The infrared spectrum of the chiral molecule CDBrClF in the range 600-1150cm^{-1}: A rovibrational analysis of the ν_4 and ν_5 band

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Abstract

The rovibrational spectrum of the chiral molecule CDBrClF has been analysed on the basis of an effective Hamiltonian [1]. The spectra have been recorded at room temperature with a Fourier transform infrared (FTIR) spectrometer (resolution 0.0024 cm^{-1}) and a supersonic jet diode laser spectrometer (resolution 0.001 cm^{-1}). The assignment of the ν_4 and ν_5 rovibrational lines of the FTIR spectrum for the two major isotopomers CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF has been carried out with an interactive Loomis-Wood program. Accurate rotational and quartic centrifugal distortion constants for the ν_4 and ν_5 vibrational state of CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF have been determined. A new experimental technique based on backward wave oscillators is proposed in order to measure the parity violation.

Introduction

CDBrClF, the deutero isotopomer of CHBrClF, is an example of one of the simplest chiral molecules. It has an asymmetric carbon with C_1 point group symmetry. CHBrClF has been analysed recently in detail with respect to its spectra and its intramolecular vibrational redistribution (IVR) dynamics [2-5]. CDBrClF offers the opportunity to investigate the effect of deutero isotopic substitution in the spectra. The vibrational spectrum of CDBrClF has been analysed from the far infrared (FIR) to the near infrared (NIR) region [6]. A rovibrational analysis of the spectrum is challenging due to the congestion of lines which results from the low symmetry of the molecule and the presence of four different isotopomers (CD^{79}Br^{35}ClF : CD^{81}Br^{35}ClF : CD^{79}Br^{37}ClF : CD^{81}Br^{37}ClF = 0.380 : 0.369 : 0.122 : 0.118) .

Another motivation to investigate the rotationally resolved spectra of this molecule arises from effects generated by parity violation [3-5,7-11]. While an unsuccessful attempt to see these effects in CHBrClF has been made already a quarter century ago [7,11], our studies seem to be the first on the D-isotopomer in this respect. Both molecules have been studied extensively in theoretical work on parity violation in our group [8-10]. New calculations including CDBrClF [9, 10] show a very small impact on relative vibrational and rotational frequency shifts due to the parity violation on the order of $\Delta\nu/\nu = 10^{-17}$ to 10^{-16} [8-10]. Recent, still unsuccessful experiments giving a limit on the order of $\Delta\nu/\nu = 10^{-13}$ are in agreement with these calculations [12].

Experimental details

The spectrum of CDBrClF has been recorded in two different ways. A Fourier transform infrared (FTIR) spectrum in the spectral region between 600-1140 cm^{-1} was measured with the Zuerich BOMEM DA 002 interferometric Fourier transform infrared (FTIR) spectrometer [13] with a resolution up to 0.004 cm^{-1}. Diode laser spectra using the Zuerich supersonic slit jet system [14] were obtained in the region 745-752 cm^{-1}. The diode laser spectra were recorded with a resolution of 0.001 cm^{-1}. In order to improve the vibrational cooling CDBrClF has been mixed with helium with a CDBrClF:He seeding ratio of 1:4, resulting in rotational temperatures in the range T_{rot}=15-40 K.

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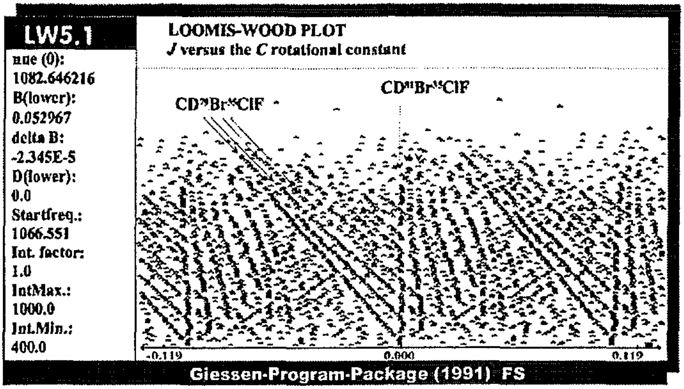

Figure 1: Loomis-Wood plot of the ν_4 band. The P-branches of the c-type series are shown. The rotational quantum number J is plotted versus the rotational constant C. The vertical series belong to the isotopomer $CD^{81}Br^{35}ClF$ and the slanted series belong to the isotopomer $CD^{79}Br^{35}ClF$.

