Freezing of molecular rotation in a paramagnetic crystal studied by $^{31}$P NMR

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We present a detailed $^{31}$P nuclear magnetic resonance (NMR) study of the molecular rotation in the compound [Cu(pz)$_2$(2-HOpy)$_2$](PF$_6$)$_2$, where pz = C$_5$H$_4$N$_2$ and 2-HOpy = C$_5$H$_4$NHO. Here, a freezing of the PF$_6$ rotation modes is revealed by several step-like increases of the temperature-dependent second spectral moment, with accompanying broad peaks of the longitudinal and transverse nuclear spin-relaxation rates. An analysis based on the Bloembergen-Purcell-Pound (BPP) theory quantifies the related activation energies as $E_a/k_B = 250$ and 1400 K. Further, the anisotropy of the second spectral moment of the $^{31}$P absorption line was calculated for the rigid lattice, as well as in the presence of several sets of PF$_6$ reorientation modes, and is in excellent agreement with the experimental data. Whereas the anisotropy of the frequency shift and enhancement of nuclear spin-relaxation rates is driven by the molecular rotation with respect to the dipole fields stemming from the Cu ions, the second spectral moment is determined by the intramolecular interaction of nuclear $^{19}$F and $^{31}$P moments in the presence of the distinct rotation modes.

I. INTRODUCTION

The mechanism of enhanced nuclear spin relaxation, caused by thermally activated local-field fluctuations at the nuclear Larmor frequency, was first introduced in 1947 [1] and elucidated in more details [2] by Bloembergen, Purcell, and Pound (BPP). Since then, the BPP mechanism of enhanced nuclear spin relaxation was observed in numerous material classes, such as cuprates [3–6], iron-based superconductors [7, 8], low-dimensional quantum magnets [9–11], materials for lithium-ion batteries [12–14], nanostructured systems [15], and several others [16–20]. Despite the diverse physical origins of the local-field fluctuations in these materials, the BPP formalism provides an adequate phenomenological description of the increased nuclear spin relaxation.

As a prominent example of the related phenomenology, the coexistence and interplay of unconventional superconductivity and low-dimensional magnetism is one of the most extensively investigated topics in the research of strongly correlated electron systems. In the iron-based and high-$T_c$ cuprate superconductors, low-energy spin dynamics are proposed as a key ingredient for the manifestation of superconductivity. Until now, it is an unresolved issue under which conditions these spin fluctuations may be constructive or rather detrimental to the formation of Cooper pairs [21]. In the case of glassy spin freezing, manifested as a peak of the nuclear spin-lattice relaxation rate, the behavior of the local-field fluctuations can be understood as a slowing down of the characteristic electronic spin-fluctuation frequency with a Lorentzian spectral density of the fluctuations at the Larmor frequency $\omega_0$. The fluctuation rate $\tau^{-1}$, describing a thermally activated process with a distribution of activation energies $E_a$, indicates, e.g., glassy spin dynamics of unresolved nature in the cuprates [3–4].

Low-dimensional quantum spin systems are model materials for the study of magnetic correlations that are also present in unconventional superconductors. In these materials, the spin-spin exchange coupling is often given by superexchange interactions. In molecular-based materials, there is a manifold of possibilities for the occurrence of thermally activated molecular motions [9]. These structural fluctuations may also affect the absolute values of the superexchange energies, as they relate to structural parameters of the exchange pathways. Therefore, a detailed knowledge of the molecular fluctuation parameters is of great interest and may represent an important input for density functional theory (DFT) calculations of the exchange constants and structural parameters.

A recent NMR study of ultrafast molecular rotation in metal-organic frameworks proposes molecular-based compounds as promising candidates for the realization of smart materials and artificial molecular machines. Here, the utilization of molecular dynamics may lead to a tuning of the thermal, dielectric, or optical properties [20].

In view of this very rich phenomenology of BPP-type local-field fluctuations, and despite of several decades of research, there is a strong need for model materials that allow for a well-defined investigation of spin relax-
ation caused by the presence of BPP-type field fluctuations. In particular, the study of rotation modes in single-crystalline materials allows to probe the anisotropy of spectral properties and to perform a detailed analysis of the local-field contributions at the nuclear sites.

