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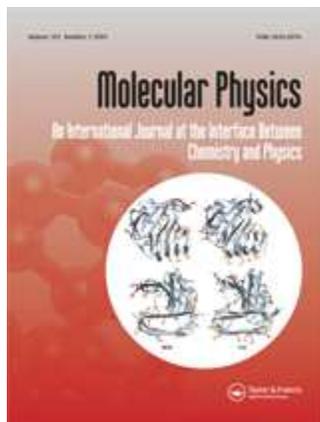
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Anharmonic Force Fields of Bromofluoromethane

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High-level *ab initio* calculations with relatively large basis sets are reported for bromofluoromethane, CH₂BrF. Correlated harmonic and anharmonic force constants are obtained from several levels of theory including second-order Møller-Plesset perturbation and coupled cluster CCSD(T). Density functional theory and to be more precise the B3LYP functional, is also employed. Results are used to determine a number of anharmonic molecular properties, including vibration-rotation interaction constants, vibrational anharmonicity constants, fundamental vibrational frequencies, sextic centrifugal distortion constants and rotational constants which include zero-point corrections. Good agreement with available experimental data is found combining coupled cluster CCSD(T) optimised geometry and harmonic force field with cubic and quartic force constants obtained at MP2 level of theory, a cost-effective computation in terms of time. Moreover, transformations of the force fields in mass-independent internal coordinates force constants suitable for other isotopologues of CH₂BrF, are also investigated.

Keywords: Anharmonic force field; internal quartic force constants; spectroscopic parameters; bromofluoromethane; vibration-rotation constants

1 Introduction

Recently bromofluoromethane (CFC-31B1), a dihalogen substituted methane having an ozone depletion potential of 0.73 with respect to CCl₃F (CFC-11), has been investigated by medium- and high-resolution infrared (IR) spectroscopy [1–3].

In Ref. [1] the vibrational spectra of CH₂BrF were studied in the region below 6200 cm⁻¹ at medium resolution and an *ab initio* investigation comprehensive of harmonic force field calculation was also performed. Employing a 90% enriched specimen of CH₂⁷⁹BrF, the high resolution infrared spectrum of the ν_4 fundamental vibration allowed the determination of the excited and ground state constants including some sextic centrifugal distortion terms [2].

Subsequently the rovibrational analysis of the tunable diode laser spectra of the ν_3 fundamental was also performed [3], keeping the ground state constants fixed to the values of Ref. [2].

Since the pioneering early days of *ab initio* calculations of harmonic force fields of polyatomic molecules as an invaluable aid for the proper assignments of their infrared spectra [4–6], in the last few decades, thanks to the progress in hardware and software, the prediction of accurate energy levels and spectroscopic parameters beyond the harmonic approximation is becoming a viable task. The theoretical development of analytical derivative methods has made it possible to determine, at moderate computer costs, the cubic and quartic force constants. The calculation of fundamental frequencies which closely correspond with the frequencies obtained from high-resolution infrared spectra, vibration-rotation interaction constants, centrifugal distortion constants and other spectroscopic parameters by use of anharmonic force fields permits direct comparison between computed and observed spectroscopic transitions.

In this article are reported the anharmonic force fields of bromofluoromethane determined by methods of quantum mechanics electronic structure theory. The theoretical predictions were performed at several levels of theory and the results were compared taking into account both the quality of the computed

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1 data and the time required to obtain them. These results, including mass-independent anharmonic force
2 constants up to 4th order, are expected to facilitate and guide experimental work on the high-resolution
3 rovibrational spectrum of bromofluoromethane and its isotopologues.
4

5 6 7 2 Computational details

8
9 Quantum-chemical calculations were carried out over a span of one year using different suites of programs
10 and levels of theory. At first, the molecular geometry was optimised and the harmonic force field was
11 computed with coupled cluster theory with single and double excitations augmented by a perturbational
12 estimate of the effects of connected triple excitations [7–9], CCSD(T), employing the Dunning correlation
13 consistent cc-pVTZ basis set [10,11] with the MOLPRO [12] system of programs. The cc-pVTZ basis is a
14 [6s5p3d1f/4s3p2d1f/3s2p1d] contraction of a (20s13p9d1f/10s5p2d1f/5s2p1d) primitive set for Br/C,F/H
15 atoms, respectively.
16

17 In another run, after geometry optimisation and calculation of the harmonic force constants, the anhar-
18 monic force field in terms of cubic and quartic semidiagonal force constants, were evaluated by numerical
19 differentiation of analytic second derivatives calculated at points that are displaced along the normal coor-
20 dinates [13] using a Density Functional Theory (DFT) method and to be more precise the Becke [14] three
21 parameters exchange functional (B3) in combination with the Lee, Yang, and Parr [15] (LYP) correlation
22 functional. A local developed procedure which includes the GAMESS-UK program [16] was used to get the
23 force constants at B3LYP/cc-pVTZ level of theory.
24

