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SPECTROCHIMICA ACTA PART A

Spectrochimica Acta Part A 60 (2004) 1967-1975

www.elsevier.com/locate/saa

Experimental and theoretical studies of the vibrational spectra of *cis*-1-bromo-2-fluoroethene

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Received 2 September 2003; received in revised form 15 October 2003; accepted 15 October 2003

Abstract

The gas-phase infrared spectrum of *cis*-1-bromo-2-fluoroethene has been studied at low resolution in the range 200–6500 cm⁻¹, leading to a complete assignment of the fundamentals, except the lowest vibrational mode ν_9 predicted at 167 cm⁻¹. The remaining vibrational structure has been mainly interpreted in terms of first overtone or two quanta combination bands. Isotopic ^{79/81}Br shift has been observed only in the ν_8 fundamental. The equilibrium structure and the quadratic force field have been investigated theoretically at CCSD(T) level of theory employing Dunning's correlation consistent triple-zeta basis set. Cubic and semidiagonal quartic force field have been calculated using second-order Møller–Plesset perturbation theory and Ahlrich' split valence (SV) contracted basis set. After a minor scaled quantum mechanical (SQM) adjustment of the quadratic force constants, the vibrational analysis, based on the second-order perturbation theory, has been carried out with the calculated force constants.

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Keywords: Bromofluoroethene; Infrared spectra; Vibrational assignment; Ab initio calculations; Anharmonic force field

1. Introduction

Dihalogenated ethenes containing fluorine and chlorine were extensively examined in the infrared region at low and high resolution, while the heavier ones, with bromine or iodine, were subjected to limited studies to dated. In this context we have focused the attention on the *cis* isomer of 1-bromo-2-fluoroethene recently examined for the first time in the microwave region [1].

The present contribution reports a detailed vibrational assignment of this molecule which is here investigated at low resolution in a large IR spectral region. The previous partial assignment of Viehe et al. [2,3] is now completed providing the assignment of all the fundamentals occurring in the region investigated, for v_9 , expected in the far infrared, we have estimated its value by means of difference of selected band centres. In order to support the assignments of the vibrational spectrum as well as to determine the molecular equilibrium geometry of *cis*-1-bromo-2-fluoroethene,

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theoretical ab initio studies have also been carried out. High level electronic structure calculations, CCSD(T), have been employed to compute the molecular structure and the harmonic force field at the optimised geometry. To take into account the anharmonic effects, which are mandatory for a comprehensive assignment of the infrared spectrum, cubic and semidiagonal quartic force constants have also been computed with the use of a finite difference procedure in the space of the dimensionless normal coordinates.

2. Experimental details

2.1. Synthesis of CHBr=CHF

CHBr=CHF was synthesised following the method of Viehe [2] based on a two steps reaction:

 $Br_2CHCHBr_2 \xrightarrow{SbF_3, Br_2} Br_2CHCHBrF + Br_2CHCHF_2$

 $Br_2CHCHF_2 \xrightarrow{Zn, C_2H_5OH} CHBr=CHF$

The reactant (Aldrich, 98%) was fluorinated with a mixture of SbF₃ and Br₂ (Aldrich, 98.8 and 99%, respectively) in a closed steel reactor at 120–125 °C for 23 h. During the first step, the formation of the most volatile 1,1-dibromo-2,2-difluoroethane was periodically checked by gas-phase IR spectroscopy. This compound (bp 107 °C), purified by fractionation, was treated with zinc powder (Aldrich, 98%) in ethanol at room temperature for about 10 min. The reaction mixture was then distilled and the *cis/trans* sample of CHBr=CHF was collected between the boiling points of 25 and 39 °C. The diastereoisomers were next separated under vacuum at low temperature. The final *cis* sample used in the analysis showed impurities of the *trans* species and ethyl alcohol, both producing weak absorptions easily recognised in the spectra.

