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Theoretical Interpretation of the Mössbauer Parameter in [1]Ferrocenophanes

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Synopsis. The smaller quadrupole splitting values in [1]ferrocenophanes than that in ferrocene were accounted for by assuming a lesser quantity of the nuclear part in the electric-field gradient at the iron nucleus; smaller quadrupole splitting could not be explained by the electron distribution among Fe 3d orbitals.

Mössbauer spectroscopy has been used as a very useful tool for probing the changes in the electronic environment around the iron nucleus.

Quadrupole splitting values (qs=2.0 mm s^{-1}) about 15% smaller than that in ferrocene were observed in (1,1′-ferrocenediyl)diphenylgermane, (1,1′-ferrocenediyl)phenylphosphine, and (1,1′-ferrocenediyl)diphenylsilane.[1] Stoeckli-Evans *et al.*[2] performed a three-dimensional X-ray analysis of these compounds, and determined the distances between the Fe and Ge atoms and between the Fe and P atoms to be 2.744 Å and 2.774 Å, respectively. They pointed out that there is clearly no bonding between these atoms, since these interatomic distances are appreciably longer than the bond lengths calculated from the metallic covalent radii ($l_{\mathrm{Fe\text{-}Ge}}$=2.47 Å and $l_{\mathrm{Fe\text{-}P}}$=2.37 Å).

On the other hand, Clemance *et al.*[3] stated that the Fe–P length of 2.77 Å does not preclude the possibility of bonding interaction between the Fe and P atoms, and that the contribution of the phosphorus' d orbitals can be present in (1,1′-ferrocenediyl)phenylphosphine.

These discussions indicate a lack of clear understanding of the reason why smaller qs values are to be expected in these [1]ferrocenophanes.

In the present note, the electronic structures and the electric-field gradients around the iron nucleus in (1,1′-ferrocenediyl)diphenylgermane and (1,1′-ferrocenediyl)phenylphosphine were estimated based on calculations by means of an *ab initio* (coreless) MO method. The smaller qs values than that in ferrocene are explained in terms of the lesser quantity of the nuclear part in the electric-field gradient at the iron nucleus.

Calculation

The pseudo-potential method of Barthelat and Durand[4] was used for the *ab initio* (coreless) MO calculations in order to account for the electronic structures and electric-field gradients around the iron nucleus. A one-electron-property-package of the MONSTER-GAUSS program[5] was installed in the PSHONDO program[6] which has been revised by Daudey in order to apply the pseudo-potential method to an original HONDO program.[7] The basis sets used for the Fe, C, and H atoms were the same as those in the previous communications;[8] only the basis set for the Fe 3d orbital was of a double-zeta quality. The contracted [2s2p1d] basis sets[9] optimized by Daudey were used for the valence of the Ge and P atoms.

The geometrical structures determined by Stoeckli-Evans *et al.*[2] were used for the calculations, but the phenyl groups were replaced by hydrogen atoms because of their large systems. These simplifications can not be expected to affect the electron distributions, especially in the 3d orbitals of the iron atom, which lies far from the phenyl groups. The original structures determined by Stoeckli-Evans *et al.*[2] were used without any modifications in calculating the nuclear part of the electric-field gradient at the iron nucleus in (1,1′-ferrocenediyl)diphenylgermane.

The usefulness of the coreless MO calculations with the pseudo-potential method has already been reported by several authors,[8,10–15] and we ourselves have discussed the ferrocene derivatives.[8]

All the calculations were performed by the use of a FACOM M380 computer at the Institute of Physical and Chemical Research.

Results and Discussion

The quadrupole splitting (qs) can be theoretically calculated by means of the principal component of the electric-field gradient (q_{zz}) around the iron nucleus: $qs=1/2\cdot eQV_{zz}(1+1/3\cdot\eta^2)^{1/2}$, where V_{zz} equals $-q_{zz}$, where Q is the nuclear electric quadrupole moment, and where η is the asymmetry parameter.[8] The qs value is, then, directly proportional to the q_{zz} values. The principal electric-field gradient (q_{zz}) is composed of the nuclear (q_{zz}^{NUC}) and electronic (q_{zz}^{ELF}) ones.

The q_{zz}^{ELF} values are proportional to the following amount, which corresponds to the electron distribution among iron's 3d orbitals: $q_{zz}^{\mathrm{ELF}}\propto[p(\mathrm{d}_{x^2-y^2}+\mathrm{d}_{xy})-\{p(\mathrm{d}_{z^2}+1/2\cdot p(\mathrm{d}_{xz}+\mathrm{d}_{yz})\}]$. Therefore, the qs values are also related to the electron distribution among the iron's 3d orbitals.

