Cooling quasiparticles in A₃C₆₀ fullerides by excitonic mid-infrared absorption

Andrea Nava¹, Claudio Giannetti², Antoine Georges³,⁴,⁵, Erio Tosatti⁶,⁷ and Michele Fabrizio¹*¹

Long after its discovery, superconductivity in alkali fullerides A₃C₆₀ still challenges conventional wisdom. The freshest inroad in such ever-surprising physics is the behaviour under intense infrared excitation. Signatures attributable to a transient superconducting state extending up to temperatures ten times higher than the equilibrium Tₑ ≃ 10 K have been discovered in K₃C₆₀ after ultra-short pulsed infrared irradiation—an effect which still appears as remarkable as mysterious. Motivated by the observation that the phenomenon is observed in a broad pumping frequency range that coincides with the mid-infrared electronic absorption peak still of unclear origin, rather than to transverse optical phonons as has been proposed, we advance here a radically new mechanism. First, we argue that this broad absorption peak represents a ‘super-exciton’ involving the promotion of one electron from the t₁₈ half-filled state to a higher-energy empty t₃₃ state, dramatically lowered in energy by the large dipole–dipole interaction acting in conjunction with the Jahn–Teller effect within the enormously degenerate manifold of (t₁₈)²(t₃₃)³ states. Both long-lived and entropy-rich because they are triplets, the infrared-induced excitons act as a sort of cooling mechanism that permits transient superconducting signals to persist up to much higher temperatures.

Superconducting alkali-doped fullerenes A₃C₆₀ are molecular compounds where several actors play together to determine an intriguing physical behaviour. The high icosahedral symmetry of C₆₀ implies, prior to intermolecular hybridization, a large degeneracy of the molecular orbitals, and thus a strong electronic response to Jahn–Teller (JT) molecular distortions lowering that symmetry. In particular, the t₁₈ lowest unoccupied molecular orbital (LUMO), which accommodates the three electrons donated by the alkali metals, is threefold degenerate and JT-coupled to eight fivefold-degenerate molecular vibrations of H₂₃ symmetry, which mediate the pairing. The JT effect, favouring low spin, is partly hindered by (Coulomb) Hund’s rule exchange, which favours high spin. Therefore, the overall singlet pairing strength g, although still sizeable, is way too small compared to the charging energy of each C₆₀ to justify by simple arguments why A₃C₆₀ are s-wave superconductors. The explanation of this puzzle proposed in refs 2, 3 and vindicated by recent experiments emphasizes the crucial role of a parent Mott insulating state where the JT coupling effectively inverts Hund’s rules, the molecular ground state therefore turning to spin S = 1/2 rather than S = 3/2 (ref. 4). A S = 1/2 antiferromagnetic insulating phase is indeed the ground state in over-expanded NH₃K₃C₆₀ (refs 5,6) and in Cs₃C₆₀ (ref. 7) at ambient pressure. In the metallic state, attained under pressure in Cs₃C₆₀ and at ambient pressure in K₃C₆₀ and Rb₃C₆₀, the incipient Mott localization slows down the coherent motion of quasiparticles while undressing them from charge correlations. As a result, the singlet pairing strength g eventually overwhelms the quasiparticle Coulomb pseudopotential and, on approaching the Mott transition, the system is effectively driven towards the top of the universal Tₑ versus g curve, where the critical temperature reaches the maximum possible value at a given non-retarded attraction TₑMAX ≃ 0.055 g. Thus, according to the theory of ref. 3, the peak Tₑ ≃ 38 K reached by Cs₃C₆₀ at P ≃ 7 kbar (refs 9,10) is actually the highest attainable at equilibrium in fullerides.

