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# Multiphoton and Multifrequency Resonances in the IR Laser Excitation of OsO<sub>4</sub> Molecules Cooled in a Supersonic Jet

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The three-frequency IR excitation of visible luminescence was used as the method for probing of the IR multiphoton absorption of OsO<sub>4</sub> molecules cooled in a supersonic jet. The first laser pulse was used to form a certain vibrational distribution below the onset of vibrational quasicontinuum. The possibility of direct excitation of the vibrational states  $\nu = 2, 3$  of pumped  $\nu_3$  mode by direct two- or three-photon absorption has been shown. The excitation spectra under the influence of the second variable laser frequency show the features attained for transitions from initially prepared vibrational levels  $\nu = 2$  or  $\nu = 3$ . The dependencies of the luminescence intensity on the IR laser fluence were studied also to prove the role of the direct multiphoton transitions. The different multiphoton and multifrequency resonances were analysed in the frame of simple spectroscopic model, and appropriate anharmonicity constants were derived.

**KEY WORDS** Multiphoton, multifrequency, infrared spectroscopy, OsO<sub>4</sub>.

## INTRODUCTION

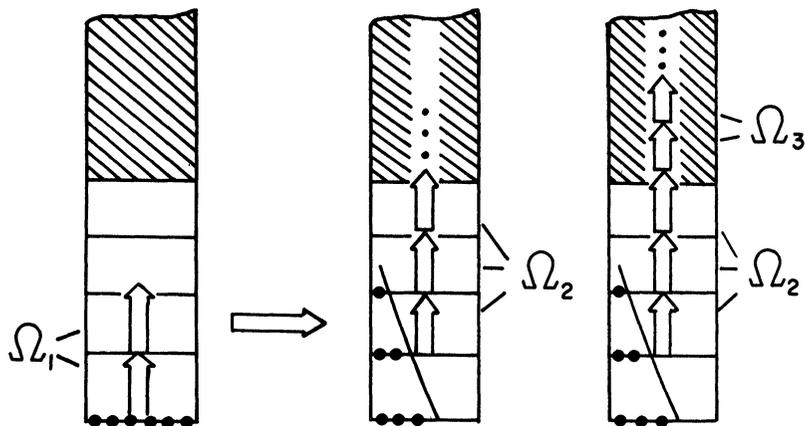
The multiphoton excitation of molecules (MPE) under the action of high-power IR laser pulses is widely used in the modern photophysics and photochemistry.<sup>1,2</sup> However, in spite of its practical value and a variety of applications, the complete adequate description of the MPE process is still lacking. One of the main theoretical problems is to

explain the effective excitation of molecules at low-lying vibrational levels up to a certain energy boundary above which the response IR excitation is connected, according to the present day knowledge, with the intramolecular broadening of the transition spectrum, i.e. with the formation of the so-called quasicontinuum (QC).

The experimental studies of the molecular excitation at low vibrational energies are of particular importance for their promise to answer some theoretical questions and, moreover, to optimize significantly the process, in particular, the isotopically selective MPE. The first MPE stage, i.e. the excitation below the QC, has the highest spectral selectivity and ensures the energy distribution needed to initiate different photochemical reactions. Even the qualitative understanding of the processes occurring in the MPE below the QC permits, for example, to improve substantially the selectivity of the process without increasing the consumption of laser energy.<sup>3</sup>

The requirements to the modern experiments aimed at probing the MPE are rather stringent. First, the MPE should start at a definite, if possible, ground vibrational state. The deep gas cooling is thereby required which, besides, decreases considerably the inhomogeneity in the rotational degrees of freedom. Secondly, it is necessary to probe *separate* vibrational levels. To meet these requirements, the experimental methods are now being developed. In particular, when the continuously tunable CO<sub>2</sub> lasers are used, the two-photon transitions arising in the MPE of the cell-cooled gas are observable,<sup>4</sup> and the CARS-probing reveals the total energy distribution below the QC.<sup>5</sup> There are also quite a number of MPE experiments in supersonic jets<sup>6-8</sup> and the attempts to probe the excited molecules with a diode laser.<sup>9</sup>

