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Published in:
Molecular Physics

DOI:
[10.1080/00268976.2016.1203036](https://doi.org/10.1080/00268976.2016.1203036)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zelovich, T., Borschevsky, A., Eliav, E., & Kaldor, U. (2017). Relativistic coupled cluster calculation of Mossbauer isomer shifts of iodine compounds. *Molecular Physics*, 115(1-2), 138-143.
<https://doi.org/10.1080/00268976.2016.1203036>

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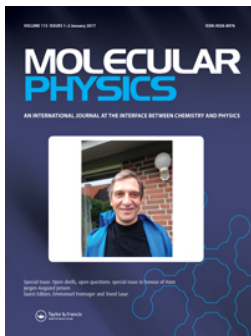
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Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: <https://www.tandfonline.com/loi/tmph20>

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To cite this article: Tamar Zelovich, Anastasia Borschevsky, Ephraim Eliav & Uzi Kaldor (2017) Relativistic coupled cluster calculation of Mössbauer isomer shifts of iodine compounds, Molecular Physics, 115:1-2, 138-143, DOI: [10.1080/00268976.2016.1203036](https://doi.org/10.1080/00268976.2016.1203036)

To link to this article: <https://doi.org/10.1080/00268976.2016.1203036>



Published online: 28 Jun 2016.



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Relativistic coupled cluster calculation of Mössbauer isomer shifts of iodine compounds

Tamar Zelovich^a, Anastasia Borschevsky^b, Ephraim Eliav^a and Uzi Kaldor^a

^aSchool of Chemistry, Tel Aviv University, Tel Aviv, Israel; ^bVan Swinderen Institute for Particle Physics and Gravity, University of Groningen, Groningen, The Netherlands

ABSTRACT

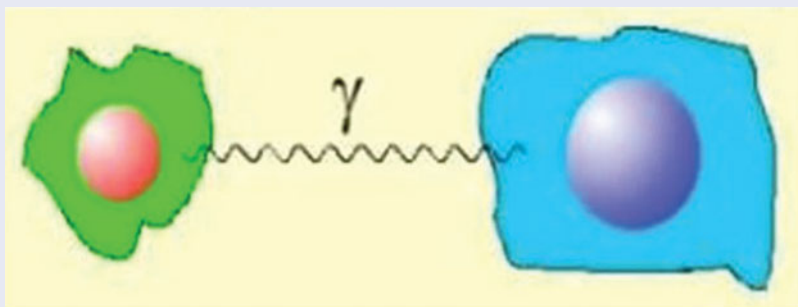
Mössbauer isomer shifts of ¹²⁹I and ¹²⁷I in the ICl, IBr and I₂ molecules are studied. Filatov's formulation is used, based on calculating the electronic energy change of the two systems involved in the Mössbauer γ transition, the source and absorber. The energy difference between the transitions in the two systems determines the shift. The effects of relativity and electron correlation on the shifts are investigated. The exact two-component (X2C) and the four-component relativistic schemes give virtually identical results; the non-relativistic approach yields about 50% of the relativistic shifts. Electron correlation is included by coupled-cluster singles-and-doubles with perturbative triples [CCSD(T)]; it reduces Hartree–Fock shifts by 15%–20%. Basis sets are increased until the isomer shifts converge. The final results, calculated with the converged basis in the framework of the X2C Hamiltonian and CCSD(T) correlation, give an agreement of 10% or better with experimental data.

ARTICLE HISTORY

Received 22 April 2016
Accepted 9 June 2016

KEYWORDS

Mössbauer isomer shifts;
relativistic effects; iodine
compounds



1. Introduction

Mössbauer spectroscopy is one of the most powerful experimental analytical techniques in modern chemistry and physics (for recent reviews, see [1–4]). More than 40 elements appear in substances identified and studied by this technique, including heavy species such as iodine, tin, gold, mercury, uranium, and rare earths [5–8]. An important feature of the Mössbauer spectroscopy is its ability to yield detailed atomic scale information about electronic structure, chemical activity and bonding. Applications range from the study of single molecules isolated in inert gas matrices [9–11] to solids and biosystems [12,13].

