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REVIEW

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Event chronology analysis of the historical development of tip-enhanced Raman spectroscopy

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Abstract

In this history review, the development of tip-enhanced Raman spectroscopy (TERS) is analyzed from the perspective of scientific instrumentation development. TERS is a powerful and label-free tool for nanocharacterization, still mainly an academic tool, built from the achievements in Raman spectroscopy, surface-enhanced Raman spectroscopy, scanning probe microscopy, near-field optics, and plasmonics. We identified three turning points in TERS history so far, based on two approaches to categorize TERS publications. Evidences from our analyses indicate that developments have been made in the scientific understanding of the technique itself, on the technology for its implementation, and on the application of TERS in other fields. Although, in total, more papers have focused on the technological development, application-oriented works became the most important type of publication in the last years. This development has participation from different actors, but it has been performed mainly by the academic community, alone or in association with national laboratories.

KEYWORDS

event frame, history review, retrospective technology roadmapping, scientific instrumentation development, tip-enhanced Raman spectroscopy

1 | INTRODUCTION

Tip-enhanced Raman spectroscopy (TERS) is a cutting-edge instrumentation technique for materials characterization because it drives Raman spectroscopy[1] into the nanoscale[2,3] (nano-Raman), with applications in condensed matter ranging from materials science to life sciences.[4] In TERS, a metal or metallized tip is illuminated with a focused excitation light beam,[5] and, by raster scanning the tip across a sample surface, it acts as a near-field light source[6] or nanoantenna, allowing optical spectroscopy and hyperspectral imaging at the nanoscale.

With the first concept of super-resolution by breaking the diffraction limit using the concept of near-field optics (NFO) theoretically introduced in 1928[7] and the first considered well-succeeded experimental TERS results appearing in 2000,[8,9] the technique has evolved, most intensely, in the past two decades. As a new scientific instrument that emerged in the beginning of the 21st century, the TERS nanoscope is currently in the transition from a laboratory device utilized by researchers devoted to the proof of concept and development of the technique itself to a mature technology apt to elucidate nanomaterials properties. Although several active authors in the field still make their own systems, a few commercial TERS brands are available. Improvements in the level of reproducibility and resolution to achieve state-of-the-art results in nanocharacterization are still requested for its diffusion as a broadly applied technique and its insertion in industry, but these assets are under way, and it is likely that TERS will become a very promising tool to boost nanotechnology in the near future.

Several review articles about the development of TERS can be found in the literature.[6,10–12] Some authors focus on aspects related to devices and instrumentation, such as tip (probe) properties.[13,14] Others review enhancement factors[15] and applications, such as the high potential of TERS for the study of carbon nanostructures[16] and two-dimensional (2D) materials at the nanoscale[17] and for the study of surfaces and interfaces.[18] In this article, we present a history review, which is the development of TERS as a scientific instrumentation technique, analyzed in an approach that is different from the up-to-date related review literature. By combining a bibliometric analysis using concepts of event frame[19] and the technology roadmapping (TRM),[20,21] mainly in the historical perspective,[22–24] we intend to shed light into how TERS has developed so far since its first theoretical concept. As a starting point, Figure 1 shows the evolution of the total number of scientific documents published in TERS, along with the evolution of the five science fields that precede the introduction and establishment of TERS, namely, Raman spectroscopy (Raman),[1] surface-enhanced Raman spectroscopy (SERS),[25] scanning probe microscopy (SPM),[26] near-field optics (NFO),[27] and plasmonics[28] (see Figure 1 for details on the search procedure). The main goal of this work is to trace the landmarks in TERS development and to make a descriptive and critical analysis based on event categorization, where "events" here are the related scientific publications. Besides learning about TERS itself, we hope to give elements to the process of understanding how a high-technology scientific instrument develops in its early stages.

This paper is organized as follows. Section 2 is a small introduction on the qualitative analysis approach. Section 3 explains the methods used and adapted to collect and treat the data. Section 4 presents the results, the descriptive analysis, and main insights. Finally, Section 5 brings the concluding remarks.