This paper suggests a new experimental method to probe the MPE—the multifrequency IR excitation of the visible luminescence of the molecules cooled in a supersonic jet. Specifically, the OsO<sub>4</sub> molecule and the three-frequency excitation induced by the TEA CO<sub>2</sub> laser radiation are considered. The method is based on the probing of the visible or UV emission which, as is known, can arise in the IR MPE of the ground electronic state up to the energies of the upper electronic state that is coupled with the ground term.<sup>10</sup> Figure 1 is an illustrative presentation of this idea. Under the action of the IR laser radiation there forms a certain vibrational distribution. The form of this distribution could shed light on the mechanisms of excitation at the



**Figure 1** Scheme of the three-frequency IR excitation of the visible emission. The field with the frequency at  $\Omega_1$  excites the molecules at the levels below the QC onset. The second field at  $\Omega_2$  probes the produced distribution. At the third frequency  $\Omega_3$  the molecule is further excited up to the luminescent states.

low-lying levels. The probing of the excited molecules is realized by the second field with a variable frequency  $\Omega_2$  which transfers the molecules distributed in the low-lying levels into the QC. The third field with a fixed frequency  $\Omega_3$  was chosen such that the QC molecules could be further excited up to the energy boundary where the visible emission occurs.<sup>10</sup> Examination of the excitation spectra will give information on the form of the distribution produced by the first field if the luminescence signal disappears in the absence of any of the three fields.

As is clear from what has been said, the method can be used if the MPE is accompanied by the visible luminescence and, besides, a different role of pulses at different frequencies is realized providing the red shift in the IR spectrum increases sufficiently with the vibrational energy. The method is applicable to many molecules which satisfy the above requirements,<sup>1</sup> and is best demonstrated using OsO<sub>4</sub>. In particular, the relatively large anharmonicity ( $2|\tilde{X}_{33}| \approx 6 \text{ cm}^{-1}$ <sup>11</sup>) and the narrow MPE spectra obtained under the two-frequency excitation in a supersonic jet<sup>12</sup> make it possible to identify the peaks in the luminescence spectra  $I_L(\Omega_L, \Omega_2)$  which correspond to the transitions from separate vibrational levels.

## EXPERIMENT

The experiments were carried out with the  $\text{OsO}_4$  molecules containing the natural mixture of Os isotopes ( $^{192}\text{Os}$  – 41.0%,  $^{190}\text{Os}$  – 26.4%,  $^{189}\text{Os}$  – 16.1%,  $^{188}\text{Os}$  – 13.3%,  $^{187}\text{Os}$  – 1.64%,  $^{186}\text{Os}$  – 1.59%). The dependence of the visible luminescence intensity  $I_L$  upon the second field frequency  $\Omega_2$  under the three-frequency excitation was measured. The  $\text{OsO}_4$  molecules were excited in the supersonic molecular jet by a train of pulses from three synchronized TEA  $\text{CO}_2$  lasers. The beams of the first two lasers propagated in the same direction at a small angle with respect to each other and overlapped completely in the irradiated region (Figure 2). The beam of the third laser was oppositely moving and superimposed the region of intersection. The radiation of each laser was multimode, the pulses were of the same shape: the peak with a duration of 80 ns (FWHM) and the 600 ns tail. The delay between the pulses of the first and the second lasers was 0.7–0.1  $\mu\text{s}$ . The laser beams were collimated, using the NaCl lenses with the focal length 200 cm, and then directed to the vacuum chamber. The maximum radiation energies:  $E_1, E_2 = 100$  mJ,  $E_3 = 1$  J. The cross sections of the beams in the radiation region were nearly the same, being 0.3  $\text{cm}^2$ .

