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The nuclear quadrupole moment of ^{115}In from molecular data

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The nuclear quadrupole moment of ^{115}In has been determined by combining the experimental nuclear quadrupole coupling constants and electric field gradients, calculated at the four-component CCSD(T) level of theory, of four indium halides. Our recommended value for the nuclear quadrupole moment of ^{115}In is 770(8) millibarn. A basis set study at the Dirac–Hartree–Fock level shows a slow convergence of the electric field gradient with respect to higher angular momentum functions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1492799]

I. INTRODUCTION

In the "year-2001"[1] set of nuclear quadrupole moments (NQM), 26 new values are tabulated, as compared to the "year-1992"[2] set. Eleven of these were solely determined via the molecular method and seven of these were determined in combination with atomic or solid state methods. The molecular method combines very accurately measured nuclear quadrupole coupling constants (NQCC) from microwave spectra, with a quantum chemical calculation of the electric field gradient (EFG) at the nucleus of interest. It has shown capable of producing accurate NQMs at relatively little expense. Since the rather inaccurate NQM of ^{115}In is not updated in the "year-2001" set it is interesting to apply the molecular method to this isotope as well.

The standard value, 810 mb, for ^{115}In[1] was obtained by Belfrage *et al.*[3] from the observed hyperfine structure of the $5p\,^2P$, $7p\,^2P$ and $8p\,^2P$ states of the ^{115}In atom in combination with empirically derived values for $\langle r^{-3} \rangle$ of these states.[4] The inaccuracy of these results is about 7%. Leiberich *et al.*[5] noted that this value is probably too high as it leads to inconsistencies between the experimental and calculated NQCCs in metallic indium. They derive a lower value of 760 mb taking the x-ray data and calculations on the muonic atom that were reported by Lee *et al.*[6] The accuracy of this NQM should be about 6%. Recently, van Lenthe and Baerends[7] computed NQCCs using the ZORA-4 DFT method for a range of compounds including the indium halides treated in this study. They also suggest a lower value of 740(30) mb for the NQM of ^{115}In.

The NQCC, $\nu_Q(X)$, in a linear molecule is given by[8]

$$\nu_Q(X) = eq(X)Q(X). \tag{1}$$

Inversion of this relation gives the NQM, Q (in barns), expressed in terms of the $\nu_Q(X)$ (in MHz) and the EFG, $q(X)$ (in atomic units):

$$Q(X) = \frac{\nu_Q(X)}{234.9647 q(X)}. \tag{2}$$

NQCCs for the indium halides tabulated to four digit accuracy or more are available from the book by Lucken.[9] Since these are already to first order corrected for vibrational effects it suffices to compute the EFG at the equilibrium geometry. Errors due to higher-order vibrational effects should be small since the first-order corrections are already small, ranging in the vibrational ground state from 0.46% for InF to 0.07% for InI.

Accurate calculation of EFGs requires large basis sets to describe the core and valence polarization. Halkier *et al.*[10] studied EFGs at the HF and CCSD level of theory for several light diatomic molecules and found that the EFG converges very slowly with standard basis set sequences, much slower than electric dipole and quadrupole moments. To make things worse, qualitative good basis sets for heavy elements are rare. For these reasons we optimized dedicated basis sets for indium at the Dirac–Coulomb Hartree–Fock (DC-HF) level of theory.

Apart from a large basis set one also needs to take relativistic effects and electron correlation effects into account to obtain an accurate description of the EFG. We do so by treating relativity at the Dirac–Coulomb (DC) level of theory, while using the CCSD(T) method to describe electron correlation.

II. METHODS AND COMPUTATIONAL DETAILS

We started by performing an extensive basis set study for In at the DC-HF level of theory. The two-step procedure to determine the optimal basis set necessary for accurate calculation of EFGs is comparable to the strategy used in earlier work[11] on the EFGs of HBr and HI. In the first step we focus on the energy of the indium atom in its ground state, while in the second step we consider the EFG of the smallest of the four indium halides, InF.

