Metal Capillaries: New Prospects for Application in Raman Spectroscopy

V.V. Vitkin[1], A.P. Kouzov[2], N.N. Filippov[2], E.E. Popov[1,2], I.K. Chubchenko[3]
[1]Institute of Advanced Data Transfer Systems, ITMO University, St.-Petersburg, Russia
[2]Department of Physics, Saint-Petersburg State University, Saint-Petersburg, Russia
[3]D.I.Mendeleyev Institute for Metrology, Saint-Petersburg, Russia

Abstract— New potentialities opened by the use of thin metal capillaries (MC) to increase the power of radiation transfer by photons scattered by an isotropic medium inside MC as well to achieve a fuller collection of a useful signal are investigated.

Keywords— Raman spectroscopy; metal capillaries; signal enhancement; multiphoton interactions.

I. Introduction

As first demonstrated by Walrafen and Stone [1], a gigantic intensification of Raman signals from a liquid put into a hollow silica fiber (*D*=75 μ, *L*=25 m) occurs reaching 3 decimal orders compared to the use of conventional Raman cells. Whereas hollow fibers are increasingly gaining attention of Raman spectroscopists [2], it is - to the best of our knowledge - not the case of metal capillaries. Here, we briefly discuss the potentialities offered by their use in the Raman and nonlinear spectroscopic tools based on the multiphoton interactions with matter.

II. Enhancement ratios

In the Raman case, the effect is mostly due to the increase of the photon-matter interaction volume V leading to enhancement of the signal by a factor $\varkappa^R=L/l$ where l is the length of caustics in a conventional Raman setup. This factor can be also estimated for the hyper-Raman (HR) case as $\varkappa^{HR}= \varkappa^R\ (d/D)^2$ where d is the caustics diameter which typically varies in the 10-20 μ range. One then can expect to achieve $\varkappa^{HR}$ in the range of 1-2 decades. It should be noted that hollow fibers and metal capillaries advantageously provide much more efficient collection of the scattered radiation. Nevertheless, light scattered at large enough angles can penetrate through the fiber walls causing signal losses which are absent when metal capillaries are used.

It is straightforward to estimate the enhancement factor $\varkappa$ for coherent nonlinear spectroscopy. With the proviso that the same incident light powers are used we obtain for the four-wave mixing techniques (such as CARS) $\varkappa=(Ld^2/lD^2)^2$. For typical caustics diameters, we get $(d/D)^4=10^{-4}$ -10^{-3} for a capillary with D=100 μm. Thus, a considerable signal enhancement can be achieved using long enough capillaries/fibers with $L\geq1$ m. Under these conditions, fibers are seemingly superior because the surface losses in the metal capillaries are expectedly higher.

Nevertheless, the mode structure of light in metal capillaries [3] is relatively simple that allows in idealized cases to mimic the phase matching conditions for coherent 3WM and 4WM responses. As anticipated, the 3WM signal enhancement $\varkappa=(Ld/lD)^2$ should be much stronger than the 4WM one.

III. Perspective applications

There are two possible 3-photon spectroscopic processes, SFG and hyper-Raman, which are dipole-allowed in macroscopically isotropic ensembles of chiral molecules and whose sensitivity may be enhanced by using capillaries or hollow fibers. The SFG signals can be produced only in non-racemic mixtures of chiral molecules. In contrast, the incoherent HR responses independently stem from both enantiomers and offer unique opportunities to detect chirality *per se*.

Another, yet unstudied effect is the 3WM generation in a nonchiral medium which can be induced by magnetic and/or quadrupolar light-matter couplings. Its incoherent analog (parity-changing Raman) was explored theoretically [4] and the first indications of its existence have been obtained [5]. The Raman and 3WM-techniques equipped with fiber/metal capillaries are promising tools to provide more accurate data on this effect.

Acknowledgment

Financial support from the Russian Science Foundation (project 24-23-00194) is gratefully acknowledged.

References

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