The three-frequency IR MPE of the visible luminescence of the  $\text{OsO}_4$  molecule was initiated in the pulsed supersonic molecular jet that was formed as a result of the free outflow of the gas mixture  $\text{OsO}_4$ :

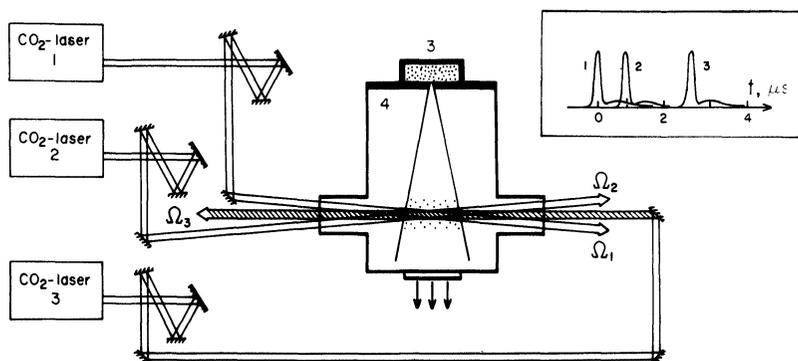


Figure 2 Experimental set-up.

Kr = 1 : 150 at the total stagnation pressure 400 Torr, through the 1 mm diameter hole into the chamber with the residual pressure  $10^{-7}$  Torr. The duration of the molecular pulse was determined with an electrodynamic-type nozzle<sup>13</sup> to be equal to 50  $\mu$ s (FWHM). The OsO<sub>4</sub> molecules were excited by laser pulses at a distance of 11.3 cm from the nozzle at the time when the gas density in the radiation zone was maximum. The maximum density of the OsO<sub>4</sub> molecules in the irradiation zone was not in excess of  $0.5 \times 10^{12} \text{cm}^{-3}$ , Kr being  $2.2 \times 10^{14} \text{cm}^{-3}$ . The visible luminescence of OsO<sub>4</sub> induced by the CO<sub>2</sub> laser radiation was registered with a photomultiplier through the side windows of the chamber in the perpendicular direction to the plane passing through the axis of the molecular jet and the laser beams.

The OsO<sub>4</sub> molecule was excited in the IR-absorption band of the  $\nu_3$  mode. The complete set of the vibrational constants of the OsO<sub>4</sub> molecule is given in Reference 11. The Q-branch frequency of the  $\nu_3$  mode equals  $960.7 \text{cm}^{-1}$  for <sup>192</sup>OsO<sub>4</sub>, the isotopic shift  $\Delta\nu_3$  for <sup>187</sup>OsO<sub>4</sub> being  $1.3 \text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

In experiment the frequency of the first field  $\Omega_1$  was chosen so as to satisfy the conditions of the two- or three-photon resonances under excitation from the ground state to the vibrational levels with  $\nu = 2$  or 3, respectively. For the OsO<sub>4</sub> molecule the positions of the Q-branches of the first<sup>11,14</sup> and second<sup>14</sup> overtones are known. According to this knowledge, the conditions of the two- and three-photon excitation are best satisfied at the CO<sub>2</sub> laser frequencies  $\Omega_1 = 957.8$  and  $954.5 \text{cm}^{-1}$  (10P(4) and 10P(8) lines, respectively). The main results of the experiment are presented in Figures 3–6.

In order to interpret the resonances arising in the excitation spectra  $I_L(\Omega_2)$ , it is convenient to record the Hamiltonian of the OsO<sub>4</sub> molecule whose triply degenerate  $\nu_3$  mode interacts with the external quasi-monochromatic field:

$$H = H_0 + H_1 - \mu \epsilon \cos \Omega_i t \quad (1)$$

Here,  $\mu$  is the operator of the dipole moment;  $\epsilon(t)$  is a slowly varying field amplitude; and  $\Omega$  is one of the frequencies in use. For the present purposes it is convenient to retain the main terms of the intramode

hamiltonian when  $H_0$  is diagonal in the coupled vibrational-rotational basis<sup>15</sup>:

$$H_0|vJR\rangle = \{v(v-1)X_{33} + [l(l+1) - 2v]G_{33} + (B_0 - \alpha v) \times \\ J(J+1) + B_0\xi_3[R(R+1) - J(J+1) - l(l+1) + 2v]\} |vJR\rangle \quad (2)$$

Here  $v$  is the occupation number of the  $\nu_3$  mode;  $J, l, R$  are the total, vibrational and rotational angular momenta, respectively;  $2X_{33}, G_{33}$  are the conventional symbols of the spectroscopic constants<sup>16</sup>. The main of the perturbation terms in  $H_1$  leads to the splitting of the vibrational  $|v\rangle$  states into the sublevels characterized by the irreducible representations of the symmetry point group  $T_d$ :

$$H_1 = T_{33} O_{33}, \quad (3)$$

where the tetrahedron operator  $O_{33}$  is designated as in Reference 16.

