1 Introduction

The knowledge of the structural properties and dynamic behavior of molecules is at the heart of a deep understanding of their stability, spectroscopy, and reactivity. The accurate determination of molecular structures is thus one of the principal aims in many areas of physical chemistry and chemical physics, which—in the last few decades—has involved the efforts of experimentalists and theoreticians. In particular, for all spectroscopists, there is a strong relationship between the experimental outcome and the underlying electronic structure of the system under consideration (see, for example, ref. 3–7). In this respect, a great advantage of molecular spectroscopy is the capability of probing molecular properties in a non-invasive manner. In the gas phase, rotational spectroscopy is the technique of choice to derive accurate structural information because of the strong dependence of the rotational constants on the molecular geometry. Unfortunately, it is seldom straightforward to retrieve the molecular structure from the experimental information. Indeed, for a given molecule, there are at most three rotational constants, with the structural parameters being up to \(3N - 6\) (where \(N\) is the number of atoms). The way-out is to resort to different isotopic species of the same molecule in order to increase the number of data. Different isotopologues of a given molecule share the same equilibrium structure \(r_0\), i.e., the minimum geometry on the Born–Oppenheimer potential energy surface but not the vibrationally averaged structure which depends on the atomic masses. This is the limitation hampering the vibrationally averaged \(r_0\) structure that is obtained from the direct analysis of the vibrational ground-state rotational constants for different isotopologues, without any explicit consideration of vibrational effects. As a consequence, vibrationally averaged structures depend on the set of isotopic species considered. To avoid these limitations, one has to resort to \(r_0\).

From a pure experimental point of view, for small molecules, it might be feasible to derive experimental vibrational contributions that can be used to correct the ground-state rotational constants. The equilibrium rotational constants then obtained for different isotopic species can be used for the determination...
of the equilibrium structure. However, such a procedure becomes unpractical already for medium-sized molecular systems. This difficulty can be efficiently tackled using the so-called semi-experimental (SE) approach.\(^2\)\(^5\)\(^\text{-}\)\(^1\)\(^7\) Within this framework, quantum-chemical calculations are employed to recover vibrational effects. For different isotopologues, computed vibrational corrections are combined with the corresponding experimental ground-state rotational constants to obtain the so-called SE equilibrium rotational constants and, from them, the SE equilibrium structure. This method proved to be powerful and allowed the derivation of the accurate equilibrium structures of small- to medium-sized molecules and non-covalent molecular complexes,\(^2\)\(^5\)\(^\text{-}\)\(^1\)\(^7\) thus superseding the previously used Kraitchman’s substitution method (the \(r_s\) structure).\(^1\)\(^8\) Since \(r_s\) structures do not explicitly and rigorously treat the vibrational contributions, they might lead to inaccurate and biased results.\(^5\)

However, the SE approach has some limitations, since a balanced fit is obtained only with a large set of experimental data including several isotopic substitutions. Ideally, one should have at least one isotopic substitution for each nucleus of the system under consideration.\(^2\) This might be unpractical from an experimental point of view, but, in some cases, it can be simply impossible because of the lack of different stable isotopes for a given atom. This is the case, for example, for fluorine and phosphorous.

Interestingly, there are other spectroscopic parameters than the rotational constants that directly depend on the molecular geometry. This is the case of the dipolar spin–spin coupling constants, which describe the interaction of two nuclear magnetic moments in a molecule. In nuclear magnetic resonance (NMR), in the spectroscopic investigation of non-isotopic media, dipolar coupling interactions are responsible for the signal splitting and represent the dominant coupling mechanism.\(^1\)\(^9\) In rotational spectroscopy, dipolar couplings are, in addition to spin-rotation interactions and nuclear quadrupole couplings, responsible for the hyperfine structure of the spectra.\(^5\)\(^,\)\(^9\) The experimentally determined dipolar spin–spin coupling constants can be used to obtain the structural information even in those cases where isotopic substitutions are not feasible.\(^5\) More generally, they can enrich the set of experimental data to be used in the SE approach.

