Extremely Long-Living Metastable State of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ Single Crystals: Optical Properties

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Below 160 K, crystalline $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ is transformed into an extremely long-living metastable state ($\tau > 10^7$ sec) by irradiation with 400–540-nm light. At $T > 160$ K and by irradiation with red light the new state decays exponentially. During population the transmission of the crystal shows characteristic time behavior with wavelength-dependent saturation. Raman spectra show the coexistence of the ground and metastable states. New infrared and visible absorption bands are interpreted in terms of an energy scheme of the metastable state.

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Optical-storage materials have recently attained significant importance because of their extremely high storage capacity and their technological impact.[1] Especially, media which can be pumped and erased by well defined wavelengths gain increasing attention. Here we report on optical properties of a potential storage material, namely sodium nitroprusside. As will be shown, data can be stored in the blue-green spectral range and erased with red wavelengths. The store/erase cycle can be repeated at any time. The stored information can easily be read either by transmission or by reflection measurements. In this Letter we study the transmission characteristics of the material. We show with the aid of Raman and absorption spectroscopy that the storage mechanism is due to an intramolecular charge transfer, which produces the extremely long-living metastable state.

$Na_2[Fe(CN)_5NO] \cdot 2H_2O$ crystallizes in the orthorhombic space group *Pnnm* with four molecules per unit cell. The $[Fe(CN)_5NO]^{2-}$ ions form slightly distorted octahedra having approximate $4m$ symmetry. In the orthorhombic lattice the slightly bent NC-Fe-NO axial units lie in the (ab)-minor plane and as a consequence of inversion symmetry are antiparallel in couples.[2] After cooling down to temperatures below 160 K, the crystals can reversibly be transformed into an extremely long-living metastable state by irradiation using polarized light in the range of 400–540 nm. This has already earlier been detected by Mössbauer spectroscopy.[3] The metastable state cannot be excited at wavelengths longer than 530 nm. During the population the transmission of the crystal shows a characteristic temporal development. It depends on the orientation of the crystallographic axes with respect to the polarization of the laser light. Additional Raman vibrational bands and new electronic absorption transitions are observed. By irradiation with light in the region of a new electronic absorption band at 676 nm, the metastable state decays within a few minutes. The results are interpreted in terms of a

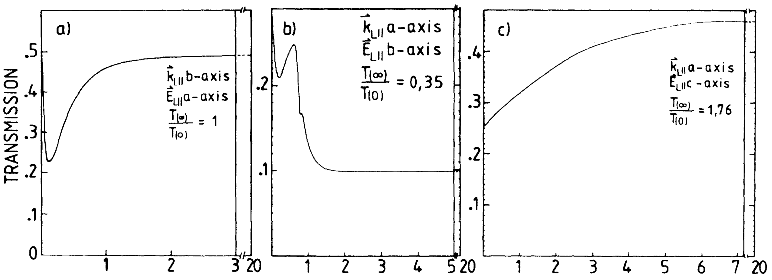

FIG. 1. Time-dependent transmission during the population of the metastable state. $\lambda = 476.5$ nm; $d = 106$ μm; $I = 100$ mW/cm^2; $T = 70$ K.

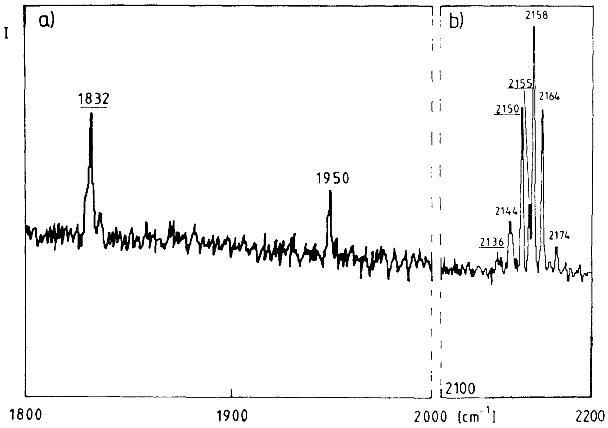

FIG. 2. Raman spectrum of a $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ single crystal in the metastable state. The underlined numbers are vibrational frequencies of the excited state. (a) $\tilde{\nu}$(NO) stretching vibrations. $K \parallel b$ axis; $E \parallel a$ axis; $T = 70$ K. (b) $\tilde{\nu}$(CN) stretching vibrations. $K \parallel a$ axis; $E \parallel c$ axis; $T = 70$ K.

modified energy level diagram based on calculations of Manoharan and Gray.[4]

Figure 1 shows typical examples of the temporal development of the optical transmission. With the electric field vector parallel to the *a* axis, the transmission decreases initially and returns to its original value. When the field vector is aligned parallel to the *b* axis, the transmission strongly decreases after some initial fluctuations. With the field vector parallel to the *c* axis, the transmission increases and is saturated on a much longer time scale. The fluctuations display the dynamical behavior of a multilevel system with different decay times and time-dependent population. The dependence of the transmission on the irradiation time, wavelength, intensity, and polarization of the incident laser beam, and thickness of the crystal will be analyzed elsewhere.[5]