On the basis of the known Q-branch frequencies it is possible to predict the positions of the main peaks in the excitation spectra  $I_L(\Omega_2)$ . In particular, at  $T_{33} = I$  the states with  $l = l_{\max} = v$  form the levels of a simple anharmonic oscillator with the effective anharmonicity constant

$$\tilde{X}_{33} = X_{33} + G_{33} \quad (4)$$

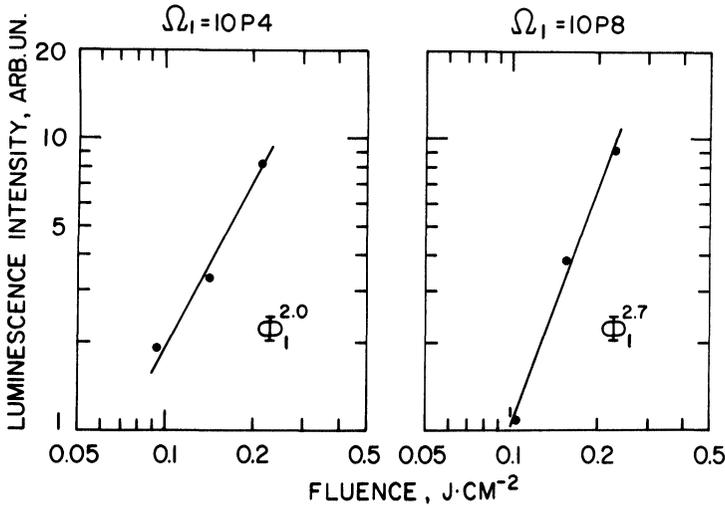
Without taking into account the possible anharmonic splitting of the  $\nu_3$  mode, the frequencies of the transitions from the ground state under the two- and three-photon excitation are expressed as:

$$\begin{aligned} \nu = 0 \xrightarrow{2\Omega_1} \nu = 2, \quad \Omega_1 = \nu_3 + \tilde{X}_{33} \\ \nu = 0 \xrightarrow{3\Omega_1} \nu = 3, \quad \Omega_1 = \nu_3 + 2\tilde{X}_{33} \end{aligned} \quad (5)$$

It is to be noted that, though the conditions (5) cannot be accurately satisfied for line-to-line tunable  $\text{CO}_2$  lasers, the taking account of the complex structure of the wide Q-branches and the isotopic shifts permits, nevertheless, the fulfillment of the conditions (5) at the 10P(4) and 10P(8) line, respectively.

An additional argument in favour of the predominant two- and three-photon excitation at  $\Omega_1 = 10\text{P}(4)$  and  $10\text{P}(8)$ , respectively, is the dependence of the luminiscent intensity  $I_L$  on the first field fluence:  $I_{L1}(\Phi_1; \Omega_1 = 10\text{P}(4))$  is  $\Phi_1^{2.0}$ ;  $I_L(\Phi_1; \Omega_1 = 10\text{P}(8))$  is  $\Phi_1^{2.7}$  (see Figure 3).

Under the excitation at different frequencies of  $\Omega_1$  the obtained excitation spectra  $I_L(\Omega_2)$  are rather different. Let us demonstrate that the main features of the spectra are in conformity with the assumption