Assignment and analysis

The assignment of the observed rovibrational transitions in the FTIR spectra belonging to a particular subband consisting of P- and R-branches has been carried out efficiently with an interactive Loomis-Wood assignment program [15]. Two types of subbands have been assigned in the spectrum of the ν_4 region. One type consists of transitions with $(J \pm 1, K_a, K_c = J \pm 1 - K_a) \leftarrow (J, K_a, K_c = J - K_a)$ (P- and R- branches) which correspond to c-type transitions. The different series can be clearly seen in the Loomis-Wood plot in Fig. 1. The spacing between two transitions of a series is approximately $2C$. The Loomis-Wood plot in the c-type region of the ν_4 band provides an easy separation of transition lines in transitions belonging to the $CD^{79}Br^{35}ClF$ or $CD^{81}Br^{35}ClF$ isotopomer. The other type of subbands consists of $(J \pm 1, K_a = J \pm 1 - K_c, K_c) \leftarrow (J, K_a = J - K_c, K_c)$ transitions (P- and R-branches) which correspond to a-type transitions.

In the ν_5 region of the spectrum, only c-type transitions have been assigned in the FTIR spectrum. The jet-cooled diode laser spectra have been used to assign the a-type transitions. The a-type Q-branches around 748 cm^{-1} in the jet-cooled diode laser spectrum have been assigned from $J = 2$ up to $J = 12$ with K_c up to 2 for $CD^{79}Br^{35}ClF$ and $CD^{81}Br^{35}ClF$. Fig. 2 shows the Q-branches for the two isotopomers.

The rovibrational analysis has been carried out with Watson's A reduced effective Hamiltonian in the I^r representation up to quartic centrifugal distortion constants

$$\tilde{H}^{vr} = A\tilde{J}_a^2 + B\tilde{J}_b^2 + C\tilde{J}_c^2 + \Delta_J\tilde{J}^4 + \Delta_{JK}\tilde{J}^2\tilde{J}_a^2 - \Delta_K\tilde{J}_a^4 - \frac{1}{2}[\delta_J\tilde{J}^2 + \delta_K\tilde{J}_a^2, \tilde{J}_+^2 + \tilde{J}_-^2] \qquad (1)$$

with $\tilde{J}_\pm = \tilde{J}_b \pm i\tilde{J}_c$. The rotational constants A, B, C and the centrifugal distortion constants Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K depend upon the vibrational level v. The spectroscopic data have been analyzed by our Wang program [16].

FTIR and jet-cooled diode laser spectra were fitted together with a standard deviation of $d_{rms} =$ 0.0006 cm^{-1}. In Table 1 the spectroscopic constants of the ν_4 and ν_5 states are presented. The A rotational constants of $CD^{79}Br^{35}ClF$ and $CD^{81}Br^{35}ClF$ are similar for the ν_4 and ν_5 states in each isotopomer; but significantly smaller than in the ground state. By contrast, the B constants

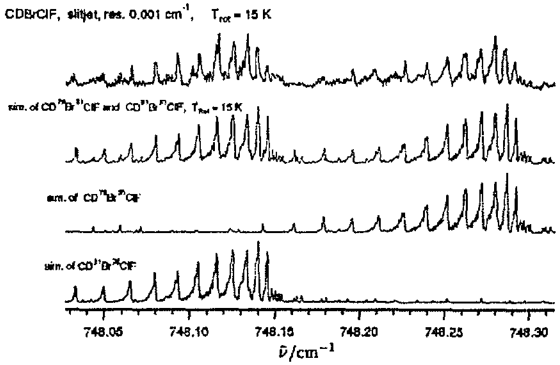

Figure 2: Part of the a-type Q-branches between $J = 2 - 12$. The upper trace shows the jet-cooled spectrum measured in absorbance. The rotational temperature T_{rot} = 15 K has been determined by comparison with the simulated spectrum. The lower trace illustrates the simulated spectrum for the two major isotopomers CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF.

are quite similar in the ground and the excited states ν_4 and ν_5 for both isotopomers. The C constants are slightly smaller in the ν_5 state than those in the ν_4 state. The shift of the ν_5 band center for CD^{79}Br^{35}ClF/CD^{81}Br^{35}ClF (0.157 cm^{-1}) is larger than that of the ν_4 band center for the CD^{79}Br^{35}ClF/CD^{81}Br^{35}ClF (0.015 cm^{-1}) pair.