2.2. Spectra

The gas-phase infrared spectra were recorded at room temperature in the range 200–6500 cm⁻¹ using the Bruker Vector 22 (400–6500 cm⁻¹) and the Nicolet Magna 750 (200–500 cm⁻¹) FTIR spectrometers, at the resolution down to 0.5 and 2.0 cm^{-1} , respectively. In the region 200–500 cm⁻¹, spectra were recorded using a 16 cm path cell equipped with KRS-5 windows and a sample pressure of 80 mbar. In the region 400–6500 cm⁻¹, a 16 cm path cell and a multipass cell, set to a path length of 22.5 m, both equipped with KBr windows, were employed, sample pressures were 13 and 40 mbar in the former and 7 mbar in the latter case, respectively.

The given band centre values are believed to have an accuracy of $\pm 0.4 \text{ cm}^{-1}$ for well resolved absorption features; however they cannot be usually evaluated with this precision in low resolution spectra. For the weaker and/or unresolved bands, the reported values have been estimated with an accuracy not better than 1 cm^{-1} .

3. Computational details

Ground state structural and vibrational parameters of *cis*-CHBr=CHF were computed in the harmonic approximation at coupled cluster singles and doubles level augmented by a perturbative correction for connected triple excitations, CCSD(T) [4]. These calculations were performed with the MOLPRO 2000 program package¹ as implemented on a SGI Origin 3800 computer system. The correlation consistent triple-zeta basis set of Dunning [5], which comprises 161 contracted Gaussian-type orbital (cGTO), was used in

conjunction with the CCSD(T) level of theory, to search the equilibrium geometry. The harmonic force field was evaluated in a Cartesian coordinate representation at the CCSD(T)/cc-pVTZ optimised geometry. The hessian matrix is calculated numerically by finite differences [6]. In addition, two other geometry optimisations and harmonic force fields were carried out employing the Møller-Plesset theory to second order (MP2) [7], using the GAUSSIAN 98 suite of programs [8] also implemented in the above mentioned computer system. The basis sets employed in these additional calculations were again cc-pVTZ and 6-311 + +G(3df, spd) with 212 cGTOs; the latter was used mainly to monitor the extension of the set used in [1]. Spherical harmonics were used throughout, and all valence electrons were correlated in MP2 and CCSD(T) calculations (frozen core approximation). MP2/cc-pVTZ harmonic force field was evaluated by analytical second derivatives of the energy; in addition the dipole moment derivatives were also computed via analytical second-derivatives in order to calculate the integrated infrared band intensities within the double-harmonic approximation.

The cubic and quartic semidiagonal normal coordinates force constants (ϕ_{ijk} , ϕ_{ijkk}) were determined with the use of a finite difference procedure involving displacements along the normal coordinates [9]. These displacements were chosen in order to vary the potential energy of each vibrational mode of 0.001 hartree. Since *cis*-CHBr=CHF has 58 electrons, to reduce the computational costs in terms either of disk space or CPU's time, the MP2/SV level of theory was employed to calculate the cubic and quartic force constants. The basis set employed in these calculations was the fully optimised contracted split valence (SV) Gaussian basis set, [10], which computes 60 cGTOs basis functions: (4s)/[2s] for H atoms, (7s4p)/[3s2p] for C and F atoms, and (14s10p5d)/[5s4p2d] for Br atom.

A dedicated PC, using the GAMESS-UK program [11], was used to calculate all the cubic and the semi diagonal quartic normal coordinates force constants. To compensate in part the limited basis set, all electrons were correlated.

4. Results and discussion

4.1. Spectral data and assignment of fundamentals

Cis-1-bromo-2-fluoroethene is a planar molecule belonging to the point group C_s, the 12 fundamental modes are distributed with nine of A' species and three of A'' species. This molecule is a near prolate asymmetric rotor with the asymmetry parameter $\kappa = -0.945$ [1]. The *a* and *b* axes lie in the molecular symmetry plane while the *c*-axis is perpendicular to this plane. Thus, vibrations of A'' species are expected to appear as C-type bands while those of A' species should appear as A-/B-hybrid bands, though one of the components might be much weaker than the other. A distinction between these two species is often possible on the

¹ MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, S.T. Elbert, C. Hampel, R. Lindh, A.W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor, M.E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorsteinsson.