The present work is, to our knowledge, the first investigation of molecular motion in a paramagnetic single crystal by a comprehensive NMR study of both static and dynamic local-field properties, including their analysis by the BPP formalism as well as calculations of the spectral properties.

II. RESULTS AND DISCUSSION

Single-crystalline samples of the molecular-based compound [Cu(pz)₂(2-HOpy)₂](PF₆)₂ (CuPOF) were grown from solution [21]. Spin moments with $S = 1/2$, hosted by the Cu$^{2+}$ ions, are coupled by a molecular matrix of pyrazine molecules (pz = C₄H₆N₂) to form quasi-2D layers with a square-lattice motif (Fig. 1), with a nearest-neighbor interlayer exchange of $J/k_B = 6.80(5)$ K. The Cu-pyrazine planes are separated by 2-pyridone molecules [2-HOpy = C₅H₄NHO], bridged to the Cu$^{2+}$ ions via oxygen. These molecules not only repel the molecular planes from each other, but also cause a shift of adjacent layers by about half of an in-plane lattice period along the crystallographic b axis. The PF$_6$ anions are located in-between the layers, thus contributing to the interlayer repulsion, as well as to the effective distribution of charge density in the molecular structure.

The $^{31}$P NMR investigations were performed at temperatures between 6 and 260 K, with applied magnetic fields between 2 and 7 T. In this temperature range, the correlations of electronic moments in CuPOF can be treated as paramagnetic in good approximation. The spectra and the nuclear spin-spin relaxation time $T_2$ were recorded with a Hahn spin-echo pulse sequence, the nuclear spin-lattice relaxation time $T_1$ was recorded by using an inversion-recovery method. For the temperature-dependent NMR measurements, the magnetic field was applied parallel to the crystallographic c axis, perpendicular to the molecular layers. The $^{31}$P magic-angle spinning (MAS) NMR spectroscopy was performed on a polycrystalline CuPOF sample at an external field of 4.7 T with a $^{31}$P resonance frequency of 80.985 MHz and a sample spinning speed of 30 kHz.

Figure 2(a) shows representative $^{31}$P-NMR spectra at selected temperatures between 6 and 200 K. Since $^{31}$P has a nuclear angular momentum of $I = 1/2$, only one transition ($m_z = -1/2$ to $+1/2$) is observed. Figure 2(b) shows a comparison of the conventional spin-echo $^{31}$P-NMR spectra and those recorded by the MAS technique at about 200 K. Due to the cancellation of local dipole fields by spinning the sample with a frequency of 30 kHz at the magic-angle orientation, the MAS spectrum is revealed as $J$ resolved with 7 lines, separated by a scalar spin-spin coupling of $J = 712$ Hz between the $^{19}$F and $^{31}$P nuclei [21]. The chemical shift of -143.2 ppm at 4.7 T and $J$ are in a good agreement with previously reported values for compounds containing PF$_6$ molecules [22-24].

The relative intensities of the septet are given by the binomial coefficients [25]. On the other hand, due to nuclear dipole-dipole broadening, the standard NMR spectrum is not $J$ resolved. The small asymmetry of the NMR spectrum is attributed to the existence of two structurally slightly non-equivalent $^{31}$P sites, see Fig. 1. The absolute values of the MAS and NMR frequency shift differ by 22 ppm. This is attributed to a residual dipolar contribution to the NMR shift at 200 K, which is absent in the MAS spectrum.

FIG. 1. In CuPOF, quasi-2D planes of Cu$^{2+}$ ions are linked by pyrazine molecules, forming the motif of a magnetic square lattice. Two structurally slightly inequivalent PF$_6$ molecules are located in-between the layers.

