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Determination of the Mössbauer Parameters of Nitrosylpentacyanoferrates (NP)

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The Mössbauer parameters isomer shift (IS), quadrupole splitting (QS), and probability of recoilless absorption f' of 26 nitroprussides have been measured at room and liquid nitrogen temperatures. The values of the QS and the IS of the different compounds are close to each other, which is supposed to result from the same short-range environment of the Fe atom in the $[Fe(CN)_5NO]^{2-}$ ion. A weak correlation between IS and electronegativity of the lattice cation, as well as between QS and CN_{trans} stretching vibrations was found. For some of the investigated nitroprussides a Goldanskii–Karyagin effect was observed. The Mössbauer parameters IS and QS for two long-living electronic metastable configurations in some nitroprusside single crystals are measured, too. Like in the case of ground state, these parameters are very close to each other, which shows that for the new metastable states the changes in the electron density distribution of the $[Fe(CN)_5NO]^{2-}$ anion do not practically depend on the kind of the metal cation.

INTRODUCTION

Sodium nitrosylpentacyanoferrate (II) dihydrate, more commonly known as sodium nitroprusside $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (we use the abbreviation NP for $[Fe(CN)_5NO]^{2-}$), is most often used in Mössbauer spectroscopy as a velocity calibration standard for the drive systems. The quadrupole splitting (QS), isomer shift (IS), and the recoilless fraction f' for the three principal crystal directions have been measured with high accuracy for Na_2NP single crystals (1). However, this material possesses surprising features. By means of Mössbauer spectroscopy a very interesting phenomenon, in connection with the formation of a new exited metastable state of the molecules, has been observed (2). The phenomenon has already been studied by means of many other methods (3–7). Two long-living electronic metastable configurations (SI and SII) can be generated in Na_2NP single crystals by irradiation with light in the spectral range 350–580 nm at temperatures below 200 K (SI) and 150 K (SII). The changes of structure and N–C–Fe–N–O bond distance at ground and electronically exited states have been directly measured by neutron diffraction (8). Population, depopulation, and transition dynamics between the ground and two metastable states have been precisely studied as a function of the intensity, wavelength, polarization, and duration of the illuminating light (9). The electronic structure of both new metastable states is investigated by means of Mössbauer spectroscopy (10). Such nearly infinitely long-living electronic states can be generated in many nitrosylpentacyanoferrates (11).

Not less interesting is the observed difference between the probabilities of recoilless resonance absorption f' and reemission f'' of gamma-quanta in single crystals of Na_2NP (12). The values of recoilless absorption f' and recoilless reemission after resonance absorption f'' are commonly assumed to be equal. Unexpectedly, the Mössbauer measurements revealed that $f'' > f'$.

For a number of nitroprussides QS and IS have been measured at room temperature, but the values of f' have not been determined (13, 14). The results from Ref. (13) have been limited by the capabilities of Mössbauer spectroscopy available at that time, so some of the numerical data are not reliable. In the present work the Mössbauer parameters QS, IS, and f' of a number of nitrosylpentacyanoferrates at room and liquid nitrogen temperatures are determined. Some of these nitroprussides have not been investigated by means of Mössbauer spectroscopy so far. The main purpose of this investigation is to find correlations between formation conditions of the metastable states and Mössbauer parameters of the ground state. An

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eventual prediction of the species with the highest temperature ($T_{\max}$) at which the metastable state still exists is of great importance. As a result of the performed studies the Mössbauer parameters IS and QS for the new metastable states populated in single crystal species of Li_2NP, Na_2NP, and K_2NP were determined as well. Another aim of this work is to find nitroprussides with Mössbauer parameters which are suitable for investigations on the inequality between f' and f''.

EXPERIMENTAL METHODS

Samples

The examined compounds are iron complexes. The general chemical formula of all nitroprussides is $M_xNP \cdot yH_2O$, where M are NH_4, H, Tl, Ce, Cr, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, Li, Na, K, Rb, Cs, Ca, Sr, Ba, and some organic cations like CN_3H_6 (guanidinium), CH_6N (methylammonium), and $C_2H_7N_2$ (acetamidinium) and $y = 0$, 1, 1.5, 2, 2.5, 3, 4, 5, and 6. The iron is located in the center of the quasi-octahedral complex nitroprusside ion $[Fe(CN)_5NO]^{2-}$ (NP) and as a normal cation in FeNP. The raw material for growing single crystals has been synthesized from Ag_2NP or Hg_2NP which were produced from aqueous solutions of Na_2NP by adding $AgNO_3$ or $HgNO_3$. Treatment of the washed precipitates with the corresponding chlorides MCl, MCl_2, or MCl_3, respectively, in water, yielded an aqueous solution or a precipitation of the required nitroprussides $M_xNP \cdot yH_2O$ (11, 13). Therefore, Na was substituted by all alkali and alkaline earth ions, some transition metals, NH_4, H, Tl, Ce, and some organic cations. Single crystals of some of the substances under investigation could be grown from aqueous solutions by slow evaporation of the solvent at about 310 K (15).

