\text{cm}^{-1}\)| 0.110955440| 0.110991590 (10)| 0.111021926 (13)| 0.11083030 (31)| 0.11086507 (30) |
| \(B_\nu/\text{cm}^{-1}\)| 0.103499682| 0.103500039 (14)| 0.103578367 (55)| 0.1033518 (26)| 0.1033950 (24) |
| \(C_\nu/\text{cm}^{-1}\)| 0.058573904| 0.0585644307 (11)| 0.058709968 (72)| 0.05847121 (57)| 0.0585121 (60) |
| \(\Delta_{\nu}/10^{-6} \text{ cm}^{-1}\)| 0.010662| 0.0106844 (27)| 0.0107001 (25)| 0.010579 (59)| 0.010626 (56) |
| \(\Delta_{\nu}/10^{-6} \text{ cm}^{-1}\)| 0.013599| 0.013570 (11)| 0.013570| 0.013599| 0.013599 |
| \(N_{\text{THz}}\)| 4318| 1019| 415 |
| \(N_{\text{GHz}}\)| 78| 44 |
| \(d_{\text{rms(FIR)}}/\text{cm}^{-1}\)| 0.00012| 0.00013| 0.00013 |
| \(J_{\text{max for fit}}\)| 70| 68| 48| 48 |
| \(J_{\text{max assigned}}\)| 70| 68| 48| 48 |
| \(K_{\text{max}}\)| 70| 68| 48| 48 |
| \(K_{\text{cmax}}\)| 57| 26| 27| 4 |

\(^a\)The uncertainties are listed in parentheses in terms of 1\(\sigma\) in units of the last digits. \(^b\)Fixed to the values from ref\(^41\). \(^x\) \(x\) is the unknown absolute value of the \(\nu_{13}\) fundamental.
Table 2. Comparison of Measured and Calculated Spectroscopic Parameters in cm⁻¹ (α being defined in a standard way by α = \( (B_0 - B_\alpha)/\nu J \))

<table>
<thead>
<tr>
<th>transition</th>
<th>( E_{\text{eq}}/(hc \ \text{cm}^{-1}) )</th>
<th>( E_{\text{ab}}/(hc \ \text{cm}^{-1}) )</th>
<th>( S/(\text{km mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{13} \to \nu_3 )</td>
<td>177.3</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>( \nu_{24} \to \nu_3 )</td>
<td>231.95</td>
<td>236.3</td>
<td>12.29</td>
</tr>
<tr>
<td>( \nu_{23} \to \nu_3 )</td>
<td>315.4</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_{24} \to \nu_{24} )</td>
<td>233.91</td>
<td>238.36</td>
<td>7.77</td>
</tr>
<tr>
<td>( 3\nu_{24} \to 2\nu_{24} )</td>
<td>235.8</td>
<td>240.4</td>
<td>3.64</td>
</tr>
<tr>
<td>( (\nu_{23} + \nu_{24}) \to \nu_{23} )</td>
<td>231.8</td>
<td>236.0</td>
<td>2.64</td>
</tr>
<tr>
<td>( (\nu_{13} + \nu_{24}) \to \nu_{13} )</td>
<td>232.58</td>
<td>237.23</td>
<td>5.18</td>
</tr>
<tr>
<td>( (\nu_{13} + 2\nu_{24}) \to (\nu_{13} + \nu_{24}) )</td>
<td>234.6</td>
<td>239.29</td>
<td>3.29</td>
</tr>
<tr>
<td>( (2\nu_{13} + \nu_{24}) \to 2\nu_{13} )</td>
<td>238.2</td>
<td>2.21</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>transition (fundamental)</th>
<th>( \Delta E_{\text{eq}}/\text{cm}^{-1} )</th>
<th>( \Delta E_{\text{ab}}/\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [2\nu_{24} \to \nu_{24}] - \nu_{24} \to \nu_3 ) ( \to \nu_{24} \to \nu_3 )</td>
<td>1.96</td>
<td>2.06</td>
</tr>
<tr>
<td>( 3\nu_{24} \to 2\nu_{24} - \nu_{24} \to \nu_3 )</td>
<td>3.8</td>
<td>4.11</td>
</tr>
<tr>
<td>( (\nu_{13} + \nu_{24}) \to \nu_{13} - \nu_{24} \to \nu_3 )</td>
<td>0.56</td>
<td>0.93</td>
</tr>
<tr>
<td>( (2\nu_{13} + \nu_{24}) \to 2\nu_{13} - \nu_{24} \to \nu_3 )</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>( (\nu_{13} + \nu_{24}) \to (\nu_{13} + \nu_{24}) - \nu_{24} \to \nu_3 )</td>
<td>2.7</td>
<td>2.98</td>
</tr>
<tr>
<td>( (\nu_{23} + \nu_{24}) \to \nu_{23} - \nu_{24} \to \nu_3 )</td>
<td>-0.15</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>vibrational state</th>
<th>rot. const</th>
<th>( -\alpha_{\text{eq}}/\text{cm}^{-1} )</th>
<th>( -\alpha_{\text{ab}}/\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{24} )</td>
<td>( (\nu_{24} - \nu_{24})/2 )</td>
<td>0.000037</td>
<td>0.000018</td>
</tr>
<tr>
<td>( \nu_{23} )</td>
<td>( (\nu_{23} - \nu_{24})/2 )</td>
<td>0.000034</td>
<td>0.000018</td>
</tr>
<tr>
<td>( \nu_{23} )</td>
<td>( B_{23} - B_0 )</td>
<td>0.000040</td>
<td>0.000033</td>
</tr>
<tr>
<td>( \nu_{23} )</td>
<td>( (\nu_{24} - \nu_{24})/2 )</td>
<td>0.000039</td>
<td>0.000033</td>
</tr>
<tr>
<td>( \nu_{23} )</td>
<td>( C_{23} - C_0 )</td>
<td>0.000070</td>
<td>0.000071</td>
</tr>
<tr>
<td>( \nu_{23} )</td>
<td>( (C_{24} - C_0)/2 )</td>
<td>0.000070</td>
<td>0.000071</td>
</tr>
<tr>
<td>( \nu_{13} )</td>
<td>( A_{13} - A_0 )</td>
<td>-0.000125</td>
<td>-0.000154</td>
</tr>
<tr>
<td>( \nu_{13} )</td>
<td>( B_{13} - B_0 )</td>
<td>-0.000150</td>
<td>-0.000157</td>
</tr>
<tr>
<td>( \nu_{13} )</td>
<td>( C_{13} - C_0 )</td>
<td>-0.000100</td>
<td>-0.000115</td>
</tr>
</tbody>
</table>