25 The installation of the GAUSSIAN 03 suite of programs [17] on computer systems available through
26 an Interuniversity Consortium Computer Center (CINECA), encouraged many other calculations taking
27 advantage of the implementation of anharmonic force constants computation included in the program
28 code [18]. Geometry optimisation, harmonic force field and anharmonic force constants calculations were
29 carried out at the correlated levels of second-order Møller-Plesset perturbation theory [19], (MP2), either
30 correlating all the electrons, MP2(full), or excluding the core electrons (frozen core), MP2(fc), all employing
31 the cc-pVTZ basis set. In addition calculations with density functional theory employing the B3LYP
32 functional in conjunction with cc-pVTZ and 6-311G++(3df,2pd) [20] basis sets, were also performed.
33

34 The implementation of analytic second derivatives of CCSD(T) molecular energies with respect to nuclear
35 coordinates, stimulated the installation of Mainz-Austin-Budapest version of ACES2 program package [21].
36 The CCSD(T) level of theory was used in conjunction with the cc-pVTZ basis set for H, C, and F atoms
37 while using TZVP, (17s13p7d)/[6s5p3d] contraction [22], for the Br atom to reduce the computation time.
38 These calculations are summarized in Table 1 with information concerning the program, computer, level
39 of theory and approximate computer time. Although the computer times have been fairly rounded, it
40 becomes clear that CCSD(T) anharmonic force constants calculation cannot be afforded with one PC.
41 The installation of ACES2 on the SP5 cluster of processors (see Table 1) made the calculations employing
42 the cc-pVTZ basis set for all the atoms of bromofluoromethane also possible in acceptable time. All ACES2
43 calculations were carried out within the frozen core approximation.
44

45 Finally, the complete quartic force fields in terms of dimensionless normal coordinates were carried out
46 at B3LYP/cc-pVTZ and MP2(full)/cc-pVTZ(H,C,F)/TZVP(Br) levels of theory employing GAMESS-UK
47 and ACES2 program packages, respectively. In order to get the full quartic force constants having four
48 different indices, Φ_{ijkl} , additional double displacements of the type $(-\Delta q_i, -\Delta q_j)$ and $(+\Delta q_i, +\Delta q_j)$ were
49 required [23]. Both runs could be carried out in less than 2 weeks on the PC workstation. Spherical
50 harmonics were used throughout.
51

52 53 3 Results and discussion

54
55 Bromofluoromethane molecule, with a symmetry plane containing the F, C, and Br atoms, belongs to
56 the C_s symmetry point group and the 9 fundamentals have the following symmetry species: $6A'$ which
57 comprise the in-plane vibrations and $3A''$ for the out-of-plane modes.
58

59 The set of chemically intuitive nonredundant internal coordinates (in parentheses), corresponds to the
60

six structural parameters: C–H (h), C–F (f), C–Br (b), $\angle\text{HCH}$ (γ), $\angle\text{HCF}$ (δ), and $\angle\text{HCB}$ (β).

For the quadratic force field, in the space of internal or symmetry coordinates, there are 27 independent force constants detailed as $21A'A' + 6A''A''$. The cubic potential consists of 92 force constants which can be detailed as $56A'A'A' + 36A'A''A''$ and the independent quartic potential constants are 267 detailed as $126A'A'A'A' + 15A''A''A''A'' + 126A'A'A''A''$. The symmetry species relative to the cubic and quartic force constants refer to the indices which span the normal modes.

The computed equilibrium geometry of bromofluoromethane at the various levels of theory investigated are reported in Table 2. For the sake of completeness also the $\angle\text{FCBr}$ angle, which can however be easily obtained from the other nonredundant structural parameters, has been reported in the same Table.

As expected, both geometries and harmonic frequencies of calculations at B3LYP/cc-pVTZ level of theory are actually equivalent since they represent the same computation performed with different programs and machines. This consideration applies also to calculations done at the CCSD(T)/cc-pVTZ level as reported in the last two columns of Table 2. Also calculations MP2(full)/cc-pVTZ and MP2(full)/cc-pVTZ(H,C,F);TZVP(Br) present closely results indicating only small differences from employing the cc-pVTZ basis set for Br instead of the less resources demanding TZVP. These arguments can be extended to calculations CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVTZ(H,C,F);TZVP(Br). Between calculations MP2(full)/cc-pVTZ and MP2(fc)/cc-pVTZ, which correlate all electrons and the valence electrons, respectively, the discrepancies become larger. As far as calculation MP2(full)/cc-pVTZ is concerned, the C–H and C–Br bond lengths are too short with respect to the CCSD(T) values.

In general, CCSD(T) calculations give very reliable results for equilibrium geometry determinations with systematic errors. On the basis of several structure optimisations, an accuracy of 0.005 Å for bond lengths and 0.2° for bond angles can be assumed [24].

The computed harmonic vibrational wavenumbers, ω_i , of $\text{CH}_2^{79}\text{BrF}$ are shown in Table 3. For the calculation at CCSD(T)/cc-pVTZ level of theory performed with ACES2 program, the analytical derivative of the dipole moment was also computed and used to determine the integrated infrared intensity of each fundamental vibration. These data are reported in parentheses, near the wavenumbers, in Table 3.

The cubic and quartic force constants, in terms of dimensionless normal coordinates are reported in Table 4. For brevity only the third and fourth potential derivatives with respect to the q_i at the equilibrium geometry having the same three and four i indices, respectively, are presented. These data however suffice for the following considerations.

