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# Parity-violation effects in the vibrational spectra of CHFClBr and CDFClBr

Guntram Rauhut[1,*] and Peter Schwerdtfeger[2,†]

[1]*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*
[2]*Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University Auckland, Private Bag 102904, 0745 Auckland, New Zealand*

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Relativistic four-component electronic structure calculations at the density functional level have been carried out to describe parity-violation (PV) energy shifts to the total electronic energy for the chiral molecule CHFClBr. An $n$-mode ($n = 3, 4$) expansion of the complete potential energy surface at the explicitly correlated coupled-cluster level has been used for the vibrational analysis of PV effects for CHFClBr and CDFClBr. The vibrational spectrum and corresponding absolute intensities for fundamental, overtone, and combination band transitions obtained from a variational configuration interaction treatment are in excellent agreement with experimental data and the most accurate so far obtained. The results show that a 3-mode expansion is sufficient for the vibrational analysis. The PV energy shifts for the fundamental, overtone, and combination bands are all in the mHz region. The data provided will be useful for future detection of PV in chiral molecules.

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## I. INTRODUCTION

Parity-violation (PV) is a manifestation of the electroweak current in fermionic interactions and important for the search of new physics beyond the standard model [1–3]. It was originally proposed by Lee and Yang [4], and subsequently observed by Wu and co-workers in the $\beta$ decay of $^{60}$Co [5]. PV has been detected in many experiments since then, for example in hadronic interactions [6] ranging from electron-quark scattering [7] to the nuclear anapole moment of Cs [8–11], or in highly forbidden electronic transitions in atoms [12,13] such as the $6^2S \rightarrow 7^2S$ transition in Cs [14–16] or the $^1S_0(6s^2) \rightarrow {}^3D_1(5d^16s^1)$ transition in Yb [17]. Atomic PV experiments serve as stringent tests to the standard model [3], and so far both experiment and theory are in good agreement [18].

In recent years, computational methods for calculating molecular spectra developed enormously [19,20] to the extent that small molecules are now considered to support precision measurements for the test of fundamental physics [21–23]. Concerning PV in molecules, these have not been discovered yet despite several experimental attempts [24,25] and many different theoretical proposals [26–32]. With few exceptions [22,33–41], most of these studies focus on chiral molecules [27,31,42–44]. Here, PV leads to a small energy difference in their spectra between left and right handed molecules (enantiomers) [43,45–48]. For vibrational transitions these PV effects are estimated to be in the mHz to Hz range [28,30,49–52] and thus accessible to future high-resolution experiments [53].

Chiral carbon compounds such as CHFClBr, as originally proposed by Lethokov [46,54], serve as prime examples for PV studies as these are reasonably stable and the rovibrational spectra albeit complex are accessible to interpretation [55,56]. CHFClBr has therefore been the most widely studied molecule for PV effects both experimentally [57,58] and theoretically [59–66]. This molecule has also been suggested as a sensitive probe for the detection of P-odd cosmic fields such as cold dark matter [67]. For the C-F stretching mode, lying conveniently in the $CO_2$ laser frequency range, the PV energy difference was calculated to be $\Delta_{RS}\nu = \nu(R) - \nu(L) = 2\Delta\nu_{\text{PV}}(R) = -2\Delta\nu_{\text{PV}}(L) = -1.7$ mHz $[\Delta\nu_{\text{PV}}(L) = \nu_{\alpha_w}(L) - \nu_{\alpha_w=0}$ for a fixed transition of frequency $\nu$ and the weak-coupling constant $\alpha_w]$ at the coupled cluster level using a single-mode analysis [63] (compare to the experimental result of $\Delta_{RS}\nu = 9.4 \pm 5.1 \pm 12.7$ Hz [57,68]). Such calculations demonstrated that anharmonicity effects contribute substantially to the PV energy shift even changing its sign [59]. Furthermore, Quack and Stohner pointed out that vibrational coupling in the deuterated compound CDFClBr becomes important [69].

In a recent paper we showed that the vibrational spectra of CHFClBr and CDFClBr can be reproduced with root-mean-square deviations (RMSDs) of a few wave numbers using coupled-cluster theory for the electronic structure and vibrational configuration interaction (VCI) including configurations with at most four different excited modals (one-mode wave functions) [70]. We also showed that the range-separated modified CAM-B3LYP functional gives results comparable to coupled-cluster calculations for typical core properties such as PV energy shifts and electric field gradients [66,71]. Quantum theoretical methods have now developed to the point where a complete vibrational analysis for PV effects in the vibrational spectrum of CHFClBr can be performed. Therefore, in this work we apply relativistic density functional theory to

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[*] rauhut@theochem.uni-stuttgart.de
[†] peter.schwerdtfeger@gmail.com

produce a hypersurface in terms of all nine vibrational modes followed by a vibrational configuration interaction (VCI) procedure to obtain the PV frequency shifts for the vibrational spectrum of CHFClBr and CDFClBr.

