

## A computational study of some electric and magnetic properties of gaseous $\text{BF}_3$ and $\text{BCl}_3$

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We present the results of an extended computational study of the electric and magnetic properties connected to Cotton-Mouton birefringences, on the trifluoro- and trichloroborides in the gas phase. The electric dipole polarizabilities, magnetizabilities, quadrupole moments, and higher-order hypersusceptibilities—expressed as quadratic and cubic frequency-dependent response functions—are computed within Hartree-Fock, density-functional, and coupled-cluster response theories employing singly and doubly augmented correlation-consistent basis sets and London orbitals in the magnetic property calculations. The results, which illustrate the capability of time-dependent density-functional theory for electron-rich systems, are compared with available experimental data. Revised values of both experimentally derived quadrupole moment of  $\text{BF}_3$ ,  $2.72 \pm 0.15$  a.u., and magnetizability anisotropy of  $\text{BCl}_3$ ,  $-0.45 \pm 0.09$  a.u., both obtained in birefringence experiments that neglect the effects of higher-order hypersusceptibilities, are presented. In the theoretical limit the traceless quadrupole moments of  $\text{BF}_3$  and  $\text{BCl}_3$  are determined to be  $3.00 \pm 0.01$  and  $0.71 \pm 0.01$  a.u., respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.2034487]

### I. INTRODUCTION

The study of the magnetic and electric properties of the boron trihalides  $\text{BX}_3$  ( $X = \text{F}, \text{Cl}, \text{Br},$  and  $\text{I}$ ) has proven a difficult proposition for experimentalists and theoreticians alike, since these systems are corrosive, highly reactive, and electron rich. Nevertheless, there is an obvious interest for chemists in the molecular properties of such species: the  $\text{BX}_3$  molecules are among the few stable  $\text{XY}_3$  gases of  $D_{3h}$  symmetry;<sup>1</sup> the fluorides and chlorides of boron are commonly used in manufacturing,<sup>2,3</sup> while the Lewis acidity of the boron trihalides is also well known and studied.<sup>4–8</sup>

The electronic charge structure of these simple molecules has been the subject of recent experimental studies, typically from linear birefringence measurements.<sup>9–14</sup> A linear birefringence is the difference in the refractive index along two axes perpendicular to each other and to the direction of propagation of linearly polarized light traversing a sample. It is usually induced by applying static electric and/or magnetic fields with components perpendicular to the direction of propagation. Birefringences constitute a sensitive probe of the response of matter to an external electromagnetic perturbation and moreover offer an attractive route

to the determination of some important molecular properties such as magnetizabilities, quadrupole moments, polarizabilities, and hyperpolarizabilities.<sup>15</sup>

Two such birefringences are the Cotton-Mouton effect<sup>16,17</sup> (CME) and the Buckingham effect (BE).<sup>18</sup> In the CME, the birefringence results from an applied magnetic field, whereas the BE is observed when an electric-field gradient (EFG) interacts with the beam and the sample. During the last two decades, there has been a growing interest in the study of birefringences both experimentally and theoretically, see Refs. 15, 19, and 20. Recent work by some of the present authors on the birefringences of benzene<sup>21</sup> and hexafluorobenzene<sup>22</sup> has illustrated the usefulness of such a theoretical approach for electron-rich systems.

Among the boron trihalides,  $\text{BCl}_3$  (bp  $12^\circ\text{C}$ ) is the optimal choice for the measurement of birefringences in the vapor phase in comparison with  $\text{BF}_3$  (bp  $-100^\circ\text{C}$ ) and  $\text{BBr}_3$  (bp  $91^\circ\text{C}$ ), considering the usual range of temperatures of a birefringence measurement. Indeed, this was one of the reasons why Ritchie and co-workers chose, among the boron trihalides, to measure the CME of  $\text{BCl}_3$ .<sup>9–11,13</sup> Still, because of the smallness of the effect in  $\text{BCl}_3$  and difficulties in measuring over a broad temperature range, it became necessary to ignore the contribution from temperature-independent terms. In an effort to separate the paramagnetic and diamagnetic contributions to the magnetizability anisotropy of  $\text{BCl}_3$ , the lack of an accurate experimental molecular quadrupole

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moment  $\Theta$  forced Lamb and Ritchie to use a theoretical value, calculated at the second-order Møller-Plesset (MP2) level of theory in a rather modest Huz-SV basis ( $\Theta = 1.18$  a.u.).<sup>9,12</sup>

Recently, the accurate determination of the quadrupole moment of  $\text{BCl}_3$  has been debated. Gierszal *et al.* reported measurements from a foreign-gas microwave pressure broadening study, yielding a value of  $1.52 \pm 0.07$  a.u.<sup>12</sup> However, questions regarding this work have been raised,<sup>13</sup> highlighting deficiencies in the experimental technique as well as limitations in the approximations made by Gierszal *et al.* The experimentally derived value assumed both a vanishing octupole moment of  $\text{BCl}_3$  and a vanishing quadrupole moment of  $\text{CHF}_3$ , neither of which are valid assumptions.<sup>23</sup> Clearly, the definitive value of this property has yet to be established.

There are no reported measurements of the CME of  $\text{BF}_3$ , but Lamb and Ritchie suggested that such an effect can be measured under high pressure.<sup>10,11</sup> The BE of  $\text{BF}_3$  has recently been measured,<sup>24</sup> whereby the quadrupole moment was determined to be  $2.81 \pm 0.16$  a.u. The procedure adopted, involving measurements at a single (room) temperature, relies on the neglect of the temperature-independent hyperpolarizability contribution  $b(\omega)$ . In a number of cases, this approximation has been proven unjustified, see Refs. 15 and 24–29. The only previously reported experimental value for the traceless quadrupole moment of  $\text{BF}_3$  is 2.50 a.u., obtained from estimates of dipole moments in van der Waals complexes of  $\text{BF}_3$  with Ar, CO, and  $\text{N}_2$ .<sup>30</sup> Keir and Ritchie also performed MP2/Huz-SV calculations for the quadrupole moment of  $\text{BF}_3$ , yielding a value of 3.21 a.u.<sup>9</sup>

Theoretical studies of the electric and magnetic properties of these interesting molecules are thus timely. The Zeeman properties—the magnetizability, the  $g$  tensor, and the quadrupole moment—of the entire series of boron trihalides have recently been the subject of an *ab initio* study by the authors, employing Hartree-Fock theory and density-functional theory (DFT), aimed at discerning trends across the series.<sup>31</sup> In this parallel work, we carry out a thorough and detailed computational investigation of the properties related to the CME and BE of  $\text{BF}_3$  and  $\text{BCl}_3$ , including other density functionals in the calculation of magnetizability and molecular quadrupole moment than in Ref. 31. More importantly, we perform an accurate coupled-cluster study. Additionally, we examine the electric dipole polarizability and higher-order response functions (hyperpolarizabilities) entering the expressions of the two linear birefringences considered.

The challenges presented to theory by these perhalogenated, electron-rich systems are worth emphasizing. For example, difficulties in calculating the magnetic properties of fluorine containing molecules are well known.<sup>32–36</sup> Ruud *et al.* have demonstrated that the additivity of magnetizabilities (known as Pascal's rule) breaks down for fluorine-containing species.<sup>34,35</sup> For calculations to match the accuracy of the experiment, extensive basis sets are required. Most significantly, the gauge dependence of magnetic properties must be taken into account.<sup>35</sup> The favored scheme to account for the gauge origin is nowadays the use of London orbitals, also known as gauge-invariant atomic orbitals (GIAOs), which in

most cases also improves basis-set convergence. The calculation of DFT magnetizabilities with London orbitals has recently been implemented by the authors<sup>37</sup> in the DALTON package.<sup>38</sup>

Studies of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{F}_6$  have highlighted the effect that perhalogenation has on the magnetic and electric properties for electron-rich systems.<sup>39,40</sup> For example, Ritchie and Vrbancich found the magnetizability anisotropy of  $\text{C}_6\text{F}_6$  to be far larger and the temperature dependence of the Cotton-Mouton and Kerr birefringences to be far more significant than may be expected from an understanding of the molecular properties of benzene.<sup>39</sup> In a Hartree-Fock study of the quadrupole moment of the fluoro- and chlorobenzenes, Hernández-Trujillo and Vela found that, whereas the quadrupole moment of  $\text{C}_6\text{H}_6$  is converged to within 1 a.u. (15%) in a small double-zeta basis, successive halogenation reduced the basis-set convergence to the point where it is no longer apparent that the Hartree-Fock quadrupole moment is converged to the same 1-a.u. accuracy (again 15%) even in a triple-zeta basis.<sup>40</sup> Since successive fluorination distorts the electron density, we also expect the response of the density to applied electric and magnetic fields and to electric-field gradients to be more complicated compared with the nonhalogenated system.