Fig. 1. The FTIR gas-phase survey spectrum of *cis*-CHBr=CHF at 1 cm^{-1} resolution: (a) path length 16 cm, pressure = 13 mbar and (b) path length 22.5 m, pressure = 7 mbar. The labelled fundamentals are reproduced in more detail in the next figures.

basis of the rotational contour. A- and C-type bands exhibit a medium and strong Q-branch, respectively, while B-type bands present a depression at their centres. Furthermore, B- and C-type bands can show Q-clusters superimposed in the P- and R-branches, in these cases the expected Q peaks separation is about 0.86 cm^{-1} by adopting the ground state rotational constants of [1].

Survey spectra of the molecule, recorded at 1 cm^{-1} resolution, are shown in Fig. 1. The labelled fundamentals are reproduced in more detail in the next figures. Frequencies and assignments of the observed bands are collected in Table 1. Eleven fundamentals happen in the region investigated; the ν_9 , expected to be very weak and out of the range, has been evaluated by difference from assignment of hot and combination bands. All assigned fundamentals were recognised in the low pressure and short path length spectra; however some of them are very weak or masked by stronger overlapping absorptions. Among overtones and combinations the most intense ones are those observed near the ν_3 , ν_4 and ν_5 fundamentals. For these bands anharmonic vibrational resonance may be occurring.

The two C–H stretching modes v_1 and v_2 , reproduced in Fig. 2, show prevalent A- and B-type envelope, respectively. Though partially overlapped, the weaker band assigned as v_2 is unambiguous since no other bands are expected in this range. The C=C stretching v_3 produces a band with predominant B-type envelope; the ^{P,R}Q rotational structure is clear and well resolved with regular spacing of 0.85 ± 0.10 cm⁻¹ in a long range. The two C–X (X = Br, F) stretching modes v_6 and v_8 exhibit envelope of hybrid A-/B- and A-type bands,

respectively, for the former band the $^{P,R}Q$ rotational structure is again regularly spaced overall the P and R branches while for the latter one the $^{79/81}$ Br isotopic splitting could be readily detected as shown in Fig. 3.

The two C–C–H in plane bendings ν_4 and ν_5 give rise to bands with a complicate structure. The ν_4 band manifests strong features irregularly displaced on both sides with respect to the band centre. The ν_5 band shows two central peaks of different intensity and a series of ^RQ lines with the expected rotational spacing; furthermore, the P-branch, though partially overlapped, appears much stronger than the R-branch. The third observed in plane deformation mode ν_7 (C–C–F) is almost completely obscured by the near perpendicular fundamental ν_{11} and only the Q-branch is detectable.

The three fundamentals of symmetry species A", two CH out of plane bendings and the torsion, show the typical structure of C-type bands. However, v_{10} is very weak and appears only in the form of a narrow spike at low pressure. In Fig. 4 is reproduced the spectral region of v_{11} which, apart the presence of red shifted satellite peaks described later, shows the Q-feature due to the v_7 band.

4.2. Overtones, combination and hot bands

Once the fundamentals were characterised, most of the additional bands were interpreted in terms of first overtone or binary combinations. Some of these bands however have an anomalous higher intensity than usually expected. Among the absorptions observed near the fundamental bands it can



Fig. 2. The FTIR spectral region of the v_1 and v_2 fundamentals of *cis*-CHBr=CHF ascribed to the C–H stretchings of the molecule showing the different envelope of the bands (resolution = 0.5 cm^{-1} , path length 16 cm, pressure = 13 mbar).

be assessed that $2\nu_{10}$, $\nu_7 + \nu_8$ and $\nu_6 + \nu_9$ enhance their intensity due to Fermi resonances with the near ν_3 , ν_4 and ν_5 , respectively.

and combination bands related to the C–H stretchings are expected to appear. Furthermore, the Fermi resonance occurring in the regions of the fundamental bands is replicated and occasionally identifications including three quanta were performed. The proposed assignment, reported in Table 1,

Spectra recorded with the multipass cell allowed the interpretation of many bands up to 6300 cm^{-1} , where overtones



Fig. 3. The FTIR spectral region of the v_8 band of *cis*-CHBr=CHF at 0.5 cm^{-1} resolution showing the isotopic ^{79/81}Br splitting (path length 16 cm, pressure = 13 mbar).