Mössbauer Study

The Mössbauer absorbers were single crystal species cut from big crystals of high quality or were prepared by pressing a powdered mixture of the investigated compound and polyvenyl alcohol (PVA). All spectra have been obtained in geometry of absorption. The source $^{57}Co[Pd]$ with activity of about 30 mCi was driven with a constant acceleration by an electrodynamic-type drive system. A scintillation detector with a thin 0.1 mm NaI(Tl) crystal was used. The velocity calibration was performed many times during the measurements with Na_2NP single crystals, for which the values of QS and IS are known with high accuracy (1). The experimental spectra were fitted to a sum of Lorentzian lines by means of a least-squares procedure.

For determination of the probability of recoilless absorption, f', a method which uses the area of the absorption lines was applied. The experimental area in the case of a single Lorentzian absorption and source lines is

$$S(t) = \frac{N_{(\infty)}\alpha\pi t\Gamma_A}{2}\exp(-t/2)\cdot[I_0(t/2) + I_1(t/2)] \qquad [1]$$
$$t = \frac{n\sigma_0 f'\Gamma_N}{\Gamma_A},$$

where $N_{(\infty)}$ is the number of impulses at infinite velocity of the source (the absorber is fixed), α is a recoilless part of the gamma-quanta in the window of the differential discriminator, Γ_N is the natural line width 0.097 mm/s determined by the lifetime of the Mössbauer level 14.4 keV, Γ_A is the line width of the absorber, I_0 and I_1 are modified Bessel functions of the first kind and zero and first order, respectively, n is the number of ^{57}Fe nuclei per cm^2 (the natural abundance of the ^{57}Fe isotope was 2.19%), and σ_0 is the maximum resonant absorption cross section (the value of $\sigma_0 = 2.57.10^{-18}$ cm^2 has been used).

The determination of the parameter Γ_A is difficult, because the width of the source line Γ_S is not known. It is usually assumed that $\Gamma_A = \Gamma_N$, which leads to higher values of f'. In our case of a well resolved quadrupole doublet and the absence of magnetic and relaxation phenomena the equality $\Gamma_A = \Gamma_N$ is fulfilled. The experimentally measured line widths of the doublet $\Gamma_{\exp} = \Gamma_A + \Gamma_S$ at room temperature lie within the range 0.250–0.280 mm/s. These values are typical for absorbers with effective nonzero thickness t and are very close to the minimum possible experimental width $\Gamma_{\exp} = 2\Gamma_N = 0.194$ mm/s. This is a strong evidence that the measurements were carried out at optimum conditions, the influence of disturbing vibrations and other artifacts causing line broadening being excluded. The observed line widths speak about well crystallized substances. In the case $\Gamma_{\exp} = 2.5\Gamma_N$ the presence of unresolved magnetic splittings and relaxation phenomena must be excluded.

The other parameter, which strongly influences the results for f' and cannot be directly determined, is α. The "control absorber" method with "black filter" was used to measure α. Transmission geometry was applied placing additionally a "black absorber" in front of the detector. The "black absorber" $^{57}FeOOH$ moves with an infinitely high velocity (±200 mm/s) at the time the Mössbauer spectrum accumulation and resonance absorption in it is therefore impossible. After this spectrum was taken two more measurements were carried out to determine α with the black filter technique. The first was done with a moving source and a moving black filter. The velocities are high (±200 mm/s) and are different for the source and the black filter, in values as in direction. In this case no resonance absorption is possible in the sample and in the black filter. The detector registers both the transmitted resonance and nonresonance emission of the source N_1. The other measurement is made with a fixed source and a fixed black filter ($v = 0$). In this case the source and the black filter are in resonance and since the black filter's ability for recoilless absorption is very high, $a \simeq 0.95$, practically all the emitted resonance gamma-quanta are absorbed. The detector registers only the nonresonance gamma-quanta emitted by the source, N_2, which pass through the absorber and the black filter. For α we obtain

$$\alpha = \frac{N_1 - N_2}{a \cdot N_1}.$$

The method is described in details in (12, 16).

For each compound the α value was determined and two spectra were taken at room and liquid nitrogen temperature, respectively. Room temperature measurements were performed without taking the sample out of the cryostat. Since in both cases the geometry of measurement is the same the recoilless part α is one and the same. The f' factors are calculated after [1]. When the precise chemical composition and the exact amount of Fe is unknown, only the f'/f'' ratio can be determined.

Population Conditions

SI has been populated in single crystal species of Li_2NP, Na_2NP, and K_2NP by irradiation from an Ar^+ laser with light in the blue spectral range (usually 457.9 nm line). The irradiated single crystal cuts are several hundred μm thick and are placed in a vacuum cryostat at about 80 K. To avoid warming of the sample, the light intensity was kept under 30 mW/cm^2. An important condition to achieve high population for all single crystal species is that the direction of the light polarization should be perpendicular to the C–N–Fe–N–O molecule axis (9), which was fulfilled in all experiments. The transfer of the population molecules from SI into SII was examined with a Nd-YAG laser (1064 nm). The irradiation was no more than 300 Ws/cm^2, since higher doses transfer SII to the ground state.