Both cubic and quartic force constants, although computed at different levels of theory, are almost comparable.

The computer time required in these calculations are nevertheless quite unlike each other as summarized in Table 1. They range from one or two days up to more than three months.

Another point to be taken into account concerns the sign of the force constants. Although many spectroscopic parameters are computed directly from the *ab initio* program packages, it is preferable, especially in the framework of the spectral analysis of small molecules, to input the theoretical force field into a computer program dedicated to determine the molecular constants from second-order perturbation theory [25, 26].

Therefore commonplace transferring of the computed force field does not ensure subsequently right calculations. In particular the vibration-rotation interaction constants α_i^B and the sextic centrifugal distortion constants might be wrongly calculated if the signs of the cubic force constants are not appropriately checked.

A displacement Δq_i along the dimensionless normal coordinate q_i leads to Cartesian displacements:

$$\Delta X_{3N}^i = \gamma_i^{-1/2} l_{3N,i} M_{3N}^{-1/2} \Delta q_i, \quad \gamma_i = \lambda_i^{1/2} / \hbar, \quad i = 1, 3N - 6$$

where λ_i and $\{l_{3N,i}\}$ are the eigenvalues and eigenvectors, respectively, of the mass-weighted quadratic force constants matrix evaluated, in terms of Cartesian coordinates, at the equilibrium geometry, while M_{3N} are the masses of the N atoms which compose the molecule.

It should be noticed that the ambiguity in the definition of the phase of q_i arise from the fact that both $l_{3N,i}$ and $-l_{3N,i}$ are column eigenvectors which solve the same secular equation with the same eigenvalues

1 λ_i . Two solutions of the same problem may be obtained with opposite phase from two computer systems
2 and programs, even when exactly the same input data are used.

3 Consequently, exactly the same eigenvector matrix $\{l_{3N,i}\}$ employed to calculate the cubic and quartic
4 force constants, must be supplied together the force field to the separate program which computes the
5 spectroscopic parameters, in order to get comparable results from different cases.

6 Since the largest discrepancies among the computed spectroscopic parameters are actually localised on
7 the harmonic wavenumbers of the normal modes (see Table 3) and it was not possible to determine the
8 eigenvector matrix used by GAUSSIAN03 program package to compute the anharmonic force field, the rest
9 of the discussion will be limited to calculation B3LYP/cc-pVTZ performed with GAMESS-UK and to the
10 MP2(full)/cc-pVTZ(H,C,F);TZVP(Br) and CCSD(T)/cc-pVTZ computations with ACES2 program. In
11 particular, the CCSD(T)/cc-pVTZ calculations of geometry, harmonic force field and anharmonic force
12 constants are assumed the better approach to the experimental values [24]. However, in order to reduce
13 the considerable amount of computer time required to obtain cubic and quartic force constants at this
14 level of theory, the results of *hybrid* force fields having the geometry and second order force constants at
15 CCSD(T)/cc-pVTZ level of theory while the cubic and quartic force constants are taken from calculations
16 B3LYP/cc-pVTZ and MP2(full)/cc-pVTZ(H,C,F);TZVP(Br) of Table 1, will be investigated.

17 Since calculations B3LYP/cc-pVTZ and MP2(full)/cc-pVTZ(H,C,F);TZVP(Br), were carried out in a
18 reasonable time also with a PC, the computations were extended to double displacements of the dimensionless
19 normal coordinates [23, 27] in order to obtain the full quartic force constants, Φ_{ijkl} . Once the
20 complete sets of force constants up to the fourth order were available, they could be converted by an
21 appropriate nonlinear transformation [28] into internal coordinates force constants defined in terms of
22 the independent geometry parameters reported in Table 2. The internal coordinates force constants are
23 mass-independent and with a second nonlinear transformation can be used to obtain the force constants
24 in terms of dimensionless normal coordinates for other isotopologues of bromofluoromethane.

25 Other hybrid force fields, now in the space of internal coordinates, may be obtained taking the internal
26 quadratic force constants from calculation CCSD(T)/cc-pVTZ and the internal cubic and quartic force
27 constants derived from the B3LYP and MP2(full) calculations as previously described.

28 It should be mentioned that these force fields give through the nonlinear coordinate transformations
29 cubic and quartic normal coordinates force constants slightly different from that obtained directly in
30 B3LYP and MP2(full) calculations. That is because the cubic Φ s depend on both cubic and quadratic
31 F s, and the quartic Φ s depend on quartic, cubic and quadratic F s. Thus, the transformations include the
32 quadratic terms of calculation CCSD(T)/cc-pVTZ which were not present in the cubic and quartic normal
33 coordinates force constants at B3LYP and MP2(full) levels of theory. The quadratic force constants in
34 terms of the internal coordinates defined in Table 2 and relative to calculation CCSD(T)/cc-pVTZ, are
35 reported in Table 5. As an examples, in Table 6, the full diagonal cubic and quartic internal coordinates
36 force constants concerning the calculations at the levels B3LYP, MP2(full), and CCSD(T) (only cubic),
37 are reported.

