

Characteristics of the rotational structure of vibrational $\nu_1(a_1)$ states of tetrahedral molecules

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The method of coherent anti-Stokes Raman scattering (CARS) spectroscopy was used to record high-resolution spectra of the $\nu_1(a_1)$ vibrational states of the CH_4 , CD_4 , and GeH_4 molecules. An analysis was made of the characteristics of the rotational structure and theoretical models of the structure were discussed allowing for the interaction of the state ν_1 with the nearby vibrational states.

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§1. INTRODUCTION

Two trends are noticeable in the current stage of experimental and theoretical investigations of isolated simple molecules in gaseous media: studies are being made of exotic nonclassical molecules, for example KrF_2 or KCN , in order to obtain the initial data on their structure and properties in their ground energy states and further investigations are being made of classical molecules such as H_2 , CO_2 , CH_4 , SF_6 , etc. with the aim of describing particularly their excited states.

The main difficulties in both types of investigation is the high density of the energy levels which makes it difficult to interpret the results, to carry out theoretical analyses, and to use them later. A natural simplifying approach in the studies of excited states is the allowance for the symmetry of the molecular system under consideration, which makes it possible to study independently certain sets of states. The greatest simplifications due to symmetry can be achieved in the case of spherical top molecules.

A theoretical analysis of the structure of the vibrational-rotational states of spherical top molecules can now be carried out in a variety of ways.¹⁻⁸ The most consistent formalism suitable for the description of the rotational structure of any group of vibrational states was developed by Moret-Bailly *et al.*^{1,2,5,6,9,10} Further development of theoretical models requires the use of experimental data on changes in the rotational structure due to transition from an isolated vibrational state to a set of interacting vibrational states. Such information is easiest to obtain by comparison of similar molecules exhibiting changes in the relative positions of the vibrational states. A characteristic example of such a change in the structure of the vibrational states is the mutual approach of the vibration frequencies ν_1 and ν_2 of the XY_4 -type tetrahedral molecules when the central atom X becomes heavier than the atom of Y . This tendency is due to weak coupling of the valence and deformation vibrations and it has the result that in the case of heavy molecules an independent analysis of the states ν_1 and ν_2 is inconvenient, particularly in the case of high rotational quantum numbers.

Attempts to investigate experimentally the ν_1 band of tetrahedral molecules have up to now been unsuccessful

because direct vibrational-rotational transitions to the state ν_1 from the ground state are forbidden and well-developed high-resolution infrared spectroscopy methods¹¹ are inapplicable. Raman transitions are allowed only between the states with $\Delta J = 0$ (Q branch of the Raman scattering spectrum). Since the spectra of the Q branches lie within a narrow frequency range $\sim 1-10 \text{ cm}^{-1}$, the only method for investigating the rotational structure of the vibrational state ν_1 is high-resolution Raman spectroscopy. However, the sensitivity of the traditional spontaneous Raman spectroscopy methods can at best be used to record spectra of gases with a resolution not exceeding 0.1 cm^{-1} (Ref. 12). The recent progress in the development of tunable lasers has been responsible for the appearance of new coherent methods which are capable providing a resolution in Raman spectra limited only by the Doppler broadening.

§2. EXPERIMENTAL COHERENT RAMAN SPECTROSCOPY METHODS

The main coherent Raman spectroscopy methods are stimulated amplification (attenuation) due to the scattering, optical Kerr effect induced by a Raman resonance, and coherent anti-Stokes Raman scattering (CARS). A general feature of these methods is the action on the investigated molecules of biharmonic pumping from coherent laser sources emitting at frequencies differing by an amount which can be varied and which can be tuned to the frequency of the investigated vibrational-rotational transition.

This ensures predominance of the resonance effects in the interaction of the field with molecules in the investigated medium. Depending on the frequency difference $\nu_1 - \nu_2$ of the frequencies of the pump waves, an analysis is made of the following features: a change in the intensity of one of the pump components in the stimulated amplification (attenuation) method,^{13,14} a change in the state of polarization of the pump radiation in the optical Kerr effect induced by Raman scattering,¹⁵ and the intensity or polarization of the anti-Stokes signal resulting from parametric mixing in the CARS method.¹⁶⁻¹⁸ The spectral resolution of each of these methods is governed by the widths of the lines emitted by lasers.

