Connection between vibrational instabilities of molecules in surface-enhanced Raman spectroscopy and Raman lasing

V. Yu. Shishkov,[1,2,3] E. S. Andrianov,[1,2] A. A. Pukhov,[1,2,3] A. P. Vinogradov,[1,2,3] and A. A. Lisyansky [4,5]

[1]*Dukhov Research Institute of Automatics (VNIIA), 22 Sushchevskaya, Moscow 127055, Russia*
[2]*Moscow Institute of Physics and Technology, 9 Institutskiy Pereulok, Dolgoprudny 141700, Moscow Region, Russia*
[3]*Institute for Theoretical and Applied Electromagnetics, 13 Izhorskaya, Moscow 125412, Russia*
[4]*Department of Physics, Queens College of the City University of New York, Flushing, New York 11367, USA*
[5]*The Graduate Center of the City University of New York, New York, New York 10016, USA*

To observe a vibrational instability in a molecule or Raman lasing, the molecules should be placed in a resonator and illuminated by a laser. Both these phenomena are self-oscillations of either photons in a resonator or nuclei in molecules. We show that, thanks to the coupling of the forced oscillations of electrons in a molecule with its nucleus vibrations, these two effects are manifestations of the same phenomenon. When the ratio of damping rates of the molecule and the resonator is large, the number of coherent photons is also large, causing Raman lasing. In this case, the number of quanta of the coherent molecular vibrations is negligible. In the opposite case, the number of coherent vibration quanta is large, causing vibrational instability. This leads to the nonlinear response in Raman scattering, which was recently observed in a surface-enhanced Raman spectroscopy (SERS) experiment [A. Lombardi *et al.*, Phys. Rev. X **8**, 011016 (2018)].

I. INTRODUCTION

Raman scattering, discovered in 1928 [1,2], was explained [2] as a parametric effect of a vibration of a molecular nucleus (VMN) on Rayleigh scattering of a molecule. Since the classical approach could not explain the difference between the amplitudes of the Stokes and anti-Stokes scattering, a quantum theory of the phenomenon based on the Plachek spectral theory [3] was developed [4]. In this theory, inelastic scattering involves absorption of a quantum of incident radiation followed by emission or absorption of a VMN quantum simultaneously with the emission of a quantum of light at the anti-Stokes or Stokes frequencies, respectively. This two-photon theory makes a visually clear picture of the phenomenon. The approach, however, requires an artificial addition of two nonexistent (virtual) energy levels to the energy level diagram of the molecule [5]. The nature of the virtual levels cannot be specified even at the phenomenological level.

Later, thanks to using coherent laser light in spectroscopy, coherent anti-Stokes Raman spectroscopy (CARS) and stimulated Raman scattering (SRS) were developed. In these phenomena, molecules are illuminated by two coherent light beams, and therefore the theory has to include four-photon processes. Consequently, the quantum theory of the spontaneous Raman scattering was modified by increasing the number of virtual levels [6]. This theory also did not explain the nature of these virtual levels. Moreover, an additional question arose about the coherence of reemitted light. It is not clear why, in the spontaneous Raman two-photon theory, the scattered light is incoherent, while the four-photon theory, which describes CARS, gives a coherent response.

The problem of the coherent Raman scattering is significantly simplified because the coherent properties of laser light are close to those of a classical plane electromagnetic (EM) wave, and the nonlinear optics of coherent light has been well developed. Thus, the use of high-power laser radiation in CARS has brought nonlinear coherent optics into the arena, and nonlinearity of the third order has been considered as the reason for the coherent Raman scattering. Along with this classical approach, a nonlinear quantum theory has also been developed. In this theory, within the paradigm of absorption and emission of photons and VMNs, a term describing the interaction of a VMN with an external EM field has been added to the Hamiltonian [7]. It has been assumed that this Hamiltonian is nonlinear, and the interaction term appears in the third order of the expansion of the interaction Hamiltonian in the external field. Although the theory gives a qualitative description of the phenomenon, the nature of the phenomenologically introduced Hamiltonian remains unclear. Moreover, the theory implies the existence of virtual levels because transitions between vibrational levels require absorption and emission of optical photons.

Moreover, the emission of EM waves is entirely associated with the vibrations of the nuclear subsystem of the molecule. Disregarding the dynamics of the high-frequency electronic subsystem raises some questions. It is clear how two coherent optical waves can excite a low-frequency VMN: this happens when the beat frequency of the total field coincides with the natural frequency of the VMN. It is not clear, however, how a low-frequency VMN can emit high-frequency optical waves. The more consistent theory based on the optomechanical Hamiltonian [8,9], in which the dynamics of electronic subsystems is taken into account by introduction of a

phenomenological effective dielectric constant or polarizability, has the same problem.

Below, by considering the behavior of a molecule driven by classical coherent light, we give a detailed analysis of both well-known effects of Raman physics, e.g., Raman lasing, and recently observed vibrational instability [10]. In this approach, the vibrational molecular subsystem does not directly interact with an external field; it interacts with the electronic subsystem that experiences forced oscillations due to the EM field. According to the Born-Oppenheimer approximation [11], the motion of electrons is responsible for changing the equilibrium position of nuclei and leads to the parametric excitation of VMNs. This interaction can be described by the Fröhlich Hamiltonian of the interaction between electronic and vibrational nucleus subsystems [12], well known in solid-state physics. It is this Hamiltonian that is responsible for the inverse effect, in which low-frequency VMNs modulate high-frequency vibrations of the dipole moments associated with forced oscillations of the electronic subsystem. As a result, an oscillating dipole moment of the system arises. This dipole moment emits various optical quanta. This approach does not require phenomenological assumptions about the indirect coupling between the VMN and the external field.

This approach has successfully been applied to describe the enhancement of Raman scattering by direct excitation of a VMN by IR radiation [13]. Now we consider a more complicated phenomenon: the connection of Raman lasing with the vibrational instability.