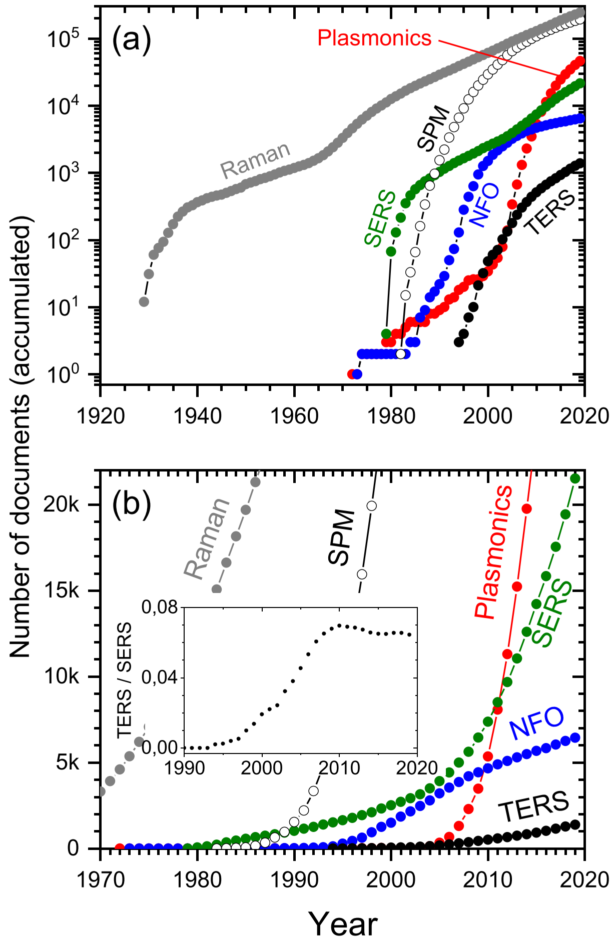

FIGURE 1 Evolution in the number of documents on Raman spectroscopy (Raman), scanning probe microscopy (SPM), plasmonics, surface-enhanced Raman spectroscopy (SERS), and near-field optics (NFO). The data are built based on the Scopus database using the following search expressions in the "keyword, title, or abstract" fields (date of search, September 17, 2020): RAMAN: "Raman spectr*" OR "Raman microsc*" OR "Raman scat*"; SPM: "scanning tunneling microsc*" OR "atomic force microsc*"; PLASMONICS: "plasmonic*"; SERS: "surface enhanced Raman"; NFO: "near field optic*"; tip-enhanced Raman spectroscopy (TERS) (see Section 3). (a) One century period with all data in a logarithmic scale; (b) 1970–2019 period on a linear scale up to the higher value observed for SERS. The inset shows the ratio between the number of documents TERS/SERS

2 | SHORT INTRODUCTION TO QUALITATIVE ANALYSIS

The qualitative analysis that gives the foundation of the methodological approach has its roots in two social sciences backgrounds: technology roadmapping (TRM) and event frame.

TRM is a method used in industry to support strategic planning, providing a structured and graphical means for exploring and communicating the relationships between markets, products, and technologies over time.[20] It supports the development, communication, and implementation of technology in the business strategy, helping innovation management and planning. It is a tool to articulate consensus about visions of future attractive technologies.[21]

More recently, the TRM method has been applied to capture the elements in industrial emergence, extending the timeline of the maps back into the past.[22–24] The aim of this approach is to study the historical milestones aiming to support future-oriented strategy and innovation, with focus on technology-intensive product-based sectors. By applying the roadmapping concepts in a retrospective view, it is intended to inform strategy and decision making for current and future industrial emergence. The framework to map industrial emergence is based on phases and transitions and requires information from the past, generally obtained by interviews and documental analysis.

In this work, the TRM retrospective method is adapted, and the information is obtained in a more structured way using the approach of event frame.

In event frame, the description of a productive event is done by partitioning it into elements such as agent, action, object, instrument, alignment, setting, product, and beneficiary.[19] Elaborating these elements into categories provides a formal ground for the description of events. The categories can be chosen according to the sociological phenomenon under study, the reasoning being supported by the field of knowledge. Operationally, a computer program can be employed to implement the frame and facilitate both data management and analysis.

The combination of elements of event frame and TRM in the retrospective approach is done here to construct a chronology about the development of a new scientific instrument, in terms of time span, geographic distribution, institutional participation, and technical issues from the outcomes of the events. In this adaptation, the input for database that generates the events is the relevant publication so far in the field of TERS technique and instrumentation, the relevance determined by two selection criteria, as will be shown in Section 3. The agent and setting categories are derived from the affiliations of the authors of the documents. The products—meaning the main results of the documents—are categorized according to two approaches, as will be shown in Section 4.3.

3 | METHOD OF DOCUMENT SELECTION

In addition to the consideration of the five main influential techniques examined in Section 1, to analyze the history of the development of TERS as a scientific instrument, a database of TERS publications was collected using two main sources. The first one was obtained by a search in the Scopus database for documents having specific expressions in the search field "keywords, title, or abstract." The search expressions were "tip enhanced Raman spectroscopy" OR "tip enhanced Raman scattering" OR "tip enhanced Raman microscopy" OR "tip enhanced Raman microscope" OR "tip enhanced Raman spectroscope" OR "near field optic* AND Raman" OR "nano-Raman" OR "near field Raman," returning 1382 documents since 1994. This search gives a view of the development of the field in number of documents, and the results are summarized in Figures 1 and 2a,b. For a more qualified analysis, two filtering criteria were then applied to the papers (date of search May 7, 2019). First, documents with the Field-Weighted Citation Impact (FWCI)*—only available in Scopus—equal or higher than 5 were selected. FWCI is used for comparative research impact "regardless of differences in entity, size, disciplinary profile, age, and publication-type composition."[29] For those documents with FWCI less than 5, we selected the ones with more than 100 citations in both filters, excluding book chapters and conference papers. Review articles were included only if they obeyed the FWCI criterion. This procedure resulted in 109 qualified papers, from which 27 were not about TERS development specifically. Therefore, the first Scopus set resulted in 82 documents.

To complement the first source of qualified publications, a personal collection of TERS papers considered important by the senior author of this work—a researcher with more than 30-year experience in the field of Raman spectroscopy and more than 15-year experience in the field of TERS—was consulted. To this collection, composed by 114 documents, the same criteria used for the Scopus database were applied, resulting in a set of 37 documents, 16 of which were already in the previously selected Scopus data. This routine resulted in 21 additional documents. The inclusion of these 21 papers was an attempt to build a merge between the database that uses explicitly the term TERS and database on SERS, NFO, and plasmonics (including nanoantennas), thus considering the experimental achievements that lead to the detection of the TERS effect, works that at that time did not include the word "Raman" alone or in the search expressions used for the Scopus search. Finally, six other historical papers of the senior author collection that did not fill the bibliometric criteria were included, considered essential to represent either the very early or very recent developments of TERS. These papers were included based on the senior author's understanding that, according with the TERS community, historically, the seed for the TERS development was a theoretical concept introduced about a century ago.[7] After Synge's proposal in transposing the diffraction limit of light, it took almost

*The FWCI is the ratio of the total citations received by the denominator's output and the total citations that would be expected based on the average of the subject field.