38 These force fields, determined using for the non-linear transformation, the appropriate eigenvectors
39 matrix of each calculation, display the same sign for every force constant in all sets, although before the
40 transformation, normal coordinates force constants had different signs.

41 In Table 7 are summarized the vibrational fundamental frequencies, ν_i , obtained from the harmonic
42 frequencies ω_i and anharmonicity constants x_{ij} , both computed with the force constants of calculations
43 B3LYP/cc-pVTZ, MP2(full)/cc-pVTZ(H,C,F);TZVP(Br), CCSD(T)/cc-pVTZ and the hybrid force fields
44 CCSD(T)+B3LYP and CCSD(T)+MP2(full) both in normal coordinates space and internal coordinates
45 space. In the same Table, the experimental wavenumbers from Ref. [1] and the approximate description
46 of each vibrational mode, are also given.

47 The anharmonicity constants x_{ij} , depend on the quadratic, cubic, and quartic force constants. Breakdown
48 of their calculation takes place when strong anharmonic interactions between fundamentals and overtones
49 or combination bands are present. In these cases it is necessary define effective constants by excluding the
50 respective contributions from the perturbational formulas [25, 26]. Such effective anharmonicity constants
51 are introduced here to take into account for the Fermi resonances $2\nu_6/\nu_5$, $2\nu_5/\nu_3$, and $\nu_6 + \nu_9/\nu_8$.

52 Table 7 shows that wavenumbers from calculation CCSD(T)/cc-pVTZ are in good agreement with the
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observed values. Good results are obtained also from the hybrid force fields which display almost the same discrepancies from the experiment. The largest differences among computed and observed values are in calculations B3LYP and MP2(full); these may be ascribed in large extent to the quadratic force field (see also Table 3). The theoretical values of the ν_4 fundamental are all too distant from the experimental value. The potential energy distribution indicates this vibration as 100% C–F stretching. Therefore the corresponding computed quadratic force constant reported in Table 5 should be considered overestimated, a problem which is known for polar bonds [29]. The use, for example, of aug-cc-pVTZ basis set on fluorine atom would improve the results but would also increase considerably CPU time requirements. Interestingly, the B3LYP calculations give underestimated results for this vibrational mode.

Table 8 lists the results for the vibration-rotation interaction constants along with the available experimental data. The α_i^X ($X = A, B, C$) constants are computed with the same force fields previously described. The agreement between theory and experiment is good and all the constants, also if computed with different force constants, exhibit comparable values.

In Table 9, the rotational and centrifugal distortion constants, calculated with the anharmonic force fields B3LYP, MP2(full), CCSD(T), and the hybrid CCSD(T)+MP2(full), CCSD(T)+B3LYP both in normal and internal coordinates space as previously depicted are reported together with the corresponding experimental data for $\text{CH}_2^{79}\text{BrF}$. The theoretical ground-state rotational constants (A_0, B_0, C_0) have been obtained from the associated equilibrium constants (A_e, B_e, C_e) by taking into account the effects of vibration-rotation coupling through perturbation theory [25, 26]. Even for these spectroscopic parameters there is a general satisfactory agreement between theory and experiment.

Finally, as an example, the hybrid force field composed by the quadratic force constants of calculation CCSD(T)/cc-pVTZ together the cubic and full quartic force constants of calculation MP2(full)/cc-pVTZ(H,C,F);TZVP(Br), all in the space of the mass-independent internal coordinates, was used to compute significant spectroscopic parameters for the isotopologues $\text{CH}_2^{81}\text{BrF}$, $\text{CD}_2^{79}\text{BrF}$, and $\text{CHD}^{79}\text{BrF}$. The results are collected in Table 10. These data may be useful for further investigations on the high-resolution rovibrational spectra of bromofluoromethane.

4 Conclusions

Ab initio calculations of anharmonic force fields of bromofluoromethane were performed at B3LYP, MP2, and CCSD(T) levels of theory employing basis sets of spdf quality for both the harmonic and anharmonic parts. These calculations make use of analytic second derivatives, which are differentiated numerically in reduced normal coordinates. The CCSD(T) results are in good agreement with the available experimental data, however the cost in terms of computation time makes this approach almost impracticable for the anharmonic part. Observing that cubic and quartic force constants, do not change in appreciable manner going from medium-level (B3LYP, MP2) to high-level (CCSD(T)) theory in spite of their very big difference in computation time, hybrid force fields — composed by high-level quadratic part and medium-level anharmonic parts — are proposed. The overall agreement between theory and experiment supports this approach.

In addition, complete quartic force fields were also computed to allow non-linear transformations and get mass-independent internal coordinates force constants suitable to predict the spectroscopic parameters for the isotopologues of bromofluoromethane.