This perspective inspects the use of dipolar spin–spin coupling constants in support of the SE structure determination. In particular, we explore their role when the isotopic substitution is limited or not feasible. For this purpose, we have selected three light hydrides and their fully fluorinated counterparts: (i) \(\text{H}_2\text{O}\) and \(\text{OF}_2\), (ii) \(\text{NH}_3\) and \(\text{NF}_3\) and, (iii) \(\text{PH}_3\) and \(\text{PF}_3\). These have been chosen because they range from systems for which a large number of data are available with great precision, such as \(\text{NH}_3\) and \(\text{H}_2\text{O}\), to systems for which isotopic substitution is limited (\(\text{OF}_2\) and \(\text{NF}_3\)) or not possible at all (such as \(\text{PF}_3\)). In the following, all relevant theoretical details of the form of the dipolar spin–spin coupling tensor are provided. Then, computational details and the methodology for the derivation of structural parameters are given. Subsequently, the results are collected and discussed.

2 Theoretical details

The dipolar interaction between the \(I_L\) and \(I_M\) nuclear magnetic moments is described by the following Hamiltonian

\[
H_{\text{dip}}^{LM} = I_L \cdot D^{LM} I_M, \tag{1}
\]

where \(D^{LM}\) is the dipolar spin–spin coupling tensor, whose components in SI units are given by\(^5\)\(^,\)\(^8\)\(^,\)\(^1\)\(^9\)

\[
D^{LM}_{\text{dip}} = \frac{g_L g_M \mu_N}{4 \pi \varepsilon_0 c^2} \frac{3 (R_{LM})_L (R_{LM})_M - \delta_{LM} R_{LM}^2}{R_{LM}^2}, \tag{2}
\]

Four members of the ROT&Comp lab. From left to right: Cristina Puzzarini, Luca Bizzocchi, Silvia Alessandrini and Mattia Melosso

From left to right: Cristina Puzzarini, Luca Bizzocchi, Silvia Alessandrini and Mattia Melosso

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where \( \mathbf{R}_{LM} \) denotes the vector from nucleus L to M, \( g_L \) and \( g_M \) are the corresponding nuclear g-factors, \( \epsilon_0 \) is the vacuum permittivity, \( c \) is the speed of light, and \( \delta_{\beta \gamma} \) is Kronecker's delta with \( x, y, z \), cyclically. From eqn (2), it appears clear that the dipolar spin–spin coupling tensor is completely determined by the molecular geometry.

The tensor \( \mathbf{D} \) is symmetric and traceless by definition and it is customary to express its diagonal elements (for a prolate-type rotor) as \( D_{zz} \) and \( D_{xx} = D_{yy} \). For linear molecules, these reduce to one independent component due to the cylindrical symmetry around the z-axis:

\[
\frac{1}{2} D^{LM}_{zz} = -D^{LM}_{xz} = -D^{LM}_{yz} = D^{LM}_{xx},
\]

(3)

where the scalar quantity \( D^{LM} \) is customarily used as the coefficient of the spin–spin interaction. This equality also holds for symmetric-tops once all the equivalent interactions involving off-axis nuclei are summed over. By expressing \( \mathbf{D} \) as a rank-2 spherical tensor, it is readily seen that, for a prolate top, \( D_{zz} \) accounts for the \( K \)-diagonal contribution of the spin–spin interaction via the tensor component \( T_{2,0}(\mathbf{D}) \) (see e.g., eqn. (8).442 of ref. 20). In the symmetric-top basis, its matrix elements of interest (\( J = \hat{J} \)) are

\[
\langle J, K' \cdots \mid T_{2,0}(\mathbf{D}) \mid J, K \cdots \rangle = -\sqrt{6} D^{LM}_{zz} (-1)^{J-K'} \begin{pmatrix} J & 2 & J \\ -K' & 0 & K \end{pmatrix}
\]

\times \langle J, I_1, I_2, \cdots \mid T_2(\mathbf{D}) \mid J, I_1, I_2, \cdots \rangle,
\]

(4)

and, due to the symmetric properties of the \( \delta \)-symbol, only the terms implying \( K = K' (\Delta K = 0) \) are non-vanishing. Nonetheless, as demonstrated in some NH3 pivotal studies,\(^{21,22} \) off-diagonal matrix elements with \( \Delta K = \pm 2 \) can arise in some cases and, when connecting states with the same rotational energy, may become important.\(^{23} \) Such energy contributions are generated by the \( T_{2,\pm 2}(\mathbf{D}) \) tensor components, whose definition in the Cartesian axis system is

\[
T_{2,\pm 2}(\mathbf{D}) = -\frac{g_L g_M \mu_e^2}{4 \pi \epsilon_0 c^2} \frac{1}{R_{LM}^3} \left[ (\mathbf{R}_{LM})_x^2 - (\mathbf{R}_{LM})_y^2 \right. \\
\left. \pm i (\mathbf{R}_{LM})_y (\mathbf{R}_{LM})_x + (\mathbf{R}_{LM})_y (\mathbf{R}_{LM})_y \right].
\]