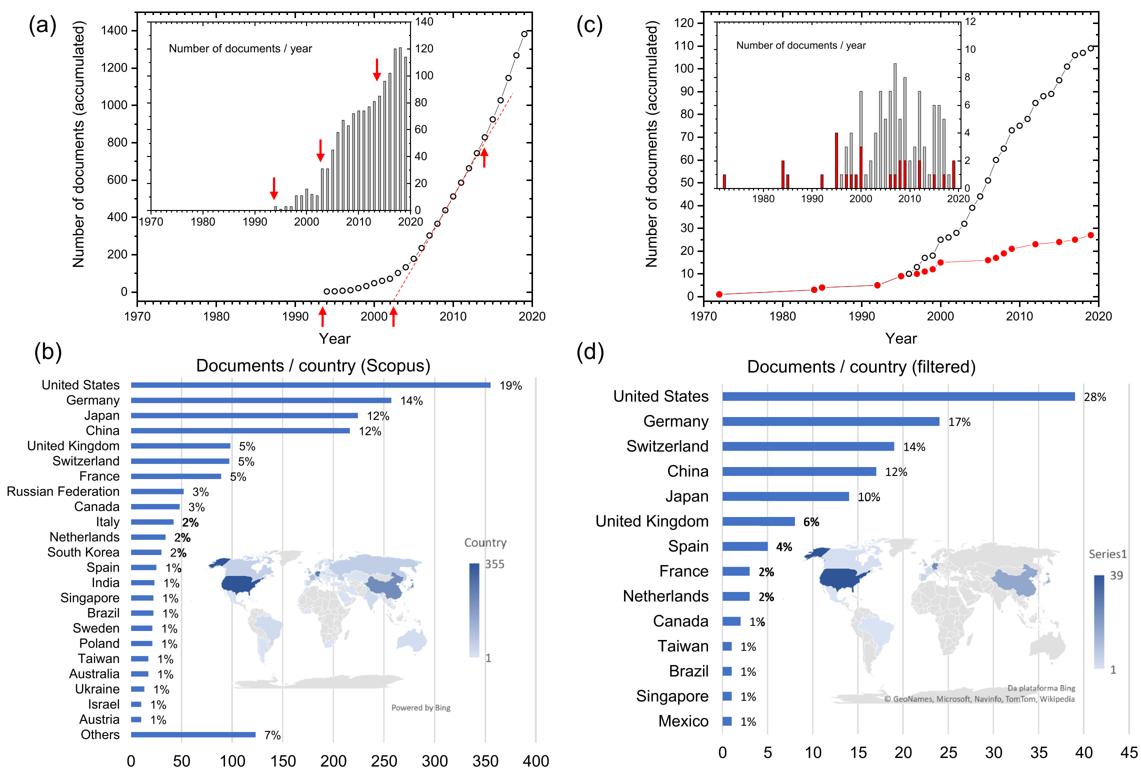

FIGURE 2 Evolution of tip-enhanced Raman spectroscopy documents in (a,b) the Scopus database and (c,d) the filtered ones. (a,c) Accumulated number of events; the inset shows the annual distribution; (b,d) geographical distribution. The red arrows and dashed line in (a) evidence changes in behavior. The red data in (c) represent the articles included from the second source

50 years until Ash and Nicholls first executed near-field microscopy in the microwave region with aperture tip.[30] In the following years, the combined evolution in the areas of SERS, plasmonics, SPM, and NFO was key to establish TERS. At the end, the filtered database for the analysis discussed here contains 109 qualified documents,[2,4,8,9,12,15,30–132] as shown in Figure 2c; that is, after the combination of the two criteria, we came up with a qualified sample that represents 10% of the whole data. The goal of this qualified data is to understand the type of work was being performed during the development of the field and the type of agents behind the developments, as discussed in Section 4, without the intention of defining or limiting the authors who contributed.

Our qualified database was integralized on May 7, 2019, and no further search or reanalysis of filtering parameters was performed thereafter. An event table was set up with the final database (109 documents), each document as an event in a row, where specific information was separated in columns, such as year of publication, authors, affiliations, title, and abstract, including the criteria of inclusion for each paper (see supporting information).

4 | RESULTS AND DISCUSSION

4.1 | TERS and the preceding techniques

The TERS system is an NFO instrument devoted to nano-Raman spectroscopy, composed of a Raman spectrometer coupled to an SPM. In terms of plasmonics, the precursor of the TERS technology is the SERS effect. In SERS, the incident and scattered radiation fields are enhanced by an entire layer or a 2D array of objects with plasmonic properties that couples to light. In TERS, this interaction is localized in the neighborhood of a single plasmonic device, the nanoantenna, that has its position controlled by an SPM system. Figure 1 shows the accumulated number of Scopus documents for the five techniques preceding and related to TERS, which are Raman spectroscopy, SPM, plasmonics, SERS, and NFO. TERS documents are also included for comparison. The first Raman spectroscopy document appears in the Scopus database in 1929, and the Nobel Prize in Physics 1930 was awarded to Sir Chandrasekhara Venkata Raman "for his work on the scattering of light and for the discovery of the effect named after him." A related technique that evolved around the 80s, based on the Raman effect, was SERS.

