NONLINEAR SPECTROSCOPY OF HIGHLY-EXCITED
MOLECULES AND CONDENSED MEDIA

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INTRODUCTION

Optical excitation of highly-nonequilibrium states in atoms, molecules and condensed media has undoubtedly become one of the most interesting trends in modern laser physics.

Nonequilibrium states of isolated molecules selectively excited due to linear and, particularly, nonlinear laser absorption are certainly one of the most interesting subjects of modern laser chemistry.

A high optical excitation of a semiconductor surface layer results in a rapid amorphization or epitaxial regrowth of crystals.

Generally the processes mentioned above occur in subnanosecond and even in femtosecond time-scale.

A detailed understanding of their physics calls for the data of the population of levels, of the crystal structure, etc obtained in real time.

The subject of the present paper is to consider the results showing that nonlinear optical spectroscopy is an important and sometimes unique method of studying these short-lived states of substance and dynamic processes.

1. COHERENT ACTIVE (ANTI-STOKES) RAMAN SPECTROSCOPY (CARS) IN
STUDYING SELECTIVELY EXCITED MOLECULAR ENSEMBLES

1.1. Kinetics of Population Changes of Two-Photon Raman Excited Vibrational States

The subject of the research by means of CARS¹ with nanosecond time resolution as described in the present section is the ensembles of multiatomic molecules, for example, carbon dioxide (CO₂) and sulfur hexafluoride (SF₆), selectively excited into certain vibrational states. These problems are among the most important ones in vibrational laser photophysics and photochemistry as well as in physical kinetics^{2,3}.

Nonlinear optics gives an opportunity not only to examine the population exchange between the excited vibrational states using CARS⁴⁻¹⁰, but also an opportunity to provide a high selective excitation of certain vibrational modes by means of so called two-photon Raman excitation technique (TRE) in an intensive biharmonic light with specially selected frequencies ω_1, ω_2 :

$$\omega_1 - \omega_2 \approx \Omega \quad (1)$$

where Ω is the frequency of excited Raman active transition.

In CARS a biharmonic light field with frequencies satisfying (1) only couples the phases of molecular oscillators without breaking the equilibrium population distribution of vibrational states. In contrast, a biharmonic field in TRE, being much more intensive, redistributes greatly the populations of vibrational levels thus a considerable excitation of Raman active modes occurs. The condition on the intensity of biharmonic pumping components is as follows:

$$I_1 I_2 \geq I_{\text{sat}}^2 = \omega_1^3 \omega_2^2 [16 \pi^2 c^2 (d\sigma/d\omega) T_1 T_2]^{-1} \quad (2)$$

where I_{sat} is intensity of two-photon Raman saturation, T_1, T_2 are times of "longitudinal" (energy) and "transverse" (phase) relaxation of the vibrational mode under investigation, $d\sigma/d\omega$ is Raman cross section. For typical molecules (N₂, H₂, O₂, ...) at standard

pressure, I_{sat} has the order of $0.1 - 1 \text{ GW/cm}^2$. In our experiments we succeeded in effective inducing vibrational and rotational excitation in molecules SF_6 , CO_2 , H_2 by means of TRE⁸. Up to 40% of the molecules could be excited. The nonlinear-optical method of a selective deposition of energy into a certain vibrational mode due to TRE is an alternative to another well-known method of excitation of molecular vibrations due to resonante one-photon absorption of infra-red radiation which frequency coincides with frequency of an excited transition. Selection rules are responsible for the difference between these methods: in the first case dipole inactive (but Raman allowed) modes are excited, in the second case, vice versa, IR-active transition (and, as a rule, forbidden in Raman scattering) are excited.

We used the combined TRE - CARS technique to study a vibrational exchange and channels of "thermalization" of energy selectively deposited into totally symmetric excited states 10^0_0 and 02^0_0 in CO_2 molecule. (They can't be selectively populated from the ground state by resonant IR absorption because of the "alternative ban" mentioned above.) Although the kinetics of the "collisional" population and deactivation of the upper laser level $\text{CO}_2(00^0_1)$ is well established the corresponding data for either of the two low laser levels, $\text{CO}_2(10^0_0)$ and $\text{CO}_2(02^0_0)$ has been known by the beginning of our study in 1982 with a considerably less accuracy just because of the difficulties connected with their selective population.

