



Cite this: *Phys. Chem. Chem. Phys.*,  
2020, 22, 8485

# Direct magnetic-field dependence of NMR chemical shift†

Anu M. Kantola,<sup>a</sup> Perttu Lantto,<sup>a</sup> Ivo Heinmaa,<sup>b</sup> Juha Vaara<sup>a</sup> and  
Jukka Jokisaari<sup>a</sup>

Nuclear shielding and chemical shift are considered independent of the magnetic-field strength. Ramsey proposed on theoretical grounds in 1970 that this may not be valid for heavy nuclei. Here we present experimental evidence for the direct field dependence of shielding, using  $^{59}\text{Co}$  shielding in  $\text{Co}(\text{acac})_3$  [tris(acetylacetonate)cobalt(III)] as an example. We carry out NMR experiments in four field strengths for this low-spin diamagnetic  $\text{Co}(\text{III})$  complex, which features a very large and negative nuclear shielding constant of the central Co nucleus. This is due to a magnetically accessible, low-energy  $e_g \leftarrow t_{2g}$  orbital excitation of the  $d^6$  system. The experiments result in temperature-dependent magnetic-field dependence of  $-5.7$  to  $-5.2$  ppb  $\text{T}^{-2}$  of the  $^{59}\text{Co}$  shielding constant, arising from the direct modification of the electron cloud of the complex by the field. First-principles multiconfigurational non-linear response theory calculations verify the sign and order of magnitude of the experimental results.

Received 11th March 2020,  
Accepted 6th April 2020

DOI: 10.1039/d0cp01372b

rsc.li/pccp

## Introduction

Nuclear magnetic resonance (NMR) parameters,<sup>1</sup> nuclear shielding, its associated chemical shift, spin–spin coupling and quadrupole coupling, are normally considered independent of the applied magnetic field. Due to the increasing field strengths used in contemporary NMR instrumentation, currently reaching 1.2 GHz proton resonance frequency, the validity of this approximation should be investigated. In 1970, Ramsey<sup>2</sup> published a theoretical study predicting a quadratic,  $O(B_0^2)$ , leading-order dependence on the field strength,  $B_0$ . Ramsey concluded that “in some molecules, especially where the magnetic shielding is abnormally large, it is possible that the field dependence of the shielding could be large enough to be observable”. Inspired by this prediction, Bendall and Doddrell<sup>3</sup> carried out  $^{59}\text{Co}$  NMR experiments of diamagnetic cobalt compounds. The authors claimed a field dependence of  $^{59}\text{Co}$  shielding constant in  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  and  $\text{Co}(\text{acac})_3$ , with values  $-70(30)$  and  $-80(50)$  ppb  $\text{T}^{-2}$ , respectively. Such  $\text{Co}(\text{III})$  complexes feature a broad chemical shift range and show a sensitivity of the NMR signal on temperature, pressure and solvent,<sup>4</sup> which can be ascribed to the existence of low-lying, magnetically accessible d–d excitations<sup>5</sup> at the metal centre and, correspondingly, a large tendency of the electron cloud to accommodate to changing interactions with surroundings.

About 25 years later, Manninen and Vaara<sup>6</sup> presented a theory and computed from first principles the field-dependence of  $^{59}\text{Co}$  shielding in the same compounds, with results that are by an order of magnitude smaller than the experimentally derived values in ref. 3. This effect can be termed direct field dependence, arising from the modification of the molecular electron cloud by the magnetic field. In contrast, the indirect effect results from a slight influence on the orientational distribution of molecules in liquid samples due to the interaction of magnetic field with the anisotropy of the molecular susceptibility, causing incomplete rotational averaging of NMR parameters.<sup>7</sup>

Further computational work on the direct field dependence of nuclear shielding has been reported at both semi-empirical<sup>8,9</sup> and first-principles<sup>10–12</sup> levels. The field dependence of spin–spin coupling has been elaborated in ref. 13 and 14. So far, the only both experimentally observed and theoretically confirmed case of direct field dependence of an NMR parameter is that of  $^{131}\text{Xe}$  quadrupole coupling in atomic xenon.<sup>15–18</sup> The  $^{131}\text{Xe}$  NMR spectrum consists of a 3 : 4 : 3 triplet when the nuclear electric quadrupole moment interacts with a non-vanishing electric field gradient (EFG) at the nuclear site. In this case, the non-zero EFG stems from the slight deformation of the atomic electron cloud induced by the magnetic field.<sup>16</sup>

In the present work, we report experiments carried out at four magnetic fields, as well as improved first-principles non-linear response theory computations on the direct field effect on the  $^{59}\text{Co}$  shielding in  $\text{Co}(\text{acac})_3$ . We eliminate the difficulty of precise temperature control of the experiments in different NMR instruments by using the gaseous and solution-state  $^{129}\text{Xe}$  NMR signal as a chemical shift and temperature reference,

<sup>a</sup> NMR Research Unit, University of Oulu, P.O. Box 3000, FI-90014, Finland.

