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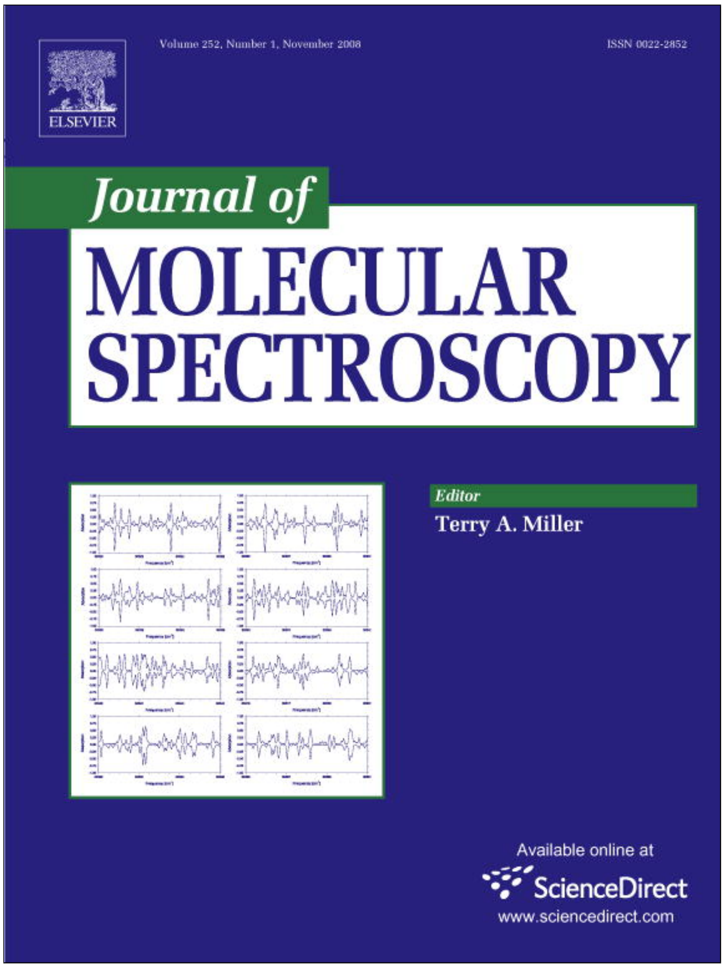
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FTIR spectra and rovibrational analysis of the ν_{11} band of *trans*-ClHC=CHF and ν_{10} of *trans*-ClHC=CDF

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ABSTRACT

High-resolution Fourier transform infrared spectra of natural *trans*-ClHC=CHF and of its isotopologue *trans*-ClHC=CDF have been recorded in the region between 700 and 1150 cm^{-1} with the purpose to analyze the ν_{11} fundamental of the main species and the ν_{10} of its deuterated compound. Both bands, of symmetry species A'', present *c*-type envelope absorptions. Beside the expected features, the *K* structure of the $P(J)$, $Q(J)$, and $R(J)$ manifolds was resolved and identified; the assignment of the rovibrational transitions was extended up to $J = 92$ and $K_a = 13$ for the *trans*-^{35}ClHC=CHF and up to $J = 86$ and $K_a = 10$ for *trans*-^{35}ClHC=CDF. More than 2900 and 2700 lines for the main and deuterated species, respectively, were analyzed by a least-squares procedure and reliable spectroscopic molecular parameters were determined for both isotopologues.

1. Introduction

In the past decade, halogenated ethylenes have been extensively investigated by spectroscopic techniques due to their significance in processes affecting the environment, such as stratospheric ozone depletion and other serious environmental quality concerns. The most important transformation reactions of halogen-containing molecules, released into the atmosphere by natural as well as anthropogenic emissions, involve ozone [1] and hydroxyl radicals [2]. Although chlorofluoroethylene molecules have not been directly recognized and studied, they are potentially involved in this kind of atmospheric processes. Accurate high-resolution spectroscopic studies can be useful for identifying these species in the atmosphere.

