

Mössbauer Effect in Frozen Solutions of Nitroprusside

Cite as: J. Chem. Phys. 50, 3127 (1969); <https://doi.org/10.1063/1.1671525>

Submitted: 12 November 1968 . Published Online: 19 December 2003

W. A. Mundt, and T. Sonnino



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Mössbauer Hyperfine Interactions in Sodium Nitroprusside Single Crystals](#)

The Journal of Chemical Physics 47, 382 (1967); <https://doi.org/10.1063/1.1711904>

Lock-in Amplifiers

Zurich Instruments

Watch the Video

TABLE I. Observed lines of the $c\ ^3\Pi-X\ ^1\Sigma^+$ transition.

J	$P(J)$	$Q(J)$	$R(J)$
1			92 084.99
2	92 068.41		089.15
3	065.81		093.31
4	062.51		097.36
5	058.16		101.73
6	055.00		105.88
7	052.14		110.54
8	047.96	92 078.97	115.07
9	045.09	080.21	119.89
10	042.95	081.02	124.59
11	039.73	081.86	129.45
12	036.36	082.79	
13	032.99	083.95	
14	030.11	084.99	
15		086.24	
16		087.63	
17		089.15	
18		090.38	
19		091.91	

of figure). Branches of the new transition are illustrated at the top of the figure.

A condensed Q branch is consistent with either a $\Pi^{-1}\Sigma^+$, $\Delta^{-1}\Sigma^+$, or $^3\Sigma^{-1}\Sigma^+$ transition but not with a $^3\Sigma^+1\Sigma^+$ transition. For a $^3\Sigma^-$ upper state, three Q -type branches are expected, but no P or R branches are permitted. Therefore, the upper state of this transition must be Π or Δ in disagreement with the previous assignment^{2,5} (unless two electronic states in the CO molecule occur within $\sim 0.5\text{ cm}^{-1}$ of each other which is extremely unlikely).

On the basis of the strength of this transition in absorption, the near-ultraviolet transition in emission,⁵ theoretical calculations¹⁰ which correlate very well with other low-lying Rydberg states in CO,^{7,9} and recent high-angle electron scattering observations,¹¹ it is most probable that the c state is a $^3\Pi$ state. As stated earlier,⁹ reanalysis of Gerö's data⁵ does not preclude the assignment of the near-ultraviolet transition to a $^3\Pi-^3\Pi$ transition; however, the apparent resolution of the older data is too poor to make a definite decision.

If the upper state is $^3\Pi$ we have observed a transition to only one of the triplet components, unless the $^3\Pi$ state is pure Hund's case "b" in which there would be no spin splitting. Because of the uncertainty in the Λ -type doubling in the upper state, the $Q(J)$ lines may be in error by 2 or more J numbers. The $Q(J)$ lines

were assigned to minimize the splitting between the Π^+ and Π^- components in the upper state.

Observed band lines are tabulated in Table I. Values of $B^+=1.963\text{ cm}^{-1}$ and $\nu_0=92076.9\text{ cm}^{-1}$ have been derived from a least-squares fit of the data. Within the limits of error for the two sets of data, these quantities are in good agreement with those determined from the near-ultraviolet data of Gerö.⁵

¹ P. H. Krupenie, Natl. Std. Ref. Data Ser., Natl. Bur. Std. (U.S.) NSRDS-NBS 5 (1966).

² R. Schmid and L. Gerö, Nature **139**, 928 (1937).

³ L. Gerö, G. Herzberg, and R. Schmid, Phys. Rev. **52**, 467 (1937).

⁴ G. H. Dieke and J. W. Mauchly, Phys. Rev. **43**, 12 (1933).

⁵ L. Gerö, Z. Physik **109**, 210 (1938).

⁶ P. G. Wilkinson and E. T. Byram, Appl. Opt. **5**, 581 (1965).

⁷ S. G. Tilford, J. T. Vanderslice, and P. G. Wilkinson, Can. J. Phys. **43**, 450 (1965).

⁸ S. G. Tilford and J. T. Vanderslice, J. Mol. Spectry. **26**, 419 (1968).