Fig. 4. The FTIR spectral region of *cis*-CHBr=CHF at 0.5 cm^{-1} resolution showing the strong perpendicular v_{11} band and the weaker obscured v_7 hybrid band. The weaker red-shifted Q-peaks of v_{11} have been attributed to hot bands involving the lowest vibrational level v_9 . (a) Path length 16 cm, pressure = 13 mbar and (b) path length 16 cm, pressure = 40 mbar.

has been obtained taking into account harmonic approximation, relative intensity and the expected band contour derived from symmetry species of the relative normal vibrations. In addition, the anharmonicity constants determined from the ab initio force field (see later) have been also considered.

Hot bands could also be detected. In particular the presence of satellite features observed in the fundamental band regions were analysed in detail giving further information. In terms of thermal distribution they can be attributed to the lower vibrational level v_9 , expected at about 170 cm^{-1} : taking the intensity of v_i band as 100%, the expected relative one of $v_i + v_9 - v_9$ at room temperature is calculated to be 44%.

Seven of the fundamental bands, showing prevalent Aor C-type contour, present features attributed to hot bands having v_9 as lower level. One of these, namely $v_6 + v_9 - v_9$, was used to calculate the lower vibrational energy level by applying the Ritz principle.

4.3. Equilibrium geometry and harmonic force field

Table 2 collects the set of chemically intuitive internal coordinates **R** and the optimised values of the nine determinable structural parameters which define the geometry of *cis*-CHBr=CHF. The first column reports the results from CCSD(T)/cc-pVTZ calculations where numerical gradients were employed using the default step-size. In general, CCSD(T) calculations give very reliable results for equilibrium geometry determinations and present systematic errors. On the basis of the vast literature on these ab initio

structure optimisations, an accuracy of 0.005 Å for bond lengths and 0.2° for angles can be assumed. The second column of Table 2 reports the optimised geometrical parameters using the analytical gradients as provided by the MP2 level of theory and employing the same basis set. This calculation was carried out mainly to have the analytical derivatives of the dipole moment in order to compute the integrated infrared band intensities. We have also tried to improve the basis set quality used in [1] performing a geometry optimisation also at MP2/6-311 + +G (3df, 2pd) level. The results, listed in the third column of Table 2, do not show any improvement from the data reported in [1].

Assuming the CCSD(T)/cc-pVTZ optimised equilibrium structure as the nearest to the true molecular geometry, the harmonic force field was evaluated at the same level of theory in a Cartesian coordinates representation. Since the theoretical harmonic force field provided a very good overall description of the spectroscopic parameters, it was used as the starting point for an additional empirical refinement through a scaled quantum mechanical (SQM) adjustment of the quadratic force constants. Employing the 12 scaling factors associated to the respective internal coordinates, the quadratic Cartesian force constants were first transformed to the internal coordinates space and then scaled within the SQM formalism [12]:

$$F_{ij}^{\text{scaled}} = \sqrt{s_i s_j} F_{ij}.$$

The experimental data consisted of rotational and centrifugal distortion constants from [1] and the harmonised wavenumbers of the fundamental vibrations obtained employing the

Table 1 Observed band centres (cm⁻¹) of the gas-phase IR spectra of *cis*-CHBr=CHE