Illumination of a molecule with EM waves, having different frequencies ω_S (the Stokes frequency) and ω_P, may cause a resonant excitation of a VMN when the frequency difference of these waves is equal to the vibrational eigenfrequency of the molecule, ω_v [4,14]. The reason for such excitation is the nonlinear parametric coupling of nucleus subsystem of the molecule and EM waves [7,13,14]. The parametric coupling may be described in terms of the additional nonlinear polarization $P(\omega_S) \sim \chi^{(3)}(\omega_S, \omega_P, \omega_S, -\omega_P)E(\omega_P)E(\omega_S)E^*(\omega_P)$ [4,13,15] (see also a phenomenological description in Ref. [7]). Within this approach, it has been shown that when the relation $\omega_P - \omega_S = \omega_v$ is satisfied, the phase of $\chi^{(3)}(\omega_S, \omega_P, \omega_S, -\omega_P)E(\omega_P)E(\omega_S)E^*(\omega_P)$ is ahead of the phase of the incident field $E(\omega_S)$, and therefore the work is done on the field. As a result, the wave $E(\omega_S)$ is amplified, while the field $E(\omega_P)$ is attenuated. If $E(\omega_S)$ is the field in the resonator, in which the Raman active molecule is placed, such an amplification leads to lasing [4,16–29].

The vibrational instability has been observed [10] in a typical surface-enhanced Raman spectroscopy (SERS) setting, in which the difference between the frequency of incident laser radiation and the eigenfrequency of the plasmonic nanocavity is equal to the frequency of the VMN. It has been shown that when the intensity of radiation of the pumping laser exceeds a certain threshold, this system can reach the vibrational instability that manifests itself in nonlinear dependencies of the Stokes and anti-Stokes intensities on the intensity of incident radiation.

In this paper, we show that both the resonator field and vibrations of molecules become coherent and synchronized above a certain threshold of the pump rate. There are two regimes of self-oscillations. The qualitative difference between them is in the distribution of the total number of quanta between the EM field and VMNs. This distribution is controlled by the ratio of the relaxation rates of the EM field in the resonator and VMNs. If this ratio is much smaller than unity, then, at the resonant frequency of a VMN, conditions for gain for photons in the resonator are satisfied, and the system is a Raman laser. In the opposite case, the number of coherent quanta of the vibrational motion may become so large that Raman scattering enters a nonlinear regime as has been observed in the recent experiment [10]. We show that an increase in the number of molecules is stabilized by the regime of nonlinear Raman scattering. Typically, due to anharmonicity, two or three vibration quanta should break a molecule. In the experiment described in Ref. [10], the molecular bonds should be very strong because nonlinearity is observed when the number of quanta is about 10. Thus, when the number of excited quanta is low, the system may be described as a harmonic oscillator. We show that an increase in the number of molecules leads to a decrease in the number of coherent quanta of the vibrational motion. Thus, by increasing the number of molecules, one can more easily achieve the regime of nonlinear Raman scattering. Although it seems that the larger the number of quanta of a VMN, the greater the gain in the Raman laser, it is not so. In the regime of the vibrational instability, a decrease in the relaxation rate in a VMN not only amplifies the VMN but also decreases the EM field in the resonator. Moreover, in the intermediate case, when the relaxation rates of the EM field in the resonator and molecule vibrations are about the same, the number of generated photons in the resonator and the quanta of the vibrations of the molecule drop drastically.

II. DESCRIPTION OF THE MODEL

We consider N molecules placed into a cavity (resonator). The molecules are Raman active, i.e., they have a zero dipole moment of their VMN transitions. The vibrational molecular subsystem does not directly interact with an external EM field, while the electronic subsystem of a molecule interacts with the external EM field through an induced dipole moment [30]. Since the electronic subsystem interacts with VMNs via parametric coupling, the EM field indirectly affects VMNs [11,31–37]. We assume that the external field only excites the resonator. This assumption is valid if the field of the resonator mode is much greater than the field of the external wave, which is possible when the resonator has high Q factor [17,19,21–23,25] or Purcell factor [10].

The total Hamiltonian of the system may be written as

$$\hat{H} = \hat{H}_{\text{cav}} + \sum_{j=1}^{N} (\hat{H}_{\text{mol}})_j + \sum_{j=1}^{N} (\hat{H}_{\text{mol-cav}})_j + \hat{H}_{\text{field-cav}}(t),$$

(1)

where the sum in Eq. (1) runs over all the molecules in the cavity. The Hamiltonian of the cavity $\hat{H}_{\text{cav}}$ is

$$\hat{H}_{\text{cav}} = \hbar\omega_a \hat{a}^\dagger \hat{a},$$

(2)

where ω_a is the resonant frequency of the cavity, $\hat{a}^\dagger$ and $\hat{a}$ are creation and annihilation operators of the field mode in the cavity. The frequency ω_a plays a role of the signal frequency ω_S in a Raman laser.

We assume that all the molecules are equivalent and the corresponding Hamiltonian of the jth molecule has the form

$$(\hat{H}_{\text{mol}})_j = \hbar\omega_0\hat{\sigma}_j^\dagger\hat{\sigma}_j + \hbar\omega_v\hat{b}_j^\dagger\hat{b}_j + \hbar g\hat{\sigma}_j^\dagger\hat{\sigma}_j(\hat{b}_j^\dagger + \hat{b}_j). \quad (3)$$

The electronic subsystem of the molecules can be treated as an effective two-level system (TLS) with the transition frequency ω_0. In Hamiltonian (3), the first term describes the energy of the jth TLS, $\hat{\sigma}_j^\dagger$ and $\hat{\sigma}_j$ are the raising and lowering TLS operators, and $\hat{b}_j^\dagger$ and $\hat{b}_j$ are the creation and annihilation operators of the VMN. Below, we disregard the effects of anharmonicity of the VMN and only consider a single VMN mode with the frequency ω_v. It should be noted that anharmonicity plays an important role in some types of the molecules when the number of quanta of a VMN is about 3–4, e.g., for H_2O and NH_3 [38]. However there are molecules for which the harmonic approximation works well, e.g., N_2 [39] and CH_3 [40].

The Hamiltonian of the interaction of the electronic subsystem with a VMN is taken in the form of the Fröhlich Hamiltonian $\hbar g\hat{\sigma}_j^\dagger\hat{\sigma}_j(\hat{b}_j^\dagger + \hat{b}_j)$, where g is the interaction constant of the electronic and vibrational subsystems of the molecule [11,31–37]. In Hamiltonian (3), the sum of the first and third terms can be represented as the energy of a TLS with the transition frequency modulated by the frequency of the VMN. Such modulation is responsible for the Raman effect.