FIG. 2. (a) $^{31}$P-NMR spectra at different temperatures for CuPOF in an external field of 7 T applied parallel to the c axis. The vertical line indicates the Larmor frequency for zero shift. (b) Comparison between conventional spin-echo $^{31}$P-NMR and MAS spectra at about 200 K.
The full width at half maximum (FWHM) of the NMR spectrum at 200 K is less than 5 kHz (41 ppm at 7 T), indicating a high homogeneity of the single-crystalline CuPOF sample. As shown in Fig. 2(a), the linewidth increases significantly upon cooling. Since the $^{31}$P-NMR spectrum is slightly asymmetric, the second spectral moment $M_2$, the square root of which is proportional to the FWHM, is used to characterize the spectral width. The $n$th spectral moment is defined as $M_n = \int (\omega - \omega_0)^nf(\omega)d\omega$, where the resonance curve is described by a normalized function $f(\omega)$ with a maximum at the frequency $\omega_0$ [26]. The temperature dependence of the $^{31}$P second spectral moment is shown in Fig. 3(a). Instead of a simple Curie-type behavior, i.e., a monotonic increase of $M_2$, the square root of which would denote a continuously growing width of the magnetic dipole-field distribution stemming from the Cu$^{2+}$ moments, the temperature dependence of the linewidth shows several step-like increases. At temperatures below about 60 K, the $^{31}$P-NMR spectrum resembles a Gaussian lineshape. With increasing temperatures, the spectral lineshape gradually changes, and a purely Lorentzian form is observed above around 145 K. At intermediate temperatures, between about 60 and 145 K, the $^{31}$P-NMR spectrum can be described by a superposition of Lorentzian and Gaussian functions. Furthermore, the temperature-dependent spin-spin and spin-lattice relaxation rates, $1/T_2$ and $1/T_1$, display several broad maxima, compare Figs. 3(b) and 3(c). The enhancements of $1/T_2$ coincide with temperature regimes for which the step-like changes of the linewidth are found, whereas the related maxima of $1/T_1$ are observed at higher temperatures. The broad maxima of the temperature-dependent $1/T_1$ and $1/T_2$ rates, as well as the step-like behavior of the linewidths, are ascribed to a motional narrowing process, as described further below.

According to the BPP model [1, 2], a time-dependent local magnetic field $\vec{h}(t)$, stemming from either nuclear or electronic moments, with a characteristic fluctuation rate close to the nuclear Larmor frequency $\omega_0$, represents a mechanism of nuclear spin-lattice relaxation: 

$$\frac{1}{T_1} = \gamma^2 \langle h_{\perp}^2 \rangle \frac{\tau_c}{1 + (\omega_0 \tau_c)^2}. \quad (1)$$

Here, $\gamma$ is the nuclear gyromagnetic ratio, and $h_{\perp}$ is the perpendicular component of $\vec{h}(t)$ with a mean-square amplitude of $\langle h_{\perp}^2 \rangle$. In the case of liquids, where the effect was first observed, $\tau_c$ is a correlation time associated with local Brownian motion, whereas in gases, $\tau_c$ is the average time between molecular collisions. Gutowsky and Pake showed that the same approach can be applied to the study of atomic motion in solids, by treating $\tau_c$ as an average time between jumps from one atomic site to another [28]. Typically, the temperature dependence of the correlation time can be described as a thermally acti-

![FIG. 3. (a) Temperature dependence of the square root of the $^{31}$P-NMR second spectral moment at 7 T. (b) Temperature dependence of the $^{31}$P nuclear spin-spin relaxation rate at 7 T. (c) Temperature dependence of the $^{31}$P nuclear spin-lattice relaxation rate at 7 and 2 T. The black (red) lines represent fits with the BPP model to the 7 T (2 T) data.](image)

tivated process:

$$\tau_c = \tau_0 \exp \left( \frac{E_a}{k_BT} \right), \quad (2)$$

with the activation energy $E_a$ and the infinite-temperature correlation time $\tau_0$.

In most experiments, only one broad maximum of the spin-lattice relaxation rate is observed, accompanied by a step-like change of the temperature-dependent second moment, with only a few exceptions [17, 18]. However, in the present case of CuPOF, each $1/T_1$ peak and related constant regime of the temperature-dependent second moment can be attributed to a different set of characteristic rotational modes of the PF$_6$ molecules. The temperature-dependent $1/T_1$ data at 7 T was modeled using Eqs. (1) and (2) and a weak linear contribution, with two separate sets of BPP parameters for the two distinguishable maxima, compare Fig. 3(c).
The perpendicular component of the local fluctuating field is determined as \((\langle h_{\perp,1}^2 \rangle)_{1/2} = 11 \text{ Oe}\) for the low-
temperature peak, while for the high-temperature peak, we find \((\langle h_{\perp,2}^2 \rangle)_{1/2} = 18 \text{ Oe}\). Since these values are very
similar, we conclude that both processes are related to motional modes of the same physical object. The activation
energies and related correlation times are \(E_{a,1}/k_B = 250 \text{ K}\) and \(\tau_{0,1} = 20 \text{ ps}\) for the low-temperature process,
and \(E_{a,2}/k_B = 1400 \text{ K}\) and \(\tau_{0,2} = 3 \text{ ps}\) for the high-
temperature one, respectively. Both the activation energies and the correlation times, are in the parameter range observed for other compounds with a BPP-type enhancement
of \(1/T_1\) by thermally activated reorientation modes \[18, 29, 30\].