Using TRE - CARS we discovered the absence of "kinetic manifestation" of Fermi resonance between states $\text{CO}_2(10^0_0)$ and $\text{CO}_2(02^0_0)$ ^{8,9}. In striking contrast to the generally accepted but not experimentally confirmed views, the population exchange between these states appeared to occur very slowly, with the rate constant being less than $7 \cdot 10^4 \text{ s}^{-1} \text{ Torr}^{-1}$. Figure 1 shows the most effective

FIGURE 1 The most effective channels (wavy lines, revealed by CARS) of energy (and population) transfer from the states $\text{CO}_2(10^0 0)$ (a) and $\text{CO}_2(02^0 0)$ (b), selectively populated from the ground state $\text{CO}_2(00^0 0)$ by TRE technique.

channels of energy relaxation from states (10^0_0) and (02^0_0) into other modes of this molecule, determined by TRE-CARS.

1.2. Local CARS-Thermometry of Vibrationally-Excited Molecular Gases

CARS spectroscopy brings much new to the study of energy processes in molecular ensembles subjected to selective multiple-photon excitation (MPE) through IR-active modes by a strong IR resonant radiation. The most complete data currently available concern gas SF_6 resonantly excited by CO_2 laser radiation. Relaxation diagnostics is carried on by means of CARS technique. A variable time delay can be easily introduced between the pulse inducing MPE and the probing pulses. Thus, it is possible to obtain the necessary data at various stages of excitation and relaxation of high vibrational states of the studied molecules. For the first time this technique (MPE-CARS) was reported by us in paper⁴, then it was successfully used in the experiments of Lebedev Institute group⁵.

The recent papers on this subject were reviewed by S. S. Alimpiev at our seminar. Thus, I do not intend to delve on them in detail, I'd like to stress the fact that equilibrium Boltzmann distribution of vibrational level populations has proved to be very fast in collisional regime, namely in the order of $1\ \mu\text{sec}$ at pressure 1 Torr, or even faster in the vibrational subsystem of SF_6 molecule. It undoubtedly is identical to the distribution occurring in the molecule as a result of an ordinary thermal heating when it receives the same energy as in the process of excitation by MPE technique.

When SF_6 gas is heated, the transformation of its CARS spectrum can be calculated by the direct summation of individual contributions of all possible Raman-active transitions "starting" from the populated ro-vibrational levels, into a coherent signal, taking into account the Boltzmann distribution^{7,10}. In Figure 2

FIGURE 2 Calculated (solid lines) and experimentally determined (dots) dependences of the frequency shift of the Q-bands of totally symmetric (ν_1) and doubly degenerated (ν_2) modes of SF_6 molecules on the temperature of the gas.¹¹

solid lines indicate the calculated temperature dependences of peak locations of CARS spectra of totally symmetric ν_1 and doubly degenerated ν_2 normal modes of SF_6 molecular gas.

The dots show the experimental results with the thermally heated gas. A good correlation is obvious, though the ro-vibrational spectra and the corresponding calculations are exclusively complicated.

CARS also allows to carry on the local thermometry of gas samples, transiently heated, for example, when the shock wave travels in the gas. Figure 3 shows the time evolution of the CARS signal from nitrogen molecules in air when a strong shock wave caused by the breakdown of gas near the metal target by the 3 J pulse of TEA CO_2 laser propagated through the volume of probing (that is 0.25 mm away from the target as shown in Figure 3). It is not only possible to detect the presence of shock wave but also to

FIGURE 3 The influence of the shock wave propagation in air on the CARS signal from nitrogen molecules. One can easily see the variation of the CARS intensity with the time delay, τ , between the pulse, causing air breakdown, and probing pulse, as shock wave travels through the probing volume (see insert for details of the experimental conditions).

measure its velocity and other parameters¹².