RESULTS AND DISCUSSION

Isomer Shift

All nitroprussides display Mössbauer spectra with a well resolved quadrupole doublet. An example with $(CN_3H_6)_2NP$ is shown in Fig. 1. Only the spectrum of FeNP is more complex (13, 14). We observe two doublets due to the Fe in the center of the NP ion and the Fe^{2+} as a normal cation. Table 1 lists the experimental values of IS, QS, Γ_{exp}, and f' for our samples. The isomer shift parameter of the NP ion is weakly dependent on the cations. Hence the population and distribution of the 3*s* and 4*s* electron density in the molecular orbitals (18) remain practically the same. This has been expected since the crystal lattices of all nitroprussides consist of the same structure units: metal ions, complex nitroprusside ions, and (not always) crystal water molecules. The short-range environment of the Fe atom is the same in all nitroprussides. The NP anion is schematically drawn for the case of Na_2NP in Fig. 2. For other lattice cations the interatomic distances may vary by 0.05 Å and in the case of nonideal octahedral symmetry the angles Fe–N–O, N–Fe–Cl, or others may differ by up to 2° (17). This can explain the narrow interval in which IS varies, from −0.025 to 0.025 mm/s at room temperature and from 0.05 to 0.09 mm/s at liquid nitrogen temperature.

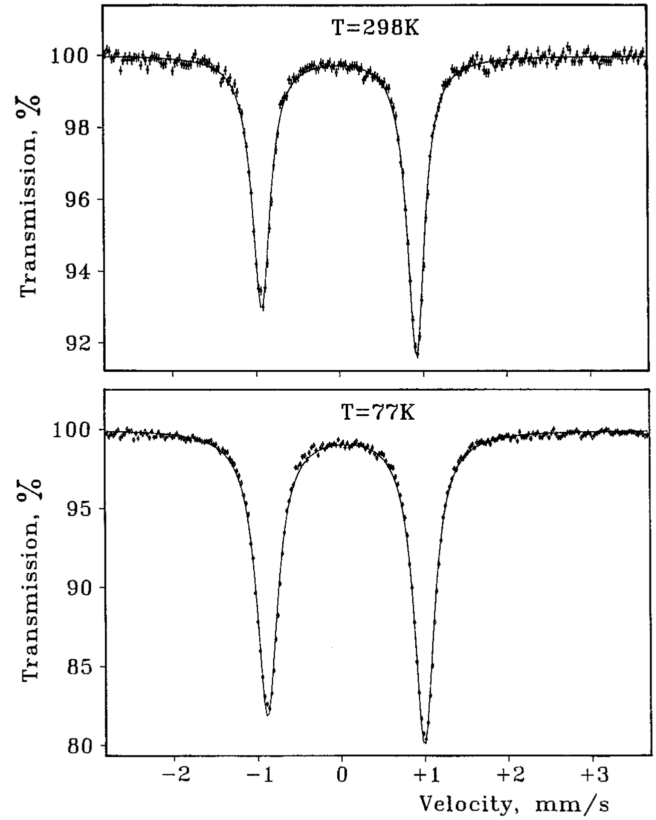

FIG. 1. Mössbauer spectra of a $(CN_3H_6)_2NP$ polycrystal sample at room and liquid nitrogen temperature.

It can be seen that the second order Doppler shift is virtually the same for all the compounds and is on the order of 0.06 to 0.08 mm/s at temperatures between 77 and 295 K. From the average value it is possible to calculate that the iron in these compounds shows an average effective recoil mass of about 140 g/mol. This value indicates extensive covalent bonding with first neighbors: five carbon and one nitrogen atom (recoil mass 131 g/mol), as would be expected for these materials.

The isomer shift correlates with the electron density which could be proved by calculating the number of electrons in each unit cell and dividing it by the unit cell volume.

TABLE 1

Data for IS (Related to Na_2NP at Room Temperature), QS, Γ_{exp} (Γ_1, Γ_2 for the Left and Right Lines, Respectively), and f' Factors of the Examined Nitroprussides at Room and Liquid Nitrogen Temperatures