(5)

Analogous to eqn (4), for the matrix elements of \( T_{2,\pm 2}(\mathbf{D}) \), one has

\[
\langle J, K' \cdots \mid T_{2,2}(\mathbf{D}) + T_{2,-2}(\mathbf{D}) \mid J, K \cdots \rangle = -D^{LM}_{zz} (-1)^{J-K'} \begin{pmatrix} J & 2 & J \\ -K' & 2 & K \end{pmatrix} \\
\times \langle J, I_1, I_2, \cdots \mid T_2(\mathbf{D}) \mid J, I_1, I_2, \cdots \rangle
\]

(6)

This term has a non-negligible importance for \( K = \pm 1 \) only, i.e. when it connects two rotationally degenerate states. As discussed by Kukolich\(^{23} \) for NH3, this contribution is non-zero for the N–H interaction only, and it is particularly important for \( ^{15}\text{NH}_3 \), since the \( ^{15}\text{N} \) nucleus has no quadrupole moment and terms off-diagonal in \( F_1 \) may be as large as the diagonal terms.

From an experimental point of view, the geometry that determines dipolar spin–spin coupling effects is that of the molecule at the moment of the measurements, which is usually that the molecule assumes in the vibrational ground state. Hence, in analogy to what is performed for rotational constants within the SE approach, dipolar spin–spin coupling constants should be corrected for zero-point vibrational (ZPV) effects:

\[
\Delta D^{LM}_{ZPV} = D^{LM}_{ZPV} - D^{LM}_{ZPVT},
\]

(7)

where the vibrational correction, \( \Delta D^{LM}_{ZPV} \), can be computed as implemented in CFOUR.\(^{24} \) The procedure consists of expanding the expectation value over the vibrational wavefunction in a Taylor series around the equilibrium value with respect to normal-coordinate displacements, with the expansion being then truncated after the quadratic term. In the retained terms, the expectation values over normal coordinates are evaluated using perturbation theory. From a computational point of view, this procedure requires harmonic and cubic force constants being evaluated within a normal-coordinate representation. This approach has already been successfully employed for the calculation of vibrational effects on dipolar spin–spin coupling constants and other rotational parameters (see, for example, ref. 5, 25–28).

### 3 Methodology

As briefly mentioned in the Introduction, to demonstrate the use of the dipolar spin–spin coupling constants in structural determination, we have chosen three model systems: NH3, PH3, and H2O. The hyperfine structures of these species have been extensively studied in the past and various experimental determinations of dipolar spin–spin coupling constants are present in the literature. Furthermore, their molecular geometry is completely determined by two parameters (one bond length and one angle) and, in the parent species, only two independent rotational constants are available for the structure determination. All these species possess a fluorinated counterpart, namely NF3, PF3, and OF2, for which access to isotopologue data is limited, if not impossible (i.e. PF3). These molecules thus provide an ideal benchmark to assess how the additional information provided by the dipolar spin–spin coupling can assist the structure determination by breaking the correlations among determinable parameters and by estimating more statistically sound uncertainties for the retrieved geometry parameters.

As a starting point of our analysis, we determined a SE equilibrium structure for each of the model molecules using a set of isotopologues: 8 for NH3, 4 for PH3 and 6 for H2O. Following the standard procedure, ground state rotational constants \( X_0 \) (where \( X = A, B, \) and \( C \)) taken from experimental studies were computationally corrected for ZPV contributions (see Section 3.1) to obtain SE equilibrium rotational constants:

\[
X^{SE}_e = X_0 + \sum_r \frac{\delta X_r}{2} x^2_r,
\]

