# Rotational dynamics of $C_{60}$ in $(ND_3)K_3C_{60}$

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The orientational dynamics of $C_{60}$ in the ammoniated fulleride $(ND_3)K_3C_{60}$ are studied by the neutron inelastic-scattering technique. Well-defined excitations are observed in the low-energy spectra with energies varying between 3.11(7) and 2.38(5) meV, as the temperature increases from 30 to 310 K. The dependence of their intensities on the scattering vector is consistent with their assignment to small-amplitude librational motion of the $C_{60}^{3-}$ ions. The librations in $(ND_3)K_3C_{60}$ are both softer and broader than those in the parent fulleride $K_3C_{60}$, reflecting the existence of a weaker and more anisotropic orientational potential upon ammoniation. The estimated barrier of the hindrance potential, $E_a \sim 250$ meV is approximately half the size of that in $K_3C_{60}$ and comparable to that found in the primitive cubic fulleride $Na_2RbC_{60}$. The temperature dependence of the energies and widths of the librational peaks in $(ND_3)K_3C_{60}$ is also more reminiscent of the behavior of $Na_2RbC_{60}$ rather than $K_3C_{60}$. The result has been rationalized by involving crystal-packing arguments, related to the increase in size of the tetrahedral interstices upon ammoniation. [S0163-1829(99)13401-5]

## I. INTRODUCTION

Ternary alkali fullerides $A_cC_{60}$ ($A$=alkali metal) exhibit superconductivity with $T_c$'s as high as 33 K at ambient pressure ($RbCs_2C_{60}$, fcc structure).[1] The well-known relationship in which the transition temperature $T_c$ scales monotonically with the cubic unit cell size $a_0$ can be rationalized in terms of an increasing density of states at the Fermi level, $N(\varepsilon_F)$, with increasing interfullerene separation, resulting from the decrease in the overlap between the molecules that leads to band narrowing.[2] As a consequence, in order to obtain high-$T_c$ fullerides, large interfullerene spacings are needed. The lattice expansion which can be achieved by using alkali metals alone in the interstitial sites of the cubic structure is limited by the maximum size of the metal cations used for intercalation. Larger lattice constants can be achieved by using as structural "spacers" alkali ions solvated with neutral molecules, such as ammonia; in such cases, the extent of charge transfer is also maintained. For instance, upon ammoniation of $Na_2CsC_{60}$, the lattice expands, while the cubic symmetry is maintained: the lattice constant increases by $\sim 0.39$ Å, and the $T_c$ increases significantly from 10.5 to 29.6 K.[3] However, this behavior is not general as the introduction of $NH_3$ in the interstitial sites of other alkali fullerides has been found to lead to diverse responses in the structural and conducting properties. The $(NH_3)_xNaA_2C_{60}$ ($0.5 \leq x \leq 1$, $A$= K, Rb) series displays reduced $T_c$'s which, in addition, decrease with increasing lattice constant.[4] In $K_3C_{60}$, the introduction of one ammonia molecule in the octahedral site of the fcc structure to form $(NH_3)K_3C_{60}$ produces an anisotropic expansion of the fulleride array, inducing a symmetry reduction to body-centered tetragonal (bct) and the suppression of superconductivity at ambient pressure;[5] application of a pressure >1

GPa leads to the recovery of superconductivity with $T_c = 28$ K.[6] A structural phase transition has been identified below 150 K and attributed to the ordering of the orientation of the $K^+$-$NH_3$ pair residing in the interstitial sites.[7] Measurements of the electronic and magnetic properties by electron-spin resonance (ESR) and $^{13}C$ NMR have shown $(ND_3)K_3C_{60}$ to be a narrow-band metal which exhibits a transition to an insulating ground state at 40 K.[8,9] zero-field-$\mu$SR measurements have characterized the low-temperature state of $(NH_3)K_3C_{60}$ as a long-range-ordered antiferromagnet,[10–12] thus providing unambiguous evidence that the suppression of superconductivity at large interfullerene spacings is of magnetic origin, in analogy with the well-established results in high-$T_c$ and organic superconductors.[13]

