



# Polarons and anharmonicity in high $T_c$ cuprates through vibrational spectroscopies

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## ABSTRACT

The discovery in 1986 of superconductivity at high critical temperatures attracted the attention of many researchers not only for its potential applications but also because it represented a theoretical challenge to understanding the mechanism that goes beyond the BCS model. Over 35 years of research, both theoretical and experimental, have not been sufficient to reach a comprehensive description of mechanism governing high  $T_c$  superconductivity. We summarize here the experimental signature of polarons and of the anharmonic behavior of the strongly polarizable  $O^{-2}$  ion, two of the possible ingredients of superconductivity in  $HT_c$  materials, evidenced by Raman and by photoinduced infrared spectroscopy.

## 1. Introduction

The discovery of high critical temperature superconductors ( $HT_c$ ) by Alex Müller and Georg Bednorz [1] was triggered by the idea that strong electron-phonon coupling, together with a low density of states at the Fermi Energy, could lead to the emergence of superconductivity at high temperature. Perovskites and oxides in general, due to their intrinsically strong electron-phonon interaction, have been considered by the authors as natural candidates for what they have actually discovered. Although there is still no commonly accepted theory explaining the mechanism of the superconductivity in  $HT_c$ , several experimental evidences indicate that in these materials the electron-phonon coupling is strong [2] and cannot be eluded in approaching a compelling model of superconductivity.

In the early 90s I was lucky enough to know and collaborate with Alex. In particular, Alex was interested in the uniqueness of the information that could be obtained with techniques such as NIR-excited Raman spectroscopy with which the relaxation of the crystalline structure around the chain segments, formed in low-doped YBCO, could be observed. This technique, well known in chemistry fluorescent materials, was scarcely used in solid state physics and including  $HT_c$  superconducting materials. Alex proposed to investigate possible evidence of

anharmonic behavior of oxygen by monitoring the energy shift by isotope substitution of oxygen at different doping levels. His interest in studying the possible anharmonicity of oxygen at the apex stemmed from his awareness of its possible role in superconductivity [3]. In one of his writings he stated: "... we then do not pretend to have found the mechanism to generate Copper pairs, but that anharmonicity is part of it" [4].

I remember with pleasure the time Alex came in Bologna in 1992 to discuss the preliminary results of our collaboration and visit our Institute. This was not his first time in Bologna and, during the welcome meeting organized by the municipality at Palazzo D'Accursio, the town Hall, he asked explicitly, speaking in his fluent Italian, to visit the Anatomy theater which he knew by reputation but had never managed to visit because at that time it was not easily accessible to the public. The Anatomy theater is an hall within the Archiginnasio building, one of the historical headquarters of the University of Bologna; the building was built in the 16th century to bring together all teaching activities in one place. The hall, a 17th-century masterpiece with walls entirely covered in spruce wood and adorned with statues, is known above all for the two statues called "spellati" (skinned men) which flank the lecturer's desk. Thanks to the Assessor for Relations with the University of the time, Mrs. Silvia Bartolini, Alex was finally able to see the Anatomy Theater.

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Bologna - July 1992. At dinner, during Alex's visit to the CNR. From left: Roberto Zamboni, José Lorenzana, Victor Denisov, Alex Müller, Giampiero Ruani - Photo by Anvar Zakhidov



Bologna - July 1992. In the Sala Rossa of Palazzo D'Accursio. Among those present: Alex Müller and his wife Ingeborg Marie Louise Winkler, José Lorenzana, Silvia Bartolini, Victor Denisov, Roberto Zamboni, Giampiero Ruani - Photo by Anvar Zakhidov

I summarize here some of the experimental evidences of polaron formation in these materials and a presence of anharmonic potential associated with oxygen ions focusing on a single class of compounds:  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (YBCO). In this brief review of our laboratory's contribution to the  $\text{HT}_c$  field, I will report the formation of photoinduced local lattice deformations (polarons) in undoped or lightly doped parent compounds ( $x \approx 0$ ) [5–7], evidencing the similarity of these deformations with those induced by chemical doping [8–12], and the presence of anharmonic potentials associated with oxygen [13,14].

