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ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · JULY 2005

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Density-functional theory study of electric and magnetic properties of hexafluorobenzene in the vapor phase

Antonio Rizzo,^{a)} Chiara Cappelli,^{b)} and Branislav Jansík

Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, via G. Moruzzi 1, I-56124 Pisa, Italy

Dan Jonsson

Department of Physics, Stockholm University, AlbaNova SE-10691, Stockholm, Sweden

Paweł Sałek

Laboratory of Theoretical Chemistry, The Royal Institute of Technology, SE-10691 Stockholm, Sweden

Sonia Coriani

Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, via L. Giorgieri 1, I-34127 Trieste, Italy

David J. D. Wilson and Trygve Helgaker

Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway

Hans Ågren

Laboratory of Theoretical Chemistry, The Royal Institute of Technology, SE-10691 Stockholm, Sweden

(Received 6 April 2005; accepted 25 April 2005; published online 21 June 2005)

A series of electric and magnetic properties of hexafluorobenzene have been calculated, including the electric dipole polarizability, magnetizability, electric quadrupole moment, and nonlinear mixed electric dipole-magnetic dipole-electric quadrupole hyperpolarizabilities needed to obtain estimates of the Kerr, Cotton-Mouton, Buckingham, Jones, and magnetoelectric birefringences in the vapor phase. Time-dependent density-functional theory was employed for the calculation of linear-, quadratic, and cubic response functions. A number of density functionals have been considered, along with Sadlej's triple- ζ basis set and the augmented correlation-consistent polarized valence double zeta and augmented correlation-consistent polarized valence triple zeta basis sets. Comparisons have been made with experiment where possible. The analysis of results allows for an assessment of the capability of time-dependent density-functional theory for high-order electromagnetic properties of an electron-rich system such as hexafluorobenzene.

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I. INTRODUCTION

In a recent paper,¹ the authors presented the results of an extended computational study, carried out by employing density-functional and coupled-cluster theories up to cubic response of five linear birefringences,² namely, Kerr, Cotton-Mouton, Buckingham, Jones, and magnetoelectric in vapors of benzene. The analysis yielded values for electric dipole polarizability, magnetizability, and electric quadrupole moment in excellent agreement with the available experimental data. The experimental reference was a recent study of the temperature dependence of the Buckingham effect in benzene and hexafluorobenzene carried out by Ritchie and Watson,³ who derived, compiled, and discussed several electric and magnetic properties of C_6H_6 and C_6F_6 .

The magnetic and electric properties of benzene have been widely studied, largely due to the relationship existing between benzene and the chemical concept of aromaticity. The perfluorinated benzene species have also attracted significant experimental^{4,5,3} and theoretical⁶⁻⁸ attention. These

studies have highlighted the differences in molecular magnetic and electric properties between C_6H_6 and C_6F_6 . For example, from birefringence studies Ritchie and Vrbancich⁵ found that the derived magnetizability anisotropies of C_6F_6 and C_6Cl_6 were far larger than may be expected, since halogenation of benzene should *reduce* the magnetizability anisotropy. Traditionally, it was assumed that the temperature-dependent contribution to the measured birefringence of the halogenated benzenes was negligible.^{9,10} However, Ritchie and Vrbancich⁵ concluded that this assumption was invalid for halogenated benzenes. This observation led to a re-evaluation of some of the basic postulates made in the analysis of the measured birefringences.⁵

Hernández-Trujillo and Vela⁸ have carried out a Hartree-Fock study of the electric quadrupole moment of the series of fluoro- and chlorobenzenes. While the quadrupole moment of C_6H_6 is converged within 1 a.u. (15%) with a modest double- ζ basis set, successive fluorination significantly reduces the basis set convergence to the point that it is not apparent, if the Hartree-Fock quadrupole moment might be considered converged within the same 1-a.u. accuracy (again 15%) with a triple- ζ basis set. Successive fluorination of ben-

^{a)}Electronic mail: rizzo@ipcf.cnr.it

^{b)}Present address: PolyLab, INFN, Pisa.

zene distorts the electron density, thus it might be expected that the response of the density to the applied electric and magnetic fields and electric field gradients would also be more complicated compared to that of benzene.

The challenges faced in calculating the magnetic properties of fluorine-containing molecules are well known.^{11,7,12–14} For example, it was demonstrated by Ruud *et al.*^{12,13} that the additivity of magnetizabilities (known as Pascal's rule) actually breaks down for fluorine-containing species. To calculate experimentally accurate results, extensive basis sets are required. Moreover, where applicable, the gauge dependence of magnetic properties must be taken into account.¹³

In this work we extend the detailed analysis of C₆H₆ given in Ref. 1, presenting and discussing the results of a computational study of the optical Kerr, Cotton-Mouton, Buckingham, Jones, and magnetoelectric linear birefringences of C₆F₆. In light of the significant challenges that this large and electron-rich species poses to theory, we have taken a different approach from that exploited for C₆H₆. While for benzene we could employ coupled-cluster theory, it is not yet feasible to carry out routine coupled-cluster calculations of higher-order properties for such a system as C₆F₆, with more than twice the number of electrons as benzene. However, with the availability of experimental data for comparison, C₆F₆ is an ideal choice to test the efficacy and accuracy of density-functional theory (DFT) for such higher-order properties. Moreover, the system is a good test for the recently implemented code allowing the calculation of DFT magnetizabilities with London atomic orbitals [i.e., gauge-invariant atomic orbital (GIAO)].¹⁵ In Ref. 1 the effect of employing different functionals for the energy and property calculations was investigated for C₆H₆. This approach was based on the hypothesis of van Gisbergen *et al.*¹⁶ that the functional requirements for ground-state energies and other properties may be different. However, it was concluded that the “standard” single-functional approach in general yields more satisfactory results than does the dual-functional approach.¹ As a result we employ the usual single-functional approach in this work, with only one exception; we have included in our choice of functionals a combination of the local density approximation (LDA) functional¹⁷ and the van Leeuwen–Baerends exchange-correlation potential (LB94),¹⁸ where the LB94 correction is only employed to the LDA potential and not to the higher-order kernels (labeled LB94/LDA as in Ref. 1).