To further test the validity of the BBP model in the present case, additional \(1/T_1\) measurements at 2 T were
performed. According to the BBP theory, a decrease of the magnetic field and the corresponding NMR fre-
quency leads to an increase of the peak amplitude and a temperature downshift of the peak position. The para-
eters \((h_{\perp,1}^2), \tau_0\), and \(E_a\) remain unchanged by a vari-
ation of the field amplitude, as the molecular rotation itself. These predictions are in full compatibility with
our experimental results. The BPP modeling of the \(1/T_1\) data at 2 T gives \((\langle h_{\perp,1}^2 \rangle)_{1/2} = 10 \text{ Oe}, \tau_{0,1} = 20 \text{ ps},\) and
\(E_{a,1}/k_B = 255 \text{ K}\).

In the rather complex molecular-based structure of CuPOF, there are several candidates for yielding molecular
reorientation modes, namely the pyrazine molecules, the 2-pyridone molecules, and the PF\(_6\) anions. The
pyrazine molecules are bridging the Cu\(^{2+}\) ions, constituting a superexchange pathway for the electronic
moments, so that a rotational motion about the axis that links nearest copper neighbors might influence the related
Heisenberg exchange coupling \(J [21]\). However, both the pyrazine as well as the 2-pyridone molecules may be ex-
pected to yield only one characteristic set of rotational modes, as they are chemically bound to the layered struc-
ture.

Since the PF\(_6\) molecules are not bound to any other part of the molecular structure, they have the highest
degree of freedom, which makes them the most likely candidates to yield complex motional modes. There are
a few NMR studies of the rotational motions of the PF\(_6\) anions in alkali hexafluorophosphates to compare with \[17, 18, 30\].

In order to obtain further quantitative understanding of the rotation of the PF\(_6\) molecules and the related moti-
ional narrowing of the NMR spectra, measurements of the angular-dependent \(^{31}\)P resonance were performed at
10, 35, 100, and 200 K, selecting characteristic regions of the step-wise temperature dependence of \(\sqrt{M_2}\), see
Fig. 3(a). Numerical estimates of the anisotropic NMR shift for the two structurally slightly non-equivalent \(^{31}\)P
sites were performed by a summation of the dipole fields from the localized Cu\(^{2+}\) electronic moments in a volume
of \((100 \text{ Å})^3\). The results of these calculations are in very good agreement with the experimental data, see Fig. 4

and reveal that the full magnetic moment is, in fact, local-
ized at the Cu\(^{2+}\) sites. The isotropic chemical-shift con-
duction is determined as -168 ppm.

At all temperatures, the anisotropy of the frequency shift is much smaller than the spectroscopic linewidth.
Furthermore, by lowering the temperature from one step of \(\sqrt{M_2}\) to another, the periodicity of the \(\sqrt{M_2}\)
anisotropy changes, see Fig. 4. The periodicity of the frequency shift is observed at all tem-
peratures. The anisotropy amplitude scales with the magnetic dipole-field distribution stemming from the Cu\(^{2+}\) moments. These findings strongly suggest that the formation of the first \((\nu_{\text{res}})\) and the second \((M_2)\) spectral
moments are determined by different physical mechanisms.