E-mail: Jukka.Jokisaari@oulu.fi

<sup>b</sup> National Institute of Chemical Physics and Biophysics, Akadeemia tee 23,  
EE-12618 Tallinn, Estonia

† Electronic supplementary information (ESI) available: Details of experiments and computations. See DOI: 10.1039/d0cp01372b



respectively.<sup>19</sup> Our experiments demonstrate the existence of the direct field dependence of shielding and, hence, verify the prediction by Ramsey.

## Results and discussion

Due to the requirement of time-reversal symmetry, terms in the molecular energy expression have to contain the nuclear spin  $I_K$  and external magnetic field  $B_0$  appearing to even total power.<sup>2,6</sup> The nuclear Zeeman term in the standard NMR spin Hamiltonian<sup>1</sup> is  $O(I_K^2 B_0^2)$  (total power 2) and the next term in increasing powers of the magnetic field is  $O(I_K^4 B_0^4)$  (total power 4). Consequently, to the leading order, the  $B_0$ -dependent NMR shielding tensor component  $\sigma_{K,\alpha\beta}$  for nucleus  $K$  can be expressed as<sup>2,6</sup>

$$\sigma_{K,\alpha\beta} = \sigma_{K,\alpha\beta}^{(0)} + \sum_{\gamma\delta} \tau_{K,\alpha\beta\gamma\delta} B_{0,\gamma} B_{0,\delta}, \quad (1)$$

where  $\sigma_K^{(0)}$  is the standard field-independent shielding and the 4-index tensor  $\tau$  parameterises the leading-order field dependence. In a liquid or gas-phase sample, isotropic molecular tumbling renders observable the average<sup>8</sup>

$$\begin{aligned} \tau = \frac{1}{15} & (3\tau_{xxxx} + 3\tau_{yyyy} + 3\tau_{zzzz} + \tau_{zzxx} + \tau_{zzyy} + \tau_{xxzz} + \tau_{yyzz} + \tau_{xxyy} \\ & + \tau_{yyxx} + \tau_{zxzx} + \tau_{zyyz} + \tau_{zxzx} + \tau_{zyyz} + \tau_{xzzx} + \tau_{yzyy} + \tau_{xzxz} \\ & + \tau_{yzyz} + \tau_{yxxy} + \tau_{xyyx} + \tau_{yxxy} + \tau_{xyxy}), \end{aligned} \quad (2)$$

which is a combination of the tensor components of  $\tau$  expressed in a molecule-fixed Cartesian frame.

A sample consisting of saturated solution of tris(acetylacetonate)cobalt(III) [Co(acac)<sub>3</sub>] in CDCl<sub>3</sub> and natural xenon gas of about 2 atm was prepared into a 5 mm (o.d.) NMR tube. Resonance frequency of natural abundance gaseous <sup>129</sup>Xe (2 atm in a 5 mm tube) was used as an external chemical shift reference for both <sup>59</sup>Co and <sup>129</sup>Xe resonance frequencies in the solution. Experiments were carried out at four magnetic fields, 18.8, 14.1, 9.4 and 7.0 T, and five temperatures at each field strength, on Bruker Avance III instruments. Following Ramsey, <sup>59</sup>Co resonance frequency can be presented in the form

$$\nu_{\text{Co}}^s = \frac{\gamma_{\text{Co}} B_0}{2\pi} (1 - \sigma_{\text{Co}}^s - \tau_{\text{Co}} B_0^2), \quad (3)$$

where  $\gamma_{\text{Co}}$  is the gyromagnetic ratio of <sup>59</sup>Co,  $\sigma_{\text{Co}}^s$  is the field-independent part of the isotropic shielding constant in solution and  $\tau_{\text{Co}}$  follows from eqn (2).

There is a strong temperature dependence of <sup>59</sup>Co chemical shift in Co(acac)<sub>3</sub>, e.g., reported in ref. 20 at +2.79 ppm K<sup>-1</sup> in CHCl<sub>3</sub> solution. Therefore, one must guarantee that the <sup>59</sup>Co frequencies in different magnetic-field instruments are obtained at the same temperature. To this end, we used the <sup>129</sup>Xe chemical shift in solution,  $\delta_{\text{Xe}}^s$ , as an internal temperature reference (see ESI†), and ensured that  $\delta_{\text{Co}}^s$  at each magnetic field corresponds to the same  $\delta_{\text{Xe}}^s$  value. This procedure is based on the extreme sensitivity of  $\delta_{\text{Xe}}^s$  upon temperature<sup>19</sup>

and is done to gain a precise value for  $\tau_{\text{Co}}$ . The resonance frequencies of xenon in gas (g) and in solution (s) can be approximately written as

$$\nu_{\text{Xe}}^{g/s} = \frac{\gamma_{\text{Xe}} B_0}{2\pi} (1 - \sigma_{\text{Xe}}^{g/s}) = \nu_{\text{Xe}}^0 (1 - \sigma_{\text{Xe}}^{g/s}). \quad (4)$$

Consequently, the <sup>129</sup>Xe chemical shift in solution, referenced to <sup>129</sup>Xe gas, is

$$\delta_{\text{Xe}}^s = \frac{\nu_{\text{Xe}}^s - \nu_{\text{Xe}}^g}{\nu_{\text{Xe}}^g}. \quad (5)$$