We used so-called dual family basis sets[12] where the large component $(\ell+2)$-exponents are a subset of the large component (ℓ)-exponents. The exponents in these sets were constrained by the even tempered prescription[13] to limit the number of variable parameters. For the In atom this means that only four variables, α_s and β_s for $\ell=0$, 2, 4 and α_p and β_p for $\ell=1$, 3, 5 had to be varied, which can readily be done

with a modified[14] version of GRASP.[15] In this energy optimization step we used a $23s$, $17p$, and $12d$ basis set as starting point. When the optimal parameters were found, we performed three new calculations, in which the basis set was extended with one tight s, p or d function, respectively, followed by reoptimization of α_s, β_s, α_p and β_p. The set that gave the largest energy lowering formed the starting point for new extensions. The procedure was repeated until the energy lowering upon extending the basis set became less than $10mE_h$.

In the second step, the α and β parameters were fixed and the convergence of the EFG as a function of basis set extension was studied. To allow for polarization in the molecule we first added three f functions, centered around the exponent closest to that of the f-function in the cc-pVDZ basis of Dyall,[16] (1.562 709 4). Next we systematically extended the basis to converge the EFG on In. Beginning with s functions we added diffuse functions until the change in EFG became less than 0.001 a.u., after which we added additional tight functions until the same convergence was reached. The same procedure was repeated, with the extended basis, for higher angular momentum functions until the EFG with respect to g functions was converged.

The results of this optimization are described in Sec. III A. The differences between the strategy applied here and the one of Ref. 11 are that in the old procedure all exponents were a subset of the s exponents and that in the study of the convergence of the EFG, several functions with different ℓ values were added simultaneously. In this new study, we add one function of one particular ℓ value at a time and also include g functions that were not considered previously.

For the correlated calculations we used a similar strategy as proposed by Kellö and Sadlej[17,18] in the context of Douglas–Kroll EFG calculations. The valence and subvalence electrons are correlated at the CCSD(T) level of theory, while the electron correlation contribution due to the deeper lying shells is computed at the MP2 level of theory. This means that at the CCSD(T) level for InF 28 electrons are correlated, for InCl 36 electrons are correlated, and for InBr and InI 46 electrons are correlated. We thereby found that virtual spinors with orbital energies higher than 13 a.u. could be neglected (see Sec. III B). All correlation contributions to the EFG are calculated using the finite field method, in which the correlation energy is differentiated with respect to the perturbation strength. The perturbation strength for these calculations was taken equal to $\pm 0.000\,01$ a.u. The total EFG of a method is the finite field correlation contribution plus the analytical HF (expectation) value. This mixed analytical/finite field scheme was introduced in Ref. 19, where an almost perfectly linear dependence of the correlation energy to the applied field strength was found.

All calculations of the electric field gradient were performed at the experimental equilibrium bond distances: $R_e(\text{InF}) = 3.752$ a.u.,[20] $R_e(\text{InCl}) = 4.538$ a.u.,[21] $R_e(\text{InBr}) = 4.806$ a.u.[22] and $R_e(\text{InI}) = 5.204$ a.u.[23] In all our calculations we used fully uncontracted basis sets. The fluorine, chlorine, and bromine basis sets were the same as used by Pernpointner and Visscher,[19] except for chlorine where an extra diffuse p (0.0419) is added. For iodine we used the cc-pVTZ basis from Visscher and Dyall[24] augmented by one diffuse s (0.02457), one tight p (250937.5944142), and one diffuse p (0.040), the resulting iodine basis is a $(22s18p12d1f)$ set. All these basis sets can be considered as of approximately triple-zeta quality, the ones for the lighter atoms being close to the original cc-pVTZ basis sets of Dunning and co-workers.[25–27] The electric field gradient calculations were performed using the DIRAC[28] electronic structure code using the standard Gaussian charge distribution for the nucleus.[29] In order to study the importance of scalar relativistic and spin-orbit contributions we not only performed relativistic DC calculations but also nonrelativistic (NR) and scalar relativistic calculations. The nonrelativistic (NR) calculations are based on the Levy–Leblond Hamiltonian, the scalar relativistic calculations are based on the spin-free (SF) Dirac equation introduced by Dyall.[30] In all DC and SF EFG calculations we neglected the (SS|SS) type of integrals, since earlier studies have shown that these are negligible for the EFG.[31] As a check we performed one DC-HF calculation with (SS|SS) integrals included for InF and found a difference in the EFG on In of only 0.02%.