In Table 1, the total energies, the electron populations among iron's 3d orbitals, the net atomic charges, the electric-field gradients around the iron nucleus, and the asymmetry parameters are summarized. In the present *ab initio* (coreless) MO calculations, the phenyl moiety was replaced by a hydrogen atom because of its large system. The values in ferrocene, as calculated by means of the *ab initio* coreless MO method, have already been found to be in agreement with them obtained by using the all-electron MO method.[8]

The q_{zz}^{ELF} values in (1,1′-ferrocenediyl)diphenylgermane and (1,1′-ferrocenediyl)phenylphosphine are quite similar to that in ferrocene. These results come from the fact that the electron distribution among iron's 3d orbitals (in these molecules) agrees well with that in ferrocene, as is shown in the table. The η values in these compounds are quite small.

Table 1. Total energies, electron populations, net atomic charges, electric-field gradients, and asymmetry parameters in [1]ferrocenophanes

	Ferrocene	(1,1′-Ferrocenediyl)-diphenylgermane	(1,1′-Ferrocenediyl)-phenylphosphine	
			(A)[a]	(B)[b]
E_t[c]	−81.1477	−84.6464	−86.4948	−86.6835
$p(d_{x^2-y^2})$[d]	1.891	1.888	1.898	1.892
$p(d_{xy})$	1.891	1.896	1.901	1.899
$p(d_{xz})$	0.433	0.433	0.429	0.427
$p(d_{yz})$	0.433	0.460	0.426	0.429
$p(d_{z^2})$	1.947	1.954	1.963	1.960
$n(\mathrm{Fe})$[e]	6.734	6.825	6.758	6.742
$n(\mathrm{C})$	4.359	4.38—4.39	4.35—4.50	4.35—4.39
$n(\mathrm{H})$	0.767	0.77—0.78	0.77—0.78	0.77—0.78
$n(\mathrm{Ge})$	—	3.272	—	—
$n(\mathrm{P})$	—	—	4.128	4.431
q_{zz}^{NUC}[f]	−0.97	−0.73(−0.69)[g]	−0.81	−0.81
q_{zz}^{ELE}[h]	−3.18	−3.12	−3.21	−3.20
q_{zz}	−4.15	−3.85(−3.81)	−4.01	−4.01
η[i]	0.00	0.12	0.01	0.00

a) 3d Function was not added on the P atom. b) 3d Function was added on the P atom. c) Total energies in a.u. d) Electron populations among Fe 3d orbitals. e) Net atomic charges. f) Nuclear part of the electricfield gradient in a.u. g) We used the geometrical structures determined by Stoeckli-Evans *et al.*,[2] in which diphenyl was not replaced by hydrogen atoms. h) Electronic part of the electric-field gradient in a.u. The correction due to core electrons (shielding effect) was not performed. See Ref. 8. i) Asymmetry parameters.

The nuclear part of the electric-field gradient (q_{zz}^{NUC}) does not show a negligible value. It is worthwhile to note that the q_{zz}^{NUC} value in (1,1′-ferrocenediyl)diphenylgermane, in which the experimetal geometry determined by Stoeckli-Evans *et al.*[2] is used without any modifications, is lower by about 0.3 a.u. than that in ferrocene. This quite important result indicates that the total electric-field gradient in (1,1′-ferrocenediyl)diphenylgermane is also lower by 0.30 a.u. than that in ferrocene. (The overlap populations between the Fe and Ge atoms are −0.030, showing that there is no bonding between these two atoms.) Therefore, the smaller *qs* value in (1,1′-ferrocenediyl)diphenylgermane than that in ferrocene cannot be ascribed to the change in the electron distribution among iron's 3d orbitals caused by a direct bonding between the Fe and Ge atoms, but it can clearly be accounted for by the contribution of a smaller quantity of the nuclear part of the electric-field gradient around the iron nucleus in (1,1′-ferrocenediyl)diphenylgermane.

For the (1,1′-ferrocenediyl)phenylphosphine, two types of the calculations were performed; one (A) does not include the 3d polarization function for the phosphorus atom, while the other (B) does include it. As is shown in the table, the two sets of data are almost identical, indicating that the contribution of the phosphorus' 3d polarization function to the electron distribution among the iron's 3d orbitals does not exist in this system; the same q_{zz}^{ELF} values are obtained in these two types of calculations. The nuclear part of the electric-field gradient (q_{zz}^{NUC}) is smaller by 0.2 a.u. than that in ferrocene. (The q_{zz}^{NUC} value is estimated to become even smaller if the experimental geometry determined by Stoeckli-Evans *et al.*[2] is used, for in it the phenyl group is not replaced by a hydrogen atom.)

In (1,1′-ferrocenediyl)phenylphosphine, also the smaller experimental *qs* value can be accounted for by assuming a lesser contribution of the nuclear part to the electric-field gradient.

In conclusion, the smaller experimental *qs* values can be ascribed by the lesser q_{zz}^{NUC} values, without using any unreasonable supposition such as that reported by Clemance *et al.*[3]

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