The physical basis of Mössbauer spectroscopy is the recoilless resonance absorption of γ rays by an atomic nucleus embedded in a crystalline or disordered solid environment. The frequency of the nuclear γ transition depends on the interaction with the surrounding

electronic density, and can therefore vary according to the chemical environment of the resonating atom. Quantities measured by Mössbauer spectroscopy, such as the isomer shift of the γ transition, the quadrupole splitting and the hyperfine constants, serve therefore as sensitive probes of the surrounding electronic structure. One parameter measured in Mössbauer spectroscopy is the isomer shift δ , defined as the energy difference between the γ transition in the sample (absorber) nucleus and the reference (source) nucleus. The value of δ is determined by the variation of the nuclear charge radius during the γ transition and by the electronic density in the vicinity of the nucleus [8,14]. These physical parameters cannot be obtained by direct experimental measurements. *Ab initio* high-precision quantum chemical studies of electronic density distributions and isomer shifts are, therefore, important tools in the interpretation of Mössbauer spectra.

An efficient and straightforward *ab initio* method for isomer shift calculations has been developed and implemented in the last decade by Filatov and coworkers [15–19], using a direct ‘all-order’ approach. Earlier schemes were based on finite-order perturbation theory, yielding less precise results. Filatov’s approach has been modified and refined by other researchers [20]. Most elements studied by Mössbauer spectroscopy are heavy, exhibiting large electron correlation and relativistic effects. Calculations demonstrated strong dependence of the isomer shift on the quality of the wave function, in particular on the level of electron correlation and relativistic effects included. A quantum chemical approach aiming at high accuracy must therefore include both correlation and relativistic effects at the highest possible level. High-quality calculations of Mössbauer isomer shifts are still rather scarce, particularly for molecular species containing heavy elements.

The present paper applies Filatov’s model of the Mössbauer isomer shift, in combination with a state-of-the-art relativistic coupled cluster approach, to calculate the isotope shift in iodine-containing diatomic molecules. The theory of the isomer shift is outlined briefly in Section 2.1. Section 2.2 describes the details of the implementation of Filatov’s theoretical model, using a relativistic coupled cluster approach with numerical differentiation of the energy as a function of the nuclear radius. The results of applying the method to iodine-containing diatomics are presented in Section 3, and a summary is given in the final section.

2. Methodology

2.1. Mössbauer isomer shifts

The interaction energy between the nucleus and the surrounding electrons depends on the nuclear volume, which changes during a γ transition. The frequency of this transition will be slightly different for different electronic environments, and the isomer shift is defined as a measure of the energy difference between the γ transitions occurring in the source and absorber nucleus. The isomer shift is used to probe the difference in the electronic environments of the two systems.

The model used most commonly in theoretical studies of the isomer shifts is [7,8]

$$\delta = \frac{c}{E_\gamma} \frac{4\pi}{5} ZS(Z) R^2 \left(\frac{\Delta R}{R} \right) (\bar{\rho}_e^a - \bar{\rho}_e^s), \quad (1)$$

where δ is the isomer shift measured in terms of the Doppler velocity necessary to achieve the resonance

absorption, E_γ is the frequency of the nuclear γ transition, Z is the atomic number, R and ΔR are the nuclear radius and its variation during the transition, and $\bar{\rho}_e^a$ and $\bar{\rho}_e^s$ are the electron densities inside the absorber and source nucleus, respectively. These densities are usually replaced by the non-relativistic electronic density at the nucleus, and an $S(Z)$ scaling factor is employed as a relativistic correction. Most studies based on Equation (1) focus on the correlation between the calculated electron density at the nucleus and the observed values of the isomer shift. The model is presented in greater detail in [7,8].