In this context, the characterization of spectroscopic properties is of considerable interest and the vibrational spectroscopy plays an important role in deriving molecular parameters which provide an insight into intramolecular interactions. Among the series of dihalogenated ethylene derivatives, those containing F and Cl atoms and in particular the *cis*- and *trans*-isomers were extensively investigated both experimentally and theoretically.

As far as the *cis*-1-chloro-2-fluoroethylene molecule is concerned, its molecular structure has been investigated from the combination of experimental ground-state constants of eight isotopologues [3] and accurate quantum chemistry calculations [4]. The molecular dipole moment from Stark spectrum [5] and the diagonal and off-diagonal quadrupole coupling constants of both ^{35}Cl and ^{37}Cl were also determined [6]. High-resolution IR spectra of the ν_4 [7], ν_5 [8], and ν_6 [9] fundamentals of the main species have been recorded with a diode laser spectrometer, and molecular constants for the corresponding vibrational excited states have been determined. In addition, a comprehensive anharmonic vibrational analysis of *cis*-ClHC=CHF and its deuterated isotopologues has been performed on the basis of a complete ab initio quartic force field [10].

As far as the *trans*-1-chloro-2-fluoroethylene molecule is concerned, a thorough computational study at high level of theory of the equilibrium structure, dipole moment and chlorine quadrupole tensor has been performed recently together with calculation of the harmonic force field [11]. The anharmonic part of the force field completed the theoretical studies on this molecule [12]. Afterwards, in spite of the small molecular dipole moment, the millimeter-wave and submillimeter-wave spectra of eight isotopologues of *trans*-ClHC=CHF were successfully recorded and investigated [12,13] enabling thus the determination of the rotational and centrifugal distortion constants. Moreover, the diagonal elements of the chlorine quadrupole-coupling tensor were also determined.

Low-resolution infrared measurements on the *trans*-ClHC=CHF molecule were performed in 1970 by Craig et al. [14], who assigned the vibrational fundamentals, overtones and combination bands. The lack of high-resolution infrared spectra, which play an important role for gas trace detection in the atmosphere, stimulated the present work to obtain reliable molecular parameters from the

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rovibrational analysis of selected bands. High-resolution Fourier transform infrared spectra were thus recorded in the atmospheric windows region and the interpretation of the rovibrational details of ν_{11} band ($\approx$785 cm^{-1}) of *trans*-ClHC=CHF, and ν_{10} fundamental ($\approx$817 cm^{-1}) of *trans*-ClHC=CDF, were carried out. From the whole sets of the assigned transitions, accurate band origins and excited-state molecular parameters for both bands were obtained.

2. Experimental details

2.1. Synthesis of trans-ClHC=CHF and trans-ClHC=CDF

The sample used was obtained in laboratory from the initial synthesis of both *cis*- and *trans*-isomers of ClHC=CHF, containing ^{35}Cl and ^{37}Cl in natural abundance. This two-step reaction scheme, reported in details in a previous work [5], can be summarized as follows:

(i) $Cl_2HC–CHCl_2$ (99% Aldrich) was fluorinated with SbF_3 (99.8% Aldrich) using SbF_5 (54% Aldrich) as activating reactant,
(ii) the resulting $Cl_2HC–CHClF$ was then dechlorinated by 1,2 elimination reaction with Zn powder in refluxing ethanol.

Finally, the specimen of *trans*-ClHC=CHF was recovered from the *E*/*Z* mixture by trap-to-trap condensation at low temperature under dynamic vacuum. Purity of *trans*-1-chloro-2-fluoroethylene was checked by gas-phase low-resolution infrared spectroscopy [14].

Samples of *trans*-ClDC=CDF were synthesized by H/D exchange of *trans*-ClHC=CHF with D_2O (99.75 atom% D, Merck), saturated with CaO (99.9%, Aldrich), at 125 °C for 1 day. A sample of *trans*-ClHC=CDF was then obtained by D/H exchange of *trans*-ClDC=CDF with H_2O, saturated with CaO, at 85 °C for 1 day.