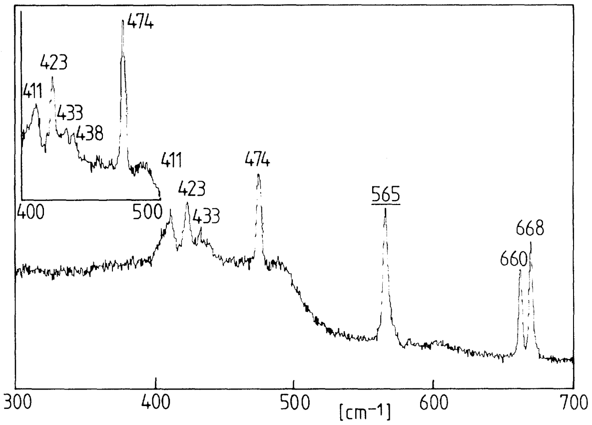

FIG. 3. Low-frequency Raman spectrum of a $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ single crystal. $K \parallel a$ axis; $E \parallel b$ axis; $T = 70$ K.

TABLE I. $\tilde{\nu}$(CN) stretching modes in the ground and metastable states.

Ground state (cm^{-1})	Metastable state ($cm^{-}1$)	Assignment
2174	2166	A_1 axial
2164	2156	A_1 equatorial
2158	2150	B_1 equatorial
2144	2136	E equatorial

Figures 2 and 3 show Raman spectra of thin single-crystalline plates measured in forward scattering geometry with a resolution < 1 cm^{-1}. Experimental details have been described elsewhere.[6] The metastable state was populated to the saturation limit with $\lambda = 514.5$ nm. The saturation was controlled by transmission spectroscopy. Vibrational bands of the ground and metastable states are simultaneously observed. Thus both states coexist in the crystal. The vibrational bands of the ground state can be identified with the $\lambda = 674.4$-nm line of a krypton-ion laser because the metastable state is depopulated by red illumination. An assignment of vibrational bands is given by several authors.[7-9] Especially, the $\tilde{\nu}$(Fe-N) and δ(FeNO) vibrations at 660 and 668 cm^{-1}, respectively, have been identified by isotopic substitution.[8] With population of the metastable state, the $\tilde{\nu}$(NO) stretching vibration suffers the most dramatic shift. It shifts by 118 cm^{-1} from 1950 to 1832 cm^{-1}. Simultaneously a new line appears at 565 cm^{-1}. Since there is no preferential polarization observed, we assign this vibrational band to the shifted degenerate δ(FeNO) deformation vibration of the metastable state. At a resolution of ~ 0.8 cm^{-1} no splitting of degenerate modes is observed in the ground nor in the metastable states. Therefore, the symmetry of the $Fe(CN)_5$ core is at most undetectably influenced by the population. In the ground-state configuration we observe four $\tilde{\nu}(C\equiv N)$ stretching vibrations according to the 4*m* symmetry (Fig. 3). When the metastable state is populated, we find four additional vibrational bands, which are all equally shifted by 8 cm^{-1} to smaller energies. Assignments are given in Table I.

In optical absorption spectra of the metastable state we observe new bands at 4063, 5415, and 14 800 cm^{-1} (676 nm). Simultaneously the band at

20 620 cm^{-1} (485 nm) decreases, whereas the uv band at 31 550 cm^{-1} (317 nm) increases in intensity.

In order to understand these results in a qualitative sense we refer to the electronic energy level diagram computed for the ground state by Manoharan and Gray[4,10] (Fig. 4). The degenerate $6e\,(d_{xz};d_{yz})$ orbital has predominantly metal d character and is occupied with four electrons. The $2b_2(d_{xy})$ level is the highest occupied molecular orbital. It contains two electrons and has mainly metal d character. The lowest unoccupied orbital is the antibonding $7e\,(\pi^*\mathrm{NO})$ ligand orbital about 20 400 cm^{-1} (2.53 eV) above the ground state. The higher $3b_1$ and $5a_1$ levels are mainly formed of metal $d_{x^2-y^2}$ and d_{z^2} orbitals, respectively. The unusual position of the $7e$ ligand orbital between the metal d states is responsible for the formation of the metastable state. With the $2b_2$ initial state, only the $7e\,(\pi^*\mathrm{NO})$ orbital can be populated by the lines of an argon-ion laser. Therefore, the metastable state is formed upon a charge transfer from the $2b_2(d_{xy})$ orbital to the antibonding $7e\,(\pi^*\mathrm{NO})$ orbital. Accordingly the NO-bond strength decreases as indicated by the strong shift of the $\tilde{\nu}(\mathrm{NO})$ vibrational frequency.