Band	Envelope	Relative intensity	Wavenumber ^a
			$(167.5 \pm 0.6)^{b}$
$v_{12} + 2v_9 - 2v_9$			413.8
$v_{12} + v_9 - v_9$			414.9
v_{12}	С	m	416.1
$v_5 - v_{11}$			491.9
$v_8 + v_9 - v_9$			(567.0/565.5) ^c
ν_8	А	m	(568.2/567.0) ^c
$v_{11} + 2v_9 - 2v_9$			728.0
$v_{11} + v_9 - v_9$			729.0
v_{11}	С	S	730.1
ν_7	А	W	750.1
$2v_{12}$	А	VW	829.9
$v_{10} + v_9 - v_9$			857.0
v_{10}	С	VW	857.9
$v_6 + v_9 - v_9$			1042.8
ν_6	A/B	VS	1045.4
$v_{11} + v_{12}$	A	W	1144.3
$v_7 + v_{12}$	С	VW	1165.2
$v_6 + 2v_9 - v_9$			1209.1
$v_6 + v_9$	A/B	m	1210.3
ν_5	A/B	S	1222.0
$v_5 + v_9 - v_9$	_		1224.7
$v_{10} + v_{12}$	В	VW	1273 ± 1
$\nu_7 + \nu_8$	A	m	(1310.9/1309.8)
ν ₄	A/B	S	1327.5
$v_6 + 2v_9$	A/B	VW	1377.5
$v_5 + v_9$	A/B	vw	1392.1
2v ₁₁	В	vw	$145/\pm 1$
$v_{10} + v_{11}$	A A/D	m -	1584.1
V3	A/B	S	1051.8
$2v_{10}$	A/B	m	1/14.2
$v_3 + v_9$	A	vw	1010.0
$v_6 + v_{10}$	^	VW	1901.5 1950 \pm 1
$v_6 + v_7 + v_9$	A A	vw vw	1939 ± 1 1071 ± 1
$\nu_5 \pm \nu_7$	A/B	vw w	2087.2
$2v_0$	C	VW VW	2184.0
$v_4 + v_{10}$	B	VW VW	22104.0 2217 ± 1
$2v_{6} + v_{8}$	A	W	2217 ± 1
$v_5 + v_6$	A	w	2263.7
$v_4 + v_6$	A	vw	2367.8
$v_3 + v_{11}$	C	vw	2376.5
$v_3 + v_7$	A	vw	2388 ± 1
$v_5 + v_6 + v_9$	В	W	2430 ± 1
$2v_5$	В	w	2444 ± 1
$v_5 + v_7 + v_8$	А	vw	2527 ± 1
$v_4 + v_5$	А	vw	2545 ± 1
$\nu_4 + \nu_7 + \nu_8$	A/B	VW	2632 ± 1
$2v_4$	A/B	VW	2651 ± 2
$v_3 + v_6$	A/B	W	2689.8
$v_3 + v_6 + v_9$	А	VW	2854 ± 1
$v_3 + v_5$	А	VW	2865 ± 1
$\nu_3 + \nu_7 + \nu_8$	А	W	2948 ± 1
$v_3 + v_4$	A/B	W	2967 ± 1
ν_2	A/B	w	3091.8
$v_1 + 2v_9 - 2v_9$			3115.0
$v_1 + v_9 - v_9$			3116.5
ν_1	А	m	3118.1
$2v_3$	A/B	w	3289.4
$\nu_2 + \nu_8$	В	w	3656 ± 2
$\nu_1 + \nu_7$	A/B	w	3858 ± 2
$\nu_1 + \nu_{10}$	С	VW	3968 ± 1

Tbale 1 (Continued).

Band	Envelope	Relative intensity	Wavenumber ^a
$v_2 + v_6$	A/B	w	4134.5
$v_1 + v_6$	A/B	W	4154 ± 1
$v_2 + v_5$	А	VW	4306 ± 1
$v_1 + v_6 + v_9$	А	W	4319 ± 1
$v_1 + v_5$	А	W	4332 ± 1
$\nu_2 + \nu_7 + \nu_8$	А	VW	4397 ± 1
$v_2 + v_4$	А	W	4413 ± 1
$\nu_1 + \nu_7 + \nu_8$	А	VW	4429 ± 2
$v_1 + v_4$	А	VW	4443 ± 1
$v_1 + v_3$	A/B	VW	4780 ± 2
$v_1 + v_2$	A/B	W	6004 ± 1
$2\nu_1$	В	W	6125 ± 2

Abbreviations used are as follows: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

^a The experimental error is $\pm 0.4 \text{ cm}^{-1}$ unless otherwise quoted.

^b From hot and combination bands implying ν_6 .

^c The two values indicate the ^{79/81}Br measurements.

empirical procedure proposed by Duncan et al. [13] on the base of the Dennison's rule [14]. The 12 scaling factors were then determined from a least squares fit of the observed data.