## II. THEORETICAL AND COMPUTATIONAL DETAILS

### A. Electronic structure calculations

The dominant PV contribution to the total electron energy comes from the Z-boson exchange between the electron and the nucleons (protons and neutrons), and can be strictly derived at the quark level from electroweak coupling theory [72]. For chiral molecules, the dominant PV Hamiltonian is nuclear spin independent and for a specific atom is given by [3,73]

$$H_{\rm PV}^{A} = \frac{G_F}{2\sqrt{2}} Q_W^A \gamma^5 \rho^A(\mathbf{r}). \tag{1}$$

Here, $G_F$=1.1663787(6)×$10^{-5}$ GeV$^{-2}$=2.22252×$10^{-14}E_h a_0^3$ is the Fermi coupling constant [74], $\rho^A$ is the normalized nuclear charge density of atom $A$, and $\gamma^5$ is the pseudoscalar Dirac matrix, coupling the large with the small Dirac component,

$$\gamma^5 = \begin{pmatrix} 0_2 & 1_2 \\ 1_2 & 0_2 \end{pmatrix}, \tag{2}$$

with $1_2$ and $0_2$ being the 2×2 identity and zero matrix, respectively. The weak charge of nucleus $A$ is given by $Q_W^A = -N^A + Z^A(1 - 4\sin^2\theta_W)$, where $N^A$ and $Z^A$ are the number of neutrons and protons of nucleus $A$, respectively. The Weinberg mixing angle, $\theta_W$, is given by $\sin^2\theta_W = 0.23125$ [75]. The energy contribution to the PV term at a fixed molecular geometry $\{\mathbf{R}_A\}$, $E_{\rm PV}(\mathbf{R}_A)$, for different isotopic combinations of CHFClBr is thus obtained as an expectation value at the Dirac-Kohn-Sham level of theory,

$$E_{\rm PV} = \sum_A E_{\rm PV}^A, \tag{3}$$

$$E_{\rm PV}^A = \sum_i^{N_{\rm occ}} \langle \phi_i | H_{\rm PV}^A | \phi_i \rangle = \frac{G_F}{2\sqrt{2}} Q_W^A M_{\rm PV}^A, \tag{4}$$

where $\phi_i$ are the occupied Kohn-Sham (KS) orbital spinors. The most common isotopes were used, i.e., $^{1,2}$H, $^{12}$C, $^{19}$F, $^{35}$Cl, and $^{79}$Br. The detailed results are provided as a separate file in the Supplemental Material [76].

Dirac-Kohn-Sham theory was used for all PV calculations with a Gaussian distribution for the nuclear charge density [77]. The set of coordinates for $\{\mathbf{R}_A\} = \{X_A, Y_A, Z_A\}$ for CHFClBr were taken from an $n$-mode expansion described in the next section. The CAM-B3LYP* functional with the parameters of the adjusted functional $\alpha = 0.20$, $\beta = 0.12$, and $\mu = 0.90$ as defined in Ref. [66] was applied as it produced accurate results for both parity-violation energy shifts and electric field gradients as compared to more accurate coupled-cluster results. We used uncontracted Dyall's augmented core-valence double-zeta (acvDZ) [78] and triple-zeta (acvTZ) basis sets [79]. Because of the large number of single-point calculations involved, the TZ basis set was used only for the 3-mode case. The parallel version of program DIRAC was used distributing 100 jobs at a time over 4 cores each on the Massey University CTCP computer cluster [80,81]. The CPU time for the parallel jobs with the acvDZ (acvTZ) basis set was on average 30 min (7 h). All PV results refer to the $S$ configuration of CHFClBr.

### B. Vibrational analysis

The equilibrium structure and the normal coordinates of CHFClBr were determined at the level of explicitly correlated coupled-cluster theory in conjunction with an augmented basis set of triple-$\zeta$ quality, i.e., CCSD(T)-F12b/aug-cc-pVTZ [82–85], using the MOLPRO program package [86]. For bromine an ECP10MDF effective core potential [87] together with an aug-cc-pVTZ-PP basis set was used in all calculations and aug-cc-pVTZ/JKFIT and aug-cc-pVTZ/MP2FIT fitting bases of Weigend [88] were employed throughout. The same basis sets were also used for the resolution of the identity (RI). The complementary auxiliary basis set (CABS) approach was employed; i.e., the union of the atomic orbital (AO) and RI basis sets was used to approximate the resolution of the identity. The $n$-mode expansion of the potential energy surface (PES), which is nothing else than a many-body expansion of the multidimensional PES with respect to the normal modes, and the related dipole moment surface were truncated after the 4-mode coupling (4D) terms [89,90]. A multilevel approach [91] was used; i.e., the 1D and 2D terms were computed at the CCSD(T)-F12b/aug-cc-pVTZ level, while the explicitly correlated distinguishable cluster approximation including single and double excitations (DCSD) of Kats and Manby [92] was used for the 3D and 4D terms, i.e., DCSD-F12b/aug-cc-pVTZ. It was shown by Kats *et al.* [92,93] and by Martin and co-workers [94] that DCSD yields remarkably accurate geometries and harmonic vibrational frequencies of near-CCSD(T) quality. Due to the neglect of the time-consuming (perturbative) triple excitations, DCSD calculations are computationally significantly less demanding than comparable CCSD(T) calculations. Note that for technical reasons dipole moments were determined at the corresponding conventional computational levels, i.e., CCSD(T) and DCSD instead of CCSD(T)-F12b and DCSD-F12b. In total, the potential is represented by 1596 CCSD(T)-F12b (1D and 2D) calculations and 45 288 DCSD-F12b (3D and 4D) energy points. At these grid points PV values were determined as described above. The energy, dipole, and PV grids were used to determine analytical representations of corresponding polynomials up to 8th order per dimension by efficient Kronecker product fitting [95].