The interaction Hamiltonian $(\hat{H}_{\text{int}})_j$ of the jth molecule and the cavity is

$$(\hat{H}_{\text{int}})_j = \frac{\hbar\Omega_{Rj}}{2}(\hat{a}\hat{\sigma}_j^\dagger + \hat{a}^\dagger\hat{\sigma}_j), \quad (4)$$

where Ω_{Rj} is the Rabi frequency of the cavity and the jth molecule [41–43]. For simplicity, we assume that all the Rabi frequencies are real.

The interaction Hamiltonian, $\hat{H}_{\text{field-cav}}(t)$, describes the excitation of the resonator by the external classical field with the frequency ω:

$$\hat{H}_{\text{field-cav}}(t) = \frac{\hbar\Omega}{2}(\hat{a}e^{i\omega t} + \hat{a}^\dagger e^{-i\omega t}), \quad (5)$$

where Ω is the interaction constant. We assume that the external field excites the cavity mode only. We also assume that the relation between the frequency of the external field ω and the frequency of the resonant mode coincides with the relation in the SRS:

$$\omega = \omega_a + \omega_v. \quad (6)$$

Condition (6) is valid for both Raman lasing [44] and the vibrational instability [10].

We consider the case when the transition frequency of the TLS, ω_0, is far from the external field ω and the cavity frequency ω_a:

$$|\omega - \omega_0| \gg \gamma_\sigma, \qquad |\omega_0 - \omega_a| \gg \gamma_\sigma, \quad (7)$$

where γ_0 is the relaxation rate of the electronic subsystem of the molecule.

III. SELF-OSCILLATION IN THE SYSTEM

One of the main features of a Raman laser is that it is pumped by a coherent wave. Consequently, it is difficult to distinguish self-oscillations from forced oscillation because both of them are coherent. This especially concerns VMNs. According to Ref. [4], after Raman lasing begins, a molecule is illuminated by two coherent waves: an incident (pump) wave and a lasing resonator mode. The frequency of the latter is equal to the Stokes frequency. Such a combination of frequencies is characteristic of CARS, in which it results in the resonant excitation of coherent VMNs. Thus, for coherence in quanta of VMNs, the coherent Stokes wave is sufficient. The self-oscillation regime is not required. In contrast, with Raman lasing, coherence may arise only as a result of self-oscillations. Thus, the pump intensity at which Raman laser generates coherent radiation, determines the appearance of coherent vibrations. Moreover, Raman lasing does not require coherent VMNs. The existence of incoherent thermal vibrations is sufficient. Thus, one can expect that the threshold for molecular self-oscillations observed in Ref. [9] may be independent of the threshold for self-oscillations of the EM field. Below we show that this is not so. There is a close connection between these phenomena, and the system has unique threshold of self-oscillations for both the EM field in the resonator and VMNs.

To find the dynamics of the system governed by Hamiltonian (1), we proceed in two steps. First, we write the equation for the average values of the operators $a = \langle\hat{a}\rangle$, $\sigma_j = \langle\hat{\sigma}_j\rangle$, and $b_j = \langle\hat{b}_j\rangle$ and neglect quantum correlations between operators. At this step, we deal with the coherent dynamics of the system in the mean-field approximation. Also at this step, we obtain the self-oscillating solution which arises above the threshold for the external field amplitude Ω. Below the threshold, all average values of the operators are equal to zero. This means that there are no coherent oscillations. At the second step, we add noise terms, which take into account spontaneous excitations of both the resonator EM field and VMNs below the threshold and describe the incoherent field and excitations of VMNs.

This procedure is standard for an open quantum system [43,45]: the first step corresponds to the semiclassical approximation for the corresponding quantum Heisenberg equation, while the second step enables one to describe the leading quantum correction to quantities obtained in the first step (for details see [45]).

The equations of motion for the mean value of the operators $a = \langle\hat{a}\rangle$, $\sigma_j = \langle\hat{\sigma}_j\rangle$, and $b_j = \langle\hat{b}_j\rangle$ have the form

$$\frac{da}{dt} = -(i\omega_a + \gamma_a)a - \frac{1}{2}i\sum_{j=1}^{N}\Omega_{Rj}\sigma_j - \frac{1}{2}i\Omega e^{-i\omega t},$$

$$\frac{d\sigma_j}{dt} = -(i\omega_0 + \gamma_0)\sigma_j - ig\sigma_j(b_j^* + b_j) + \frac{1}{2}i\Omega_{Rj}(2|\sigma_j|^2 - 1)a,$$

$$\frac{db_j}{dt} = -(i\omega_v + \gamma_v)b_j - ig|\sigma_j|^2, \quad (8)$$

where the relaxation is described in the standard way [41–43] by constants γ_v and γ_a characterizing the relaxation rates of VMNs and the EM field in the cavity, respectively. We represent Eqs. (8) in the form of slowly varying amplitudes $a = \tilde{a}(t)e^{-i\omega t}$ and $\sigma_j = \tilde{\sigma}_j(t)e^{-i\omega t}$. Then, these equations take

the form

$$\frac{d\tilde{a}}{dt} = -[i(\omega_a - \omega) + \gamma_a]\tilde{a} - \frac{1}{2}i\sum_{j=1}^{N}\Omega_{Rj}\tilde{\sigma}_j - \frac{1}{2}i\Omega,$$

$$\frac{d\tilde{\sigma}_j}{dt} = -[i(\omega_0 - \omega) + \gamma_0]\tilde{\sigma}_j - ig\tilde{\sigma}_j(b_j^* + b_j)$$
$$+ \frac{1}{2}i\Omega_{Rj}(2|\tilde{\sigma}_j|^2 - 1)\tilde{a},$$

$$\frac{db_j}{dt} = -(i\omega_v + \gamma_v)b_j - ig|\tilde{\sigma}_j|^2. \qquad (9)$$

Assuming that $\gamma_\sigma \gg \gamma_v, \gamma_a$, we can adiabatically exclude variables of the electronic subsystem from Eqs. (9) by setting $d\tilde{\sigma}_j/dt = 0$:

$$0 = -[i(\omega_0 - \omega) + \gamma_0]\tilde{\sigma}_j - ig\tilde{\sigma}_j(b_j^* + b_j)$$
$$+ \frac{1}{2}i\Omega_{Rj}(2|\tilde{\sigma}_j|^2 - 1)\tilde{a}. \qquad (10)$$