II. DEFINITIONS

Linear birefringences—that is, differences in the refractive index for linearly polarized light along two optical axes perpendicular to each other and to the direction of propagation—are most commonly induced by applying static electric and/or magnetic fields perpendicular to the direction of propagation of the beam. They provide a route to the experimental determination of some important molecular properties and constitute a sensitive probe of the response of matter to an external electromagnetic perturbation.²

The anisotropy of the refractive index $\Delta n(\omega, T)$ at a circular frequency ω (the corresponding wavelength is

$\lambda = 2\pi c/\omega$, c is the speed of light in the medium), temperature T , and for an optical path length l is related to the retardance ϕ (the observable) by

$$\phi = \frac{2\pi l}{\lambda} \Delta n(\omega, T). \quad (1)$$

The general expression for $\Delta n(\omega, T)$ as a function of molecular properties and of the parameters characterizing the electromagnetic radiation can be expressed as

$$\Delta n(\omega, T) = n_\theta - n_{\theta+90^\circ} = k_i F_1^{n_1} F_2^{n_2} {}_m W(\omega, T), \quad (2)$$

where F_1 and F_2 identify the field strengths raised to the corresponding powers n_1 and n_2 . θ is the angle formed by the direction of the primary optical axis and that of the field \mathbf{F}_1 . The quantity k_i is a combination of fundamental constants, which depends on the specific process, as does the molar quantity ${}_m W(\omega, T)$. The latter is usually identified as the “constant” for the particular birefringence in question (Kerr, Cotton-Mouton, Buckingham, or Jones). At a fixed pressure and in the absence of permanent magnetic dipole moments, ${}_m W(\omega, T)$ can be written as

$${}_m W(\omega, T) = A_0(\omega) + \frac{A_1(\omega)}{T}. \quad (3)$$

In Table I we list (for D_{6h} symmetry molecules) the specific field dependence of the birefringences of interest in this work—that is, the identity of the various parameters in Eqs. (2) and (3). The angle θ dependence detailed in Table I relates to the specific birefringence phenomenon considered. In the Kerr (KE) and Cotton-Mouton (CME) effects, the birefringences are quadratic in the electric- and magnetic-induction field strengths, respectively. The Jones (JB) and magnetoelectric (MEB) birefringences are both bilinear in the two fields—they share the molar constant expression, ${}_m J(\omega)$, but differ in the direction of the optical axes. Buckingham's effect (BE) is linear in the strength of the electric-field gradient.

The molecular properties mediating the $A_1(\omega)$ contribution to the birefringences studied here are the anisotropies of the static and frequency-dependent electric dipole polarizabilities $\alpha_{\alpha\beta}(0)$ and $\alpha_{\alpha\beta}(\omega)$ as (z is the principal symmetry axis in this section)

$$\alpha_{\text{ani}}(\omega) = \alpha_{zz}(\omega) - \alpha_{xx}(\omega); \quad (4)$$

the anisotropy of the magnetizability, $\xi_{\alpha\beta}$, defined as

$$\xi_{\text{ani}} = \xi_{zz} - \xi_{xx} \quad (5)$$

and the permanent traceless electric quadrupole moment (symmetry-unique component) $\Theta = \Theta_{zz}$. The $A_0(\omega)$ coefficient relates to specific combinations of higher-order frequency-dependent properties such as the dynamic second electric dipole hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}(-\omega; \omega, 0, 0)$ (Refs. 19–21) [the wavelength arguments are sometimes omitted below for brevity],

TABLE I. The birefringences studied here. W indicates the symbol commonly used to indicate the molar constant, ϵ_0 is the vacuum permittivity, μ_0 is the vacuum permeability, V_m is the molar volume, k is the Boltzmann constant, N_A is Avogadro's number, and E , B , and ∇E are the strengths of the electric field, the magnetic induction field, and the electric field gradient, respectively.

	θ	F_1	n_1	F_2	n_2	k_i	W	$A_0(\omega)$	$A_1(\omega)$
Kerr	0°	E	2	\cdots	\cdots	$\frac{27}{2V_m}$	K	$\frac{N_A}{81\epsilon_0}\gamma_K(\omega)$	$\frac{N_A}{405k\epsilon_0}\alpha_{\text{ani}}(\omega)\alpha_{\text{ani}}(0)$
Cotton-Mouton	0°	B	2	\cdots	\cdots	$\frac{27}{2V_m(4\pi\epsilon_0)}$	C	$\frac{2\pi N_A}{27}\Delta\eta(\omega)$	$\frac{4\pi N_A}{405k}\alpha_{\text{ani}}(\omega)\xi_{\text{ani}}$
Buckingham	0°	∇E	1	\cdots	\cdots	$\frac{3}{2V_m}$	Q	$\frac{N_A}{3\epsilon_0}b(\omega)$	$\frac{2N_A}{45k\epsilon_0}\Theta\alpha_{\text{ani}}(\omega)$
Jones ^a	-45°	E	1	B	1	$\frac{\sqrt{\epsilon_0\mu_0}}{V_m}$	J	$\frac{N_A}{30\epsilon_0}\Lambda(\omega)$	0
Magnetoelectric ^b	0°	E	1	B	1	$\frac{\sqrt{\epsilon_0\mu_0}}{V_m}$	J	$\frac{N_A}{30\epsilon_0}\Lambda(\omega)$	0

^aThe two fields (electric and magnetic) are parallel to each other and are both perpendicular to the direction of propagation of the beam.