Any properties of the two isotopologs were determined at the grid points of the parent compound CHFClBr. As these grids are expanded in terms of mass-dependent normal coordinates and thus they belong to CHFClBr, a subsequent Duschinsky-like transformation [96] was used to transform the energy and property surfaces to grids expanded in terms of normal coordinates $\vec{q}$ belonging to CDFClBr:

$$\vec{q}\,' = \mathbf{L}'' \mathbf{M}'^{1/2} \mathbf{T} \mathbf{M}^{-1/2} \mathbf{L} \vec{q}. \tag{5}$$

Within this equation primed quantities refer to the original system, while unprimed ones refer to the new one. **L** denotes the displacement vectors, **M** the diagonal matrix of atomic masses, and **T** is the Eckart transformation matrix. For details see Ref. [96]. As the $n$-mode expansion is truncated and its

TABLE I. Equilibrium $r_e$ and vibrationally averaged $r_a$ and $r_g$ bond length (in pm) and equilibrium angles $\alpha$ (in degrees) for $S$-CHFClBr obtained from explicitly correlated coupled-cluster calculations, dipole moment $\mu$ (in D), and parity-violation matrix elements $M^A_{\mathrm{PV}}$ (in atomic units) at the CAMB3LYP* level using various uncontracted basis sets (acvDZ to acvQZ). Experimental structural parameters from Ref. [102].

| Distances | $r_e$ | $r_a$ | $r_a$ (exp.) | $r_g$ | Angles | $\alpha$ | $\alpha$ (exp.) | PV | acvDZ | acvTZ | acvQZ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $R$(C-H) | 108.4 | 109.3 | 113.2(5) | 110.6 | $\alpha$(H-C-F) | 109.75 | 108.5(3) | $M^{\mathrm{H}}_{\mathrm{PV}}$ | $-1.219\times10^{-8}$ | $-1.310\times10^{-8}$ | $-1.619\times10^{-8}$ |
| $R$(C-F) | 134.6 | 135.1 | 134.8(5) | 135.4 | $\alpha$(H-C-Cl) | 109.05 | 108.8 | $M^{\mathrm{C}}_{\mathrm{PV}}$ | $8.636\times10^{-7}$ | $9.429\times10^{-7}$ | $9.960\times10^{-7}$ |
| $R$(C-Cl) | 175.6 | 176.7 | 175.3(5) | 176.3 | $\alpha$(H-C-Br) | 107.67 | 109.95(1.1) | $M^{\mathrm{F}}_{\mathrm{PV}}$ | $8.421\times10^{-6}$ | $9.165\times10^{-6}$ | $9.624\times10^{-6}$ |
| $R$(C-Br) | 193.3 | 193.8 | 192.7(6) | 193.9 | $\alpha$(F-C-Cl) | 109.52 | 109.6(6) | $M^{Cl}_{\mathrm{PV}}$ | $-1.455\times10^{-5}$ | $-1.599\times10^{-5}$ | $-1.677\times10^{-5}$ |
| | | | | | $\alpha$(F-C-Br) | 109.14 | 109.2(6) | $M^{\mathrm{Br}}_{\mathrm{PV}}$ | $8.522\times10^{-6}$ | $9.712\times10^{-6}$ | $1.028\times10^{-5}$ |
| | | | | | $\alpha$(Cl-C-Br) | 111.69 | 111.5(4) | $\mu$ | 1.228 | 1.220 | 1.219 |

transformation does not conserve the order of terms, inaccuracies will be introduced by this transformation step. However, a comparison of the fundamental frequencies of CDFClBr obtained from the transformation of the potential energy surfaces of CHFClBr and those obtained from an energy surface explicitly calculated for CDFClBr shows that the deviations are tiny, typically less than 1.0 cm$^{-1}$. Therefore, the results presented below are based on the assumption of transferability of this observation to any other properties.

An optimized basis of one-mode wave functions (modals) was determined by vibrational self-consistent field (VSCF) theory using a primitive basis of 20 distributed Gaussians [89]. The modals were used in subsequent configuration-selective vibrational configuration interaction (VCI) calculations [97] in order to account for vibration correlation effects. Within these calculations the correlation space was restricted to quintuple excitations, excitations up the 6th root per mode, and a sum of quantum numbers of 15. This led to 302 254 Hartree products in the VCI calculations. The full Watson Hamiltonian [98] for nonrotating molecules was employed with the $\mu$ tensor being truncated after the 0th-order term [99]. State-specific vibrational averaging was used to determined the final PV expectation values.

The calculation of infrared intensities is based on the integrated absorption coefficients (see for example Refs. [100,101]):

$$I_{rf} = \frac{8N_A\pi^3}{3c^2h^2(4\pi\epsilon_0)}|\langle\Psi^{\mathbf{n}^f}|\mu|\Psi^{\mathbf{n}^r}\rangle|^2\Delta E_{rf}\Delta n_{rf}, \tag{6}$$

where $N_A$ is Avogadro's number, and $\Psi^{\mathbf{n}^r}$ and $\Psi^{\mathbf{n}^f}$ denote the wave functions in the initial and the final vibrational state characterized by the quantum number vectors $\mathbf{n}^r$ and $\mathbf{n}^f$, respectively. $\Delta E_{rf}$ is the energy difference between these two states and $\Delta n_{rf}$ is the temperature-dependent difference in the fraction of molecules in these states, which is assumed to be 1. Within this representation and the VSCF framework, the working equation for the expression given above can be written as

$$I_{rf} = \frac{2N_a\pi^2}{3c^2\epsilon_0h^2}\Delta E_{rf}\sum_{\alpha\in\{x,y,z\}}\Bigg[\mu^0_\alpha + \sum_i\langle\varphi_i^{n_i^f}|\mu_\alpha(q_i)|\varphi_i^{n_i^r}\rangle + \sum_{i<j}\langle\varphi_i^{n_i^f}\varphi_j^{n_j^f}|\mu_\alpha(q_i,q_j)|\varphi_i^{n_i^r}\varphi_j^{n_j^r}\rangle + \cdots\Bigg]^2. \tag{7}$$

Note that in the corresponding VCI calculations strictly orthogonal ground-state-based modals were used.