*Calculations were carried out at the B3LYP level of theory (see Supporting Information).*

approximate positions estimated from the Q branches as \( (\nu_{24} + \nu_{23}) \to \nu_{24} \) at 231.8 cm⁻¹, \( (2\nu_{24} + \nu_{24}) \to (\nu_{13} + \nu_{24}) \) at 234.6 cm⁻¹, and \( 3\nu_{24} \to 2\nu_{24} \) at 235.8 cm⁻¹.

The rovibrational analysis has been carried out with Watson’s A reduced effective Hamiltonian⁵³ in the \( \Pi \) representation up to sextic centrifugal distortion constants using our WANG program⁵⁴

\[
\hat{H}^{\text{rot}} = A_{\nu} J_{\nu}^2 + B_{\nu} J_{\nu}^2 + C_{\nu} J_{\nu}^2 - \Delta J^2 - \Delta_{xy} J_x^2 J_y^2 - \Delta_{yz} J_y^2 J_z^2
\]

\[
- \frac{1}{2} (\delta J^2 + \delta K^2 J_{\nu}^2), (J_x^2 + J_y^2) + \Phi J(J^2)^3
\]

\[
+ \Phi_{xy} J_x^2 J_y^2 + \Phi_{xz} J_x^2 J_z^2 + \Phi_{yz} J_y^2 J_z^2
\]

\[
+ \frac{1}{2} (\phi J_x^2 J_y^2 + \phi_{xy} J_x^2 J_z^2 + \phi_{xz} J_y^2 J_z^2), (J_x^2 + J_y^2) J_{\nu}^2
\]

(2)

Equation 2 defines the notation used for the parameters. The angular momentum operators are given by \( \hat{J} = \hat{J}_x + \hat{J}_y + \hat{J}_z \) and \( J_{\nu} = J_{\nu} \pm i \hat{J}_{\nu} \). The \( \Pi \) representation was chosen to reduce correlations during the fit. The spectroscopic constants were fitted for each band separately according to the A reduction. The Hamiltonian in eq 2 shows distortion terms through second order, but only terms through first order were retained in the final fit, as given in Table 1.

According to the calculated transition moments for the \( \nu_{24} \) fundamental the \( b \)- and \( c \)-type absorption lines are predicted to be of similar intensity. Around 2000 \( b \)-type transitions and around 2300 \( c \)-type transitions have been used in the adjustment, where around 1500 lines are from coinciding nonsplit \( c \)-type and \( b \)-type transitions for \( K_z \leq 11 \). Pure \( b \)-type transitions (~500) have been assigned. Pure \( c \)-type transitions (~800) have been assigned in the entire spectrum. Overall, 4318 \( b \)- and \( c \)-type transitions for \( J \leq 70 \), \( K_z \leq 70 \), and \( K_z \leq 57 \) of the terahertz spectrum and the 78 \( b \)-type transitions from the gigahertz spectrum were used for the fit of the spectroscopic constants. There were no important perturbations observed in the spectrum, as the very small root-mean-square deviation \( d_\text{rms} = 0.00012 \text{ cm}^{-1} \) for the terahertz lines indicates. The constants of the ground state have been held fixed to the values in Table 1, and the constants of \( \nu_{24} \) have been adjusted in the least-squares analysis.