In view of the challenges that these systems present to theory, we have investigated a number of methods and basis sets for all properties. In particular, the popularity and general usefulness of DFT make it interesting to assess its performance for higher-order properties. Since only a few experimental results of limited accuracy are available, we have also performed high-level *ab-initio* coupled-cluster singles and doubles<sup>41</sup> (CCSD) calculations. In particular, for the molecular quadrupole moment, whose accurate determination is a primary aim of our work, we have carried out extensive coupled-cluster calculations with basis-set extrapolation to determine a theoretical limit for this property.

The paper is organized as follows: in Sec. II, we outline the essential definitions and introduce the relevant molecular properties and their link to time-dependent response theory; in Sec. III, computational details are given; the results are presented and discussed in Sec. IV. Some concluding remarks are collected in Sec. V.

## II. THEORY

The Cotton-Mouton effect is the birefringence induced on linearly polarized light by an applied external magnetic field.<sup>16,17</sup> It is the magnetic equivalent of the electric-field-induced Kerr birefringence.<sup>42,43</sup> For the CME, the anisotropy of the refractive index  $\Delta n(\lambda, T) = n_{\parallel} - n_{\perp}$  at wavelength  $\lambda$  (frequency  $\omega$ ) and temperature  $T$  is connected to the microscopic molecular properties of the sample through the molecular function labeled as the “Cotton-Mouton constant”  ${}_m C(\lambda, T)$ ,<sup>19,44</sup> which, for diamagnetic axial molecules in the limit of an ideal gas at fixed pressure, can be written as

$$\Delta n(\lambda, T) = \frac{27B^2}{2V_m(4\pi\epsilon_0)} {}_m C(\lambda, T), \quad (1)$$

$${}_m C(\lambda, T) = \frac{2\pi N_A}{27} \left[ \Delta \eta(\omega) + \frac{2}{15kT} \alpha_{\text{ani}}(\omega) \xi_{\text{ani}} \right], \quad (2)$$

where  $k$  is the Boltzmann constant,  $N_A$  is Avogadro's number,  $\epsilon_0$  the vacuum permittivity,  $V_m$  the molar volume, and  $B$  the intensity of the magnetic field. Equation (2) introduces the anisotropies of the frequency-dependent electric dipole polarizability ( $z$  axis along the principal molecular axis)

$$\alpha_{\text{ani}}(\omega) = \alpha_{zz}(\omega) - \alpha_{xx}(\omega), \quad (3)$$

of the magnetizability

$$\xi_{\text{ani}} = \xi_{zz} - \xi_{xx}, \quad (4)$$

and of the frequency-dependent hypermagnetizability

$$\Delta \eta(\omega) = \frac{1}{5} \left[ \eta_{\alpha\beta, \alpha\beta}(\omega) - \frac{1}{3} \eta_{\alpha\alpha, \beta\beta}(\omega) \right]. \quad (5)$$

For comparison with experimental observations, we use a definition of  $\Delta n(\lambda, T)$  that corresponds to the anisotropy observed for a magnetic induction of 1 T and a pressure of 1 atm, indicated as  $\Delta n_u$ .<sup>19</sup>

In the BE, the birefringence is observed when linearly polarized light traverses the sample in a direction perpendicular to an applied external electric-field gradient  $\nabla E$ .<sup>18,25</sup> With  $\nabla E$  arranged so that  $\nabla E = \nabla E_{xx} = -\nabla E_{yy}$  and  $\nabla E_{zz} = 0$ , the anisotropy in the refractive index is observed as  $\Delta n(\lambda, T) = n_x - n_y$ . The ‘‘Buckingham constant’’  ${}_m Q(\lambda, T)$  connects the anisotropy of the refractive index to the strength of the EFG and to the microscopic properties of the gas.<sup>45–47</sup> For an axial molecule,

$$\Delta n(\lambda, T) = \frac{3 \nabla E}{2V_m} {}_m Q(\lambda, T), \quad (6)$$

$${}_m Q(\lambda, T) = \frac{N_A}{3\epsilon_0} \left[ b(\omega) + \frac{2}{15kT} \alpha_{\text{ani}}(\omega) \Theta \right], \quad (7)$$

where  $\Theta$  is the symmetry unique traceless permanent electric-quadrupole moment ( $\Theta_{zz}$ ) and

$$b(\omega) = \frac{2}{15} B_{\alpha\beta, \alpha\beta} - \frac{2}{15} \mathcal{B}_{\alpha, \alpha\beta, \beta} - \frac{2}{3\omega} \epsilon_{\alpha\beta\gamma} J'_{\alpha, \beta, \gamma} \quad (8)$$

includes tensor components of the electric dipole–electric dipole–electric quadrupole hyperpolarizability  $B$ , the electric dipole–electric quadrupole–electric dipole hyperpolarizability  $\mathcal{B}$ , and the electric dipole–magnetic dipole–electric dipole hyperpolarizability  $J'$ . The symbol  $\epsilon_{\alpha\beta\gamma}$  represents the Levi-Civita alternating tensor.

In Eqs. (2) and (7), the quantities within the square brackets are separated into a temperature-independent contribution involving higher-order frequency-dependent response properties  $\Delta \eta(\omega)$  and  $b(\omega)$ , respectively, and a temperature-dependent contribution. For theoretical calculations, it is practical to express all these properties in terms of response functions<sup>19,27,48,49</sup>

$$\alpha_{\alpha\beta}(\omega) = -\langle\langle \mu_\alpha; \mu_\beta \rangle\rangle_\omega, \quad (9)$$

$$\eta_{\alpha\beta, \gamma\delta}(\omega) = \eta_{\alpha\beta, \gamma\delta}^{\text{para}}(\omega) + \eta_{\alpha\beta, \gamma\delta}^{\text{dia}}(\omega), \quad (10)$$

$$\eta_{\alpha\beta, \gamma\delta}^{\text{para}}(\omega) = -\langle\langle \mu_\alpha; \mu_\beta, m_\gamma, m_\delta \rangle\rangle_{\omega, 0, 0}, \quad (11)$$

$$\eta_{\alpha\beta, \gamma\delta}^{\text{dia}}(\omega) = -\langle\langle \mu_\alpha; \mu_\beta, \xi_{\gamma\delta}^{\text{dia}} \rangle\rangle_{\omega, 0}, \quad (12)$$

$$B_{\alpha\beta, \gamma\delta}(-\omega; \omega, 0) = \langle\langle \mu_\alpha; \mu_\beta, \Theta_{\gamma\delta} \rangle\rangle_{\omega, 0}, \quad (13)$$

$$\mathcal{B}_{\alpha, \beta\gamma, \delta}(-\omega; \omega, 0) = \langle\langle \mu_\alpha; \Theta_{\beta\gamma}, \mu_\delta \rangle\rangle_{\omega, 0}, \quad (14)$$

$$J'_{\alpha, \beta, \gamma}(-\omega; \omega, 0) = i\langle\langle \mu_\alpha; m_\beta, \mu_\gamma \rangle\rangle_{\omega, 0}. \quad (15)$$

Here the superscripts para and dia distinguish the paramagnetic and diamagnetic contributions (see Ref. 19 for a review of the subject),  $\mu_\alpha$  is the electric dipole operator,  $m_\alpha$  is the magnetic dipole operator,  $\xi_{\alpha\beta}^{\text{dia}}$  is the diamagnetic susceptibility operator, and  $\Theta_{\alpha\beta}$  is the traceless electric quadrupole moment operator.

### III. COMPUTATIONAL DETAILS

Experimental  $D_{3h}$  equilibrium geometries were employed in all calculations, with BF and BCl bond lengths of 130.70 pm (Ref. 50) and 174.21 pm,<sup>51</sup> respectively. With the exception of some of the higher-order electric moments, all calculations were performed with a locally modified version of the DALTON program<sup>38</sup> that includes DFT modules up to cubic response.<sup>52,53</sup> The octupole-moment and MP2 quadrupole-moment calculations were performed within GAUSSIAN.<sup>54</sup>

All properties were calculated with the Hartree-Fock, DFT, and CCSD methods. Three density functionals were considered: the local-density approximation (LDA),<sup>55</sup> Becke-3-parameter-Lee-Yang-Parr (B3LYP)<sup>56</sup> and Keal-Tozer KT1 (Ref. 57) functionals. Although the latter has been shown to be particularly accurate in the calculation of molecular magnetic properties,<sup>37,57</sup> its performance for electric properties has not been thoroughly investigated.<sup>58</sup> It is therefore of some interest to compare the KT1 functional with the LDA and B3LYP functionals for mixed magnetic and electric properties. The B3LYP results for the magnetizability tensor and quadrupole moments of BF<sub>3</sub> and BCl<sub>3</sub> were presented in Ref. 31, together with Hartree-Fock and KT2 functional<sup>59</sup> results.

The singly and doubly augmented correlation-consistent basis sets of Dunning<sup>60</sup> were employed for all calculations. For all higher-order response properties, we considered the aug-cc-pVXZ and daug-cc-pVXZ (where  $X = D, T$ ) basis sets. For BF<sub>3</sub>, we also carried out aug-cc-pVQZ calculations of all properties. Convergence to the basis-set limit for the quadrupole moments of BF<sub>3</sub> and BCl<sub>3</sub> was investigated for the Hartree-Fock, DFT, MP2, and coupled-cluster models.