Compounds NP= $[Fe(CN)_5NO]$	IS [mm/s]		QS [mm/s]		Γ_1/Γ_2 [mm/s]		f'	
	77 K	298 K	77 K	298 K	77 K	298 K	77 K	298 K
$[Cr(H_2O)_6]_2NP_3$	0.072	0.008	1.796	1.753	0.363/0.353	0.324/0.316	4.5**	
$MnNP \cdot 2H_2O$	0.052	-0.014	1.848	1.854	0.312/0.312	0.271/0.265	0.80	0.42
$FeNP \cdot 3H_2O$								
Fe in NP ion	0.057	-0.021	1.884	1.879	0.311/0.323	0.289/0.297	0.62	0.35
Fe in lattice	1.498	1.373	2.153	1.367	0.324/0.321	0.311/0.312	0.78	0.34
$CoNP \cdot 5H_2O$	0.061	-0.013	1.925	1.899	0.308/0.319	0.288/0.294	0.65	0.28
$NiNP \cdot 6H_2O$	0.062	-0.002	1.931	1.899	0.313/0.300	0.270/0.270	0.68	0.29
$CuNP \cdot 2H_2O$	0.060	0.005	1.648	1.641	0.319/0.314	0.273/0.264	0.64	0.37
Ag_2NP	0.081	-0.001	1.767	1.774	0.330/0.340	0.253/0.248	0.54	0.23
$ZnNP \cdot 3H_2O$	0.049	-0.025	1.874	1.847	0.319/0.316	0.267/0.263	0.76	0.37
$CdNP \cdot 2H_2O$	0.059	-0.007	1.835	1.853	0.310/0.313	0.273/0.269	0.69	0.41
$Hg_2NP \cdot 1.5H_2O$	0.055	-0.025	1.796	1.762	0.330/0.327	0.298/0.267	0.59	0.31
Tl_2NP	0.086	0.005	1.779	1.772	0.275/0.278	0.251/0.228	0.53	0.23
$H_2NP \cdot 3H_2O$	0.093	0.003	1.777	1.863	0.301/0.307	0.276/0.284	0.63	0.18
$Li_2NP \cdot 4H_2O$	0.083	-0.007	1.866	1.858	0.326/0.328	0.264/0.263	0.70	0.19
$Na_2NP \cdot 2H_2O$	0.061	0.000*	1.722	1.7048*	0.307/0.298	0.275/0.267	0.68	0.37
$K_2NP \cdot 2.5H_2O$	0.071	0.026	1.897	1.842	0.325/0.307	0.272/0.265	0.66	0.26
$Rb_2NP \cdot H_2O$	0.079	-0.001	1.894	1.879	0.336/0.335	0.268/0.267	0.70	0.27
$Cs_2NP \cdot H_2O$	0.081	0.006	1.850	1.780	0.303/0.309	0.287/0.291	0.68	0.24
$CaNP \cdot 4H_2O$	0.057	-0.003	1.819	1.790	0.324/0.323	0.270/0.271	0.70	0.38
$SrNP \cdot 4H_2O$	0.083	0.013	1.850	1.800	0.307/0.303	0.259/0.255	0.59	0.29
$BaNP \cdot 3H_2O$	0.066	0.008	1.870	1.856	0.321/0.325	0.280/0.282	0.58	0.30
Ce_2NP_3	0.064	-0.003	1.818	1.843	0.303/0.293	0.277/0.272	0.51	0.33
$(NH_4)_2NP \cdot H_2O$	0.084	0.002	1.899	1.882	0.316/0.318	0.282/0.276	0.74	0.30
$(CN_3H_6)_2NP$	0.060	0.004	1.879	1.854	0.308/0.294	0.261/0.249	0.66	0.16
$(CH_6N)_2NP \cdot 1.5H_2O$	0.074	0.005	1.876	1.790	0.328/0.326	0.274/0.272	0.60	0.16
$(C_2H_7N_2)_2NP$	0.072	-0.003	1.837	1.837	0.312/0.319	0.272/0.269	0.62	0.18
	±0.012		±0.008		±0.008	±0.012	±0.03	±0.02

Note. In case that the precise chemical composition and the exact amount of Fe is unknown, only the f'_{77K}/f'_{295K} ratio can be determined. The errors of the measured f' factors are only statistical and should be referred to only as a lower limit of the error interval. When measuring polycrystal species the influence of dispersity, inhomogeneity of the absorber, and eventual impurities may increase the error about 2 times.

* Calibration values after R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.* **178,** 523 (1969).

** f'_{77K}/f'_{298K}.

Unfortunately, there is no precise data of the crystal structure for most of the nitroprussides. The powder diffraction patterns taken from all samples do not give enough information about the unit cell. Single crystal diffraction measurements are needed to get unambiguous data for the crystal lattice.

The lattice cations are bound to the CN groups from the equatorial plane only. Therefore, the type and size of the cation can slightly affect only the bonds on this plane. A weak correlation between the cation radius and the isomer shift is really observed but only for nitroprussides with similar crystal structure and cations belonging to one and the same group of the periodic table.

A small change in the isomer shift can be caused by a number of factors, like the cations valence and their number in the unit cell, respectively, the cation radius, its electronegativity, the number and orientation of the NP anions, the presence of crystallized water and its quantity, and the space group in which the corresponding nitroprusside crystallizes. The influence of all these factors

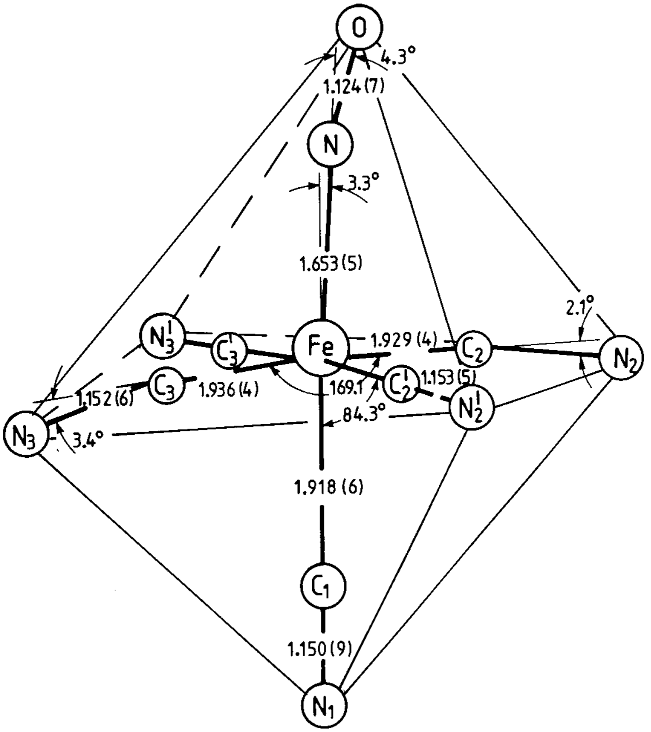

FIG. 2. The structure of the NP ion in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ after (21). All distances are in Å.

on the isomer shift can hardly be distinguished. All the 26 measured values of the IS lie within a 50 μm interval, only.