2. OPTICAL NONLINEARITY OF LASER PLASMA

Until recently optical nonlinearities of homogeneous plasma were thought to be small since they are due to the relatively small Lorentz and hydrodynamic nonlinearities. In view of this fact nonlinear-optical methods of plasma diagnostics have not been considered to be promising, and there have been practically no experiments on the study of nonlinear optical plasma response (except¹⁴). At the same time there are many theoretical papers on this subject (see¹⁵ and the references given there).

We managed to find experimentally that the optical nonlinearity of plasma created by laser breakdown of gases is, in contrast, relatively large and possesses a number of puzzling properties¹⁹.

In the experiment, plasma was created by the laser breakdown

FIGURE 4 The enhancement of "non-resonant" CARS signal from air in the presence of the target-assisted laser breakdown as a function of time delay between CO_2 laser pulse (initiating the gas breakdown) and a pair of pulses, used for CARS probing.

of the gas in the vicinity of a metal target. The breakdown was produced either by a Q-modulated Nd:Yag laser with pulse energy of up to 0.5 J or by a TEA CO_2 laser pulse with energy up to 3 J. The CARS signal ($\omega_a = 2\omega_1 - \omega_2$) was studied when $\omega_1 - \omega_2$ did not coincide with any frequency of neutral molecular resonances, i.e. when the anti-Stokes signal from the neutral gas was generated by "nonresonant" electron gas susceptibility, $\chi^{(3)\text{NR}}$. As plasma was created, the intensity of the "nonresonant" signal I_{CARS}^P sharply increased, see Figure 4.

The enhancement of the CARS signal in the presence of a laser breakdown was found to have the universal character: it was observed both in molecular (SF_6 , O_2 , N_2 , CO_2) and atomic (Ar) gases at the atmospheric or at higher pressure; in the self-breakdown of a gas (i.e. in case of initiating a breakdown by one of the beams used in CARS scheme) as well as in a spark caused by an independent laser source (irrespective of this source wavelength, $\lambda = 1.06 \mu\text{m}$ or $\lambda = 10.6 \mu\text{m}$); in a "free spark" occurring directly in the gas, or in a breakdown near metal or dielectric targets and even in case of a breakdown in the vapours of a metal target placed into a evacuated volume.

Nonlinear-optical plasma response proved to possess a slight frequency dependence, decreasing a little both at $|\omega_1 - \omega_2| \rightarrow 0$ and at $(\omega_1 - \omega_2)/2\pi c \gtrsim 3000 \text{ cm}^{-1}$, but still easily detectable at frequency detuning as large as $(\omega_1 - \omega_2)/2\pi c \approx 8000 \text{ cm}^{-1}$. Even the enhancement of third harmonic generation in the presence of laser breakdown of a gas has been experimentally observed, although the net enhancement was not so greatly pronounced as in the case of CARS-type mixing process.

We are leaning now towards describing the observed effect in terms of self-focusing of the probing beams due to ponderomotive forces¹⁵, which become especially high when the difference frequency, $\omega_1 - \omega_2$, is tuned to the frequency of Langmuir's oscillations of a plasma, Ω_p :

$$\Omega_p = (4\pi N e^2 / m)^{1/2} \quad (3)$$

where N is the electron density, e and m are electron charge and mass, respectively.

At a complete single-fold ionization of a gas at atmospheric pressure, $\Omega_p/2\pi c = 1650 \text{ cm}^{-1}$. The absence of well-pronounced frequency dependence of the effect in the vicinity of Ω_p can be ascribed to the high degree of inhomogeneity and nonstationarity

of real laser-produced plasma. A small enhancement (up to 10 times) of the CARS intensity have been experimentally observed also in a plasma created by electric discharge with electron density not more a few times 10^{17} cm^{-3} , 30 μsec after the leading front of the discharge.

It is also possible to study the nonlinear optical response of ionic component of a plasma.