## 2. Raman at 1.16 eV in semiconducting YBCO parent compounds

Raman scattering is a resonant process, consequently, the Raman features can vary in intensity by using different photon excitation energies (related to the energy and the symmetries of the different electronic states involved in the resonant process). In some cases, the energy of the phonons can depend on the photon excitation energy as in the case of the  $G'$  band in graphene where a double resonance process induce the emission of phonons far from the  $\Gamma$  point in the reciprocal

space [15]. Also in the case of different crystalline phases present within the same investigated sample, different photon energy, being in resonance with one of the phase, can enhance the phonons associated with that phase.

This is the case of oxygen doping in YBCO where the oxygen concentration and the thermal history of the system can determine the presence within the same sample of one or more orthorhombic phases as well as local defects. Because of the different electronic transitions associated to the different crystalline phases, different photon excitation energies can emphasize one crystalline phase with respect to others because of resonance with the electronic level of that phase. As an example [7], we report in Fig. 1 the NIR-excited Raman (NIR-Raman) of undoped and lightly doped YBCO. The spectrum of the  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_6$  in Fig. 1 is characterized by three peaks at 387, 457 and 548  $\text{cm}^{-1}$  which correspond respectively to the out of plane oxygen mode, the apex oxygen (O(IV)) mode and the single oxygen in the chain vibration. The same peaks (with different relative intensities and widths) are observed by exciting in the visible. This is not the case when the oxygen content increases enough to allow the formation of short chain segments. While the visible excited Raman scattering of YBCO in low doping regime does not depend on the oxygen content [9,16], NIR-Raman shows the appearance of a strong Raman band around 477  $\text{cm}^{-1}$  in the  $^{18}\text{O}$

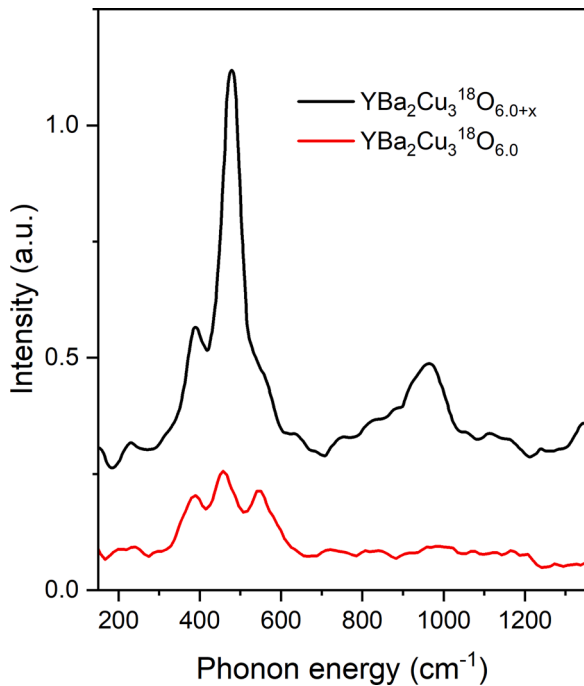


Fig. 1. NIR-excited (1.16 eV) Raman spectra of  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_6$  (red line)  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{6+x}$  (black line).

compounds ( $508\text{ cm}^{-1}$  in  $^{16}\text{O}$  one) with a large number of overtones; in some cases, we observed up to six overtones. The presence of harmonics confirms the association of the strong Raman peak to a localized mode related to the crystalline defect with electronic states in resonance with the excitation energy of the laser (in a defect state, the Raman selection rules that inhibit Raman scattering processes with the generation of multiple phonons are relaxed and the appearance in the spectrum of overtones become possible). Furthermore, the energy of this feature is very close to that attributed to the mode of the apex oxygen along the c-axis observed in fully doped YBCO [9]. The association with a O(IV) mode was confirmed by site selective oxygen isotope substitution [8].

The intensity of this band, and the overtones increases with the oxygen doping; at  $x > 0.2$  both the intensity and the overtones decrease indicating a shift in energy of the resonant electronic band [8].