⁹ J. E. Hesser and K. Dressler, J. Chem. Phys. **45**, 3149 (1966).

¹⁰ H. Lefebvre-Brion, C. M. Moser, and R. K. Nesbet, J. Mol. Spectry. **13**, 418 (1964).

¹¹ H. H. Brongersma and L. J. Oosterhoff, Chem. Phys. Letters **1**, 169 (1967).

Mössbauer Effect in Frozen Solutions of Nitroprusside*

W. A. MUNDT AND T. SONNINO†

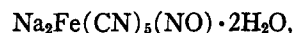
Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil

(Received 12 November 1968)

The results of Mössbauer-effect experiments are very often interpreted in terms of molecular electronic structure, but if the Mössbauer nucleus is bound in a covalent charged complex, the effects of the external ions are ignored. The lattice effects on the electronic structure are also ignored in the case of molecular crystals. Frozen solutions can be used to study those effects.

In recent years the Mössbauer effect has been applied to frozen aqueous solutions of some inorganic iron salts,^{1,2} in order to study the crystalline arrangement of water molecules and its effect, at temperatures between about -190° – 0°C . The effects of the lattice have been demonstrated to be quite important in the case of molecular I_2 using ^{129}I in the inert organic solvents.³ Our purpose was to follow another line, investigating iron complexes, in which the influence of water dipoles in the frozen solution would be presumably negligible and certainly the interaction solute-solvent smaller than the effects that are to be measured.³

In this Note we report an experiment carried out to test the effect of ions external to the complex. We have chosen sodium nitroprusside