^bThe two fields (electric and magnetic) are perpendicular to each other and are both perpendicular to the direction of propagation of the beam.

$$\gamma_K(\omega) = \frac{1}{5}(\gamma_{xyxy} - \gamma_{xxzz} + 7\gamma_{xyyx} + 6\gamma_{zxxz} - \gamma_{zzxx} + \gamma_{zzzz}), \quad (6)$$

the anisotropy of the hypermagnetizability, $\eta_{\alpha\beta,\gamma\delta}(-\omega; \omega, 0, 0)$,^{22,23}

$$\Delta\eta(\omega) = \frac{1}{15}(7\eta_{xx,xx} - 5\eta_{xx,yy} + 2\eta_{zz,zz} - 2\eta_{xx,zz} - 2\eta_{zz,xx} + 12\eta_{xz,xz}), \quad (7)$$

and²⁴⁻²⁶

$$b(\omega) = \Sigma B(\omega) - \Sigma \mathcal{B}(\omega) - \Sigma J'(\omega), \quad (8)$$

where $b(\omega)$ is a linear combination of electric dipole-electric dipole-electric quadrupole $B_{\alpha\beta,\gamma\delta}(-\omega; \omega, 0, 0)$, electric dipole-electric quadrupole-electric dipole $\mathcal{B}_{\alpha,\beta\gamma,\delta}(-\omega; \omega, 0, 0)$, and electric dipole-magnetic dipole-electric dipole $J'_{\alpha,\beta,\gamma}(-\omega; \omega, 0)$ mixed hypersusceptibilities,

$$\Sigma B(\omega) = \frac{2}{15}(B_{zz,zz} - B_{xx,yy} + 3B_{xx,xx} + 4B_{xz,xz}), \quad (9)$$

$$\Sigma \mathcal{B}(\omega) = \frac{2}{15}(\mathcal{B}_{z,zz,z} + 2\mathcal{B}_{x,xx,x} + 2\mathcal{B}_{x,xy,y} + 2\mathcal{B}_{z,z,x} + 2\mathcal{B}_{x,x,z}), \quad (10)$$

$$\Sigma J'(\omega) = \frac{4}{3\omega}(J'_{x,y,z} + J'_{z,x,y} + J'_{y,z,x}). \quad (11)$$

Finally, in the Jones and magnetoelectric birefringences,²⁷⁻³⁰ the “Jones constant”¹ $mJ(\omega)$ has, to the lowest order in perturbation theory, only a T -independent contribution A_0 , which is proportional to $\Lambda(\omega)$,

$$\Lambda(\omega) = G_\Lambda(\omega) + \omega a'_\Lambda(\omega), \quad (12)$$

which is a combination of mixed electric dipole, electric quadrupole, and magnetic dipole hypersusceptibilities, $G_{\alpha,\beta\gamma,\delta}$ and $a'_{\alpha,\beta\gamma,\delta,\epsilon}$,

$$G_\Lambda(\omega) = 8G_{x,xx,x} + 6G_{x,yx,y} + 6G_{z,xz,x} + 6G_{x,zx,z} + 6G_{x,yy,x} + 6G_{z,xx,z} + 6G_{x,zz,x} - 4G_{x,xy,y} - 4G_{z,zx,x} - 4G_{x,xz,z} + 4G_{z,zz,z}, \quad (13)$$

$$a'_\Lambda(\omega) = a'_{x,xz,y} - a'_{x,yy,z} + 2a'_{x,xz,y,y} + a'_{x,zz,y,z} + a'_{y,xx,z,x} + a'_{y,xy,y,z} + a'_{y,xy,z,y} + 2a'_{y,xz,z,z} - a'_{y,yz,y,x} - a'_{y,zz,z,x} - a'_{z,xx,x,y} + 2a'_{z,xy,x,x} - a'_{z,xz,z,y} + a'_{z,yy,y,y} + a'_{z,yz,x,z}. \quad (14)$$

The nonlinear optical properties introduced above may conveniently be expressed in terms of quadratic and cubic response functions^{31,23,32,33} (see Ref. 1 for more details). As a result, all properties discussed here can be computed with high efficiency using analytical response theory with a variety of electronic structure models.³⁴

III. COMPUTATIONAL DETAILS

Development versions of the DALTON program,³⁵ which include DFT modules up to cubic response theory^{36,37} and magnetizabilities with London orbitals,¹⁵ are employed for all calculations. These were carried out at the experimental geometry.³⁸

The following DFT functionals were employed: LDA,¹⁷ Becke–Lee–Yang–Parr (BLYP),³⁹⁻⁴¹ Becke-3-parameter–Lee–Yang–Parr (B3LYP),^{42,40,39} and LB94/LDA (see Ref. 1). Note that our implementation of LDA and B3LYP corre-

TABLE II. Static and frequency-dependent electric dipole polarizability of C₆F₆. Atomic units, $\lambda=632.8$ nm.