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References

- [1] A. Baldacci, A. Baldan, A. Gambi and P. Stoppa, *J. Mol. Struct.* **517-518**, 197 (2000).
- [2] A. Baldacci, P. Stoppa and A. Gambi, *J. Mol. Spectrosc.* **201**, 280 (2000).
- [3] A. Baldacci, P. Stoppa, A. Pietropolli Charmet and S. Giorgianni, *J. Mol. Spectrosc.* **220**, 7 (2003).
- [4] P. Pulay, *Molec. Phys.* **17**, 197 (1969).
- [5] P. Pulay, *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Plenum, New York, (1977).
- [6] P. Pulay, *Advan. Chem. Physics* **69**, 241 (1987).
- [7] G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- [8] K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- [9] C. Hampel, K. A. Peterson and H. -J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).
- [10] T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- [11] D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- [12] MOLPRO (version 2002.6) is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.
- [13] W. Schneider and W. Thiel, *Chem. Phys. Lett.* **157**, 367 (1989).
- [14] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [15] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- [16] M. F. Guest, I. J. Bush, H. J. J. Van Dam, P. Sherwood, J. M. H. Thomas, J. H. Van Leuthe, R. W. A. Havenith and J. Kendrick, *Molec. Phys.* **103**, 719 (2005).
- [17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, GAUSSIAN03, revision B.05, Gaussian, Inc., Pittsburgh PA, (2003).
- [18] V. Barone, *J. Chem. Phys.* **122**, 014108 (2005).
- [19] C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).
- [20] M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.* **80**, 3264 (1984).
- [21] ACES2 (Mainz-Austin-Budapest) program package by J. F. Stanton, J. Gauss, J. D. Watts, P. G. Szalay, R. J. Bartlett with contributions from A. A. Auer, D. B. Bernholdt, O. Christiansen, M. E. Harding, M. Heckert, O. Heun, C. Huber, D. Jonsson, J. Jusélius, W. J. Lauderdale, T. Metzroth, C. Michauk, D. P. O'Neill, D. R. Price, K. Ruud, F. Schiffrmann, A. Tajti, M. E. Varner, J. Vázquez and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen). Version 2005, see also <http://www.aces2.de>
- [22] A. Schafer, C. Huber and R. Aldrichs, *J. Chem. Phys.* **100**, 5829 (1994).
- [23] A. G. Császár, in *The Encyclopedia of Computational Chemistry*, P. v. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III and P. R. Schreiner (Eds), pp. 13-80, Wiley, Chichester, (1998).
- [24] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker and J. F. Stanton, *J. Chem. Phys.* **114**, 6548 (2001).
- [25] I. M. Mills, in *Molecular Spectroscopy: Modern Research*, K. Narahari Rao, C. W. Mathew (Eds), Vol. 1, pp. 115-140, Academic Press, New York, (1972).
- [26] D. Papoušek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra*, Elsevier, Amsterdam, (1982).
- [27] G. Cazzoli, C. Puzzarini and A. Gambi, *J. Chem. Phys.* **120**, 6495 (2004).
- [28] A. R. Hoy, I. M. Mills and G. Strey, *Molec. Phys.* **24**, 1265 (1972).
- [29] X-G. Wang, E. L. Sibert III and J. M. L. Martin, *J. Chem. Phys.* **112**, 1353 (2000).

Table 1. Summary of the various quantum-chemical calculations performed to compute optimised geometries, harmonic and anharmonic force fields of CH₂BrF.

Program Package	Machine ^a	Theory	Basis Set	Time ^b
GAMESS-UK	PC	B3LYP	cc-pVTZ	2
GAUSSIAN03	SP5	B3LYP	cc-pVTZ	1
	SP5	B3LYP	6-311G++(3df,2pd)	1
	SP5	MP2(full)	cc-pVTZ	1
	SP5	MP2(fc)	cc-pVTZ	1
ACES2	PC	MP2(full)	cc-pVTZ (H,C,F); TZVP (Br)	2
	PC	CCSD(T)	cc-pVTZ (H,C,F); TZVP (Br)	110
	SP5	CCSD(T)	cc-pVTZ	15
MOLPRO	SP5	CCSD(T)	cc-pVTZ	1

^aPC is Intel/Linux with Pentium 4 processor at 2.4 GHz clock and SP5 is a Cluster of 512 IBM Power5 processors at 1.9 GHz.

^bComputer time in days. These data are estimated and for the SP5 machine additional queue's waiting time might be added.

Table 2. Optimised geometries of CH₂BrF molecule obtained at the various level of theory reported in Table 1. Bond lengths in units of ångström (Å) and bond angles in degree (°). The data are reported following the order of Table 1.

		B3LYP VTZ ^a	B3LYP VTZ	B3LYP 6-311G ^b	MP2(full) VTZ	MP2(fc) VTZ	MP2(full) TZVP ^c	CCSD(T) TZVP	CCSD(T) VTZ	CCSD(T) VTZ
<i>h</i>	C–H	1.0848	1.0849	1.0844	1.0794	1.0835	1.0790	1.0853	1.0857	1.0857
<i>f</i>	C–F	1.3592	1.3587	1.3598	1.3564	1.3588	1.3582	1.3614	1.3584	1.3585
<i>b</i>	C–Br	1.9625	1.9617	1.9574	1.9195	1.9249	1.9146	1.9302	1.9450	1.9450
γ	∠HCH	113.37	113.20	113.30	112.50	112.54	112.15	112.21	112.66	112.70
δ	∠HCF	109.83	109.87	109.63	109.65	109.66	109.33	109.38	109.78	109.75
β	∠HCB _r	106.55	106.59	106.85	107.15	107.15	107.58	107.54	107.01	107.00
	∠FCB _r	110.62	110.62	110.52	110.70	110.64	110.86	110.79	110.54	110.57

^acc-pVTZ

^b6-311G++(3df,2pd)

^ccc-pVTZ (H,C,F); TZVP (Br)

Table 3. Fundamental modes of CH₂⁷⁹BrF computed from the harmonic force constants obtained at the optimised geometries and levels of theory reported in Table 2. All wavenumber data in cm⁻¹. For the calculation at CCSD(T)/cc-pVTZ level, the intensities in units of km/mol, are also reported in parentheses. For the basis sets, see footnotes of Table 2.