As indicated above, the CCSD, CCSD with a perturbative triples correction [CCSD(T)], and coupled-cluster-triples<sup>61</sup> [CC(3)] calculations were carried out with DALTON.<sup>38</sup> The CCSD implementation in DALTON, including response-function modules, is described in Refs. 62–64. At the CCSD level, traceless quadrupole moments were calculated by direct contraction of the corresponding density matrix with the appropriate integrals<sup>63</sup> and without orbital relaxation effects, which are small. To extrapolate to the basis-set limit for the coupled-cluster and MP2 methods,

TABLE I.  $\text{BF}_3$ . Electric dipole polarizability at  $\lambda=632.8$  nm and molecular magnetizability anisotropy (in a.u.).

Wave function	Basis	$\alpha_{xx}(\omega)$	$\alpha_{zz}(\omega)$	$\alpha_{iso}(\omega)$	$\alpha_{ani}(\omega)$	$\xi_{ani}$
HF <sup>a</sup>	aug-cc-pVDZ	14.32	11.32	13.32	-2.99	-0.37
	daug-cc-pVDZ	14.74	11.73	13.74	-3.01	-0.22
	aug-cc-pVTZ	14.63	11.77	13.68	-2.86	-0.33
	daug-cc-pVTZ	14.69	11.90	13.76	-2.78	-0.32
	aug-cc-pVQZ	14.66	11.88	13.74	2.79	-0.33
LDA-DFT	aug-cc-pVDZ	18.34	13.84	16.84	-4.49	-0.53
	daug-cc-pVDZ	18.82	14.40	17.35	-4.42	-0.47
	aug-cc-pVTZ	18.69	14.37	17.25	-4.33	-0.50
	daug-cc-pVTZ	18.79	14.59	17.39	-4.20	-0.49
	aug-cc-pVQZ	18.74	14.52	17.33	-4.21	-0.50
B3LYP-DFT <sup>a</sup>	aug-cc-pVDZ	17.27	13.20	15.91	-4.07	-0.46
	daug-cc-pVDZ	17.72	13.72	16.38	-4.00	-0.39
	aug-cc-pVTZ	17.57	13.68	16.27	-3.88	-0.43
	daug-cc-pVTZ	17.66	13.89	16.40	-3.77	-0.42
	aug-cc-pVQZ	17.61	13.82	16.35	-3.78	-0.43
KT1-DFT	aug-cc-pVDZ	18.66	14.25	17.19	-4.41	-0.45
	daug-cc-pVDZ	19.16	14.83	17.71	-4.33	-0.37
	aug-cc-pVTZ	19.05	14.84	17.65	-4.20	-0.42
	daug-cc-pVTZ	19.16	15.07	17.80	-4.08	-0.41
	aug-cc-pVQZ	19.12	15.01	17.75	-4.11	-0.42
CCSD	aug-cc-pVDz	16.94	12.98	15.62	-3.97	
	daug-cc-pVDZ	17.46	13.54	16.16	-3.93	
	aug-cc-pVTZ	17.11	13.39	15.87	-3.72	
HF <sup>b</sup>	Huz-SV	13.9	10.7	12.9	-3.2	
MP2 <sup>b</sup>	Huz-SV	16.6	12.4	15.2	-4.1	
HF (IGLO) <sup>c</sup>	H-III					-0.33
Expt.		17.7 <sup>b</sup>	13.9 <sup>b</sup>	16.4 <sup>d</sup> 22.3 <sup>e</sup>	-3.8±0.2 <sup>b</sup>	

<sup>a</sup>For detailed data on the magnetizability, including tensor components and isotropic average, see Ref. 31.

<sup>b</sup>From Ref. 9.

<sup>c</sup>From Ref. 32.

<sup>d</sup>From Ref. 69.

<sup>e</sup>From Ref. 74.

we used the two-point extrapolation formula<sup>65-67</sup>

$$P_\infty = \frac{P_X X^3 - P_Y Y^3}{X^3 - Y^3}, \quad (16)$$

where  $P_X$  and  $P_Y$  are the property values calculated with the correlation-consistent basis sets (d)aug-cc-pVXZ and (d)aug-cc-pVYZ, respectively. For the Hartree-Fock and DFT methods, we estimated the limit by inspection of the properties calculated with the (d)aug-cc-pVXZ basis sets.

## IV. RESULTS AND DISCUSSION

The results obtained in this study of the birefringences of  $\text{BF}_3$  and  $\text{BCl}_3$  are presented and discussed with reference to Tables I-V. We note that a comparison of the calculated properties with experiment is made difficult by the absence of information regarding the effect of molecular vibrations, which in some cases can be large. An example is the electric dipole polarizability of hexafluorobenzene, where the zero-point vibrational (ZPV) contributions yield an anomalous experimental dispersion, with the static value of the isotropic

electric dipole polarizability being larger than at (small) non-vanishing frequencies.<sup>68,22</sup> In most cases, however, the vibrational corrections are smaller, making a comparison of the purely electronic contributions with the experiment meaningful.

## A. The electric dipole polarizability and magnetizability anisotropy

### 1. $\text{BF}_3$

The calculated frequency-dependent dipole polarizabilities and molecular magnetizability anisotropies of boron trifluoride are listed in Table I. For the elements of the polarizabilities  $\alpha_{\alpha\beta}(\omega)$ ,  $\alpha_{iso}(\omega)$ , and  $\alpha_{ani}(\omega)$ , the tabulated data indicate that the CCSD/aug-cc-pVTZ results are within 0.1 a.u. of the CCSD basis-set limit. With the aug-cc-pVQZ basis set, the Hartree-Fock and DFT methods both appear to be within 0.15 a.u. of their respective basis-set limits. A comparison of experimental and computational results indicates that the KT1 functional performs less satisfactorily for electric properties than it does for magnetic properties. To exam-

ine further the suitability of the  $KT_n$  functionals for electric properties, we have carried out polarizability calculations with the  $KT3$  functional, presumably the best such functional for this property.<sup>58</sup> However, although the  $KT3$  isotropic and anisotropic values are closer to the experiment than those given by the  $KT1$  functional ( $KT3/aug\text{-}cc\text{-}pVQZ$  values of  $\alpha_{iso}$  and  $\alpha_{ani}$  are 16.89 and  $-3.99$  a.u., respectively), it does not alter our impression that these functionals do not perform as well as  $B3LYP$  for electric properties. Note, however, that our comparisons are made without vibrational corrections.

Whereas the Hartree-Fock method yields polarizability components that are significantly smaller in magnitude than the experimental values,<sup>9</sup> the LDA and  $KT1$  functionals overestimate the polarizability of BF<sub>3</sub>. The  $B3LYP$  and CCSD models both reproduce experiment within the given error bars, supporting the  $\alpha_{iso}$  estimate of 16.4 a.u. of Keir and Ritchie<sup>9</sup> rather than the older value of 22.3 a.u. of Watson and Ramaswamy.<sup>69</sup>

For all models, basis-set expansion and augmentation reduce (in absolute value) the polarizability anisotropy. In Table I, we have included two *ab initio* results reported by Keir and Ritchie.<sup>9</sup> From an analysis of our data, the basis used by these authors may be considered too small for accurate calculations of this property.

The results obtained for the magnetizability tensor of BF<sub>3</sub> with Hartree-Fock theory and the  $B3LYP$  and  $KT2$  density functionals were presented and discussed in Ref. 31. Since only the anisotropic magnetizability enters the Cotton-Mouton constant Eq. (2), only this component is listed in Table I. The LDA and  $KT1$  magnetizabilities are within 0.1 a.u. of the previous  $B3LYP$  and  $KT2$  results, for the Cartesian as well as isotropic and anisotropic components.<sup>31</sup>

The Hartree-Fock and DFT magnetizabilities of BF<sub>3</sub> were obtained employing London orbitals, which are not yet available for coupled-cluster methods in DALTON.<sup>38</sup> An approach that is able to cope with the magnetic gauge-origin dependence is mandatory for a reliable treatment of magnetizabilities—non-London Hartree-Fock and CCSD results (not tabulated here) differ significantly from the London results and from the experiment. The London results converge rapidly with basis-set extension, the  $aug\text{-}cc\text{-}pVTZ$  magnetizability components being within 0.01 a.u. of the  $aug\text{-}cc\text{-}pVQZ$  results.

The Hartree-Fock magnetizability anisotropies are consistently more paramagnetic than the DFT values. In our experience, the  $KT1$  and  $B3LYP$  functionals are equally well suited to magnetic properties;<sup>37</sup> their anisotropies here differ by more than 0.01 a.u. Assuming that these functionals give accurate results, we conclude that the Hartree-Fock magnetizability anisotropies are too paramagnetic.