Wave function	Basis	$\alpha_{xx}(0)$	$\alpha_{zz}(0)$	$\alpha_{iso}(0)$	$\alpha_{ani}(0)$	$\alpha_{xx}(\omega)$	$\alpha_{zz}(\omega)$	$\alpha_{iso}(\omega)$	$\alpha_{ani}(\omega)$
HF-SCF	Sadlej	79.75	41.05	66.85	-38.69	81.91	41.58	68.47	-40.33
LDA		91.64	43.67	75.65	-47.97	95.08	44.27	78.14	-50.81
LB94/LDA		87.79	40.46	72.01	-47.33	91.02	40.93	74.32	-50.08
BLYP		91.84	43.58	75.75	-48.26	95.29	44.19	78.26	-51.10
B3LYP		88.17	42.47	72.93	-45.69	91.20	43.04	75.14	-48.16
HF-SCF	aug-cc-pVDZ	79.48	40.27	66.41	-39.21	81.63	40.79	68.02	-40.84
LDA		90.87	42.66	74.80	-48.21	94.26	43.24	77.25	-51.02
LB94/LDA		87.03	39.88	71.32	-47.15	90.22	40.36	73.60	-49.85
BLYP		91.15	42.58	74.96	-48.56	94.57	43.18	77.44	-51.38
B3LYP		87.60	41.58	72.26	-46.02	90.60	42.14	74.45	-48.47
HF-SCF	aug-cc-pVTZ	79.92	40.97	66.94	-38.95	82.08	41.50	68.55	-40.59
LDA		91.74	43.71	75.73	-48.03	95.15	44.29	78.20	-50.86
LB94/LDA		88.21	41.07	72.50	-47.14	91.47	41.56	74.83	-49.91
BLYP		91.91	43.75	75.85	-48.15	95.34	44.36	78.35	-50.99
B3LYP		88.29	42.64	73.07	-45.65	91.31	43.20	75.27	-48.11
Expt. ^a		96.01±0.97	45.43±1.64	79.15±0.61	-50.58±2.30	84.91±1.03	42.09±1.46	70.66±0.61	-42.82±1.27

^aFrom Ref. 3.

sponds to the Vosko, Wilk, and Nusair (VWN) correlation functional V of Ref. 17. For comparison we have also carried out Hartree-Fock calculations. The basis sets used in this work for both carbon and fluorine are the augmented correlation-consistent polarized valence double zeta (aug-cc-pVDZ, 276 contracted functions) and augmented correlation-consistent polarized valence triple zeta (aug-cc-pVTZ, 552 contracted functions) sets together with Sadlej's triple- ζ set [10s6p4d|5s3p2d] (288 contracted functions).

All frequency-dependent properties are determined at a wavelength λ of 632.8 nm. Unless otherwise specified, atomic units are used. For conversion factors between atomic units and SI units, see Refs. 43 and 44 and the Appendix in Ref. 1.

IV. RESULTS AND DISCUSSION

The results obtained in this study for the electric and magnetic properties of hexafluorobenzene are presented in Tables II–V. A comparison between experiment and our results for the KE, CME, and BE is given in Figs. 1–3.

A. Electric dipole polarizability, magnetizability, and electric quadrupole moment

In Table II, the calculated static and dynamic ($\lambda = 632.8$ nm) electric dipole polarizabilities of hexafluorobenzene are reported and compared with experimental estimates taken from Ref. 3. Comparing Hartree-Fock and DFT results, it can be seen that electron correlation is important, particu-

TABLE III. Magnetizability and quadrupole moment of C₆F₆. Atomic units.

Wave function	Basis	ξ_{xx}	ξ_{zz}	ξ_{iso}	ξ_{ani}	Θ_{zz}
HF-SCF	Sadlej	-11.56	-13.60	-12.24	-2.04	7.11
LDA		-12.93	-13.81	-13.22	-0.87	5.19
LB94/LDA		-13.51	-15.50	-14.17	-1.98	9.63
BLYP		-13.53	-15.39	-14.15	-1.86	6.07
B3LYP		-13.53	-15.90	-14.32	-2.37	6.33
HF-SCF	aug-cc-pVDZ	-14.58	-15.63	-14.93	-1.05	7.18
LDA		-13.65	-19.96	-15.76	-6.31	5.12
LB94/LDA		-14.21	-21.61	-16.67	-7.40	9.49
BLYP		-13.57	-19.18	-15.44	-5.61	6.02
B3LYP		-13.80	-18.95	-15.52	-5.15	6.31
HF-SCF	aug-cc-pVTZ	-14.31	-23.04	-17.22	-8.73	7.30
LDA		-13.44	-21.42	-16.10	-7.97	5.18
LB94/LDA		-14.04	-23.08	-17.05	-9.04	9.46
BLYP		-13.38	-21.12	-15.96	-7.73	5.99
B3LYP		-13.60	-21.66	-16.29	-8.06	6.31
Expt. ^a		-14.1±0.5	-22.1±0.5	-16.7±0.5	-7.95±0.29	6.31±0.47

^aFrom Ref. 3.

TABLE IV. Dynamic second electric dipole hyperpolarizability and mixed electric dipole hypersusceptibilities (see text for definitions). Atomic units, $\lambda=632.8$ nm.

Wave function	Basis	$\gamma_K(\times 10^3)$	$b(\omega)$	$\Delta\eta(\omega)$	$\Lambda(\times 10^3)$
HF-SCF	Sadlej	3.24	-322	441	4.57
LDA		6.07	-443	582	8.27
LB94/LDA		4.19	-367	431	5.59
BLYP		6.61	-440	624	8.99
B3LYP		5.04	-397	551	7.13
HF-SCF	aug-cc-pVDZ	2.87	-293	315	2.52
LDA		5.39	-415	409	6.04
LB94/LDA		3.82	-344	293	3.31
BLYP		5.76	-411	452	6.93
B3LYP		4.64	-368	396	5.05
HF-SCF	aug-cc-pVTZ	3.25	-312	389	4.71
B3LYP		5.09	-395	479	7.05
Expt.		$(11 \pm 11) \times 10^3$ ^a	-2900 ± 2000 ^b	-100 ± 880 ^c	

^aReference 45.^bReference 3.^c $\lambda=441.6$ nm and $T=304.1$ K, with measurements in the temperature range 304.1–453.5 K, Ref. 47.

larly for the polarizability anisotropy. Including the correlation with DFT changes α_{xx} by 10%–16%, α_{zz} by 3%–5%, $\alpha_{iso} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz})$ by 7%–13%, and α_{ani} by 18%–26%. Basis set effects are much smaller.

