Magnetoelastic Coupling through the Antiferromagnet-to-Ferromagnet Transition of Quasi-Two-Dimensional \([\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4\) Using Infrared Spectroscopy

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We investigated magnetoelastic coupling through the field-driven transition to the fully polarized magnetic state in quasi-two-dimensional \([\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4\) by magnetoinfrared spectroscopy. This transition modifies out-of-plane ring distortion and bending vibrational modes of the pyrazine ligand. The extent of these distortions increases with the field, systematically tracking the low-temperature magnetization. These distortions weaken the antiferromagnetic spin exchange, a finding that provides important insight into magnetic transitions in other copper halides.

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As a candidate for a molecular solid with small \(J\) that can exhibit substantial magnetoelastic coupling, we consider the quasi-two-dimensional (2D) Heisenberg antiferromagnet \([\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4\). This compound consists of 2D square nets of \(\text{Cu}^{2+}\) ions \([\text{Fig. 1(a)}]\) in which the intralayer AFM spin exchange between \(\text{Cu}^{2+}\) centers is mediated by pyrazine with \(J = 6.1(3)\) K, and the interlayer FM spin exchange between \(\text{Cu}^{2+}\) ions by the \(\text{HF}_2^-\) bridging ligand with \(J_L = 0.010(5)\) K \([8,18–20]\). Here, we employ a spin Hamiltonian of the form \(- \sum J_{ij} S_i \cdot S_j\). Because of these overall low energy scales, a powered magnet can drive the system through the magnetic transition. \([\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4\) reaches the fully saturated state in an applied field of approximately 18 T at 500 mK and 1.5 K \([8]\). The sharp “elbow” denoting the critical field broadens at 4.2 K \([8]\). This is so because \(T_N = 1.54\) K. Nevertheless, there is a strong similarity between the 4.2 and 1.5 K magnetization curves, demonstrating the well-
established fact that spin correlations in low-dimensional AFM materials are present well above the long-range magnetic ordering temperature [21]. These short range correlations are also manifested as a broad low-temperature maximum in the susceptibility [21,22].

Here, we investigate the field-induced transition to the fully polarized magnetic state in \([\text{Cu(HF}_2(\text{pyz})_2)]\text{BF}_4\). We find that, in reaction to the change in state, the system lowers its magnetic exchange energy, in this case \(|J_{AFM}|\), through magnetoelastic coupling. The beauty of the present experiment is that exchange is mediated by a molecular ligand, pyrazine, the value of the coupling being sensitively dependent on the geometry of the Cu-pyz-Cu path. Because the ligand is soft, it is easily distorted. We follow these local distortions by magnetoinfrared spectroscopy and demonstrate that they track the magnetic transition. This finding is relevant to field-driven magnetic ordering transitions in other low-dimensional quantum Heisenberg antiferromagnets such as the copper halides and complex materials with higher energy scales such as copper oxides, where AFM fluctuations of \(S = 1/2\) centers may play a crucial role in establishing superconductivity but the size of the critical field precludes straightforward investigation of magnetostructural interactions [23]. These results are also important for understanding materials with more complicated noncollinear magnetic ordering transitions [13,24,25].

Single crystals were grown by solution techniques [26] and mixed with paraffin or KBr powder to form isotropic pellets for unpolarized transmittance measurements in the far and middle infrared, respectively [27]. Variable temperature studies were done at several temperatures between 300 and 4.2 K with 0.5 cm\(^{-1}\) resolution, and absorption was obtained as \(\alpha(\omega) = -\frac{i}{h} \ln T(\omega)\), where \(h\) is the loading, \(d\) is the pellet thickness, and \(T(\omega)\) is the measured transmittance. Magnetoinfrared experiments were carried out at the NHMFL at 4.2 K using a 33 T resistive magnet. To emphasize field-induced changes in the optical properties, we calculated the absorption difference spectra \([\alpha(H) - \alpha(0\ \text{T})]\) and spin density distributions for the AFM and FM states were calculated using the Vienna \textit{ab initio} simulation package [28–30] with the generalized-gradient approximation [31], a 400 meV plane-wave cutoff energy, and 50 \(k\) points for the irreducible Brillouin zone. \(U_{\text{eff}} = 4\ \text{eV}\) was employed for the Cu 3\(d\) states [32].