The approach of Equation (1) is computationally straightforward, but suffers from some drawbacks. The most serious problems are its inherently non-relativistic character and the use of the point nucleus model, ignoring the finite nuclear extent, which is nonnegligible for heavy atoms. In addition, this approach makes it difficult or impossible to account for electron correlation effects on the electron density inside the nucleus.

A new theoretical model for calculating the Mössbauer isomer shift was suggested by Filatov and coworkers [15–19]. The advantage of the new scheme is that it avoids the explicit use of the electronic density, thus allowing straightforward incorporation of both relativity and electron correlation. Below we follow the presentation of [15].

Mössbauer isomer shifts have the same origin as the isotope shift of the electronic energy [21]. The energy shift of the electronic terms due to the change in the nuclear radius during a γ transition is, in fact, equal to the energy shift of the nuclear terms. Thus, assuming that the electronic wavefunction Ψ_e does not change during the Mössbauer nuclear transition, the transition energy E_γ^e of a nucleus in a given electronic environment e may be expressed as

$$E_\gamma^e = E_\gamma^0 + \langle \Psi_e | \hat{H}_e(V_{Ne}^{(e.s.)}) | \Psi_e \rangle - \langle \Psi_e | \hat{H}_e(V_{Ne}^{(g.s.)}) | \Psi_e \rangle, \quad (2)$$

where $\hat{H}_e(V_{Ne}^{(g.s.)})$ and $\hat{H}_e(V_{Ne}^{(e.s.)})$ are the electronic Hamiltonians, which depend on the electron–nuclear attraction potentials in the ground and excited states of the nucleus, $V_{Ne}^{(g.s.)}$ and $V_{Ne}^{(e.s.)}$, respectively; E_γ^0 is the transition energy of a bare nucleus. The variation of the nuclear radius during a γ excitation is quite small, $\Delta R/R \approx 10^{-4}$, and Equation (2) can be rewritten as the Taylor series

$$E_\gamma^e = E_\gamma^0 + \left. \frac{\partial E_e(R_N)}{\partial R_N} \right|_{R_N=R} \Delta R + \frac{1}{2} \left. \frac{\partial^2 E_e(R_N)}{\partial^2 R_N} \right|_{R_N=R} (\Delta R)^2 + \dots \quad (3)$$

Here, $E_e(R_N)$ is the electronic energy calculated using a finite-size nuclear model characterised by the nuclear

radius R_N . Thus, the energy shift of the Mössbauer γ transition may be defined as the change in the electronic energy due to the variation of the nuclear radius. Keeping only the lowest order term of (3), the Mössbauer isomer shift is

$$\delta = \frac{c}{E_\gamma} \left(\left. \frac{\partial E_e^a(R_N)}{\partial R_N} \right|_{R_N=R} - \left. \frac{\partial E_e^s(R_N)}{\partial R_N} \right|_{R_N=R} \right) \Delta R, \quad (4)$$

where E_e^a and E_e^s are the electronic energies of the systems containing the absorber and source nuclei, respectively. Relating $\partial E_e(R_N)/\partial R_N$ to the electron density inside the nucleus, $\bar{\rho}_e$, and using some other assumptions, Filatov [15] showed that Equation (4) is equivalent to Equation (1).

The use of Equation (4) for calculating Mössbauer isomer shifts has a number of advantages, most importantly allowing the *ab initio* treatment of relativity. Isomer shifts originate from the interaction of the s electrons with the nucleus. Since these electrons experience strong relativistic effects, the treatment of relativity as a perturbation or by scaling parameters does not give the correct picture of the underlying physics of the phenomenon. An additional advantage of this scheme is eliminating the calculation of the electron density at the nucleus, thus allowing straightforward incorporation of correlation effects. In the present work, we explore both advantages by combining Filatov's model with the relativistic coupled cluster method.