Eqn (4) and (5) neglect any field dependence of shielding in atomic <sup>129</sup>Xe, which has been shown by correlated *ab initio* response theory calculations to be of the order of 10<sup>-6</sup> ppb T<sup>-2</sup>, i.e., hardly observable.<sup>11</sup> The minute field dependence can be understood to be due to the large difference between the occupied and vacant energy levels of the noble gas atom, a situation vastly different from that of Co(acac)<sub>3</sub> with low-energy magnetically accessible excitations. The <sup>129</sup>Xe gas frequency has a negligible temperature dependence compared to that of both <sup>59</sup>Co and <sup>129</sup>Xe in solution.<sup>20–23</sup>

The <sup>59</sup>Co resonance frequency relative to the chosen shift reference, xenon gas, is

$$\begin{aligned} \nu_{\text{Co}}^s - \nu_{\text{Xe}}^g &= \frac{\gamma_{\text{Co}} B_0}{2\pi} (1 - \sigma_{\text{Co}}^s - \tau_{\text{Co}} B_0^2) - \frac{\gamma_{\text{Xe}} B_0}{2\pi} (1 - \sigma_{\text{Xe}}^g) \\ &= \nu_{\text{Co}}^0 (1 - \sigma_{\text{Co}}^s) - \nu_{\text{Xe}}^0 (1 - \sigma_{\text{Xe}}^g) - \nu_{\text{Co}}^0 \tau_{\text{Co}} B_0^2, \end{aligned} \quad (6)$$

leading to the chemical shift

$$\delta_{\text{Co}}^s = \frac{\nu_{\text{Co}}^s - \nu_{\text{Xe}}^g}{\nu_{\text{Co}}^0} = \left[ 1 - \sigma_{\text{Co}}^s - \frac{\gamma_{\text{Xe}}}{\gamma_{\text{Co}}} (1 - \sigma_{\text{Xe}}^g) \right] - \tau_{\text{Co}} B_0^2 \quad (7)$$

with the field-dependence coefficient appearing in the second term. The function in eqn (7) was least-squares fitted to the experimental data at different magnetic fields using two adjustable parameters:  $c = 1 - \sigma_{\text{Co}}^s - \frac{\gamma_{\text{Xe}}}{\gamma_{\text{Co}}} (1 - \sigma_{\text{Xe}}^g)$  and  $\tau_{\text{Co}}$ . The results, obtained at the <sup>129</sup>Xe chemical shift values of 200, 202, 205, 206 and 208 ppm, are listed in Table 1 and illustrated in Fig. 1. Fig. 1(b) shows linear dependence of  $c$  on temperature. The slope of the line is  $2.793 \pm 0.007$  ppm K<sup>-1</sup>, corresponding to the temperature coefficient of the <sup>59</sup>Co chemical shift in chloroform/xenon solution, in excellent agreement with the value of  $2.79 \pm 0.02$  ppm K<sup>-1</sup> reported in ref. 20 for a sample without xenon gas.

At this point we may assess the significance of the temperature dependence of  $\sigma_{\text{Xe}}^s$ , which we neglected in the above analysis. As this effect does not depend on the external magnetic field, it could be absorbed in the field-independent fitting parameter  $c$  in eqn (7). Using the ideal gas law to approximate the number density of a 2 atm Xe gas at room temperature and the temperature-dependent second virial coefficient,  $\sigma_{\text{Xe},1}$ , of <sup>129</sup>Xe shielding constant reported in ref. 22, one can arrive at a (linearized) contribution to the temperature dependence of  $c$  amounting to just  $-0.0019$  ppm K<sup>-1</sup>. This change would be inside the error margins of the present fit results for  $c$  and those of the previous experiment of ref. 20.



**Table 1** Fits of the  $^{59}\text{Co}$  chemical shift in  $\text{Co}(\text{acac})_3$  in solution with respect to  $^{129}\text{Xe}$  in gas

$\delta_{\text{Xe}}^{\text{a}}$ (ppm)	$T^{\text{a}}$ (K)	$c^{\text{b}}$ (ppm)	$\tau_{\text{Co}}$ (ppb $\text{T}^{-2}$ )
200	319.9	$-153932.2 \pm 0.2$	$-5.2 \pm 1.0$
202	314.7	$-153946.7 \pm 0.2$	$-5.4 \pm 0.9$
205	307.0	$-153968.4 \pm 0.2$	$-5.5 \pm 1.1$
206	304.4	$-153979.7 \pm 0.2$	$-5.6 \pm 0.8$
208	299.2	$-153990.1 \pm 0.2$	$-5.7 \pm 0.8$