(8)
where \( d_r \) represents the degeneracy of the normal mode \( r \) and \( \chi_x^c \) is the corresponding vibration–rotation interaction constant for the \( X \) parameter. The structural parameters have then been obtained by a least-squares fit over the set of the \( \chi_x^c \) constants, considering only the \( B, C \) pair for the planar H\(_2\)O species. Such a procedure provided the reference SE structure which the subsequent determinations are compared to. Since we do not aim at computing the “best” equilibrium structure possible for each molecule, the level of theory employed to compute the ZPV contributions has not been pushed to the limit. Furthermore, the electronic contributions to the rotational constants, \( \Delta X_{el} \), which are usually of minor importance,\(^3,3^4\) have been neglected for simplicity. However, this missing contribution is taken into account when estimating the expected uncertainties for the \( \chi_x^c \) used in the data weighting scheme. Given that the fractional precision of the experimental ground state rotational constants obtained by rotational or high-resolution infrared spectroscopy is very high (10\(^{-8}\)–10\(^{-9}\)), the two main sources of uncertainties for \( \chi_x^c \) are those due to the error on the \( ab \ initio \) computed ZPV contributions (\( \Delta X_{ZPV} \)) and the lack of the electronic term \( \Delta X_{el} \).

Based on a series of previous case studies (see e.g. ref. 5), we assume an error of about 1% for the ZPV contributions. The corresponding relative error on the SE equilibrium rotational constants is then summed in quadrature with the fractional uncertainty due to the neglected \( \Delta X_{el} \):

\[
\left( \delta \chi_x^c \right)^2 = \left( \frac{0.01 \Delta X_{ZPV}}{\chi_x^c} \right)^2 + \left( \frac{\Delta X_{el}}{\chi_x^c} \right)^2 ,
\]

where \( \Delta X_{ZPV} \) is the total ZPV contribution to a given rotational constant.

The second step is to insert the equilibrium values of the dipolar spin–spin \( D \) tensor elements into the structural least-squares fit. The experimental values are available for 4 isotopic species of NH\(_3\), 6 isotopic species of H\(_2\)O and for the parent species of PH\(_3\), NF\(_3\), and OF\(_2\) (see Tables 1–3). The experimental dipolar spin–spin coupling constants are corrected for the corresponding ZPV contributions using eqn (7) and then incorporated in the analysis with a weight derived from their corresponding 1σ experimental error. Given the small effect produced in the hyperfine structures by these constants, they are usually determined with a moderate precision, even when obtained by very high-resolution molecular beam measurements (i.e. 1% at best). Such an uncertainty is clearly dominant over the inherent inaccuracy of the \( ab \ initio \) ZPV contributions \( \Delta D_{ZPV} \).

Lastly, we computed a set of SE equilibrium structures using a mixed rotational/spin–spin data set from a single isotopologue for each species considered. The goodness of this last approach is evaluated in comparison with the corresponding reference structure.

### 3.1 Quantum chemical calculations

To have highly accurate reference values for the equilibrium dipolar spin–spin coupling constants, the equilibrium structures of the selected molecules have been obtained at the \( ab \ initio \) level of theory, with all electrons (ae) correlated but the 1s for third-row atoms. In the acronym above, \( \text{CCSD(T)} \) stands for coupled-cluster (CC) singles and doubles with perturbative treatment of triples,\(^{42}\) and \( \text{cc-pCVQZ} \)\(^{43}\) is a weighted core-valence quadruple-zeta set, purposely set up for accurately describing core–core and core–valence correlation effects. For small molecules containing first- to third-row atoms,
4 Results and discussion

4.1 Ammonia (NH₃)

Six isotopic species have been considered for NH₃ structural determination. For each SE parameter, an average fractional uncertainty of $3 \times 10^{-4}$ has been considered, which has been obtained through eqn (9) by considering average values of 3 GHz for the ZPV contribution and 75 MHz for the electronic effects. This average fractional uncertainty has been used to determine the weights adopted in the fitting procedure. The structural parameters derived from 20 SE equilibrium rotational constants are listed in the first row of Table 4 and are labeled as “reference”. Within the quoted error ranges (3σ for the present calculation), they are consistent with the most recent SE results from the literature (also reported in Table 4), with discrepancies of 0.0003 Å for $r_e$(NH) and 0.11 deg. for $\theta_e$(HNH).