Low-energy neutron inelastic-scattering (NIS) measurements have been successfully used to probe the rotational dynamics of pristine $C_{60}$ (Ref. 14) and $C_{70}$ (Ref. 15) as well as of $C_{60}^{3-}$ and $C_{60}^{6-}$ ions in a variety of fullerides.[16–20] In all cases, the excitations observed at low temperatures at nonzero energy transfer are due to fullerene molecules librating about their equilibrium orientations. It is of particular interest to see how the introduction of ammonia in the lattice and the consequent solvation of the alkali ions modify the intermolecular orientational potential of the $C_{60}^{n-}$ ions in fullerides. For this reason, we performed NIS measurements of the low-energy rotational excitations in $(ND_3)K_3C_{60}$ between 30 and 310 K. The fully deuterated sample was chosen for the present study in order to eliminate the strong contributions to the scattering arising from the hydrogen atoms of the $NH_3$ molecules. The momentum-transfer $Q$ dependence of the intensity of the low-energy excitations in $(ND_3)K_3C_{60}$ leads to their assignment as librational modes whose ener-

gies are substantially lower than those in the parent material $K_3C_{60}$,[16] indicating a substantial change in the orientational potential between the two fullerides. Softening and broadening of the librational peaks are observed on heating. Considerable similarities with the behavior of $Na_2RbC_{60}$ (Ref. 17) are also encountered.

## II. EXPERIMENTAL DETAILS

$(ND_3)K_3C_{60}$ was prepared by following the procedure employed earlier in the synthesis of $(NH_3)K_3C_{60}$.[5] The starting $K_3C_{60}$ was synthesized by direct reaction of K vapor and $C_{60}$ powder, followed by annealing for 1 month at 400 °C. The single-phase $K_3C_{60}$ powder thus obtained was then loaded in a glass tube (18 mm in outer diameter), evacuated to $10^{-3}$ Torr, and exposed to 0.5 atm $ND_3$ gas at room temperature for 1 h. After the reaction, the glass tube was sealed under a 0.5 atm partial pressure of $ND_3$ and the sample was annealed at 100 °C for 2–3 months. Phase purity was confirmed by powder x-ray-diffraction measurements performed with a Siemens D5000 diffractometer at ambient temperature.

The neutron-scattering measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research using the BT4 triple-axis spectrometer with fixed incident neutron energy $E_i$ of 28 meV. The incident neutron beam was monochromated using the Cu(220) reflection, and the scattered neutrons were analyzed using the pyrolytic graphite (004) reflection. The measured resolution at the elastic lie for 60′-40′-40′-40′ collimations was 0.9093 meV full width at half maximum (FWHM). For the present experiment, 0.83 g of powder sample was loaded in an indium-wire-sealed aluminum cylindrical can and placed inside a closed-cycle helium refrigerator. In the analysis of the inelastic-scattering measurements,[21] background runs were first subtracted, the intensities were corrected for changes in the scattered energy contribution to the spectrometer resolution, and then the spectra were symmetrized. The corrected data were subsequently fitted using the measured resolution function at zero energy transfer ($\hbar\omega = 0$) and two Lorentzians centered at nonzero energy transfer, convoluted with the instrumental resolution function.

## III. RESULTS AND DISCUSSION

Detailed NIS measurement for $(ND_3)K_3C_{60}$ were performed as a function of $Q$ and $\omega$ at several temperatures. Figure 1 shows representative spectra for temperatures between 30 and 310 K at a scattering vector $Q = 5.5$ Å$^{-1}$. The solid circles are the corrected experimental data, and the lines are the fits described in the previous section. Well-defined peaks are observed at nonzero energy transfer at all temperatures and may be assigned to librational modes of the $C_{60}^{3-}$ ions from the dependence of their integrated intensity on the scattering vector $Q$. This is apparent from Fig. 2 where the integrated intensity of the librational peaks is shown as a function of $Q$ at 125 and 310 K, together with Monte Carlo calculations for uncorrelated isotropic molecular librations with root-mean-square amplitudes $\theta_{rms} = 2.86°$ (solid line), 4.29° (dotted line), 5.72° (dash-dotted line), and 8.59° (dashed line). The measured values at 125 K were
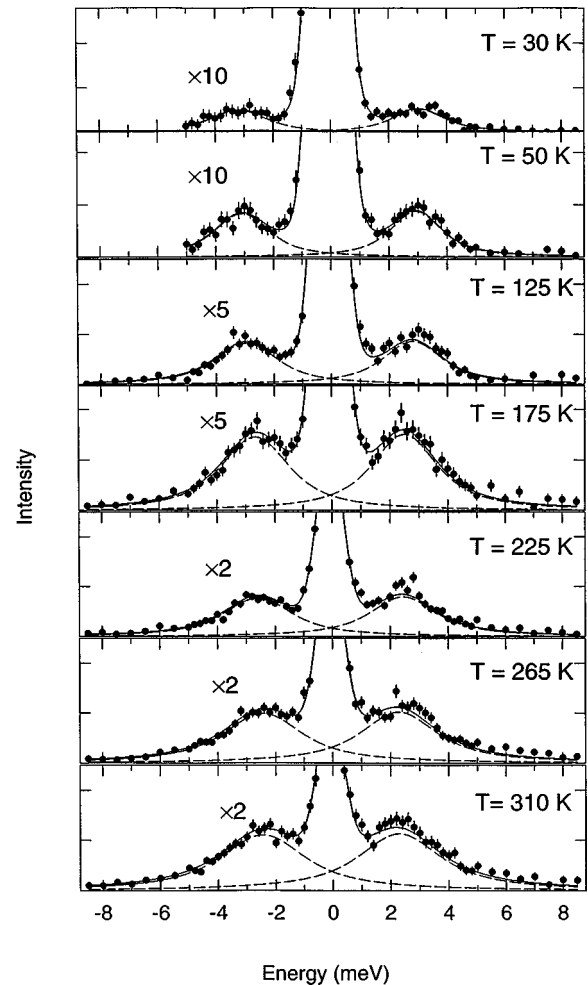