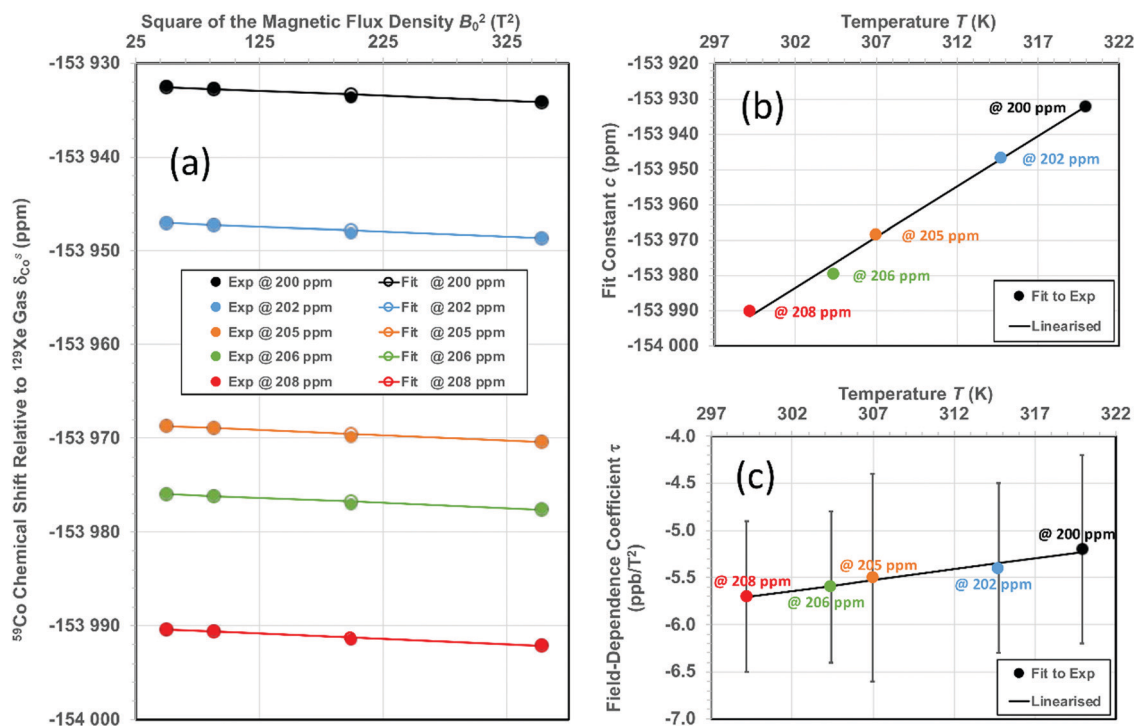
<sup>a</sup>  $^{129}\text{Xe}$  chemical shift of xenon in the solution,  $\delta_{\text{Xe}}^{\text{s}}$ , is used to approximately detect the temperature  $T$ . The given temperatures were determined from the equation given in ref. 19. In this case, the sample contained only  $\text{D}_2$ -chloroform and xenon gas. Therefore, the tabulated temperatures may not be correct. One should note that the knowledge of exact temperatures is not essential in this case, but that of the  $^{129}\text{Xe}$  chemical shift is. <sup>b</sup> Parameters  $c$  and  $\tau_{\text{Co}}$  appearing in eqn (7) are listed for a fit of a series of measurements at different magnetic fields. Each series is performed at a constant value of  $\delta_{\text{Xe}}^{\text{s}}$ .

Another physical influence that should be considered is the correction due to the difference of the bulk magnetic susceptibilities of the chloroform solution,  $\chi_{\text{s}}$ , and that of the external xenon gas reference,  $\chi_{\text{r}}$ . At the limit of an infinitely long cylindrical sample oriented along  $B_0$ , the associated chemical shift contribution (in SI units) to eqn (7) equals approximately

$$\delta_{\text{b}} = \frac{1}{3} \left( \chi_{\text{s}} - \frac{\gamma_{\text{Xe}}}{\gamma_{\text{Co}}} \chi_{\text{r}} \right). \quad (8)$$

Using the molar susceptibilities  $\chi_{\text{m}}$  listed in ref. 24,  $-58.9 \times 10^{-6} \times 4\pi$  and  $-45.5 \times 10^{-6} \times 4\pi \text{ cm}^3 \text{ mol}^{-1}$  for chloroform and xenon, respectively, we obtain  $\chi_{\text{s}} = -9.19$  and  $\chi_{\text{r}} = -0.02509$  ppm, corresponding to  $\delta_{\text{b}} = -3.07$  ppm from eqn (8). This is an additional, magnetic field-independent contribution to the parameter  $c$ . We are not aware of data on the temperature dependence of the susceptibility of either chloroform or xenon, which hinders us from accurately evaluating the contribution of the  $\delta_{\text{b}}$  term to the temperature dependence of  $c$ . Presumably the susceptibility of liquid  $\text{CHCl}_3$ , which is bigger than that of gaseous Xe by three orders of magnitude, dominates also the temperature dependence of  $\delta_{\text{b}}$ . Ref. 25 reported a close-to-linear temperature dependence of the relative mass susceptibility of water at temperatures in the liquid range as  $\chi(T)/\chi(20\text{C}) \approx 1 + 1.39 \times 10^{-4} (T - 20\text{C})$ . Using  $\chi_{\text{m}}(\text{H}_2\text{O}) = -12.96 \times 10^{-6} \times 4\pi \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>24</sup> hence  $\chi(\text{H}_2\text{O}) = -9.01$  ppm, corresponds to  $\frac{1}{3} \frac{d\chi(\text{H}_2\text{O})}{dT} = -0.000417 \text{ ppm K}^{-1}$ . Presumably the same property for chloroform does not deviate very much from this result for liquid water. Therefore, also the bulk susceptibility effect falls well within the error margins obtained in the present fit of the  $c$  parameter.