2.2. Measurements of the spectra

The high-resolution spectrum of the main isotopic species of *trans*-ClHC=CHF was recorded in the region between 700 and 1150 cm^{-1} with a Bruker IFS 120HR vacuum Fourier transform spectrometer at the University of Giessen, Germany. A globar source, a Ge:KBr beam-splitter and a Ge:Cu detector were employed. A detailed description of the instrument configuration has been reported elsewhere [15]. The measurements were carried out using a 3 m path cell fitted with KBr windows containing a sample pressure of about 0.2 mbar and kept cooled at -10 °C. The collected interferograms were coadded, apodized with a boxcar function, and Fourier transformed to give a nominal resolution of 0.0019 cm^{-1}. Calibration was performed using suitable CO_2 lines [16].

The spectrum of the deuterated specimen, *trans*-ClHC=CDF, was recorded with a BOMEM Fourier transform spectrometer at the University of Bologna. The instrument was equipped with a KBr beamsplitter and an Hg:Cd:Te detector. The spectrum was recorded at room temperature employing an optical pathlength of 15 cm and a pressure of 2 mbar. In order to have a better signal to noise ratio, 494 scans were coadded and Fourier transformed to give a resolution of 0.004 cm^{-1}.

3. Results and discussion

The molecule of *trans*-1-chloro-2-fluoroethylene is a planar near-prolate asymmetric top ($\kappa = -0.996$) belonging to the C_s symmetry point group. The *a* and *b* principal inertial axes lie in the molecular symmetry plane, while the *c*-axis is perpendicular to it. The molecule has 12 fundamental vibrations, of which nine of species A′(ν_1–ν_9) give rise to *a*/*b*-type hybrid bands and three of species A''(ν_{10}–ν_{12}) produce *c*-type band envelope absorptions.

3.1. The ν_{11} of trans-^{35}ClHC=CHF

The ν_{11} fundamental located at $\sim$785 cm^{-1} may be approximately described as a C–H out-of-plane bending mode and exhibits the typical *c*-type band contour. The survey spectrum of this band is given in Fig. 1, where the spectral region of the rovibrational transitions investigated spans a range of about 80 cm^{-1}, from 745 up to 824 cm^{-1}.

The following selection rules have been taken into account: $\Delta J = 0, \pm 1$, $\Delta K_a = \pm 1$, and $\Delta K_c = 0, \pm 2$. Therefore many transitions are expected in the *P*, *Q*, and *R* branches, which will produce several even ($J'' = K''_a + K''_c$) and odd ($J'' + 1 = K''_a + K''_c$) subbands. In addition, the spectrum presented tangled patterns due to the *trans*-^{37}ClHC=CHF isotopologue (in natural abundance, i.e. about 1/3 with respect to the species containing ^{35}Cl) and traces of the *cis* diastereomer.

For the numerical analysis of the rovibrational transitions, effective Hamiltonians were fitted for the ground and excited vibrational states. The wavenumbers, in units of cm^{-1}, of the transition lines, were then given by

$$\nu(\Delta J, \Delta K_a, \Delta K_c) = \nu_0 + E_{\rm rot}(J', K'_a, K'_c) - E_{\rm rot}(J'', K''_a, K''_c)$$

where ν_0 is the band origin of the fundamental vibrational mode. The Watson's *A*-reduced Hamiltonian in the I^r representation [17] was employed to compute the rotational energy levels in both ground and excited states, including the centrifugal distortion constants up to the sixth order.

The assignment of the rovibrational transitions followed a well-established pattern: the structure of a *c*-type band is mainly dominated by ^pQ_K and ^rQ_K clusters having a separation between neighboring characteristics approximately corresponding to $2(A - \bar{B}) \approx 3.4$ cm^{-1} where $\bar{B} = (B + C)/2$. These clusters, which could be identified for several K_a values, appear as groups of closely spaced lines showing distinct patterns and could be easily assigned since the adjacent features differ by one unit in *J*.