This equilibrium upper limit has been far surpassed in out-of-equilibrium conditions in a recent remarkable pump–probe experiment on K₃C₆₀ (ref. 11). After irradiation by an intense femtosecond infrared pulse between 80 and 200 meV, K₃C₆₀ showed a transient regime of some picoseconds where the optical properties looked like those of a superconductor up to a temperature T ≥ 200 K, ten times higher than the equilibrium Tₑ ≃ 20 K (Fig. 1b). This tantalizing observation has already elicited various theoretical efforts¹²–¹⁵, where it was mainly assumed, as in the original work¹¹, that transverse optical (TO) phonon infrared (IR) absorption acts as the crucial ingredient increasing the pairing efficiency. Here we follow another route, directly inspired by experimental features, which leads to a totally different perspective.

First of all, the transient ‘superconducting’ gap does increase¹¹, yet not as much as the transient Tₑ (see Fig. 1b). More importantly, we note in ref. 11 that the transient reduction of optical conductivity (suggestive of a transiently enhanced superconducting state) is broadly distributed over the infrared-pumping frequency range from 80 to 200 meV (see Fig. 1a). Although that includes the two highest Tₑ₁₈ infrared-active modes near 150 and 170 meV (ref. 17), the enhancement does not especially peak there, extending instead to lower frequencies (see Fig. 1a). There is instead an intriguing similarity between a long-known¹⁸–²¹ broad absorption peak that characterizes the equilibrium infrared response of K₃C₆₀ and Rb₃C₆₀. This peak is present and strong in the equilibrium optical data of ref. 11, centred around ~50 meV and ~100 meV in width (see Fig. 1b). Given these characteristics, the underlying excitation is not a phonon, and can only be electronic; yet, nobody seems to know exactly what it is²⁰–²³.

Intriguingly, it now appears that the superconducting enhancement follows rather closely the shape of this infrared absorption

¹International School for Advanced Studies (SISSA), Via Bonomea 265, I-34136 Trieste, Italy. ²Intercalation Laboratory for Advanced Materials Physics (ILAMP), Università Cattolica del Sacro Cuore, Brescia I-25121, Italy. ³Centre de Physique Théorique, École Polytechnique, CNRS, Université Paris-Saclay, 91128 Palaiseau, France. ⁴Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France. ⁵Department of Quantum Matter Physics, University of Geneva, 24 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland. ⁶International Centre for Theoretical Physics (ICTP), Strada Costiera 11, I-34151 Trieste, Italy. ⁷CNR-IOM Democritos, Via Bonomea 265, I-34136 Trieste, Italy. *e-mail: fabrizio@sissa.it

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feature. Our first task is therefore to understand this excitation, which might provide a precious clue to superconductivity enhance-
ment alternative to the resonance with infrared-active TO modes.

In $A_1C_{3u}$ the conduction electrons occupy the narrow band originated by the threefold degenerate $t_{1u}$ LUMO of $C_{6u}$. The Coulomb interaction projected onto the $t_{1u}$ manifold includes a charge repulsion, the Hubbard $U \sim 1\, \text{eV}$, plus a quadrupole–quadrupole electronic interaction providing an intramolecular Hund’s rule exchange $J_{H} \gg 0$. The latter splits the twenty possible $\{t_{1u}\}$ configurations of $C_{6u}$, assumed at first with nuclei rigidly frozen in their ideal icosahedral positions, as

$$E(\{t_{1u}\}) - E(\{t_{1u}\}) = 10J_{H}$$

$$E(\{1g\}) - E(\{1u\}) = 6J_{H}$$

(1)

The highest-spin state, $^{4}A_{g}$, has therefore the lowest energy (see Table 1). Once the nuclei defreeze, and the molecular ion can distort, the resulting JT energy $E_{JT}$ strongly competes against exchange $J_{H}$, since now the quadrupole operators of the $t_{1u}$ electrons couple with the quadrupole of the $H_{2}$ vibrational modes, but with opposite sign. In $C_{6u}$, the JT effect actually prevails over Coulomb exchange, effectively inverting Hund’s rules. The real ground state thus becomes the low-spin $^2T_{1u}$ multiplet 24–29.