3. NONLINEAR-OPTICAL DIAGNOSTICS OF A STATE AND OF FAST LASER-INDUCED PHASE TRANSFORMATIONS OF A SEMICONDUCTOR SURFACE

3.1. Harmonic Generation in Reflection

Methods of optical spectroscopy have been playing an important role in the study in "real time" of processes, occurring in a pulsed laser annealing (PLA) of semiconductor surfaces and other laser-induced phase transformations of a solid surface (see, for example,¹⁶). Nonlinear-optical methods have gained recently even greater significance. The latter are extremely informative, local, fast and, which is the most important, they supply inaccessible by other optical methods structural information of the processes occurring on the surface^{16,17}.

In the recent papers^{17,18} carried out in our laboratory the phenomenon of second harmonic generation (SHG) at the reflection from a noncenter-symmetrical GaAs crystal was applied to study the dynamics of pulsed laser annealing (PLA) in nanosecond time-scale.

The essence of the effect used consists in the following: the surface layer of a crystal as a result of melting under PLA (or as a result of amorphization in the condition of ion bombarding used for ion implantation) becomes center-symmetrical and thus makes no dipole contribution to the reflected SH. Crystal lattice regrowth in the course of PLA causes the SH reflected wave of probing incident on the studied surface with a small variable time delay with respect to the annealing pulse. Measuring the intensity

of this SH as a function of the time delay allows to study the dynamics of melting and the following fast recrystallization of the sample surface during PLA. Analysing polarization characteristics of SH allows to obtain information of the regrown crystal lattice quality after PLA as well as of the degree and character of the surface amorphization before laser annealing.

Soon after publishing our first results on SHG in GaAs¹⁷ there appeared a number of papers²⁰ considering SHG in reflection from silicon crystal possessing the center of inversion due to the presence of quadrupolar second-order nonlinear polarization (see below) in the conditions close to PLA. The effect was (apparently by mistake) interpreted in the terms of varying local symmetry of the subsurface layers of a crystal (before its melting) and of generating Frenkel's excitations. Shank and others²¹ using the data obtained by Tom and others²² correctly interpreted SHG in Si as a consequence of the quadrupole nonlinearity. They used this effect for the diagnostics of the Si surface structural changes at the initial PLA stage-melting the surface layer-in femtosecond time scale.

3.2. Nonlinear Surface Source of Reflected Optical Harmonics

To describe the phenomena of second (SHG) and third (THG) harmonic generation and that of sum (SFG) and (or) difference (DFG) frequencies under reflection from the surface of a solid we shall introduce, as is conventional in nonlinear optics, the nonlinear polarization of a surface part of a medium induced by incident fields in the form of power series taking into account dipole and quadrupole contributions:

$$P_i^{NL} = P_i^{(2)} + P_i^{(2)S} + P_i^{(3)} + P_i^{(3)S} + \dots \quad (4)$$

where

$$P_i^{(2)} = P_i^{(2)D} + P_i^{(2)Q} = \chi_{ijk}^{(2)D} E_j E_k + \chi_{ijkl}^{(2)Q} E_j \nabla_k E_l \quad (5)$$

- bulk second-order and

$$P_i^{(3)} = P_i^{(3)D} + P_i^{(3)Q} = \chi_{ijkl}^{(3)D} E_j E_k E_l + \chi_{ijklm}^{(3)Q} E_j E_k \nabla_l E_m \quad (6)$$

- third-order nonlinear susceptibilities of dipole (D) and quadrupole (Q) types, and

$$P_i^{(2)S} = \chi_{ijk}^{(2)S} E_j E_k \quad (7)$$

$$P_i^{(3)S} = \chi_{ijkl}^{(3)S} E_j E_k E_l \quad (8)$$

- analogous surface polarization terms taking into account dipole contributions only (see, for instance, ²³). Identical indexes in eqs. (5)-(8) imply summation from 1 to 3. The symmetry and structure of the tensors of nonlinear susceptibilities $\chi_{ijk}^{(2)D}$, $\chi_{ijkl}^{(2)Q}$, $\chi_{ijkl}^{(3)D}$, $\chi_{ijklm}^{(3)Q}$, ... are determined by the point symmetry group of the crystal in the bulk, and those of the surface susceptibilities $\chi_{ijk}^{(2)S}$ and $\chi_{ijkl}^{(3)S}$ - by the symmetry of corresponding surface subgroup of the crystal point group.