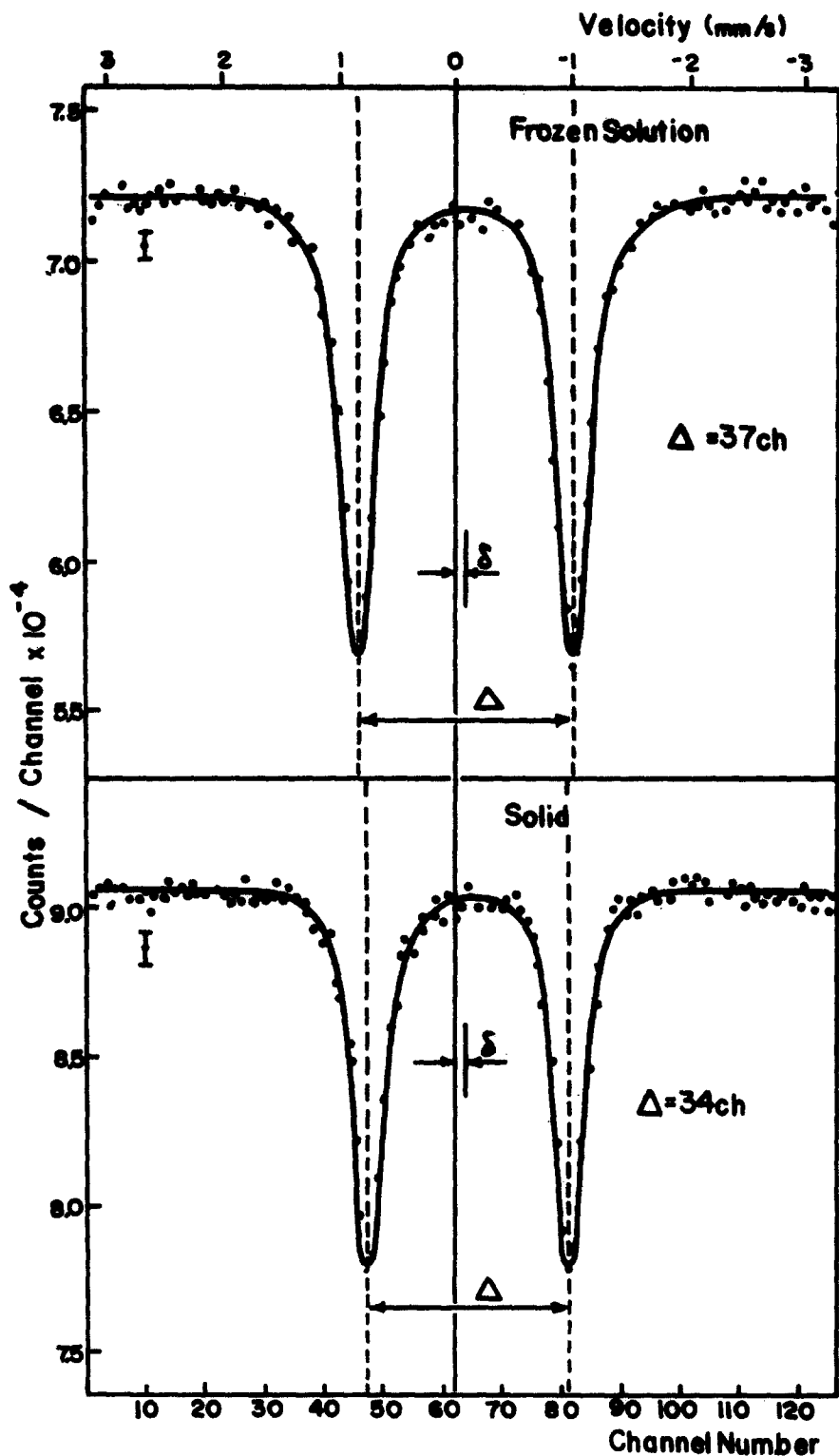


FIG. 1. The Mössbauer effect of aqueous frozen solution (upper) and of solid (lower) nitroprusside, both at liquid-nitrogen temperature.

whose properties have been exhaustively studied⁴ and the results interpreted using electronic structure calculations.⁵ The nitroprusside molecule has the structure of a distorted octahedron, the iron atom occupying nearly the center and four CN groups being equatorial

and the fifth CN group colinear with the Fe nucleus and NO group on the axial direction.

Aqueous solutions of sodium nitroprusside were prepared with concentrations between 0.05M and 1.4M (saturated solution).

Solutions in ethyl alcohol with a concentration smaller than 0.05M were also investigated, to test the possible influence of the solvent. These solutions were introduced in an absorber holder with Mylar windows and rapidly cooled with liquid nitrogen. To test the influence of ionic concentration another series of solutions was prepared with a nitroprusside concentration of 0.1M and an NaCl concentration up to 2M. The Mössbauer effect was measured using a constant acceleration setup and a ^{57}Co source in a Cr matrix. The results were reproducible and are shown in Fig. 1, compared with solid nitroprusside at liquid-nitrogen temperature.

The quadrupole splitting $\Delta = \frac{1}{2}e^2qQ$ increased in the frozen solutions to 1.86 ± 0.03 mm/sec as compared to 1.71 mm/sec in the solid, independently of concentration and ionic strength. The isomer shift δ is equal for solid and frozen solutions, except for the second-order Doppler shift.⁶

The same increase in quadrupole coupling was observed in the alcoholic solution, thus confirming the negligible effect of water dipoles in the behavior of the iron complex.

The difference in $\frac{1}{2}e^2qQ$ in the solid and frozen solutions can be explained as an effect of polarization of the cations on the CN ligand groups. Direct effects can be ruled out, as the two Na^+ ions in the solid are too far away to contribute directly to the electric field gradient.

According to Danon,⁴

$$q = (4/7)\langle r^{-3} \rangle (n_{xy}) - (2/7)\langle r^{-3} \rangle (n_{zz} + n_{yz}),$$

where n is the electron population in the various iron d orbitals. From Ref. 5 the charge distribution of the complex is $(\text{Fe})^{+0.3166}(\text{CN})_4^{-2.200}(\text{CN})^{-0.5809}(\text{NO})^{+0.4643}$, where $(\text{CN})_4$ are the four equatorial ligands in the xy plane, the other (CN) being axially colinear with the NO group in the z direction.

In the solid the two Na^+ ions will polarize the negative CN groups, hence also the Fe-CN bonds, and affect the electron populations of the iron orbitals. This effect will result in a different contribution of q for axial and equatorial bonds, as lower population in the equatorial bonds (xy) will decrease q , the opposite for the axial.