Fig. 1 shows the principal result of the paper: the field-dependence coefficient  $\tau$  resulting from the slope of  $^{59}\text{Co}$  shift with respect to  $B_0^2$  [Fig. 1(a)]. The magnitude of the field



**Fig. 1** (a)  $^{59}\text{Co}$  chemical shift relative to  $^{129}\text{Xe}$  gas,  $\delta_{\text{Co}}^{\text{s}}$ , when  $\delta_{\text{Xe}}^{\text{s}}$  is (from top to bottom) 200, 202, 205, 206 and 208 ppm, corresponding to approximate temperatures 319.9, 314.7, 307.0, 304.4 and 299.2 K as given in Table 1. Fit parameters for (b) the field-independent part of the shift,  $c = \left[ 1 - \sigma_{\text{Co}}^{\text{s}} - \frac{\gamma_{\text{Xe}}}{\gamma_{\text{Co}}} (1 - \sigma_{\text{Xe}}^{\text{s}}) \right]$  and (c) the leading field-dependence coefficient  $\tau_{\text{Co}}$  [see eqn (7)] as functions of temperature. Colour coding is used to indicate corresponding data points in panel (a) and panels (b) and (c). The error margins resulting from the statistical uncertainty of the fit are in panel (b) smaller (circa  $\pm 0.2$  ppm) than the used symbols and in (c) circa  $\pm 1$  ppb  $\text{T}^{-2}$ .



dependence is around  $-5.5 \pm 0.9$  ppb T $^{-2}$ , which is significant in view of the NMR instruments with 1.2 GHz proton frequency (28.2 T field strength) in production use soon. This result deviates clearly from the experimental data reported by Bendall and Doddrell,<sup>3</sup> where a distinctly larger magnitude of the field dependence, at  $\tau = -80 \pm 50$  ppb T $^{-2}$ , was found. The underlying reasons of the difference include the limitation of the 40-year-old experiment to the modest maximum field of 2.1 T in contrast to the 18.8 T field strength used in the present work. In a similar vein, the precise temperature control enabled by using  $^{129}\text{Xe}$  signal in solution is instrumental to the present success. Despite the sizable statistical error margins,  $\tau$  from the present measurements shows evidence of temperature dependence: its magnitude decreases with temperature with a least-squares fitted slope of  $2.29 \times 10^{-2}$  ppb T $^{-2}$  K $^{-1}$ .

Theoretical electronic-structure formulation of the field-dependence tensor  $\tau_K$  was presented in the form of four distinct linear and nonlinear response functions<sup>26</sup> in ref. 6:

$$\tau_{K,\alpha\beta\gamma\delta} = \tau_{K,\alpha\beta\gamma\delta}^{\text{dia}} + \tau_{K,\alpha\beta\gamma\delta}^{\text{dia-para}} + \tau_{K,\alpha\beta\gamma\delta}^{\text{para-dia}} + \tau_{K,\alpha\beta\gamma\delta}^{\text{para}} \quad (9)$$

where the last, fourth-order perturbation theory term<sup>6</sup>

$$\tau_{K,\alpha\beta\gamma\delta}^{\text{para}} = \frac{1}{3!} \frac{1}{\hbar \gamma_K} \frac{P_{\beta\gamma\delta}}{3!} \left\langle \left\langle h_{K,\alpha}^{\text{PSO}}, h_{B_0,\beta}^{\text{OZ}}, h_{B_0,\gamma}^{\text{OZ}}, h_{B_0,\delta}^{\text{OZ}} \right\rangle \right\rangle_{0,0,0} \quad (10)$$

was found in ref. 6 to overwhelmingly dominate for  $^{59}\text{Co}$  nucleus (see ESI† for the other terms). Indeed, the other contributions remained three or more orders of magnitude smaller than  $\tau^{\text{para}}$ . In eqn (10),  $\langle\langle A;B,C,D \rangle\rangle_{0,0,0}$  is a cubic response function<sup>26</sup> involving  $h_{K,\alpha}^{\text{PSO}}$ , the Cartesian  $\alpha$ -component of the orbital hyperfine interaction and  $h_{B_0,\beta}^{\text{OZ}}$  etc. the corresponding components of the Zeeman interaction of the orbital motion of the electrons with the external field,<sup>27</sup> as static perturbations. The symbol  $P_{\beta\gamma\delta}$  denotes a sum over all six permutations of its three indices.