For a further quantitative analysis of the experimental data, we calculated the second spectral moment. Ac-
cording to the Van Vleck theory of the nuclear-resonance linewidth in a rigid lattice \[31\], the second moment \(M_2^2\)
of the resonance absorption of the nuclear species \(j\) with angular momentum \(I\) and gyromagnetic ratio \(\gamma_I\) can be written as

\[
M_2^2 = (\Delta \omega)^2 = \frac{3}{4} I (I + 1) \sum_k \left[ \gamma_I^2 \frac{1 - 3 \cos^2 \theta_{jk}}{\gamma_{jk}^2} \right]^2 + \frac{1}{3} S(S + 1) \sum_{k'} \left[ J_{IS} + \gamma_I \gamma_S \frac{1 - 3 \cos^2 \theta_{jk'}}{\gamma_{jk'}^2} \right]^2,
\]

where \(\theta_{jk}\) is the angle between the position vector \(\vec{r}_{jk}\) of the magnetic moments \(j\) and \(k\) and the magnetic field,
and \(J_{IS}\) is the scalar coupling between unlike spins. The first term of Eq. \(3\) represents the broadening by like
nuclear moments, whereas the second term of equation \(3\) accounts for all other magnetic moments \(S'k'\). The line
broadening caused by different types of spin systems, \(I^k\) and \(S'k'\), is additive, and the broadening by like spins is
9/4 times more efficient than by unlike spins.

Since electronic magnetic moments are about 1000

![FIG. 4. Angular dependence of the \(^{31}\)P-NMR frequency shift, recorded for a field rotation in the crystallographic \(ac\) plane at 7 T and 10 K (circles). For both the \(P_{11}\) and \(P_{21}\) sites, the experimental data is compared to the calculated anisotropy of the dipolar-field contribution, stemming from the Cu\(^{2+}\) ions.](image-url)
times larger than nuclear magnetic moments (depending on the isotope), we first consider the line broadening due to dipole fields stemming from the Cu$^{2+}$ ions. Our calculations of the anisotropic dipole broadening using the second term of equation 3 gives magnitudes of 46-156 kHz, where 46 kHz results for an external magnetic field perpendicular to the $ab$ planes. The calculated values significantly exceed the experimentally determined second moment, e.g., $\sqrt{M_2} = 19$ kHz at 10 K for the out-of-plane orientation. The reason for this discrepancy is found by considering the exchange interactions between the Cu$^{2+}$ moments, contributing strongly to the fourth spectral moment, which leads to a narrowing of the absorption line [21]. The effective linewidth can be estimated as $(\Delta \omega)^2_{\text{Cu},\text{eff}} = (\Delta \omega)^2_{\text{Cu}} h (\Delta \omega)_{\text{obs}} / A$, where $(\Delta \omega)^2_{\text{Cu}}$ is the calculated second moment of the electronic copper moments, $(\Delta \omega)_{\text{obs}}$ is the experimentally observed width and $A/h$ is the exchange frequency [22]. In the case of CuPOF, $A/h \approx 4 \cdot 10^{11}$ Hz is estimated from the known Heisenberg exchange value of $J/k_B = 6.80(5)$ K [21]. Thus, the effective second moment contribution of the copper ions for an out-of-plane orientation of the external magnetic field is only about $\sqrt{M_2} = 25$ Hz. In consequence, whereas the Cu$^{2+}$ moments mainly determine the first spectral moment of the $^{31}$P absorption line, they yield no significant contribution to the second moment due to the exchange narrowing.

Since the second moment is inversely proportional to the sixth order of the distance between the interacting magnetic moments, the nuclear intramolecular broadening of PF$_6$ is examined as the next possible mechanism of the $^{31}$P line broadening. As mentioned, there are two structurally non-equivalent PF$_6$ molecules in the structure, see Fig. 1 giving rise to different second-moment anisotropies for the corresponding sites P$_{11}$ and P$_{21}$. Using the second term of Eq. 3, where $J_{1S} = J_{PF} = 712$ Hz, as determined by the MAS NMR experiments, see Fig. 2, the calculated anisotropy for the P$_{21}$ site agrees very well with the experimental data, compare Fig. 3(a). Due to almost identical first-moment anisotropies of the sites P$_{11}$ and P$_{21}$, see Fig. 4, the broader P$_{21}$ spectrum determines the experimentally observed anisotropy of the second moment.

The second-moment contribution from the dipolar broadening by the $^{13}$C, $^{14}$N, $^{15}$N, $^{63}$Cu, and $^{65}$Cu nuclei, as well as the intermolecular broadening by $^{31}$P and $^{19}$F nuclei, was evaluated by the second term of Eq. 3. The total calculated contribution yields only $\sqrt{M_2} = 26$ Hz, and is neglected in the following.