As can be seen from the portion of high-resolution spectrum illustrated in Fig. 2, the resolved details in the $^rQ_0(J)$ manifold move to the lower wavenumber side with increasing *J*. The fine structure appear more regular for the ^pQ_K clusters, and the degradation of the resolved lines occurs toward higher wavenumbers.

The investigation was carried out using the ATIRS package software [18]. This suite is composed by three programs: (a) VLW for the assignment of spectral lines based on the procedure suggested by Nakagawa and Overend [19]; (b) VCALPGM, a graphical interface to the Pickett's programs SPFIT and SPCAT [20], to fit the experimental data and predict the transitions, respectively; and (c) VSS for the simulation of the spectra. In the fitting process, the ground state constants were fixed at the value reported in Table 1. The starting values of the rotational constants for $\nu_{11} = 1$ were obtained from the theoretical rotation vibration interaction constants α^X_{11} (with *X* = *A*, *B*, and *C*), computed from the cubic anharmonic force field of [12], while for the band origin the experimental ν_{11} band center was taken.

The transitions wavenumbers were fitted by assuming uncertainties of ±0.001 and ±0.002 cm^{-1} for apparently single and blended lines, respectively. The analysis led to the assignment of 2910 rovibrational lines in the ^pP_K, $^{p,r}Q_K$, and ^rR_K subbranches with K'_a ranging from 0 to 12 and J' up to 92.

All assigned rovibrational transitions were employed to obtain the set of molecular constants for the vibrationally excited state $\nu_{11} = 1$ listed in Table 1. The rotational and quartic centrifugal distortion constants appear well determined and the standard devia-

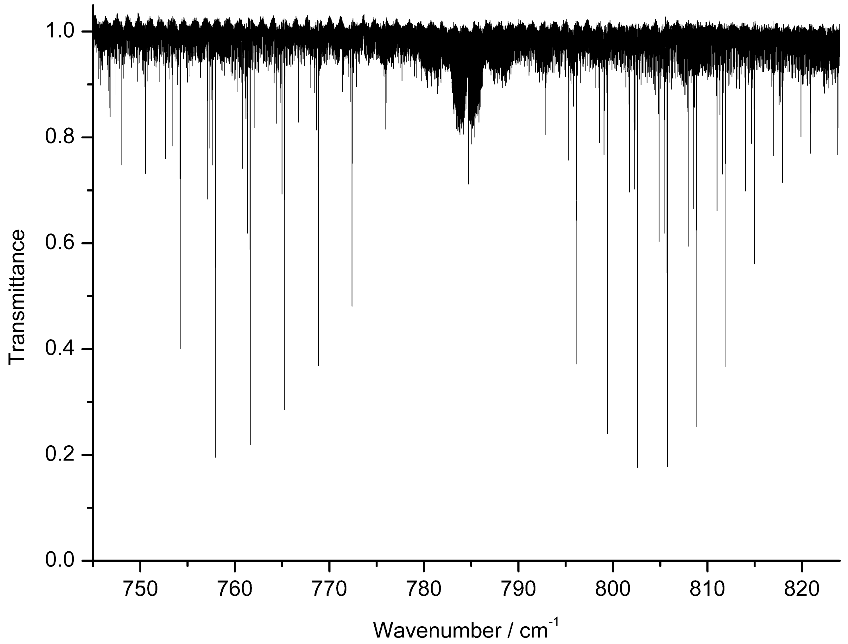

Fig. 1. Survey spectrum ($P = 0.2$ mbar, 300 cm cell, $T = 263$ K) of the ν_{11} fundamental of *trans*-ClHC═CHF.