It is known that there is a correlation between isomer shift and electronegativity (19). Figure 3 shows the dependence of IS on the electronegativity of the metal cation of the nitroprussides. The values of IS change weakly, notwithstanding the considerable changes in electronegativity of the cation (from 0.7 to 2.3). It slightly increases with decreasing electronegativity. The IS change may be considerable when the electronegativity of the ligands changes. For example, the IS of the ferrous halides strongly increases as the electronegativity increases (22). In the case of NP an important characteristic should be taken into account. The metal cation is located in the second coordination sphere and changes the distribution of the formally negatively charged CN^- groups which in turn changes the distribution of the electron density of the central Fe atom in the NP ion. As a consequence of the indirect interaction the IS change in respect to the electronegativity change is reverse—it decreases with the increase of electronegativity and it is very weak, too. The H_2NP is an exception because of its specific lattice structure (15); the proton together with the crystal water form a H_3O^+ ion. The structural formula is $(H_3O)_2^+ \cdot [Fe(CN)_5NO]^{2-} \cdot H_2O$ and the ions bond through hydrogen bridges. The Fe–N bonding is shortest in this nitroprusside—1.635 Å (15). The NO^+ ligand is a strong acceptor and the electron density withdraws toward it, while around the Fe^{2+} it reduces. Because of the smaller s electron density, the isomer shift of this nitroprusside is larger.

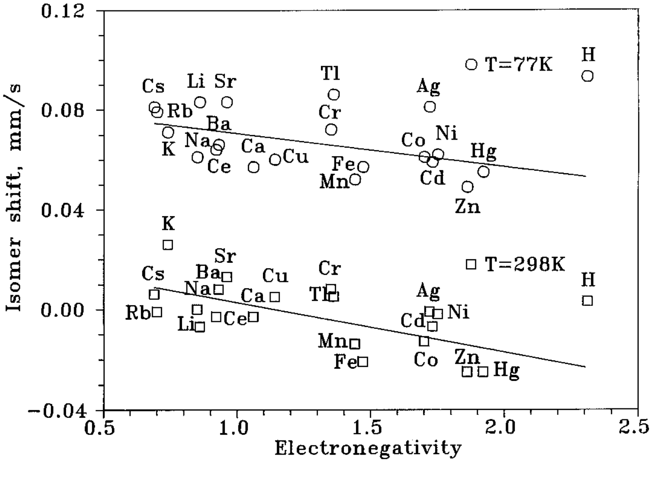

FIG. 3. Dependence of IS on the electronegativity of the cation. The range of error for all values of isomer shift is ±12 μm/s. the data for the electronegativity are taken from Ref. (20).

Based on the results from Fig. 3, we suppose that the metal ion has a very weak influence on the electron density at the site of the Mössbauer nucleus ^{57}Fe. A qualitative evaluation shows that the influence of the second coordination sphere is about 10 times weaker than the influence of the first. For this reason and because of the greater experimental errors of the IS determination, no correlation between IS and electronegativity has been observed in Ref. (13).

Further, no correlation between the IS and the decay temperatures $T_{\max}$ of the new states (11) was found.

Quadrupole Splitting

The change of QS for different cations is also weak (from 1.64 to 1.90 mm/s at room temperature). The value of QS is proportional to the electric field gradient (EFG) q in the Fe nucleus when the asymmetry parameter $\eta = 0$, which is valid for NP ions with slightly distorted octahedra—nearly $4m$ symmetry (1). The EFG is conveniently expressed as

$$q = (1 - R)q_{\mathrm{val}} + (1 - \gamma_\infty)q_{\mathrm{lat}}.$$

The lattice cation cannot substantially change the first term which involves the valence contribution q_{val} and the Sternheimer shielding effect, but a change of the lattice charges or small changes in their coordination can strongly influence the second term because the

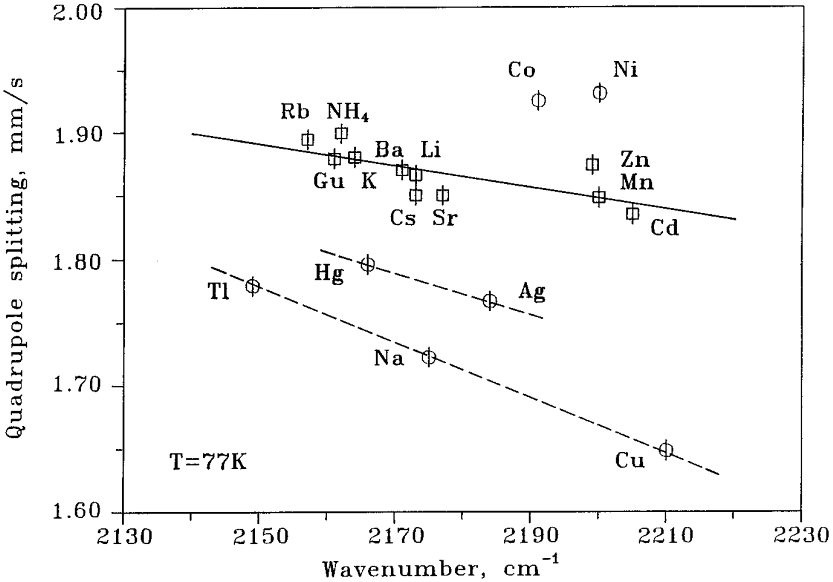

FIG. 4. Dependence of QS on wavenumber $\tilde{\nu}(\mathrm{CN})_{\mathrm{trans}}$ of the C–N stretching vibrations trans to the N–O. Gu = CN_3H_6.