SERS is the mother technique of TERS, introducing the concept of using the near field from a plasmonic nanoparticle to locally enhance the Raman scattering effect. Notice the steadier increase in the number of SERS publications after the 2005–2010 period, which is when the plasmonics field also exhibits a considerable evolution, jumping from tens of papers to tens of thousands. Parallelly, an initially unrelated field evolved, the SPM, with the first document also published in the 80s, and very soon experimenting a big raise. The NFO field exhibits documents starting from 1973. However, the NFO papers start growing significantly around 1995, after SPM has matured, enabling the use of the scanning probe procedure for the development of NFO. TERS, as a specific type of NFO, also appears around this period. The slowdown in NFO publications after the 2005–2008 period, coincident to TERS rise, happens because TERS is a specialization or subfield of NFO. Interestingly, a sum of NFO + TERS documents generate a roughly straight line (not shown). Focusing on the evolution of TERS, it is the establishment of SERS and plasmonics as mature fields that enables the TERS field to evolve significantly after this 2005–2010 period. As Figure 1b shows, SERS and plasmonics grow extraordinarily around 2003–2005, when TERS publications also start raising, indicating that SERS and plasmonics are behind the establishment of TERS. The relation between SERS and TERS evolution in the last decade is evident in the inset of Figure 1b, which shows the ratio between TERS and SERS publications—TERS raises, comparatively with SERS between 1995 and 2010, and after that time, the growth of the two techniques is the same, making a constant evolution of the TERS/SERS ratio. This trend indicates that, after 2010, TERS started to play a more significant role as a scientific tool. To continue this research, we further introduce a deeper analysis of the TERS-specific documents.

4.2 | TERS data and evolution of number of documents

Figure 2a shows the evolution in the total number of TERS documents of the Scopus database (see searching criteria in Section 3), a total of 1382 documents since 1994, up to the end of 2019. The accumulated numbers are shown in the main panel and the year distribution, in the inset.

Figure 2b shows the country participation in these 1382 documents. The main groups come from the United States (Northwestern University and the University of Rochester), Germany (Institut für Photonische Technologien, Friedrich-Schiller-Universität Jena, Universität Tübingen, Ludwig-Maximilians-Universität München, Fritz Haber Institute of the Max Planck Society, and Leibniz Institute for Analytical Sciences), Japan (Osaka University, Riken, and Kwansei Gakuin University), China (Xiamen University), the United Kingdom (National Physical Laboratory), Switzerland (Eidgenössische Technische Hochschule—ETH Zürich), and France (École Polytechnique).

Figure 2c shows the evolution of total number of TERS documents in the qualified database, a total of 109 documents since 1972, up to May 7, 2019, when the event frame was set up. The red data in the main graphic and in the inset represent the articles from the personal collection, as defined in Section 3. Figure 2d shows the distribution of countries, in number of events and respective percentages. The six leading countries are the same of Scopus database without filters (Figure 2b). In chronological order, the United Kingdom starts the events (1972),[30] followed by Switzerland and the United States (1984),[100,111] and Germany (1995)[42], although here we must remind the readers that these papers were introduced from our personal collection, not from the Scopus database, which starts having entries only after 1994. Based on these 109 qualified documents, the history of TERS seems to start in Europe, joined by North America and subsequently by Asia. South America joins in 2008 and is represented by our group of the Federal University of Minas Gerais (UFMG), in collaboration with the National Metrology and Technology Institute (Inmetro)[98] (this is the only paper of ours in the list that fulfilled the FCWI and citation criteria). Europe dominates the events until the end of the 1990s. From 2004 on, Asia starts to alternate protagonism with Europe, North America having the lead only in 2003 and 2017. There is a growing tendency of Asian participation in the last years.

In terms of the accumulated evolution of documents, besides what has been shown in Figure 1 and discussed in Section 4.1, the plot line in Figure 2a indicates three inflections in the increasing tendency, marked in the main panel by the red arrows: (i) 1994–1995, when the first documents start to appear in the Scopus database; (ii) 2002–2003, when a large increase in the number of documents takes place; and (iii) 2014–2015, when a further inflection takes place, increasing even more the number of contributions appearing in the literature. These markers in the history of TERS will be further elaborated in the following section.

4.3 | Classification of TERS documents

To understand the inflections shown by red arrows in Figure 2a, we structured the qualified documents in categories. First, we categorized the articles in four groups according to the main emphasis of the work: science (S), technology (T), application (A), or market (M) dominated, named here the STAM approach. Science (S) category means the development of TERS knowledge, specifically, that is, works with emphasis on activities to establish the supporting scientific phenomena, including demonstrations of the potential to applied science. Examples of S category papers are the studies of light propagation and confinement in scanning near-field optical microscopy (SNOM) by means of the multiple multipole method[43]; the theoretical model for the gradient-field Raman effect to explain the origin and intensity of some Raman modes observed in SERS and through a near-field optical microscope (NSOM-Raman)[58]; and the work on the vibrational spectra of *p*-aminothiophenol (PATP) molecules on a gold substrate and high-vacuum TERS (HV-TERS) by means of detailed first-principles calculations.[118] Technology (T)-oriented documents are those reporting mostly technical advances to improve TERS, its reliability, and its performance to the point that it can be demonstrated in the field. Examples of T category papers are the work on optical fiber tips for SNOM produced by etching with the protection layer method and metallization leading to improved optical transmission[47]; the description of an apertureless near-field Raman spectroscopy setup using side-illumination geometry[77]; and the construction of a high-vacuum TERS system that allows in situ sample preparation and measurement.[130] Scientific papers that use TERS to advance, for example, molecular biology or materials science, are classified with main emphasis in application (A), meaning activities that aim to improve the performance of the instrument for that specific application. Examples of such A-dominated papers are the near-field Raman spectroscopy and imaging of single isolated single-walled carbon nanotubes with a spatial resolution of approximately 25 nm[62]; the TERS spectra of a tobacco mosaic virus as an example of the potential of TERS to rapid and direct detection of different species of single viruses[101]; and the demonstration of spectral fingerprint patterns of individual self-assembled peptide nanotapes using TERS.[119] Market (M) oriented are works linked to commercial activity studies, and they are absent in our data. Taking exemplary samples from another area, for instance, in the case of the electron microscopy development, examples of market-dominated works are the launching of the first commercial scanning electron microscope, the StereoScan, by the Cambridge Instrument Company[133]; the introduction of the Philips TWIN lens for the EM400 series of transmission electron microscopes[134]; and the launching of the commercial scanning tunneling electron microscope HB5 by Vacuum Generators.[135]