Next, what about the $\{t_{1u}\}^{2}(\{t_{1g}\})^{1}$ configuration? Within each $C_{3u}$ molecule, the lowest dipole-allowed excitation corresponds to transferring one electron from the $t_{1g}$ LUMO to the $t_{1u}$ LUMO+1, which is also threefold degenerate and whose single-particle energy level lies $\Delta E \sim 1.2\, \text{eV}$ above. High as this energy is, the $\{t_{1u}\}^{2}(\{t_{1g}\})^{1}$ subspace comprises as many as 90 states, and hence is many times more susceptible to exchange splitting and JT effects than the lowest energy $\{t_{1g}\}^{3}$ subspace. In addition, the Coulomb interaction projected onto the enlarged $t_{1u}$ manifold also includes a dipole–dipole interaction, which is stronger than the quadrupole–quadrupole. Through a fully quantitative multipole expansion of the Coulomb interaction, Nikolaev and Michel found (omitting JT couplings) 30 that the split $\{t_{1u}\}^{2}(\{t_{1g}\})^{1}$ subspace spans a gigantic 2 eV range, four times wider than the splitting $10J_{H} \simeq 476 \,\text{meV}$ of the $\{t_{1u}\}^{2}$ (see Table 1).

The two lowest $\{t_{1u}\}^{2}(\{t_{1g}\})^{1}$ states with symmetry $^4H_{g}$ and $^2T_{1g}$ lie at only 494 meV and 525 meV, respectively, above the $^4A_{g}$ ground state, and that is before JT coupling. After allowing for the JT effect, there is a further lowering, and the situation becomes richer 25,31. The quadrupole moment of the $t_{1u}$ LUMO+1 has opposite sign to the $t_{1u}$ LUMO, and its absolute value is 2.6 times larger, which makes JT couplings much more effective. In particular, and unlike the $\{t_{1u}\}$ manifold, the JT effect in $\{t_{1u}\} \cup \{t_{1g}\}$ is stronger in the high-spin $S=3/2$ subspace than in the low-spin $S=1/2$ subspace. The reason is that in the $S=3/2$ subspace the $H_{2}$ vibrations couple together the lowest energy $^4H_{g}$ with the $^4A_{g}$ term, which is a mere 124 meV above (see Table 1). In the $S=1/2$ subspace, by contrast, the lowest energy $^2T_{1g}$ is coupled only to states higher than 600 meV above, which reduces the effect.

We further note that the new $t \otimes H (t_{1u}) \otimes (t_{1g})$ JT problem within configurations $^4H_{g}$ and $^4A_{g}$ is equivalent to that of $C_{60}^{-}$ in the $\{t_{1u}\}^{2}$ subspace of the $\{t_{1u}\}^{2}$ manifold, which involves the configurations $^4H_{g}$ and $^4A_{g}$ and where the JT energy gain is known to be maximum 24,26,28. On the other hand, the Coulomb exchange splitting $E(\{t_{1u}\}) - E(\{t_{1g}\}) = 124\, \text{meV}$ of the $\{t_{1u}\}^{2}(\{t_{1g}\})^{1}$ subspace is smaller than $E(\{t_{1u}\}) - E(\{t_{1g}\}) = 697\, \text{meV}$ of the $S=0 (\{t_{1u}\}^{2})$ case, implying a larger JT energy gain.