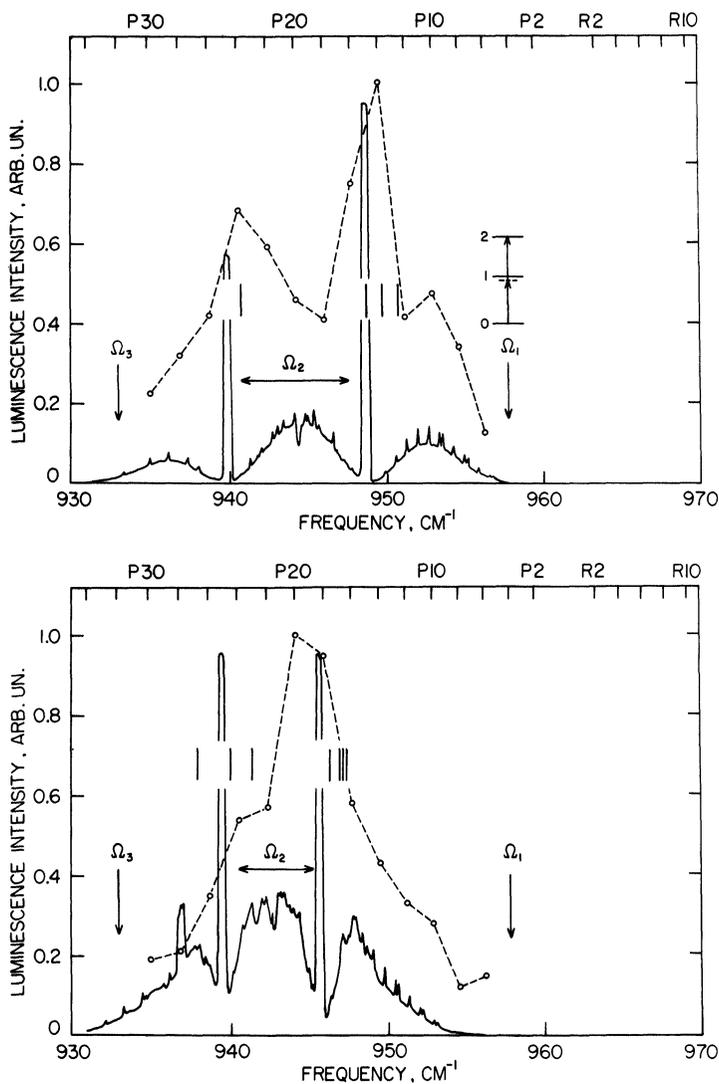
**Figure 3** Visible luminescence intensity of the OsO<sub>4</sub> molecule versus the fluence  $\Phi_1$  of the first field at  $\Omega_1 = 957.8 \text{ cm}^{-1}$  (10P(4)) (a) and  $954.5 \text{ cm}^{-1}$  (10P(8)) (b). The other parameters of the experiment: a)  $\Omega_2 = 949.5 \text{ cm}^{-1}$  (10P(14)),  $\Phi_2 = 0.3 \text{ J/cm}^2$ ,  $\Phi_3 = 0.75 \text{ J/cm}^2$ ; b)  $\Omega_2 = 944.2 \text{ cm}^{-1}$  (10P(20)),  $\Phi_2 = 0.25 \text{ J/cm}^2$ ,  $\Phi_3 = 0.75 \text{ J/cm}^2$ . In both cases  $\Omega_3 = 933.0 \text{ cm}^{-1}$  (10P(32)),  $\Delta\tau_{1-2} = 0.7 \mu\text{s}$ ,  $\Delta\tau_{1-3} = 2.5 \mu\text{s}$ .

about the principal role of the two- or three-photon excitation at  $\Omega_1$ . If the field at  $\Omega_2$  exerts influence upon the states with  $v = 2$  (or  $v = 3$ ), the spectrum  $I_L(\Omega_2)$  should exhibit the peaks corresponding to the transitions  $v = 2 \rightarrow v = 3$  (or  $v = 3 \rightarrow v = 4$ ) and, besides, the two-photon transitions are also possible. The corresponding frequencies of the transitions can be estimated from the relations:

$$\begin{aligned}
 v = 2 \xrightarrow{\Omega_2} v = 3, \quad \Omega_2 &= \nu_3 + 4\tilde{X}_{33} \\
 v = 2 \xrightarrow{2\Omega_2} v = 4, \quad \Omega_2 &= \nu_3 + 5\tilde{X}_{33} \\
 v = 3 \xrightarrow{\Omega_2} v = 4, \quad \Omega_2 &= \nu_3 + 6\tilde{X}_{33}
 \end{aligned} \tag{6}$$

The main peak of the spectrum  $I_L(\Omega_2)$  under the two-photon excitation of OsO<sub>4</sub> ( $\Omega_1 = 10P(4)$ ) is observed at the 10P(14) CO<sub>2</sub> laser line ( $\Omega_2 = 949.5 \text{ cm}^{-1}$ ), see Figure 4a, and in the three-photon case ( $\Omega_1 = 10P(8)$ ), at the 10P(20) line ( $\Omega_2 = 944.2 \text{ cm}^{-1}$ ), see Figure 5. This is in agreement with the interpretation of the transitions (6)—the main peaks of the differently excited molecules are shifted by about  $2\tilde{X}_{33}$ .