## 2. BCl<sub>3</sub>

The calculated frequency-dependent electric dipole polarizabilities and magnetizability anisotropies of BCl<sub>3</sub> are listed in Table II. Except for  $B3LYP$  and  $KT1$ , adding a second set of diffuse functions and going from a double-zeta to a triple-zeta basis both make the Cartesian components as well as the isotropic and anisotropic components of the polarizability tensor more positive. We estimate that the  $aug\text{-}cc\text{-}pVTZ$  isotropic and anisotropic polarizabilities are converged to within 1.0 and 0.5 a.u. (2%), respectively, of the basis-set limit. Compared with the experiment, the Hartree-Fock method underestimates the in-plane polarizability in the same manner as for BF<sub>3</sub>, resulting in an underestimation of the isotropic and anisotropic polarizability. The agreement of the CCSD and  $B3LYP$  results with the experiment is not as good as for BF<sub>3</sub>, but the  $aug\text{-}cc\text{-}pVTZ$  results are within twice the reported error bars. The  $KT1$  results are again similar to the LDA results, indicative of the less satisfactory performance of this gradient-corrected functional for electric properties. As for BF<sub>3</sub>, the  $KT3/aug\text{-}cc\text{-}pVTZ$  isotropic and anisotropic values of 57.72 and  $-24.25$  a.u., respectively, are closer to the experiment than the  $KT1$  values but less accurate than the  $B3LYP$  values.

In Table II, we have also included the two results reported by Keir and Ritchie.<sup>9</sup> As discussed previously, the basis employed by these authors is too small for high accuracy, the Hartree-Fock results, in particular, deviating significantly from the experiment. The agreement of their MP2 result with the experiment is fortuitous, in view of the limitation of the basis set.

As for BF<sub>3</sub>, the LDA and  $KT1$  magnetizability components (not listed) are very similar to the  $B3LYP$  or  $KT2$  values, differing by a few tenths of an a.u.<sup>31</sup> The Hartree-Fock and DFT magnetizability anisotropies converge rapidly, the  $aug\text{-}cc\text{-}pVTZ$  results being within 0.01 a.u. (1%) of the basis-set limit. The  $KT1$  and  $B3LYP$  magnetizabilities are again similar, the anisotropy differing by less than 0.01 a.u.

In agreement with Lamb and Ritchie,<sup>10,11</sup> the magnetizability anisotropy of BF<sub>3</sub> and BCl<sub>3</sub> are both negative, supporting their hypothesis that boron bonds to carbon, oxygen, fluorine, and chlorine are less magnetizable along than across the internuclear axis. The foundation for this hypothesis originates from Pauling,<sup>70</sup> who recognized the  $p\pi\text{-}p\pi$  interactions, ionic-covalent resonance, partial double-bond character, and electron delocalization characteristic of the boron bonds, which is surmised to account for the observed negative magnetizability anisotropy.<sup>10,11</sup> In our previous Zeeman study of the boron trihalides,<sup>31</sup> the anisotropies of BBr<sub>3</sub> and BI<sub>3</sub> were found to be negative and positive, respectively. Thus, although the hypothesis of Lamb and Ritchie may hold in most cases, at least BI<sub>3</sub> is an exception.

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## B. The quadrupole moment

The traceless electric quadrupole moments of BF<sub>3</sub> and BCl<sub>3</sub> have recently been the subject of debate in the literature.<sup>9,12,13,24</sup> The calculated and experimental quadrupole moments are listed in Table III, with only the  $aug\text{-}cc\text{-}pVXZ$  results tabulated. Concerning the calculated results, several points are worth making.

First, the Hartree-Fock and DFT quadrupole moments are larger and smaller, respectively, than the coupled-cluster theory results. Second, the poor LDA and  $KT1$  performance for dipole polarizabilities is reflected in the quadrupole moments, with the  $KT1$  functional behaving in a manner similar to the  $KT2$  functional.<sup>31</sup> As observed in Sec. IV A, although the  $KT3$  functional improves on the  $KT1$  and  $KT2$  results, it

TABLE II.  $\text{BCl}_3$ . Electric dipole polarizability at  $\lambda=632.8$  nm and molecular magnetizability anisotropy (in a.u.).

Wave function	Basis	$\alpha_{xx}(\omega)$	$\alpha_{zz}(\omega)$	$\alpha_{\text{iso}}(\omega)$	$\alpha_{\text{ani}}(\omega)$	$\xi_{\text{ani}}$
HF <sup>d</sup>	aug-cc-pVDZ	57.22	38.67	51.04	-18.55	-0.67
	daug-cc-pVDZ	58.22	40.19	52.21	-18.03	-0.54
	aug-cc-pVTZ	58.43	40.14	52.33	-18.29	-0.69
	daug-cc-pVTZ	58.57	40.45	52.53	-18.12	-0.70
LDA-DFT	aug-cc-pVDZ	66.62	41.36	58.20	-25.26	-0.90
	daug-cc-pVDZ	68.24	43.33	59.94	-24.92	-0.82
	aug-cc-pVTZ	68.49	43.17	60.05	-25.31	-0.92
	daug-cc-pVTZ	68.77	43.63	60.39	-25.14	-0.93
B3LYP-DFT <sup>a</sup>	aug-cc-pVDZ	63.84	40.48	56.06	-23.36	-0.80
	daug-cc-pVDZ	65.31	42.38	57.67	-22.94	-0.71
	aug-cc-pVTZ	65.43	42.22	57.69	-23.21	-0.79
	daug-cc-pVTZ	65.69	42.71	58.03	-22.99	-0.81
KT1-DFT	aug-cc-pVDZ	67.05	41.95	58.68	-25.10	-0.62
	daug-cc-pVDZ	68.66	43.96	60.43	-24.70	-0.54
	aug-cc-pVTZ	68.82	43.80	60.48	-25.02	-0.62
	daug-cc-pVTZ	69.13	44.29	60.85	-24.84	-0.65
CCSD	aug-cc-pVDZ	63.41	40.45	55.76	-22.96	
	daug-cc-pVDZ	64.77	42.32	57.29	-22.45	
	aug-cc-pVTZ	64.39	41.98	56.92	-22.41	
HF <sup>b</sup>	Huz-SV	54.9	37.1	49.0	-17.8	
MP2 <sup>b</sup>	Huz-SV	62.1	40.1	54.8	-22.0	
Expt.		62.5 <sup>b</sup>	41.2 <sup>b</sup>	55.6 <sup>c</sup>	-21.5±0.7 <sup>b</sup>	-0.71±0.09 <sup>d</sup>
						-0.45±0.09 <sup>e</sup>

<sup>a</sup>For detailed data on the magnetizability, including tensor components and isotropic value, see Ref. 31.

<sup>b</sup>From Ref. 9.

<sup>c</sup>From Ref. 75.

<sup>d</sup>From Refs. 10 and 11.

<sup>e</sup>From the data in Refs. 10 and 11 fitted in this work, assuming linear regression with a  $T \rightarrow \infty$  value of  ${}_m C(\lambda, T)$  equal to our B3LYP-DFT/daug-cc-pVTZ “best value” of  $\Delta\eta(\omega)=701.3$  a.u., see Table V.

does not perform quite as well as the B3LYP functional, suggesting that the performance of the  $KTn$  functionals for electric properties does not match their performance for magnetic properties.<sup>37</sup>

For all models, basis-set convergence is achieved in the daug-cc-pVTZ basis, whose errors are within 0.010 a.u. of the basis-set limit. We have not listed the singly augmented results but found that the effect of a second set of diffuse functions is small.

Noting that the daug-cc-pVQZ results are close to the basis-set limit, we turn our attention to the coupled-cluster  $N$ -electron (excitation-level) convergence. Relative to the CCSD basis-set limit, the CCSD(T) model reduces the quadrupole moment of  $\text{BF}_3$  by 2.4% and the CC(3) model by another 0.1%. In the daug-cc-pVTZ basis, the CC(3) result is predicted to be within 0.3% of the basis-set limit. For  $\text{BCl}_3$ , the triples contribution is larger, with a CCSD(T) reduction of 9.8% and a further CC(3) reduction of 0.3%. Assuming a  $\text{BCl}_3$  basis-set convergence similar to that of  $\text{BF}_3$ , we predict CCSD(T) and CC(3) basis-set limits of 0.713 and 0.711 a.u., respectively.

Having established theoretical values for the quadrupole moments of  $\text{BF}_3$  and  $\text{BCl}_3$ , which we assign to be  $3.00 \pm 0.01$  and  $0.71 \pm 0.01$  a.u., respectively, we may comment on pre-

vious studies of this property. From our basis-set study, it appears that the split-valence results of Ritchie and co-worker<sup>9,13</sup> are quite far from the MP2 basis-set limit. To illustrate the sensitivity of the quadrupole moment to polarization and diffuse functions in small basis sets, we note that, for the  $\text{BF}_3$  molecule, MP2 calculations in the 6-31G, 6-31G\*, and 6-31+G\* basis sets give widely different values of 3.83, 2.81, and 3.20 a.u., respectively. The good agreement between the MP2/Huz-SV and coupled-cluster basis-set limits is therefore fortuitous.