All of the above calculations are performed for a rigid lattice, i.e., under the assumption that the lengths and orientations of the vectors describing the relative positions of the magnetic moments are time independent. A different situation appears for liquids and gases, as well as for atomic diffusion in solids. In these cases, due to the rapid relative motion of magnetic moments, the resulting local fields at the nuclear sites fluctuate in time and only their average value is observed experimentally. This mechanism is known as motional narrowing, and can be observed under the condition that the average is taken over a time period which is long compared to the characteristic time scale of the fluctuations. The criterion for motional narrowing is $(\Delta \omega_0)^2 \cdot \tau_c \ll 1$, where $(\Delta \omega_0)^2$ is the second moment in the rigid lattice, described by Eq. 3, and $\tau_c$ is the correlation time characterizing the

| Calculation | Rotational mode | $\sqrt{M_2}$ (kHz) | $\Delta \omega_1$ (($\Delta \omega_0^2$)$^{1/2}$ E$_d$/k$_B$) | $\tau_0$ (K) | $\tau_0$ (ps) |
|-------------|----------------|-----------------|---------------------------------|-----------|---------|
| None, rigid lattice | 20.16 | 10 | 19.14 | |
| $^{3}$C$_4$ | 14.21 | 35 | 12.95 | 11 | 250 | 20 |
| $^{6}$C$_2$ | 3.62 | 100 | 3.59 | - | - | - |
| $^{4}$C$_3$ | 2.49 | 200 | 2.53 | 18 | 1400 | 3 |

Table I. Comparison between the calculated and experimentally recorded second moment $\sqrt{M_2}$, for the rigid lattice and rotations around two-, three-, and fourfold symmetry axes.

![Fig. 5](image-url) Angular dependence (with $H \parallel a$ or $c$ corresponding to $\theta = 0$ or 90 degrees, respectively) of the $^{31}$P second spectral moment at (a) 10, (b) 35, (c) 100, and (d) 200 K, compared to calculations for the nuclear P$_{11}$ and P$_{21}$ sites for (a) a rigid lattice and in presence of PF$_6$ molecular reorientations around the symmetry axes (b) $^{3}$C$_4$, (c) $^{6}$C$_2$, and (d) $^{4}$C$_3$. The inset in (a) shows a sketch of the local P$_{11}$ and P$_{21}$ symmetry with respect to the in- (H || a, horizontal) and out-of-plane (H || c, vertical) field orientation. The insets in (b), (c), and (d) show sketches of the molecular symmetry axes, around which the PF$_6$ molecular reorientations occur.
rate of the local field fluctuations. In the present case of CuPOF, this criterion is satisfied, since $\tau_c$ is of the order of a few ps, whereas $\sqrt{(\Delta\omega_0)^2}$ is of the order of a few ten kHz, see Table I. Since the second moment of the $^{31}$P resonance is mainly determined by the interaction with the six neighboring $^{19}$F nuclei of the same PF$_6$ molecule, it is reasonable to consider that the motional narrowing is related to reorientation modes of the PF$_6$ molecule itself. These molecules form almost perfect octahedral structures, the simplest and foremost motion of which are rotations around well-defined symmetry axes. The rotation about the two-, three-, and fourfold ($C_n$, $n = 2, 3, 4$) symmetry axes narrows the $^{31}$P line. To account for the molecular rotation, the angular-dependent coefficient $(1 - 3\cos^2 \theta_{jk})$ in Eq. (3) needs to be replaced by its average over all possible angles $\theta_{jk}$ [29]. According to the theorem for spherical harmonics,

$$\frac{3\cos^2 \theta_{jk} - 1}{2} \frac{3\cos^2 \gamma - 1}{2} \left(3\cos^2 \theta' - 1\right),$$