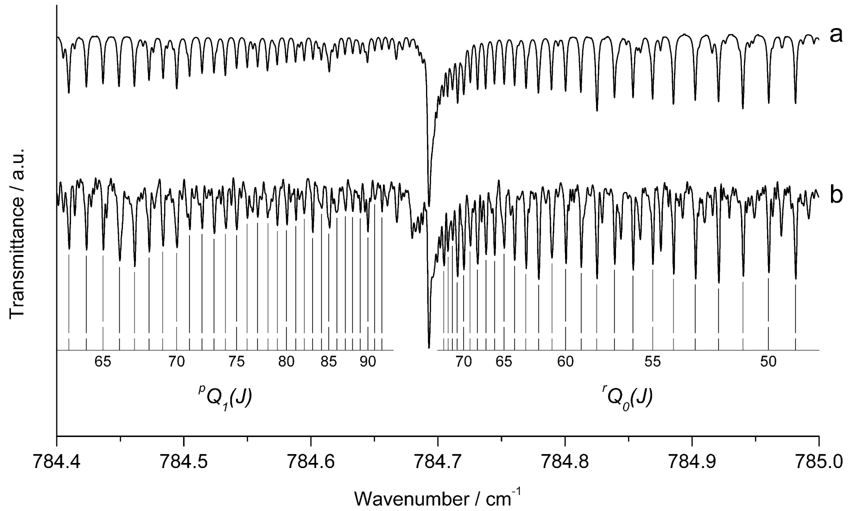

Fig. 2. Portion of the central *Q* branch of the ν_{11} band of *trans*-ClHC═CHF showing the assignment of the $^{p}Q_1(J)$ and $^{r}Q_0(J)$ manifolds. (a) Simulated spectrum of ^{35}Cl isotopologue. (b) Experimental spectrum ($P = 0.2$ mbar, 300 cm cell, $T = 263$ K) of natural *trans*-ClHC═CHF.

tion of the fit is consistent with the resolution of the experimental spectrum. The sextic terms could not be significantly determined and therefore were constrained to their ground state values.

3.2. The ν_{10} of trans-^{35}ClHC═CDF

The ν_{10} fundamental vibrational mode of *trans*-ClHC═CDF, of symmetry species A'' and centered at ≈817 cm^{-1}, may be approximately described as the torsion mode. The overall spectral region of this band is shown in Fig. 3. The absorption exhibits the typical *c*-type envelope with a strong *Q* branch and settled P- and R-branch groups; since this isotopologue is also a near-prolate symmetric top rotator ($\kappa = -0.994$), the spectral features approach those of a perpendicular band.

The procedure for the assignment of the rovibrational transitions followed the pattern carried out for the main isotopologue. Since the wavenumbers of the strongest $^{p}Q_K$ and $^{r}Q_K$ subbranch transitions can be easily identified (see Fig. 3), they were selected as starting point of the analysis. The assigned transitions were fitted as described in Section 3.1. The ground state constants were kept fixed while the upper state parameters, together with the band origin, were refined. The uncertainties associated to the transitions ranged from ±0.001 to ±0.003 cm^{-1}. This procedure was repeated for successively larger sets of assigned lines with increasing K_c values (see Fig. 4).

After a few cycles, leading to reasonable improvement in the agreement between the observed and the computed lines, other transitions from the *P* and *R* branches could also be inserted into the fitting procedure.

The complete analysis in the *P*, *Q*, and *R* branches led to the assignment of about 2800 transitions with J'up to 86 and K'_a up to 9. Further attempts to extend the assignment could not be afforded because the several mingled lines of *trans*-^{37}ClHC═CDF, and impurities from the *cis* isomer and its deuterated isotopologues.