For  $\text{BF}_3$ , an early result of 2.50 a.u., derived from a study of van der Waals complexes,<sup>30</sup> may be dismissed as too low. A Buckingham birefringence study yields an “apparent” value of  $2.81 \pm 0.16$  a.u., with the temperature-independent  $b(\omega)$  contribution neglected.<sup>24</sup> Including this term in Table III, we obtain a revised value of  $2.72 \pm 0.15$  a.u., see details in Sec. IV C 1 below. This inclusion reduces the magnitude of the quadrupole moment of  $\text{BF}_3$ , taking it further away from our best *ab initio* results. This comparison neglects vibrations, which may in principle account for some of the difference between our best value and the revised experimental value. A preliminary study of the effect of ZPV average on the quadrupole moment of  $\text{BF}_3$ , carried out at Hartree-

TABLE III. Traceless quadrupole moments of BF<sub>3</sub> and BCl<sub>3</sub> calculated with daug-cc-pVXZ basis sets (in a.u.).

Wave function	BF <sub>3</sub>				BCl <sub>3</sub>			
	DZ	TZ	QZ	Limit <sup>a</sup>	DZ	TZ	QZ	Limit <sup>a</sup>
HF	3.307	3.416	3.418	3.42	1.174	1.177	1.151	1.13
LDA-DFT	2.613	2.704	2.703	2.70	0.529	0.474	0.453	0.44
B3LYP-DFT	2.885	2.981	2.981	2.98	0.886	0.839	0.814	0.80
KT1-DFT	2.540	2.643	2.641	2.64	0.468	0.476	0.454	0.44
KT3-DFT	2.635	2.782	2.780	2.78	0.621	0.660	0.625	0.60
MP2	2.926	2.986	2.988	2.990	0.829	0.723	0.701	0.685
CCSD	2.985	3.067	3.075	3.081	0.888	0.793	0.796	0.798
CCSD(T)	2.929	2.997	3.001	3.005	0.829	0.715		
CC(3)	2.927	2.995	2.999	3.003	0.828	0.713		
Experiment and other values								
Ref. 9 <sup>b</sup>	3.21				Ref. 9 <sup>b</sup>	1.18		
Ref. 24 <sup>c</sup>	2.81±0.16				Ref. 12 <sup>d</sup>	1.52±0.07		
Ref. 24, revised <sup>e</sup>	2.72±0.15							
Ref. 30 <sup>f</sup>	2.50							

<sup>a</sup>Hartree-Fock and DFT values estimated from daug-cc-pVTZ and daug-cc-pVQZ calculated values. Coupled-cluster and MP2 values are extrapolated with the relationship given in Ref. 67.

<sup>b</sup>*Ab initio* study, MP2/Huz-SV.

<sup>c</sup>Buckingham birefringence study.

<sup>d</sup>Derived from microwave pressure-broadening observations. See text for discussion.

<sup>e</sup>Revised in this work, as  $\Theta^{\text{rev}} = \Theta^{\text{app}} - 15bkT/2\alpha_{\text{ani}}$ , where  $\Theta^{\text{app}}$  is the value estimated in Ref. 24 by neglecting the contribution of  $b(\omega)$ ,  $b$  is our best estimate, see Table IV,  $b(\omega) = -47.6$  a.u.,  $k$  is Boltzmann constant,  $T = 293.15$  K, and  $\alpha_{\text{ani}}$  is taken from Ref. 9.

<sup>f</sup>Extrapolated from measured dipole moments of van der Waals complexes containing BF<sub>3</sub>.

Fock level with the daug-cc-pVTZ basis set, yielded on the other hand a correction on the order of  $\approx -0.015$  a.u., rather small although somehow pointing towards the right direction.

As BF<sub>3</sub>, we do not expect the BCl<sub>3</sub> quadrupole moment of Keir and Ritchie<sup>9</sup> to be close to the MP2 basis-set limit. Indeed, the large differences between their and our BCl<sub>3</sub> results support the conclusion that the agreement for BF<sub>3</sub> occurs by error cancellation.

The only reported experimental quadrupole moment of BCl<sub>3</sub> was derived from a microwave pressure-broadening experiment, with CHF<sub>3</sub> as the absorbing species.<sup>12</sup> However, Ritchie has raised objections to the assumptions made in that work,<sup>13</sup> arguing that the absorber-perturber collision cross section  $\sigma$  is not proportional to  $(\Theta^2 M)^{1/3}$  where  $M$  is the reduced mass of the absorber-perturber collision pair, and that the observed spectral broadening cannot be interpreted solely on the basis of dipole-quadrupole interactions. The first assumption relied on old  $\Theta$  values, for which Ritchie has shown that, when more recent and reliable values are used, the assumed proportionality is qualitatively and quantitatively incorrect.<sup>13</sup> The second assumption ignores higher-order interactions such as CHF<sub>3</sub>-BCl<sub>3</sub> quadrupole-quadrupole and CHF<sub>3</sub>-BCl<sub>3</sub> dipole-octupole interactions, which are proportional to  $R^{-5}$  and thus shorter ranged than the  $R^{-4}$  dipole-quadrupole interactions. Using symmetry arguments, Buckingham demonstrated that  $C_{3v}$  species such as CHF<sub>3</sub> possess a nonzero quadrupole moment, whereas  $D_{3h}$  species such as BCl<sub>3</sub> exhibit a nonzero molecular octupole moment.<sup>23</sup>

In this work, we investigated the magnitude of these higher-order multipole moments for BCl<sub>3</sub>. There are two ex-

perimental values for the quadrupole moment of CHF<sub>3</sub>: the measurement of Meerts and Ozier at  $2.79 \pm 0.04$  a.u.,<sup>71</sup> and that of Ellenbroek and Dymanus at  $2.875 \pm 0.018$  a.u.<sup>72</sup> Russell has carried out Bruekner-double calculations with a perturbative treatment of triple excitations [BD(T)], yielding a value of 2.746 a.u.<sup>73</sup> Our aug-cc-pVQZ values are 2.97 a.u. (Hartree-Fock), 2.40 a.u. (LDA), 2.57 a.u. (B3LYP), and 2.24 a.u. (KT1). The experimental measurements and the BD(T) value are thus between our Hartree-Fock and B3LYP values, in agreement with the performance of these methods for BF<sub>3</sub>. Our daug-cc-pVTZ results for the traceless octupole moment of BCl<sub>3</sub> are 11.87 a.u. (Hartree-Fock), 11.99 a.u. (B3LYP), and 12.57 a.u. (CCSD).

Our results thus quantitatively support the objections raised by Ritchie<sup>9</sup> regarding the assumptions in the microwave pressure-broadening experiment<sup>12</sup> and identify the source of the discrepancy between the experimental values and the results from the current work.

### C. The Cotton-Mouton and Buckingham linear birefringences

In Tables IV and V, we have collected our results for the hypermagnetizability anisotropy  $\Delta\eta(\omega)$ , the combination of quadratic responses  $b(\omega)$ , and the CME, Eq. (2), and Buckingham, Eq. (7), birefringences of BF<sub>3</sub> and BCl<sub>3</sub>, respectively.

#### 1. BF<sub>3</sub>

As defined in Sec. II, the Cotton-Mouton and Buckingham constants of BF<sub>3</sub> are obtained by combining the electric dipole polarizability anisotropies, the magnetizability

TABLE IV. CME and BE for  $\text{BF}_3$  at  $\lambda=632.8$  nm and  $T=273.15$  K. a.u., with  ${}_mC(\lambda, T)$  in cgs units of  $\text{cm}^3 \text{G}^{-2} \text{mol}^{-1}$  ( $4\pi\epsilon_0$ ).  $\Delta n_u$  is the birefringence defined for an induction field  $B$  of 1 T and a pressure  $P$  of 1 atm according to Ref. 19.  $\Delta n$  for Buckingham birefringence is given for a pressure of  $P=1$  bar and EFG of  $\nabla E=-1 \times 10^9 \text{V m}^{-2}$ .