where $\gamma$ and $\theta'$ are the angles between the symmetry-axis direction vector and $\vec{r}_{jk}$ or the externally applied magnetic field, respectively. The angular dependence of the $^{31}$P-NMR second moment $M_2$ of the P$_{11}$ and P$_{21}$ sites was calculated in the presence of PF$_6$ molecular reorientations around the symmetry axes 6$C_2$, 4$C_3$, and 3$C_4$, using Eqs. (3) and (4). The angular dependences for each rotational PF$_6$ motion are compared to the experimental values of $M_2$ at 35 K ($3C_4$), 100 K ($6C_2$), and 200 K ($4C_3$), as shown in Figs. 5(b)-5(d). Excellent agreement between the calculations for the phosphorous site P$_{21}$ and the experimental data is observed. For the given rotation in the $ac$ plane, the different crystallographic orientations of the PF$_6$ molecules of the sites P$_{11}$ and P$_{21}$, as depicted in the inset of Fig. 5(a), result in quantitative differences of the calculated second moment anisotropies for the respective sites, depending on the symmetry axes of the given molecular rotation mode. Note that the calculations of $M_2$ do not include any free parameter.

As the only small deviation, at 100 K, the experimentally determined $\sqrt{M_2}$ mostly follows the calculations for the P$_{21}$ site, although a broader line is expected for the P$_{11}$ site. Nevertheless, the excellent overall agreement between the experimental and calculated second moment allows to assign the PF$_6$ molecular reorientation modes to the respective temperature regimes of constant $\sqrt{M_2}$. The motional modes in the different temperature regimes can be described as depicted by the insets in Figs. 5(b)-5(d).

At temperatures above 155 K, the PF$_6$ molecules are rotating around the four three-fold symmetry axes 4$C_3$, which pass through the centers of the octahedron surfaces. With decreasing temperature, these molecular reorientation modes are contiously freezing out, as is manifested by the broad high-temperature maximum of the $^{31}$P spin-lattice relaxation rate, see Fig. 3(c). At temperatures between about 130 and 80 K, molecular reorientation takes place with respect to the six two-fold symmetry axes 6$C_2$, which pass through the centers of the octahedron edges. Although these motional modes are freezing out with further decrease of temperature, no distinct maximum of the $^{31}$P spin-lattice relaxation rate, associated with a slowing of this specific molecular reorientation, is observed. Likely, this is due to a significant change of the reorientation frequency, leading to an abrupt change of the correlation time of the local-field fluctuations. As a consequence, the slowing down of the field fluctuations does not cross the Larmor frequency upon cooling. Below around 50 K, the PF$_6$ molecules rotate around the three four-fold symmetry axes 3$C_4$, which coincide with the space diagonals of the octahedron. The freezing of these molecular motions causes another BPP peak in the $^{31}$P spin-lattice relaxation rate, see Fig. 3(c).

Finally, at around 10 K, all PF$_6$ reorientation modes are frozen out, and the rigid-lattice condition is reached. Any of the aforesaid rotations does not necessarily need to be described in a classical formalism. If a molecule has more than one equivalent position with respect to the symmetry axis, separated by energy barriers, it may flip between these positions with a given frequency. A classical description of the rotation and averaging over a discrete number of possible positions will, in case of more than two equivalent orientations, give the same result for the calculation of the second moment [29]. A summary of all experimental and calculated characteristic parameters is presented in Table II.

III. CONCLUSIONS

In summary, we used a combined approach by probing static and dynamic local-magnetic-field properties by means of NMR spectroscopy, as well as molecular-motion models, to investigate the freezing of molecular rotation modes in the paramagnetic crystal CuPOF. By analyzing the temperature-dependent relaxation rates, the activation energies $E_{a,l}/kB = 250$ K and $E_{a,h}/kB = 1400$ K, with the corresponding correlation times $\tau_{a,l} = 20$ ps and $\tau_{a,h} = 3$ ps of the molecular reorientations, were determined. The angular-dependent frequency shift and second moment, compared with our calculations, reveal the origin of the low-frequency local-field fluctuations. The excellent agreement between the calculations and experimental data allows for a well-defined investigation and identification of the temperature-dependent evolution of the PF$_6$ molecular rotation modes. Perspectively, the knowledge of the microscopic environment of the Cu$^{2+}$ ions and its variation with temperature can be used as an important input for detailed DFT calculations of the electronic properties in CuPOF. The presented approach can be used for a broad range of similar molecular-based compounds with localized magnetic moments, and, thus, opens new possibilities for the exploration of molecular rotational modes in paramagnetic single crystals.
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