

NOTAS DE FÍSICA

VOLUME X

Nº 17

NUCLEAR ISOMER SHIFT AND COVALENCY IN IRON COMPLEXES

by

J. Danon

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71

RIO DE JANEIRO

1963

•

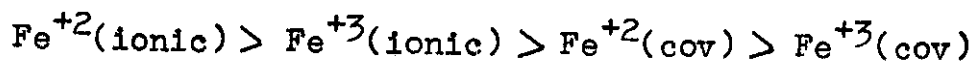
NUCLEAR ISOMER SHIFT AND COVALENCY IN IRON COMPLEXES *

J. Danon

Centro Brasileiro de Pesquisas Físicas
Rio de Janeiro - Brasil

(Received July 17, 1963)

In a recent study of the Mossbauer effect with spin-free and spin-paired iron complexes we have shown ¹ that the isomer shift of the resonance curves follows the order:



These shifts are relative to the same material (stainless steel) and they measure the increase in total s-electron density at the Fe⁵⁷ nucleus ^{2,3} on going from Fe⁺²(ionic) to Fe⁺³(cov) (decreasing shift = increasing s-electron density).

For the ionic configurations which follow Hund's rule it has been possible to give a quantitative interpretation of the isomer shift ² on the basis of the wave function calculations of Watson. The increase in s-electron density at the iron

* Accepted for publication in the Journal of Chemical Physics.

nucleus on going from $3d^n$ to $3d^{n-1}$ configurations arises as a consequence of the decrease in shielding of the 3s electrons by the remotion of the d electron ^{2, 4}.

In the spin-paired iron complexes the 3d electrons are more or less delocalized according to the strength of π -bonding between the d_{π} orbitals of the metal and the appropriate orbitals of the ligands. The spread of the charge cloud of the d-electrons due to this covalent bonding will decrease the shielding of the s-electrons and it is thus possible to explain the relatively small isomer shift observed with these complexes.

The isomer shift observed with the isoelectronic ligands CN^- , CO, NO^+ in the complexes $Fe^{II}(CN)_6^{(1)}$, $Fe(CO)_5^{(5,6)}$ and $Fe^{II}(CN)_5NO^{(1,5)}$ give the following order for the s-electron density at the Fe nucleus:



The extent of back-donation of the d_{π} electrons of the metal to the π antibonding orbitals of the ligands follow also the same order, as expected from the relative electronegativity of those ligands ⁷. The extensive deslocalization of the d_{π} electrons in the Fe-NO π bonds leads to a large increase of s-electron density at the iron nucleus in the nitrosyl complex.

These ideas are also useful for the interpretation of Mössbauer measurements of several iron-nitrosyl complexes. Table I gives the results of these measurements with the same apparatus described in our previous work ¹.

Table I

Complex	Temperature	Isomer shift (cm/sec)	Quadrupoles coupling (cm/sec)
$\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}$	room	-0.012 ± 0.005	0.185 ± 0.005
$\text{Fe}^{\text{II}}(\text{H}_2\text{O})_5\text{NO}^*$	room	$+0.140 \pm 0.010$	0.170 ± 0.010
$\text{Fe}^{\text{II}}[\text{S}_2\text{CN}(\text{CH}_3)]_2\text{NO}$	room	$+0.038 \pm 0.005$	0.085 ± 0.005
$\text{Fe}^{\text{II}}[\text{S}_2\text{CN}(\text{CH}_3)]_2\text{NO}$	liq. N_2	$+0.046 \pm 0.005$	0.081 ± 0.005
$\text{Fe}^{\text{II}}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2\text{NO}$	room	$+0.043 \pm 0.005$	0.076 ± 0.005

Extensive π -bonding in the NO^+ complexes of the transition metals have been assumed by Gray and Ballhausen⁸. Confirming this idea it has recently been found that the Fe-NO distance (1.63 \AA) is shorter than the Fe-CN distance (1.92 \AA) in the $\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}$ complex⁹. The isomer shift for this complex (-0.012 ± 0.005) indicates the largest s-electron density observed with an octahedral or substituted octahedral iron complex.