III. RESULTS AND DISCUSSION

A. Convergence of the electric field gradient in the Hartree–Fock calculations

For the indium atom the result of the optimization is a $(25s19p12d)$ even tempered basis which gives an energy of $-5880.410\,40\,E_h$, $21mE_h$ above the DC-HF limit as calculated with GRASP.[15] The β_s for the s and d functions was 2.272 and the β_p of the p functions was 2.234. The highest s, p, and d exponents after the energy optimization were 20 702 066.70, 120 828.7227 and 2483.704 644, respectively.

The convergence of the EFG and the energy of InF by extending this basis is given in Table I. The first g function that we used in the convergence study had exponent 0.67707, which is comparable to the most diffuse f. The convergence of the EFG on In is very slow for the f and g functions, and we see that especially many tight functions are needed. The final basis, for which the EFG on In is converged within 0.001 a.u., is a $25s23p15d9f8g$ basis. The highest s, p, d, f, and g exponents were 20 702 066.70, 1 347 862.219 141 1, 12 823.109 75, 434.534 442 5 and 41.007 795 7, respectively. To analyze the cause of this slow convergence we studied the individual orbital contributions to the EFG on In in InF. In Table II we list partial sums of orbital contributions and the differences in these partial sums upon adding $6f$ functions to the $25s23p15d3f$ basis and adding $8g$ functions to the resulting $25s23p15d9f$ basis. The main difference to the EFG on In upon extending the basis with f functions arises from the $2p$ orbitals. When the basis is subsequently extended with g functions the main differences arise from the $3p$ and $3d$ orbitals. This dependence can be understood by realizing that the EFG operator connects functions that differ by two units of angular momentum. It thereby weights the small admixture of the f character in the closed p shell and similarly the small admixture of g character in the closed d shell that occurs due to the molecule formation. Surprising is that this effect is so large that it needs to be taken into account to

TABLE I. Electric field gradients at the indium and fluorine nuclei in InF in atomic units using different basis sets for indium. The fluorine basis is the cc-pVTZ basis with two additional p functions (see Ref. 19). The convergence (Δq^{In}) of the EFG at indium is also given. All calculations were performed at the DC-HF level of theory.