Table 4 SE equilibrium structural parameters of NH₃ derived using different isotopic data sets

| Data set | Iso³ (data) | $r_e$(NH)/Å | $\theta_e$(HNH)/deg. | $\sigma_{w,ROT}$ | $\sigma_{w,SS}$ |
|----------|-------------|--------------|----------------------|-----------------|-----------------|
| Reference | 8[20]       | 1.0107(4)    | 106.83(9)            | 4.1             | —               |
| Mixed     | 8[30]       | 1.0106(4)    | 106.8338(16)         | 4.1             | 1.5             |
| NH₃       | 1[5]        | 1.0104(4)    | 106.88(6)            | 0.3             | 1.1             |
| $^{15}$NH₃ | 1[5]        | 1.0104(8)    | 106.87(13)           | 0.2             | 2.3             |
| ND₃       | 1[4]        | 1.0110(4)    | 106.98(2)            | 0.0             | 0.3             |
| $^{15}$ND₃ | 1[4]        | 1.0110(4)    | 106.98(4)            | 0.0             | 0.8             |
| Literature² |            | 1.0110(2)    | 106.94(2)            |                 |                 |

Note: numbers in parentheses indicate 3σ uncertainties in units of the last quoted digit. ³ Number of isotopologues and, in parentheses, number of data. ⁴ Weighted rms deviation of the rotational constants. ⁵ Weighted rms deviation of the dipolar spin–spin coupling constants. ⁶ Ref. 11.

For the four top-symmetric ammonia isotopologues (NH₃, $^{15}$NH₃, ND₃, and $^{15}$ND₃), the dipolar spin–spin interaction constants were experimentally determined. In this work, values for NH₃ and $^{15}$NH₃ have been newly derived by re-analyzing the molecular beam hyperfine data for several rotation–inversion transitions available in the literature. For ND₃ and $^{15}$ND₃, the spin–spin coupling parameters have been directly taken from the corresponding literature studies. In total, 10 $D_M$ constants have been corrected for the ZPV contribution through eqn (7) and fitted together with the 20 SE equilibrium rotational constants. This new geometry is labelled as “mixed” and the corresponding parameters are reported in the second row of Table 4. It can be noticed that the inclusion of the dipolar spin–spin information has a beneficial effect in alleviating the correlation between the two geometry parameters of ammonia without producing any significant structural distortion. Indeed, the quality of the two fits is essentially the same, but the statistical uncertainty of the $\theta_e$(HNH) is reduced by a factor of ~60.

Single-isotopologue data sets, containing both rotational and SE dipolar spin–spin constants, have then been analyzed separately for each top-symmetric variant of ammonia; the derived structural parameters are presented in Table 4. The values of the structural parameters are mainly determined by the rotational constants, which are almost exactly reproduced in all cases. Still, the independent and uncorrelated information provided by the dipolar spin–spin constants (3 for NH₃ and $^{15}$NH₃ and 2 for ND₃ and $^{15}$ND₃) prevents a major distortion of the retrieved geometry and provides a meaningful estimate of the uncertainty interval. Indeed, all obtained $r_e$(NH) and $\theta_e$(HNH) agree well within the statistical uncertainties.
4.2 Phosphine (PH₃)

Four isotopic variants of phosphine have been considered in the “reference”: PH₃, PD₃, PH₂D, and PHD₂. An average fractional uncertainty of 1 × 10⁻⁴ has been used to estimate the weights of their SE equilibrium rotational constants. This corresponds essentially to 1% of the theoretical ZPV contributions, as the ΔE_{el} is very small (~1 × 10⁻⁵).⁴⁹ Studies of the hyperfine spectra of PH₃ are scarcer than those of NH₃ and only two experimental determinations of dipolar spin–spin coupling constants actually exist, namely D_{PH} and D_{OH} for the parent isotopeologue.³⁶ These two values were corrected for the ZPV contribution and used in the “mixed” structural fit. Inspection of Table 5 points out that the “reference” and “mixed” structures are essentially identical and very close to the best SE structure presently available in the literature,⁴⁹ with minor discrepancies of 7 × 10⁻⁵ Å and 0.003 deg. for r_{d}(PH) and θ_{d}(PH), respectively. Use of the parent species only (which implies two rotational constants and two spin–spin constants as input data) does not change significantly the picture, as the derived structural parameters remain consistent within the uncertainties. Only a minor increase of the statistical error is produced, in spite of the much less parameters employed, i.e. 4 vs. 14 employed in the “mixed” structure.