Wave function	Basis	CME			Buckingham		
		$\Delta\eta(\omega)$	${}_mC(\lambda, T) \times 10^{19}$	$\Delta n_u \times 10^{14}$	$b(\omega)$	${}_mQ(\lambda, T) \times 10^{-27}$	$\Delta n \times 10^{15}$
HF	aug-cc-pVDZ	44.6	8.09	4.87	-26.3	-3.84	3.87
	daug-cc-pVDZ	57.1	5.94	3.58	-33.6	-3.95	3.98
	aug-cc-pVTZ	44.5	7.20	4.33	-30.7	-3.89	3.92
	daug-cc-pVTZ	47.8	7.01	4.22	-34.0	-3.79	3.81
	aug-cc-pVQZ	46.7	7.13	4.24	-32.9	-3.79	3.82
LDA-DFT	aug-cc-pVDZ	81.9	16.85	10.12	-45.7	-4.51	4.54
	daug-cc-pVDZ	104.8	16.06	9.64	-58.2	-4.64	4.67
	aug-cc-pVTZ	85.9	15.85	9.52	-53.3	-4.71	4.74
	daug-cc-pVTZ	95.0	15.60	9.37	-59.8	-4.56	4.60
	aug-cc-pVQZ	90.6	15.69	9.43	-57.1	-4.58	4.61
B3LYP-DFT	aug-cc-pVDZ	71.6	13.59	8.16	-40.6	-4.53	4.56
	daug-cc-pVDZ	91.3	12.50	7.50	-51.8	-4.62	4.66
	aug-cc-pVTZ	74.5	12.50	7.51	-47.3	-4.65	4.68
	daug-cc-pVTZ	81.9	12.24	7.35	-53.2	-4.50	4.53
	aug-cc-pVQZ	78.0	12.39	7.36	-50.5	-4.52	4.56
KT1-DFT	aug-cc-pVDZ	87.0	15.01	9.01	-51.4	-4.33	4.36
	daug-cc-pVDZ	111.1	13.53	8.12	-64.5	-4.44	4.47
	aug-cc-pVTZ	92.5	13.61	8.17	-60.0	-4.49	4.52
	daug-cc-pVTZ	102.4	13.56	8.14	-66.9	-4.37	4.40
	aug-cc-pVQZ	97.7	13.58	8.15	-64.0	-4.39	4.42
CCSD <sup>a</sup>	aug-cc-pVDZ	60.5	12.89	7.66	-30.0	-4.58	4.62
	daug-cc-pVDZ	79.5	11.87	7.06	-41.9	-4.56	4.59
	aug-cc-pVTZ	60.1	11.54	6.86	-47.6	-4.68	4.71

<sup>a</sup>B3LYP GIAO magnetizability anisotropies are employed in place of the non-GIAO CCSD results.

anisotropies, and the electric quadrupole moments of Tables I and III with the temperature-independent contribution given in Table IV. The temperature-independent contribution to the CME  $\Delta\eta(\omega)$  is significant, constituting more than 20% of  ${}_mC(\lambda, T)$ . By contrast,  $b(\omega)$  contributes less than 5% to  ${}_mQ(\lambda, T)$ .

In the absence of London coupled-cluster calculations, we have used B3LYP magnetizability anisotropies in our CME studies. For  $\text{BF}_3$ , the anisotropy varies little with the functional—for example, use of the KT1 rather B3LYP anisotropy changes the CME constant and birefringence by only 3% in the aug-cc-pVTZ basis.

The higher-order electric properties offer a different challenge to theory than do dipole polarizabilities, as illustrated by the slower basis-set convergence and the larger electron-correlation contribution. Thus, the inclusion of correlation at the DFT level increases  $\Delta\eta(\omega)$  and  $b(\omega)$  relative to the Hartree-Fock value by at least 60% and 50%, respectively; sometimes by more than 100%. Note that  $\Delta\eta(\omega)$  is obtained, at all levels of theory, without London orbitals, which have not yet been implemented for cubic response functions in DALTON. In these calculations, we used the center of nuclear mass as the gauge origin.

The slower convergence without London orbitals is reflected in the calculated birefringence constants  ${}_mC(\lambda, T)$

and  ${}_mQ(\lambda, T)$ , and in the related birefringences. From our results, we conservatively estimate a Cotton-Mouton constant of  ${}_mC(\lambda, T)=(12 \pm 1) \times 10^{-19} \text{cm}^3 \text{G}^{-2} \text{mol}^{-1}$  ( $4\pi\epsilon_0$ ) and an associated birefringence of  $\Delta n_u(\lambda, T)=(7 \pm 1) \times 10^{-14}$ , defined for the conditions in Table IV. Similarly, we predict the BE constant to be  ${}_mQ(\lambda, T)=(-4.5 \pm 0.3) \times 10^{27}$  a.u., with an associated birefringence of  $\Delta n(\lambda, T)=(4.6 \pm 0.3) \times 10^{-15}$ .

The CME of  $\text{BF}_3$  has not yet been measured, but its Buckingham birefringence has been measured by Graham *et al.* in Ref. 24. These authors report a value of  $\Theta + 15b(\omega)kT/2\alpha_{\text{ani}}$  of  $(12.6 \pm 0.7) \times 10^{-40} \text{C m}^2$  at 20 °C, corresponding, once they assume a vanishing  $b(\omega)$  contribution, to  $\Theta=2.81 \pm 0.16$  a.u. Taking a few steps back in their derivation, considering that they assumed  $\alpha_{\text{ani}}(\omega)$  at 632.8 nm to be  $(-0.63 \pm 0.03) \times 10^{-40} \text{C}^2 \text{m}^2 \text{J}^{-1}$  ( $-3.8 \pm 0.2$  a.u.) and using for  $b(\omega)$  our CCSD/aug-cc-pVTZ result of Table IV ( $-47.6$  a.u.), we obtain the revised experimental quadrupole moment of  $\text{BF}_3$  of  $2.72 \pm 0.15$  a.u. introduced in Sec. IV B. In a similar manner, we can reconstruct a value of  ${}_mQ(\lambda, T)$  of  $(-3.9 \pm 0.2) \times 10^{27}$  a.u. at  $T=293.15$  K, as experimentally observed in Ref. 24, somewhat less negative than predicted *ab initio*. The discrepancy reflects the difference observed between the *ab initio* and revised quadrupole moments of boron trifluoride.



TABLE V. CME and BE for BCl<sub>3</sub> at  $\lambda=632.8$  nm and  $T=273.15$  K. a.u., with  ${}_mC(\lambda, T)$  in cgs units of  $\text{cm}^3 \text{G}^{-2} \text{mol}^{-1}$  ( $4\pi\epsilon_0$ ).  $\Delta n_u$  is the birefringence defined for an induction field  $B$  of 1 T and a pressure  $P$  of 1 atm according to Ref. 19.  $\Delta n$  for Buckingham birefringence is given for a pressure of  $P=1$  bar and EFG of  $\nabla E=-1 \times 10^9 \text{V m}^{-2}$ .

Wave function	Basis	CME			Buckingham		
		$\Delta\eta(\omega)$	${}_mC(\lambda, T) \times 10^{18}$	$\Delta n_u \times 10^{13}$	$b(\omega)$	${}_mQ(\lambda, T) \times 10^{-27}$	$\Delta n \times 10^{15}$
HF	aug-cc-pVDZ	410.6	8.78	5.29	-207.4	-9.509	9.58
	daug-cc-pVDZ	597.4	7.82	4.71	-278.9	-8.931	9.00
	aug-cc-pVTZ	488.7	9.14	5.50	-260.2	-9.221	9.29
	daug-cc-pVTZ	505.0	9.21	5.55	-285.0	-9.008	9.07
LDA-DFT	aug-cc-pVDZ	547.8	15.31	9.20	-247.6	-6.035	6.08
	daug-cc-pVDZ	874.4	15.19	9.12	-344.6	-5.996	6.04
	aug-cc-pVTZ	707.8	16.27	9.78	-311.7	-5.618	5.66
	daug-cc-pVTZ	775.4	16.54	9.94	-352.8	-5.521	5.56
B3LYP-DFT	aug-cc-pVDZ	509.5	12.72	7.65	-235.7	-9.002	9.07
	daug-cc-pVDZ	799.6	12.45	7.47	-328.1	-8.733	8.80
	aug-cc-pVTZ	642.8	13.13	7.89	-296.3	-8.592	8.65
	daug-cc-pVTZ	701.3	13.34	8.01	-336.2	-8.341	8.40
KT1-DFT	aug-cc-pVDZ	571.0	11.25	6.76	-261.9	-5.555	5.59
	daug-cc-pVDZ	905.2	11.21	6.73	-360.6	-5.401	5.44
	aug-cc-pVTZ	739.8	11.87	7.13	-325.9	-5.631	5.67
	daug-cc-pVTZ	812.0	12.47	7.49	-369.8	-5.532	5.57
CCSD <sup>a</sup>	aug-cc-pVDZ	446.6	12.30	7.31	-227.6	-9.206	9.27
	daug-cc-pVDZ	692.4	11.84	7.04	-310.1	-8.536	8.60
	aug-cc-pVTZ	547.7	12.40	7.37	-284.7	-7.809	7.87
Extrapolated from experiment			$8.2 \pm 0.7^b$	$4.9 \pm 0.7^b$			

<sup>a</sup>B3LYP-DFT GIAO magnetizability anisotropies are employed in place of the non-GIAO CCSD results.

<sup>b</sup>Data in Refs. 10 and 11 fitted in this work, assuming linear regression with a  $T \rightarrow \infty$  value of  ${}_mC(\lambda, T)$  equal to our B3LYP-DFT/daug-cc-pVTZ “best value” of  $\Delta\eta(\omega)=701.3$  a.u.