In the solutions, where the complex is presumably surrounded by solvent molecules, this polarization will be removed, and the charge in the Fe-CN bond increased. This effect in the four equatorial bonds will result in higher electron population in the d_{xy} orbitals of iron, (n_{xy}), and hence increase the quadrupole splitting as has been actually found.

* Work supported partially by CNPq (Brasil), CPq (UFGGS), Air Force Office of Scientific Research, and I.A.E.A.

† I.A.E.A. Visiting Professor. Permanent address: Soreq Nuclear Research Center, Yavne, Israel.

¹I. Dezi, L. Keszthelyi, B. Molnar, and L. Pocs, Proc. Conf. Hyperfine Structure Nucl. Radiations, Asilomar, Calif., 1967, 566 (1968).

²A. J. Nozik and M. Kaplan, J. Chem. Phys. **47**, 2960 (1967).

³S. Buckshpan, C. Goldstein, and T. Sonnino **49**, 5477 (1968).

⁴J. Danon and L. Iannarella, J. Chem. Phys. **47**, 382 (1967) and references cited therein. It is interesting also to remember that nitroprusside has been proposed as a standard material for the Mössbauer effect in ^{57}Fe . Intern. At. Energy Agency, Tech. Rept. Ser. **50**, 254 (1966).

⁵P. T. Manoharan and H. B. Gray, J. Am. Chem. Soc. **87**, 3340 (1965).

⁶W. Kerler and W. Neuwirth, Z. Physik **167**, 176 (1962).

Quenching of $\text{N}_2(A \ ^3\Sigma_u^+)$ in High Vibrational Levels by Nitrogen Atoms

MICHAEL P. WEINREB AND GENE G. MANNELLA

Electronics Research Center, Cambridge, Massachusetts

(Received 18 October 1968)

Several researchers¹ have suggested that the primary process in removing $\text{N}_2(A \ ^3\Sigma_u^+)$ in low ($v=0,1$) vibrational levels from active nitrogen is



with a rate coefficient, k_1 , of 5×10^{-11} cm³ sec⁻¹, corresponding almost to the kinetic cross section; Thrush² estimated k_1 at 5×10^{-12} cm³ sec⁻¹. Also interesting is the value of k_1 where Reaction (1) involves $\text{N}_2(A \ ^3\Sigma_u^+)$ in high vibrational levels, since, for example, this reaction might interfere with the mechanism suggested by Campbell and Thrush³ for populating the $\text{N}_2(B \ ^3\Pi_g)$ state in active nitrogen.

In studies on surface-catalyzed excitation of nitrogen,⁴ we have deduced an upper limit of 5×10^{-13} cm³ sec⁻¹ for k_1 when Reaction (1) involves $\text{N}_2(A \ ^3\Sigma_u^+)$ in high levels.

Surface-catalyzed excitation of nitrogen⁴ occurs when a mixed stream of nitrogen atoms and discharged oxygen passes over a nickel, cobalt, or copper surface. A red glow appears in the gas above the surface, its intensity decreasing with increasing height above the surface until it disappears in the background at a height of several centimeters. This glow contains only first positive bands of N_2 . The most intense bands originate from $v=6$ of the $B \ ^3\Pi_g$ state, and bands from levels above the eighth are suppressed. The evidence indicates⁴ that nitrogen atoms recombining at the surface form molecules in high ($v \geq 7$) levels of the A state. These molecules diffuse into the gas and cross into the B state through collisions, i.e., $\text{N}_2(A \ ^3\Sigma_u^+) + \text{M} \rightarrow \text{N}_2(B \ ^3\Pi_g) + \text{M}$. These B -state molecules radiate immediately in transitions to low levels of the A state.

In this paper we use measurements of the intensity of this glow to determine k_1 . Above the surface, the steady-state concentration of A -state molecules in high levels is mainly governed by three processes: the diffusion of these A -state molecules from the surface where they were formed; the A - to B -state crossing; and Reaction (1). Solution of the rate equation yields