Resolved Raman spectra of the ν_1 vibrations of tetrahedral molecules were obtained by us using the CARS method. The CARS process involves parametric mixing, due to the cubic nonlinearity of the investigated medium, of coherent pump waves of frequencies ν_1 and ν_s , the result of which is coherent radiation at the frequency $\nu_{as} = 2\nu_1 - \nu_s$. The dependence of the intensity of this radiation on the tunable frequency ν_s or on the difference $\nu_1 - \nu_s$ is recorded and this dependence represents the dispersion of the square of the modulus of the component $\chi_{1111}^{(3)}$ ($-\nu_{as}, \nu_1, \nu_1, -\nu_s$) of the cubic nonlinear susceptibility tensor.

The susceptibility dispersion near the frequencies of vibrational-rotational transitions from the ground state of a molecule, allowed in the Raman spectra, has the following form in the case of homogeneous broadening:

$$\chi_{1111}^{(3)} \propto \frac{1}{\sum_j g_j \exp(-E_j^0/kT)} \sum_{j,m} \left(\frac{d\sigma}{d\omega} \right)_{j,m} \frac{g_j \exp(-E_j^0/kT)}{(\nu_{j,m} - (\nu_1 - \nu_s)) - i\Gamma_{j,m}/2}, \quad (1)$$

where E_j^0 are the rotational energies in the ground vibrational state; $(d\sigma/d\omega)_{j,m}$, $\nu_{j,m}$, and $\Gamma_{j,m}$ are, respectively, the cross sections, frequencies, and homogeneous widths of the transition lines; g_j is the statistical weight of the j -th rotational state; T is the rotational temperature.

The nonresonance contribution to the susceptibility due to distant vibrational and electronic transitions is ignored in Eq. (1) because in the case of strong lines of gases this contribution is between three and five orders of magnitude less than the resonance contribution. The physical principles and characteristics of the CARS spectroscopic method are discussed in greater detail in Refs. 12 and 18.

We constructed a high-resolution CARS spectrometer with an automated data acquisition and analysis unit. We used it to investigate the Raman spectra of vibrational-rotational transitions in molecules. The pump sources were single-frequency lasers with high amplitude and frequency stability. The instrumental resolution of the spectrometer was 0.001 cm^{-1} . Continuous tuning of the pump frequency ν_s was possible in the range $0-12 \text{ cm}^{-1}$. A detailed description of the spectrometer was given in Refs. 19 and 20.

§3. SPECTRA OF THE Q BRANCH OF ν_1 (a_1) VIBRATIONS OF TETRAHEDRAL CH_4 , CD_4 , AND GeH_4 MOLECULES

According to the theory of the rotational spectra of isolated vibrational states of tetrahedral molecules of the XY_4 type, which allows for the flexibility of these molecules, the rotational levels with a specific total momentum J split into sublevels of different types of symmetry corresponding to vibrational-rotational wave functions with statistical weights depending on nuclear spins. In the case of a totally symmetric vibrational state the effective rotational Hamiltonian can be written in the form

$$H = \sum_{\alpha, \beta, \gamma} t^{\alpha(\beta, \gamma)} R^{\alpha(\beta, \gamma)}, \quad (2)$$

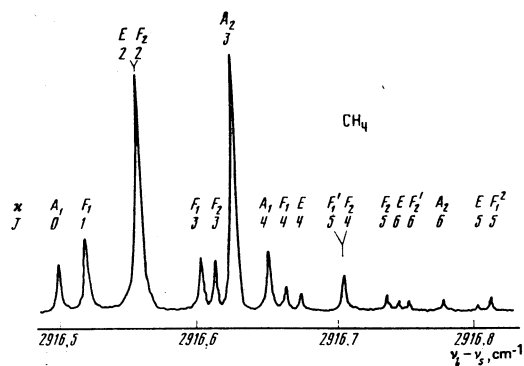


FIG. 1. Spectrum of the Q branch of the ν_1 vibration of the CH_4 molecule with a completely resolved structure ($P = 0.5 \text{ Torr}$, $T = 80 \text{ }^\circ\text{K}$).

where $R^{\alpha(\beta, \gamma)}$ is the effective rotational operator of degree Ω and rank K ; $t^{\alpha(\beta, \gamma)}$ is an empirical parameter. The notation is the same as that adopted in Ref. 5. The order of smallness of terms in the expansion (2) is governed by the degree Ω relative to elementary rotational operators. A good convergence of the expansion (2) demonstrates that the vibrational state is isolated. In the more general case we can easily go over from a Hamiltonian of the type (2) to an effective Hamiltonian for a set of degenerate or quasidegenerate states (see Ref. 5 and also the discussion in §4).

