Comment on “Enhancement of the Raman Effect by Infrared Pumping”

Zhenhuan Yi, Zhedong Zhang, Alexei V. Sokolov, and Vladislav V. Yakovlev

Phys. Rev. Lett. **124**, 159401 — Published 15 April 2020

DOI: 10.1103/PhysRevLett.124.159401

Comment on "Enhancement of the Raman Effect by Infrared Pumping"

Zhenhuan Yi,* Zhedong Zhang,† Alexei V. Sokolov, and Vladislav V. Yakovlev
Texas A&M University, College Station TX 77843

A recent Letter [1] describes a method for producing coherent molecular vibrations, and then argues that this method results in orders-of-magnitude enhancement of Raman signals. We believe this Letter misleads the readers in that (1) it presents a well-established result of Raman signal enhancement due to molecular coherence [2], and (2) it omits simple analysis showing that their method is inferior to other, well-established techniques for coherence preparation. In addition, some numbers the authors calculated are incorrect and misleading. We elaborate on these points in the following paragraphs.

In spectroscopic detection and sensing, coherent enhancement is given by the ratio of the number of coherently scattered photons to that of incoherently scattered photons via the Scully equation [3, 4], which illuminates most of the misleading claims in Ref. [1]:

$$\frac{\langle n^{\text{coh}}_{\text{Stokes}}\rangle}{\langle n^{\text{incoh}}_{\text{Stokes}}\rangle} \cong \lambda^2 L \frac{N}{V}\frac{|\rho_{01}|^2}{\rho_{00}} \tag{1}$$

where n_{Stokes} denotes the Stokes photon number, ρ_{01} is the coherence between the vibrational levels $v = 0$ and 1, and ρ_{00} is the population at the $v = 0$ level (replace by ρ_{11} for the anti-Stokes case). We note that Ref. [1] used $n_b^{\text{coh}}/n_b^{\text{incoh}}$ to denote phonons, and that ratio is equivalent to $|\rho_{01}|^2/\rho_{11}$. We have also found that the "intensity" $I(\omega)$ used in Ref. [1] has units of energy, thus is consistent with photon numbers, not *power per unit area*.

The coherence ρ_{01} plays a central role in the whole business of coherent Raman scattering. From 2nd-order time-dependent perturbation theory, one can obtain results in terms of coherence for the Ref. [1] technique, visible-light pumped CARS and MIRA CARS. The Ref. [1] technique and visible-light pumped CARS employ the same scheme for creating vibrational coherence, i.e., using the same transition dipoles between electronic ground and excited states. Visible-light pumped CARS is shown to achieve stronger coherence than the Ref. [1] technique due to smaller detuning from electronic excited levels. In practice, visible sources achieve higher intensity more easily, and therefore higher coherence.

MIRA CARS entails a completely different scenario as it relies on transition dipoles within the electronic ground state of a molecule, regardless of excited states, and is applicable to molecules having both IR- and Raman-active vibrational modes. Those molecules make up the majority of the chemical world. To this end, one may refer to Herzberg's classic volumes [5].

The "coherence volume" defined in Ref. [1] is the volume in which molecules are coherently excited. Assuming the radius of the cross section is *w* (the waist of a beam, usually), and putting $V = w^2 \times L$ into Eqn. 1, we get a factor λ^2/w^2, which shows that diffraction governs the photon number ratio in addition to the coherence [6], and it defines the emission solid angle. A solid angle $\Delta\Omega$ for collecting signals should enter the denominator of Eqn. 1 [4], and only if $\Delta\Omega = \lambda^2/w^2$, one recovers an N dependence of the signal ratio, otherwise, N/V remains to be the number density. We estimate Eqn. 1 using parameters from Ref. [1] as follows.

For "typical ... organic molecules", $n_b^{\text{coh}}/n_b^{\text{incoh}} \sim 10^{-7}$. From $\lambda^2 \times L = 10^{-9}$ cm^3, assuming $\lambda = 1$ μm, and $N/V \sim 10^{18} - 10^{19}$ cm^{-3}, we get a photon number ratio $\langle n^{\text{coh}}_{\text{Stokes}}\rangle/\langle n^{\text{incoh}}_{\text{Stokes}}\rangle$ of $10^2 - 10^3$. The emission solid angle of the coherent photons is $4\pi \times 10^{-4}$ (a reasonable estimation based on Ref. [1]), and the incoherent signal's is 4π. By collecting signals within the $4\pi \times 10^{-4}$ solid angle, the ratio of the collected signals will increase to $10^6 - 10^7$. This procedure is consistent with experiment [7]. For "a single [nitrogen] molecule", $n_b^{\text{coh}}/n_b^{\text{incoh}} \sim 10^{-3}$; $N = 1$, so $1 \times n_b^{\text{coh}}/n_b^{\text{incoh}} \sim 10^{-3}$. For light scattering from single-molecule coherence, the emission solid angle is on the same order of 4π. So limiting the solid angle will suppress both signals, and the ratio will stay at $\sim 10^{-3}$. For both cases, Ref. [1] gets quite different estimations, thus we assume the authors made mistakes in their calculations. Lastly, it is worth noting that the results of Ref. [1] do not apply to high temperature conditions, due to the lack of a thermal distribution factor in their expression for the coherent signal.

In conclusion, visible-light pumped CARS always gives a stronger signal than the technique proposed in Ref. [1], while MIRA CARS is fundamentally different. The Scully equation gives correct estimations of real-world numbers.

* Electronic address: yzh@tamu.edu
† Electronic address: zhedong.zhang@tamu.edu

[1] V. Y. Shishkov, E. S. Andrianov, A. A. Pukhov, A. P. Vinogradov, and A. A. Lisyansky, Phys. Rev. Lett. **122**, 153905 (2019).
[2] M. O. Scully, G. W. Kattawar, R. P. Lucht, T. Opatrný, H. Pilloff, A. Rebane, A. V. Sokolov, and M. S. Zubairy, Proc. Nat. Acad. Sci. USA **99**, 10994 (2002).
[3] A. J. Traverso, B. Hokr, Z. Yi, L. Yuan, S. Yamaguchi, M. O. Scully, and V. V. Yakovlev, Phys. Rev. Lett. **120**, 063602 (2018).
[4] G. I. Petrov, R. Arora, V. V. Yakovlev, X. Wang, A. V. Sokolov, and M. O. Scully, Proc. Nat. Acad. Sci. USA **104**, 7776 (2007).
[5] G. Herzberg and K.-P. Huber, *Molecular spectra and molecular structure, I. II.* (New York : Van Nostrand, [©1945-1966], 1950).
[6] M. O. Scully and A. A. Svidzinsky, Science **325**, 1510 (2009).
[7] D. Pestov, G. O. Ariunbold, X. Wang, R. K. Murawski, V. A. Sautenkov, A. V. Sokolov, and M. O. Scully, Opt. Lett. **32**, 1725 (2007).