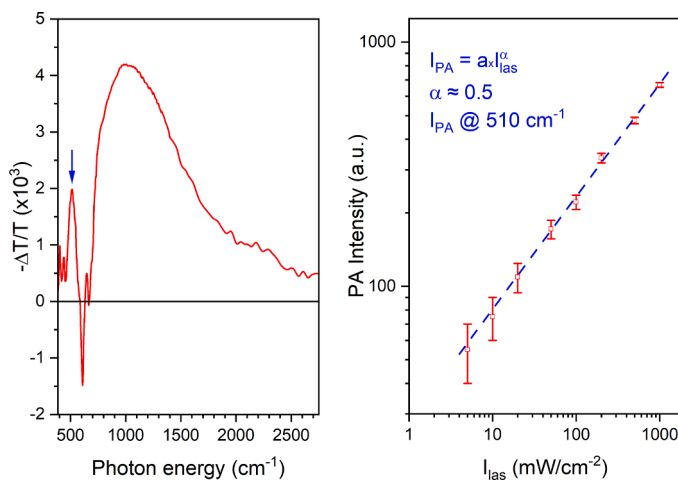


Fig. 2. Photoinduced absorption spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.21}$  at 34 K exciting with a He-Ne laser at 1.96 eV (left). Laser power dependence of the peak at  $510\text{ cm}^{-1}$  (indicated with the arrow in the PA spectrum) represented in log-log scale (right).

### 3. Photoinduced absorption in semiconducting YBCO parent compounds

Steady-state photoinduced absorption (PA) in the mid and far spectral region is a powerful tool to study semiconducting systems in which the photogenerated excitations evolve into separate carriers (electrons and holes) with a relatively long lifetime. The relatively long lifetime of the photogenerated carriers can be associated either with the trapping in defect states of one or both of the two types of carriers or, in systems with strong electron-phonon interactions, to the formation of polarons (bipolarons). The new electronic state and the local variation/reduction of the symmetry are associated with the distortion of the lattice around the photoinduced carriers, resulting in a modification of the optical absorption spectra of the investigated system. As a result, new electronic transitions are detected within the optical gap of the semiconducting compound associated to the new electronic states as well as changes in the vibrational spectra. The local deformation around the carriers determines a reduction of the symmetry of the crystal by relaxing the selection rules, e.g. allowing active Raman phonons to be detected as a direct transition in IR absorption. Furthermore, the presence of “free” carriers can shield the phonon absorption with dipole parallel to the conduction plane.

Representing PA as variation of the transmission spectrum ( $-\Delta T/T$ ), the positive features are new electronic or phononic transitions induced by photoexcitation while the negative peaks are bleached modes. The PA spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  includes all these spectral changes. A broad band at  $1000\text{ cm}^{-1}$  is associated with the low energy (bi)polaron state, while at lower energies, below  $700\text{ cm}^{-1}$ , some new phonon peaks are observed as well as bleached modes associate with the undoped perovskite (see Fig. 2 left). The intensity dependence of the PA spectrum scales with the square root of the power density of the laser radiation (in Fig. 2 right the intensity dependence of the peak at  $510\text{ cm}^{-1}$ , the same behavior is observed for the band at  $1000\text{ cm}^{-1}$ ). This indicates a bimolecular recombination of the photogenerated species that means that neither of them is trapped or pinned. Similar square-root dependence (at  $T = 45\text{ K}$ ) were observed in other parent compounds of HTc systems like  $\text{La}_2\text{CuO}_4$  and  $\text{Nd}_2\text{CuO}_4$ , [17]. In that case, at lower temperature 4 K, the laser intensity dependence switch to fourth-root. The four molecule recombination dynamic observed at lower temperatures is

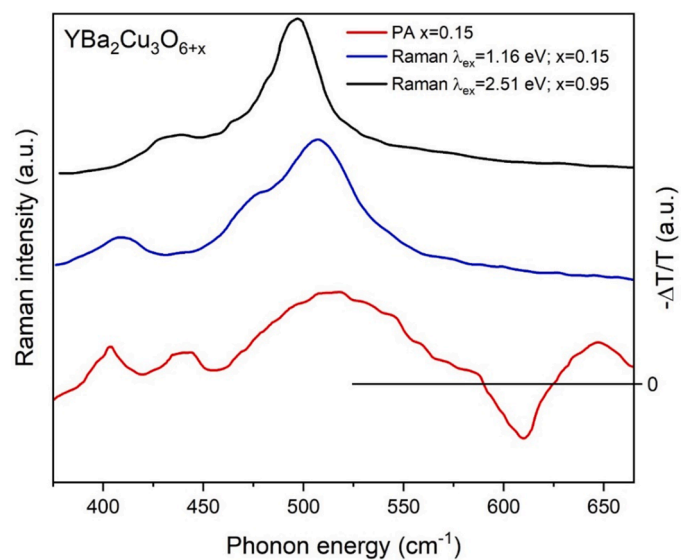


Fig. 3. Comparison between 1.16 eV excited Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  single crystal in  $x(\text{zz})x$  geometry (black line), of polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$  (blue line) and the PA spectrum at 34 K of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.21}$  obtained by exciting at 1.96 eV (red line).