## 2. BCl<sub>3</sub>

The data employed in the study of the Cotton-Mouton and Buckingham birefringences of BCl<sub>3</sub> in Table V are listed in Tables II and III, combined with the higher-order contribution in Table V. Figure 1 reports the experimental data obtained in the 295.6–361.9-K temperature range by Lamb and Ritchie<sup>10,11</sup> for the CME of boron trichloride, comparing it with the *ab initio* results obtained in the largest basis sets.

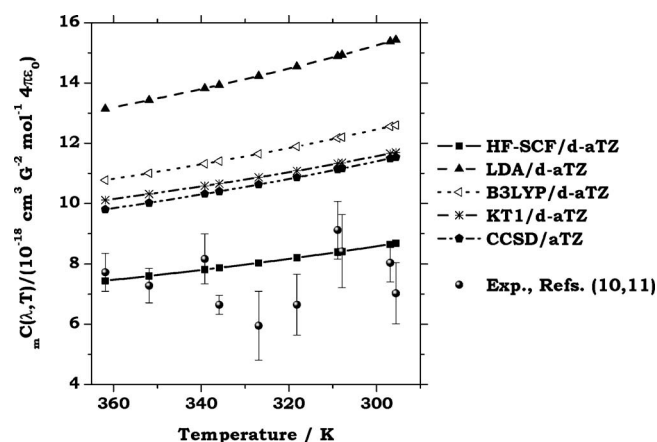


FIG. 1. The temperature dependence of the CME of BCl<sub>3</sub> as computed here, compared to the experiment. The labels “aTZ” and “d-aTZ” stand for aug-cc-pVTZ and daug-cc-pVTZ, respectively.

As for BF<sub>3</sub>, the London B3LYP (rather than non-London CCSD) magnetizability anisotropies are used for the Cotton-Mouton constant and for the corresponding birefringence. The magnetizability anisotropy depends more critically on the density functional for BCl<sub>3</sub> than for BF<sub>3</sub>; for example, use of the KT1 rather than B3LYP anisotropies modifies the aug-cc-pVTZ Cotton-Mouton constant by about 20%.

The results presented here allow us to compare the performance of KT1 for electric and magnetic properties. Thus, for the CME constant (which includes magnetic properties via  $\xi_{\text{ani}}$ ) and associated birefringence, the KT1 values agree well with the CCSD results and with B3LYP, and they are close to the area where experimental data are distributed, see Fig. 1. Still, it is the Hartree-Fock method that yields results closest to the experiment, whereas LDA is rather off target. By contrast, for the BE, which depends only on the electric properties, the agreement of KT1 with the CCSD (and B3LYP) results is poorer and similar to that of the LDA functional.

The temperature-independent CME contribution is similar to that of BF<sub>3</sub>, with  $\Delta\eta(\omega)$  contributing about 20% to  ${}_mC(\lambda, T)$ . By contrast,  $b(\omega)$  contributes more than 10% to the Buckingham constant  ${}_mQ(\lambda, T)$  of BCl<sub>3</sub>, twice the amount of BF<sub>3</sub>. In their experimental study of the CME, Lamb and Ritchie<sup>10,11</sup> were unable to identify the temperature-independent contribution by extrapolation to infinite tem-

perature because of the smallness of the effect and limited experimental precision, forcing the authors to ignore  $\Delta\eta(\omega)$  in the derivation of  $\xi_{\text{ani}}$ . However, they did suggest that the temperature-independent contribution may easily account for 10% of the measured value of  ${}_mC(\lambda, T)$ , increasing the magnitude of the experimentally derived  $|\xi_{\text{ani}}|$ . Indeed, our study indicates a temperature-independent contribution of about 20%. In Table V, we have listed an experimental value for the CME of  $\text{BCl}_3$ , but note that this value has been extrapolated to 273.15 K from a linear regression of the experimental data.<sup>10,11</sup>

In view of the neglected temperature-independent contribution in the paper of Ritchie and Lamb,<sup>10,11</sup> we have re-derived the value for  $\xi_{\text{ani}}$ . If their experimental data are fitted such that the line, Eq. (2), passes through our estimated intercept (B3LYP/daug-cc-pVTZ,  $\Delta\eta=701.3$  a.u.), and if the same value assumed by Lamb and Ritchie is taken for the anisotropy of the electric dipole polarizability ( $\alpha_{\text{ani}}=-21.5\pm 0.7$ ),<sup>9</sup> then the experimental estimate for  $\xi_{\text{ani}}$  is revised to  $-0.45\pm 0.09$  a.u. We have no estimates of the effects of vibrations on the magnetizability of  $\text{BCl}_3$ . However, some preliminary results for  $\text{BF}_3$ , obtained as for the quadrupole moment, see Sec. IV B, at the Hartree-Fock level and with the daug-cc-pVTZ basis set, indicate that the effect of ZPV average on the magnetizability anisotropy is in that case of  $\approx 5\%$  the purely electronic property. We have no reason to suspect that ZPV average might play a much stronger role in  $\text{BCl}_3$ . Other sources of error, as, for example, the effect of relativity, are most likely even less important. We therefore conclude that the error bar of 0.09 a.u. given in Ref. 10 for the magnetizability anisotropy of  $\text{BCl}_3$ , and which takes into account also systematic errors, is probably too small.

We predict a Cotton-Mouton constant of  ${}_mC(\lambda, T)=(13\pm 2)\times 10^{-18}$  cm<sup>3</sup> G<sup>-2</sup> mol<sup>-1</sup> ( $4\pi\epsilon_0$ ) with an associated birefringence of  $\Delta n_u(\lambda, T)=(7.5\pm 1.0)\times 10^{-13}$ , under the conditions in Table V. With the exception of Hartree-Fock, which displays a surprisingly excellent performance, we are outside the error bars of the experiment, and overestimate the effect. In view of what we have shown above, it is rather unlikely that the causes of discrepancy between our electron-correlated results and the experiment would be removed by a proper account of the effect of molecular vibrations.

Finally, we predict the BE constant to be  ${}_mQ(\lambda, T)=(-8\pm 1)\times 10^{27}$  a.u. with an associated birefringence of  $\Delta n(\lambda, T)=(8\pm 1)\times 10^{-15}$ . No experimental measurements are available for these constants.

## V. CONCLUSION

We have presented the results of the Hartree-Fock, DFT, and CCSD studies of the electric and magnetic properties of  $\text{BF}_3$  and  $\text{BCl}_3$ —including the magnetizability anisotropy, quadrupole moment, frequency-dependent electric dipole polarizability, and higher-order response properties—all associated with Cotton-Mouton and Buckingham linear birefringences. Basis-set convergence has been examined and basis-set limits established. The performance of DFT is excellent. In particular, the hybrid B3LYP functional gives the best

results, with the Keal-Tozer functionals performing less satisfactorily for electric properties than for magnetic properties.

The agreement with the experimental data is satisfactory, particularly in view of the neglect of molecular vibrations. The temperature-independent contribution to the Cotton-Mouton birefringence is about 20% for both molecules, whereas the contributions to the BE are about 5% and 10% for  $\text{BF}_3$  and  $\text{BCl}_3$ , respectively.

We have carried a detailed and systematic investigation of the molecular quadrupole moment of both molecules, yielding  $3.00\pm 0.01$  and  $0.71\pm 0.01$  a.u. for  $\text{BF}_3$  and  $\text{BCl}_3$ , respectively. For  $\text{BF}_3$ , this value is within two standard deviations of our revised experimental measurement, while for  $\text{BCl}_3$  our value supports the claims of Ritchie<sup>10,11,13</sup> that the measurement of Gierszal *et al.*<sup>12</sup> is inaccurate.

A revision of the linear regression analysis of the CME measurements in  $\text{BCl}_3$  performed by Lamb and Ritchie<sup>10,11</sup> yields a revised value of the magnetizability anisotropy of boron trichloride,  $\xi_{\text{ani}}=-0.45\pm 0.09$  a.u., almost 40% less negative than the original estimate, and in disagreement with our best *ab initio* results. The Cotton-Mouton constant of  $\text{BCl}_3$  is indeed overestimated by our electron-correlated approaches in the whole range of temperatures of the original experiment, whereas Hartree-Fock performs excellently. The origin of these discrepancies is apparently not ascribable to the neglect of the effect of molecular vibrations.

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<sup>1</sup> Y. Pak and R. C. Woods, J. Chem. Phys. **106**, 6424 (1997).

<sup>2</sup> K. K. Baeck and R. J. Bartlett, J. Chem. Phys. **106**, 4604 (1997).

<sup>3</sup> C. W. Bauschlicher and A. Ricca, J. Phys. Chem. A **103**, 4313 (1999).

<sup>4</sup> H. C. Brown and R. R. Holmes, J. Am. Chem. Soc. **78**, 2173 (1956).

<sup>5</sup> F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1980).

<sup>6</sup> T. Brinck, J. S. Murray, and P. Politzer, Inorg. Chem. **32**, 2622 (1993).