The shift of the $\tilde{\nu}(\mathrm{CN})$ stretching vibrations can be explained with the aid of a Mulliken population analysis of the $2b_2$ and $7e$ orbitals. According to Manoharan and Gray the $2b_2$ level is composed of 84.5% d_{xy}(Fe), 13.89% π(CN), and 1.58% π^*(CN), whereas the $7e$ level is composed of 72.53% π^*(NO), 22.9% (d_{xz},d_{yz}) (Fe), 0.4% π(CN), and 0.33% π^*(CN). The charge transfer $2b_2 \rightarrow 7e$ reduces the charge density in the $2b_2$ ground state with about 14% π(CN) character. Therefore, all $\mathrm{C{=}N}$ bonds become weaker and the $\tilde{\nu}(\mathrm{CN})$ stretching vibrations are shifted to smaller energies.

The metal-NO group in chemically similar nitrosyl complexes is either linear or bent, depending on the population of the π^*(NO) orbital.[10,11] The Fe-N-O group in $[\mathrm{Fe(CN)_5NO}]^{3-}$ is known to be nonlinear.[12] Therefore, it is reasonable to assume that the charge transfer $2b_2 \rightarrow 7e$ causes a change of the Fe-N-O bond angle. As a consequence, the originally degenerate $7e\,(\pi^*\mathrm{NO})$ orbital is split into two orbitals π_1^*(NO) and π_2^*(NO) as shown in Fig. 4. Such a splitting can originate from lowering of the symmetry, spin-orbit coupling, or static or dynamic Jahn-Teller effects. In $4m$ symmetry an electronic degenerate term is unstable with respect to the vibrations of B_1 and B_2 symmetry. Therefore two B_1 and four B_2 modes are Jahn-Teller active to split the $7e$ level. This change of the electonic structure results in the three new absorption bands. We tentatively assign them as shown in Fig. 4. In the ground state the separation of the $6e$ and $2b_2$ levels is approximately 5500 cm^{-1}. Since one electron is removed from the $2b_2$ level during population of the metastable state, an optical transition becomes possible between these two levels. The new band at 4515 cm^{-1} closely corresponds to this energy separation and is assigned to the $6e \rightarrow 2b_2$ transition. The depopulation of the $2b_2$ state also leads to the decrease of the $2b_2 \rightarrow 7e$ absorption band at 475 nm. The line at 676 nm corresponds to the transition $\pi_1^*(\mathrm{NO}) \rightarrow 3b_1$ observed at 630 nm for the $[\mathrm{Fe(CN)_5NO}]^{3-}$ molecular ion.[12] From the $3b_1$ level the ion relaxes back to the ground state, so that the metastable state is destroyed. The band at 4063 cm^{-1} may be assigned to the $\pi_1^*(\mathrm{NO}) \rightarrow \pi_2^*(\mathrm{NO})$ transition. The excitation wavelength is simultaneously in resonance with the $2b_2(d_{xy}) \rightarrow 7e\,(\pi^*\mathrm{NO})$ and $\pi_1^* \rightarrow 5a_1(d_{z^2})$ transitions. Therefore, population of the metastable state and depopulation via higher orbitals takes place simultaneously. In addition, transitions from lower states to the $2b_2$ or from the π_1^* level to higher unoccupied states become possible and are reflected by the increase of the uv-absorption band at 317 nm. These dynamical multilevel cycles result in the temporal optical transmission behavior of Fig. 1. The thermal decay channels at $T > 160$ K result from interactions with phonons $> 110\ \mathrm{cm}^{-1}$. These phonons may activate the recombination.

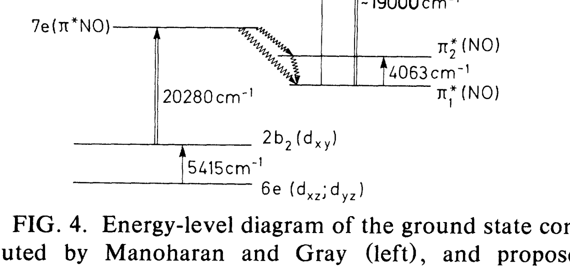

FIG. 4. Energy-level diagram of the ground state computed by Manoharan and Gray (left), and proposed modified level scheme for the metastable state (right).

These results show that sodium nitroprusside can be used as a light storage material, when it is pumped with blue light and erased with red light. In order to change the wavelength range and the temperature range for the production of the metastable state we suggest the replacement of the central iron ion by other transition-metal ions. Further the NO ligand may be replaced by other ligands having low-lying antibonding π^* orbitals. Replacement of the $2Na^+$ by Ba^{2+} already allowed us to raise the decay temperature by an amount of 30 K.

In conclusion we have shown that the metastable state of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ is caused by a charge transfer from the $2b_2(d_{xy})$ to the $7e(\pi^*NO)$ orbital. The electronic absorption behavior and Raman spectra can qualitatively be explained by this picture. An energy-level diagram to explain the optical behavior is proposed. Potential applications as a data-storage material are indicated. Ultraviolet photoelectron spectroscopy measurements are currently under investigation to fix the energetical position of the metastable state. The FeNO bond angle will be studied by neutron and x-ray scattering in the near future. Chemically related materials are currently being studied.

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