## III. RESULTS

The calculated CAMB3LYP* atomic PV energy contributions and dipole moment at the coupled-cluster equilibrium structure are listed in Table I together with the computed bond distances and angles. Our $r_e$ equilibrium bond lengths agree nicely with the values obtained from conventional coupled-cluster calculations as provided in Ref. [70]. While $r_a$ distances were determined from zero-point averaged atomic positions, $r_g$ parameters present an average value of an instantaneous internuclear distance and were calculated from a VCI expectation value of the bond lengths expanded in terms of normal coordinates. The $r_a$ bond lengths are in very good agreement with gas phase electron diffraction results of Jacob [102] except for the C-H bond length where we believe that our value is more accurate (see also the discussion in Refs. [103,104]). We also have good agreement with the experimental bond angles considering the uncertainties in the original gas phase electron diffraction experiment, see Table I, and the dipole moment is also in excellent agreement with our previous CCSD(T) results of 1.19 D [70]. Moreover, the rotational constants and quartic centrifugal distortion constants in Watson's $A$-reduced form are provided in Table II. Furthermore, the PV matrix elements are in reasonable agreement with previous results [66] considering the

TABLE II. Rotational constants (in MHz) and quartic centrifugal distortion constants in the Watson $A$-reduced form (in kHz) of CHFClBr and CDFClBr.

| Property | CHFClBr | CDFClBr |
|---|---|---|
| $A_e$ | 6476.75 | 6266.85 |
| $B_e$ | 2030.11 | 2008.06 |
| $C_e$ | 1596.81 | 1592.82 |
| $A_0$ | 6446.00 | 6237.08 |
| $B_0$ | 2022.64 | 2000.58 |
| $C_0$ | 1589.77 | 1585.77 |
| $\Delta_J$ | 0.421 | 0.404 |
| $\Delta_{JK}$ | $-0.505$ | $-0.519$ |
| $\Delta_K$ | 7.520 | 6.649 |
| $\delta_J$ | 0.099 | 0.093 |
| $\delta_K$ | 2.803 | 2.646 |

TABLE III. Frequencies (in cm$^{-1}$) and infrared intensities (in km/mol) for the fundamental transitions in $^{12}\mathrm{C}\,^{1,2}\mathrm{H}\,^{19}\mathrm{F}\,^{35}\mathrm{Cl}\,^{79}\mathrm{Br}$. For the transitions the notation $k^m$ is used, where $k$ is the cardinal number from the lowest to the highest frequency, and $m = n''_k - n'_k$ is the difference in the vibrational quantum numbers. The main stretching (s) and bending (b) contributions are also listed. Experimental values taken from Refs. [105,106].

| | | | 3-mode | | | | 4-mode | | Exp. | |
|---|---|---|---|---|---|---|---|---|---|---|
| Molecule | Transition | $\tilde{\nu}_{\mathrm{harm}}$ | $\tilde{\nu}_{\mathrm{VSCF}}$ | $I_{\mathrm{VSCF}}$ | $\tilde{\nu}_{\mathrm{VCI}}$ | $I_{\mathrm{VCI}}$ | $\tilde{\nu}_{\mathrm{VCI}}$ | $I_{\mathrm{VCI}}$ | $\tilde{\nu}$ | $I$ |
| CHFClBr | $E_{\mathrm{ZPE}}$ | 4642.0 | 4601.8 | | 4594.6 | | 4594.6 | | | |
| | $1^1$ ClCBr b | 224.9 | 223.7 | 0.004 | 223.4 | 0.004 | 223.4 | 0.004 | 223.6 | 0.024 |
| | $2^1$ FCBr b | 316.1 | 313.9 | 0.132 | 312.9 | 0.108 | 312.9 | 0.109 | 313.0 | 0.096 |
| | $3^1$ FCCl b | 429.4 | 426.5 | 0.70 | 425.2 | 0.66 | 425.2 | 0.66 | 425.2 | 0.51 |
| | $4^1$ CBr s | 671.2 | 665.3 | 43.5 | 663.4 | 42.7 | 663.4 | 42.8 | 663.6 | 52.4 |
| | $5^1$ CCl s | 803.6 | 791.3 | 165 | 788.7 | 164 | 788.7 | 164 | 787.0 | 179 |
| | $6^1$ CF s | 1107.3 | 1082.7 | 167 | 1079.2 | 154 | 1079.2 | 154 | 1077.18 | 168 |
| | $7^1$ HCCl/Br b | 1232.0 | 1216.2 | 58 | 1204.6 | 31 | 1204.8 | 31 | 1202.8 | 57 |
| | $8^1$ HCF b | 1336.5 | 1313.1 | 10.7 | 1306.6 | 9.1 | 1306.6 | 9.2 | 1306.2 | 11.2 |
| | $9^1$ CH s | 3163.1 | 2982.4 | 0.70 | 3022.0 | 0.61 | 3022.3 | 0.77 | 3025.5 | 0.82 |
| CDFClBr | $E_{\mathrm{ZPE}}$ | 3863.2 | 3839.6 | | 3834.6 | | 3834.7 | | | |
| | $1^1$ ClCBr b | 223.9 | 222.8 | 0.024 | 222.5 | 0.027 | 222.5 | 0.004 | 222.7 | 0.024 |
| | $2^1$ FCBr b | 315.4 | 313.3 | 0.234 | 312.4 | 0.215 | 312.4 | 0.122 | 312.7 | 1.1 |
| | $3^1$ FCCl b | 427.3 | 424.4 | 0.71 | 423.2 | 0.68 | 423.3 | 0.71 | 423.2 | 0.74 |
| | $4^1$ CBr s | 629.4 | 624.6 | 34 | 619.5 | 25 | 619.7 | 23 | 619.9 | 36 |
| | $5^1$ CCl s | 760.9 | 751.4 | 88 | 749.3 | 82 | 749.4 | 82 | 748.37 | 105 |
| | $6^1$ DCBr/Cl b | 938.4 | 930.1 | 145 | 919.2 | 90 | 919.7 | 90 | 917.86 | 114 |
| | $7^1$ DCF b | 988.9 | 976.9 | 16.82 | 972.5 | 15.29 | 972.8 | 9.04 | 974.3 | 9.56 |
| | $8^1$ CF s | 1112.1 | 1089.7 | 190.5 | 1085.1 | 186.2 | 1085.4 | 167.7 | 1082.67 | 181.3 |
| | $9^1$ CD s | 2330.0 | 2231.6 | 1.38 | 2264.7 | 0.68 | 2264.3 | 1.80 | 2265.33 | 1.41 |