The rotational and quartic centrifugal distortion constants for both isotopomers, *cis*-CH⁷⁹Br=CHF and *cis*-CH⁸¹ Br=CHF, obtained with the scaled harmonic force constants, are given in Table 3, and are compared with the experimental ones [1]. There is a general overall good agreement between the calculated and observed data. In the lower part of the same table, the sextic centrifugal distortion constants of the main species, which requires the cubic force field (see later), are also included.

The elements of the bromine inertial nuclear quadrupole coupling tensor, evaluated from an applied field gradient q_{ij} , are computed as:

$\chi_{ij} = e Q q_{ij}, \quad i, j = a, b, c$

where χ_{ij} is the *ij*-element of the nuclear quadrupole coupling tensor, *e* the electronic charge, *Q* the nuclear electric quadrupole moment of bromine nucleus and *a*, *b*, *c* are the inertial axes. Since *cis*-1-bromo-2-fluoroethene is a planar molecule, the inertial nuclear quadrupole tensor has only one off-diagonal element, χ_{ab} . The values of q_{ij} were computed at HF/cc-pVTZ level and then converted into the χ_{ij} values by using the following expression:

 $\chi_{ii}(\text{MHz}) = 234.9647 Q(\text{barn})q_{ii}(\text{amu})$

where Q (⁷⁹Br) = +0.331 barn and Q (⁸¹Br) = +0.276 barn, both taken from [15]. These results, compared with the experimental data obtained from the microwave spectra [1], are given in Table 4. There is a very good agreement between the calculated and observed values, only the off-diagonal element χ_{ab} exhibits a larger error which however does not reach the 5%. The scaled quadratic force field, in terms of the internal coordinates defined in Table 2, is reported in Table 5.

Table 2

		CCSD(T)/cc-pVTZ	MP2/cc-pVTZ	MP2/6-311++G(3df, 2pd)
A'				
R_1	C ₁ –Br	1.8823	1.8617	1.8652
R_2	$C_1 - C_2$	1.3311	1.3282	1.3281
R_3	C ₂ –F	1.3336	1.3315	1.3306
R_4	C ₁ –H	1.0782	1.0765	1.0776
R_5	C ₂ -H	1.0818	1.0799	1.0802
R_6	$\angle BrC_1C_2$	123.32	123.31	123.44
R_7	$\angle HC_1C_2$	120.39	119.93	119.83
R_8	$\angle HC_2C_1$	123.02	122.86	123.11
R_9	$\angle FC_2C_1$	123.25	123.31	123.12
Α″				
R_{10}	C ₁ -H out-of-plane	bending		
R_{11}	C ₂ -H out-of-plane	bending		
<i>R</i> ₁₂	Torsion			

Internal coordinates of *cis*-CHBr=CHF and theoretical equilibrium geometry computed at the levels of theory used to determine the harmonic force field and the band intensities (see text)

Distances in Å and angles in degree.

4.4. Ab initio anharmonic force field

The cubic and quartic semidiagonal force constants were calculated in the normal coordinates space with the use of a finite difference procedure, as outlined in Section 3, through the calculation of analytical second derivatives (rel-

Table 3 Observed ([1]) and calculated rotational constants (MHz), quartic (kHz) and sextic (in 10^2 Hz) centrifugal distortion constants for *cis*-CHBr=CHF

	cis-CH ⁷⁹ Br=C	HF	cis-CH ⁸¹ Br=Cl	HF
	Observed	Calculated	Observed	Calculated
$\overline{A_0}$	15107.019	15209.1783	15098.604	15200.6747
B_0	2494.8890	2445.7913	2474.7752	2426.0586
C_0	2139.3039	2106.9552	2124.3304	2092.1339
Δ_J	1.345	1.2876	1.326	1.2683
Δ_{JK}	-10.75	-10.4705	-10.60	-10.3652
Δ_K	57.7	62.1843	56.2	61.9737
δ_J	0.2643	0.2466	0.2605	0.2413
δ_K	4.95	4.2014	4.82	4.1561
Φ_J		0.3301		
Φ_{JK}		-1.6058		
Φ_{KJ}		-5.1539		
Φ_K		33.2301		
ϕ_J		0.1088		
ϕ_{JK}		2.5766		
ϕ_K		71.0031		