$\text{Fe}(\text{H}_2\text{O})_5\text{NO}$ is an interesting spin-free complex of NO^+ as shown by magnetic and infra-red measurements¹⁰. π bonding in this complex is absent or very small^{10,11}. The delocalization of the d-electrons of Fe and that of the unpaired electron of NO on the $\pi^* - 2p$ orbital should in consequence be negligible. In agreement both the isomer shift and the quadrupole interaction for this complex are typical of Fe^{+2} ionic compound.

The magnetic moment of nitroso-bis (dimethyldithiocarbamate) iron (II) shows that the complex has one unpaired electron¹². The M. O. level scheme is $(e)^4(b_2)^2(b_1)^1$ with a

* $\text{Fe}(\text{H}_2\text{O})_5\text{NO}$ is contained in the complex $(\text{FeSO}_4)_2 \cdot \text{NO} \cdot 13 \text{ H}_2\text{O}$ (10).

2B_1 ground state with electron in the (b_1) antibonding orbital¹³.

The hyperfine splitting structure of the electron spin resonance spectra of this complex shows that the unpaired electron is delocalized in respect to the N nucleus^{12, 13, 14}. The extent of delocalization is however smaller than that observed with $Cr(CN)_5NO$ ⁽¹⁵⁾. This difference has been attributed to the fact that in $Cr(CN)_5NO$ the delocalization concerns a non-bonding orbital of the transition metal whereas with the nitroso-carbomato complex an antibonding orbital of iron is involved.

By these arguments the extent of delocalization of d electrons and consequent increase in s-electron density at the iron nucleus should be smaller in $Fe^{II}[S_2CN(CH_3)_2]_2NO$ than in $Fe(CN)_5NO$ which is in agreement with the isomer shift values for these complexes.