FIG. 1. Representative NIS spectra of $(ND_3)K_3C_{60}$ in the temperature range 30–310 K at constant $Q = 5.5$ Å$^{-1}$. The solid circles are experimental points, and the solid lines are best fits, as discussed in the text. The dashed lines show the individual Lorentzian components at nonzero energy transfer. Note changes in the intensity scale in the various panels.

scaled to the average value of the 2.86° and 4.29° calculations at $Q = 3.5$ Å$^{-1}$, and the same factor was used to scale the data at 30 K. There is good agreement between the experimental data and the librational model calculations at both temperature, confirming the assignment of the low-energy inelastic-scattering peaks as arising from molecular librations.

A comparison of the temperature evolution of the energies of the librational modes in $(ND_3)K_3C_{60}$ with those reported before in $C_{60}$ (Ref. 14), $Na_2RbC_{60}$ (Ref. 17), and $K_3C_{60}$ (Ref. 16) is shown in Fig. 3. At low temperatures, the librational energy in $(ND_3)K_3C_{60}$ [3.11(7) meV at 30 K] is comparable to those in $C_{60}$ [2.77(6) meV at 20 K] and $Na_2RbC_{60}$ [2.83(17) meV at 50 K], but considerably smaller than that in $K_3C_{60}$ [4.04(3) meV at 12 K]. Ammoniation of $K_3C_{60}$ thus leads to a considerable weakening of the orientational potential. The librations in $(ND_3)K_3C_{60}$ also soften as the temperature increases (Fig. 3), in agreement with the behavior of the other systems studied; however, the softening is markedly higher in $(ND_3)K_3C_{60}$ (~23% between 30 and 310 K) compared to $K_3C_{60}$ (~11% between 12 and 300 K), showing a behavior much more similar to that observed for $C_{60}$ and $Na_2RbC_{60}$. In addition, there is no measurable effect on the
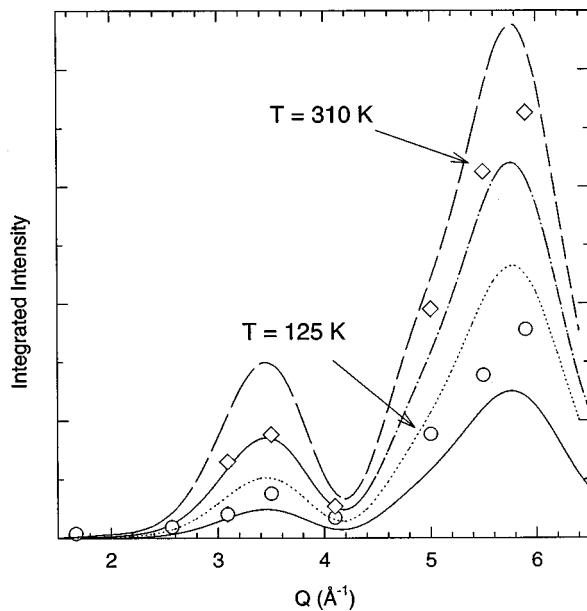
FIG. 2. $Q$ dependence of the intensity of the librational peaks in (ND$_3$)K$_3$C$_{60}$ at 310 K (rhombi) and 125 K (circles). The lines represent the intensity variation calculated for uncorrelated isotropic librations with root-mean-square amplitude of 2.86° (solid line), 4.29° (dotted line), 5.72° (dash-dotted line), and 8.59° (dashed line). The measured values at 125 K are normalized to the average value of the 2.86° and 4.29° calculations at $Q = 3.5$ Å$^{-1}$, and the same factor is used to normalized the data at 310 K.