Sternheimer antishielding factor γ_∞ has a large negative value (about -10 (23)). In our case the indirect interaction between the lattice cation and the Fe atom should lead to a decrease of QS. The NP ion which is not bound to any other ions in the crystal structure is therefore expected to give considerably larger QS than the bounded NP one. We have not found a dependence of the QS from the electronegativity of the lattice cation. There is a weak, but distinct, correlation between QS and $\tilde{\nu}(\mathrm{CN})_{\mathrm{trans}}$ stretching vibrations shown in Fig. 4. It can be expected that for very weak bonds between the CN groups and the cations (quasi-free NP) the value of QS will be about 1.95 mm/s. Experimentally measured values for QS as well as semiempirical self-consistent field molecular calculations are presented by Trautwein *et al.* (25). Similar values of QS are given for NP ions in solid solution (24) where the NP ion can be considered quasi-free. For CoNP and NiNP, which are X-ray amorphous and so the near crystal surrounding is absent, the QS values are very close to 1.95 mm/s, too. All theoretical calculations (18, 25) of the orbital population of the NP ion should be fitted not to the QS value 1.73 mm/s which corresponds to Na_2NP (crystal) but to the value 1.95 mm/s. Knowing that the Sternheimer shielding effect is normally $(1 - R) \cong 0.8$ (23) the pure valence contribution q_{val} in EFG for the free NP ion should give values for QS of about 2.3 mm/s.

No distinct correlation between the Mössbauer parameter QS and the important decay temperature $T_{\max}$ of metastable states is observed. The CuNP with the highest $T_{\max} = 222$ K (11) shows the smallest value of QS = 1.641 mm/s.

The results for IS and QS of all the nitroprussides we have examined make us consider some values of IS and QS cited in Ref. (13) to be not quite real (for example for Cs_2NP, IS = 0.4 mm/s and QS = 2.00 mm/s).

Probability of Recoilless Absorption

Most of the nitroprussides have spectra with a symmetric quadrupole doublet. In the case of $(NH_4)_2NP$, $(CN_3H_6)_2NP$, $(CH_6N)_2NP$, and $(C_2H_7N_2)_2NP$ a well pronounced asymmetry in intensities of the two lines was observed. Figure 1 shows the Mössbauer spectra of absorption for $(CN_3H_6)_2NP$ at room and liquid nitrogen temperatures. The observed asymmetry can be caused by the Goldanskii–Karyagin effect (GKE) or simply by oriented texture in the absorber. The unit cell of this nitroprusside is shown in Fig. 5 after Ref. (17). The coordination of NP is different along the three principal axes which leads to an anisotropy of the intermolecular vibrations. This means that f' for the different directions has different values and the observed asymmetry in the Mössbauer spectrum results from the Goldanskii–Karyagin effect. It is also possible that an anisotropy of the intermolecular vibrations of NP exists, but it cannot be significant since for most of the nitroprussides the quadrupole doublet is symmetric. Magic angle measurements are known as a tool to prove the isotropy of the crystal (i.e., the absence of the Goldanskii–Karyagin effect) but it can be applied only if the EFG has only one direction in the crystal. Then at an angle of 54°44′ between the gamma beam and the EFG direction the measured intensities for the two lines will be equal. In our case though, this method cannot be applied since the NP ions

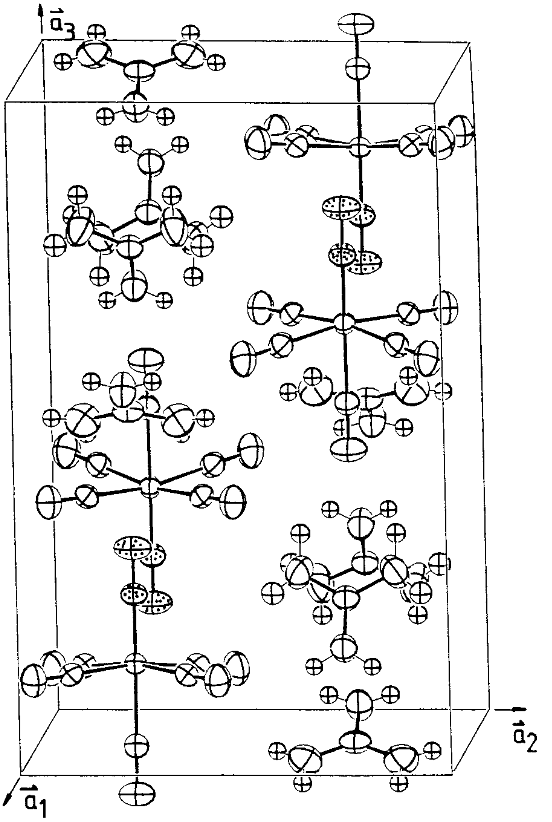

FIG. 5. The unit of guanidinium nitroprusside after (17).

have two different orientations in the crystal. The axis N–C–Fe–N–O which coinsides with the EFG direction has two different orientations, about ±9° to the *c* axis of the crystal (15, 17). We are going to investigate the GKE in more details with single crystals of $(CN_3H_6)_2NP$. For this reason we have already measured the f' factors at room temperature for the three principal crystal directions using single crystal *a*, *b*, and *c* cuts. The differences between the respective f' values, $f'_a = 0.130(5)$, $f'_b = 0.167(6)$, and $f'_c = 0.198(6)$, give clear evidence for crystal vibration anisotropy and GKE.