2.2. Computational details

The Mössbauer isomer shifts of IBr, ICl and I_2 are calculated relative to the negative iodine ion. We examine free molecules rather than a solid-state model. The equilibrium internuclear distances are taken from experiments: $R_e(\text{IBr}) = 2.469 \text{ \AA}$ [22], $R_e(\text{ICl}) = 2.321 \text{ \AA}$ [23], and $R_e(I_2) = 2.666 \text{ \AA}$ [24].

All energy calculations were performed using the DIRAC08 computational package [25]. The systems under study have closed-shell ground states; the single-reference coupled cluster approach was therefore employed. Energy calculations were performed for three different nuclear radii (within the expected change of the radius upon γ transition) to obtain the dependence of the electronic energy on the nuclear radius. The derivative $\partial E^e/\partial R_N$ was obtained by numerical differentiation. The DIRAC08 program employs the finite nucleus model with a Gaussian charge distribution. The nuclear radius was changed by using different nuclear exponents [26] in the input files.

Uncontracted Huzinaga–Klobukowski basis sets [27] were employed. Basis functions were added until the

isomer shifts converged, indicating that the basis was effectively complete. This approach gave excellent results in many previous applications, most recently in the experimental and theoretical study of the first ionisation potential of atomic lawrencium [28], where the computed IP was within the error bounds of the measurements. Twenty-six electrons were correlated in I^- , 40 electrons in ICl, and 50 electrons in IBr and I_2 . Virtual orbitals with energies above 100 au were omitted for all systems.

E_γ , the energy of the γ transition appearing in Equation (4), has been measured experimentally. Two resonant lines are given in [29] for the iodine isotopes, $^{127}E_\gamma = 57.60 \text{ keV}$ and $^{129}E_\gamma = 27.72 \text{ keV}$. Upon γ excitation, the radius R of the iodine nucleus changes. The values of $\Delta R/R$ found in the literature vary over a range of more than one order of magnitude. Thus, for ^{129}I one can find values from 0.3×10^{-4} [30] to 7.2×10^{-4} [31]. Most measurements cluster between 4×10^{-4} and 5×10^{-4} [32–38]. We use the most up-to-date (to our knowledge) value, $\Delta R/R = 4.3 \times 10^{-4}$, reported by Hartmann and Winkler [39] and characterised by them as the best experimental data available. For ^{127}I , we use $\Delta R/R = -3.4 \times 10^{-4}$, taken from the same work [39].

3. Results and discussion

All isomer shifts presented here are relative to I^- . Experimental values measured relative to other species (ZnTe or NaI) are shifted as necessary, using the known differences $\delta(I_2 - \text{ZnTe}) = 0.83 \text{ mm/sec}$ [40] and $\delta(I_2 - I^-) = 1.48 \text{ mm/sec}$ [32]. To assess relativistic effects and choose the proper relativistic Hamiltonian, isomer shifts were obtained in the framework of the fully relativistic four-component Dirac Hamiltonian, the exact two-component relativistic Hamiltonian (X2C) [41], and the non-relativistic (NR) Schrödinger equation. Due to the heavy computational demands of four-component calculations, this stage was carried out with the relatively limited basis set A, consisting of 23s19p12d3f uncontracted Gaussians on iodine and 21s17p10d2f on Cl and Br. Table 1 presents the isomer shifts of molecules containing ^{129}I , calculated at the different levels of relativistic treatment. The X2C values coincide in all cases with the full four-component numbers at the precision given, and this two-component approach is, therefore, sufficient (and less costly) for isomer shift calculations. The non-relativistic calculations underestimate the isomer shifts by about 50% for all molecules, indicating the importance of explicit treatment of relativity. The last column in Table 1 gives the results for the converged basis B, which are about 50% higher than basis A values. The convergence of basis B is demonstrated in Table 2, which shows

Table 1. Calculated isomer shifts (mm/s) of ^{129}ICl , ^{129}IBr and $^{129}\text{I}_2$, relative to $^{129}\text{I}^-$. A and B in parentheses give the basis set used, described in the text and in Table 2.