Including in the expansion (2) the fourth-rank tensors and retaining only the diagonal parts of the sixth-rank tensors, we find that the rotational energies in the state ν_1 are^{3,4}

$$E(J, \kappa) / hc = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + [D_t + H_t J(J+1)] f(J, \kappa) + H_6 g(J, \kappa), \quad (3)$$

where the coefficients $f(J, \kappa)$ and $g(J, \kappa)$ are tabulated in Refs. 3 and 4.

Since the Raman transitions of interest to us are allowed only between the states of the same type of symmetry and with the same rotational momentum, the ex-

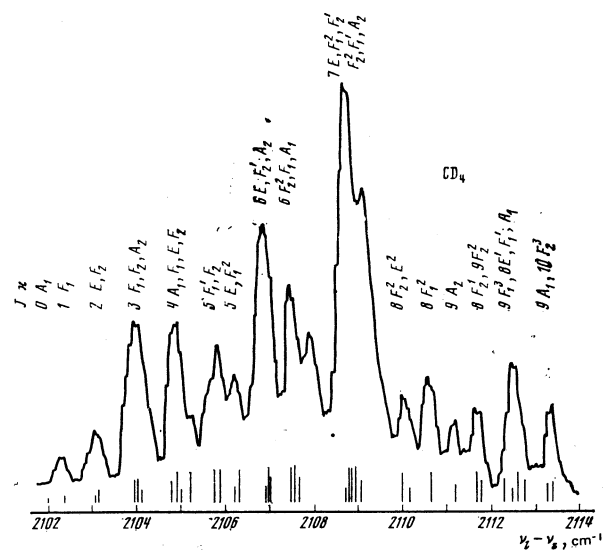


FIG. 2. Spectrum of the Q branch of the ν_1 vibration of the CD_4 molecule ($P = 1 \text{ atm}$, $T = 293 \text{ }^\circ\text{K}$).

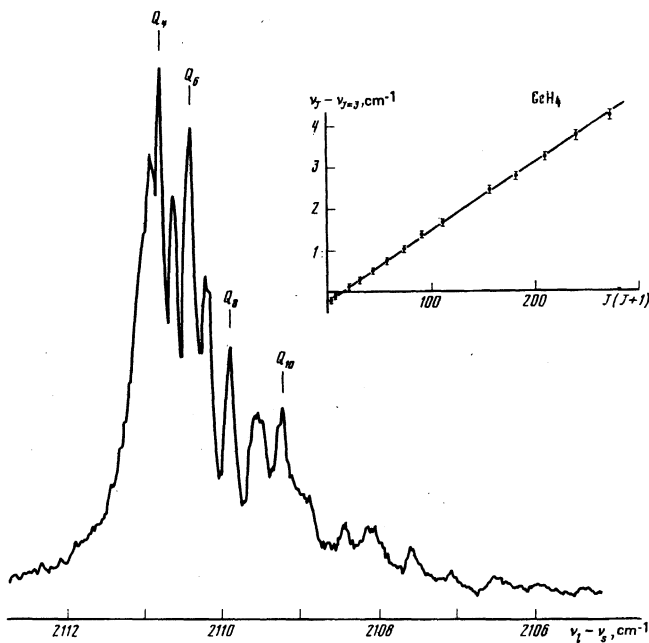


FIG. 3. Spectrum of the Q branch of the ν_1 vibration of the GeH_4 molecule. The inset shows the dependence of the frequency positions of the J lines on the value of $J(J+1)$ ($P=1$ atm, $T=293^\circ\text{K}$).

pression for the transition frequencies deduced from Eq. (3) is

$$\nu_{j, \kappa} = \nu_i - \alpha J(J+1) - \beta J^2(J+1)^2 + \gamma J^3(J+1)^3 + [\beta_t + \gamma_t J(J+1)]f(J, \kappa) + \gamma_{6t} g(J, \kappa), \quad (4)$$

where the parameters $-\alpha$, β , β_t , γ , γ_{4t} , and γ_{6t} represent increments in the rotational constants B , D , D_t , H , H_{4t} , and H_{6t} in the upper vibrational state.