4.3 Water (H₂O)

The data set for the “reference” structure of the water molecule comprises seven isotopic species: H₂¹⁷O, H₂¹⁸O and their singly and doubly deuterated variants plus H₂¹⁵O. Given the planarity of the molecule, only two out of three equilibrium rotational constants are actually independent and can be used simultaneously in a structural least-squares fit.⁸ In the present case, the B₀, C₀ pair has been adopted. Their SE equilibrium values have been obtained, as already described for NH₃ and PH₃, by subtracting the ZPV (ae-CCSD(T)/cc-pwCVQZ) contributions from the experimental B₀, C₀. The SE equilibrium parameter weights have been estimated assuming the fractional uncertainty of 33 × 10⁻⁴, which is obtained from eqn (9) when using average values of 5 GHz for the ZPV contribution and 150 MHz for the electronic effects.³³ The derived “reference” structural parameters are reported in the first row of Table 6.

A number of detailed studies devoted to the hyperfine structure of water rotational transitions are present in the literature. As a consequence, dipolar spin–spin coupling constants are available for six isotopologues. They are presented in Table 3 along with the corresponding literature references. The correction for the ZPV contribution through eqn (7) allowed us to obtain the set of SE equilibrium dipolar spin–spin tensor elements to be employed in the “mixed” structural calculation. For water, the “reference” and “mixed” equilibrium structures are identical, thus indicating that the structural information brought by the dipolar spin–spin coupling constants perfectly matches that established by the rotational parameters. The comparison with the most up to date SE equilibrium structure available in the literature¹¹ reveals small, but significant discrepancies, with r_{d}(OH) longer by 0.0007 Å and θ_{d}(HOH) smaller by 0.14 deg., both slightly exceeding the overlap range of the corresponding quoted uncertainties. This is likely due to the different treatment of the electronic contribution to the rotational constants, which may have a magnified effect on the estimate of geometrical parameters due to the planarity relationship.

Six single-isotopologue “mixed” structure calculations have been finally performed to evaluate the spread of the parameter values determined using the supporting contribution of the dipolar spin–spin coupling constants. Although determined with different precision, the six pairs of structural parameters make up a consistent (within 3σ) data set symmetrically spread around the “reference” geometry. This proves that the additional geometric information carried by the SE D tensor elements is capable of providing a reliable estimate of the distortion effects typically produced by the H–D isotopic substitution.

4.4 Fluorinated species (NF₃, OF₂, and PF₃)

Minimal data sets are available for the fluorinated analogues of the chosen model molecules. For NF₃, the experimental values of the B₀ and C₀ constants were determined, while only B₀ is available for ¹⁷NF₃.⁵³,⁵⁴ The experimental value of the dipolar spin–spin D_{FF} constant for the main isotopic species has been reported by Novick et al.¹⁵ The B₀ and C₀ constants of PF₃ have been determined in several infrared investigations; here, we use the value provided by Najjib (2014).⁵⁵ Instead, no experimental information on its hyperfine structure is presently available in the literature. To the best of our knowledge, only the rotational parameters determined using the supporting contribution of the dipolar spin–spin coupling constants are listed in Table 4 for the H–F isotopic substitution.

### Table 6 SE equilibrium structural parameters of H₂O derived using different isotopic data sets

| Data set | Iso³ (data) | r_{d}(OH)/Å | θ_{d}(HOH)/deg. | σ_{w,ROH}² | σ_{w,SS}² |
|----------|-------------|--------------|-----------------|-------------|-----------|
| Reference | 7(14)       | 0.95798(19)  | 104.39(5)       | 1.1         | —         |
| Mixed     | 7(24)       | 0.95798(17)  | 104.39(5)       | 1.1         | 0.7       |
| H₂O       | 1(3)        | 0.95813(3)   | 104.36(6)       | 0.0         | 0.5       |
| HDO       | 1(3)        | 0.95832(5)   | 104.238(17)     | 0.0         | 0.1       |
| D₂O       | 1(3)        | 0.95795(5)   | 104.422(12)     | 0.0         | 0.1       |
| H₂¹⁷O     | 1(5)        | 0.95812(1)   | 104.36(5)       | 0.0         | 0.4       |
| HD¹⁸O     | 1(5)        | 0.95786(6)   | 104.42(18)      | 0.1         | 1.0       |
| D₂¹⁵O     | 1(3)        | 0.95775(5)   | 104.48(11)      | 0.1         | 1.0       |
| Literature | 7(14)       | 0.9573(1)    | 104.53(1)       | 0.1         | —         |

Note: numbers in parentheses indicate 3σ uncertainties in units of the last quoted digit. ² Number of isotopologues and, in parentheses, number of data. ³ Weighted rms deviation of the rotational constants. ⁴ Weighted rms deviation of the dipolar spin–spin coupling constants. ⁵ Ref. 49.
spectrum of the parent species of OF\(_2\) has been investigated and its ground state rotational constants still come from a microwave study performed in the 60’s. An estimate of the F–F dipolar spin–spin coupling constants was obtained by molecular beam electric resonance measurements more than twenty years later.