		NR(A)	X2C(A)	4-comp(A)	X2C(B)
ICl	HF	0.54	1.00	1.00	1.51
	MP2	0.47	0.90	0.90	1.28
	CCSD	0.45	0.89	0.89	1.32
	CCSD(T)	0.44	0.85	0.85	1.25
IBr	HF	0.51	1.02	1.02	1.42
	MP2	0.44	0.84	0.84	1.23
	CCSD	0.43	0.83	0.83	1.25
	CCSD(T)	0.40	0.80	0.80	1.19
I_2	HF	0.45	0.90	0.90	1.24
	MP2	0.42	0.80	0.80	1.14
	CCSD	0.40	0.76	0.76	1.13
	CCSD(T)	0.39	0.74	0.74	1.08

Table 2. Basis set dependence of the isomer shift of ^{129}ICl and ^{129}IBr , relative to $^{129}\text{I}^-$ (mm/s). Calculations were performed at the CCSD(T) level with the X2C Hamiltonian. The top six lines demonstrate convergence of the more diffuse basis functions, whereas the bottom two describe the addition of high-exponent Gaussian functions on the I atom.

	I	Cl/Br	$\delta(\text{ICl})$	$\delta(\text{IBr})$
Basis A	23s19p12d3f	21s17p10d2f	0.85	0.80
	23s19p12d3f1g	21s17p10d2f1g	0.96	0.91
	24s20p13d4f2g	22s18p11d3f1g	0.99	0.94
	25s21p14d5f3g	23s19p12d4f2g	1.00	0.97
	26s22p15d5f3g	24s20p13d4f2g	1.11	1.06
	27s23p16d5f3g	25s21p14d4f2g	1.11	1.06
Basis B	31s22p15d5f3g	24s20p13d4f2g	1.25	1.19
	35s22p15d5f3g	24s20p13d4f2g	1.25	1.19

results of gradually increasing basis sets, carried out in the framework of the X2C Hamiltonian, with correlation included at the CCSD(T) level. The converged basis B consists of 35s22p15d5f3g uncontracted Gaussians on I and 24s20p13d4f2g functions on Cl and Br. Since isomer shifts depend strongly on the electron density inside the nucleus, high-exponent *s* functions are of considerable importance, and special care was taken to assure convergence of the high-exponent part of the basis (see two last lines in Table 2) as well as the more diffuse part.

The contribution of electron correlation to the isomer shifts was examined by calculating Hartree–Fock (HF) values, then including correlation at different levels, starting with the second-order Møller–Plesset perturbation theory (MP2) and proceeding to coupled cluster methods with singles and doubles (CCSD) and with perturbative triples [CCSD(T)]. The results, collected in Table 1, show that correlation lowers the isomer shifts by 15%–20%; the effect is larger for the higher order methods, which account for more electron correlation, but most of the change is already given at the low-order MP2 level. It is worth noting that the effect of adding perturbative triples

is larger than that of going from MP2 to the infinite-order CCSD.

The experimental studies of the ^{129}I isomer shifts have been reviewed critically by de Waard [36], and his recommended values are used below. Less information is available for ^{127}I [42]. Data for many iodine compounds in the solid state have been presented recently by Wdowik *et al.* [43]. Direct comparison of the results obtained from Equation (4) with experiment is problematic, due to the inherent large uncertainty in the value of ΔR . Filatov and co-workers [15–19] avoid using an explicit value for ΔR by employing a calibration constant, α , which connects between the calculated density at the nucleus and the experimentally measured isomer shift (see, e.g. Equation (2) in [15]). This scheme tests the proportionality of calculated and measured isomer shifts for several molecules. Eriksson *et al.* [44], who calculated the density in the nuclear region by a non-relativistic DFT approach, also used a multiplication factor *C*, obtained by dividing the experimental isomer shift for I_2 [36] by the calculated electron density at the nucleus. This factor accounts for the nuclear parameters as well as the relativistic increase of the electron density at the nucleus, and is then used for all the other iodine compounds studied. Here, we adopt a similar strategy, fitting the calculated isomer shifts of I_2 to the experimental values taken from [36] for the 129 isotope and from [42] for the 127 isotope, obtaining multiplication factors for the ICl and IBr species.