	ν_5		ν_4	
	CD^{79}Br^{35}ClF	CD^{81}Br^{35}ClF	CD^{79}Br^{35}ClF	CD^{81}Br^{35}ClF
A	0.207 965 6 (34)	0.207 787 6 (32)	0.207 983 6 (18)	0.207 818 1 (19)
B	0.067 094 9 (70)	0.066 598 2 (57)	0.067 117 9 (68)	0.066 612 7 (55)
C	0.053 193 72 (83)	0.052 749 59 (84)	0.053 237 41 (82)	0.052 793 63 (82)
$\Delta_J \times 10^{-6}$	−0.035 1 (21)	−0.030 4 (23)	0.073 2 (27)	0.138 0 (16)
$\Delta_{JK} \times 10^{-6}$	−0.084 5^2	−0.092 4^3	−0.166 9 (96)	−0.395 6 (61)
$\Delta_K \times 10^{-6}$	0.125 9 (22)	0.138 4 (22)	0.099 5 (70)	0.204 1 (46)
$\delta_J \times 10^{-6}$	0.015 1 (30)	0.056 3 (21)	0.074 9 (13)	0.041 09 (77)
$\delta_K \times 10^{-6}$	−0.128 7 (35)	−0.051 9 (24)	−0.107 59 (81)	−0.117 96 (67)
ν_0	748.299 262 (80)	748.152 728 (80)	1082.811 77 (11)	1082.796 56 (10)
n	345	352	834	828
d_{rms}	0.0006	0.0006	0.0006	0.0006

Table 1: Rotational constants and centrifugal distortion constants of the ν_5 and ν_4 states of CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF from the ν_4 and ν_5 fundamental band transitions. The standard deviations of the parameter values are given in parentheses. d_{rms} is the root-mean-square deviation of the fit. All constants are given in cm^{-1}.

For the simulation of the ν_5 band of CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF the following transition moment components obtained with *ab initio* calculations [6] were used: $\mu_a = 0.191$ D, $\mu_b = -0.0774$ D, $\mu_c = -0.0348$ D for ν_5. Fig. 2 illustrates the a-type Q-branches of the ν_5 band of CD^{79}Br^{35}ClF and CD^{81}Br^{35}ClF recorded with a diode laser in a seeded supersonic slit expansion with an effective rotational temperature T_{rot} = 15 K. The Q-branches have been assigned from $J = 2$ up to $J = 12$. There is a good agreement between the experimental and calculated spectra.

Conclusion

A rovibrational analysis of the ν_4 and ν_5 bands has determined the spectroscopic constants of the ν_4, ν_5 and the ground state of $CD^{79}Br^{35}ClF$ and $CD^{81}Br^{35}ClF$ for the first time. The patterns of the ν_4 and ν_5 bands have also been found in the ν_8 and ν_3 spectral regions of CDBrClF.
The assignment of the highly resolved infrared spectrum of CDBrClF is expected to increase the possibility of finding spectral regions in order to carry out double resonance experiments as described in [7] to measure the energy difference between the two enantiomers caused by the parity violation potential or to measure infrared frequency shifts [12], as recent calculations [8–10] predict. With the ground work presented in [10] and here, it might be possible to detect rotational absorption line shifts caused by the parity violation potential with a phase locked submillimeter spectrometer in the terahertz region [17, 18]. Backward wave oscillators have frequency purity better than 1 Hz. If they are phase locked the ratio is in the range of $\Delta\nu/\nu = 10^{-10} - 10^{-11}$ in the THz region. This ratio is not sufficient to observe the effect in the CDBrClF spectra, but perhaps in heavier molecules. In the spectra presented here no splitting due to parity violation potential has been observed. This is in agreement with recent calculations [8–10].

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