As a result, we obtain

$$\tilde{\sigma}_j \approx -\frac{1}{2}\tilde{a}\frac{\Omega_{Rj}}{\omega_0 - \omega} + \frac{1}{2}\tilde{a}(b_j^* + b_j)\frac{\Omega_{Rj}g}{(\omega_0 - \omega)^2}. \qquad (11)$$

Using Eqs. (9) and (11) we can obtain equations for the amplitudes a and b_j:

$$\frac{da}{dt} = -(i\omega_a + \gamma_a)a - \frac{i}{4}\sum_{j=1}^{N}\frac{g\Omega_{Rj}^2}{(\omega_0 - \omega)^2}(b_j^* + b_j)a - \frac{1}{2}i\Omega e^{-i\omega t},$$
$$(12)$$

$$\frac{db_j}{dt} = -(i\omega_v + \gamma_v)b_j - \frac{i}{4}\frac{g\Omega_{Rj}^2}{(\omega_0 - \omega)^2}|a|^2. \qquad (13)$$

Here, we neglect the shift of the eigenfrequency of the cavity caused by the interaction with the molecules. We multiply Eq. (13) by Ω_{Rj}^2, sum over the molecules, and regroup the terms to obtain

$$\frac{da}{dt} = -(i\omega_a + \gamma_a)a - \frac{i}{4}\frac{g\sum_{j=1}^{N}\Omega_{Rj}^2}{(\omega_0 - \omega)^2}$$
$$\times \left(\frac{\sum_{j=1}^{N}\Omega_{Rj}^2 b_j^*}{\sum_{j=1}^{N}\Omega_{Rj}^2} + \frac{\sum_{j=1}^{N}\Omega_{Rj}^2 b_j}{\sum_{j=1}^{N}\Omega_{Rj}^2}\right)a - \frac{1}{2}i\Omega e^{-i\omega t},$$
$$(14)$$

$$\frac{d}{dt}\left(\frac{\sum_{j=1}^{N}\Omega_{Rj}^2 b_j}{\sum_{j=1}^{N}\Omega_{Rj}^2}\right) = -(i\omega_v + \gamma_v)\left(\frac{\sum_{j=1}^{N}\Omega_{Rj}^2 b_j}{\sum_{j=1}^{N}\Omega_{Rj}^2}\right)$$
$$- \frac{i}{4}\frac{g}{(\omega_0 - \omega)^2}\left(\frac{\sum_{j=1}^{N}\Omega_{Rj}^4}{\sum_{j=1}^{N}\Omega_{Rj}^2}\right)|a|^2.$$
$$(15)$$

Introducing the VMN amplitude averaged over all molecules,

$$b = \frac{\sum_{j=1}^{N}\Omega_{Rj}^2 b_j}{\sum_{j=1}^{N}\Omega_{Rj}^2}, \qquad (16)$$

the Rabi frequency averaged over positions of the molecules,

$$\Omega_R = \sqrt{\frac{1}{N}\sum_{j=1}^{N}\Omega_{Rj}^2}, \qquad (17)$$

and the effective coupling constant between the field in the cavity and the VMN,

$$G = \frac{g\sum_{j=1}^{N}\Omega_{Rj}^2}{4N(\omega - \omega_0)^2} = \frac{g\Omega_R^2}{4(\omega - \omega_0)^2}, \qquad (18)$$

and assuming that

$$\sqrt[4]{\frac{1}{N}\sum_{j=1}^{N}\Omega_{Rj}^4} \approx \sqrt{\frac{1}{N}\sum_{j=1}^{N}\Omega_{Rj}^2}, \qquad (19)$$

one can rewrite Eqs. (14) and (15) as

$$\frac{da}{dt} = -(i\omega_a + \gamma_a)a - iNGa(b^* + b) - \frac{1}{2}i\Omega e^{-i\omega t}, \qquad (20)$$

$$\frac{db}{dt} = -(i\omega_v + \gamma_v)b - iG|a|^2. \qquad (21)$$

The last term in the right-hand side of Eq. (20) describes the effect of the external harmonic field on the resonator.

Since Eq. (20) is linear in a, below, we suppose that the electric field in the resonator has the form $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r})[\alpha \exp(-i\omega t) + A \exp(-i\omega_a t)]$, i.e., it oscillates on both the frequency of the external field ω and the resonator eigenfrequency ω_a. With this assumption, we seek the stationary solution of Eqs. (20) and (21) as a linear combination of driven oscillations and eigenoscillations of the EM field and the VMN:

$$a(t) = \alpha e^{-i\omega t} + A e^{-i\omega_a t}, \quad b(t) = \beta + B e^{-i\omega_v t}, \qquad (22)$$

where α, β, A, and B do not depend on time. Recall that we imply $\omega = \omega_a + \omega_v$. Under this condition, the nonlinear term in Eq. (20), which is proportional to ab, oscillates with the frequency of the pumping field $\omega = \omega_a + \omega_v$.

Substituting Eq. (22) into Eqs. (20) and (21) and using Eq. (6), one obtains

$$0 = -(-i\omega_v + \gamma_a)\alpha - iGN\alpha(\beta + \beta^*) - iGNAB - \frac{1}{2}i\Omega, \qquad (23)$$

$$0 = -(i\omega_v + \gamma_v)\beta - iG(|\alpha|^2 + |A|^2), \qquad (24)$$

$$0 = -\gamma_a A - iNG\alpha B^* - iNGA(\beta + \beta^*), \qquad (25)$$

$$0 = -\gamma_v B - iG\alpha A^*. \qquad (26)$$

Using the assumption $\omega_v \gg \gamma_a, \gamma_v$, one can find the amplitudes α and β up to the first order of G/ω_v:

$$\alpha \approx \frac{\Omega}{2\omega_v} + \frac{GN}{\omega_v}AB, \qquad (27)$$

$$\beta \approx -\frac{G}{\omega_v}|\alpha|^2 - \frac{G}{\omega_v}|A|^2. \qquad (28)$$