Generally, 36% of the documents are technology dominated; 28% application dominated; and 25% science dominated. Eleven percent of the documents were classified as a combination of categories, where it was difficult to attribute only one. Therefore, documents with focus on science (S), technology (T), and application (A) are roughly equally present (see inset in Figure 3a, which considers the disaggregation of the 11% of combined

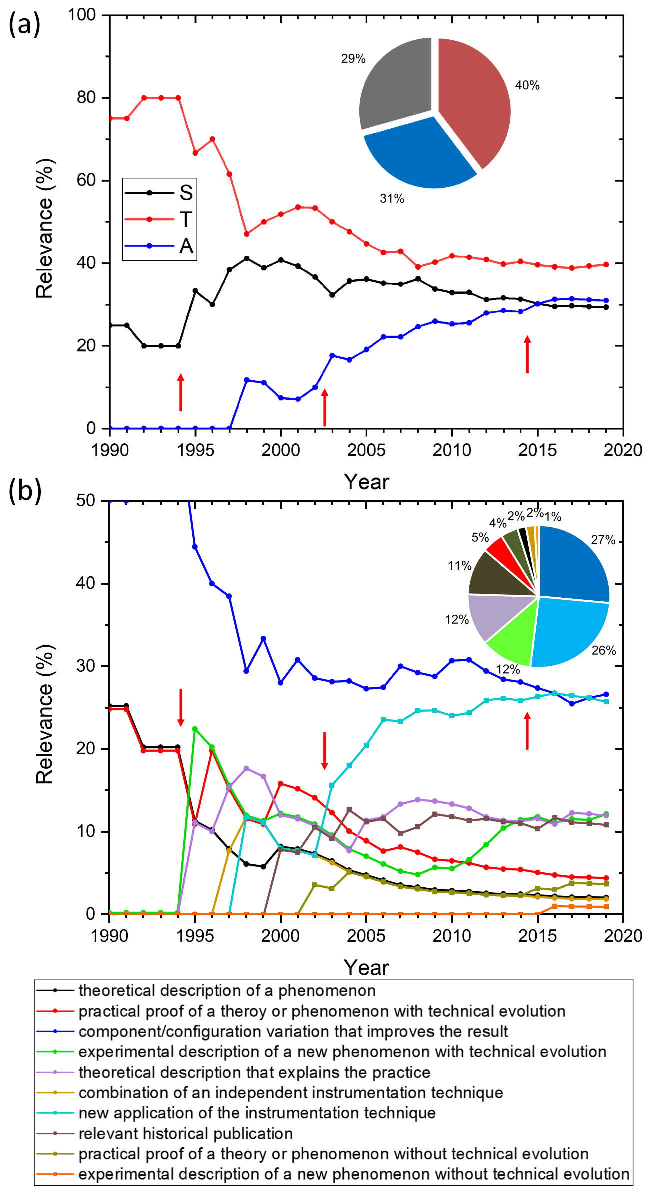

FIGURE 3 Evolution of relevance (in %) of documents according to (a) the science (S), technology (T), application (A), or market approach and (b) the scientific instrument development approach (see legend in the bottom). The insets show the total accumulated % distribution. The red arrows point to the years of changes in behavior identified in Figure 2a

categories). None of the documents was market (M) dominated. In this respect, the database was biased, because it considers a science and technology literature per se. However, the absence of market-dominated study is consistent with the consideration that TERS is still in the scientific realm. Actors from the industry sector are indeed present in the event table, especially in the beginning of TERS history, although in most events, especially the recent ones, they appear in association with other organization(s), as we will see in Section 4.4. This can reflect that, despite being commercially available, TERS technology has been mostly developed by the scientific community so far, both as users and as consumers. As noted, the application (A)-dominated events are still in other research areas, not in the industrial sector, and TERS have not gone through all the potential diffusion paths.

Figure 3a shows the evolution of the S, T, and A documents' relevance, measured by the percentage of total documents in the qualified literature, year by year, in a cumulative way. We focused in the period after 1990 because, before this date, there are only four papers in the qualified data, one S and three T related. TERS history starts with three technology-dominated events in 1972 and 1984, and it is followed by the first science-dominated event in 1985 (see inset in Figure 2c).