fact that larger basis sets are used here and the equilibrium geometry differs slightly from the previously published result [63]. Concerning the basis sets, extending from acvDZ to acvTZ (or even acvQZ) does not affect the dipole moment significantly, but the PV matrix elements can change up to 11.4% ($M^{\mathrm{Br}}_{\mathrm{PV}}$) in value from the acvDZ to the acvTZ basis set. Here we include the results with the much larger and computationally expensive uncontracted acvQZ basis set, which shows that the acvTZ set is a good compromise. Regarding what is computationally feasible, we decided to use the larger acvTZ uncontracted basis set in conjunction with the 3-mode analysis to correct for basis set incompleteness errors.

### A. Vibrational spectra

Tables III and IV report fundamental and overtone transitions and intensities for CHFClBr and CDFClBr at different levels of theory for the most abundant isotope of each atom in comparison with experimental data [105,106]. Results for combination bands are provided in the Supplemental Material [76]. The vibrational spectra have been discussed in detail by Beil *et al.* [105,106] and we concentrate on the comparison to our calculated values here. In the following and for better comparison we report intensities and PV contributions to three decimal places even though it does not reflect the accuracy of our calculations.

Our transition frequencies are in excellent agreement with experimental data considering that the experimental frequencies reported have sometimes errors of the order of 1 cm$^{-1}$. This error bar is in the same range as for our calculations, as small changes in the fitting of the potential or enlarged correlation spaces within the VCI calculations will lead to variations of the same magnitude. The mean absolute deviation (MAD) of our computed values with respect to the experimental ones for the fundamentals modes of CHFClBr is 1.1 cm$^{-1}$ and 0.9 cm$^{-1}$ for CDFClBr. Even though this accuracy is excellent, it still relies on error compensation as several contributions to the total energy in the electronic structure calculations have been neglected, e.g., core-correlation effects, high-order coupled-cluster contributions, diagonal Born-Oppenheimer corrections, etc. The fundamental transition $7^1$ of CHFClBr at 1204.8 cm$^{-1}$ shows a strong Fermi resonance with the combination band $3^1 5^1$ at 1214.7 cm$^{-1}$, but the assignment is unambiguous. In that context, we like to note that the experimentally determined intensities suffer from the usual resolution problem; i.e., often one finds more than one transition contributing to the experimental IR intensity, especially for the dense spectrum of the deuterated species, and a direct comparison with computed values is error prone. For example, according to our VCI(3D) calculations for CHFClBr the overtone $8^2$ splits into two bands, one at 2599.8 cm$^{-1}$, the other at 2599.1 cm$^{-1}$. The leading VCI coefficients are 0.69 and 0.51, respectively. Although these states can clearly be distinguished computationally, due to line broadening it is difficult in experimental work to correctly assign the intensity to the individual transitions. We note here that computed weak infrared intensities also inherit a considerable uncertainty as parameters within the calculations have certain impact on these values; see the discussion about vibrational transitions above. However, due to the high accuracy of our calculations, we were able to reassign some of the

TABLE IV. Frequencies (in cm$^{-1}$) and infrared intensities (in km/mol) for the overtone transitions in $^{12}$C$\,^{1,2}$H$\,^{19}$F$\,^{35}$Cl$\,^{79}$Br. Experimental values taken from Refs. [105,106]. For details see Table III. Experimental intensities set in parentheses contain more than one vibrational transition and are therefore upper limits.