Now, we substitute solutions (27) and (28) into Eqs. (25) and (26) to obtain

$$0 = -\gamma_a A - iN \frac{G\Omega}{2\omega_v} B^* - iN^2 \frac{G^2}{\omega_v} A|B|^2 - 2iN \frac{G^2}{\omega_v} A|A|^2,$$

$$0 = -\gamma_v B - i \frac{G\Omega}{2\omega_v} A^* - iN \frac{G^2}{\omega_v} |A|^2 B. \qquad (29)$$

To determine the generation regimes, we move to new variables: the number of quanta of a VMN, $n_v = |B|^2$, the number of quanta of photons in the cavity, $n_a = |A|^2$, and the product of VMN and cavity electric field amplitudes, $s = AB$:

$$0 = -2\gamma_a n_a - iN \frac{G\Omega}{2\omega_v}(s^* - s), \qquad (30)$$

$$0 = -2\gamma_v n_v - i \frac{G\Omega}{2\omega_v}(s^* - s), \qquad (31)$$

$$0 = -(\gamma_a + \gamma_v)s - i\frac{G\Omega}{2\omega_v}(Nn_v + n_a) - iN\frac{G^2}{\omega_v}s(Nn_v + 3n_a). \qquad (32)$$

Equations (30) and (31) have a trivial solution $n_v = |B|^2 = 0$, $n_a = |A|^2 = 0$, and $s = AB = 0$. One can see that there is another solution to Eqs. (30)–(32) in which the number of cavity photons n_a, the number of quanta of molecule vibrations n_v, and the total number of photons and quanta of the VMN, $n_a + Nn_v$, have nonzero values

$$n_a = \frac{1}{4} \frac{\gamma_a + \gamma_v}{\gamma_a + 3\gamma_v} \frac{\Omega_{th}}{\gamma_a} \frac{\sqrt{\Omega^2 - \Omega_{th}^2}}{\omega_v}, \qquad (33)$$

$$n_v = \frac{1}{4N} \frac{\gamma_a + \gamma_v}{\gamma_a + 3\gamma_v} \frac{\Omega_{th}}{\gamma_v} \frac{\sqrt{\Omega^2 - \Omega_{th}^2}}{\omega_v}, \qquad (34)$$

$$n_a + Nn_v = \frac{1}{4} \frac{\gamma_a + \gamma_v}{\gamma_a + 3\gamma_v} \frac{\Omega_{th}}{\omega_v} \sqrt{\Omega^2 - \Omega_{th}^2} [\gamma_a^{-1} + \gamma_v^{-1}], \qquad (35)$$

where the threshold amplitude of the external field Ω_{th} is determined by the expression

$$\Omega_{th} = \frac{2\omega_v}{G} \sqrt{\frac{\gamma_a \gamma_v}{N}}. \qquad (36)$$

The situation is typical to the Hopf bifurcation leading to self-oscillations [46].

It should be noted that below the threshold $n_a = n_v = 0$, there are no coherent oscillations with the resonator frequency ω_a and vibrational frequency ω_v. However, there are driven oscillations with the frequency of the external field. Using Eqs. (27) and (28), these driven oscillations can be written as

$$a = \alpha e^{-i\omega t} \approx \frac{1}{2} \frac{\Omega}{\omega - \omega_a} e^{-i\omega t},$$

$$b = \beta \approx -i \frac{G\Omega^2}{4(\omega - \omega_a)^2}. \qquad (37)$$

The self-oscillating solutions in the resonator with the frequency ω_a and molecule with the vibrational frequency ω_v arise simultaneously. The dependencies of n_a and n_v on the relaxation rate γ_v at fixed γ_a, Ω, G, and N are shown in
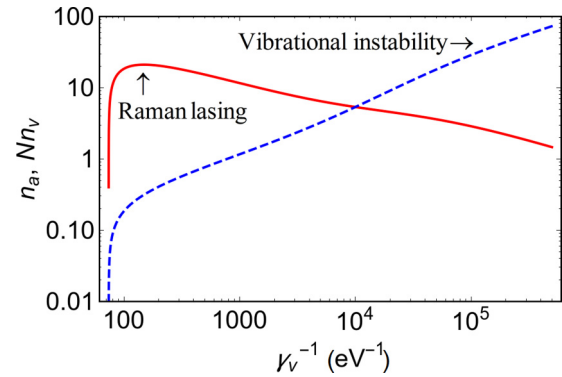

FIG. 1. The dependence of the number of photons n_a (the red solid line) and the number of quanta of a VMN n_v (the blue dashed line) on the inverse dissipation rate of VMNs γ_v^{-1}. Note that changing γ_v^{-1} implies a transition to a different physical system. $\omega_a = 2\,\text{eV}$, $\Delta = \omega_v = 0.2\,\text{eV}$, $G = 0.38 \times 10^{-3}\,\text{eV}$, $\Omega = 0.083\,\text{eV}$, and $\gamma_a^{-1} = 2 \times 10^4\,\text{eV}^{-1}$.

Fig. 1. When $\gamma_a \ll \gamma_v$, n_a is much greater than the number of quanta of a VMN n_v (Fig. 1). This corresponds to Raman lasing, in which the energy of the external field is transferred to the cavity quanta resulting in self-oscillations of the field in the cavity with the cavity eigenfrequency [15,17,19,21–23,25,27]. In the opposite case $\gamma_a \gg \gamma_v$, above the threshold, $n_a \ll n_v$ (Fig 1). This is the case of the vibrational instability observed in the experiment [10]. When the relaxation rates of photons in the cavity and vibrations of the molecule are of the same order, the EM field in the resonator and the generation molecule vibrations are weak because the function $n_a + Nn_v \propto \gamma_a^{-1} + \gamma_v^{-1}$ has a minimum at $\gamma_a = \gamma_v$. Note that γ_v is a characteristic of a molecule; therefore, in Fig. 1, by changing this parameter we, in fact, change the physical system.

Thus, according to Eqs. (33)–(35), VMN and EM field oscillations in the resonator are a unique self-oscillation process. Figure 1 provides a clear illustration of this fact. If VMNs are driven oscillations caused by the beating of the pumping and lasing fields [4], then the quality factor of the molecular subsystem cannot decrease the number of photons in the resonator. Our computer simulation shows the opposite result. The number of photons decreases with an increase in the Q factor of the VMN (see Fig. 1).