The three inflection points identified in Figure 2a are also indicated in Figure 3a. Notice that after the inflection (i), 1994–1995, S-oriented papers start to gain importance, showing that the technological aspects of TERS implementation were available, making possible the development of S. A-oriented works also appear and start to gain importance after the inflection (ii), 2002–2003. Finally, after inflection (iii), 2014–2015, clearly, A-oriented works take over the S-oriented ones. S-dominated events, although consistently present, have the lowest participation after the last inflection, which can indicate that the majority of scientific discoveries or understandings have been made for the field to grow. On the other hand, the growing tendency of A-oriented works is a good indicator for the development of TERS—or any scientific instrumentation technique—once it means that the technology is diffusing to other research fields that can both take advantage from it and help spread its use. Further on, it can generate more developments and adaptations optimized to those new applications, with science, technology, and application coexisting in a synergistic way.

To gain further understanding on the inflections shown by red arrows in Figure 2a, another approach was used to analyze the documents, based on *scientific instrument development* characteristics (simplified here as the SID approach). An initial set of 17 categories was idealized, but after the articles analysis, only 10 categories were relevant: theoretical description of a new phenomenon (THEORY); practical proof of a theory or phenomenon with technical evolution (PRACTICAL PROOF WITH THECHNICAL EVOL.); component or configuration variation that improves the result (COMPONENT VARIATION); experimental description of a new phenomenon with technical evolution (NEW PHENOMENON WITH TECHNICAL EVOL.); theoretical description that explains the practice (THEORY AFTER PRACTICE); combination of an independent instrumentation technique (COMBINATION); new application of the instrumentation technique (APPLICATION); relevant historical publication (PUBLICATION); practical proof of a theory or phenomenon without technical evolution (PRACTICAL PROOF NO TECHNICAL EVOL.); and experimental description of a new phenomenon without technical evolution (NEW PHENOMENON NO TECHNICAL EVOL.).

The chronological order of categories, according to SID approach, starts with "practical proof of a theory with technical evolution," in 1972,[30] that proves Synge's theory, followed by "component/configuration variation that improves the result" (1984),[100,111] related to minor improvements in the microscope and, consequently, in the resolution. In the sequence, follows the work of Wessel on the surface-enhanced optical microscope,[122] categorized as "theoretical description of a phenomenon". In 1995, it comes the first events categorized as "experimental description of a new phenomenon with technical evolution", and TERS is able to give new experimental results not yet explained or described by theory.[41,44] Coincidently, in the same year, there is the first event categorized "theoretical description that explains the practice", that is, theory after experiment.[43] This year has also another event classified as "component/configuration variation that improves the result".[42] In 1996, there is only one event, categorized as "practical proof of a theory or phenomenon with technical evolution".[45] In 1997, the three events are about a scheme for optical trapping and alignment of dielectric particles in aqueous environments at the nanometer scale,[46] categorized as "theoretical description that explains practice"; the production of optical fiber tips for SNOM by etching with the protection layer method and subsequent metallization,[47] and the development of a near-field Raman microscope for nanometer-scale vibrational spectroscopy at room temperature, with SERS and tapered single-mode fiber probes,[48] both categorized as "component/configuration variation that improves the result". The first events classified as "new application of the instrumentation technique" come in 1998: TERS to study stress in silicon[52] and TERS in DNA with SERS substrates.[51] The other events in 1998 are related to computer-simulated results of an electromagnetic field near the apex of a metallic probe, categorized as "theoretical description that explains practice",[50] and the combined use of SNOM and SERS, categorized as "combination of an independent instrumentation technique".[49] The only event in 1999 presents a new scheme for near-field fluorescence imaging using a metal tip illuminated with femtosecond laser pulses of proper polarization and was categorized as "component/configuration variation that improves the result".[53] In 2000, there is the first "relevant historical publication", related to the dissemination of general knowledge about TERS. In chronology, the categories without technical evolution are also the last to appear (in 2002 and 2016, respectively).

The three inflection points identified in Figures 2a and 3a are also shown in Figure 3b. Notice that before the inflection (i), 1994–1995, the "component/configuration variation that improves the result" category is majoritarian and it starts to decay at this inflection point, with the raise of "experimental description of a new phenomenon with technical evolution" and "theoretical description that explains the practice", followed by "combination of an independent instrumentation technique", the birth of "new application of the instrumentation technique", and the appearance of "relevant historical publication". These categories are consistent with the message delivered by Figure 1, which shows that this inflection is a domino effect triggered by the establishment of SPM, necessary for the development of the NFO techniques, enabling technology transfer to the field SERS, to implement the TERS. Inflection (ii), 2002–2003, is clearly marked by a steady increase in importance of category "new application of the instrumentation technique". Nanotechnology itself has a huge increase in the number of publications after the year 2000, thus enabling SERS and plasmonics to evolve, having a pronounced raise in the number of publications, as shown in Figure 1. This evolution in the realm of nano turned these research areas and consequently the TERS to be used for new applications. One example of an intensively studied nanomaterial at that time was the carbon nanotubes. In 2001, it was demonstrated that carbon nanotubes could be measured with Raman spectroscopy in the single molecule without any enhancement.[136] In this context, the extremely large Raman response of carbon nanotubes was a key factor for demonstrating the potential of TERS as a powerful tool for nanoscience. As such, from 2003, the TERS community adopted by the carbon nanotubes as a prototype sample,[62,64,73,80,82,83,89,137–141] spreading the technique into the materials science community. The latest inflection (iii), after the 2014–2015 period, is marked by the "new application of the instrumentation technique" category, reaching the same importance as the majoritarian category "component/configuration variation that improves the result", and also by the raise of categories that are independent on further technical developments, for example, a raise in importance of "practical proof of a theory or phenomenon without technical evolution" and the birth of "experimental description of a new phenomenon without technical evolution". This last inflection marks the maturity of TERS as an applied technique, and it happens along with SERS and plasmonics reaching maturity (Figure 1).