Computations of eqn (9) were carried out for  $\text{Co}(\text{acac})_3$  in 2004 using Hartree–Fock (HF) and density-functional theory (DFT) levels.<sup>6</sup> The result of HF calculation,  $\tau_{\text{Co}}^{\text{para}} \sim O(1)$  ppb T $^{-2}$  agrees with the experiment carried out presently. In view of the importance of electron correlation effects on high-order valence-like response properties such as  $\tau$  a question remains whether this agreement is coincidental. Since then, cubic response functions at electron-correlated *ab initio* levels have become feasible for systems of the present size in the DALTON software.<sup>28</sup> We employ the multiconfigurational self-consistent field (MCSCF) level of theory<sup>29</sup> to address this question here, on models of  $\text{Co}(\text{acac})_3$  described in the ESI.†

All the tensorial components of the four terms in eqn (9) were computed using HF and MCSCF response theory. In the latter, restricted active-space (RASSCF)-type wave functions<sup>30</sup> correlating 18, 32 or 38 electrons [denoted RASSCF (18/32/38 el.)] were used for a truncated molecular model. The ESI† is referred to for details of the used MCSCF wave functions (Table S7, ESI†) and basis sets. For calculating the magnetic properties of a low-gap  $\text{Co}(\text{acac})_3$  complex, multireference-type wave functions are preferred over single configuration-based methods such as

**Table 2** Computational results for the field-dependence coefficient  $\tau$  for  $^{59}\text{Co}$  nuclear shielding constant. The leading  $\tau^{\text{para}}$  term and the total value are listed separately for methods which the latter is available. Results obtained for the truncated model and the small, locally dense basis set as described in the ESI

Computational method	$\tau^{\text{para}}$ (ppb T $^{-2}$ )	$\tau^{\text{total}}$ (ppb T $^{-2}$ )
HF	−1.445	−1.441
RASSCF (18 el.)	−0.943	— <sup>a</sup>
RASSCF (32 el.)	−0.843	−0.839
RASSCF' (32 el.)	−0.992	— <sup>a</sup>
RASSCF (38 el.)	−0.742	— <sup>a</sup>
BHandHLYP	−0.086	−0.084
Expt. <sup>b</sup>		(−5.7 to −5.2) ± 1.0

<sup>a</sup> Not calculated. <sup>b</sup> This work.

DFT, second-order many-body perturbation theory, or coupled-cluster theory at low excitation level.<sup>31</sup> Even the present truncated model of  $\text{Co}(\text{acac})_3$  is currently prohibitively large for beyond-singles and doubles (CCSD) coupled-cluster theory-based nonlinear response theory calculations.<sup>32</sup>

Table 2 lists the computational results for the dominating  $\tau^{\text{para}}$  contribution to the field-dependence coefficient, as well as the total  $\tau$  (the latter using three of the methods: HF, RASSCF (32 el.) and DFT/BHandHLYP<sup>33,34</sup>). While the results depend on the method used, both HF and the different RASSCF wave functions lead to  $\tau$  in an order-of-magnitude agreement with the experimental datum, with the largest result,  $-1.4$  ppb T $^{-2}$  obtained at the HF level. Increasing the number of correlated electrons tends to lower the final result as evidenced by the 10% decrease between RASSCF (18 el.) and RASSCF (32 el.), and further to RASSCF (38 el.), whereas increasing the virtual orbital space, *e.g.*, from the RASSCF (32 el.) to the RASSCF' (32 el.) wave function has the opposite effect. In contrast, the DFT result is at a much smaller value. The small difference between the  $\tau^{\text{para}}$  and  $\tau^{\text{total}}$  results reassures us of the earlier finding that the 4th-order term dominates in the field dependence in  $\text{Co}(\text{acac})_3$ . The small contributions of the other terms are listed in Table S9 of the ESI.†

The present calculations of  $\tau$  at optimised, static molecular geometries lead to negative field-dependence coefficient of  $^{59}\text{Co}$  nuclear shielding constant in agreement with the experimental findings, and at the *ab initio* level similar order of magnitude of the coefficient as in the experimental data. At the same time, the new calculations result also in smaller  $\tau^{\text{para}}$  than what was found earlier<sup>6</sup> at the HF level. The well-known sensitivity of  $^{59}\text{Co}$  chemical shift on temperature in this complex suggests that both thermal rovibrational and solvation effects, which are neglected in the present computations, may significantly influence  $\tau$ . To investigate this possibility, we repeated the HF calculations of  $\tau^{\text{para}}$  in modified models obtained by varying the Co–O bond distance from the value 1.885 Å of the optimised truncated model (for reference, 1.880 Å was obtained for the optimised full model). The results (Fig. 2 and Table S10 in the ESI†) indicate, expectedly, a strong dependence of  $\tau$  on the Co–O bond lengths of the coordination shell of the Co ion. Indeed, coincidence with the range of present experimental data for  $\tau$  is reached at the HF level by relatively modest modification of  $r(\text{Co–O})$ .





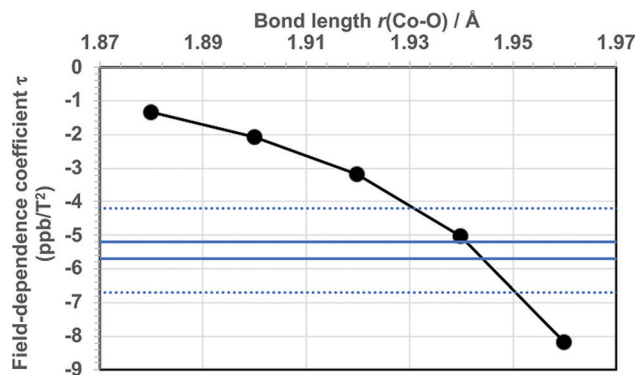


Fig. 2 Calculated field-dependence coefficient  $\tau$  as a function of the Co–O bond length in  $\text{Co}(\text{acac})_3$ . The bonds are symmetrically extended, maintaining the  $D_3$  point-group symmetry. The range of present experimental data is indicated by horizontal lines (error margins as dotted lines). The bond length in the results of Table 2 is 1.885 Å.