In cubic crystals with the center of inversion of class m3m (which Si and Ge crystals belong to) and isotropic media expression (5) can take the following vector form:

$$P_i^{(2)Q} = \beta E_i (\vec{\nabla} \vec{E}) + \gamma \nabla_i (\vec{E} \vec{E}) + (\delta - \beta - 2\gamma) (\vec{E} \vec{\nabla}) E_i + \chi_{Qij} E_i \nabla_j E_i; \quad (9)$$

$$P_i^{(2)D} = 0;$$

where

$$\beta = \chi_{1122}^{(2)Q}, \quad \gamma = \frac{1}{2} \chi_{1212}^{(2)Q}, \quad \delta - \beta - 2\gamma = \chi_{1221}^{(2)Q} \quad \text{and}$$

$$\chi_{Qij} = \chi_{1111}^{(2)Q} - (\chi_{1122}^{(2)Q} + \chi_{1212}^{(2)Q} + \chi_{1221}^{(2)Q})$$

- anisotropy parameter of quadrupole nonlinearity (in linear optics these crystals are isotropic); in isotropic media $\chi_Q = 0$.

In cubic crystals of class $\bar{4}3m$ lacking the center of inversion (semiconductors GaAs, GaP, and others belong to them) there is a dipole contribution to second-order polarization, as there is a nonvanishing component $\chi_{123}^{(2)D}$ of the tensor of the second order nonlinear susceptibility (other components of $\chi_{ijk}^{(2)D} \neq 0$ can be obtained from $\chi_{123}^{(2)D}$ by permutation of indexes).

3.3. Studying Structural Changes of the Surface by SHG and SFG

The crystalline anisotropy of class $m\bar{3}m$ and $\bar{4}3m$ crystals which are isotropic from the point of view of linear optics, manifests itself in the dependence of the intensity of the reflected SH and other nonlinear signals upon the crystal orientation with respect to the probe radiation plane of incidence i.e. upon angle ψ .

In this case the symmetry of $I_{SH}(\psi)$ dependence reflects the local symmetry of the crystal surface, from which reflection occurs.

In particular, melting the surface layer of noncenter-symmetrical crystal GaAs subjected to PLA results in forming center-symmetrical liquids giving no dipolar SH at all.

The structural change of GaAs surface subjected to ion-implantation by fast ions results in a partial or even complete loss of the far order in the crystal lattice, i.e. in the amorphization of the surface layer. This is easily observed by SHG: SH efficiency decreases in the course of reflecting from the amorphous section¹⁸. Nonlinear-optical technique of the surface state probing is proved in this case to be much more sensitive to small implantation doses than the traditionally used for these purposes methods¹⁸.

The structure of partially amorphous GaAs surface, as our polarizational measurements by means of SHG and SFG have shown, retains the main symmetry elements of the initial crystal lattice,

FIGURE 5 Sum-freequency generation (SFG) in reflection from (100) GaAs surface as a technique for the characterization of the presence of a thin amorphized layer caused by a picosecond UV pulsed irradiation. The SFG intensity is shown as a function of the sample displacement across the focused probe laser beam.

i.e. amorphization under ion implantation occurs in "spots" surrounding the trace of a fast particle, whereas the rest of the surface remains unchanged.

GaAs surface amorphization can also be carried out by means of laser radiation. For example the action of strong enough pulse of the fourth harmonic of picosecond Nd:YAG laser on the (100) GaAs surface results in forming a thin amorphous film (thickness $d = 15$ nm) either in the center or in the periphery of the irradiated spot. This film was discovered in our SFG experiments: $\omega_{SF} = 2\omega + \omega$, where ω , 2ω are the fundamental and second harmonic frequencies of Nd:YAG probing laser (see Figure 5).

"Quadrupole" SH generation in reflecting from the plane (111) of a center-symmetrical silicon crystal in the course of PLA was used by Shank and others to register directly the surface melting with time resolution of 100 fsec.²¹

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