Exploring further the SID approach, the most frequent category is "component/configuration variation that improves the result" (27% of the events), showing that incremental developments in devices or systems for TERS are predominant so far in its history; that is, it is a technique that is still being improved and studied to reach the best performance results. Almost with same share (26%) is "new application of the instrumentation technique." This is a promising result to prove the value of the technology in other areas of expertise, apart from the optics field, that originated it. Although the "application-dominated" events are frequent, the areas of application are still in the fundamental physics and chemistry fields, in most events, with some in biology. Besides applied to semiconductor, virus, and bacteria investigations, TERS is not broadly diffused to engineering or health studies yet. But the relative importance of application-dominated events is a good indicator that TERS has its relevance in other fields distinct of its origins, which shows some level of maturity in the diffusion process.

The third most frequent SID category is the "experimental description of a new phenomenon with technical evolution" (12%). It shows the importance of TERS in making possible the experiment, even before having a theory to explain it—moreover, *with* technical improvement, in contrast to the less relevant category "experimental description of a new phenomenon *without* technical evolution." This feasibility of science through a new device that was not available before and that does not have yet a theory to explain it is described in scientific instrumentation literature. It is interesting to note that "theoretical description that explains the practice" has the same frequency (12%); it is related to theoretical concepts and calculation dedicated to offer theory models to describe the experimental results already achieved.

In the sequence, with 11% participation, comes the "relevant historical publication" category, which integrates compilation papers (mainly reviews) that, despite not revealing new information (either theoretical or experimental), are important for the dissemination of knowledge about TERS.

Something worth noting is that both categories representing events with technical evolution ("experimental description of a new phenomenon *with* technical evolution" and "practical proof of a theory or phenomenon with technical evolution"), 12% and 5%, respectively, are more frequent than their counterparts with no technical evolution (1% and 4%, respectively). Additionally, "experimental description of a new phenomenon with technical evolution" is much more frequent (12%) than "practical proof of a theory or phenomenon with technical evolution" (5%); that is, experiment before the subjacent theory is more frequent than experiment after theory. This is also a feature that reflects the evolution of a scientific instrument development, because the experiment enables new facts and brings new data to be studied by theory afterward. Moreover, "pure" theory, before experimentation (category "theoretical description of a phenomenon"), comes first in history, but it is much less frequent (2%) than "theoretical description that explains practice" (12%), that is, theory that is developed to explain the experiment already done.

"Combination of an independent instrumentation technique" has 2% in frequency, related to the combination of NFO and SERS to enable TERS (in 1997 and 1998). Once the combination was enabled, few other events aggregated other whole techniques to develop TERS. Instead, the variation of components or devices was more important (first category in frequency, "component/configuration variation that improves the result"). The works in this direction mostly target achieving better sensitivity and lateral resolution, by the design of new routes to nanoantenna production, by changing the setup configuration (illumination geometries), or by performing measurements in controlled conditions (ultrahigh vacuum, low temperature), all representing routes exploring the plasmonic effects that result in better SERS. The qualified database shows that the SERS and plasmonics fields are transversally important for the development of TERS. SERS-related papers are represented by at least seven of the SID categories: "component/configuration variation that improves the result"[56,85,93]; "theoretical description that explains practice"[95]; "practical proof of a theory without technical evolution"[36]; "relevant historical publication"[61]; "new application of the instrumentation technique"[51]; "theoretical description of a phenomenon"[122]; and, as already pointed, "combination of an independent instrumentation technique".[48,49] Plasmonics-related papers are represented by eight categories: "component/configuration variation that explains the result"[38,39,65,91,93,103,108,109,117,123,130]; "theoretical description that explains practice"[33,37,43,50,78,92,95,104,124]; "relevant historical publication"[4,12,15,32,70,81,96,99]; "experimental description of a new phenomenon with technical evolution"[40,105,115,116,126]; "practical proof of a theory or phenomenon without technical evolution"[36,127]; "new application of the instrumentation technique"[35,114]; and "experimental description of a new phenomenon without technical evolution".[132]

4.4 | Classification of TERS documents according to the triple-helix agent

To identify the type of institutions responsible for TERS development within the innovation ecosystem, we categorized the documents according to institutions within the entities considered in the triple-helix concept,[142] the main categories being academy, government (here represented by the national laboratories), and industry sector (firm). It was possible to identify combinations of two or three categories and hybrid organizations.[142]

Figure 4a displays the institutional roadmap for the time span under consideration, with disaggregate data, that is, considering the net institutional participation; the diameter of the circle is proportional to the number of qualified publications. The inset shows that academy is responsible for 64% of the publications, followed by government (28.5%). Hybrid institutions have 4% participation. Industry has 3.5% of share, but in most of the events, it is in cooperation, with academy and/or government; in two publications, industry is the actor alone (the first two of this actor). This result corroborates that TERS development is still inside universities and national laboratories. After Synge's paper on the concept of NFO, universities started to develop it joined by industry (1984) and government representatives (1985). Industry participation is interrupted from 1996 to 2006 and after 2007. The presence of hybrid institutions occurs only after 2009.