Basis set		Energy	q^{In}	Δq^{In}	q^{F}
$[25s19p12d]$	(b1):	−5980.184 06	−4.4336		0.5438
$[25s19p12d3f]$	(b2): (b1+3 diffuse f)	−5980.187 26	−4.4704	−0.0367	0.5348
$[26s19p12d3f]$	(b3): (b2+diffuse s)	−5980.187 31	−4.4705	−0.0002	0.5362
	(b4): (b2+tight s)	−5980.189 51	−4.4703	0.0000	0.5348
$[25s20p12d3f]$	(b5): (b2+diffuse p)	−5980.187 31	−4.4688	0.0015	0.5350
	(b6): (b5+diffuse p)	−5980.187 31	−4.4688	0.0001	0.5350
	(b7): (b5+tight p)	−5980.190 38	−4.4723	−0.0034	0.5350
	(b8): (b7+tight p)	−5980.191 65	−4.4741	−0.0018	0.5350
	(b9): (b8+tight p)	−5980.192 19	−4.4756	−0.0015	0.5350
	(b10): (b9+tight p)	−5980.192 42	−4.4761	−0.0005	0.5350
$[25s23p13d3f]$	(b11): (b9+diffuse d)	−5980.193 13	−4.4813	−0.0057	0.5287
	(b12): (b11+diffuse d)	−5980.193 14	−4.4814	0.0000	0.5288
	(b13): (b11+tight d)	−5980.193 25	−4.4828	−0.0015	0.5287
	(b14): (b13+tight d)	−5980.193 27	−4.4847	−0.0019	0.5287
	(b15): (b14+tight d)	−5980.193 27	−4.4850	−0.0003	0.5287
$[25s23p15d4f]$	(b16): (b14+diffuse f)	−5980.194 32	−4.4850	0.0000	0.5139
	(b17): (b14+tight f)	−5980.193 27	−4.4809	0.0037	0.5288
	(b18): (b17+tight f)	−5980.193 29	−4.4798	0.0012	0.5287
	(b19): (b18+tight f)	−5980.193 29	−4.4750	0.0048	0.5287
	(b20): (b19+tight f)	−5980.193 30	−4.4659	0.0091	0.5287
	(b21): (b20+tight f)	−5980.193 30	−4.4625	0.0034	0.5287
	(b22): (b21+tight f)	−5980.193 30	−4.4604	0.0021	0.5287
	(b23): (b22+tight f)	−5980.193 30	−4.4604	0.0000	0.5287
$[25s23p15d9f1g]$	(b24): (b22+diffuse g)	−5980.194 18	−4.4396	0.0208	0.5289
	(b25): (b24+diffuse g)	−5980.194 26	−4.4405	−0.0009	0.5288
	(b26): (b25+diffuse g)	−5980.194 44	−4.4419	−0.0014	0.5280
	(b27): (b26+diffuse g)	−5980.194 45	−4.4421	−0.0002	0.5281
	(b28): (b26+tight g)	−5980.194 46	−4.4340	0.0079	0.5284
	(b29): (b28+tight g)	−5980.194 46	−4.4319	0.0021	0.5285
	(b30): (b29+tight g)	−5980.194 47	−4.4285	0.0034	0.5285
	(b31): (b30+tight g)	−5980.194 47	−4.4238	0.0047	0.5285
	(b32): (b31+tight g)	−5980.194 47	−4.4211	0.0027	0.5285
$[25s23p15d9f9g]$	(b33): (b32+tight g)	−5980.194 47	−4.4202	0.0008	0.5285

reach the desired accuracy. As could be expected, since we have no occupied f shell in In, the addition of h functions is not necessary. Adding an h function to the $25s23p15d9f8g$ basis, with the h exponent comparable to the most diffuse g exponent, gave a difference of the EFG of only 0.0009 a.u.

We also did a minor study on the stability of the EFG on In for extending the fluorine basis. We hereby used the mentioned cc-pVTZ, the aug-cc-pVTZ, aug-cc-pVQZ, and the aug-cc-pV5Z basis sets. The difference between the cc-pVTZ and aug-cc-pVQZ is −0.011 a.u., the difference between the aug-cc-pVQZ and aug-cc-pV5Z basis is −0.001 a.u. This means that with the $25s23p15d9f8g$ basis for In and the aug-cc-pV5Z for F, the EFG on In should be converged to almost 0.001 a.u. at the DC-HF level.

When doing correlated calculations, we have to compromise between basis set size and computational feasibility. For $\ell=0$, $\ell=1$, and $\ell=2$, we took those exponents from the HF EFG convergence study which made the EFG converge within about 0.01 a.u. For f and g we only took the most important functions, which could be chosen such that the EFG deviates less than 0.01 a.u. from the benchmark HF value. The final In basis which we used for the correlated calculations became then a $25s19p13d4f2g$ basis where the selected f exponents were 87.035 571 1, 3.491 740 3,

1.562 709 4, and 0.699 382 1 and the selected g exponents were 7.942 788 8 and 1.538 436 6. In Table III results for the four indium halides are presented. The deviation between these benchmark results and the results with the basis that we used for the correlated calculations is less than 0.01 a.u. and is used to correct the correlated EFG values calculated in the smaller basis.