The vibrational contribution to the electric dipole polarizability in hexafluorobenzene is large, particularly at the static limit.³ Indeed, the experimental static isotropic value, $\alpha_{iso}(0)$, is 8.5 a.u. (12%) larger than the

value at $\lambda=632.8$ nm. The significant influence of the intense in-plane stretching modes gives $\alpha_{xx}(0) \gg \alpha_{xx}(\omega)$, with a difference of about 12 a.u. leading to a negative experimental dispersion of the anisotropy: $\alpha_{ani}(0) > \alpha_{ani}(\omega)$. These strong vibrational effects make the comparison with experiment difficult for our purely electronic results.

One of the consequences is that neither Hartree-Fock nor the DFT functionals considered here were able to reproduce

TABLE V. Linear birefringences of C_6F_6 , $\lambda=632.8$ nm. Atomic units except where noted.

Wave function	Basis	Kerr effect ^a		CME ^b		Buckingham ^c		Jones ^d	
		${}_mK \times 10^{26}$	$\Delta n \times 10^{11}$	${}_mC \times 10^{16}$	$\Delta n_u \times 10^{12}$	${}_mQ \times 10^{-28}$	$\Delta n \times 10^{14}$	${}_mJ \times 10^{-26}$	$\Delta n \times 10^{15}$
HF-SCF	Sadlej	1.91	7.66	0.46	2.58	-11.23	11.31	11.52	3.54
LDA		2.98	11.98	0.26	1.47	-10.36	10.44	20.85	6.41
LB94/LDA		2.89	11.62	0.55	3.10	-18.84	18.97	14.10	4.33
BLYP		3.02	12.14	0.54	3.01	-12.17	12.26	22.67	6.97
B3LYP		2.69	10.81	0.64	3.58	-11.96	12.05	17.99	5.53
HF-SCF	aug-cc-pVDZ	1.95	7.85	0.24	1.36	-11.48	11.57	6.36	1.96
LDA		3.01	12.08	1.75	9.83	-10.26	10.34	15.23	4.68
LB94/LDA		2.87	11.51	2.00	11.24	-18.49	18.62	8.35	2.56
BLYP		3.05	12.26	1.57	8.83	-12.13	12.21	17.49	5.37
B3LYP		2.72	10.95	1.36	7.64	-11.98	12.06	12.73	3.91
HF-SCF	aug-cc-pVTZ	1.93	7.76	1.93	10.82	-11.60	11.68	11.88	3.65
B3LYP		2.69	10.79	2.11	11.84	-11.90	11.99	17.78	5.46
Derived from experiment		2.61 ± 0.17 ^e		1.46 ± 0.03 ^f	8.81 ± 0.18 ^f	-11.2 ± 1.2 ^g			
				1.68 ± 0.03 ^h	10.11 ± 0.17 ^h				

^a ${}_mK$ given in SI units of $V^{-2} m^5 mol^{-1}$. Pressure of 1 bar, $T=273.15$ K, and electric field strength E of 2.6×10^6 V m^{-1} .^b ${}_mC$ given in CGS units of $cm^3 G^{-2} mol^{-1}$ ($4\pi\epsilon_0$). Δn_u defined for an induction field B of 1 T, pressure P of 1 atm, and $T=273.15$ K.^c $T=273.15$ K, $P=1$ bar, and $\nabla E = -1 \times 10^9$ V m^{-2} .^d $T=273.15$ K, $P=1$ bar, $B=3$ T, and $E=2.6 \times 10^6$ V m^{-1} .^e $\lambda=632.8$ nm from Ref. 45. We have extrapolated their fitted temperature-dependence linear equation to $T=273.15$ K to calculate ${}_mK$.^f Δn from Ref. 46 with $\lambda=632.8$ nm and $T=273.15$ K. We have extrapolated their data to calculate ${}_mC$ to $T=273.15$ K.^g $\lambda=632.8$ nm from Ref. 3. We have extrapolated their fitted temperature-dependence linear equation to $T=273.15$ K to calculate ${}_mQ$.^h Δn measured at $\lambda=441.6$ nm and $T=304.1$ K across the temperature range 304.1–453.5 K, Ref. 47. We have extrapolated their data to 273.15 K to calculate ${}_mC$.

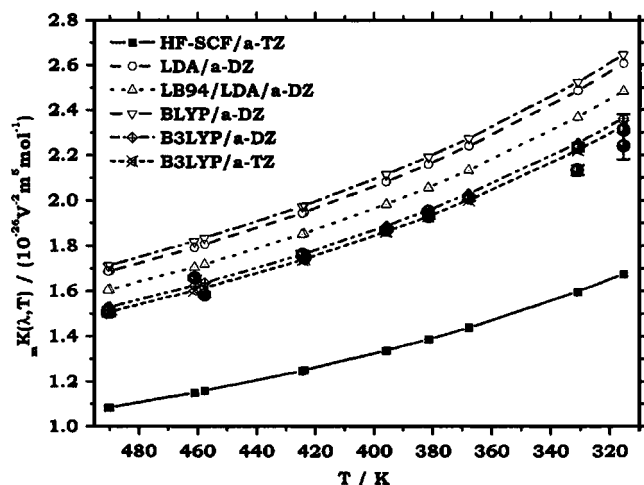


FIG. 1. The Kerr constant of hexafluorobenzene $mK(\lambda=632.8 \text{ nm}, T)$ as a function of temperature. Experimental data taken from Ref. 45. "a-DZ" and "a-TZ" here and in the remaining figures are shorthand notations for the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively.

the experimental perpendicular component of the electric dipole polarizability, in particular, $\alpha_{xx}(0)$. In contrast, the parallel component is typically calculated within the reported experimental error bars. The failure to reproduce the perpendicular component results in isotropic and anisotropic polarizabilities that differ from experiment, although correlated results agree for $\alpha_{\text{ani}}(0)$, mainly due to the large experimental error bar. To highlight the different responses of the electronic density in C_6F_6 and C_6H_6 , note that both Hartree-Fock and DFT/B3LYP accurately reproduce the experimental perpendicular component of C_6H_6 ,¹ whereas both methods yield parallel components outside three experimental standard deviations from the measured value.