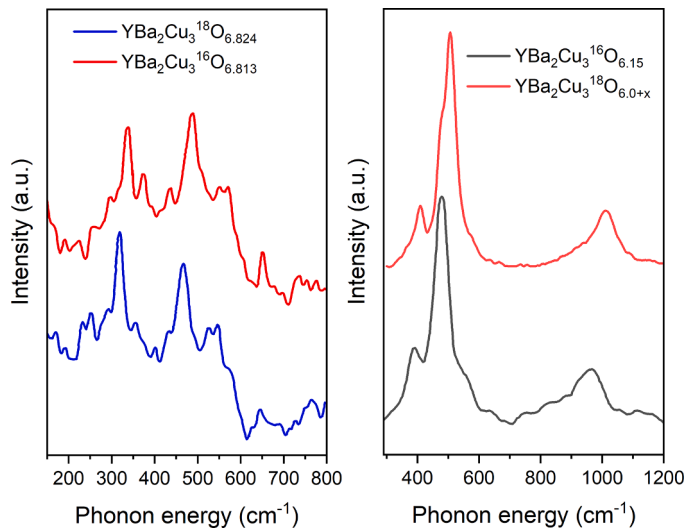


Fig. 4. NIR-excited (1.16 eV) Raman spectra of  $^{16}\text{O}$  and  $^{18}\text{O}$  YBCO at different oxygen content.

consistent with bipolarons clustering when polaron density is large enough. [18]

To identify PA signatures we compare the photoinduced infrared active vibration (IRAV) to the Raman spectra of YBCO at different excitation energies and oxygen concentration. The IRAV at approximately  $510\text{ cm}^{-1}$  is very closed in energy to the Raman active mode associated with the apex oxygen of the doped perovskite, or in the low doping regime, in 1.16 eV Raman excited spectrum (Fig. 3). Likewise, IRAV at  $430\text{ cm}^{-1}$  is associated to the in phase motion of oxygens of the conduction  $\text{CuO}_2$  plane along the c-axis in the metallic phase. These findings indicate that the local deformation associated with the photoinduced polaron is similar to that induced by chemical doping. Both the bleachings (above  $600\text{ cm}^{-1}$ ) are associated with in-plane oxygen IR active modes with dipole parallel to the  $\text{CuO}_2$  conduction plane; as already mentioned, this can be associated to the screening effect of mobile carriers in the plane. A detailed review of PA measurements in HTc parent compounds and their interpretation in terms of polarons is written by Mihailovic [18] in the book Polarons in Advanced Materials.

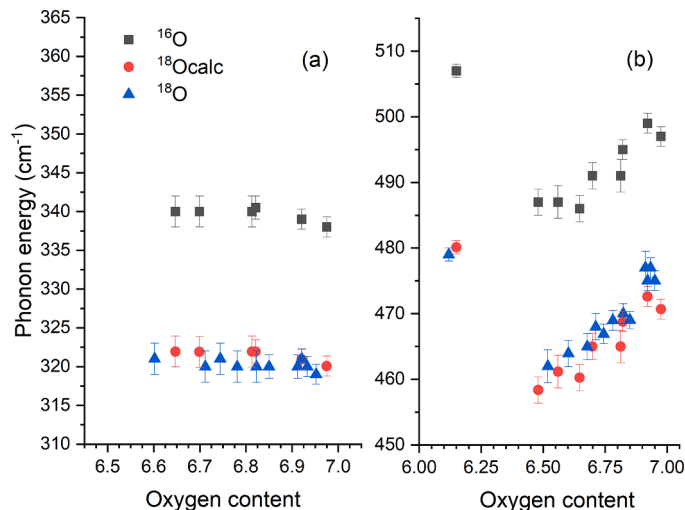


Fig. 5. Phonon energies of the Raman peaks associated (a) to the out-of-phase  $B_{1g}$  oxygen mode ( $\text{CuO}_2$  plane) along the c-axis and (b) to the  $A_g$  apex oxygen mode along the c-axis as a function of oxygen content.  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{6+x}$  measured values (black squares),  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{6+x}$  measured values (blue triangles) and  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{6+x}$  calculated values (red circles).

#### 4. Isotope effect in Raman and photoinduced absorption: the oxygen anharmonicity

The isotope effect in  $\text{HT}_c$  has been the center of debates on the mechanism of superconductivity in this class of materials for long time both in favor or against a phonon-mediated coupling mechanism. The isotope effect, almost zero on  $T_c$  in optimal doped systems, increases progressively in underdoped systems up to values approximately two times larger of the value predicted in the BCS theory. A good review of the experimental results and models proposed for their interpretation is reported in the article by H. Keller et al. [19]

Isotopic substitution, approached from the point of view of vibrational spectroscopy, can provide other information complementary to that of the direct influence on the critical temperature or on the superconducting gap, for example on the type of potential in which the different oxygen ions move. Vibrational spectroscopies are well known and effective tools for investigating anharmonic potentials related to a particular atom or group of atoms.

We investigated, using NIR excited Raman, a large number of YBCO powder samples at different oxygen concentrations both with both natural oxygen and 96% substituted  $^{18}\text{O}$  [20]. The NIR excited Raman spectra (Fig. 4) of the metallic phases of YBCO are characterized by two relatively narrow bands that shift on the isotope substitution and a broad feature between  $300$  and  $600\text{ cm}^{-1}$  that do not depends on the oxygen isotope and is probably associated with an interband transition between quasi-degenerate electronic levels around the Fermi energy associated with the apical oxygen [21]. The two narrow bands are observed, for the  $^{16}\text{O}$  samples, at approximately  $340$  and  $500\text{ cm}^{-1}$  (the latter strongly dependent on the oxygen concentration) respectively assigned to the out-of-phase  $B_{1g}$  mode of the oxygen of the  $\text{CuO}_2$  conduction plane along the c-axis and to the  $A_g$  mode of O(IV) along the c-axis. As described in Section 2, the Raman spectrum of semiconducting YBCO is dominated by a single band at  $508\text{ cm}^{-1}$  and its overtones associated with the chain segments induced localized state within the charge transfer gap. To evaluate the possible anharmonic contribution of a vibrational mode we compared [20] the energy shift associated with the isotopic substitution with that derived from the shell model calculation for a harmonic potential [22,23].

Fig. 5 shows the energies of the two Raman active mode observed

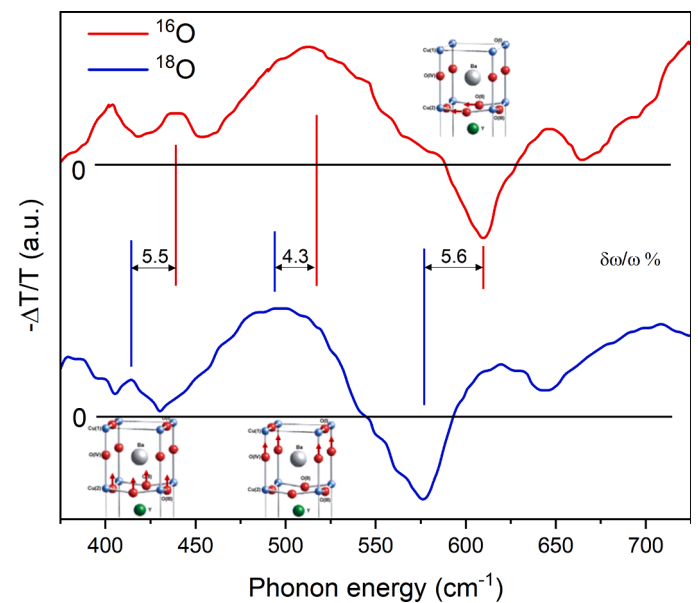


Fig. 6. Low temperature photoinduced absorption spectra of  $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{6+x}$  and  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{6+x}$ . The peak energy shift percentage with oxygen isotope substitution ( $\delta\omega/\omega$ ) is calculated with respect to  $^{16}\text{O}$ .

exciting at 1.16 eV both for  $^{16}\text{O}$  and  $^{18}\text{O}$  samples at different oxygen concentrations. Experimental  $^{18}\text{O}$  values are compared with those derived from  $^{16}\text{O}$  samples shifting the phonon energy of 5.6%. In the case of the phonon mode associated with the  $B_{1g}$  oxygen mode ( $\text{CuO}_2$  plane), the observed shift associated with the isotope substitution coincides, within the experimental error, with that expected for a harmonic potential. This is not the case for all oxygen concentrations for the phonon mode associated with apex oxygen. In this case the experimentally observed values differ from the expected values for the harmonic potential, although this result is not constant across the oxygen concentration range.

It is worth noting that, in the semiconducting phase ( $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ,  $x < 0.3$ ), the localized mode associated with apex oxygen adjacent to isolated chain fragments, the isotope shift is nearly that expected for a harmonic oscillator (Fig. 2b).

Liarokapis et al. have shown that, in the case of YBCO, there is a strong dependence of the anharmonic contribution both for the apex oxygen and for those of the  $\text{CuO}_2$  plane from the single phases of the compound (tetra, ortho-I, ortho-II). [24] They monitored, as we also observed, that the  $\text{CuO}_2$  out-of-phase oxygen mode is harmonic at all oxygen concentrations, while the in-phase mode shows anharmonic behavior (this mode is not detected exciting at 1.16 eV). With respect to the O(IV) mode, they observed the presence of an anharmonic potential only in ortho-II, ortho-III phases but not in the optimally doped (ortho-I) phase. Again, the difference in the obtained results is to ascribe to the very different resonance conditions in YBCO, or rather, to the resonance with the different phases of YBCO, when the system is excited at 1.16 eV or at 2–2.5 eV. Indeed, the apex oxygen phonon energies we observed by exciting at 1.16 eV in the YBCO orthorhombic phases are lower than those observed by exciting in the visible, even at optimal doping.

We also investigated the effect of oxygen isotope substitution in photodoped parent compound (Fig. 6). The bleached IR active mode related to the  $\text{CuO}_2$  oxygen mode and the IRAV peak associated to the in-phase  $A_g$  Raman mode of the orthorhombic phase show a isotope shift ( $\delta\omega/\omega \approx 5.6\%$ ), compatible with harmonic potentials. Instead, the apex oxygen associated IRAV shows a much smaller isotope shift ( $\delta\omega/\omega \approx 4.3\%$ ). Oxygen isotope substitution was investigated by Yusupov et al. in  $\text{La}_2\text{CuO}_4$  ( $^{16}\text{O}/^{18}\text{O}$ ) [25], in that case the authors found an isotope shift of the bands consistent with harmonic potentials.

Unlike chemical doping in the semiconducting phase, when the system is photo-excited (photo-doped) the oxygen mode at the apex shows an anharmonic nature. The difference is probably associated with the coupling of the phonon mode with the  $\text{CuO}_2$  photoinduced free carriers [26]. The polaronic states that are generated when holes are transferred to the  $\text{CuO}_2$  are coupled with O(IV) and can account for the presence of the observed anharmonic potential of the apex oxygen ion in the PA measurements. This is not the case which occurs in the tetragonal parent compound in low oxygen doping regime. In this case, the extra oxygen present at the chain sites induce a relaxation of the apex oxygens nearby in a similar way to the superconducting phase (as is deduced by the vibrational energy of observed in NIR-Raman) but without mobile holes in the conduction plain with which to couple. The different behavior is also consistent with the model proposed by Mustre de Leon et al. [27] for an electron-phonon system exhibiting polaron tunneling.

## 5. Conclusions

This paper summarizes the experimental evidences we collected by photoinduced IR and Raman scattering indicating that cuprates are characterized by strong electron-phonon coupling. In particular, we observed the generation of polarons by photodoping in the semiconducting parent compound of the superconducting YBCO. By isotopic oxygen substitution, we observed the presence of anharmonic potential associated with apex oxygen that could be interpreted also as a signature of polarons. All these findings, together with many others reported in literature, are consistent with the significant role of polarons in the high-

temperature superconductivity mechanism [1,19,28,29].

## Author statement

G.R. participate as principal investigator in performing and elaborating the experiments reported in this review.

No use of AI have been done in writing the submitted manuscript

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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