B. Convergence of the electric field gradient in the correlated calculations

The uncontracted basis sets that we use generates many high-lying virtuals spinors that are unimportant for the correlation of valence and subvalence shells. To achieve better computational efficiency these virtuals are eliminated by applying an energy threshold for inclusion in the correlation calculation. To study the effect of truncating the active virtual space in this manner we varied this threshold in the spin-free formalism. Raising the virtual spinor threshold from 13 to 100 a.u. gave a change in the calculated EFG at the CCSD(T) level for InF, InBr, and InI of 0.06% and for InCl of 0.21%. In the all-electron calculations at the MP2 level, which we use to estimate the effect of core correlation, the effect of higher virtuals should be more important be-

TABLE II. Orbital contributions to the EFG (in atomic units) at indium in InF for the $25s23p15d3f$ basis. Partial sums of orbital contributions are also given, as well as differences in these partial sums between the different indium basis sets. The contribution of the F $1s_{1/2}$ orbital is added to the partial sum of the In $3p$ shell because its energy is just between the $3p_{1/2}$ and the $3p_{3/2}$ indium. All calculations have been performed at the DC-HF level of theory.

| | $25s23p15d3f$ | | $25s23p15d9f$ | $25s23p15d9f8g$ |
Orbital	q_i	Partial sum q_i	Partial sum Δq_i	Partial sum Δq_i
$1s_{1/2}$	0.0086	0.0086	−0.0002	−0.0003
$2s_{1/2}$	0.0129	0.0129	−0.0002	−0.0006
$2p_{1/2}$	0.4598			
$2p_{3/2}$	3206.8787			
$2p_{3/2}$	−3207.4583	−0.1198	0.0187	0.0061
$3s_{1/2}$	0.0052	0.0052	0.0000	−0.0004
$3p_{1/2}$	1.7863			
F$1s_{1/2}$	−0.0757			
$3p_{3/2}$	595.4546			
$3p_{3/2}$	−597.4780	−0.3129	0.0082	0.0175
$3d_{3/2}$	92.7105			
$3d_{3/2}$	−92.1772			
$3d_{5/2}$	123.4478			
$3d_{5/2}$	−25.1868			
$3d_{5/2}$	−98.8341	−0.0399	0.0001	0.0171
$4s_{1/2}$	−0.0006	−0.0006	0.0000	0.0003
$4p_{1/2}$	3.3431			
$4p_{3/2}$	97.2239			
$4p_{3/2}$	−101.2474	−0.6804	−0.0024	−0.0005
F$2s_{1/2}$	−0.4570	−0.4570	−0.0001	−0.0002
$4d_{3/2}$	11.0968			
$4d_{3/2}$	−9.7183			
$4d_{5/2}$	13.2589			
$4d_{5/2}$	−3.6756			
$4d_{5/2}$	−10.5747	0.3871	−0.0002	0.0078
$5s$−F$2p$	−1.4601	−1.4601	−0.0005	−0.0027
F$2p$	−0.0246			
F$2p$	−0.0338	−0.0585	−0.0003	−0.0006
$5sp$−F$2p$	−2.1102	−2.1102	−0.0008	−0.0020
Total	−4.8255	−4.8255	0.0222	0.0414

cause we then also consider core correlation. In these calculations we did therefore take all the virtual spinors into account. These all-electron results can be compared to the smaller MP2 calculation (with the same active space as in the coupled-cluster calculations) to provide an estimate of the joint contribution of core correlation and the effect of higher lying virtual spinors on the valence spinors. Because of the small effect of the virtual spinors with energies between 13 and 100 a.u. on the valence correlation, and because the all-electron MP2 calculations will also give a good estimate of this effect, we conclude that it is justified to put the energy threshold at 13 a.u. in the coupled-cluster calculations. The correction obtained by comparing the full active space DC-MP2 and the small active space DC-MP2 calculations gives changes in EFG ranging from 0.04% for InI to 0.36% for InCl and is included in the CC values of Table III.