	B3LYP VTZ	B3LYP VTZ	B3LYP 6-311G	MP2(full) VTZ	MP2(fc) VTZ	MP2(full) TZVP	CCSD(T) TZVP	CCSD(T) VTZ	CCSD(T) VTZ
ω_1	3094	3092	3095	3163	3143	3166	3110	3109 (17.14)	3108
ω_2	1497	1498	1493	1529	1519	1528	1507	1510 (0.16)	1510
ω_3	1328	1333	1330	1367	1362	1377	1357	1349 (50.26)	1349
ω_4	1083	1084	1070	1118	1113	1116	1108	1114 (173.55)	1113
ω_5	626	624	628	683	679	686	667	657 (56.86)	656
ω_6	307	306	308	324	322	327	319	315 (0.53)	314
ω_7	3178	3176	3179	3232	3231	3230	3187	3190 (5.60)	3190
ω_8	1247	1249	1246	1279	1270	1282	1263	1262 (2.94)	1262
ω_9	937	938	939	962	962	968	952	948 (≈ 0)	948

Table 4. Cubic and quartic force constants of $\text{CH}_2^{79}\text{BrF}$ in the space of dimensionless normal coordinates from the first eight calculations depicted in Table 1. Only the constants with the same indices are reported. For the basis sets, see footnotes of Table 2.

		B3LYP VTZ	B3LYP VTZ	B3LYP 6-311G	MP2(full) VTZ	MP2(fc) VTZ	MP2(full) TZVP	CCSD(T) TZVP	CCSD(T) VTZ
Φ_{iii}	$i = 1$	-1358.12	-1354.88	-1353.28	-1361.42	-1352.55	-1361.42	-1363.38	-1361.32
	2	-106.80	-108.80	-110.91	-113.38	-104.31	-120.57	-110.24	-105.42
	3	-93.20	-94.51	-93.92	-87.00	-84.67	91.41	86.87	87.75
	4	-439.83	435.78	434.76	431.63	430.48	-431.31	-433.99	-433.97
	5	-156.39	165.36	165.34	166.96	167.05	165.95	171.39	166.57
	6	41.14	40.58	40.18	36.55	37.33	36.78	38.78	39.03
Φ_{iiii}	$i = 1$	527.13	529.74	530.60	530.12	520.93	529.7	525.68	525.04
	2	40.97	39.82	40.83	37.94	40.96	46.06	50.89	36.12
	3	117.15	114.39	121.79	122.56	115.68	115.01	108.97	110.96
	4	166.56	159.92	160.45	154.58	154.83	154.07	153.18	153.20
	5	42.59	54.56	53.81	44.31	43.93	44.05	44.44	43.20
	6	7.50	7.54	6.19	7.17	7.49	6.68	7.56	7.68
	7	585.05	585.27	584.50	595.91	573.71	601.63	586.92	581.92
	8	132.09	132.48	141.65	124.58	124.58	127.08	124.56	120.12
	9	302.12	304.12	303.94	304.26	294.66	287.73	290.59	297.35

Table 5. The quadratic internal coordinates force constants of CH_2BrF , from calculation at CCSD(T)/cc-pVTZ level performed with ACES2 on SP5 machine. Diagonal force constants are indexed with only one symbol identifying the internal coordinate. The ' indicates two different force constants involving the same coordinates. The units are consistent with energy in aJ, bond length in \AA and bond angle in radian.

F_h	5.4507	F_{bf}	0.5312	$F_{\delta\delta}$	1.2359
F_f	6.1510	$F_{\gamma h}$	0.1088	$F_{\beta h}$	0.0021
F_b	2.8222	$F_{\gamma f}$	-0.3863	$F_{\beta h'}$	-0.0264
F_γ	1.8812	$F_{\gamma b}$	-0.3942	$F_{\beta f}$	-0.3976
F_δ	2.1519	$F_{\delta h}$	0.0621	$F_{\beta b}$	0.0251
F_β	1.7217	$F_{\delta h'}$	-0.0081	$F_{\beta\gamma}$	1.1781
F_{hh}	0.0362	$F_{\delta f}$	0.1266	$F_{\beta\delta}$	1.2073
F_{fh}	0.1907	$F_{\delta b}$	-0.3424	$F_{\beta\delta'}$	1.0844
F_{bh}	0.0437	$F_{\delta\gamma}$	1.3088	$F_{\beta\beta}$	1.0453

Table 6. The full diagonal cubic and quartic internal coordinates force constants of CH_2BrF from calculations at B3LYP/cc-pVTZ, MP2(full)/cc-pVTZ(H,C,F);TZVP(Br) and CCSD(T)/cc-pVTZ levels of theory. See Table 2 for the definition of the internal coordinates. The units are consistent with energy in aJ, bond length in \AA and bond angle in radian.