Figure 2 displays close-up views of several important infrared-active molecular vibrational modes in \([\text{Cu(HF}_2(\text{pyz})_2)]\text{BF}_4\). Assignments were made using a combination of dynamics calculations, independent measurements on chemically similar model materials, and known functional group patterns [26]. Low-temperature mode splitting and redshifting were discussed extensively in Ref. [26] and attributed to a local structural distortion driven by improved low-temperature hydrogen bonding. The latter is evidenced by low-temperature redshifting of vibrational modes, an effect shown clearly in Fig. 2(e). This behavior is observed across the copper-pyrazine-based family of low-dimensional molecular magnets [33,34] and in related magnetic materials as well. A notable difference between these new measurements and the previous set is the presence of modest splitting in the Cu-pyz lattice mode centered at \(~138\ \text{cm}^{-1}\) at 4.2 K [Fig. 2(a)], indicative of a weak low-temperature distortion of the Cu\(^{2+}\) environment. Below, we focus on trends in the out-of-plane pyrazine ring deformation near 468 cm\(^{-1}\), the out-of-plane pyrazine bend between 480 and 508 cm\(^{-1}\), and the out-of-plane C-H bend of the pyrazine ring near 805 cm\(^{-1}\) [Figs. 2(b) and 2(c)]. These modes are molecular in nature.

Figure 3 displays the magnetoinfrared response of \([\text{Cu(HF}_2(\text{pyz})_2)]\text{BF}_4\). Panels (a) and (b) show the absolute absorption in the two frequency regimes of interest: 450–510 cm\(^{-1}\) and 790–830 cm\(^{-1}\). Field-induced spectral modifications are often difficult to see in \(\alpha(\omega)\). As a consequence, we calculate absorption differences \([\alpha(H) - \alpha(0\ \text{T})]\) to emphasize field-induced changes in the vibrational properties [Figs. 3(c) and 3(d)]. With increasing field, the out-of-plane pyrazine ring deformation, out-of-plane pyrazine bend, and pyrazine out-of-plane C-H bend-
ing modes redshift and increase slightly in intensity. The overall trend toward a softer lattice in applied magnetic field can be seen in the absolute absorption data [Figs. 3(a) and 3(b)], but it is more obvious in the absorption difference data where the characteristic derivativelike line shape is observed [Figs. 3(c) and 3(d)] [35]. Changes in the aforementioned ring-related modes are small but systematic at low fields, increase through \( H_{c2} \), and start to saturate above 25 T. At full field, the out-of-plane pyrazine ring deformation at 468 cm\(^{-1}\) displays an 11% change, the out-of-plane pyrazine bend at 488 cm\(^{-1}\) shows a 13% difference, the pyrazine out-of-plane C-H bend near 805 cm\(^{-1}\) has a 3.5% difference, and the small trio of peaks between 810 and 825 cm\(^{-1}\) change by about 30% at 33 T. In contrast, the frequency range (~515–520 cm\(^{-1}\)) where the BF\(_4^-\) mode resonates shows only fluctuations within our noise level, which is less than 0.05%. These results indicate that the field-driven transition to the fully polarized state is accompanied by strong changes in the out-of-plane pyrazine ring distortion and bending modes.