Usually, the f' factors for NP with inorganic cations differ by about 2 times for room and liquid nitrogen temperature. Larger differences (about 4 times) are observed only in the case of NP with organic cations. The f' factor at room temperature is comparatively low, 0.16–0.18. The elastic stiffness and the Debye temperature of these materials is low resulting in low values of f'. A very interesting characteristic of these materials is their low critical temperatures $T_{\max}$ of decay of the new states. This fact confirms the assumption in Ref. (11) that there exists a distinct correlation between the energy distribution in the phonon spectrum and the decay temperature. Probably one can expect metastable states with higher decay temperatures existing in nitroprussides with larger lattice energy and harder phonon spectra, respectively.

From all measured NP the $(CN_3H_6)_2NP$ turns out to be most suitable for further investigations on the metastable states and the difference between f' and f''. The fact that the f' values are different for the three principal crystal directions allows one to measure f'' for each output direction at two input directions with different f'. The strong temperature dependence and the presence of a Goldanskii–Karyagin effect down to liquid nitrogen temperature allows one to carry out such measurements for different values of the f' factor in a large temperature range.

Mössbauer Parameters of Exited States

The Mössbauer spectra of three single crystal absorbers, Li_2NP, Na_2NP, and K_2NP, populated in SI are shown on Fig. 6. The measured values of the Mössbauer parameters are summarized in Table 2. The analysis and the comparison between the Mössbauer parameters of unpopulated crystals species and those of species with populated SI (or SII) leads to the following conclusions.

1. The Mössbauer parameters of the new metastable electron states are very close to each other, like in the case of the crystal in ground state. The isomer shifts (referred to Na_2NP at liquid nitrogen temperature) for SI lie in the interval 0.18–0.20 mm/s. The quadrupole splittings are traditionally high and lie in the interval 2.75–2.95 mm/s. This shows that for the new metastable states the changes in the electron density distribution of the $[Fe(CN)_5NO]^{2-}$ anion depend weakly on the kind of the metal cation.

2. The quadrupole splitting ratios QS_{SI}/QS_{GS} are very close to each other. For not a very high degree of population of SI (about 20%) this ratio is about 1.57(1) (Li_2NP and K_2NP). For a high population 40–50% (Na_2NP) it is larger, 1.605(5). This fact may be explained by a very weak dependence of the Mössbauer parameters for the GS and for SI on the degree of population. Similar results are published in Ref. (24).

3. The above conclusions (points 1 and 2) are valid for the new state SII, too. Here we should only point out that the great differences between SI and GS do not already exist between SI and SII. The isomer shifts of SII lie in the interval 0.19–0.21 mm/s, the quadrupole splittings within 2.86–3.00 mm/s. The corresponding Mössbauer parameters of SII are always a little larger than those of SI. A precise analysis of the case of Na_2NP is carried out in our work (10). We may say that a totally new distribution of the electron densities in the complex $[Fe(CN)_5NO]^{2-}$ at SII cannot be expected. Probably only a dynamic change of the new electron density distribution in SI may explain the Mössbauer parameters of SII. Although, with very close values of the Mössbauer parameters the new states should be referred to as two completely different physical