		B3LYP VTZ	MP2(full) TZVP	CCSD(T) VTZ
F_{iii}	$i = h$	-31.65	-32.57	-31.93
	f	-36.58	-37.25	-37.55
	b	-11.73	-14.24	-13.31
	γ	10.70	10.07	10.25
	δ	4.88	4.21	4.53
	β	3.31	3.54	3.24
F_{iiii}	$i = h$	165.57	174.36	^a
	f	209.65	204.28	
	b	48.82	61.47	
	γ	101.04	91.19	
	δ	41.60	33.18	
	β	23.76	23.00	

^aFor this calculation only the cubic force constants are available.

Table 7. Fundamental vibrations of $\text{CH}_2^{79}\text{BrF}$ calculated with the anharmonic force fields described in the text. The approximate description of the normal modes are reported in the rightmost column. All data in cm^{-1} .

Mode	B3LYP VTZ	MP2(full) TZVP	CCSD(T) VTZ	CCSD(T)+ MP2(full) ^a	CCSD(T)+ B3LYP ^a	CCSD(T)+ MP2(full) ^b	CCSD(T)+ B3LYP ^b	Exp ^c	Approximate Description	
A'	ν_1	2977	3054	2992	3000	2998	2987	2998	2992	CH_2 sym stretch
	ν_2	1459	1490	1470	1472	1473	1472	1472	1465	CH_2 deformation
	ν_3	1297	1346	1319	1318	1321	1311	1323	1314	CH_2 wag
	ν_4	1057	1089	1086	1087	1088	1087	1089	1068	C-F stretch
	ν_5	619	676	645	646	647	643	649	650	C-Br stretch
	ν_6	304	323	311	311	312	311	312	312	$\angle\text{FCBr}$ bend
A''	ν_7	3030	3092	3041	3049	3045	3039	3046	3047	CH_2 asym stretch
	ν_8	1218	1253	1232	1233	1236	1231	1236	1226	CH_2 twist
	ν_9	923	954	934	933	936	933	936	936	CH_2 rock

^aHybrid force field in normal coordinate space.

^bHybrid force field in internal coordinate space.

^cFrom Ref. [1].

Table 8. Vibration-rotation interaction constants of $\text{CH}_2^{79}\text{BrF}$ calculated from the cubic force fields described in the text. The last column reports the available observed values. All data in MHz.

	B3LYP VTZ	MP2(full) TZVP	CCSD(T) VTZ	CCSD(T)+ MP2(full) ^a	CCSD(T)+ B3LYP ^a	CCSD(T)+ MP2(full) ^b	CCSD(T)+ B3LYP ^b	Exp ^c	
α_i^A	$i = 1$	111.706	112.427	110.209	113.600	112.040	114.016	109.513	
	2	130.108	122.619	129.074	120.076	128.867	110.573	123.781	
	3	118.312	95.574	112.300	100.123	108.379	131.422	66.375	113.532
	4	277.726	252.109	287.274	278.146	270.444	280.138	273.133	257.417
	5	-42.469	-26.641	-24.712	-20.444	-50.489	-17.758	-46.492	20.116
	6	-193.331	-193.169	-199.053	-191.734	-200.844	-199.959	-202.920	
	7	57.613	59.111	60.016	64.804	58.779	65.718	55.002	
	8	234.696	242.080	230.929	233.893	222.737	232.987	234.485	
	9	105.821	91.626	90.780	71.361	88.497	71.219	85.079	
α_i^B	$i = 1$	-2.980	-1.282	-1.632	-1.309	-2.901	-1.759	-1.749	
	2	1.319	1.360	1.377	1.642	1.075	2.317	1.256	
	3	1.839	1.229	1.494	0.876	2.083	0.539	3.064	1.289
	4	5.225	6.518	6.266	6.888	4.741	6.385	5.896	6.529
	5	20.246	18.490	19.303	18.977	20.206	21.009	17.095	15.757
	6	5.645	3.698	4.723	4.007	5.431	5.121	4.069	
	7	-5.727	-3.404	-3.705	-3.478	-5.653	-4.064	-3.974	
	8	-2.126	-2.316	-1.928	-2.431	-1.972	-2.439	-2.446	
	9	9.829	9.397	9.376	9.419	9.725	10.204	9.073	
α_i^C	$i = 1$	-2.924	-1.421	-1.758	-1.445	-2.843	-1.898	-1.850	
	2	-3.830	-4.871	-4.215	-4.090	-4.470	-3.583	-4.346	
	3	10.858	11.009	10.977	10.357	11.474	10.219	12.046	
	4	5.597	6.740	6.463	6.963	5.007	6.518	6.033	6.879
	5	21.025	19.542	20.161	19.900	20.766	21.692	18.093	23.233
	6	7.062	5.560	6.353	5.782	6.960	6.700	5.762	
	7	-4.936	-2.806	-3.150	-2.888	-4.833	-3.451	-3.389	
	8	-5.172	-5.304	-4.973	-5.383	-5.041	-5.409	-5.379	
	9	11.055	10.449	10.642	10.529	10.934	11.199	10.331	

^aHybrid force field in normal coordinate space.