The SE equilibrium values for the rotational and spin–spin coupling constants of these three species have been obtained using the ZPV contributions computed in this work (fc-MP2/jun-cc-pVTZ) and then employed to derive the “mixed” equilibrium structures. As performed for the model molecules in previous sections, the weights of the rotational constants have been set to \(1 \times 10^{-4}\) of the corresponding values, mostly on the basis of the ZPV contribution accuracy. The impact of the electronic contributions has been estimated from the \(g\) constants and was found to be essentially negligible. The derived structural parameters are reported in Table 7 together with the best available equilibrium geometries from the literature.

For NF\(_3\) and OF\(_2\), our “mixed” SE approach yields equilibrium geometrical parameters more precise than those available in the literature, with the set two sets of values agreeing within the quoted error ranges. The only exception is the O–F bond length in OF\(_2\) for which our determination provides a value 0.001 Å longer than the corresponding literature value. However, it should be noted that the values of \(r_{e}(XF)\) and \(\theta_{e}(XF)\) from ref. 50–52 were obtained using a minimal set of constants and, being purely experimental, they may also be affected by residual perturbations on the retrieved equilibrium rotational constants. This aspect is particularly critical for PF\(_3\), for which the two structural parameters were derived from only two rotational constants and the uncertainty range, estimated by error propagation, is clearly underestimated (Table 7). Unfortunately, the lack of any experimental information on the dipolar spin–spin coupling prevents us from computing a “mixed” equilibrium structure for PF\(_3\) and providing a reliable uncertainty range on its geometry parameters. In Table 7, the structural parameters optimized at the ae-CCSD(T)/cc-pwCVQZ level of theory are also reported. Their comparison with the literature and SE results points out a good agreement. In view

| Data set | Iso\(^a\) (data) | \(r_{e}(XF)/\text{Å}\) | \(\theta_{e}(XF)/\text{deg.}\) | \(\sigma_{w,\text{ROT}}/\text{Å}\) | \(\sigma_{w,\text{SS}}/\text{deg.}\) |
|----------|-----------------|----------------|----------------|----------------|----------------|
| NF\(_3\)  | 2(4)            | 1.36797(3)    | 101.878(3)    | 0.0            | 0.1            |
| Theory\(^c\) |                 | 1.366        | 101.86(10)    |                |                |
| Literature\(^d\) |             | 1.3675(10)   | 101.86(10)    |                |                |
| PF\(_3\)  | 1(2)            | 1.56111      | 97.561        |                |                |
| Literature\(^d\) |             | 1.560986(43) | 97.566637(64) |                |                |
| Theory\(^c\) |                 | 1.561        | 97.6          |                |                |
| OF\(_2\)  | 1(3)            | 1.40625(18)  | 103.08(2)     | 0.0            | 0.3            |
| Literature\(^b\) |             | 1.4053(4)    | 103.07(5)     |                |                |
| Theory\(^c\) |                 | 1.403        | 103.1         |                |                |

Note: Numbers in parentheses indicate 3\(^e\) uncertainties in units of the last quoted digit. \(^a\) Number of isotopologues and, in parentheses, number of data. \(^b\) Weighted rms deviation of the rotational constants. \(^c\) Weighted rms deviation of the dipolar spin–spin constants. \(^d\) Average values from ref. 50. \(^e\) At the ae-CCSD(T)/cc-pwCVQZ level of theory. \(^f\) No degrees of freedom, thus errors cannot estimated. \(^g\) Experimental value from ref. 51. Uncertainties obtained by error propagation. \(^h\) Experimental value from ref. 52.