Figure 4b shows the type of institution distribution into the publication categories for STAM approach (reminding M is absent). Most of the events in which academy is responsible are technology (T) dominated. For the government actor, the distribution is almost equal for S, T, and A. Industry participates in only five events (two S, two T, and one A), two of which are in association with academy (S and A) and one with academy and government (S). The only two events that industry participates alone are technology dominated and occur before the first inflection (1984 and 1992). In hybrid institutions, the prevalent events are science (S) dominated. This result indicates that TERS

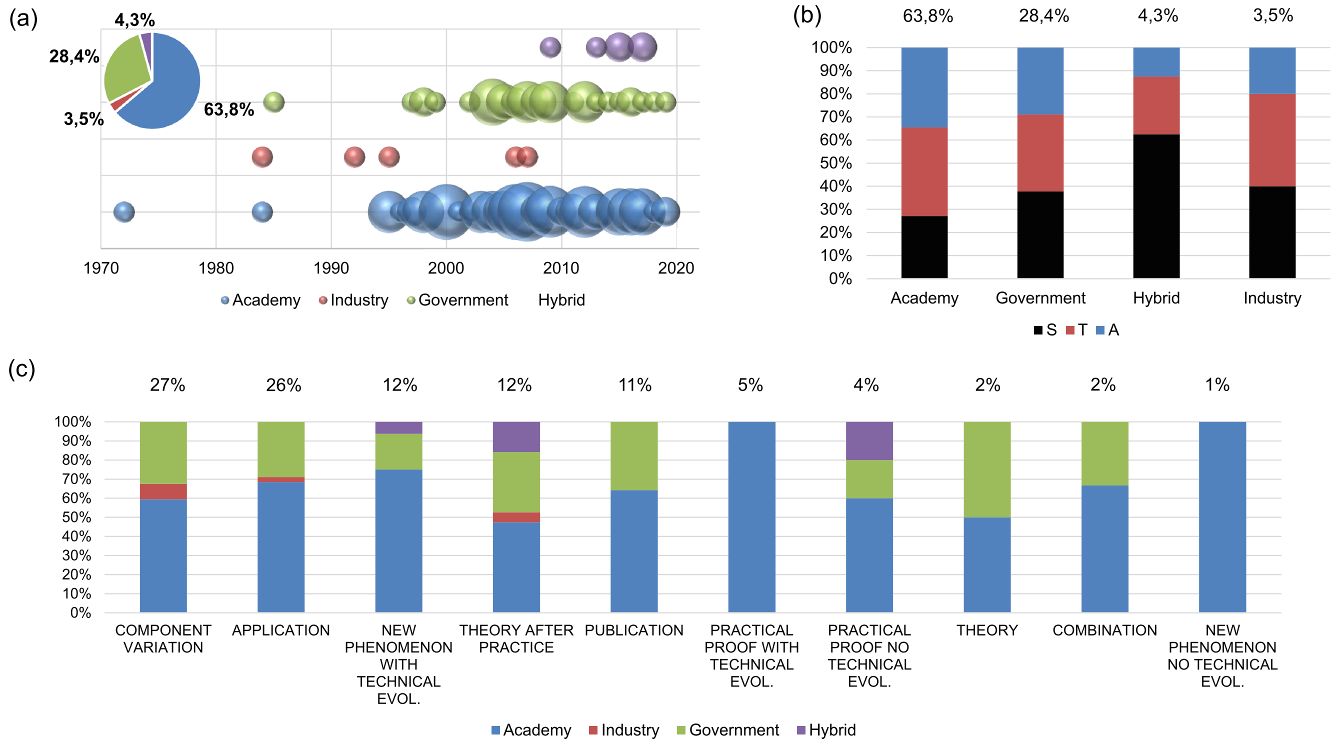

FIGURE 4 (a) Institutional contribution in the history of tip-enhanced Raman spectroscopy development by year. The size of the circle is proportional to the number of qualified documents; the inset shows the net institutional participation. (b) The type of institution distribution for the categories according to science (S), technology (T), application (A), or market (M, absent) approach (STAM) of the events. (c) Distribution of events by institutional participation according to scientific instrument development (SID) approach, considering disaggregate data. Percentages show the net participation of categories

technology is still being developed, and mainly by its users, that is, inside academy and national laboratories. Industry has timid participation with no apparent focus and no market-dominated studies yet.

The institutional distribution of events in the SID approach is shown in Figure 4c. Academy has participation in all categories. Government participates in eight out of 10 categories. It is worth noting that industry participates in only three categories, namely, component variation, application, and theory after practice, component variation being the most important for this actor.

Proportionally, the main activity in academy, government, and industry is related to technical evolution. Academy and government are the only institutions producing technical publications about the field. Academy is the only actor producing theoretical description (prior to experiment) and observation of new phenomena (prior to theory to explain it).

5 | CONCLUDING REMARKS

By analyzing the development of TERS based on the number of related publications and on the category of these published works, we characterized the increasing tendency and identified three positive inflections in the growth: (i) 1994–1995, when the first documents start to appear, greats to the combination of SERS/plasmonics with SPM/NFO; (ii) 2002–2003, when a large increase in the number of documents takes place, greats to the boom of nanotechnology that highly boosted SERS/plasmonics and the application in novel materials, such as carbon nanotubes; and (iii) 2014–2015, when the number of contributions related to applications of the technique surpassed the number of articles development to the development and understanding of the technique itself, thus establishing that SERS, plasmonics and, consequently, TERS reached maturity.

In total, most TERS events over the time focused more on the technological development than on the scientific understanding of the technique or its application in other fields as a characterization tool. However, this picture changed in the last decade, indicating that TERS is in the verge of raising the community of users by its diffusion to other areas. Academic institutions have been the leading actors in this endeavor.

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