Table 4

Observed ([1]) and HF/cc-pVTZ calculated inertial quadrupole tensor for $cis\mbox{-}CHBr\mbox{=}CHF$

	cis-CH ⁷⁹ Br=	CHF	cis-CH ⁸¹ Br=CHF			
	Observed	Calculated	Observed	Calculated		
Хаа	278.044	278.338	233.04	232.089		
$\chi_{bb} - \chi_{cc}$	256.32	257.267	215.81	214.519		
$ \chi_{ab} $	431.50	414.331	360.27	345.485		

All data are in MHz.

ative precision $\varepsilon \le 10^{-6}$) at these displaced geometries. At the MP2/SV equilibrium geometry of *cis*-CHBr=CHF, the internal gradient components were less then 10^{-7} amu.

The anharmonic spectroscopic constants were then determined from the theoretical normal coordinates cubic and quartic force constants by applying the formulas based on second-order perturbation theory [16]. The anharmonicity constants x_{ij} of *cis*-CH⁷⁹Br=CHF, calculated using the theoretical force field determined so far, are reported in Table 6. Since the anharmonic interactions between fundamentals and overtones or combination bands may lead to indefinitely large terms in the corresponding perturbational formulas, it is necessary to exclude such contributions from the perturbational summations [17] and define therefore effective constants. These effective anharmonicity constants were introduced in the present work to account for the following Fermi resonances: $v_1/2v_3, v_3/2v_{10}$, and $v_2/v_3 + v_4(x_{ij}$ values marked with an asterisk in Table 6).

In Table 7 are summarised the vibrational fundamentals computed with the scaled harmonic CCSD(T)/cc-pVTZ force field together with the total energy distribution (TED) values [18] in terms of the internal coordinates defined in Table 2, and the corresponding approximate description of the vibrational mode. Only for the vibrational mode ν_8 , which corresponds to the C–Br stretching, the calculated harmonic value shows ^{79/81}Br isotopic shift.

The integrated infrared band intensities were computed with the formula:

$$A_i = 42.25472 \ |\partial \mu / \partial Q_i|^2$$

where A_i is in km/mol, and $\partial \mu / \partial Q_i$ in D/(Å amu^{1/2}) are the dipole moment derivatives evaluated via analytical derivatives computed at MP2/cc-pVTZ level of theory.

Applying the anharmonic constants of Table 6, the calculated wavenumbers are obtained and listed in the penultimate column of Table 7. The wavenumbers of the first three

Table 5			
Scaled quadratic	force	constants	F_{ij}

i	j	F _{ij}	i	j	F _{ij}	i	j	F _{ij}	i	j	F_{ij}
1	1	3.4787	5	4	0.0113	7	6	0.4889	9	4	0.0441
2	1	0.2371	5	5	5.6508	7	7	0.9226	9	5	-0.1084
2	2	9.4698	6	1	0.1023	8	1	0.0563	9	6	0.0471
3	1	0.0560	6	2	0.2664	8	2	0.1942	9	7	0.1080
3	2	0.4556	6	3	-0.0936	8	3	-0.4872	9	8	0.7179
3	3	6.7534	6	4	-0.0442	8	4	-0.0023	9	9	1.8101
4	1	0.0336	6	5	0.0263	8	5	0.0207			
4	2	0.0059	6	6	1.2654	8	6	0.0756	10	10	0.4190
4	3	-0.0232	7	1	-0.3236	8	7	-0.0094	11	10	-0.2034
4	4	5.7929	7	2	0.1988	8	8	1.1541	11	11	0.5898
5	1	-0.0156	7	3	0.0691	9	1	-0.0876	12	10	0.3313
5	2	0.0450	7	4	0.0901	9	2	0.4012	12	11	-0.4075
5	3	0.1821	7	5	-0.0012	9	3	0.1174	12	12	0.5351

The units of the force constants are consistent with energy in aJ, bond length in Å and bond angles in radian.