The adjustments of the constants for the \( 2\nu_{24} \) state have been carried out using the \( b \)-type transitions of the terahertz spectrum. Around 1000 lines have been used. During the adjustment of the constants of the lower level, the \( \nu_{24} \) state has been held fixed to the values determined from the adjustment of the \( \nu_{24} \) fundamental, which confirmed the assignment as \( \nu_{24} \to \nu_{24} \). The rotation–vibration \( \alpha \) constants of the rotation constants of the \( \nu_{24} \) vibrational state agree very well with the calculated values shown in Table 2 and confirm the assignment. The constants for \( \nu_{13} + \nu_{24} \to \nu_{13} \) band have been adjusted using around 400 \( b \)-type transitions from the terahertz spectrum and the 44 rotational lines from the gigahertz spectrum. Therefore, some of the quartic constants have been fixed to the values of the ground state. The shifts of the center of the \( 2\nu_{24} \to \nu_{24} \) and \( (\nu_{13} + \nu_{24}) \to \nu_{13} \) hot bands as shown in Table 2 confirm the assignments, too. In particular, the \( \alpha \) constants of the \( \nu_{13} \) state show a very good agreement with the calculated values. Also, the calculations indicate that the
fundamentals $\nu_{23}$ and $\nu_{13}$ are too weak to be detected in our experiment.

A comparison of the measured spectrum with the simulated spectrum calculated with the parameters listed in Table 1 is shown in Figure 4 for the R and P branch regions. The upper trace shows the experimental spectrum, the second trace is the sum of all simulations, the third trace is the $\nu_{24}$ fundamental simulation, the fourth trace is the $\nu_{13} + \nu_{24} \leftarrow \nu_{13}$ simulation, and the lower trace is the $2\nu_{24} \leftarrow \nu_{24}$ simulation. As one can see, the agreement is very good. One recognizes the importance of hot bands to simulate the measured spectrum.

The ideal setup of the very stable synchrotron light source at the SLS with the currently highest resolution interferometric Fourier transform spectrometer is able to reduce noise levels in absorbance spectra to values by a factor of 100 lower than with conventional thermal sources. We have shown here that as a consequence of this advance high-resolution analyses are possible for the spectra of 1,2-dithiine in the very di-terahertz range, for a chiral molecule that may at first sight seem exotic but is in fact one of the very few realistic candidates to measure the parity violating energy difference $\Delta_{pv}E$ between enantiomers, so far never detected. The fundamental $\nu_{24}$ at 231.95 cm$^{-1}$ agrees reasonably well with our theoretical results at the B3LYP level (236.3 cm$^{-1}$; see the Supporting Information). Also, the agreement between theory and the experimental anharmonic shifts of several hot band centers and the rotation vibration interaction constants is satisfactory. The rotational parameters for the $\nu_{13}$ and $\nu_{13} + \nu_{24}$ levels should be useful for the study of interactions of excited vibrational levels of $\nu_{13}$ with other vibrations, which will be relevant for future analyses, perhaps best starting with a reanalysis of the polyad associated with the $\nu_{23}$ fundamental (at 600 cm$^{-1}$, Figure 2).

The tunneling splitting $\Delta E_{\pm} (\nu = 0)$ in the ground state predicted at several levels of theory all consistently indicate that it is much smaller (by many orders of magnitude) than the predicted parity violating energy difference between the enantiomers, which is favorably large for a molecule containing no nucleus heavier than sulfur ($\Delta_{pv}E = 1.1 \times 10^{-11}$ (hc) cm$^{-1}$), leading to a relatively short “parity violating time” (1.5 s period) for which the initial evolution in the millisecond range should be detectable. The present first high-resolution analysis and characterization of the spectrum of the low-frequency modes for this molecule provide an important step toward future analyses aiming at identifying combination levels at higher energy, which would be suitable for parity selection in the experiment on molecular parity violation.

**ASSOCIATED CONTENT**

 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01674.

Tables of calculated vibrational wavenumbers, inversion potentials, tunneling splittings, anharmonic constants, and wavenumber shifts. Tables of measured and fitted line frequencies and wavenumbers with the assignments. (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*S.A.: E-mail: albert@ir.phys.chem.ethz.ch. Phone: +41446327918. Fax: +41446321021.

*MLQ.: E-mail: martin@quack.ch. Phone: +41446324421.

Notes
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