The spin-orbit effect on the EFG can be calculated by comparing the Dirac–Coulomb and the spin-free calculations. By comparing the DC-HF with the NR-HF calculations we see that relativistic effects are indeed very important. The relativistic contribution to the EFG ranges from −0.435 a.u. (9.83%) for InF to 0.300 a.u. (7.97%) for InI. The main contribution to the relativistic effects comes from

scalar relativistic effects. For the benchmark basis the spin-orbit contributions range from −0.019 a.u. (0.47%) for InBr to −0.015 a.u. (0.41%) for InI at the HF level. If we compare the CCSD(T) calculations using the SF formalism and the DC formalism, including the contribution of the all-electron MP2 calculations, we see that the spin-orbit effect ranges from −0.021 a.u. (0.53%) for InCl to −0.013 a.u. (0.40%) for InI, so the electron correlation effects do not affect the magnitude of spin-orbit effects much in this case. The total relativistic contribution and the correlation contributions are of roughly the same magnitude but of opposite sign, so that we see a fortuitous agreement between the NR-HF and the DC-CCSD(T) values. A similar cancellation was found for the EFG at Ag in AgCl by Pernpointner et al.[32]

C. Nuclear quadrupole moment of In

The resulting nuclear quadrupole moments of In extracted by the different methods from the four indium halides are presented in Table IV. At the HF level we see an average absolute deviation of 3.7 and 3.8 mb for the DC and spin-free formalisms, respectively, and 8.4 mb at the nonrelativistic level (for the small basis). At the correlated level the

TABLE III. EFG values at the indium nucleus (in atomic units) in different indium halides, calculated using different methods. The ''benchmark'' values are calculated using the $25s23p15d9f8g$ basis for indium and the aug-cc-pV5Z basis for the halides, except for iodine where an aug-cc-pVTZ basis is used. All other values are calculated using the $25s19p13d4f2g$ basis for indium and the extended cc-pVTZ basis for the halides. NR means nonrelativistic, SF spin-free, and DC Dirac–Coulomb.

Method	InF	InCl	InBr	InI
NR HF	−3.990	−3.671	−3.553	−3.462
SF HF	−4.409	−4.051	−3.898	−3.750
SF HF_benchmark	−4.414	−4.054	−3.896	−3.739
SF MP2	0.413	0.460	0.450	0.435
SF MP2c[a]	0.408	0.453	0.443	0.438
SF CCSDc[b]	0.330	0.337	0.320	0.310
SF CCSD(T)c[b]	0.424	0.424	0.406	0.397
DC HF	−4.425	−4.067	−3.910	−3.762
DC HF_benchmark	−4.432	−4.074	−3.914	−3.754
DC MP2	0.416	0.462	0.452	0.439
DC MP2c[a]	0.404	0.449	0.441	0.438
DC CCSDc[b]	0.326	0.347	0.318	0.309
DC CCSD(T)[b]	0.420	0.422	0.405	0.400
DFT ZORA-4[c]	−4.144	−3.783	−3.637	−3.475

[a]The MP2 contribution to the EFG due to all electrons and all virtual spinors.
[b]Corrected for the contribution due to the core electrons and higher lying virtuals estimated from the difference between the MP2c and MP2 results.
[c]Reference 7.

TABLE IV. NQMs of ^{115}In (in mb) derived using different methods and from different indium halides. The ''benchmark'' values are calculated using the $15s23p15d9f8g$ basis for indium and the aug-cc-pV5Z basis for the halides, except for iodine where an aug-cc-pVTZ basis is used. The correlation contributions are calculated using the $25s19p13d4f2g$ basis for indium and the extended cc-pVTZ basis for the halides. NR means nonrelativistic, SF spin-free, and DC Dirac–Coulomb. At the correlated level the NQMs are corrected for the contribution due to core correlation and higher lying virtuals.

Method	InF	InCl	InBr	InI	Average
NR HF	775.7	764.7	760.2	746.7	761.8±8.4
SF HF	701.8	693.0	692.9	689.5	694.3±3.8
SF HF_benchmark	701.1	692.4	693.4	691.6	694.6±3.3
SF MP2	772.6	779.4	782.3	783.2	779.4±3.4
SF CCSD	757.8	755.2	755.5	754.1	755.6±1.6
SF CCSD(T)	775.6	773.3	774.0	773.8	774.2±1.0
DC HF	699.4	690.2	690.9	687.2	691.9±3.7
DC HF_benchmark	698.3	689.1	690.1	688.7	691.6±3.3
DC MP2	768.3	774.6	777.6	779.7	775.1±3.6
DC CCSD	753.7	750.7	751.1	750.6	751.5±1.1
DC CCSD(T)	771.4	768.8	769.6	770.8	770.2±1.0
DFT ZORA-4[a]	746.8	742.1	742.8	744.0	743.3±1.5