The MPE spectrum of the <sup>187</sup>OsO<sub>4</sub> molecule whose Q-branch of the two-photon transition does not coincide with the 10P(4) line, is also



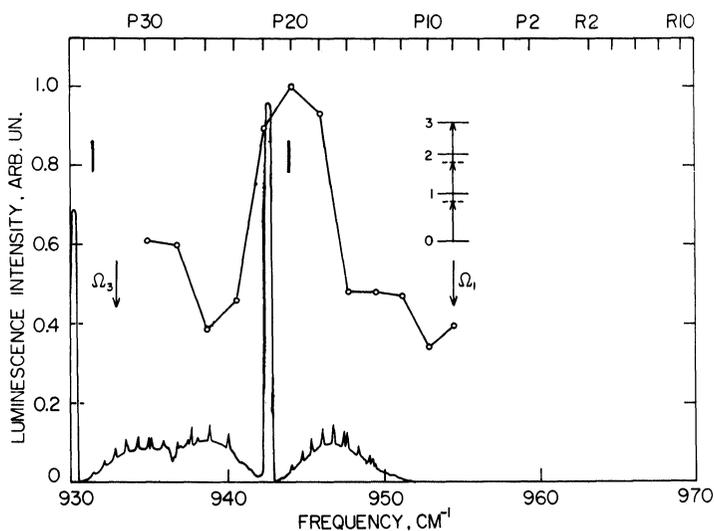
**Figure 4** Excitation spectra of the visible luminescence of  $\text{OsO}_4$  molecules  $I_L(\Omega_2)$  at  $\Omega_1 = 957.8 \text{ cm}^{-1}$  (10P(4)) and  $\Phi_2 = 0.3 \text{ J/cm}^2$  (a) and  $0.6 \text{ J/cm}^2$  (b). The other parameters of the experiment are:  $\Phi_1 = 0.2 \text{ J/cm}^2$ ,  $\Phi_3 = 0.75 \text{ J/cm}^2$ ,  $\Omega_3 = 933.0 \text{ cm}^{-1}$  (10P(32)),  $\Delta\tau_{1-2} = 0.7 \mu\text{s}$ ,  $\Delta\tau_{1-3} = 2.5 \mu\text{s}$ . The broken line represents the calculated spectra at  $T_{\text{rot}} = 50\text{K}$  and  $G_{33} = 0.9 \text{ cm}^{-1}$  (see the text). The calculated frequencies of the Q-branches of the transitions  $v = 2 \rightarrow v = 3$  and  $v = 2 \rightarrow v = 4$  (b) at  $T_{33} = 0.1 \text{ cm}^{-1}$  are marked in the insert in the middle of the figure.

strong evidence for the predominant population of the  $\nu = 2$  level at  $\Omega_1 = 10P(4)$  for one of the isotopic OsO<sub>4</sub> molecule (for example, <sup>192</sup>OsO<sub>4</sub>). For <sup>187</sup>OsO<sub>4</sub> the spectrum  $I_L(\Omega_2)$  at  $\Omega_1 = 10P(4)$  is qualitatively different: there is a structureless band without any peculiarities in the 950 cm<sup>-1</sup> region<sup>12</sup>.