In addition to the direct magnetic field effect, molecular properties may also depend upon the indirect magnetic-field effect.<sup>7</sup> It arises from partial alignment of molecules because of the interaction of the anisotropy of the molecular susceptibility with the magnetic field. In partially aligned molecules, the NMR properties become dependent on the orientational order parameter.<sup>35</sup> In the case of  $\text{Co}(\text{acac})_3$ , the  $^{59}\text{Co}$  chemical shift, when excluding the direct field effect, can be presented in the form<sup>36,37</sup>

$$\delta_{\text{Co}}^{\text{exp}} = \delta_{\text{Co}}^{\text{iso}} - \frac{2}{3} \Delta\sigma_{\text{Co}} S_{\parallel}(T). \quad (11)$$

Here  $\delta_{\text{Co}}^{\text{iso}}$  is the isotropic average of the standard, field-independent chemical shift,  $\Delta\sigma_{\text{Co}}$  is anisotropy (relative to the molecular symmetry axis) of the shielding tensor and  $S_{\parallel}(T)$  is the orientational order parameter of the symmetry axis.  $S_{\parallel}(T)$  can be shown to be<sup>7</sup>

$$S_{\parallel}(T) = \frac{\Delta\chi}{15kT} B_0^2, \quad (12)$$

when higher than second-order terms in  $B_0$  are omitted. Here,  $\Delta\chi$  is the anisotropy of the molecular susceptibility tensor,  $k$  is the Boltzmann constant and  $T$  temperature. Substitution of the right-hand side of eqn (12) for  $S_{\parallel}(T)$  to (11) results in

$$\delta_{\text{Co}}^{\text{exp}} = \delta_{\text{Co}}^{\text{iso}} - \frac{2}{3} \Delta\sigma_{\text{Co}} \frac{\Delta\chi}{15kT} B_0^2. \quad (13)$$

Consequently, the indirect (anisotropic) effect, the latter term in eqn (13), on the  $^{59}\text{Co}$  chemical shift is proportional to the square of the magnetic flux density similarly to the direct field-dependence effect. This means that the indirect contribution may confuse the determination of the direct contribution, except if it is negligible. We computed the anisotropies of the shielding and susceptibility tensors at the DFT/BHandHLYP level, on the DALTON program. The computations resulted in  $\Delta\sigma_{\text{Co}} \approx -619$  ppm and  $\Delta\chi \approx -188 \times 10^{-30} \text{ J T}^{-2}$ . With these values, the indirect contribution to the  $^{59}\text{Co}$  chemical shift is about three orders of magnitude smaller than the direct

contribution within the present temperature and magnetic field ranges, and therefore is insignificant in the present analysis.

## Conclusions

We have both experimentally and computationally verified the 50-year-old prediction of Ramsey of direct magnetic-field dependence of nuclear magnetic shielding and the associated NMR chemical shift. The present experiments on  $^{59}\text{Co}$  NMR in  $\text{Co}(\text{acac})_3$  resulted in significant field-dependence coefficient by using a range of high-field instruments and both external and internal  $^{129}\text{Xe}$  reference in solution-state experiments. The external xenon gas, with its well-known and modest temperature and pressure dependence of the NMR frequency acted as the shift reference for  $^{59}\text{Co}$ . On the other hand, the xenon resonance in the liquid state is extremely sensitive to the experimental conditions, which was used to adjust the temperature to constant value in NMR instruments of different field strengths. This way, the effects due to the temperature dependence of the  $^{59}\text{Co}$  signal could be effectively eliminated. Similarly, the bulk magnetic susceptibility and field-induced molecular orientation (the indirect field dependence) were shown to be insignificant in the present results.

*Ab initio* nonlinear response theory computations confirmed the order of magnitude of the field dependence and indicated its strong dependence on the coordination distance of the  $\text{Co}(\text{III})$  ion, as expected based on the well-known temperature dependence of the  $^{59}\text{Co}$  chemical shift. The magnitude of the observed field dependence in  $\text{Co}(\text{acac})_3$ , *circa*  $-5.5 \text{ ppb T}^{-2}$ , corresponds to an experimentally significant frequency shift in, *e.g.*, the 28.2 T field of a 1.2 GHz  $^1\text{H}$  frequency instrument, and the phenomenon is expected to gain importance in pursuit of even higher fields and resolution in contemporary NMR. The verification of the fundamental field dependence of shielding and chemical shift adds a new parameter to the panoply of NMR observables, for which one can envision applicability in future high-field experiments designed to specifically make use of the explicit field dependence. Questions for future work remain also in finding the specific molecular characteristics that predict a significant field dependence.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

Financial support has been obtained from the University of Oulu (Kvantum Institute), and the Academy of Finland (projects 285666 and 296292). Computational resources due to CSC (Espoo, Finland) and the Finnish Grid and Cloud Infrastructure project (persistent identifier urn:nbn:fi:research-infras-2016072533), were used. IH was supported by European Regional Development Fund (TK134).