Table 1
Spectroscopic constants (cm^{-1}) for the $\nu_{11} = 1$ state of *trans*-$^{35}ClHC{=}CHF$

	Ground state[a]	$\nu_{11} = 1$
ν_0		784.538 647(64)[b]
A	1.789 762 489 6	1.769 703 0(26)
B	0.082 610 718 98	0.082 589 976(140)
C	0.078 934 954 73	0.078 961 836(113)
$\Delta_J \times 10^7$	0.106 420	0.106 817(173)
$\Delta_{JK} \times 10^6$	−0.345 920	−0.313 49(71)
$\Delta_K \times 10^4$	0.253 506	0.219 73(21)
$\delta_J \times 10^9$	0.691 1	0.691 8(107)
$\delta_K \times 10^7$	0.747 5	0.56(20)
$\Phi_J \times 10^{14}$	0.250	0.250[c]
$\Phi_{JK} \times 10^{12}$	−0.157 9	−0.157 9[c]
$\Phi_{KJ} \times 10^{11}$	−0.681	−0.681[c]
$\Phi_K \times 10^9$	0.269	0.269[c]
$\phi_J \times 10^{15}$	0.57	0.57[c]
Number of data		2910
J_{max}		92
$K_{a\,max}$		13
$\sigma \times 10^3$		0.267

[a] From Ref. [13].

[b] Quoted uncertainties in parenthesis are one standard deviation in units of the last significant digits.

[c] Constrained to the ground state value.

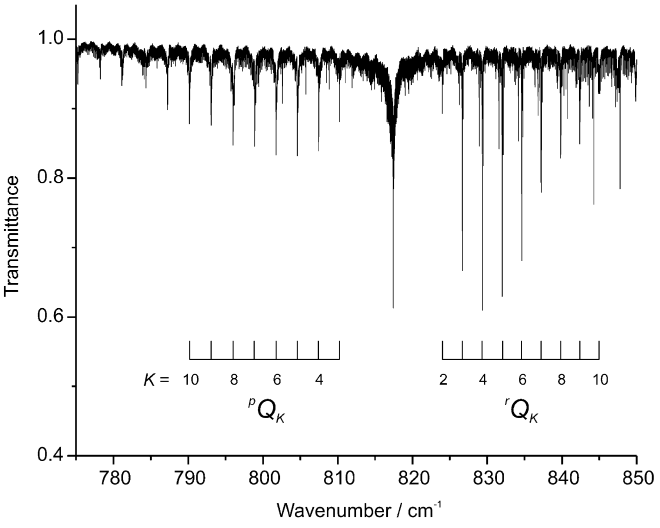

Fig. 3. An overview spectrum of the ν_{10} fundamental band of *trans*-$ClHC{=}CDF$ between 775 and 850 cm^{-1} ($P = 2$ mbar, 15 cm cell, $T = 298$ K). The main features are highlighted.

With the ground state parameters fixed at the values of Ref. [13], reported in the first column of data in Table 2, the upper constants were refined obtaining in the final fit of 2715 lines a standard deviation of about $0.8 \times 10^{-3}\ cm^{-1}$; the derived molecular parameters for the $\nu_{10} = 1$ state of *trans*-$^{35}ClHC{=}CDF$ are given in the second column of Table 2. The band origin, the excited rotational and quartic centrifugal distortion constants were all well determined and the standard deviation of the whole fit is consistent with the experimental resolution of the infrared spectrum.

During the assignment procedure a number of lines could be identified as belonging to the ^{37}Cl-containing species of both isotopologues, but they were too weak and/or too overlapped to be assigned and fitted. Indeed, the most visible features were the Q-branch lines. The large sets of data analyzed for both molecules stimulated the use of combination differences in order to ameliorate the ground state constants. Such attempts, however, did not lead to any significant improvement and therefore were not carried out further.