We investigated experimentally the CH_4 , CD_4 , and GeH_4 molecules. We record resolved CARS spectra of the Q branches of the $\nu_1 = 2916.5 \text{ cm}^{-1}$ vibration of the CH_4 molecule²¹ (Fig. 1), of the $\nu_1^{\text{max}} = 2108.9 \text{ cm}^{-1}$ vibration of the CD_4 molecule²² (Fig. 2), and of the $\nu_1^{\text{max}} = 2110.6 \text{ cm}^{-1}$ vibration of the GeH_4 molecule²³ (Figs. 3 and 4). The individual lines in the resolved spectra represented transitions between different tetrahedral sublevels of the lower and upper vibrational-rotational states.

In the CH_4 and CD_4 molecules we were able to identify the lines and to describe their frequencies suf-

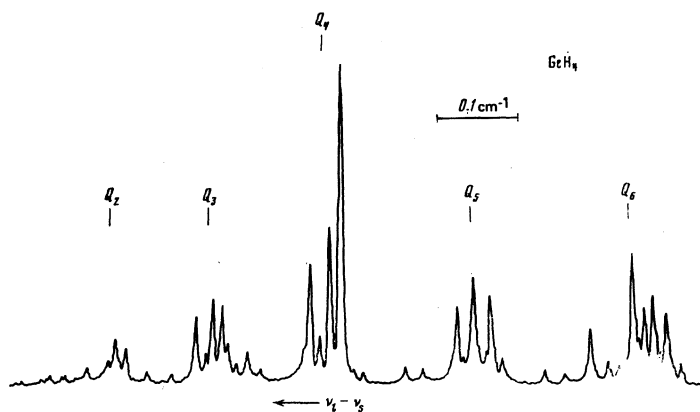


FIG. 4. Spectrum of the Q branch of the ν_1 vibration of the GeH_4 molecule ($P=20$ Torr, $T=170^\circ\text{K}$).

TABLE I.

Rotational parameter	Numerical value, cm^{-1}	
	CH_4	CD_4
B_0	5.2410356 ± 0.0000096	2.63264 ± 0.00013
α	$-(1.023 \pm 0.033) \cdot 10^{-2}$	-0.190 ± 0.017
D_0	$(1.10864 \pm 0.00074) \cdot 10^{-4}$	$(2.74 \pm 0.15) \cdot 10^{-5}$
β	$(6.23 \pm 0.64) \cdot 10^{-5}$	$(2.57 \pm 0.27) \cdot 10^{-3}$
H_0	$(5.78 \pm 0.18) \cdot 10^{-9}$	—
γ	$(3.77 \pm 0.39) \cdot 10^{-7}$	$(2.37 \pm 0.13) \cdot 10^{-3}$
D_0^0	$(4.4252 \pm 0.0070) \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
β_t	$(4.097 \pm 0.090) \cdot 10^{-5}$	$(4.10 \pm 0.13) \cdot 10^{-4}$
H_{4t}^0	$-(5.40 \pm 0.39) \cdot 10^{-10}$	—
γ_{4t}	$-(2.09 \pm 0.11) \cdot 10^{-7}$	$-(7.40 \pm 0.17) \cdot 10^{-6}$
H_{6t}^0	$(3.63 \pm 0.15) \cdot 10^{-10}$	—
γ_{6t}	$-(1.004 \pm 0.051) \cdot 10^{-7}$	$-(1.133 \pm 0.067) \cdot 10^{-6}$

ficiently accurately with the aid of relationships of the (4) type. The calculated parameters in the dependences (4) are listed in Table I. This table includes also, for the sake of comparison, the experimental values of the rotational constants of the ground state of CH_4 (Ref. 24) and CD_4 (Ref. 25). It should be noted that the parameters for methane agreed, within the limits of the errors, with the results of Ref. 26 obtained by the method of stimulated amplification of the Stokes component of biharmonic pumping.

It is worth noting the following features of the results obtained. Firstly, the majority of the parameters under discussion exceed (sometimes by one to three orders of magnitude) the corresponding constants of the ground state and, therefore, cannot be regarded as small increments to the latter. Secondly, the quantity α , introduced as an increment in the rotational constant B_0 is small compared with B_0 but it is positive, whereas in the state corresponding to a totally symmetric valence vibration the value of B should decrease because of an increase in the moment of inertia of the molecule.