| | | 3-mode | | | | 4-mode | | Exp. | |
|---|---|---|---|---|---|---|---|---|---|
| Molecule | Transition | $\tilde{\nu}_{\mathrm{VSCF}}$ | $I_{\mathrm{VSCF}}$ | $\tilde{\nu}_{\mathrm{VCI}}$ | $I_{\mathrm{VCI}}$ | $\tilde{\nu}_{\mathrm{VCI}}$ | $I_{\mathrm{VCI}}$ | $\tilde{\nu}$ | $I$ |
| CHFClBr | $1^2$ ClCBr b | 447.4 | 0.001 | 446.8 | 0.003 | 446.8 | 0.003 | | |
| | $2^2$ FCBr b | 627.6 | 0.004 | 625.1 | 0.666 | 625.2 | 0.671 | 625.5 | 1.5 |
| | $3^2$ FCCl b | 852.5 | 0.011 | 850.3 | 0.669 | 850.4 | 0.675 | 849.7 | 1.4 |
| | $4^2$ CBr s | 1326.9 | 0.105 | 1324.9 | 0.742 | 1325.0 | 0.700 | 1324.9 | 0.08 |
| | $5^2$ CCl s | 1573.5 | 0.959 | 1569.3 | 0.964 | 1569.4 | 0.969 | 1564.1 | 1.0 |
| | $6^2$ CF s | 2146.4 | 3.349 | 2140.1 | 3.164 | 2140.2 | 3.164 | 2135.6 | 3.5 |
| | $7^2$ HCCl/Br b | 2445.3 | 3.362 | 2396.1 | 0.161 | 2396.4 | 0.180 | 2392.6 | (0.48) |
| | $8^2$ HCF b | 2633.2 | 1.781 | 2599.8 | 0.136 | 2600.0 | 0.083 | 2599.4 | 0.25 |
| CDFClBr | $1^2$ ClCBr b | 445.6 | 0.001 | 445.0 | 0.003 | 445.1 | 0.002 | | |
| | $2^2$ FCBr | 626.3 | 0.006 | 626.6 | 9.132 | 626.7 | 8.554 | 625.74 | (35) |
| | $3^2$ FCCl b | 848.4 | 0.015 | 846.0 | 0.045 | 846.1 | 0.038 | 844 | (0.944) |
| | $4^2$ CBr s | 1246.2 | 0.184 | 1239.7 | 1.237 | 1239.9 | 0.896 | 1240 | 1.352 |
| | $5^2$ CCl s | 1495.8 | 0.453 | 1493.4 | 0.608 | 1493.6 | 0.562 | 1491.69 | 0.84 |
| | $6^2$ DCBr/Cl b | 1863.3 | 0.480 | 1828.1 | 0.053 | 1829.4 | 0.061 | 1828 | 0.1 |
| | $7^2$ DCF b | 1954.9 | 0.023 | 1940.0 | 0.108 | 1940.8 | 0.118 | 1941.67 | 0.032 |
| | $8^2$ CF s | 2162.2 | 3.772 | 2149.5 | 3.208 | 2149.7 | 2.458 | 2145.14 | 2.74 |

combination bands compared to the experimental assignment; see the Supplemental Material [76]. One can also see that in general a 3-mode treatment is already sufficient for the vibrational transitions, i.e., a 4-mode treatment results in little

TABLE V. PV frequency shift $\Delta\nu_{\mathrm{PV}}(k^m) = [E_{\mathrm{PV}}(k^m) - E_{\mathrm{PV}}(0)]/h$ (in mHz) for the fundamental transitions in $^{12}$C$\,^{1,2}$H$\,^{19}$F$\,^{35}$Cl$\,^{79}$Br at different levels of theory and basis sets used. $E_{\mathrm{PV}}(0) = h\nu_{\mathrm{PV}}(0)$ denotes the ground vibrational PV energy shift (in $10^{-18}$ a.u.) and $E_{\mathrm{PV}}(k^m)$ the PV energy shift for the excited vibrational state. acvDZ+TZC denotes the 4-mode result corrected for the basis set effect due to the change from acvDZ to acvTZ from the 3-mode result. The last column contains single-mode (SM) random-phase approximation (RPA) results of Stohner and Quack [62,108] (for the conversion of $\Delta_{RS}\nu/\nu$ to $\Delta\nu_{\mathrm{PV}}(L)$ in Refs. [62,108] the experimental frequencies from Table III were used). Vibrational transitions dominated by a small leading VCI coefficient of $\leqslant$0.8 for the final state are marked by asterisks.