Table 1 | Molecular terms of undisrupted $C_{60}^{-}$

| $E$ (meV) | $(t_{1u})^{3}$ | $(t_{1u})^{2}(t_{1g})^{1}$ |
|----------|--------------|--------------------------|
| 0        | $^{4}A_{g}$  | $^{2}H_{g}$               |
| 285      | $^{2}T_{1u}$ | $^{4}A_{g}$               |
| 476      | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 494      | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 525      | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 618      | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 1,109    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 1,143    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 1,280    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 1,496    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 1,947    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 2,218    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |
| 2,549    | $^{2}T_{1u}$ | $^{2}T_{1u}$              |


Figure 2 | Molecular terms in the presence of Jahn–Teller. a, Low-lying C2v
molecular terms as function of the t_{1g} JT energy E_{JT} in the antiadiabatic approximation. Ungerade (u) and gerade (g) terms derive from (t_{1u})^3 and from (t_{1u})^2(t_{1g})^3 configurations, respectively. Terms are calculated as in Table 1, now with effective exchange parameters including JT contributions evaluated in the antiadiabatic approximation (see Supplementary Notes). The Coulomb exchange parameters such as J_{ex} are the same as in Table 1 with a 14% reduction to mimic screening effects. The t_{1g} JT energy is taken as 1.25^2 E_{JT} and ΔE = 1,240 meV to account for the overestimate of the t_{1g} downward single-particle energy shift within the antiadiabatic approximation. The vertical dashed line indicates the suggested appropriate parameter for K3C60. b, Energy as a function of the modulus of the JT distortion of the 2T_{1u} and 4A_{g} configurations. The zero of energy is set at the 4A_{g} level and we take ΔE = 1,080 meV and an interaction screening reduction of 22%. The calculation is performed within the single-mode approximation by the variational approach of ref. 28 using a mode frequency ω = 100 meV, vibrational coupling g = 1.32 for t_{1g}, which corresponds to E_{JT} = 87 meV, and 1.25 g for t_{1g}. The differences in screening reduction and ΔE with respect to a take into account the overestimated JT effect within the antiadiabatic approximation. The arrow shows the vertical Franck–Condon exciton transition.

molecular anions. Moreover, t_{1g} electrons couple preferentially to higher-frequency H_2 vibrations with tangential character, while t_{1u} electrons couple to lower-frequency radial vibrations, which might also imply a larger t_{1g} JT energy. One should finally note that, given the large size of the (t_{1u})^3(t_{1g})^3 subspace, even small variations of the many Coulomb exchange parameters and vibrational coupling constants may lead to appreciably different results.

For these reasons we opt for a less ambitious approach and, following ref. 3, we treat the JT problem within the antiadiabatic approximation, where all effects depend only on the value of the total JT energy gain E_{JT}, whose value for t_{1g} electrons is far less uncertain than the value of each vibrational coupling constant (see the Supplementary Notes for details). We use the model III interaction parameters of Nikolaev and Michel, with a 14% reduction to account for screening effects of nearby molecules, and we further assume, in accordance with the density functional results of ref. 38, that the t_{1g} LUMO+1 JT energy is 1.25^2 larger than the t_{1u} LUMO one. In Fig. 2a we show the low-lying molecular terms as a function of E_{JT} (ref. 34).

We can now consider the full multiplet spectrum for a realistic estimate of E_{JT} = 50–70 meV (ref. 34). The 2T_{1u} ground state and the lowest H_2 excitation, whose role was recently discussed, both belong to the (t_{1u})^3 manifold. The very next state, however, is the 4A_{g} term, of (t_{1u})^3(t_{1g})^3 origin, dramatically pushed down close to the ground state by JT and dipole–dipole interactions, despite the 1 eV energy of the t_{1g} LUMO+1. We also performed a different calculation, treating the JT coupling within the single-mode approximation and using a variational approach that consists of a stably distorted wavefunction projected onto a state with well-defined isosahedral symmetry (details are in the Supplementary Notes). In Fig. 2b we show the energies thus obtained of the T_{1u} and A_{g} states as a function of the distortion vector norm. As anticipated, the 4A_{g} energy minimum is reached for a larger distortion than that of T_{1u}, which entails substantial Franck–Condon effects—further strengthened by the shape difference, bimodal for T_{1u} (refs 24,25) and unimodal for 4A_{g}.