Table III lists the calculated magnetizability properties of hexafluorobenzene along with the corresponding experimental data.³ Employing Sadlej's basis, the individual components and the isotropic value increase (in absolute value) by no more than 17% relative to Hartree-Fock. For LDA, the parallel and perpendicular components change by 1.5% and

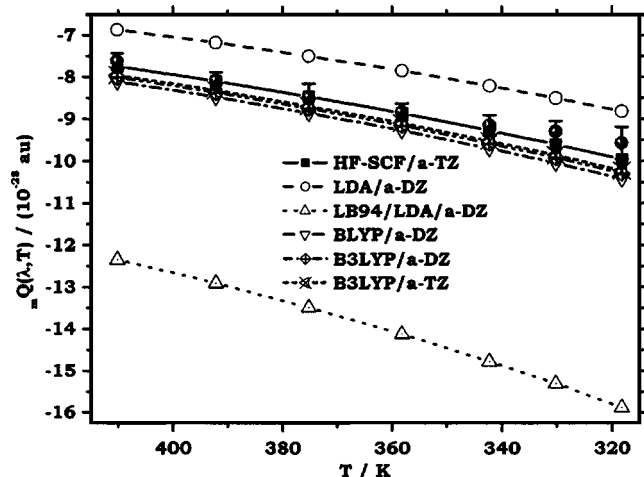


FIG. 2. The Buckingham constant of hexafluorobenzene $mQ(\lambda=632.8 \text{ nm}, T)$ as a function of temperature. Experimental data taken from Ref. 3.

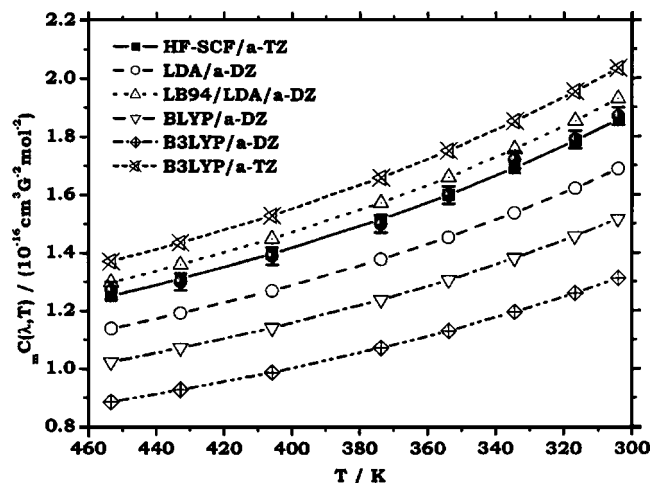


FIG. 3. The Cotton-Mouton constant of hexafluorobenzene $mC(\lambda=632.8 \text{ nm}, T)$ as a function of temperature. Experimental data taken from Ref. 47.

12%, respectively, resulting in an absolute anisotropy decrease by more than 50%. We note, however, that all anisotropies calculated with the Sadlej basis deviate significantly from experiment.

In contrast to the Sadlej basis set, the correlation-consistent sets give correlated values of the perpendicular component ξ_{xx} that are smaller than the uncorrelated ones by 6%–7%. For the parallel component, the same behavior is observed in the aug-cc-pVTZ basis (except for LB94/LDA), whereas in the aug-cc-pVDZ basis the effect is much larger, but in the opposite direction. The parallel component and thus the anisotropy are significantly underestimated at the uncorrelated aug-cc-pVDZ level, leading to the correlation contribution being of the order of 600% in the anisotropy (it is only 11% with the aug-cc-pVTZ basis) and illustrating the high sensitivity of this component to the level of electronic structure theory.

Comparison with experiment shows that only the aug-cc-pVTZ set yields results for the Cartesian components and isotropic and anisotropic magnetizabilities in agreement with experimental results from Ref. 3 for all functionals (except the LB94/LDA isotropic and anisotropic values). It is apparent that the magnetizability of C_6F_6 is difficult to reproduce, with the parallel component of the magnetizability particularly troublesome. B3LYP calculations with the doubly augmented correlation-consistent polarized valence double zeta (d-aug-cc-pVDZ) and doubly augmented correlation-consistent polarized valence triple zeta (d-aug-cc-pVTZ) basis sets yield magnetizability anisotropies of -8.86 and -8.54 a.u. respectively. The latter value represents an increase of almost 6% (in absolute value) with augmentation, with diffuse functions at the triple- ζ level. Indeed, it is not clear that convergence within 1 a.u. is achieved with the aug-cc-pVTZ basis, with further augmentation needed if adequate accuracy is sought. Comparison with benzene¹ highlights the special challenges posed to theory by the magnetic environment in C_6F_6 . For benzene, it is expected that the DFT anisotropic magnetizabilities are converged to within

0.3 and 0.1 a.u. of the basis set limit with aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. This is in direct contrast to the situation in C_6F_6 .

The traceless electric quadrupole moment of C_6F_6 is listed in Table III. For this property, basis set effects are much smaller than those of electron correlation, which decreases the quadrupole moment by about 11% for B3LYP, by 15% for BLYP, and by almost 30% for LDA; for LB94/LDA correlation increases the quadrupole moment by over 30%. Agreement with experiment is good for the GGA functionals, particularly for B3LYP. The LDA and LB94/LDA functionals perform poorly in reproducing the experiment.