Note that below the generation threshold, without noise, Eqs. (20) and (21) predict that, in the stationary state, the number of quanta of both VMNs and photons in the resonator is zero. This is due to the fact that these equations describe only the coherent dynamics of the system. To describe incoherent radiation processes, as noted at the beginning of Sec. III, it is necessary to add noise terms $F_a(t)$ and $F_b(t)$ to Eqs. (20) and (21). The noise terms arise due to elimination of (i) the thermal reservoir of free space modes into which the resonator mode radiates and (ii) the phonon thermal reservoir of the surrounding system. The interactions with these reservoirs lead to finite linewidths of the cavity mode and vibrations in the molecule. The correlation properties of these noises are uniquely related to the dissipation rates via the fluctuation-
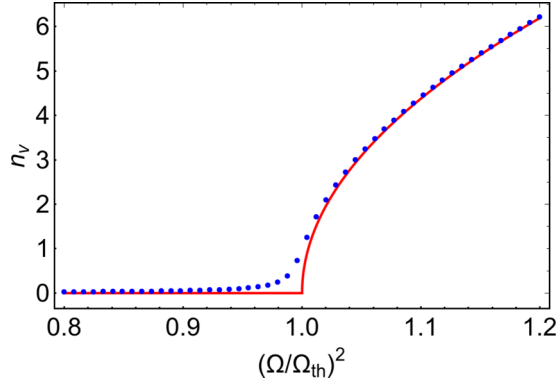
FIG. 2. The dependence of the number of generated quanta of molecule vibrations n_v on the intensity of the pump field Ω^2. The red solid line is the solution without the thermal noise of VMNs. The blue dashed line is the solution of Eqs. (39) and (40) with the thermal noise of the molecule vibrations ($n_v^{th} = 2 \times 10^{-2}$). The parameters of the system are $N = 150$, $\Delta = \omega_v$, $\omega_v = 0.1\omega_a$, $\gamma_a = 10^{-2}\omega_a$, $\gamma_v = 10^{-4}\omega_a$, and $G = 5 \times 10^{-4}\omega_v$.

dissipation theorem as follows:

$$\langle F_a(t) F_a^*(t') \rangle = 2\gamma_a \bar{n}_a^{th} \delta(t - t'),$$
$$\langle F_v(t) F_v^*(t') \rangle = 2\gamma_v \bar{n}_v^{th} \delta(t - t'), \quad (38)$$

where $\bar{n}_v^{th}$ is the number of thermal VNM quanta. Thus, Eqs. (20) and (21) take the form

$$\frac{da}{dt} = -(i\omega_a + \gamma_a)a - iNGa(b^* + b) - \frac{1}{2}i\Omega e^{-i\omega t} + F_a(t), \quad (39)$$

$$\frac{db}{dt} = -(i\omega_v + \gamma_v)b - iG|a|^2 + F_b(t). \quad (40)$$

The dependence of the number of quanta of VMNs on the pump, obtained by numerical simulation of Eqs. (39) and (40), is shown in Fig. 2. One can see that due to noise, even below the threshold, there are quanta of VMNs (Fig. 2, the blue curve). This situation is similar to the behavior of a laser below the generation threshold [46,47].

Substituting Eqs. (22) into Eqs. (39) and (40) we find the equations for the amplitude A of the resonator mode at the eigenfrequency ω_a and the amplitude B of the VMN:

$$\dot{A} = -\gamma_a A - iN\frac{G\Omega}{2\omega_v}B^* - iN^2\frac{G^2}{\omega_v}A|B|^2 - 2iN\frac{G^2}{\omega_v}A|A|^2 + F_A(t),$$

$$\dot{B} = -\gamma_v B - i\frac{G\Omega}{2\omega_v}A^* - iN\frac{G^2}{\omega_v}|A|^2 B + F_B(t). \quad (41)$$

To estimate the number of incoherent VMNs below the generation threshold, we expand the system (41) in powers of G near the equilibrium state at $G = 0$, $A_{st} = B_{st} = 0$:

$$\dot{A} = -\gamma_a A - iN\frac{G\Omega}{2\omega_v}B^* + F_A(t),$$

$$\dot{B} = -\gamma_v B - i\frac{G\Omega}{2\omega_v}A^* + F_B(t). \quad (42)$$

By considering only the linear terms in A and B, it is easy to obtain the exact solution for the average number of VMNs,
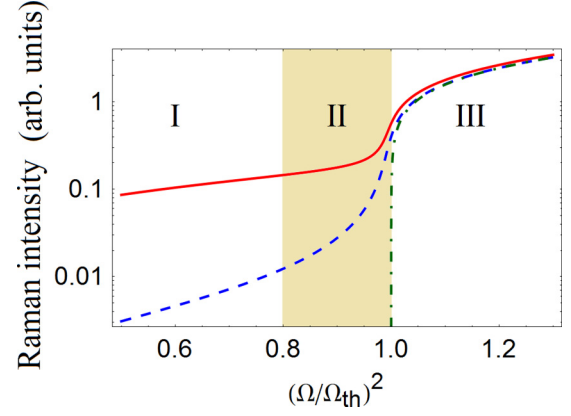

FIG. 3. The Stokes (the red solid line), and anti-Stokes (the blue dashed line) signal intensities as functions of the intensity of the coherent external field. The green dot-dashed line denotes the intensity of the emitted light in the case when noises in molecule are neglected. The parameters of the system are the same as in Fig. 2.

Since the number of thermal photons in the resonator is much smaller than those of VMNs ($\bar{n}_a^{th} \ll \bar{n}_v^{th}$) and, given Eq. (38), we arrive at the following expressions for mean number of incoherent VMN quanta, $n_v^{incoh} = \langle |B|^2 \rangle$:

$$n_v^{incoh} = \bar{n}_v^{th}\left(1 + \frac{N(G\Omega/2\omega_v)^2\gamma_a}{(\gamma_a\gamma_v - N(G\Omega/2\omega_v)^2)(\gamma_a + \gamma_v)}\right). \quad (43)$$

On can see that at zero pump intensity, when $G = 0$, the number of incoherent VMN quanta is completely determined by thermal fluctuations ($n_v^{incoh} = \bar{n}_v^{th}$). However, with nonzero pumping, there is a linear increase in the number of incoherent VMNs with the pump intensity, Ω^2 : $n_v^{incoh} = \bar{n}_v^{th}(1 + N(G\Omega/2\omega_v)^2/\gamma_v(\gamma_a + \gamma_v))$. The situation here is similar to amplified spontaneous emission (ASE) or conventional laser below the generation threshold, where the number of incoherent photons below the threshold also increases linearly with the intensity of the pumping field [43,45].