We propose that the infrared peak observed in A_{g}C_{60} corresponds precisely to the low-lying 4A_{g} state, the T_{1u} → A_{g} transition essentially turning into a genuine triplet exciton in the bulk material. The parity-allowed but spin-forbidden optical creation of this exciton can actually acquire oscillator strength and appear in the infrared optical spectrum of a narrow band nearly (antiferro)magnetic metal, through the simultaneous absorption/emission of a low-energy spin-triplet particle–hole excitation—that is a paramagnon. For that it is important to recall that A_{g}C_{60} are indeed narrow quasiparticle–band metals, close to a transition into an antiferromagnetic Mott insulator state, so much so that the transition is realized when the cation A merely changes from Rb to Cs. The absorption process is schematically shown in Fig. 3. The photon induces a virtual spin-conserving transition T_{1u} → T_{1g}. This intermediate state then transforms into the triplet exciton by absorbing/emitting a paramagnon via intermolecular exchange. One should note that this absorption mechanism is of the very same nature as that introduced by Rice and Choi, which is necessary to explain why uncharged T_{1u} vibrations acquire oscillator strength and thus are observed in optics. The contribution of the T_{1u} → (A_{g} ± paramagnon) peak to the optical conductivity reads

\[ \delta\sigma(\omega) \propto \int_{0}^{\infty} \frac{d\epsilon}{\epsilon} A(\epsilon) \left[ \theta(\omega - \epsilon) b(\epsilon - \omega) \chi''(\epsilon - \omega) 
+ \theta(\epsilon - \omega) (1 + b(\epsilon - \omega)) \chi''(\epsilon - \omega) 
- b(\epsilon + \omega) \chi''(\epsilon + \omega) \right] \]

where A(\epsilon) is the exciton absorption spectrum, b(\epsilon) the Bose distribution function, \theta(\epsilon) the Heaviside step function, and \chi''(\epsilon) the imaginary part of the dynamical local spin susceptibility. Equation (2) suggests that the large width of the absorption peak, which experimentally corresponds to a timescale of about 7 fs, is the result of a convolution between the paramagnon bandwidth and a Franck–Condon broadening, rather than a radiative lifetime of the exciton. In fact, the expectedly strong Franck–Condon effect must cause a large broadening in \chi''(\epsilon), corresponding to the non-radiative relaxation of the triplet exciton to a dark state whose lifetime might be much longer, possibly picoseconds or more, before eventual (phosphorescent) recombination. In agreement with this exciton–paramagnon interpretation, the infrared absorption peak grows in importance and intensity from K_{3}C_{60} to Rb_{2}C_{60} (ref. 18), the latter closer to Mott insulator (realized in Cs_{2}C_{60}), thus with stronger and narrower paramagnons.

The next and central question in the present context is if and why this exciton peak should actually play a role in the apparent enhancement of T_{c} found by ref. 11, where infrared pumping is roughly in the same frequency range. We start by noting that the experimental transient superconducting-like absorption spectra suggest (see Fig. 1b) that the infrared pump can act to sweep away the thermally excited quasiparticle states that, at equilibrium, are responsible for the gap filling-up and closing with the transition to the normal state. Things superficially seem as if the pump effectively cooled down the infrared laser pulse, about 300 fs in length. Within that short time lapse, the system is effectively isolated from the environment, with which it was in thermal equilibrium before the infrared shot.
The absorption process. 