| | | 3-mode | | | | 4-mode | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | acvDZ | | acvTZ | | acvDZ | | acvDZ+TZC | | |
| Molecule | Transition | VSCF | VCI | VSCF | VCI | VSCF | VCI | VSCF | VCI | SM/RPA |
| CHFClBr | $E_{\mathrm{PV}}(0)$ | −1.48872 | −1.48771 | −1.74236 | −1.74135 | −1.48864 | −1.48740 | | | |
| | $1^1$ ClCBr b | −0.629 | −0.636 | −0.673 | −0.680 | −0.630 | −0.635 | −0.674 | −0.679 | −0.151 |
| | $2^1$ FCBr b | 2.945 | 2.952 | 3.215 | 3.223 | 2.943 | 2.950 | 3.213 | 3.221 | 1.576 |
| | $3^1$ FCCl b | −3.361 | −3.375 | −3.778 | −3.794 | −3.357 | −3.362 | −3.774 | −3.781 | −1.153 |
| | $4^1$ CBr s | −1.473 | −1.532 | −1.683 | −1.749 | −1.475 | −1.500 | −1.685 | −1.717 | −0.948 |
| | $5^1$ CCl s | 0.999 | 0.948 | 1.200 | 1.139 | 1.001 | 0.962 | 1.202 | 1.153 | 2.949 |
| | $6^1$ CF s | 1.995 | 1.627 | 2.262 | 1.847 | 1.998 | 1.647 | 2.265 | 1.867 | 1.301 |
| | $7^{1*}$ HCCl/Br b | 0.746 | 0.062 | 0.821 | 0.088 | 0.751 | 0.100 | 0.826 | 0.126 | 2.322 |
| | $8^1$ HCF b | −0.722 | −0.596 | −0.869 | −0.711 | −0.722 | −0.637 | −0.869 | −0.752 | −2.583 |
| | $9^{1*}$ CH s | −0.204 | −0.939 | −0.169 | −1.049 | −0.205 | −0.589 | −0.170 | −0.699 | −0.038 |
| CDFClBr | $E_{\mathrm{PV}}(0)$ | −1.55325 | −1.55360 | −1.82230 | −1.82237 | −1.55300 | −1.55353 | | | |
| | $1^1$ ClCBr b | −0.621 | −0.624 | −0.685 | −0.687 | −0.621 | −0.622 | −0.685 | −0.685 | −0.032 |
| | $2^1$ FCBr b | 3.115 | 3.120 | 3.323 | 3.323 | 3.113 | 3.115 | 3.321 | 3.318 | 1.319 |
| | $3^1$ FCCl b | −3.371 | −3.377 | −3.083 | −3.096 | −3.369 | −3.381 | −3.081 | −3.100 | −0.920 |
| | $4^1$ CBr s | −1.912 | 0.759 | −2.263 | 0.567 | −1.906 | 0.824 | −2.257 | 0.632 | −1.085 |
| | $5^1$ CCl s | 2.046 | 1.855 | 2.243 | 2.249 | 2.013 | 1.835 | 2.210 | 2.229 | 3.516 |
| | $6^1$ DCBr/Cl b | −0.232 | 0.207 | −0.255 | 0.250 | −0.220 | 0.262 | −0.243 | 0.305 | 1.304 |
| | $7^1$ DCF b | −0.918 | −0.672 | −1.193 | −0.875 | −0.922 | −0.806 | −1.197 | −1.009 | −2.129 |
| | $8^1$ CF s | 2.567 | 2.653 | 2.896 | 2.991 | 2.574 | 2.619 | 2.903 | 2.957 | 2.139 |
| | $9^1$ CD s | −0.102 | 0.670 | −0.050 | 0.827 | −0.108 | 0.623 | −0.056 | 0.780 | −0.090 |

TABLE VI. PV frequency shift $\Delta\nu_{\mathrm{PV}}(k^m)$ (in mHz) in $^{12}\mathrm{C}\,^{1,2}\mathrm{H}\,^{19}\mathrm{F}\,^{35}\mathrm{Cl}\,^{79}\mathrm{Br}$ for the overtone transitions at different levels of theory and basis sets used. Vibrational transitions dominated by a small leading VCI coefficient of $\leqslant 0.8$ for the final state are marked by asterisks. See Table V for further details.

| | | 3-mode | | | | 4-mode | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | acvDZ | | acvTZ | | acvDZ | | acvDZ + TZC | |
| Molecule | Transition | VSCF | VCI | VSCF | VCI | VSCF | VCI | VSCF | VCI |
| CHFClBr | $1^2$ ClCBr b | −1.198 | −1.211 | −1.283 | −1.298 | −1.120 | −1.208 | −1.205 | −1.295 |
| | $2^2$ FCBr b | 5.809 | 5.789 | 6.338 | 6.317 | 5.805 | 5.893 | 6.379 | 6.421 |
| | $3^2$ FCCl b | −6.638 | −6.578 | −7.459 | −7.390 | −6.632 | −6.561 | −7.453 | −7.373 |
| | $4^2$ CBr s | −2.942 | −3.329 | −3.358 | −3.798 | −2.944 | −3.149 | −3.360 | −3.618 |
| | $5^2$ CCl s | 2.142 | 2.023 | 2.557 | 2.414 | 2.151 | 2.053 | 2.566 | 2.444 |
| | $6^2$ CF s | 3.944 | 3.856 | 4.469 | 4.371 | 3.950 | 3.821 | 4.475 | 4.336 |
| | $7^{2*}$ HCCl/Br b | 1.434 | −1.678 | 1.584 | −1.830 | 1.445 | 0.642 | 1.595 | 0.490 |
| | $8^{2*}$ CH s | 1.345 | −0.345 | −1.625 | −0.456 | −1.348 | −0.651 | −1.628 | −0.762 |
| CDFClBr | $1^2$ ClCBr b | −1.179 | −1.181 | −1.358 | −1.358 | −1.178 | −1.179 | −1.357 | −1.356 |
| | $2^2$ FCBr b | 6.517 | 3.786 | 6.798 | 3.885 | 6.514 | 3.705 | 6.795 | 3.804 |
| | $3^2$ FCCl b | −6.771 | −6.756 | −4.654 | −4.697 | −6.767 | −6.699 | −4.650 | −4.640 |
| | $4^{2*}$ CBr s | −3.859 | −1.884 | −4.730 | −2.727 | −3.848 | −1.704 | −4.719 | −2.547 |
| | $5^2$ CCl s | 4.200 | 3.313 | 4.982 | 4.222 | 4.133 | 3.203 | 4.915 | 4.112 |
| | $6^{2*}$ DCBr/Cl b | −0.503 | 0.098 | −0.564 | 0.344 | −0.476 | 0.240 | −0.537 | 0.486 |
| | $7^2$ DCF b | −1.710 | −2.062 | −2.189 | −2.524 | −1.727 | −2.192 | −2.206 | −2.654 |
| | $8^2$ CF s | 5.028 | 5.338 | 5.685 | 6.093 | 5.033 | 5.275 | 5.690 | 6.030 |

improvement, while the infrared intensities are slightly more sensitive. This supports the general finding in quantum chemistry that energies are often faster converged than properties, which depend directly on the wave function. Nevertheless, the good performance of our VCI method implies that the vibrational wave functions produced are of good quality for the following PV treatment. We finally mention that isotope effects (other then H/D) in the vibrational spectrum are also in good agreement with available experimental results which we do not detail here.