Stokes and anti-Stokes emission intensities I_S and I_{aS} are determined by the equations [10,48]

$$I_S \propto \Omega^2 L_S(n_v + 1), \quad (44)$$

$$I_{aS} \propto \Omega^2 L_{aS} n_v, \quad (45)$$

where $L_S = [(\omega - \omega_v - \omega_a)^2 + \gamma_a^2]^{-1}$ and $L_{aS} = [(\omega + \omega_v - \omega_a)^2 + \gamma_a^2]^{-1}$ are field enhancements due to the cavity resonance with the Lorentzian profiles of the Stokes and anti-Stokes signals, respectively. These intensities are shown in Fig. 3, in which three characteristic regions of the intensity of the external field can be distinguished.

In the first region, in which $\Omega^2 \ll \Omega_{th}^2$, the intensities of the Stokes and anti-Stokes signals increase linearly with the intensity of the incident field. In this region, the regime of the spontaneous Raman scattering near the plasmonic particle (ordinary SERS) is realized. In the second region, in which $\Omega^2 \sim \Omega_{th}^2$, the intensities of the Stokes and anti-Stokes signals depend nonlinearly on the intensity of the incident field. More precisely, in this region, the intensity of the anti-Stokes signal tends toward the intensity of the Stokes signal [see Eqs. (44)
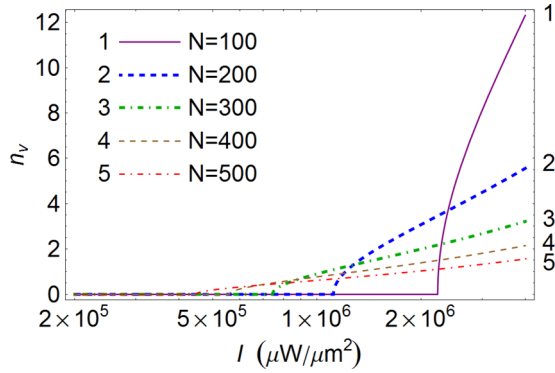
FIG. 4. Generation curves for average numbers of quanta of VMNs per molecule for different values of number of molecules N. The values of the parameters are taken from Ref. [18]: $\omega_a = 2$ eV, $\Delta = \omega_v = 0.2$ eV, $\gamma_a = 100$ meV, $\gamma_v = 0.045$ meV, and $G = 0.38$ meV. Ω is calculated by using Eq. (14) of Ref. [10].

and (45)]. This happens because the number of incoherent VMN quanta increases by the pump field. The situation is similar to ASE or a conventional laser. This is in qualitative agreement with a recent experiment on the vibrational instability [10]. Note that the interpretation of the mechanism of such nonlinearity below threshold in terms of the optomechanical Hamiltonian was discussed in Ref. [9]. In the third region, in which $\Omega^2 \geqslant \Omega_{th}^2$, the regime of the self-oscillation is realized. In this regime, the dependence of the number of VMN quanta on the pump intensity becomes nonlinear (the square-root dependence). In a sence, this regime is similar to CARS [13]. Indeed, two coherent fields, the incident field and the field of the resonator mode, whose frequency difference is equal to the eigenfrequency of the VMN, resonantly excite coherent VMN quanta. Note that there is also a significant difference from CARS: the field of the resonator mode now depends on the the pump rate.

From the equation for the average number of generated quanta of VMNs, Eq. (34), one can see that an increase in the number of molecules, N, interacting with a plasmonic structure results in two effects: (i) the decrease of the laser generation threshold and (ii) a flatter curve of the generation of VMNs per molecule, n_v. Both of these effects may help in achieving the regime the "phonon laser." The first effect

has been discussed in Ref. [10]. The second effect, as far as we know, is noted in the present paper for the first time. As one can see from Fig. 4, above the generation threshold, when the number of molecules interacting with the plasmonic particle increases, the average number of VMN quanta per molecule decreases. In the regime of the developed generation, this number may reach $n_v \sim 1$. This justifies neglecting anharmonicity even when harmonic potential (3) for VMNs for one molecule cannot be used.

IV. CONCLUSION

We consider the impact of external laser radiation on the collective dynamics of vibrations of a Raman-active molecule and oscillations of the EM field in the resonator containing this molecule. We show that, above a certain pump threshold, two different regimes of self-oscillations may be observed. The first regime, Raman lasing, requires the relaxation rate of the EM field in the resonator to be much greater than the relaxation rate of molecule vibrations, $\gamma_a \ll \gamma_v$. The second regime, the vibrational instability, is realized in the opposite limit, $\gamma_a \gg \gamma_v$ [10].

These two self-oscillation regimes have the same criterion for thresholds but different observable outcomes. The regimes are characterized by the number of quanta of the EM field and the number of quanta of oscillations in the molecule. When the relaxation rates of photons in the cavity and VMNs differ significantly, one of the regimes is realized, and the numbers of generated quanta of VMNs or of photons in the resonator are dramatically enhanced. When the relaxation rates of photons in the cavity and vibrations of the molecule are of the same order, the EM field in the resonator and the generation molecule vibrations are weak.

[1] C. V. Raman and K. S. Krishnan, Nature (London) **121**, 501 (1928).

[2] G. Landsberg and L. Mandelstam, Naturwissenschaften **16**, 557 (1928).

[3] G. Placzek, *Rayleigh-Streuung und Raman-Effekt* (Acadeische-Verlag, Leipzig, 1934).

[4] A. Penzkofer, A. Laubereau, and W. Kaiser, Prog. Quantum Electron. **6**, 55 (1979).

[5] E. Smith and G. Dent, *Modern Raman Spectroscopy: A Practical Approach* (Wiley, New York, 2019).