Before we discuss the consequences of out-of-plane pyrazine ring distortions for spin exchange interactions between Cu\(^{2+}\) centers, it is important to note that several characteristic vibrational modes of structurally important functional groups do not display any magnetic field dependence within our sensitivity. These include the Cu-pyrazine lattice modes, bifluoride linkers, and the BF\(_4^-\)-related modes. That the BF\(_4^-\) bend near 520 cm\(^{-1}\) [Fig. 3(c)] is rigid is not such a surprise because it resides in the anion pocket without strong connectivity to the 2D spin exchange network. On the other hand, the low frequency Cu-pyrazine lattice modes and biflouride linkers are intimately involved in the 2D structural and magnetic framework and the interlayer connectivity and spin exchange interaction, respectively. From these spectral results, we see that the HF\(_2^-\) anion remains symmetric in the high field phase. Further, we find that interlayer magnetoelastic interactions as represented by the bifluoride group are unchanged in the fully polarized state. The behavior of the BF\(_4^-\) and HF\(_2^-\) molecular vibrations and the copper-pyrazine lattice modes clearly differs from that of the pyrazine ligands.

We can quantify trends in the out-of-plane pyrazine vibrations by integrating the absolute value of the absorption difference data and plotting the results as a function of field (Fig. 4). Here, integrations were carried out over two independent frequency regimes in order to follow the contrast in different modes. Strikingly, the spectral data track the magnetization, albeit with a small lag that may be
related to slower lattice relaxation. That the size of these field-induced molecular-level distortions tracks the bulk magnetization demonstrates that the magnetoelastic interactions are coupled to the field-driven transition. This kind of coupling has not been observed before in any material to the best of our knowledge.

Magnetostructural correlations in chemically similar materials highlight the possible relationship between pyrazine ring tilt and magnetic exchange [8,36–39]. Considering this traditional interpretation and ring tilt data in [Cu(HF2)(pyz)2]BF4 (31.6° away from c at 300 K, increasing at lower temperature), it is reasonable to anticipate field-driven orientational effects involving the pyrazine ligand. Instead, we found that the pyrazine ring distorts to accommodate the fully polarized magnetic state. Because the AFM term \( J_{AF} \) is determined by the overlap of the N lone pair orbitals of the pyrazine ring with the Cu \( x^2-y^2 \) orbital [Fig. 1(b)], the Cu-pyz-Cu spin exchange path is most effective when the twofold rotational axis coincides with the Cu-Cu direction and the pyrazine ring is planar. When the pyrazine ring is distorted from planarity, the hopping integral for the Cu-pyz-Cu spin exchange path becomes smaller, reducing the magnitude of \( J_{AF} \). This reduces the overall spin exchange \( J = J_F + J_{AF} \) since \( J_F < |J_{AF}| \), effectively lowering the energy of the FM state forced upon the 2D antiferromagnet by external magnetic field. It is noted from Figs. 1(b) and 1(c) that the FM state forced upon the 2D antiferromagnet by external C0 magnetic field is most effective when the twofold rotational axis coincides with the C-C bond and the pyrazine ring is planar. This destabilizing effect in the FM state is reduced by the pyrazine out-of-plane distortion. It is also important to consider the role of lattice energy in the magnetoelastic effect. That this model 2D antiferromagnet is driven into the fully polarized state by an applied field demonstrates that the energy cost of distorting the pyrazine ring must be less than the magnetic energy gain in that state. Our preliminary density-functional calculations indicate that a 1° out-of-plane bend of the pyrazine ring can be accommodated in a 33 T field; such a hypothetical distortion changes \( J \) by \( \sim 3\% \).

To summarize, we measured the vibrational properties of [Cu(HF2)(pyz)2]BF4 through the magnetic field-driven transition to the fully polarized magnetic state in order to probe magnetoelastic coupling in a model 2D molecular antiferromagnet. The out-of-plane pyrazine ring deformation and bending modes redshift with applied field, and this contrast systematically tracks the low-temperature magnetization. The magnetoelastic coupling associated with this transition occurs most likely to reduce the strength of the Cu-pyz-Cu spin exchange in the FM state. Such a balance may be important in other magnetic materials.

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[22] The broadband maximum occurs at 5.5 K but slightly above \( T_N \), where a strong remnant of the long-range ordered state still exists.
[27] High optical density precludes single crystal studies.
[35] The redshift and softer lattice may be a signature of improved hydrogen bonding in the FM state [26].