Erratum zu:

Nonlocal Susceptibilities and Molecular Electric Quadrupole Moments of 3-Fluoropyridine and 2,6-Difluoropyridine, a Rotational Zeeman Effect Study

D. Hübner, M. Stolze, and D. H. Sutter
Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik

Z. Naturforsch. **37a**, 95–96 (1982);
received November 16, 1981

The lower part of Table 4 of our paper [1] contained several printing errors. In view of the rising interest in experimental values for the second moments of the molecular charge distribution the corrected Table is given below. The abbreviations have the following meanings:

$Z_n \triangleq$ atomic number of n-th nucleus,
$a_n, b_n, c_n \triangleq$ coordinates of the n-th nucleus,
$a_\varepsilon, b_\varepsilon, c_\varepsilon$ and the ε-th electron with respect to the principal inertia axes system,
$\langle 0 |\ | 0 \rangle$ denotes an electronic ground state expection value.

For comparison we also include calculated approximate values for the second moments of the electronic charge distribution. They result from a "back of the envelope calculation" according to Eq. (20) of Ref. [2] which reads:

$$\left\langle 0 \left| \sum_{\varepsilon}^{\text{electrons}} x_\varepsilon^2 \right| 0 \right\rangle = \sum_{n}^{\text{nuclei}} Z_n x_n^2 + 0{,}19\, n_{\mathrm{H}} + 1{,}24\, n_{\mathrm{B}} + 1{,}06\, n_{\mathrm{C}} + 0{,}92\, n_{\mathrm{N}} + 0{,}81\, n_{\mathrm{O}} + 0{,}73\, n_{\mathrm{F}}\,. \quad (1)$$

with $x = a$, b or c.

Here n_{H}, n_{B} etc. are the numbers of Hydrogen atoms, Borine atoms, etc. present in the molecule. The result is given in $Å^2 = 10^{-20}\ \mathrm{m}^2$.

In essence equations such as Eq. (1) view the molecule as a superposition of neutral atomic charge distributions, each spherical, and are closely

---

Reprint requests to Prof. Dr. H. Sutter, Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, Olshausenstraße 40–60, D-2300 Kiel.

Table 1. The Table contains the corrected lower part of Table 4 of Ref. [1] supplemented by calculated approximate values for the second moments of the electron charge distribution (see Eq. (1) of the text). The rigid rotor expressions used for the evaluation of the experimental data are given at the left hand side. The experimental uncertainties are given in units of the least significant figure and correspond to one standard deviation.

		3-Fluoro-pyridin	2,6-Difluoro-pyridin
Second moments of the nuclear charge distribution from the geometry of the nuclear frame (Fig. 2 of [1]). All values are given in $Å^2 = 10^{-20}\ \mathrm{m}^2$.	$\sum_{n}^{\text{nuclei}} Z_n a_n^2$	99.7 (1)	132.2 (1)
	$\sum_n Z_n b_n^2$	50.3 (1)	73.2 (1)
	$\sum_n Z_n c_n^2$	0.00	0.00
Second moments of the electronic charge distribution in $Å^2$.	$\langle 0 \vert \sum_{\varepsilon}^{\text{electrons}} a_\varepsilon^2 \vert 0 \rangle_{\text{exp}}$	108.0 (24)	140.9 (24)
	$\langle 0 \vert \sum_{\varepsilon} a_\varepsilon^2 \vert 0 \rangle_{\text{calc}}$	107.4	140.5
Experimental values derive from the g-values, susceptibilities and rotational constants according to: $\left\langle 0 \vert \sum_{\varepsilon}^{\text{electrons}} a_\varepsilon^2 \vert 0 \right\rangle = -\frac{2mc^2}{e^2}(\chi_{bb} + \chi_{cc} - \chi_{aa}) - \frac{h}{16\pi^2 m_p}\left(\frac{g_{bb}}{B} + \frac{g_{cc}}{C} - \frac{g_{aa}}{A}\right) - \sum_{n}^{\text{nuclei}} Z_n a_n^2$	$\langle 0 \vert \sum_{\varepsilon} b_\varepsilon^2 \vert 0 \rangle_{\text{exp}}$	58.0 (24)	81.6 (24)
	$\langle 0 \vert \sum_{\varepsilon} b_\varepsilon^2 \vert 0 \rangle_{\text{calc}}$	58.0	81.5
	$\langle 0 \vert \sum_{\varepsilon} c_\varepsilon^2 \vert 0 \rangle_{\text{exp}}$	8.4 (24)	8.7 (24)
Calculated values result from Eq. (1), text.	$\langle 0 \vert \sum_{\varepsilon} c_\varepsilon^2 \vert 0 \rangle_{\text{calc}}$	7.7	8.3

0340-4811 / 82 / 0100-0095 $ 01.00/0. — Please order a reprint rather than making your own copy.

related to Steiners rule for the calculation of the moment of inertia of a larger body composed from smaller bodies of known moment of inertia.

The calculated and experimental values agree within the experimental uncertainties, and it is obvious that the experimental values are of no use as a check of quantum chemical calculations.

We note however that the second moments of the electronic charge distribution are the least accurate values determined in a rotational Zeeman effect study since they require the bulk susceptibilities as additional input data. Since the latter are usually determined in the liquid phase or are even only estimated from Pascals rules [3], they include large uncertainties if used for free molecules as are investigated in microwave spectroscopy. We further note that electronic second moments calculated from Eq. (1) would lead to zero molecular electric quadrupole moments. The latter may be also determined from a rotational Zeeman effect study. Since their determination does not require the bulk susceptibility as additional input data, they are obtained with higher accuracy and are thus better suited to check the quality of quantum chemical calculations.

Our results show that within the present experimental uncertainties, calculations based on CNDO/2- or INDO-wavefunctions appear to reproduce the observed quadrupole moments already rather well [2], especially if families of related molecules are considered [4]. However, since by use of the high resolution microwave spectrometers which are under construction in our laboratory, quadrupole moments with considerably reduced experimental uncertainties will become available in the near future, we expect them to become more and more useful as additional test data also for quantum chemical ab initio calculations.

For more detailed theoretical considerations related to the calculation of the second moments, the reader is referred to a recent paper by Maksić and Mikac [5], which also containes a simpler "back of the envelope formula" with an even wider range of application.

[1] D. Hübner, M. Stolze, and D. H. Sutter, Z. Naturforsch. **36a**, 332 (1981).
[2] E. Hamer, L. Engelbrecht, and D. H. Sutter, Z. Naturforsch. **29a**, 924 (1974).
[3] P. Pascal, Ann. Chim. Phys. **19**, 5 (1910). — P. W. Sellwood, Magnetochemistry. Interscience Publ., New York 1956.
[4] Compare for instance Figs. 6 and 7 of Ref. [1].
[5] Z. B. Maksić and N. Mikac, Mol. Phys. **40**, 455 (1980).

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg