Neutral 3*d* excitations in insulating VO₂ as seen with resonant inelastic x-ray scattering at the *V L*₃,₂ edges

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We present resonant inelastic x-ray scattering (RIXS) results on insulating monoclinic VO₂ with excitation across the $L_{2,3}$ edges of vanadium. The spectra measured near threshold in the L_3 region and in the L_2 region show a Raman behavior with a clear peak around 0.9 eV transferred energy. The analysis of the data allows the neutral excitation spectrum of the system up to about 2–2.5 eV to be determined. These excitations are due to *dd* transitions, whose main contributions are discussed. The possibility of $\{d^1; d^1 \to d^2; d^0\}$ charge fluctuations within a dimer in RIXS is also discussed. The results are compared with available information on optical constants and on electron energy loss spectroscopy. Due to the low symmetry of the system, there is a similarity between the Raman spectrum obtained with RIXS and the optical absorption spectrum.

I. INTRODUCTION

Among strongly correlated systems, VO₂ had a crucial role in the past 40 years and is still receiving much attention. This is largely due to the fact that the electronic states cannot be described by traditional bands; in particular, a pure band-like approach cannot explain the metal-insulator transition occurring in this system around 340 K, with a stable insulating monoclinic phase below the transition temperature. In VO₂ spectroscopy, the use of soft x rays has recently added important information. In particular, the *x*-ray absorption spectroscopy (XAS) at *V L*₂,₃ (Ref. [1]) together with calculations of theoretical spectra[1,2] suggests a description of the phase transition as orbital-assisted Peierls-Mott. Moreover, high energy photoemission added information on the transfer of spectral weight across the transition,[3] giving a very strong support to the theoretical spectral function by Biermann *et al.*[4] based on a cluster extension of dynamical mean-field theory.[5,6] All these results refer to final states containing either one less valence electron (photoemission) or a core hole plus an extra valence electron (XAS). Thus, it is timely to expand the experimental basis to include neutral excitations offering further experimental information useful in the discussion of the electronic states. In fact, the neutral excitations in the valence states have correlation properties different from those of valence charge subtraction or addition. Moreover, they do not involve a core hole in the final state at variance with respect to XAS.

The present paper is devoted to the study of neutral excitations and reports experimental results on insulating VO₂ obtained with resonant inelastic x-ray scattering (RIXS).[7] In this experimental approach, the sample is excited with a monochromatic incident beam (with incident photon energy $h\nu_{in}$ at selected values across an absorption resonance) and the spectrum of the emitted photons is measured vs their energy $h\nu_{out}$. Among neutral spectroscopies, RIXS is particularly important because it can be used to study the so-called *dd* excitations.[8,9] In a 3*d* ion, the scattering path across the $L_{2,3}$ edges is the dipole allowed $2p^6 3d^n \to 2p^5 3d^{n+1} \to 2p^6 3d^{n*}$, where *n* is the ground state occupation and * means either ground state or excited state. This neutral final state corresponds to a charge redistribution within the 3*d* manifold; being formally $n=1$ in VO₂, this corresponds to the transfer of the *d* electron to an excited state. Of course, this picture must not be seen in an independent particle scheme, and one has to refer to the total energies of the many body system. Moreover, the effect of the V-V dimerization in insulating VO₂ on the scattering path must also be discussed. In general, a strong reason for the interest in RIXS is that it shows the *dd* excitations that are optically dipole forbidden. In the present case, the low symmetry of the system[10] and the hybridization with oxygen[11] make these *dd* excitations visible with a reasonable intensity also in optical spectra.[12,13] Thus, in VO₂, the RIXS spectroscopy is important also because it provides an alternative excitation path with respect to optical measurements, and it will be interesting to compare RIXS and optical measurements, as done in the final part of this paper. The *dd* excitation peaks appear in the RIXS spectra as characteristic energy losses so that the peaks are seen at constant transferred energies ($h\nu_{in} - h\nu_{out}$) and disperse with $h\nu_{in}$ (Raman regime). On the other hand, the RIXS spectra contain, in general, also other features at constant $h\nu_{out}$, i.e., not dispersing and containing information typical of resonantly excited fluorescence (non-Raman regime). The competition between Raman and non-Raman regimes depends on the nature of the sample and it is already well established that the Raman features are more pronounced in insulating systems.[14] For this reason, the insulating phase is best suited for the study of neutral excitations in VO₂ as seen with RIXS. However, also in insulating VO₂,
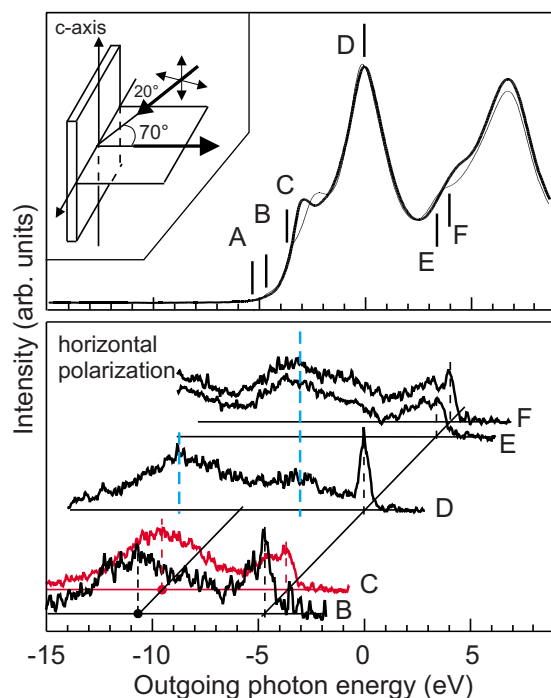
FIG. 1. (Color online) Upper panel: $L_{2,3}$ absorption curves of VO$_2$, with the vertical bars giving the energies used in RIXS. The absorption with linear polarization parallel to the c axis is given by the thin line and that perpendicular to the c axis by the thick line. The inset shows the geometry in scattering. Lower panel: a selection of RIXS spectra measured with horizontal linear polarization (one spectrum is in red for readability).

the emission spectra are dominated by the fluorescencelike contributions, so that the recovery of the dispersing features is far from being easy. Probably due to this fact, the information on the neutral dd excitations given by RIXS has been overlooked up to now. Here, we give the dd excitations up to about 2–2.5 eV above the ground state, and we point out the main orbital contributions to the transitions. This is important because it can open the way to future theoretical work. In fact, another goal of the present paper is to stimulate theoretical research. This will be very important because a theory of RIXS from VO$_2$ taking into account correlation within the modern approaches already used in non-neutral spectroscopies is lacking at present. In what follows, Sec. II summarizes the experimental method, Sec. III gives the experimental results and the extraction of the Raman spectrum, and Sec. IV presents the interpretation of the Raman spectrum. The main conclusions are summarized in Sec. V.

II. EXPERIMENTAL METHOD

The RIXS measurements have been taken on a single crystal in the geometry sketched in the inset of Fig. 1 (upper panel), i.e., with incidence at 20° to the surface and scattering at 70° included angle (normal emission) and horizontal scattering plane. The crystal was the same as in Refs. 1 and 3, cleaved in air, and oriented as in the figure. The measurements were taken at the ID08 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The beamline is based on an Apple II undulator giving full control of the polarization: about 100% linear vertical or horizontal, and circular right or left. We have exploited the linear polarization control of the incident beam by taking data both with polarization perpendicular to the scattering plane (hereafter referred to as vertical) and within the scattering plane (horizontal). The spectra were measured with the advanced x-ray emission spectrocopy (AXES) spectrometer equipped with a dedicated monochromator before the sample.[15] The AXES spectrometer is equipped with a charge coupled device detector as shown in Ref. 16. As a compromise between counting rate and resolution, we adopted a linewidth of 0.5 eV (combined effect of the incoming and scattered beam resolution). This resolution is sufficient to the purpose of the present work, and has been chosen although the ultimate resolution of the equipment is better as shown in our work on MnO (Ref. 17) (around 0.3 eV combined linewidth at 640 eV). At 70° scattering angle, an elastic peak is seen also with horizontal polarization, while this is obviously very strong with perpendicular polarization. In the horizontal polarization case, the presence of a weak elastic peak is an advantage because it helps to set the zero of the transferred energy and to test the energy scale when the polarization is changed. We stress that we have never seen energy shifts while changing the polarization of the source.

III. EXPERIMENTAL RESULTS AND DETERMINATION OF THE RAMAN SPECTRUM

A selection of the experimental results is given in Fig. 1, where the incident photon energies in RIXS are shown by the vertical bars along the L-absorption spectra in the upper panel. The absorption spectra are taken from Ref. 1 and correspond to the two orientations of the electric vector: vertical, i.e., parallel to the c axis (thin line), and horizontal, i.e., perpendicular (thick line) to the c axis of the sample. As stated above, the goal was the study of the dd excitations (Raman regime) and not of fluorescencelike emission. In general, the Raman behavior has more chance to be found in the region near threshold. In VO$_2$, this is strongly suggested by the emission work by Schmitt *et al.*[18] Thus, the excitation energies have been chosen in the threshold region of L_3 and L_2 apart from the excitation at peak L_3 taken for comparison. In order to simplify the experiment, the excitation energies around the threshold have been chosen where the absorption has no linear dichroism. The RIXS measurements have been taken with both polarizations because the change of the intensity of the elastic peak with respect to the Raman features due to polarization change is very useful, as we will show later. The identification of the dispersing Raman features is possible on the basis of Fig. 1 (lower panel), showing some spectra taken with horizontal polarization and plotted vs the outgoing photon energy with an offset proportional to the increment of the excitation energy. In this presentation, the Raman features are aligned along the inclined lines, while the fluorescencelike features do not disperse, their emission energy being independent of the incident photon energy. The elastic peak is very clear, together with a dispersing feature
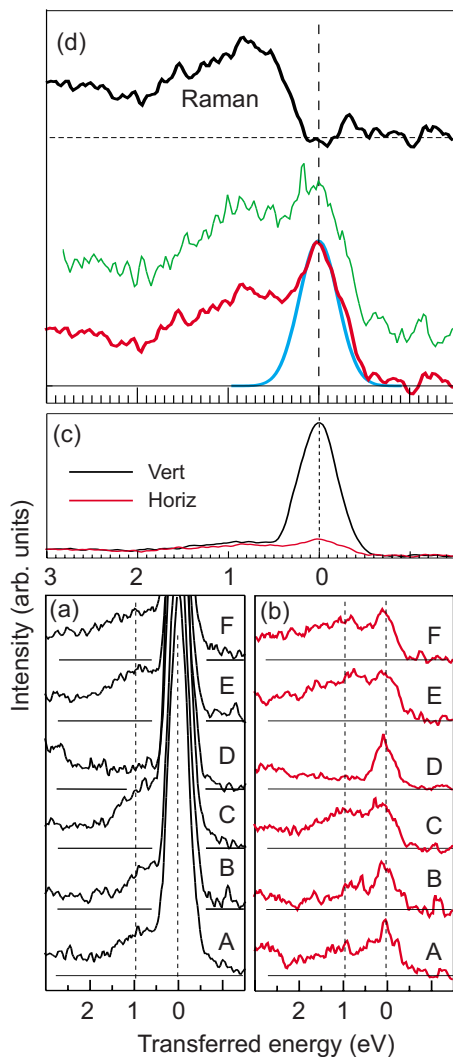
FIG. 2. (Color online) The RIXS spectra with vertical polarization [black in (a)] and with horizontal polarization [red in (b)]. The sum of spectra A, B, C, E, and F is given in (c) with both polarizations. (d) The elastic contribution to the sum spectrum with horizontal polarization (red) is fitted with the combined line shape (blue), while the green spectrum with excitation C is given for comparison. The extracted experimental Raman spectrum is given by the upper black curve in reference to the horizontal dashed line.

around 0.9 eV from the elastic peak. Also the feature around 6.5 eV from the elastic peak disperses with excitations B and C, but this trend cannot be followed in a wider energy range because of the fluorescencelike contributions shown by the vertical blue lines. This deep dispersing feature was already clear in Refs. 18–20 and will not be discussed because it is assigned to charge transfer excitations and not to pure dd excitations.[21] Thus, we will concentrate on the Raman behavior in the region from the elastic peak to about $2-2.5$ eV transferred energy. The whole set of measurements in this energy range is given in Fig. 2 vs the transferred energy [vertical polarization in black in (a) and horizontal polarization in red in (b)]. The existence of a Raman contribution near 0.9 eV is very clear with both polarizations, with all excitations near the L_3 and L_2 thresholds, whereas this is not

seen with the excitation D at the L_3 peak. The Raman feature at 0.9 eV is shown by the vertical dashed line. In the present paper, we are interested in the position of the Raman features along the transferred energy scale, while we do not discuss the shape of the Raman spectral function. To this end, we can sum the spectra A, B, C, E, and F plotted vs the transferred energy in order to gain statistics although this can produce some minor modification of the relative intensities in the Raman region. As a matter of fact, these distortions are negligible in the present case, as is seen from the comparison in Fig. 2(d) between the sum spectrum with horizontal polarization (in red) and the green spectrum with excitation C (obviously noisier). Of course, this procedure is legitimate exclusively in the Raman region where only dispersing features are present, and for this reason, we concentrate on the region of about 2.5 eV transferred energy.[22] The sum spectra with both polarizations are given in Fig. 2(c), showing very well the line-shape of the elastic peak to be used in the data analysis. Moreover, Fig. 2(c) shows that the Raman spectrum has basically no linear dichroism in the excitation range used in the present work. In order to extract the Raman contribution, we use the sum spectrum with horizontal polarization [red spectrum in Fig. 2(d)]. The extraction of the Raman spectrum is straightforward as shown in Fig. 2(d) and is done by subtracting the elastic peak well represented by a Gaussian with full width at half maximum of 0.5 eV (blue line). This width is determined on the basis of the spectra with vertical polarization. The result is the Raman spectrum in the upper part of panel Fig. 2(d) (in black).

IV. INTERPRETATION OF THE RAMAN SPECTRUM

The Raman spectrum has a rather broad feature extending up to about 2 eV transferred energy, with a maximum around 0.9 eV. This is the characteristic loss spectrum due to neutral dd excitations in the final state discussed hereafter. It should be noted that the broad Raman feature extends along an energy scale much wider than the combined instrumental linewidth (0.5 eV); thus, more than one excitation contributes to the spectrum.

The extraction of the characteristic excitations from the experimental Raman spectrum is guided qualitatively by the available knowledge on the VO_2 electron states. To this end, we rely on the scheme by Goodenough,[23] summarized in Fig. 3(a) (see also the presentation of this scheme in Ref. 4). This must be considered as a first step, while a more detailed discussion of the neutral excitations has to wait for future calculations possibly stimulated by the present paper. In metallic VO_2, the V atoms are surrounded by oxygen octahedra sharing the edges along the c axis. The d levels are split into lower t_{2g} and higher empty e_g states. These e_g states are outside the energy range where RIXS has a strict Raman behavior, so they cannot be discussed here. Due to the superposition with fluorescence, it will be very difficult and perhaps impossible to assess the position of e_g states with RIXS. The tetragonal crystal field splits the t_{2g} into $d_{\parallel}$ (along the c axis with V-V σ bonds) and antibonding V_d-O_p π^*. When the system becomes insulating the V-V dimerization splits the $d_{\parallel}$ into a bonding (partially occupied) and an antibonding fea-
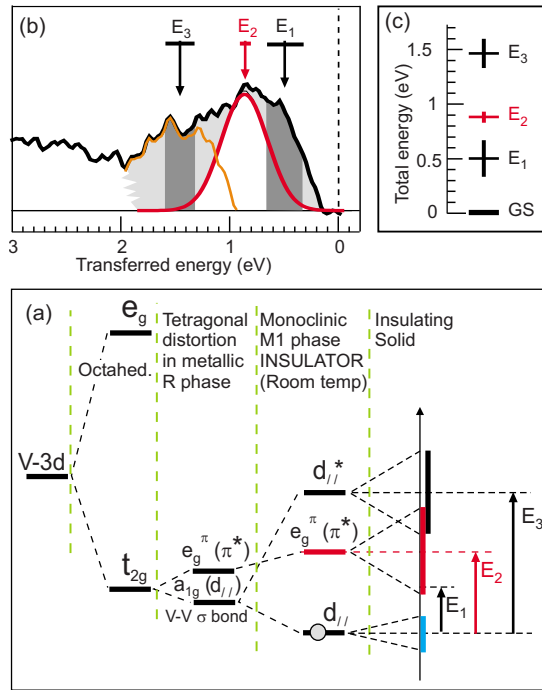
FIG. 3. (Color online) (a) Schematic origin of the VO_2 d states and of the excitations E_1, E_2, and E_3. See text for more explanations. (b) The subcomponents of the measured Raman spectrum. (c) Summary of the measured excitations in the final state of RIXS.

ture. Moreover, the antibonding V_d-O_p π^* states are pushed up in energy. In the solid, these levels become broad features derived from these orbitals, and a gap is found between the top of the bonding $d_\parallel$ states and the bottom of the π^* states. This situation is shown qualitatively in Fig. 3(a). In this scheme, we expect to see essentially three contributions to the neutral dd excitations. These excitations shown by vertical arrows start from the bonding $d_\parallel$ states that are basically concentrated in a rather narrow occupied region shown in blue (at most 0.4 eV wide) accordingly to all calculations (see, e.g., Refs. 4 and 24). The two excitations at higher energies contain a relevant contribution respectively from transitions to the π^* derived states (E_2 excitation in red) and to the $d_\parallel^*$ states (E_3 excitation in black). At energies lower than E_2, there must be a shoulder due to the lower tail of the π^* states. The position of this shoulder is indicated by E_1. The onset of this tail, corresponding to the minimum self-consistent d to d transition as seen in RIXS, is not necessarily at the optical gap. In conclusion, the RIXS must contain three major contributions E_1, E_2, and E_3 having the spectral origin just specified.

The main experimental result of the present paper is given by the information on the energies of these three excitations. The better defined excitation is around 0.9 eV and is clearly seen in the raw data. This excitation is shown in Fig. 3(b) by the peak of the red curve, in which we have assumed a width equal to the combined instrumental resolution. It is clearly impossible to fit the data with a single excitation, and there is intensity both below and above this excitation. For this reason, we assign the transition at 0.9 eV as E_2 in the model explained above. At higher transferred energies, there is

clearly another feature which can be assigned to E_3. This is shown by the orange curve that is the difference between the experimental Raman spectrum and the red excitation E_2. The position and width of the E_3 excitation depend on the assumption on the width of the E_2 excitation, and a detailed fitting has to wait for future calculations of the RIXS spectra. This gives some uncertainties. An estimate of the present uncertainties is given by the horizontal bars in Fig. 3(b). More uncertain is the position of the first shoulder E_1, but there is no doubt that there is some intensity. In conclusion the information on the dd excitations is summarized by the total energy diagram of Fig. 3(c), where GS indicates the ground state.

As far as the meaning of these excitations is concerned, we stress that they must not be considered necessarily as processes involving only one single V site, i.e., as single ion transitions seen with RIXS as a local probe of the type $2p^63d^1 \rightarrow 2p^53d^2 \rightarrow 2p^63d^{1*}$, where * means either ground or excited state. In effect, other scattering channels can contribute. As a matter of fact, the intermediate state core hole in resonant scattering can be screened also by another d electron taken from the nearby V in the V-V dimer, so that the well screened intermediate state $2p^53d^3$ (with $3d^0$ in the nearby site) can be formed besides the $2p^53d^2$ state. The intermediate $2p^53d^3$ state decays to a final d^2 state of the considered ion, with d^0 in the nearby V ion giving a $\{d^2; d^0\}$ final state. This corresponds to a neutral intersite dimer excitation $\{d^1; d^1 \rightarrow d^2; d^0\}$. The energy scale of this fluctuation is dictated by the balance of several terms. The lowest energy is obtained with two electrons in different orbitals on the same site, since in this case the Coulomb repulsion U' is smaller than the repulsion U on the same orbital. In effect, $U' = (U - J)$, where J is the exchange interaction (see Refs. 2 and 25). Moreover, the energy of the first excitation is lowered by the amount J when a triplet state is formed ($S=1$ in $\sigma\pi$ configuration), so that it is found at $U' - J$. This makes the dimer excitation $\{d^1; d^1 \rightarrow d^2; d^0\}$ very likely relevant in our energy range. The value by Tanaka[2] is $U' - J$ = 0.7 eV, and the estimate by Koo *et al.*[13] is 1.3 eV. With the parameters by Bierman *et al.*,[4] this value is 1.96 eV. On the other hand, this value is somewhat higher (3.3 eV) if one accepts the parameters from Ref. 26. Note that all these values pertain to the Hamiltonian before diagonalization, so that they must be used only to point out the energy region where these fluctuations are important and not to give a precise value. Since the $\{d^1; d^1 \rightarrow d^2; d^0\}$ fluctuations are enhanced in RIXS due to the core hole effect in the intermediate state, a future theoretical investigation of RIXS will be particularly important. In fact, this will certainly contribute to clarify the role of these charge fluctuations. These arguments on the energy scale explain the fact that these transitions have been invoked to discuss the optical absorption up to about 3 eV.[12,13]