C$_{60}$ librational motion of either the metal-insulator transition near 40 K (Refs. 8–12) or the structural transition, driven by the ordering of the NH$_3$ rotational motion, near 150 K.[7,12]

It is apparent from the present results that the magnitude of the orientational potential in (ND$_3$)K$_3$C$_{60}$ and its tempera-
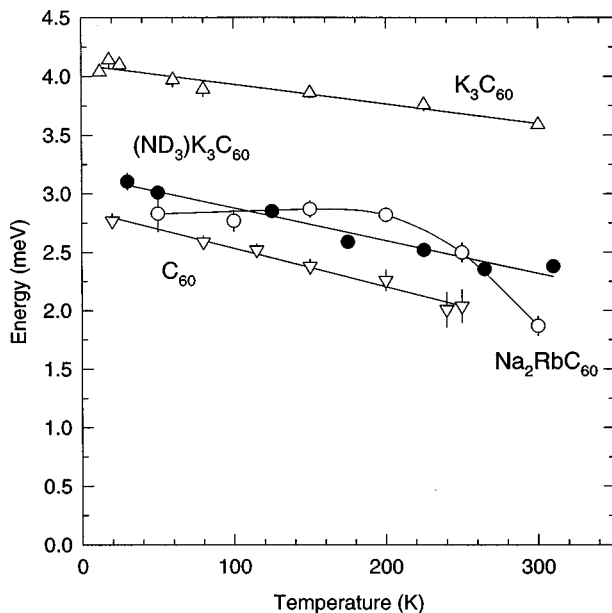


FIG. 3. Temperature evolution of the librational energy for (ND$_3$)K$_3$C$_{60}$ (solid circles). Earlier results for C$_{60}$ (inverted triangles) (Ref. 14), Na$_2$RbC$_{60}$ (open circles) (Ref. 17), and K$_3$C$_{60}$ (triangles) (Ref. 16) are included for comparison. Lines are guides to the eye.
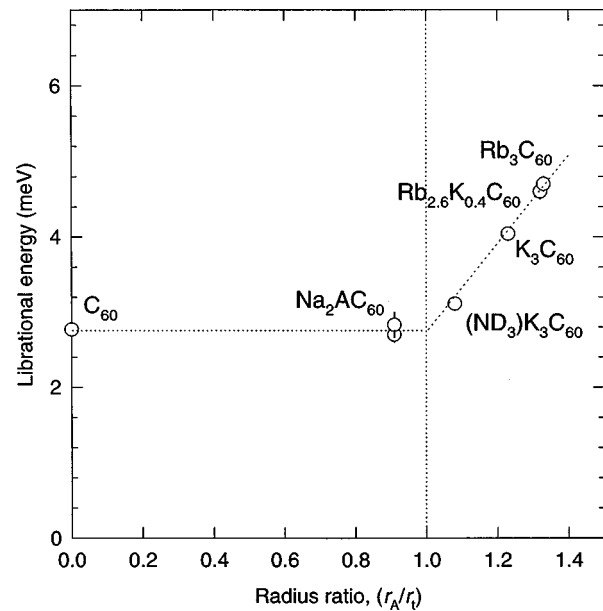


FIG. 4. Schematic diagram showing the dependence of the low-temperature librational energy on ($r_A/r_t$), where $r_t$ is the size of the tetrahedral hole and $r_A$ is the radius of the ion residing in it. Results for C$_{60}$ (Ref. 14), Na$_2$RbC$_{60}$ (Ref. 17), Na$_2$CsC$_{60}$ (Ref. 18), K$_3$C$_{60}$ (Ref. 16), Rb$_{2.6}$K$_{0.4}$C$_{60}$ (Ref. 19), and Rb$_3$C$_{60}$ (Ref. 20) are taken from the literature.