* * *

Acknowledgements

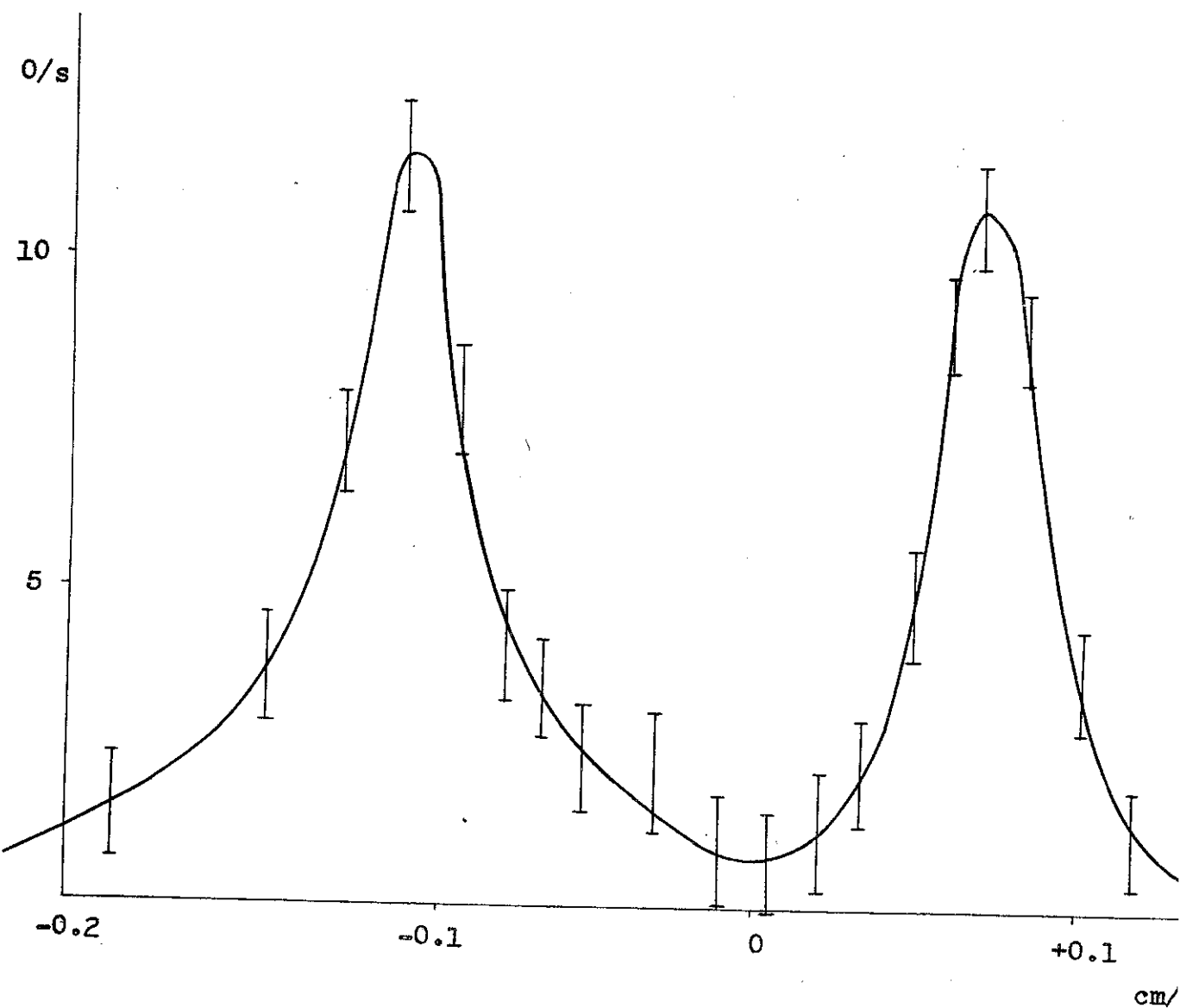
We are indebted to Professor A. L. Zamith for advice in preparing the complexes and to Dr. P. Krumholz and Professor Hans Stammreich for helpful discussions.