Since dd excitations (not necessarily intersite) contribute both to optical absorption due to low symmetry and to x-ray Raman, we expect some similarity between the Raman spectrum and the optical absorption. This comparison is illuminating and is made in Fig. 4, where we give our RIXS result and the optical absorption obtained from the optical conduc-
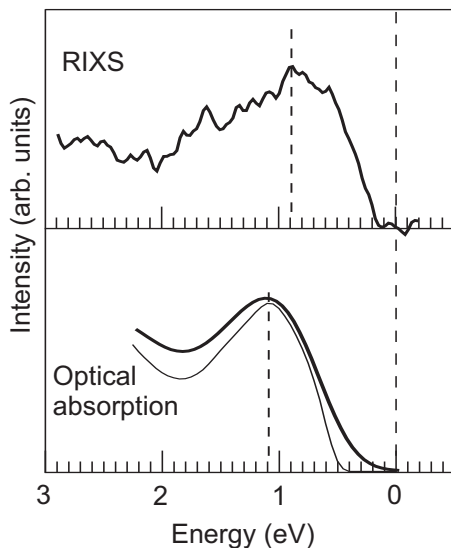
FIG. 4. Comparison between the RIXS Raman spectrum of VO_2 (present work) and the optical absorption obtained from the optical conductivity of Ref. 12. The energy corresponds to the transferred energy in the RIXS spectrum and to incident photon energy in optical absorption.

tivity of Ref. 12. The optical absorption in the lower panel of Fig. 4 is given by the thin line (derived from Ref. 12), while the thick line is the absorption measured with the same resolution of the RIXS measurements so that it can be compared directly with RIXS.[27] The similarity between the results of the two spectroscopies is remarkable and opens the way to a connection between RIXS and optical measurements in low symmetry systems where the optical dd transition can be seen. Furthermore, there is about 0.2 eV difference in the peak position, with some enhancement of the low energy region in RIXS. This difference between the two approaches will be an important experimental point to be interpreted in a unified view of insulating VO_2 spectroscopy. Also, the comparison with electron energy loss spectroscopy is interesting. In the loss spectra (raw data) by Abe *et al.*,[11] a weak feature at the limit of visibility at about 0.9 eV is seen, in agreement with our results, and a feature seen at 1.25 eV could be related to our E_3 transition. However, we do not emphasize this point because further work is needed to reconcile energy loss and optical absorption. In fact, the optical conductivity measurements[12] are not in perfect agreement with the optical conductivity one can derive from the imaginary part of the dielectric function of Ref. 11, which was obtained from electron energy loss.

V. CONCLUSIONS

We have presented experimental results on the neutral dd-excitation spectrum of insulating VO_2 as seen in RIXS up to excitation energies around 2–2.5 eV in the final states. This has been possible on the basis of RIXS measurements, with incident photon energies near the L_3 and L_2 thresholds. The excitation spectrum has been explained, and we have pointed out the main orbital contributions to these transitions. Moreover, the energy scale of neutral dd excitations, the RIXS spectral shape, and the comparison with optical spectra call for future theoretical work. The detailed interpretation of RIXS will be a further relevant test of future theoretical schemes taking into account correlation.

ACKNOWLEDGMENTS

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[21] The superposition with fluorescence makes it difficult to discuss systematically the charge transfer excitations. It is worth mentioning that the present energy (about 6.5 eV) of the charge transfer peak is consistent with a peak in measured optical conductivity (see Ref. 12). On the other hand, the measured optical conductivity shows also a charge transfer peak around 3.7 eV, not seen in RIXS. The elucidation of this problem awaits future theoretical research and is likely to be due to the differences in the selection rules of the two approaches and to the superposition with fluorescence.

[22] We also did further test in order to exclude artifacts coming from the sum. In fact, we summed spectra taken with subsets of different excitations chosen arbitrarily from the sets A, B, C, E, and F, and the results always support our conclusions.

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