^bHybrid force field in internal coordinate space.

^cFrom Refs. [2, 3].

Table 9. Equilibrium and ground state rotational constants, quartic and sextic centrifugal distortion constants of $\text{CH}_2^{79}\text{BrF}$ calculated from the force fields described in Section 3. The available experimental data are reported in the rightmost column. Rotational constants in units of MHz, quartic centrifugal distortion constants in kHz and sextic distortion constants in Hz.

	B3LYP VTZ	MP2(full) TZVP	CCSD(T) VTZ	CCSD(T)+ MP2(full) ^a	CCSD(T)+ B3LYP ^a	CCSD(T)+ MP2(full) ^b	CCSD(T)+ B3LYP ^b	Exp ^c
A_e	40215.05846	40871.77862	40270.68732					
B_e	3676.49449	3801.95150	3728.30703	As in calculation CCSD(T)/cc-pVTZ				
C_e	3444.59844	3557.50830	3489.94481					
A_0	39814.968	40493.910	39872.279	39885.775	39901.482	39876.509	39921.710	39852.671
B_0	3659.860	3785.106	3710.671	3711.012	3711.939	3709.651	3712.165	3772.924
C_0	3425.232	3538.060	3469.695	3470.082	3470.968	3468.951	3471.294	3524.060
Δ_J	1.74910	1.67193	1.70400					1.77687
Δ_K	548.57863	542.24546	541.22096					535.63918
Δ_{JK}	-24.05862	-24.26586	-24.37437	As in calculation CCSD(T)/cc-pVTZ				
δ_J	0.17059	0.16907	0.17062					0.17658
δ_K	7.58035	7.27296	7.43229					5.99585
Φ_J	0.00078	0.00088	0.00081	0.00090	0.00071	0.00075	0.00094	
Φ_K	27.07719	25.29773	26.18133	25.85091	26.27699	26.19361	26.65200	19.48651
Φ_{JK}	0.02000	0.01786	0.02130	0.01860	0.02198	0.02067	0.02184	0.02099
Φ_{KJ}	-1.99303	-1.84497	-1.95717	-1.91551	-1.92153	-1.95984	-1.96948	-1.43900
ϕ_J	0.00025	0.00026	0.00026	0.00027	0.00024	0.00025	0.00027	
ϕ_{JK}	0.00823	0.00918	0.00889	0.00934	0.00817	0.00835	0.00955	
ϕ_K	2.27767	2.10622	2.19699	2.20979	2.19186	2.19340	2.20126	

^aHybrid force field in normal coordinate space.

^bHybrid force field in internal coordinate space.

^cFrom Ref. [2].

Table 10. Spectroscopic molecular parameters for the $\text{CH}_2^{81}\text{BrF}$, $\text{CD}_2^{79}\text{BrF}$, and $\text{CHD}^{79}\text{BrF}$ isotopologues calculated from the hybrid force field in internal coordinates CCSD(T)/cc-pVTZ+MP2(full)/cc-pVTZ(H,C,F);TZVP(Br) described in Section 3. Rotational constants in units of MHz, quartic centrifugal distortion constants in kHz and sextic distortion constants in Hz. Fundamental wavenumbers in cm^{-1} .

	$\text{CH}_2^{81}\text{BrF}$	$\text{CD}_2^{79}\text{BrF}$	$\text{CHD}^{79}\text{BrF}$
A_e	40259.73930	29444.72115	33982.55193
B_e	3702.74667	3601.65341	3667.41949
C_e	3467.43203	3348.98088	3414.37519
A_0	39865.565	29191.685	33674.358
B_0	3684.228	3583.932	3649.298
C_0	3446.628	3329.717	3394.353
Δ_J	1.68198	1.47823	1.58718
Δ_K	540.59139	209.94767	325.31116
Δ_{JK}	-24.22057	-11.53276	-16.32719
δ_J	0.16735	0.16195	0.16873
δ_K	7.34844	5.39314	6.46845
Φ_J	0.00073	0.00051	0.00062
Φ_K	26.14361	5.67397	11.46299
Φ_{JK}	0.02031	0.01449	0.01742
Φ_{KJ}	-1.94405	-0.64239	-1.07372
ϕ_J	0.00024	0.00019	0.00022
ϕ_{JK}	0.00820	0.00583	0.00722
ϕ_K	2.17354	0.86762	1.37480
ν_1^a	2986.580	2176.822	3024.289
ν_2	1471.566	1139.657	2222.425
ν_3	1310.717	1019.070	1356.123
ν_4	1087.187	1001.344	1244.870
ν_5	642.565	601.390	1085.983
ν_6	310.003	309.521	955.015
ν_7	3039.281	2295.639	789.888
ν_8	1231.434	921.585	603.003
ν_9	932.649	716.410	310.221

^aFor the C_1 asymmetric isotopologue, $\text{CHD}^{79}\text{BrF}$, all the vibrations belong to the unique symmetry species and are reported in descending order.