* * *

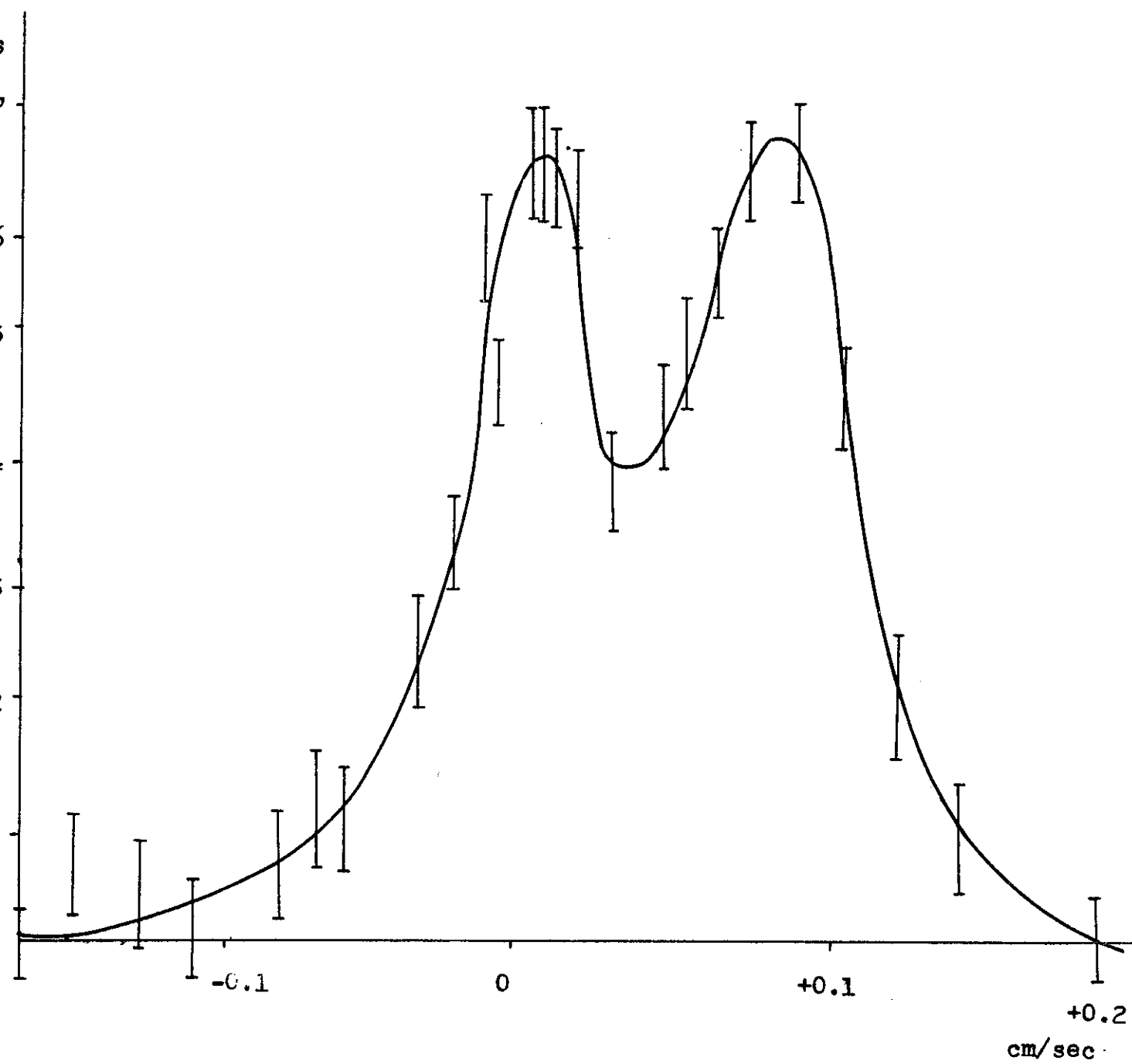
References:

1. Neyla L. Costa, J. Dancou and R. Moreira Xavier - J. Phys. Chem. Solids 23, 1738 (1962).
2. L. R. Walker, G. K. Weutheim and V. Jaccarino - Phys. Rev. Letters 6, 98 (1961).
3. S. De Benedetti, G. Lang and R. Ingalls - Phys. Rev. Letters 6, 60, (1961).
4. R. Ingalls - Thesis, Carnegie Institute of Technology (1962).
5. L. M. Epstein - J. Chem. Phys. 36, 2731 (1962).
6. M. Kalvius, U. Zahn, P. Kienle and H. Eicher - Z. Naturforschg. 17a, 494 (1962).
7. W. P. Griffith - Quart. Rev. 16, 188 (1962).
8. H. B. Gray and C. J. Ballhausen - J. Chem. Phys. 36, 1151 (1962).
9. H. B. Gray - private communication, March 1963.
10. W. P. Griffith, J. Lewis and G. Wilkinson - J. Chem. Soc. 3993 (1958).
11. J. Lewis - Sci. Prog. 47, 506 (1959).
12. J. F. Gibson - Nature 196, 64 (1962).
13. H. B. Gray, I. Bernal, and E. Billig - J. Am. Chem. Soc. 84, 3404 (1962).
14. I. Bernal and M. F. Heckings - Proc. Chem. Soc. 361 (1962).
15. I. Bernal and S. H. Harrison - J. Chem. Phys. 34, 102 (1961).

* * *



Mössbauer spectrum of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}] \text{Na}_2 \cdot 2\text{H}_2\text{O}$



Mössbauer spectrum of $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2\text{NO}$ at liquid nitrogen temperature.