The structure of the Q branch of the ν_1 vibration of the GeH_4 molecule does not show the tetrahedral splitting equally clearly and the characteristic lines in the fully resolved spectra (Fig. 3) clearly represent all the sets of transitions between the states with identical values of J . The average frequency positions of the J lines are described sufficiently accurately by the dependence $\nu_j = \nu_1 - \alpha J(J+1)$ with the parameter $\alpha = (1.70 \pm 0.03) \cdot 10^{-2} \text{ cm}^{-1}$. In contrast to CH_4 and CD_4 , the tetrahedral splitting of the J lines in the resolved spectra (Fig. 4) cannot be described by relations of the (4) type even for low values of J .

These features of the spectra of the investigated tetrahedral molecules are due to the interaction of the state ν_1 with the neighboring vibrational states, which may result either in considerable changes in the physical meaning of the parameters in the expansion (3) or may invalidate this expansion. We have pointed out earlier the need to allow for interactions such as the Fermi and Coriolis resonances between nearby states $2\nu_2$, $2\nu_4$, $\nu_2 + \nu_4$, and ν_3 in correct interpretation of the structure of the vibrational-rotational spectra of tetrahedral molecules and analysis of the spectral data.^{5,7} Reports have recently been published of the first attempt to use the relevant operators in a quantitative analysis of the structure of the sets of states $\{\nu_1, 2\nu_2, 2\nu_4, \nu_2 + \nu_4\}$ of the CH_4 molecule (Ref. 27) and $\{\nu_1, \nu_3\}$ of the SiH_4 molecule (Ref. 28).

§4. DISCUSSION OF RESULTS

We shall now consider the characteristics of the spectra of the investigated molecules. The relative positions of the vibrational states of CH_4 , CD_4 , and GeH_4 are shown in Fig. 5. In the case of the methane molecule a sufficiently detailed theoretical analysis has been made⁶ for a large set of vibrational states $\{\nu_1, 2\nu_2, 2\nu_4, \nu_2 + \nu_4, \nu_3\}$ but these calculations have not been based on the recently obtained data on the ν_1 transitions. A full quantitative analysis of the ν_1 state of methane can now be made allowing simultaneously for all the states in this set.

The most important operators of the interaction between the state ν_1 and the nearby states are

$$V_{1,22}^{(A_1, A_1)}, \quad V_{1,11}^{(A_1, A_1)}, \quad (5)$$

describing purely vibrational interactions of the Fermi resonance type with the states $2\nu_2$ and $2\nu_4$. The operator

$$V_{1,3}^{(A_1, F_2)} \times R^{(2, F_2)} \quad (6)$$

of the Coriolis interaction of the vibrational states ν_1 and ν_3 of methane can be regarded as of higher order than the Fermi interaction because the distance between the interacting vibrational states is in both cases of the same order of magnitude, whereas the Coriolis interaction operator is of a higher order. On the other

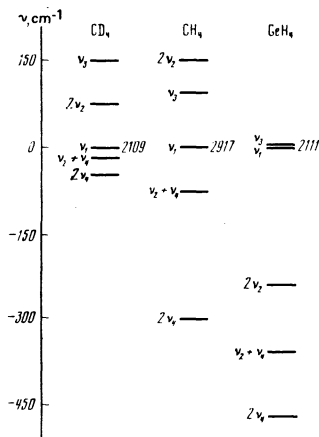


FIG. 5. Vibrational levels near the ν_1 vibrational state of the CH_4 , CD_4 , and GeH_4 molecules.

hand, the Coriolis interaction of the states $2\nu_2$ and $2\nu_4$ with $\nu_2 + \nu_4$ is described by the operator

$$V_{2,4}^{(E, F_2)} \times R^{(1, F_2)}, \quad (7)$$

which is of the same order as the operators (5) for the Fermi interaction. Partial allowance for these interaction operators in the interpretation of the ν_1 band of methane is made in Ref. 27.

Interactions of the same type, described by the operators (5)–(7) should also dominate interpretation of the ν_1 band of CD_4 (Fig. 5). However, in this case we can expect an increase in the contribution of the operators (5) relative to the Coriolis interactions (6) because compared with methane—the states ν_1 , $2\nu_2$, and $2\nu_4$ of deuteromethane are located closer than ν_1 and ν_3 .