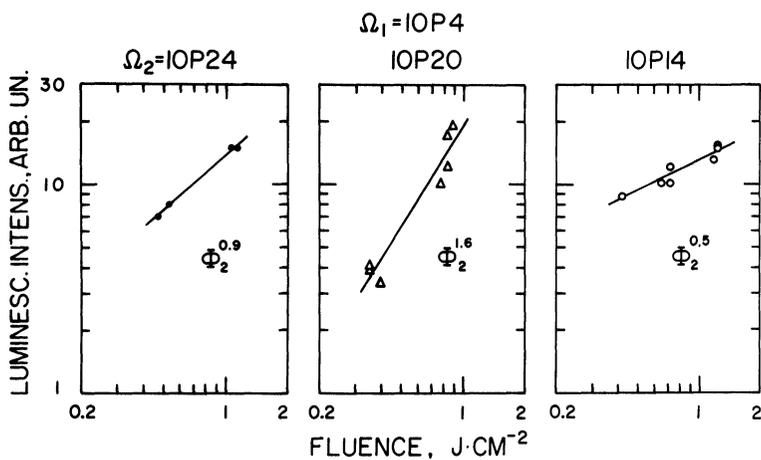
Up to here the more detailed spectroscopic information about the spectrum of transitions between the states of the Hamiltonian (2)–(3) was not needed, since the effective anharmonicity constant  $\tilde{X}_{33}$  only was known in advance from experiment which permitted the interpretation of the main peaks in  $I_L(\Omega_1, \Omega_2)$ . Consider now the second peak (at the line  $\Omega_2 = 10P(24)$ ) under the two-photon excitation of molecules in the field  $\Omega_1$  (Figure 4a). Unfortunately, neither the constant  $G_{33}$  nor the tetrahedron constant  $T_{33}$  for the OsO<sub>4</sub> molecule are known. However, on the assumption that the additional peak at  $\Omega_2 = 10P(24)$  (Figure 4a) is connected with the transition ( $\nu = 2, l = 2$ ) → ( $\nu = 3, l = 1$ ), the estimations yield  $G_{33} \approx 0.9$  cm<sup>-1</sup>. In this case the peak at  $\Omega_2 = 10P(14)$  is connected with the transition ( $\nu = 2, l = 2$ ) → ( $\nu = 3, l = 3$ ). The calculated fraction of the molecules, which are resonant with the exciting field in the interval  $\pm 0.1$  cm<sup>-1</sup>, is also shown in Figures 4 and 5. For definiteness, it was assumed that the rotational distribution corresponds to the temperature  $T_{rot}$  equal to 50K. The vertical inserts in the middle of the figures show the positions of the Q-branches of the transitions with allowance for the additional tetrahedron splitting ( $T_{33} = 0.1$  cm<sup>-1</sup>).

An independent proof of the proposed model of  $I_L$  spectrum formation (Figure 4a) is its transformation with increasing fluence  $\Phi_2$ . That is, as  $\Phi_2$  increases, the maxima in Figure 4a are both decreasing with respect to a new, strongly increasing, maximum at  $\Omega_2 = 10P(20)$ , 10P(18). The dependence  $I_L(\Phi_2)$  at  $\Phi_2 = 0.2 \div 1.2$  J/cm<sup>2</sup> can be represented in the following form:  $\Omega_2 = 10P(24) - I_L(\phi_2)$  is  $\Phi_2^{0.9}$ ;  $\Omega_2 = 10P(20) - I_L(\phi_2)$  is  $\Phi_2^{0.5}$  (Figure 6). The transformed spectrum at  $\phi_2 = 0.6$  J/cm<sup>2</sup> is shown in Figure 4b. It indicates to the contribution of the two-photon absorption from the level  $\nu = 2$  which, in turn, was excited in the field of  $\Omega_1$  also due to the two-photon process.

A slight discrepancy between the calculated and the experimental spectrum may result from the difference of the real constants  $G_{33}$  and  $T_{33}$ , or the effect of higher-order perturbations on the energy level position, and, also, from the difference in frequency between different isotope-containing molecules.



**Figure 5** Excitation spectrum  $I_L(\Omega_2)$  at  $\Omega_1 = 954.5 \text{ cm}^{-1}$  (10P(8)). The experiment was carried out at  $\Phi_1 = 0.21 \text{ J/cm}^2$ ,  $\Phi_2 = 0.24 \text{ J/cm}^2$ . The other parameters are the same as in Figure 4. The frequencies of the Q-branch of the transition  $\nu = 3 \rightarrow \nu = 4$  at  $T_{33} = 0.1 \text{ cm}^{-1}$  are marked in the insert in the middle part of the figure.