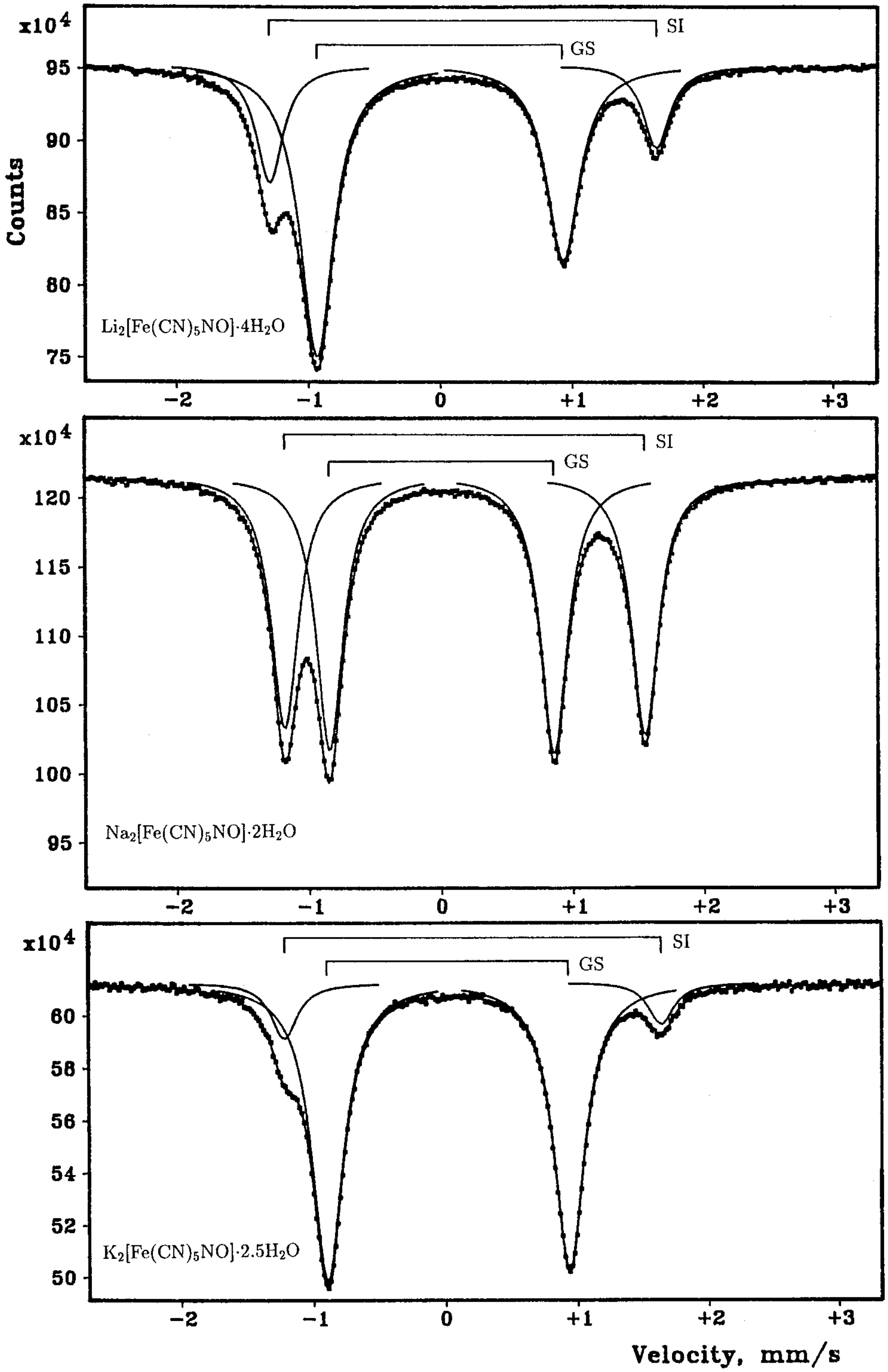

FIG. 6. Mössbauer spectra of three single crystal absorbers populated in SI. The population and the Mössbauer measurements are carried out at 80 K.

states of the complex. The transfer of SI into SII at irradiation with the Nd-YAG laser is nothing else than causing dynamic effects in distribution of electron density in the SI accompanied by processes of decay from SI and SII to GS. At doses of about 3000 Ws/cm^2 the new states are totally transferred to GS.

4. By means of Mössbauer spectroscopy we have shown (10) that the observed spectra before and after irradiation are absolutely and completely reversible. This important result has been proved by other techniques, too: optic (4, 5), calorimetric (6), structural (8), etc. The change of the crystal color after population of SI or SII state can be seen

TABLE 2
Mössbauer Parameters of the Three Single Crystal Absorbers Populated in SI

$Li_2[Fe(CN)_5NO]\cdot 4H_2O$	GS	SI
QS (mm/s)	+1.869(5)	+2.941(5)
IS (mm/s)	−0.002(5)	0.180(5)
Γ_1 (mm/s)	0.349(4)	0.249(4)
Γ_2 (mm/s)	0.352(4)	0.247(4)
Population (%)	74.8(4)	25.2(4)
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	GS	SI
QS (mm/s)	+1.716(3)	+2.755(3)
IS (mm/s)	0.000	0.178(3)
Γ_1 (mm/s)	0.261(4)	0.268(4)
Γ_2 (mm/s)	0.260(4)	0.267(4)
Population (%)	52.9(4)	47.1(4)
$K_2[Fe(CN)_5NO]\cdot 2.5H_2O$	GS	SI
QS (mm/s)	+1.833(5)	+2.86(1)
IS (mm/s)	0.023(5)	0.21(1)
Γ_1 (mm/s)	0.289(4)	0.24(1)
Γ_2 (mm/s)	0.282(4)	0.24(1)
Population (%)	87.4(2)	12.6(2)

Note. The isomer shift values are referred to Na_2NP at liquid nitrogen temperature.

on the cover of the *Laser and Optoelectronic Journal* (26). This change can be used as an optical switch, especially for information storage and retrieval. The written, read, and erased cycles together with visible information storage are discussed in detail in Ref. (27). The low critical temperature at which the states decay (200 K) does not allow practical application. New nitroprussides or other compounds must be found such that in them similar light induced long-lived metastable states can exist up to room temperature.

5. We observe weak, but distinct, differences between the Mössbauer parameters of powder samples and those of single crystal species. This can be explained by higher concentrations of impurities (Hg and Cl) present in the powder species which originate from the output components and which are strongly reduced at single crystal growth. In our opinion the cation exchange reaction between Na_2NP and $HgNO_3$ to product Hg_2NP and a successive treatment with the corresponding MCl to product M_2NP must be avoided. High purity samples can be obtained only in cation exchange reactions between Na_2NP and $AgNO_3$ and a following treatment with MCl.

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