The final isomer shifts, calculated with the converged basis B, the X2C Hamiltonian and the CCSD(T) correlation scheme, and scaled by the method outlined above, are shown and compared with known experimental values and DFT results in Table 3. The ^{127}I isomer shifts

Table 3. Calculated isomer shifts of ICl, IBr and I_2 (mm/s, relative to I^-) compared with experiment and DFT results. All theoretical values were scaled to match experiment for I_2 , see text for details.

Molecules	δ	Environment	Method	Ref.
ICl	1.71	^{129}I isotope		
		Free molecule	X2C-CCSD(T)	Present
		Solid	Expt.	[36]
		Matrix	Expt.	[36]
IBr	1.74	Free molecule	DFT	[44]
		Free molecule	X2C-CCSD(T)	Present
		Solid	Expt.	[36]
		Matrix	Expt.	[36]
I_2	1.66	Free molecule	DFT	[44]
		Free molecule	X2C-CCSD(T)	Present
		Solid	Expt.	[36]
		Matrix	Expt.	[36]
ICl	1.48	^{127}I isotope		
		Free molecule	X2C-CCSD(T)	Present
		Solid	Expt.	[42]
		Free molecule	X2C-CCSD(T)	Present
IBr	-0.64	Free molecule	X2C-CCSD(T)	Present
		Free molecule	X2C-CCSD(T)	Present
I_2	-0.58	Free molecule	X2C-CCSD(T)	Present
		Solid	Expt.	[42]

have a sign opposite to that of ^{129}I , indicating an opposite direction of the change of radius during the γ transition. When comparing with experiment, it should be noted that the reported isomer shifts depend on the environment of the molecule, which may be embedded in a solid or in a matrix (usually argon). For the ^{129}I compounds, the multiplication factor was obtained from fitting to the shift of matrix-isolated I_2 , and thus the results for ICl and IBr should also be compared to the matrix-isolated molecules [36]. For both systems, our results are in excellent agreement both with the experimental values and with the earlier theoretical investigations.

The fitting to experiment for ^{127}I was done using the measured isomer shift of solid I_2 , so that the comparison for ^{127}ICl is with the measurement for the solid compound [42]. Again, we obtain a good agreement with the experimental value for ICl ; no other theoretical investigations were carried out on the ^{127}I compounds.

4. Summary and conclusion

Filatov's scheme for Mössbauer isomer shifts allows the incorporation of relativistic and correlation effects to high order. Here, we study the shifts of ^{129}I and ^{127}I in the ICl , IBr and I_2 molecules. Non-relativistic calculations give about half the shifts of relativistic methods, and are therefore inadequate. Relativistic four-component and exact two-component Hamiltonians give essentially identical shifts, so the latter, which is computationally less demanding, may be used, allowing for future calculations of larger systems. Correlation lowers the isomer shifts by 15%–20% relative to HF values; most of the effect is given by the MP2 scheme, but going to the CCSD(T) level induces significant changes.

Basis sets were increased until the calculated shifts converged. Particular attention must be paid to high-exponent functions, since the effect is strongly dependent on the electron density inside the nucleus. Using the converged basis, isomer shifts were obtained in the framework of the X2C Hamiltonian, with correlation at the CCSD(T) level. Comparison with experiment, where available, gave agreement within a few percent.

Disclosure statement

No potential conflict of interest was reported by the authors.

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