ture dependence resemble those in C$_{60}$ and Na$_2$RbC$_{60}$, differing substantially from that in K$_3$C$_{60}$. It has been noted before[17,19] that the librational energies of cubic fullerides scale with the size of the ion, $r_A$, occupying the tetrahedral interstices in the cubic lattice. In brief, when $r_A$ is less than 1.12 Å, the low-temperature structure is primitive cubic (space groups $Pa\bar{3}$) (Ref. 22) and the librational energy remains roughly constant at ~2.8 meV (e.g., Na$_2$RbC$_{60}$, Na$_2$CsC$_{60}$).[18,19] However, when $r_A > 1.12$ Å, the structure is fcc (space group $Fm\bar{3}m$) and the librational energy increases almost linearly with increasing $r_A$ (e.g., K$_3$C$_{60}$, K$_{3-x}$Rb$_x$C$_{60}$, Rb$_3$C$_{60}$).[16,19,20] Such behavior reflects the dominance of the repulsive $A^+$-C$_{60}^{3-}$ overlap in determining the orientational potential in these systems. However, in the case of (ND$_3$)K$_3$C$_{60}$, ammoniation leads to a reduction in crystal symmetry to body-centered tetragonal (space group $I4/mmm$) (Ref. 5), and an anisotropic expansion of the unit cell to accommodate the large K$^+$-NH$_3$ units in the octahedral interstices. As a result, the size of the tetrahedral hole also becomes considerably larger, expanding to $r_t = 1.28$ Å. So in order to rationalize the measured characteristics of the orientational potential in (ND$_3$)K$_3$C$_{60}$, we now plot (Fig. 4) the low-temperature librational energies measured for the various fulleride salts as a function of the ratio of $r_A$ to the size of the tetrahedral hole, $r_t$. Hence, when the ($r_A/r_t$) ratio is less than 1, the librational energy is roughly constant at ~2.8 meV. On the other hand, when ($r_A/r_t$) > 1, the librational energy increases linearly with increasing ($r_A/r_t$). From these considerations, one can now explain the observed differences (similarities) between the orientational potentials in (ND$_3$)K$_3$C$_{60}$ and K$_3$C$_{60}$ (Na$_2$RbC$_{60}$) in terms of simple crystal-packing considerations and the continued importance of the repulsive $A^+$-C$_{60}^{3-}$ interactions. The introduction of

ammonia in the $K_3C_{60}$ structure brings about an increase in the size of the tetrahedral hole by $\sim 0.14$ Å and reduces the $(r_A / r_t)$ ratio from 1.23 in $K_3C_{60}$ to 1.08, close to the value of 1 in $Na_2RbC_{60}$.

An estimate of the rotational barrier in $(ND_3)K_3C_{60}$ can be made assuming that a simple sinusoidal hindrance potential is sufficient to describe the rotational motion of the librating group. For small amplitudes of libration,

$$E_a = (E_{lib}^2/B)(\theta/2\pi)^2, \qquad (1)$$

where $E_a$ is the potential barrier, $\theta$ is the hopping angle between neighboring potential minima, $B = 0.364 \times 10^{-3}$ meV is the rotational constant for $C_{60}$, and $E_{lib}$ is the librational energy at a given $Q$ and temperature. The bct structure of $(ND_3)K_3C_{60}$ is related to that of the $A_3C_{60}$ ($A = K$, Rb) systems, in which the reorientational mechanism involves angular jumps, $\theta \sim 44.5°$, about the threefold molecular axes, aligned with the $\langle 111 \rangle$ directions in the unit cell.[23] Assuming a similar reorientational motion in $(ND_3)K_3C_{60}$, we obtain an estimate of the activation barrier of the hindrance potential, $E_a \sim 250$ meV. In agreement with the crystal size arguments developed earlier, this is approximately half the size of the value $E_a \sim 520$ meV calculated for $K_3C_{60}$ and of the same order of magnitude as the barriers ($E_a \sim 250$–300 meV) calculated for $C_{60}$ and $Na_2RbC_{60}$. An estimate can be also made of the temperature evolution of the rms amplitude of libration, $\theta_{rms}$, within the harmonic approximation, using the expression

$$(\theta_{rms})^2 = (4B/E_{lib})\coth(E_{lib}/2kT). \qquad (2)$$

The librational amplitudes in $(ND_3)K_3C_{60}$ are found to vary from $\sim 1.7°$ at 30 K to $\sim 6.7°$ at 310 K, in good agreement with the results shown in Fig. 2.