B. Higher-order mixed electric and magnetic properties

In Table IV we detail results for the higher-order properties of C_6F_6 , namely, the dynamic second electric dipole hyperpolarizability γ_K , which is used to determine the KE, and the dynamic mixed electric dipole-electric quadrupole-magnetic dipole hypersusceptibilities, $b(\omega)$ (BE), $\Delta\eta(\omega)$ (CME), and $\Lambda(\omega)$ (JB and MEB). See Sec. II for definitions of these expressions. Further details on the individual components of these higher-order properties, as defined above, are available from the authors upon request.

The effect of electron correlation on γ_K is positive and large, ranging from about 30% to more than 100% (60% for B3LYP), but decreasing slightly as the basis set becomes larger. The experimental estimate of γ_K for hexafluorobenzene of Gentle and Ritchie⁴⁵ is $11\,000 \pm 11\,000$ a.u. roughly twice as large as their benzene value of 6400 ± 6400 a.u.. The only other reported experimental estimate of γ_K is $12\,800 \pm 6400$ a.u.,²⁰ measured at 240.14 K. Curiously, for hexafluorobenzene we compute a value between one third and one fourth that of benzene.¹

Electron correlation likewise increases the absolute value of the hypersusceptibility $b(\omega)$ by 13%–42% (26% for B3LYP/aug-cc-pVTZ). As for C_6H_6 ,¹ $\Sigma\mathcal{B}(\omega)$ and $\Sigma\beta(\omega)$ [see Eqs. (9) and (10)] experience the same effect, almost canceling each other. Thus $b(\omega)$ is well approximated by $\Sigma J'(\omega)$, and the effect of electron correlation on the hypersusceptibility contribution is approximately that of the electric dipole-magnetic dipole-electric dipole hyperpolarizability term, $\Sigma J'(\omega)$. Due to the very large error bar, we can claim agreement with the measurement of $b(\omega) = -2900 \pm 2000$ a.u. at 632.8 nm.³

For the anisotropy of the hypermagnetizability $\Delta\eta(\omega)$, inclusion of electron correlation with the LDA, BLYP, and B3LYP functionals has a large and positive effect on $\Delta\eta(\omega)$, which increases by 25%–45% (23% at the B3LYP/aug-cc-pVTZ level) with respect to Hartree-Fock. Conversely, the correction is small and negative in the mixed LB94/LDA approach (because of the paramagnetic contribution). The experimental, extrapolated infinite-temperature value of $\Delta\eta(\omega)$ is -100 ± 880 a.u. at 441.6 nm. Note that our calculated values are all positive in contrast to the center of the experimental distribution. Once again, the very large experimental error bars still allow us to claim agreement with experiment.

Table IV also collects our results for the hypersusceptibility contribution $\Lambda(\omega)$, which determines the Jones constant ${}_mJ(\omega)$, and which, as expected,¹ is strongly influenced by electron correlation. This dependence arises from a complex behavior with electron correlation of the three separate contributions $G_\Lambda^{\text{dia}}(\omega)$, $G_\Lambda^{\text{para}}(\omega)$, and $a'_\Lambda(\omega)$, see Sec. II. The latter is particularly sensitive, increasing by a factor of three when correlation is induced at the BLYP level with Sadlej's basis set. Again, the mixed LB94/LDA approach behaves in a different manner in comparison with the single-functional approaches.

C. Linear birefringences

In Table V the refractive index anisotropies, Δn , of Eq. (2) and the birefringence constants, ${}_mW(\omega, T)$, of Eq. (3) are given for radiation at a wavelength of 632.8 nm. Also, in Figs. 1–3 we compare, with experiment, the temperature dependence of the Kerr, Cotton-Mouton, and Buckingham constants, respectively, for selected representative combinations of methods and basis sets.

In hexafluorobenzene, the temperature-independent contribution of γ_K to the KE is less than 2% of the total contribution, appreciably smaller than in benzene.¹ Relative to benzene, the KE is thus less influenced by the electronic rearrangement and more dependent on the temperature-dependent Langevin contribution involving the anisotropies of the electric dipole polarizability.

The temperature dependence of ${}_mK(\lambda=632.8\text{ nm}, T)$ for C_6F_6 is illustrated in Fig. 1, where the experimental data from Ref. 45 are also plotted. Our B3LYP/aug-cc-pVTZ estimates included in Fig. 1 mirror the experimental data. Non-hybrid density functionals overestimate the Kerr constant, whereas Hartree-Fock theory strongly underestimates it; see Table V and Fig. 1. We also note that LB94/LDA is reasonably close to experiment, the closest to the experimental data points after B3LYP. The absence of vibrational corrections, in particular, for the anisotropy of the electric dipole polarizability does not affect the conclusions as the overestimation of $\alpha_{\text{ani}}(\omega)$ is balanced by the underestimation of $\alpha_{\text{ani}}(0)$.

As for KE, the temperature-independent contribution to BE of $b(\omega)$ is negligible in comparison with the temperature-dependent term involving the product $\alpha_{\text{ani}}(\omega)\Theta_{zz}$. It never exceeds 1.7% of the total quantity of ${}_mQ(\omega, T)$ in the temperature range 318.2–410.2 K of the measurements made by Ritchie and Watson,³ being approximately half as important as in benzene.¹ In Fig. 2, the experimental data from Ref. 3 are plotted together with some of our estimates. B3LYP/aug-cc-pVTZ results agree well with experiment across the whole temperature range. In contrast, the LB94/LDA approach yields results that exhibit significant deviation from experiment, largely due to the poor reproduction of the experimental quadrupole moment. Both Hartree-Fock and BLYP methods mirror the experimental temperature dependence in a similar manner as B3LYP. The LDA curve in Fig. 2 lies in the upper part of the figure, away from experiment, and it exhibits a slope larger than expected.