Table 6 Anharmonicity constants x_{ij} (cm⁻¹) of *cis*-CHBr=CHF^a

i	j											
	1	2	3	4	5	6	7	8	9	10	11	12
1	-30.0	-118.4	1.2*	-9.2	-7.9	-2.1	0.3	0.3	-0.3	-8.8	-7.8	-0.7
2		-29.8	-4.1*	-13.6*	-8.8	-1.8	-1.0	0.0	-0.3	-7.5	-6.5	-0.5
3			-8.2*	-4.4*	-8.6	-6.4	-2.3	-1.1	-1.0	-8.0*	-4.2	-4.3
4				-3.4	-8.9	-3.0	1.0	1.0	0.0	1.2	0.2	-0.3
5					-0.5	-2.8	-0.9	-1.5	2.0	-2.3	2.2	-0.9
6						-2.5	-2.1	-2.8	-1.0	-1.3	-0.8	-0.3
7							-1.1	-2.8	-0.1	-0.7	-0.8	-0.7
8								-1.1	-1.5	-1.3	-0.3	-1.1
9									0.3	0.2	-0.3	0.3
10										-1.4*	-10.4	-2.0
11											-2.8	-2.3
12												-0.5

^a The constants which are affected by Fermi resonances are marked by asterisk.

Table 7 Calculated and observed gas phase infrared frequency fundamentals (cm⁻¹) of *cis*-CHBr=CHF (see text for details)

Mode	Total energy distributions (TED) (terms ≥20%)	Approximate description	Infrared intensities (Km mol ⁻¹)	Calculated harmonic wavenumber	Calculated wavenumber	Observed wavenumber
A'						
ν_1	89 R ₄	C ₁ –H stretching	7.6	3258	3117 ^a	3118.1
ν_2	90 R ₅	C ₂ –H stretching	5.9	3209	3091 ^a	3091.8
ν_3	76 R ₂	C=C stretching	65.1	1695	1654 ^a	1651.8
ν_4	$72 R_8 + 27 R_7$	$\angle C_2 C_1 H$ bending	22.9	1352	1327	1327.5
ν_5	$43 R_7 + 34 R_3$	$\angle C_1 C_2 H$ bending	43.9	1242	1222	1222.0
ν_6	$49 R_3 + 30 R_7$	C-F stretching	70.2	1062	1045	1045.4
ν_7	$40 R_9 + 29 R_6 + 23 R_1$	∠CCF bending	3.5	758	751	750.1
ν_8	$71 R_1 + 24 R_9$	C-Br stretching	14.6	(576/575) ^b	568	(568.2/567.0) ^b
ν_9	69 R_6 + 28 R_9	∠CCBr bending	1.3	168	167	167.5
A″						
v_{10}	96 R ₁₂	Torsion	0.5	882	859	857.9
v_{11}	62 R_{11} + 24 R_{10}	C ₂ H out-of-plane bending	40.8	751	730	730.1
v_{12}	84 R_{10} + 26 R_{11}	C1H out-of-plane bending	11.8	423	416	416.1

 a Fermi resonance is taken into account. b The two values refer to $^{79/81}\mathrm{Br}$ isotopomers.

fundamentals (ν_1 , ν_2 and ν_3) were computed after diagonalization of the matrices in which effects of Fermi resonances were taken into account. To facilitate the reading of the table, the last column reports the observed fundamental wavenumbers taken from Table 1. There is a general overall good agreement between the calculated and observed values.

5. Conclusion

A thorough study of the infrared vibrational spectrum and spectroscopic properties of *cis*-1-bromo-2-fluoroethene has been carried out both experimentally and theoretically. All the fundamentals, many combination bands and overtones have been identified in a wide IR region and their assignments have been supported by ab initio calculations. The quantum mechanic computations provided accurate values of equilibrium geometry, nuclear quadrupole tensor, rotational and centrifugal distortion constants. In addition a minor empirical adjusted force field has been determined, and employing second-order perturbation theory, the fundamentals of *cis*-CHBr=CHF have been derived predicting band centres in agreement with the experimental ones.

The results of this work, along with that presented in the microwave region [1], collect basic information which can be useful for high-resolution infrared studies, in particular in the regions of the atmospheric windows.

6. Supplementary materials

The complete lists of the full cubic with the semi diagonal quartic force constants in dimensionless normal coordinate space, are available from the authors.

Acknowledgements

The authors thank Alessandro Baldan for the synthesis of *cis*-CHBr=CHF and the MIUR, Rome, for financial support.

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