Fig. 1  Spectral simulation of the \(J_{K}=1_0–0_0\) rotational transition of PF\(_3\) as can be observed using a pulsed-jet Ball–Flygare Fourier-transform microwave spectrometer. The x-axis scale is expressed as the offset with respect to the unperturbed frequency value of 15637.959 MHz. The y-axis scale indicates the absorption cross section computed at 2 K, the typical rotational temperature obtained in a supersonic-jet cooled sample. The hyperfine components are labelled as \(F’’ \rangle F’ \rangle F, \) (a) 1.5.3 \( \leftrightarrow \) 0.5.2; (b) 1.5.2 \( \leftrightarrow \) 0.5.1 and 1.5.2 \( \leftrightarrow \) 0.5.2; (c) 1.5.1 \( \leftrightarrow \) 0.5.1, 1.5.1 \( \leftrightarrow \) 0.5.2, and 1.5.0 \( \leftrightarrow \) 0.5.1; (d) 1.5.2 \( \leftrightarrow \) 0.5.1 and 1.5.2 \( \leftrightarrow \) 0.5.2; (e) 1.5.1 \( \leftrightarrow \) 0.5.1 and 1.5.1 \( \leftrightarrow \) 0.5.2. The \( h_{\text{tot}} \) for \( K = 0 \) is always 1.5 because of spin statistics.
of the accuracy of ae-CCSD(T)/cc-pwCVQZ geometries discussed above,\textsuperscript{24} the observed agreement supports the reliability of the SE/experimental structural determinations even when carried out with a very limited number of data.

To date, there are no studies devoted to the hyperfine structure of the rotational transitions of PF\textsubscript{3}, despite the fact that the $J = 1 \leftarrow 1$ line is located at 15.6 GHz, a frequency region easily achievable using a Ball–Flygare-type high-resolution Fourier-transform microwave (FT-MW) spectrometer (see e.g. ref. 58). Our theoretical calculations provide a full characterization of the hyperfine structure of this transition and provide a valuable guide for future laboratory measurements. Besides the P–F and F–F dipolar spin–spin coupling constants listed in Table 2, we have also computed the nuclear spin-rotation coupling tensor C for the P and F nuclei at the ae-CCSD(T)/cc-pwCVQZ level of theory. The values of the isotropic constant ($C_{\text{iso}} = \frac{1}{3} \text{Tr}(C)$) are $C_{\text{iso}}(C) = -12.77$ kHz and $C_{\text{iso}}(F) = -9.23$ kHz. The hyperfine pattern of the $J = 1 \leftarrow 1$ rotational transition of PF\textsubscript{3} has then been evaluated using the SPACAT program\textsuperscript{59} and is plotted in Fig. 1 assuming a typical pulsed-jet FT-MW line full width at half maximum of 3 kHz. Under these experimental conditions, the hyperfine structure of the $J = 1 \leftarrow 0$ transition is predicted to be well resolved. This indicates that its spectral analysis would lead to an accurate determination of dipolar spin–spin coupling constants, thus opening the route towards a complete structural determination of PF\textsubscript{3}.

5 Conclusions

In this perspective, we have investigated the use of dipolar spin–spin coupling constants in the structure determination of isolated molecules. The SE approach is powerful and allows the determination of equilibrium geometries with minimum experimental efforts. However, it is effective only if the number of available isotopic substitutions is greater than the number of internal coordinates describing the molecular system. Furthermore, an unbalanced set of data due to impossible isotopic substitution (as in the case of F and P) can lead to biased results. In those cases for which obtaining a sufficiently large set of data is unpractical due to the lack of isotopic data or totally unfeasible (as for PF\textsubscript{3}), dipolar spin–spin coupling constants can be considered as an additional source of information for the SE least-squares fitting procedure. Spin–spin coupling in rotational spectra only produces small effects, usually detected as perturbations of more important interactions, such as nuclear quadrupole coupling and/or nuclear spin-rotation interactions. In the past, the determination of dipolar spin–spin constants was a prerogative of molecular beam maser techniques, which are characterized by an extremely high resolving power. Nowadays, adequate resolution to reveal spin–spin coupling effects is achievable routinely using a Fourier-transform spectrometer coupled with supersonic expansions of the gas sample. Although experimentally determined with moderate precision (typically 1–10%), the dipolar spin–spin coupling constants can effectively support the determination of the molecule structural parameters within the SE approach. Their incorporation in an isotopically balanced fit does not generally alter the value of the structural parameters, but can lead to a significant reduction of their statistical error, as they provide independent and statistically uncorrelated information for the least-squares fit procedure. In critical cases, when there is a shortage of isotopic rotational data, their inclusion in the computation provides additional degrees of freedom (thus leading to a significant improvement of the fit and geometrical parameters).

Conflicts of interest

There are no conflicts to declare.

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