**Figure 6** Intensity  $I_L$  versus the fluence  $\Phi_2$  at  $\Omega_1 = 957.8 \text{ cm}^{-1}$  (10P4). The other parameters are the same as in Figure 4.

Figure 5 presents the spectrum  $I_L(\Omega_2)$  obtained in the case when the state  $v = 3$  is populated in the field  $\Omega_1 = 10P(8)$ . It is to be noted here that the uncertainty in the choice of the constants  $G_{33}$  and  $T_{33}$  has no effect on the interpretation of the transitions under the action of the first field, since the frequencies of the transitions  $v = 0 \rightarrow v = 2$  and  $v = 0 \rightarrow v = 3$  are known from experiment.<sup>11,14</sup> It is seen that the spectrum (Figure 5) differs qualitatively from the previous case (Figure 4) and its principal peak can be associated with the transition  $(v = 3, l = 3) \rightarrow (v = 4, l = 4)$ .

## CONCLUSIONS

The proposed MPE probing enabled us to prove the predominant role of the two- and three-photon transitions at the first stage of the MPE below the QC using, as an example, the OsO<sub>4</sub> molecule cooled in a supersonic jet.

Naturally, it is necessary to use a continuously tunable IR laser, at least, at the second step (the tuning of the frequency  $\Omega_2$ ) in order to interpret unambiguously the transition peaks and to determine independently the spectroscopic constants  $G_{33}$ ,  $T_{33}$ . The successful realization of our experiment with the OsO<sub>4</sub> gas containing numerous isotopic modifications is connected with a chance coincidence of the lines of the line-to-line tunable CO<sub>2</sub> laser with the frequencies of both the two- and three-photon transition.

It will also be noted that when the spectroscopic parameters are not known in advance, the detailed interpretation of the spectra is further complicated by an alternative explanation of the origin of the peak at the  $\Omega_2 = 10P(24)$  line with  $\Omega_1 = 10P(4)$ , Figure 4a. Really, in the strong field an adequate description of the excitation should consist in solving the dynamic problem (Schrödinger equation) with the Hamiltonian (1). Assuming the QC onset in the OsO<sub>4</sub> molecule at  $v > 4$  (estimate from Reference 17), it is possible to find the average population of the fourth level  $\langle p_4(t) \rangle$  in the limited basis ( $v \leq 4$ ). In this case  $I_L \sim \langle p_4 \rangle$ . The initial conditions (the  $v = 2$  level is predominantly populated) for the excitation in the field  $\Omega_2$  are specified by the preliminary excitation at the frequency  $\Omega_1 = 10P(4)$ . The result of the present calculation depends strongly on the assumed dependence  $\varepsilon(t)$  in (1). In particular, for  $\varepsilon(t) = \varepsilon_0 = \text{const}$  at  $0 < t < \tau_p$  the spectrum

$\langle p_4 \rangle (\Omega_2)$  with the start at  $\nu = 2$  exhibits a resonance at the transition  $\nu = 3 \rightarrow \nu = 4$ . In this case the peak at 10P(14), Figure 4a may be attributed, as before, to the transition  $\nu = 2 \rightarrow \nu = 3$  and at 10P(24), to  $\nu = 3 \rightarrow \nu = 4$ ; at large  $\Phi_2$  (Figure 4b) the peak at 10P(20) may be regarded to be due to the two-photon transition  $\nu = 2 \rightarrow \nu = 4$ . To match all the frequencies, it is sufficient to require that the constant  $G_{33}$  be equal to  $0.21 \text{ cm}^{-1}$  (if  $T_{33} = 0$ ).

At the same time, if the dependence  $\varepsilon(t)$  is sufficiently smooth, the system remains during a pulse in the single quasi-energy state which stems adiabatically from the  $\nu = 2$  level.<sup>18</sup> The spectral feature at the transition  $\nu = 3 \rightarrow \nu = 4$  is not observed in this case.

The ambiguous details in the interpretation are easily removed when the tunable lasers are used, or when the anharmonicity constants are measured by means of the standard spectroscopic methods. However, the main conclusion of the present work—the predominant excitation of the  $\nu = 2, 3$  vibrational levels of the cooled  $\text{OsO}_4$  molecules via the two- and three-photon transitions, holds true.

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