[a]Reference 7.

deviations between the NQMs of ^{115}In derived from the different molecules become smaller. At the DC level the average absolute deviation in going from MP2 to CCSD(T) becomes smaller, from 3.6 to 1.0 mb. The small spread in NQM values for ^{115}In determined at the CCSD(T) level from the different indium halides gives already an indication of the quality of these calculations. In addition we also did some additional calculations to check the convergence of the calculated NQM.

As mentioned, the basis set that we used for the correlated calculations gave an EFG on In in the indium halide molecules that was converged within 0.01 a.u. at the DC-HF level. To check that this basis is also good enough for the correlated calculations we extended the basis with one diffuse p and one diffuse d, with exponents 0.028 058 5 and 0.057 715 5, respectively, and performed a spin-free MP2 calculation for InF. The change in the EFG of InF was only 0.0007 a.u., so about 0.02%, again a negligibly small effect. So far our focus with respect to basis sets has mainly been on InF that has the shortest bond distance of the four halides. To see whether enough diffuse functions are present in the basis we also performed some additional calculations on InI using the same diffuse functions as mentioned for InF. At the spin-free correlated level we find that the effect on the EFG value is indeed larger than in InF, although still very small. At the MP2 level a lowering of 0.0055 a.u. (0.17%) is seen, at the CCSD(T) level 0.0038 a.u. (0.11%), giving rise to a slightly higher NQM.

Besides the spread in NQM values that is determined by comparing values from different molecules there is also a possibility of a systematic error that does not contribute to the spread. This error is difficult to estimate. Given the calculations that we performed, we believe the error in the basis

set is negligible, in any case far below 1%. The vibrational correction error is also expected to be very small. This leaves possible errors in the electron correlation contribution as the largest source of uncertainty. From their ample experience with the calculation of electric field gradients of small molecules at the Douglas–Kroll CCSD(T) level of theory, Kellö and Sadlej[17,33,34] believe that an inaccuracy of 1% to the total EFG, due to the neglect of higher-order electron correlation effects, should be an upper limit. We also take this estimate for our CCSD(T) calculations which makes our recommended value for the NQM of ^{115}In 770(8) mb. This value for the NQM of ^{115}In is in better agreement with the value favored by Leiberich et al.[5] [760(50) mb] than with the standard value from Belfrage et al.[3] [810(60) mb]; although it falls in both error bars. Our value for the NQM of ^{115}In indicates also that the value determined by van Lenthe and Baerends,[7] using ZORA-4 and the Becke–Perdew functional, is too low, even though the spread in their values is of comparable size to ours.

The NQMs of other indium isotopes can be deduced by combining the measured B factors of atomic states and the NQM of ^{115}In. Eberz et al.[35] tabulate the B factors for the $^2P_{3/2}$ states of the In isotopes 104–127. Here we only give the NQM of ^{113}In because it is, besides ^{115}In, the only stable isotope (with a natural abundance of about 4%). Using the ratio[36] Q(^{113}In)/Q(^{115}In)$=0.986\,362(15)$ we obtain a new value for Q(^{113}In) of 759(8) mb.

IV. CONCLUSIONS

A new value for the nuclear quadrupole moment for ^{115}In has been determined by combining experimental nuclear quadrupole couplings constants with four-component CCSD(T) electric field gradient calculations of four indium halides. Our recommended value for the nuclear quadrupole moment of ^{115}In is 770(8) mb. Relativistic effects are shown to be almost as important as electron correlation effects, both

about 10%, but since they are of opposite sign, they almost cancel each other. A basis set study at the Dirac–Hartree–Fock level showed that multiple tight f and g functions are needed to converge the electric field gradient for InF within 0.001 au.

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