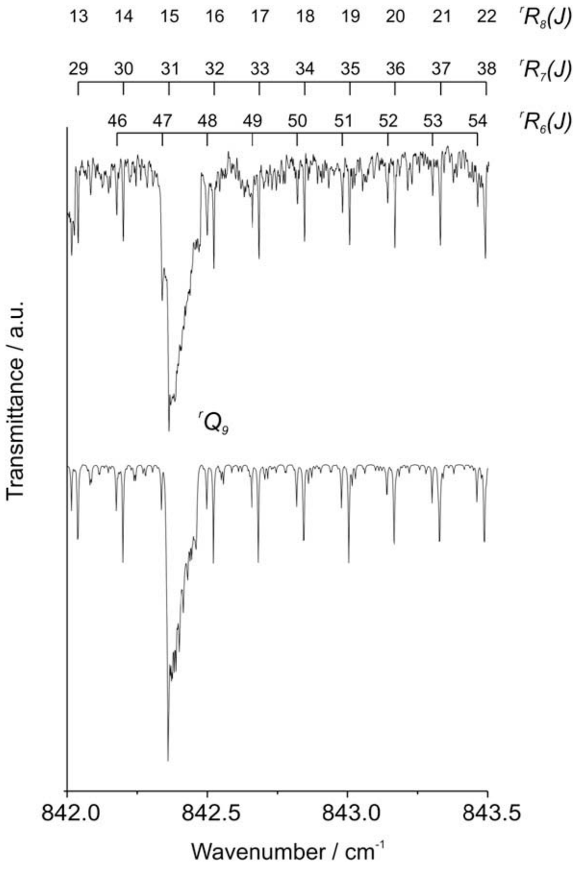

Fig. 4. A portion of the infrared spectrum ($P = 2$ mbar, 15 cm cell, $T = 298$ K) of *trans*-$ClHC{=}CDF$ between 842.0 and 843.5 cm^{-1}; upper trace observed, lower trace computed. Three main sequences of vibro-rotational transitions are shown: $^rR_6$ with $J = 46$–54, $^rR_7$ with $J = 29$–38 and $^rR_8$ with $J = 13$–22. The lines belonging to the $^rR_7$ and $^rR_8$ series are overlapped. The $^rQ_9$ branch is not resolved.

Table 2
Spectroscopic constants (cm^{-1}) for the $\nu_{10} = 1$ state of *trans*-$^{35}ClHC{=}CDF$

	Ground state[a]	$\nu_{10} = 1$
ν_0		817.195 350(64)[b]
A	1.460 567 66	1.449 891 0(36)
B	0.082 278 25	0.082 267 970(143)
C	0.077 858 66	0.077 913 855(157)
$\Delta_J \times 10^7$	0.103	0.103 942(170)
$\Delta_{JK} \times 10^6$	−0.179 84	−0.158 32(64)
$\Delta_K \times 10^4$	0.114 088	0.080 17(48)
$\delta_J \times 10^9$	0.667	0.754 9(173)
$\delta_K \times 10^7$	0.80	0.741(173)
$\Phi_{KJ} \times 10^{11}$	−0.77	−0.77[c]
$\Phi_K \times 10^{10}$	0.89	0.89[c]
Number of data		2715
J_{max}		86
$K_{a\,max}$		10
$\sigma \times 10^3$		0.75

[a] From Ref. [13].

[b] Quoted uncertainties in parenthesis are one standard deviation in units of the last significant digits.

[c] Constrained to the ground state value.

4. Conclusions

This work deals with the detailed rovibrational analysis of the ν_{11} absorption band of *trans*-$ClHC{=}CHF$ and the ν_{10} of *trans*-$ClHC{=}CDF$ occuring in a spectral region of atmospheric interest; the high-resolution infrared spectra of these molecules were never previously investigated.

From the assigned transition lines reasonable sets of molecular parameters for the $v_{11} = 1$ vibrational level of the main species and for the $v_{10} = 1$ state of the deuterated isotopologue, were obtained. These molecular spectroscopic constants of low energy vibrational excited levels can be used as guidance for further high-resolution experimental investigations of their rotational spectra.

The complete lists of all the observations used in the upper vibrational states together with the residuals are given as Supplementary data for this article.

Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2008.06.011.

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