The discrepancy between our best value of the frequency-dependent electric dipole polarizability anisotropy

and that deduced from measurement has the effect that our estimated CME does not fit within three times the experimental error bars for the two observations^{46,47} in Table V. Note, however, that the measurement in Ref. 47 was made at a temperature and wavelength slightly different from those included in Table V. Again, the temperature-independent contribution of $\Delta\eta$ (which is quite well reproduced in our calculations) to the quantity in brackets in the Cotton-Mouton constant in Table I is only a fraction of a percent at all levels of theory (in particular, in the largest basis set), within the temperatures of interest for a comparison with experiment.

In Fig. 3 we show a comparison of the temperature dependence of the CME as measured by Lukins *et al.*⁴⁷ (using a laser source tuned at 441.6 nm between 304.1 and 453.3 K) and that estimated by us in our best calculation. The B3LYP/aug-cc-pVTZ results consistently overestimate the temperature effect, which is fortuitously well reproduced at the Hartree-Fock level due to an underestimation of the electric dipole polarizability anisotropy and an overestimation of the magnetizability anisotropy. For CME, the very poor performance of Sadlej's basis set discussed above for ξ_{ani} at all levels (and that of the aug-cc-pVDZ basis at the Hartree-Fock level) reflects on the estimates for the computed anisotropies Δn_u of hexafluorobenzene. Sadlej's results for ${}_mC(\lambda, T)$, independent of the choice of functional, lay well outside the range of Fig. 3, roughly between 0.2×10^{-16} and 0.6×10^{-16} SI units across the temperature range.

Finally, in Table V, results for the Jones constant ${}_mJ(\omega)$ have been collected. The constant itself and the corresponding birefringence predicted for the experimental conditions of $P=1$ bar, $B=3$ T, $E=2.6 \times 10^6$ V m⁻¹, and $T=273.15$ K correspond to the setup already adopted in Refs. 33, 1, and 2. Since as yet there are no experimental gas-phase data for JB and MEB, we can discuss only their predicted intensity and detectability.

Previously, we have compared different birefringences—that is, the Kerr, Cotton-Mouton, Buckingham, and Jones (magnetoelectric) effects—discussing, in particular, the observability of the latter and the challenges that its observation may pose to the experimentalist.^{33,2,1} Preliminary results for hexafluorobenzene were already anticipated in Ref. 2. As before, we assume as plausible field strengths the values $E=2.6 \times 10^6$ V m⁻¹ and $\nabla E=-1 \times 10^9$ V m⁻²,⁴⁸ with $P=1$ atm and $B=1$ T (for CME),²³ while $P=1$ bar and $B=3$ T (for JB and MEB).²⁸ For hexafluorobenzene, with an optical path of $l=1$ m,²⁸ at 632.8 nm we obtain, here using the B3LYP/aug-cc-pVTZ results, retardances of 1.1×10^{-3} rad (KE) $> 1.2 \times 10^{-4}$ rad (CME) $> 1.2 \times 10^{-6}$ rad (BE) $> 5.4 \times 10^{-8}$ rad (JB, MEB). Under these experimental conditions, the Jones and magnetoelectric birefringences of hexafluorobenzene in the gas phase should be detectable, if we take as current detection limit for retardances the value of 2 nrad.⁴⁸

V. CONCLUSIONS

We have presented the results of Hartree-Fock and DFT studies of some electric and magnetic properties of hexafluoro-

robenzene, including the frequency-dependent electric dipole polarizability, magnetizability, quadrupole moment, and the temperature-dependence of five different linear birefringences, namely, the Kerr, Cotton-Mouton, Buckingham, Jones, and magnetoelectric birefringences. The studies follow closely that recently performed on benzene.¹ From a comparison of the results obtained within the Hartree-Fock and DFT approaches in Sadlej's triple- ζ and Dunning's aug-cc-pVDZ and aug-cc-pVTZ basis sets, the dependence of the calculated properties on electron correlation has been analyzed in detail.

The effect of electron correlation is quite large, even for the magnetizability, which is usually well reproduced by the Hartree-Fock theory. However, the dependence on correlation is exceptionally strong for the higher-order optical properties that contribute to the different birefringences: the electric dipole dc-Kerr second hyperpolarizability and the mixed electric dipole, electric quadrupole, and magnetic dipole hypersusceptibilities, which contribute to the Cotton-Mouton, Buckingham, Jones, and magnetoelectric birefringences.

The agreement with the experimental data collected by Ritchie and Watson in Ref. 3 is generally quite satisfactory, in view of the neglect of molecular vibrations. As is often the case, the hyperpolarizabilities and hypersusceptibilities yield negligible contributions to the Kerr, Cotton-Mouton, and Buckingham birefringences. Because of the very large experimental error bars, the comparison between our values and the experiment for these high-order properties is always favorable, although in some cases error cancellation plays a decisive role. The Jones and magnetoelectric birefringences are predicted to be one to two orders of magnitude weaker than the BE and should be detectable with current experimental equipment.

All in all, we find that time-dependent DFT performs satisfactorily for the calculation of these properties for a potentially difficult system such as hexafluorobenzene, provided that basis sets of at least triple- ζ quality are employed.

ACKNOWLEDGMENTS

This work has been supported by the European Research and Training Network "Understanding Nanomaterials from a Quantum Perspective" (NANOQUANT), Contract No. MRTN-CT-2003-506842 and the Norwegian Research Council (Grant No. 154011/420). D.J.D.W. has been supported by the Norwegian Research Council through a postdoctoral fellowship (Grant No. 155137/432). We also acknowledge a grant of computer time from the Norwegian Supercomputing Program.

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