The considerable increase in the weight of the central atom in GeH_4 results in a quasidegeneracy of the vibrational frequencies ν_1 and ν_3 . Consequently, the rotational structure of the ν_1 band is not described by a simple effective rotational Hamiltonian for a totally symmetric vibrational state. In view of the small amount of experimental data on the GeH_4 molecule, a reasonable approximation is provided by a simultaneous analysis of the vibrations ν_1 and ν_3 allowing for the succeeding purely rotational operators

$$R^{(2(0), A_1)}, \quad R^{(2(1), A_1)}, \quad R^{(2(2), A_1)}, \quad R^{(2(3), A_1)}, \quad R^{(2(4), A_1)}, \quad R^{(2(5), A_1)},$$

and for the vibrational-rotational operators quadratic in respect of the vibrational operators, which include:

a) the diagonal operators

$$V_{1,1}^{(A_1, A_1)}, \quad V_{2,3}^{(F_2, F_2) A_1}, \quad (8)$$

$$V_{2,3}^{(F_2, F_2) F_2} \times R^{(1, F_2)}, \quad (9)$$

$$V_{3,3}^{(F_2, F_2) F_2} \times R^{(2, F_2)}, \quad V_{3,3}^{(F_2, F_2) E} \times R^{(2, E)}, \quad (10)$$

b) the nondiagonal operator

$$V_{1,3}^{(A_1, F_2) F_2} \times R^{(2, F_2)}. \quad (11)$$

The operators (9) and (10) describe, respectively, the Coriolis interaction and the centrifugal distortion effects in the vibrational state of the F_2 symmetry, whereas the operator (11) represents the centrifugal distortion as a result of interaction of the vibrational states ν_1 and ν_3 . The operators (10) and (11) are of the same order because they are of the same degree with respect to elementary vibrational and rotational operators. On the other hand, the Coriolis interaction operator (9) is of a lower order. Therefore, in calculations it is convenient to describe the degenerate vibrational state ν_3 in terms of the basis of the vibrational-rotational functions which diagonalize the Coriolis interaction operator (9), i. e., it is convenient to employ basis functions with a definite quantum number of the pseudorotational angular momentum.

The formulas for the calculation of the matrix elements of the operators (9) and (10) are obtained in this basis in Ref. 10. The matrix elements of the operator (11) can also be calculated:

$$\langle K' = J_u, p_0', A_1 | [{}^{(1)} V_{1,3}^{(A_1, F_2) F_2} \times R^{(2, F_2)}]^{A_1} | K_g, p \rangle = (-1)^K \left(\frac{7(2K+1)}{3} \right)^{1/2} \left\{ \begin{matrix} 3 & K & J \\ J & 2 & 1 \end{matrix} \right\} \langle J || R^{(2, F_2)} || J \rangle. \quad (12)$$

$$\times \langle A_1 || V_{1,3}^{(A_1, F_2) F_2} || F_2 \rangle_{A_1, p, p_0}^{F_2, K_g, J_u}$$

The notation in Eq. (12) is the same as that in Ref. 10. The results of specific numerical calculations carried out using the above scheme will be considered in a separate communication.

Our work has thus provided a systematic analysis of the spectra of the vibrational states ν_1 of three spherical top molecules for which a study has been made of the features of the rotational structure associated with changes in the relative positions of the vibrational states near ν_1 . This analysis shows that interpreting the spectra of the ν_1 band and calculating the molecular parameters one has to use a model approach based on a simultaneous consideration of a set of interacting vibrational states.

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Inertialess metal glow produced by picosecond pulses

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A new phenomenon, inertialess glow of a metal produced by picosecond pulses, has been observed and is theoretically explained. The glow is due to the production of hot electrons in the metal. This phenomenon can serve as a basis for the investigation of the relaxation kinetics of the electron and phonon subsystems in metals, and can also be used for inertialess conversion of near and far IR picosecond pulses into visible light. This uncovers prospects for expanding the spectral range of modern photoelectric recorders.

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According to a hypothesis advanced in Ref. 1, temperature-induced glow, due to heating of the electron gas of the metal, should appear under certain conditions in addition to the photoemission and thermionic emission induced by ultrashort pulses in a metal.² At sufficient laser pulse-intensity the electron temperature T_e can reach several thousand degrees, and a substantial fraction of the radiation will be in the visible region of the spectrum. The glow follows without

inertia the pulse waveform if T_e is not subject to inertia delay. In Ref. 1 were reported preliminary experimental results that confirmed indirectly the advanced hypothesis. The time resolution of the measurements in Ref. 1, however, was worse than 10^{-9} sec at a laser pulse duration $\sim 10^{-11}$ sec, so that no direct confirmation of the hypothesis could be obtained.

We report in this paper experimental results ob-