**Figure 3** | The absorption process. 

- **a.** Diagrammatic representation of the absorption. The photon induces a virtual dipolar transition $t_u \rightarrow t_g$. This intermediate state spawns a triplet super-exciton and a spin-triplet particle-hole pair. The high density of the latter near a Mott transition boosts the curve (red), as function of $T$ as expected by the poor Fermi-liquid character above and if, furthermore, the quasiparticle collision rate is high enough, it be shorter than both the non-radiative exciton recombination time $\tau_{\text{nr}}$ and the decay time of a vibration into particle–hole excitations, $\tau_h$. The horizontal dashed lines from top to bottom are the values of the equilibrium microcanonical ensemble identified by an energy $E$ and quasiparticle number $N$. At a later time the quasiparticles will eventually come to equilibrium with the excitons, the lattice and the molecular vibrations. Yet, in the long transient before that happens, the infrared pulse supplies the initial normal metal with energy, which is sunk in the exciton–paramagnon excitation as well as by the vibrations that are emitted during the molecular relaxation after the vertical Franck–Condon transition. If the pulse duration happens to be shorter than both the non-radiative exciton recombination time $\tau_{\text{nr}}$ and the decay time of a vibration into particle–hole excitations, and if, furthermore, the quasiparticle collision rate is high enough, as expected by the poor Fermi-liquid character above $T_e$ (ref. 3), then the quasiparticle subsystem will exit the laser shot time in an effective microcanonical ensemble identified by an energy $E$ and quasiparticle number $N$. At a later time the quasiparticles will eventually come to equilibrium with the excitons, the lattice and the molecular vibrations. Yet, in the long transient before that happens, we can legitimately define an entropy $S(E,N)$ of the quasiparticle liquid and its effective temperature $T_{\text{eff}} = \delta S / \delta E$. Moreover, if the quasiparticle collision integral is strong enough to establish local equilibrium during the whole pulse duration, we are additionally allowed to define an entropy $S(E(t),N(t))$ that depends on the quasiparticle energy, $E(t)$, and number, $N(t)$, at time $t$ after the pulse front arrives. The absorption process of Fig. 3 implies that the creation rate of excitons is

$$ \dot{N}_{\text{exc}}(t) = \int \delta(\omega - E_{\text{exc}}) A_{\text{exc}}(\epsilon) \dot{n}_{\text{exc}}(\epsilon, t) $$

where $\dot{n}_{\text{exc}}(\epsilon, t)$ is equal to the term in square brackets of equation (2) multiplied by a parameter that we fit from equilibrium optical data (see Supplementary Notes), with the Bose distribution function and magnetic susceptibility corresponding to the instantaneous local equilibrium conditions. Since at $\omega \leq E_{\text{exc}}$ for each extra exciton a quasiparticle is annihilated then $\dot{N}_{\text{exc}}(t) = -\dot{N}(t)$. Moreover energy conservation implies that

$$ \dot{E}(t) = \int \delta(\omega - E_{\text{exc}}) A_{\text{exc}}(\epsilon) \dot{n}_{\text{exc}}(\epsilon, t) = (\omega - E_{\text{exc}}) \dot{N}_{\text{exc}}(t) $$

where $\omega$ is the laser frequency and the last equivalence holds if $A_{\text{exc}}(\epsilon) \sim \delta(\epsilon - E_{\text{exc}})$, which we shall assume hereafter for simplicity. Because of our assumption of local equilibrium, it follows that the quasiparticle entropy satisfies

$$ T(t) \dot{S}(t) = \dot{E}(t) - \mu(t) \dot{N}(t) $$

$$ = \int \delta(\omega - \epsilon + \mu(t)) A_{\text{exc}}(\epsilon) \dot{n}_{\text{exc}}(\epsilon, t) $$

$$ = (\omega - E_{\text{exc}} + \mu(t)) \dot{N}_{\text{exc}}(t) $$

where $T(t)$ and $\mu(t) = -T(t)^{-1} \langle \delta S / \partial N \rangle_t$ are, respectively, the instantaneous temperature and chemical potential. The entropy is expected to be maximum when the number of $t_u$ quasiparticles is equal to its initial value of three per molecule, so that $\mu(t) < 0$ for any $N(t) < N(0)$. Through equation (5) we thus reach the conclusion that the quasiparticle entropy can indeed

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**Figure 4** | Effective temperature $T_{\text{eff}}$ after the laser pulse. 