## References

- 1 M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance*, Wiley, 2nd edn, 2008.
- 2 N. F. Ramsey, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1970, **1**, 1320.
- 3 M. R. Bendall and D. M. Doddrell, *J. Magn. Reson.*, 1979, **33**, 659.
- 4 N. Juranic, *Coord. Chem. Rev.*, 1989, **96**, 253.
- 5 K. Kanda, H. Nakatsuji and T. Yonezawa, *J. Am. Chem. Soc.*, 1984, **106**, 5888.
- 6 P. Manninen and J. Vaara, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2004, **69**, 022503.
- 7 J. Jokisaari, A. M. Kantola and J. Vaara, *J. Magn. Reson.*, 2017, **281**, 1 and references therein.
- 8 D. M. Doddrell, D. T. Pegg and M. R. Bendall, *Aust. J. Chem.*, 1979, **32**, 1.
- 9 K. Endo and K. Yamamoto, *J. Phys. Soc. Jpn.*, 1995, **64**, 4053.
- 10 A. Boucekkine, G. Boucekkine-Yaker, M. Nait Achour and G. Berthier, *THEOCHEM*, 1988, **166**, 109.
- 11 J. Vaara, P. Manninen and J. Lounila, *Chem. Phys. Lett.*, 2003, **372**, 750.
- 12 J. Boyd, G. I. Pagola, M. C. Caputo, M. B. Ferraro and P. Lazzeretti, *J. Chem. Theory Comput.*, 2009, **5**, 1343.
- 13 W. T. Raynes and S. J. Stevens, *Magn. Reson. Chem.*, 1992, **30**, 124.
- 14 P. Manninen, PhD thesis, University of Oulu, Finland, 2004.
- 15 T. Meersmann and M. Haake, *Phys. Rev. Lett.*, 1998, **81**, 1211.
- 16 J. Vaara and P. Pykkö, *Phys. Rev. Lett.*, 2001, **86**, 3268.
- 17 P. Manninen, J. Vaara and P. Pykkö, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2004, **70**, 043401.
- 18 N. Abuzaid, A. M. Kantola and J. Vaara, *Mol. Phys.*, 2013, **111**, 1390.
- 19 J. Saunavaara and J. Jokisaari, *J. Magn. Reson.*, 2006, **180**, 58.
- 20 M. Kanakubo, T. Uda, H. Ikeuchi and G. P. Satô, *J. Solutions Chem.*, 1998, **27**, 645.
- 21 C. J. Jameson, A. K. Jameson and S. M. Cohen, *J. Chem. Phys.*, 1973, **59**, 4540.
- 22 C. J. Jameson, A. K. Jameson and S. M. Cohen, *J. Chem. Phys.*, 1975, **62**, 4224.
- 23 J. Jokisaari, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1994, **26**, 1.
- 24 Diamagnetic Susceptibility of Selected Organic Compounds and Magnetic Susceptibility of the Elements and Inorganic Compounds, in *CRC Handbook of Chemistry and Physics, Internet Version 2006*, ed. D. R. Lide, Taylor and Francis, Boca Raton, FL, 2006.
- 25 J. S. Philo and W. M. Fairbank, *J. Chem. Phys.*, 1980, **72**, 4429.
- 26 J. Olsen and P. Jørgensen, *J. Chem. Phys.*, 1985, **82**, 3235.
- 27 P. Atkins and R. Friedman, *Molecular Quantum Mechanics*, Oxford University Press, Oxford, 5th edn, 2011.
- 28 Dalton, a Molecular Electronic Structure Program, Release 2016.1, see <http://daltonprogram.org>; K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansik, H. J. A. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawłowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Snegov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski and H. Ågren, The Dalton quantum chemistry program system, *WIREs Comput. Mol. Sci.*, 2014, **4**, 269.
- 29 D. Jonsson, P. Norman and H. Ågren, *J. Chem. Phys.*, 1996, **105**, 6331.
- 30 J. Olsen, B. O. Roos, P. Jørgensen and H. J. A. Jensen, *J. Chem. Phys.*, 1988, **89**, 2185.
- 31 T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic Structure Theory*, John Wiley & Sons, Chichester, 2000.
- 32 C. Hättig, O. Christiansen and P. Jørgensen, *Chem. Phys. Lett.*, 1998, **282**, 139.
- 33 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785.
- 34 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
- 35 J. W. Emsley and J. C. Lindon, *NMR Spectroscopy Using Liquid Crystal Solvents*, Pergamon Press, 1975.
- 36 J. Lounila and J. Jokisaari, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1982, **15**, 249.
- 37 J. Jokisaari, *Encyclopedia of NMR Spectroscopy*, 1996, vol. 1, p. 83.