### B. Parity-violation contributions

Tables V and VI show the PV frequency shifts for CHFClBr and CDFClBr. Again we see that a 3-mode treatment is sufficient in most cases, but a few exceptions can be found especially in the high-frequency region. For example, the PV shift for the overtone $7^2$ in CHFClBr changes at the VCI level from $-1.678$ cm$^{-1}$ (acvDZ, 3D) to 0.642 cm$^{-1}$ (acvDZ, 4D). Due to a strong resonance with the $3^2 5^2$ state, the corresponding leading VCI coefficients are 0.57 (3D) and 0.71 (4D) and the related transition energies are 2405.5 cm$^{-1}$ (3D) and 2396.9 cm$^{-1}$ (4D). Clearly, this transition cannot be described within a single-mode treatment and the VCI(3D) wave function has a completely different composition than the VCI(4D) function, which readily explains the difference. As the 4D result is in much better agreement with the experimental transition energy (2392.6 cm$^{-1}$), the 3D result must suffer from the incompleteness of the potential energy surface. It is a well known fact that incomplete surfaces may lead to artificial resonances in the vibrational structure calculations and thus the 4D results must be considered superior in general [107]. Further examples concerning the incompleteness of the potential are the transitions $2^1 7^1$, $3^1 7^1$ and $2^1 8^1$ for CDFClBr (see the Supplemental Material [76]). Moreover, one can see that a VSCF treatment is insufficient for modes which are strongly affected by resonances (marked by asterisks in Tables V and VI), which mirrors the effects seen for the infrared intensities. For the combination bands shown in the Supplemental Material the number of such resonating states is quite large, in particular for CDFClBr, for which the state density is increased for low-lying transitions, VCI calculations appear to be mandatory, and a sufficiently large correlation space must be provided in order to obtain converged results. Moreover, although the molecules being considered in this study are quite heavy, a consequent inclusion of the vibrational angular momentum terms as occurring in the Watson-Hamiltonian was found to be important and lead to a stabilization of the VCI wave functions, while the impact on the transition energy was very moderate. Likewise, basis set effects in the electronic structure calculations for the PV shifts appear to be important and thus results based on double-$\zeta$ calculations must be considered unreliable. All this shows that PV shifts are fairly sensitive to different individual components of the calculations and need to be carefully converged in any respect.

We now compare with previous calculations. Using the random-phase approximation for the PV calculations, Quack and Stohner report PV effects including anharmonicity corrections in a single-mode analysis for the fundamental transitions as shown in Table V [62]. For CHFClBr, the signs for the PV shifts all agree with our results, but the values often differ from each other substantially. Notably our 4-mode VCI result with the acvDZ basis set for the C-H stretching fundamental of $\Delta\nu_{\mathrm{PV}}(S) = -0.70$ mHz appears to be rather large, but this is a result of the strong correlation effects for this high-lying state, which describe couplings to other coordinates. Only 53% arise from the C-H stretching coordinate and thus the PV shift must differ significantly with respect to a single-mode analysis, which is in agreement with the much lower VSCF value. Concerning the C-F fundamental mode, which has been in the focus for experimental measurements [57,68]), our TZ-corrected VCI result of $\Delta\nu_{\rm PV}(S) = 1.87$ mHz compares to 0.85 mHz [63] from Dirac-Hartree-Fock results and 1.30 mHz [62] from RPA results within a single-mode coupled-cluster treatment. For comparison, Berger and Stuber obtained 1.08 and 1.51 mHz at the HF and B3LYP level of theory, respectively [65].

For CDFClBr we see much larger deviations with the single-mode analysis of Quack and Stohner [108], but they seem to agree qualitatively on the PV frequency shift for the C-F stretching mode. For CDFClBr Quack and Stohner present a four-dimensional potential energy surface using the random-phase approximation for PV calculations and coupling the C-F stretching mode with the C-D stretching and the $X$-C-D ($X$ = F, Cl, Br) bending modes. They obtain for the C-D stretching mode (our values are given in parentheses) $\nu_{\rm PV}(S) = 0.45$ mHz (0.78 mHz), C-F stretching mode 3.48 mHz (2.96 mHz), D-C-F bending mode −0.89 mHz (−1.01 mHz), and D-C-Br/Cl bending mode 2.69 mHz (0.31 mHz). We see larger deviations from Quack and Stohner's values for the D-C-Br/Cl bending mode. We also get a large enhancement in the PV vibrational shift for the C-F stretching mode due to deuterium substitution.

## IV. CONCLUSIONS

We presented a comprehensive vibrational analysis coupling all modes for the vibrational spectrum and PV frequency shifts of the chiral molecule CHFClBr and its isotopologs. We believe that the data presented will be very useful for detecting PV effects in chiral molecules. For the fundamental transitions the deviations to experimental data are on the order of a few wave numbers only, the most accurate spectrum obtained so far by theoretical methods for such molecules. We showed that a 3-mode analysis at the VCI level is sufficient for the vibrational spectrum and PV frequency shifts. The largest error for the PV data comes perhaps from the density functional treatment and basis sets used. However, a coupled-cluster treatment for PV effects for the 3-mode hypersurface was beyond our computational means.

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