<sup>7</sup> V. Jones, G. Frenking, and M. T. Reetz, J. Am. Chem. Soc. **116**, 8741 (1994).

<sup>8</sup> S. Fau and G. Frenking, Mol. Phys. **96**, 519 (1999).

<sup>9</sup> R. I. Keir and G. L. D. Ritchie, Chem. Phys. Lett. **290**, 409 (1998).

<sup>10</sup> D. W. Lamb and G. L. D. Ritchie, Chem. Phys. Lett. **310**, 150 (1999).

<sup>11</sup> D. W. Lamb and G. L. D. Ritchie, Chem. Phys. Lett. **317**, 653 (2000).

<sup>12</sup> S. Gierszal, J. Galica, and E. Miś-Kuźminńska, Phys. Scr. **67**, 525 (2003).

<sup>13</sup> G. L. D. Ritchie, Phys. Scr. **69**, 403 (2004).

<sup>14</sup> E. B. Graham and R. E. Raab, Mol. Phys. **52**, 1241 (1984).

<sup>15</sup> A. Rizzo and S. Coriani, Adv. Quantum Chem. (in press).

<sup>16</sup> A. Cotton and H. Mouton, C. R. Hebd. Seances Acad. Sci. **141**, 317 (1905).

<sup>17</sup> A. Cotton and H. Mouton, C. R. Hebd. Seances Acad. Sci. **141**, 349 (1905).

<sup>18</sup> A. D. Buckingham, J. Chem. Phys. **30**, 1580 (1959).

<sup>19</sup> C. Rizzo, A. Rizzo, and D. M. Bishop, Int. Rev. Phys. Chem. **16**, 81 (1997).

- <sup>20</sup> S. Coriani, A. Halkier, and A. Rizzo, in *Recent Research Developments in Chemical Physics*, edited by G. Pandarai (Transworld Scientific, Kerala, India, 2001), Vol. 2, p. 1.
- <sup>21</sup> A. Rizzo, C. Cappelli, B. Jansík, D. Jonsson, P. Salek, S. Coriani, and H. Ågren, *J. Chem. Phys.* **121**, 8814 (2004).
- <sup>22</sup> A. Rizzo, C. Cappelli, B. Jansík *et al.*, *J. Chem. Phys.* **122**, 234314 (2005).
- <sup>23</sup> A. D. Buckingham, in *Physical Chemistry, an Advanced Treatise*, edited by H. Eyring, D. Henderson, and W. Yost (Academic, New York, 1970), Vol. 4.
- <sup>24</sup> C. Graham, D. A. Imrie, and R. E. Raab, *Mol. Phys.* **93**, 49 (1998).
- <sup>25</sup> A. D. Buckingham and R. L. Disch, *Proc. R. Soc. London, Ser. A* **273**, 275 (1963).
- <sup>26</sup> R. I. Keir, D. W. Lamb, G. L. D. Ritchie, and J. N. Watson, *Chem. Phys. Lett.* **279**, 22 (1997).
- <sup>27</sup> S. Coriani, C. Hättig, P. Jørgensen, A. Rizzo, and K. Ruud, *J. Chem. Phys.* **109**, 7176 (1998).
- <sup>28</sup> C. Cappelli, U. Ekström, A. Rizzo, and S. Coriani, *J. Comput. Methods Sci. Eng.* **4**, 365 (2004).
- <sup>29</sup> J. M. Junquera-Hernández, J. Sánchez-Marín, V. Pérez-Mondéjar, and A. S. de Merás, *Chem. Phys. Lett.* **378**, 211 (2003).
- <sup>30</sup> S. E. Novick, *J. Phys. Chem.* **90**, 3871 (1986).
- <sup>31</sup> D. J. D. Wilson, T. Helgaker, and A. Rizzo, *Mol. Phys.* (in press).
- <sup>32</sup> U. Fleischer and M. Schindler, *Chem. Phys.* **120**, 103 (1988).
- <sup>33</sup> P. O. Åstrand and K. V. Mikkelsen, *Magn. Reson. Chem.* **36**, 92 (1998).
- <sup>34</sup> K. Ruud, T. Helgaker, P. Jørgensen, and K. L. Bak, *Chem. Phys. Lett.* **223**, 12 (1994).
- <sup>35</sup> K. Ruud, P. O. Åstrand, and P. R. Taylor, *J. Phys. Chem. A* **105**, 9926 (2001).
- <sup>36</sup> H. Fukaya and T. Ono, *J. Comput. Chem.* **25**, 51 (2003).
- <sup>37</sup> D. J. D. Wilson, C. E. Mohn, and T. Helgaker, *J. Chem. Theory Comput.* (to be published).
- <sup>38</sup> DALTON, a molecular electronic structure program, Release 2.0, 2005; see <http://www.kjemi.uio.no/software/dalton/dalton.html>
- <sup>39</sup> G. L. D. Ritchie and J. Vrbancich, *Aust. J. Chem.* **35**, 869 (1982).
- <sup>40</sup> J. Hernández-Trujillo and A. Vela, *J. Phys. Chem.* **100**, 6524 (1996).
- <sup>41</sup> G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- <sup>42</sup> J. Kerr, *Philos. Mag.* **50**, 337 (1875).
- <sup>43</sup> J. Kerr, *Philos. Mag.* **50**, 446 (1875).
- <sup>44</sup> A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc. London, Sect. B* **69**, 1133 (1956).
- <sup>45</sup> A. D. Buckingham and H. C. Longuet-Higgins, *Mol. Phys.* **14**, 63 (1968).
- <sup>46</sup> A. D. Buckingham and M. J. Jamieson, *Mol. Phys.* **22**, 117 (1971).
- <sup>47</sup> D. A. Imrie and R. E. Raab, *Mol. Phys.* **74**, 833 (1991).
- <sup>48</sup> J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Pt. II, p. 857.
- <sup>49</sup> A. Rizzo and S. Coriani, *J. Chem. Phys.* **119**, 11064 (2003).
- <sup>50</sup> S. Yamamoto, R. Kuwabara, M. Takami, and K. Kuchitsu, *J. Mol. Spectrosc.* **115**, 333 (1986).
- <sup>51</sup> J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pole, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Group II Atomic and Molecular Physics*, edited by K. H. Hellwege and A. M. Hellwege (Springer, New York, 1976), Vol. 7, Chap. 2, p. 15.
- <sup>52</sup> B. Jansík, P. Salek, D. Jonsson, O. Vahtras, and H. Ågren, *J. Chem. Phys.* **122**, 054107 (2005).
- <sup>53</sup> B. Jansík, *Density functional theory for molecular properties*, Ph.D. thesis, KTH Biotechnology, Stockholm, Sweden, 2004.
- <sup>54</sup> M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.
- <sup>55</sup> S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- <sup>56</sup> A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>57</sup> T. W. Keal and D. J. Tozer, *J. Chem. Phys.* **119**, 3015 (2003).
- <sup>58</sup> T. W. Keal and D. J. Tozer, *J. Chem. Phys.* **121**, 5654 (2004).
- <sup>59</sup> T. W. Keal, D. J. Tozer, and T. Helgaker, *Chem. Phys. Lett.* **391**, 374 (2004).
- <sup>60</sup> T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>61</sup> K. Hald and P. Jørgensen, *Phys. Chem. Chem. Phys.* **4**, 5221 (2002).
- <sup>62</sup> O. Christiansen, A. Halkier, H. Koch, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **108**, 2801 (1998).
- <sup>63</sup> A. Halkier, H. Koch, O. Christiansen, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **107**, 849 (1997).
- <sup>64</sup> C. Hättig, O. Christiansen, H. Koch, and P. Jørgensen, *Chem. Phys. Lett.* **269**, 428 (1997).
- <sup>65</sup> T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Phys. Chem.* **106**, 9639 (1997).
- <sup>66</sup> A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- <sup>67</sup> T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 1999).
- <sup>68</sup> G. L. D. Ritchie and J. N. Watson, *Chem. Phys. Lett.* **322**, 143 (2000).
- <sup>69</sup> H. E. Watson and K. L. Ramaswamy, *Proc. R. Soc. London, Ser. A* **156**, 144 (1936).
- <sup>70</sup> L. Pauling, *The Nature of the Chemical Bond*, 2nd. ed. (Cornell University Press, Ithaca, NY, 1940).
- <sup>71</sup> W. L. Meerts and I. Ozier, *J. Chem. Phys.* **75**, 596 (1981).
- <sup>72</sup> A. W. Ellenbroek and A. Dymanus, *Chem. Phys.* **35**, 227 (1978).
- <sup>73</sup> A. J. Russell and M. A. Spackman, *Mol. Phys.* **98**, 633 (2000).
- <sup>74</sup> A. A. Maryott and F. Buckley, *Circular No. 537* (National Bureau of Standards, Washington DC, 1953), p. 11.
- <sup>75</sup> R. J. W. LeFèvre, *Proc. Chem. Soc.*, London **1958**, 283.