[6] C. L. Evans and X. S. Xie, Annu. Rev. Anal. Chem. **1**, 883 (2008).

[7] C. Flytzanis, *Quantum Electronics: A Treatise* (Academic, New York, 1975).

[8] M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg, and J. Aizpurua, Faraday Discuss. **205**, 31 (2017).

[9] P. Roelli, C. Galland, N. Piro, and T. J. Kippenberg, Nat. Nanotechnol. **11**, 164 (2016).

[10] A. Lombardi, M. K. Schmidt, L. Weller, W. M. Deacon, F. Benz, B. de Nijs, J. Aizpurua, and J. J. Baumberg, Phys. Rev. X **8**, 011016 (2018).

[11] M. Born and R. Oppenheimer, in *Quantum Chemistry: Classic Scientific Papers* (World Scientific, Singapore, 2000), p. 1.

[12] H. Fröhlich, Adv. Phys. **3**, 325 (1954).

[13] V. Y. Shishkov, E. S. Andrianov, A. A. Pukhov, A. P. Vinogradov, and A. A. Lisyansky, Phys. Rev. Lett. **122**, 153905 (2019).

[14] R. W. Boyd, *Nonlinear Optics* (Elsevier, New York, 2003).

[15] N. T. Otterstrom, R. O. Behunin, E. A. Kittlaus, Z. Wang, and P. T. Rakich, Science **360**, 1113 (2018).

[16] N. Bloembergen, Am. J. Phys. **35**, 989 (1967).

[17] J. K. Brasseur, P. A. Roos, K. S. Repasky, and J. L. Carlsten, J. Opt. Soc. Am. B **17**, 1223 (2000).

[18] G. Eckhardt, R. Hellwarth, F. McClung, S. Schwarz, D. Weiner, and E. Woodbury, Phys. Rev. Lett. **9**, 455 (1962).

[19] J.-P. M. Feve, K. E. Shortoff, M. J. Bohn, and J. K. Brasseur, Opt. Express **19**, 913 (2011).

[20] A. Grasiuk, I. Z. A. Mooradian, T. Jaeger, and P. Stokseth, in *Tunable Lasers and Applications: Proceedings of the Loen Conference* (Springer, Berlin, 1976), p. 88.

[21] J. T. Green, J. J. Weber, and D. D. Yavuz, Phys. Rev. A **82**, 011805(R) (2010).

[22] Y.-G. Han, C.-S. Kim, and J. U. Kang, IEEE Photon. Technol. Lett. **15**, 3 (2003).

[23] T. J. Kippenberg, S. M. Spillane, D. K. Armani, and K. J. Vahala, Opt. Lett. **29**, 1224 (2004).

[24] L. S. Meng, K. S. Repasky, P. A. Roos, and J. L. Carlsten, Opt. Lett. **25**, 472 (2000).

[25] L. S. Meng, P. A. Roos, K. S. Repasky, and J. L. Carlsten, Opt. Lett. **26**, 426 (2001).

[26] L. F. Mollenauer, J. C. White, and C. R. Pollock, *Tunable Lasers* (Springer, Berlin, 1992).

[27] P.-C. Peng, H.-Y. Tseng, and S. Chi, IEEE Photon. Technol. Lett. **16**, 3 (2004).

[28] Y. R. Shen and N. Bloembergen, Phys. Rev. **137**, A1787 (1965).

[29] E. J. Woodbury and W. K. Ng, Proc. IRE **50**, 2367 (1962).

[30] R. Loudon, *The Quantum Theory of Light* (Oxford University Press, Oxford, 2000).

[31] L. Droenner and J. Kabuss, in *Physics and Simulation of Optoelectronic Devices XXIII* (International Society for Optics and Photonics, 2015), p. 93570P.

[32] J. Kabuss, A. Carmele, T. Brandes, and A. Knorr, Phys. Rev. Lett. **109**, 054301 (2012).

[33] J. Kabuss, A. Carmele, and A. Knorr, Phys. Rev. B **88**, 064305 (2013).

[34] H. Köuppel, W. Domcke, and L. S. Cederbaum, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley Online Library, 1984), Vol. 57, p. 59.

[35] R. Merlin, Solid State Commun. **102**, 207 (1997).

[36] N. L. Naumann, L. Droenner, W. W. Chow, J. Kabuss, and A. Carmele, J. Opt. Soc. Am. B **33**, 1492 (2016).

[37] D. Wigger, H. Gehring, V. M. Axt, D. E. Reiter, and T. Kuhn, J. Comput. Electron. **15**, 1158 (2016).

[38] G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Krieger, Malabar, Forida, 1991).

[39] S. B. Bayram and M. V. Freamat, Am. J. Phys. **80**, 664 (2012).

[40] B. Urban and V. E. Bondybey, Phys Chem. Chem. Phys. **3**, 1942 (2001).

[41] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2007).

[42] Y. I. Khanin, *Fundamentals of Laser Dynamics* (Cambridge International, Cambridge, 2006).

[43] M. O. Scully and M. S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, 1997).

[44] Y. Feng, L. Zhang, V. R. Supradeepa, J. W. Nicholson, V. Fortin, M. Bernier, R. Vallée, M. N. Islam, G. Qin, P. S. Westbrook, K. S. Abedin, T. Kremp, S. A. Babin, S. I. Kablukov, E. A. Zlobina, E. V. Podivilov, S. R. Abdullina, Ivan A. Lobach, A. G. Kuznetsov, I. D. Vatnik, D. V. Churkin, and S. K. Turitsyn, *Raman Fiber Lasers* (Springer, New York, 2017).

[45] H. J. Carmichael, *Statistical Methods in Quantum Optics 2: Non-Classical Fields* (Springer, New York, 2007).

[46] H. Haken, *Laser Light Dynamics* (North-Holland, Amsterdam, 1985).

[47] I. V. Doronin, E. S. Andrianov, A. A. Zyablovsky, A. A. Pukhov, Y. E. Lozovik, A. P. Vinogradov, and A. A. Lisyansky, Opt. Express **27**, 10991 (2019).

[48] F. Benz, M. K. Schmidt, A. Dreismann, R. Chikkaraddy, Y. Zhang, A. Demetriadou, C. Carnegie, H. Ohadi, B. de Nijs, and R. Esteban, Science **354**, 726 (2016).