$T_{\text{eff}}$ is calculated as explained in the main body of the text, for initial values $T = 300, 200, 150, 100, 50, 25$ K, from the top curve (black) to the bottom curve (red), as function of $\omega - E_{\text{exc}}$, where $\omega$ is the light frequency, with an assumed quasiparticle bandwidth of 100 meV and a sharp exciton line. The coefficient that multiplies the process in Fig. 3 is fixed to reproduce in linear response the excitonic peak value of the optical conductivity at equilibrium. The horizontal dashed lines from top to bottom are the values of the equilibrium $T_e$ at 0, 0.5, 1 and 2 GPa, respectively.
decrease, and so the effective temperature, especially for frequencies \( \omega \leq E_{\text{exc}} \) when exciton creation requires absorption of thermal quasiparticle–quasihole triplet pairs. To simplify the calculation of \( T_{\text{eff}} = T (t \simeq 300 \text{ fs}) \) at the end of the laser pulse, besides assuming \( A_{\text{exc}} (\epsilon) \sim \delta (\epsilon - E_{\text{exc}}) \), we also neglect the contribution from the change in quasiparticle density—that is, we take \( \mu (t) = 0 \) in (5), which implies that the entropy may decrease only below resonance. Furthermore, we assume for \( \chi'' (\epsilon) \) the expression of non-interacting quasiparticles at half-filling and temperature \( T \) with a reduced bandwidth of 100 meV, and model the evolution of their distribution function by a Boltzmann type of equation (see Supplementary Notes). In Fig. 4 we show \( T_{\text{eff}} \) thus obtained for equilibrium sample temperatures \( T = 25, 50, 100, 150, 200, 300 \text{ K} \). The result of this modelling, crude but we believe inevitable, is that the effective temperature \( T_{\text{eff}} \) can indeed be substantially lower than the equilibrium value—thermal triplet quasiparticle–quasihole pairs being absorbed so that infrared pumping can reach the exciton energy. The final step is straightforward: since the quasiparticle effective temperature \( T_{\text{eff}} < T \), the gap equation may have a superconducting solution despite \( T > T_c \). From this perspective, our proposal of a light-induced intramolecular exciton \( ^3\text{A}_2 \), without charge transfer among nearby molecules, as opposed to the alternative \(^3\text{A}_1\), a term which besides spin is also parity forbidden, and thus much weaker as it requires additional intermolecular excitations. It may be noted, on the other hand, that the lack of inversion symmetry in merohedrally disordered face-centred cubic fullerides might partly allow the parity-forbidden dipole transitions\(^{21,23}\), mixing in this case the spin-quartet \(^4\text{A}_2\) state with the \(^4\text{A}_1\). Our theory of pumping-induced cooling is sufficiently general and would apply to that case as well.

To assess the validity of the above calculation, we have to make sure that the decay of vibrations and the exciton non-radiative recombination become indeed effective on timescales comparable to or longer than the pulse duration. The decay of \( H_2 \) vibrations into \( t_{\text{int}} \) particle–hole excitations occurs on timescales that vary among the eight \( H_2 \) modes between 30 fs and 3.7 ps. In particular, the modes more strongly coupled to the \( t_{\text{int}} \) electrons are also those with the longest decay times (3.7 and 0.8 ps, respectively). On the other hand, the exciton decays non-adiabatically via intermolecular dipole–dipole interactions: the electron hops from the \( t_{\text{exc}} \) into the \( t_{\text{int}} \) and concurrently a dipolar particle–hole excitation is created some distance apart, which corresponds to a \( t_{\text{int}} \) electron that hops from a molecule to a neighbouring one. This process is thus hindered by the Hubbard \( U \), which is the cost of such dipole excitations, but also by the Debye–Waller factor due to the molecular distortion brought by the exciton. The non-adiabatic decay rate \( \tau_{\text{exc}}^{-1} \) can be overestimated neglecting the Debye–Waller factor through the absorption rate \( \tau^{-1} \simeq 1 \text{ fs}^{-1} \) corresponding to the optical conductivity peak of 300 \( \text{cm}^{-1} \) at 50 meV, suppressed by the probability of creating dipolar excitations, which can be approximated by \( J/4U \), where \( J \simeq 2 \text{ meV} \) is the nearest-neighbour spin exchange.\(^{45}\) We thus estimate a non-adiabatic decay time \( \tau_{\text{exc}} \geq 2 \text{ ps} \), which is still longer than the pulse duration.