The FWHM of the librational peaks in $(ND_3)K_3C_{60}$ (Fig. 5) are not resolution limited. Their values are comparable to those in $Na_2RbC_{60}$,[17] but considerably broader than those in $K_3C_{60}$,[16] implying an increased anisotropy of the orientational potential upon ammoniation. In $K_3C_{60}$, the FWHM do not increase significantly with increasing temperature ($\sim 20\%$ between 12 and 300 K), in sharp contrast with the present ammoniated sample in which there is a substantial increase ($\sim 70\%$ between 30 and 310 K). This is again reminiscent of the situation encountered in $Na_2RbC_{60}$ in which there is a doubling of the FWHM of the librations on approaching the primitive cubic→fcc phase transition.[17] No evidence for a similar orientational order→disorder transition has been identified for $(ND_3)K_3C_{60}$ yet. However, the present experimental data imply that the system is gradually approaching such a transition at temperatures somewhat higher than 310 K, and it will be of interest to search for its occurrence up to the decomposition temperature.

The temperature dependence of the reduced integrated intensity of the librational modes ($I_{lib}/I_{tot}$) can be accounted for if the librational intensity $I_{lib}$ is associated not only with one-phonon scattering, but with all the inelastic scattering. Then,

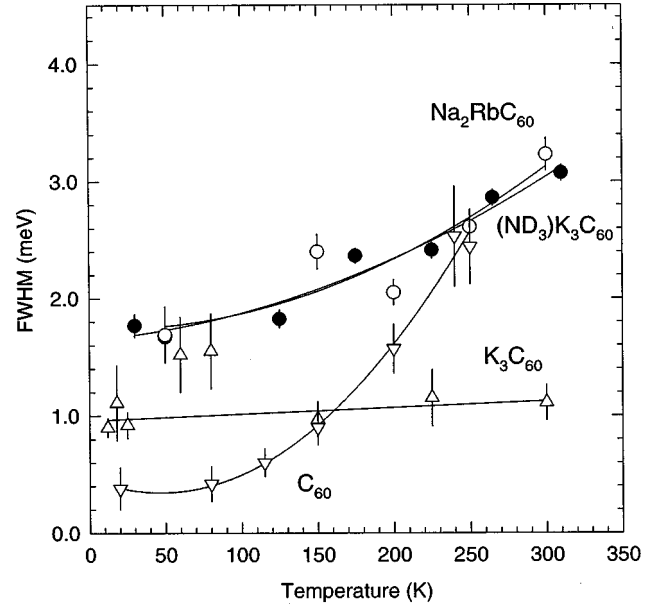$$(I_{lib}/I_{tot}) = 1 - \exp[-2W], \qquad (3)$$



FIG. 5. Temperature evolution of the FWHM of the librational peaks for $(ND_3)K_3C_{60}$ (solid circles). Earlier results for $C_{60}$ (inverted triangles) (Ref. 14), $Na_2RbC_{60}$ (open circles) (Ref. 17), and $K_3C_{60}$ (triangles) (Ref. 16) are included for comparison. Lines are guides to the eye.

where $\exp[-2W]$ is the librational Debye-Waller factor.[24] Within the incoherent approximation and for harmonic librational motion, $2W$ is identical to the one-phonon scattering expression $(4BQ^2R^2/3E_{lib}\coth(E_{lib}/2kT)$, where $R = 3.5$ Å is the radius of the $C_{60}$ molecule. This expression completely describes the temperature dependence of the intensities seen in Fig. 1.

## IV. CONCLUSIONS

We have measured the low-energy NIS spectra of $(ND_3)K_3C_{60}$ as a function for the scattering vector $Q$ at various temperatures between 30 and 310 K. The fulleride units are found to undergo small-amplitude librations about their equilibrium position, giving rise to well-defined librational peaks near 3.1 meV at low temperature. The librational motion is not sensitive either to the antiferromagnetic transition at 40 K or to the structural transition at 150 K, driven by the ordering of the $K^+$-coordinated $NH_3$ molecules. The librational energy is smaller than in the parent $K_3C_{60}$ salt, and the peaks are much broader, reflecting a weaker and more anisotropic orientational potential. There is a striking similarity, both in the magnitude of the hindrance potential and the temperature dependence of the librational excitations, between $(ND_3)K_3C_{60}$ and the primitive cubic salt $Na_2RbC_{60}$. As the orientational potential is determined by the strength of the Coulomb repulsions in these systems, we were able to rationalize this behavior by noting the increased size of the tetrahedral interstices in the body-centered tetragonal structure of $(ND_3)K_3C_{60}$. Thus these can accommodate the $K^+$ ions with considerably reduced repulsive $K^+$-$C_{60}^{3-}$ overlap than in $K_3C_{60}$. Finally, the similarities in behavior with $Na_2RbC_{60}$ raise the possibility of an order→disorder transition in $(ND_3)K_3C_{60}$ before its decomposition temperature.

## ACKNOWLEDGMENTS

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