Conclusions

The apparently tenfold critical temperature enhancement discovered by infrared pumping in \( \text{K}_{x}\text{C}_{60} \) (ref. 11) is explained by a novel mechanism. First, noting that the effect broadly overlaps in frequency with the unexplained equilibrium mid-infrared absorption peak observed in all \( A_{\text{C}_{60}} \) fullerenes, that peak is argued, on the basis of single-molecule calculations, to correspond to the creation of a triplet exciton, Frank–Condon broadened and downshifted from its high LUMO–LUMO+1 energy by large intramolecular interactions. Spin conservation requires this process to be accompanied by absorption/emission of a paramagnon.

Second, we propose that the transient \( T_c \) enhancement occurs because, in the process of promoting quasiparticles into these long-lived triplet excitons, the laser pulse effectively cools down the quasiparticles system. This also explains why the experiment at 300 K (ref. 11) or those under pressure\(^{44}\) still show a transient increase of reflectivity, even though the optical data cannot be fitted by a model for a superconducting state.

Differently from other laser cooling techniques\(^{46}\), this mechanism relies on the triplet excitons generated by the laser pulse, which effectively act as a charge and spin reservoir soaking up entropy from quasiparticles\(^{47}\), and might also be functioning in other correlated metals on the verge of a Mott transition showing infrared absorption peaks attributable to excitons or other long-lived localized excitations that could equally well play the role of entropy sinks.

Although compatible with existing data, various aspects and implications of the present theory can be tested against further experiments. For one, the exciton and its spin-triplet nature could be tackled by magnetic fields and other spectroscopic tools, including, for example, detection of phosphorescence in pumped Cs\(_3\)C\(_{60}\).

The possible existence and detection at ambient pressure of the same broadband infrared absorption peak near 50 meV in the Mott insulating A15–\( \text{Cs}_{x}\text{C}_{60} \) at ambient pressure would provide support to our proposal of a light-induced intramolecular exciton \( ^3\text{A}_2 \), without charge transfer among nearby molecules, as opposed to the alternative \(^3\text{A}_1\), a term which besides spin is also parity forbidden, and thus much weaker as it requires additional intermolecular excitations. It may be noted, on the other hand, that the lack of inversion symmetry in merohedrally disordered face-centred cubic fullerides might partly allow the parity-forbidden dipole transitions\(^{21,23}\), mixing in this case the spin-quartet \(^4\text{A}_2\) state with the \(^4\text{A}_1\). Our theory of pumping-induced cooling is sufficiently general and would apply to that case as well.

Also important would be a re-examination of nuclear magnetic resonance data, where signatures of a 75 meV spin gap in Rb\(_x\)C\(_{60}\) (ref. 48) have so far been attributed to thermal population of the \(^4\text{A}_1\) state, for the possible presence of another, possibly even lower energy \(^4\text{A}_2\) spin-quartet state.

Finally, the role of the triplet exciton in the infrared-pumping enhancement of \( T_c \) could be addressed in a variety of ways and of materials. The strongest candidate remains pressurized Cs\(_3\)C\(_{60}\), which metallizes and superconducts above 5 kbar, and where the full range of parameters becomes available as a function of pressure. The ideal maximum equilibrium \( T_c = 38 \text{ K} \) of fullerides being achieved near 7 kbar (ref. 9), it would be exciting to explore whether the transient \( T_c \) might conceivably be raised even closer to room temperature.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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