

MULTIPHOTON EXCITATION AND DISSOCIATION OF CH₃OH MOLECULES BY INTENSE BROADBAND YSGG:Cr:Er LASER RADIATION IN THE RANGE 2.7 μm

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Abstract

We have observed efficient multiphoton excitation of CH₃OH molecules by broadband pulsed YSGG:Cr:Er-laser radiation ($\lambda = 2.7 \mu\text{m}$, $\tau_p = 60 \text{ ns}$, and $\Delta\nu_{\text{las}} \sim 1.5 \text{ cm}^{-1}$) at fluences of 0.3–600 J/cm² under collisional and collisionless conditions. Multiphoton dissociation of CH₃OH has been realized. We discuss the role of intermode interaction, the intensity of the laser radiation, and the laser bandwidth in the excitation process.

1. Introduction

Multiphoton excitation (MPE) of characteristic vibrations of O–H and C–H bonds in polyatomic molecules is of interest from the viewpoint of searching for highly excited localized vibrational states (local modes) in addition to various applications based on the vibrational kinetics of organic molecules and realization of direct chemical reactions involving molecules adsorbed on a surface. Pioneering papers of R. V. Khokhlov et al. [1, 2] stimulated such investigations.

The substantial difference in the character of MPE of light (CH₃OH, H₂O, and CD₃OH) and heavy (C₂H₅OH and CF₃CH₂OH) molecules is explained by intermode interaction, which is more pronounced in the case of a greater mass for the radical R in molecules of an R–OH type [3]. It is obvious that intermode interaction is crucial for the total vibrational energy absorbed by the molecule from the laser field and the mode selectivity of excitation. The intensity and bandwidth of the laser radiation determine the efficiency of MPE and are important factors in such investigations. Thus, the experiments should involve light molecules in which the effect of the factors mentioned is noticeable on the background of strong intermode interaction.

The CH₃OH molecule is an interesting experimental object, first of all due to a low density of energy levels in the quasicontinuum region [3]. Strong anharmonicity is characteristic of the O–H vibrations in organic molecules (including the CH₃OH molecule, for which we have $B = -86.2 \text{ cm}^{-1}$ [4]), and under collisionless conditions the “bottle-neck” effect is likely, due to the noticeable frequency difference in sequential transitions caused by anharmonicity. This takes place in excitation of the O–H vibrations in the CH₃OH molecule by “narrow-band” (with a spectral bandwidth of 0.03 cm⁻¹) radiation of an HF laser [5], where the “bottle-neck” effect restricts the degree of excitation to 1 quant/molecule and prevents the multiphoton dissociation (MPD) of the CH₃OH molecules by HF-laser radiation under collisionless conditions.

Excitation of CH₃OH molecules through hydroxylic O–H bonds by “narrow-band” radiation of an HF laser [5] at an energy density (4 J/cm²) and a number of collisions per pulse that are close to those in the case of “broad-band” radiation of an optical parametric oscillator (OPO) [6] (with a line width of $\sim 5 \text{ cm}^{-1}$) yields a number of absorbed quanta per molecule of 0.016, which is 20 times less than the corresponding value in the case of OPO excitation. It seems that the low energy of the OPO pulse prevents it from achieving a level of excitation greater than 0.3 quant/molecule [6]. Thus, comparing the results of O–H

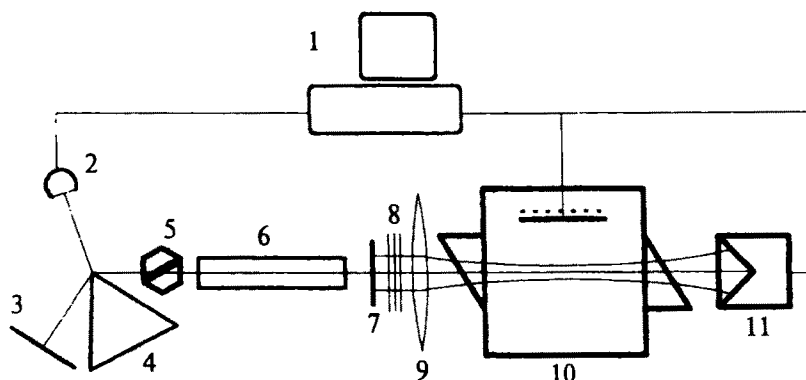


Fig. 1. Diagram of the experimental setup: 1) data acquisition and processing unit; 2) Ge–Au photodetector; 3) 100% back mirror; 4) LiF prism; 5) shutter; 6) YSGG:Cr:Er crystal; 7) output couplers; 8) attenuators; 9) focusing lens; 10) gas cell with an OAD; 11) calorimeter.

bond excitation of CH_3OH molecules by broadband (OPO [6]) and narrow-band (HF laser [5]) radiation under similar experimental conditions one can conclude that an intermode interaction sensitive to the laser bandwidth is present in this molecule, which reduces the “bottle-neck” effect and increases the MPE efficiency in the case of broadband irradiation.

More efficient MPE of molecules with O–H bonds by intense broadband radiation is expected for recently developed Er^{3+} ion solid-state lasers, in particular, a YSGG:Cr:Er laser operating in the Q-switched regime [7, 8]. The spectral bandwidth of YSGG:Cr:Er-laser radiation is close to that of OPO radiation, and the available pulse energy is considerably higher. Thus, a YSGG:Cr:Er laser provides investigation of MPE of O–H vibrations in organic molecules at a much higher level of excitation.

In the present paper, we investigate multiphoton excitation of O–H vibrations in CH_3OH molecules by radiation of a YSGG:Cr:Er solid-state laser under collisional and collisionless conditions and study the influence of the laser bandwidth and Stark broadening on the MPE efficiency of strongly anharmonic O–H vibrations in CH_3OH molecules at a high level of excitation.

2. Experimental Setup

The characteristics of MPE of O–H vibrations in CH_3OH molecules were investigated using Q-switched YSGG:Cr:Er laser with intracavity spectral selector [9]. The YSGG:Cr:Er laser radiation was focused into a gas cell with an optical-acoustic detector (OAD). The schematic diagram of the experimental setup is presented in Fig. 1. The YSGG:Cr:Er laser provided giant pulses with a duration of 60 ± 10 ns. The spectral bandwidth was 1.2 cm^{-1} at a wavelength of $2.70 \mu\text{m}$ (3701.5 cm^{-1}) and 3 cm^{-1} at a wavelength of $2.79 \mu\text{m}$ (3577.8 cm^{-1}). It is worth noting that generation at a wavelength of $2.64 \mu\text{m}$ was observed in the range of pump energy from 60 to 70 J. At a pump energy of 64 J, the pulse energies at 2.64, 2.70, and $2.79 \mu\text{m}$ were 2.6, 34, and 45 mJ, respectively (0.07:0.7:1), which agrees with data reported in [8] for the case of free running regime.

The fluence of the exciting radiation is the principal parameter in MPE investigations. That is why we controlled the intensity distribution across the laser beam to determine its effective area S and, correspondingly, the laser fluence F . The cross-sectional profile of the intensity at the focus of a lens with $f = 130$ mm was a super-Gaussian distribution with an index of 4 and an effective diameter at half-height of 0.215 mm,

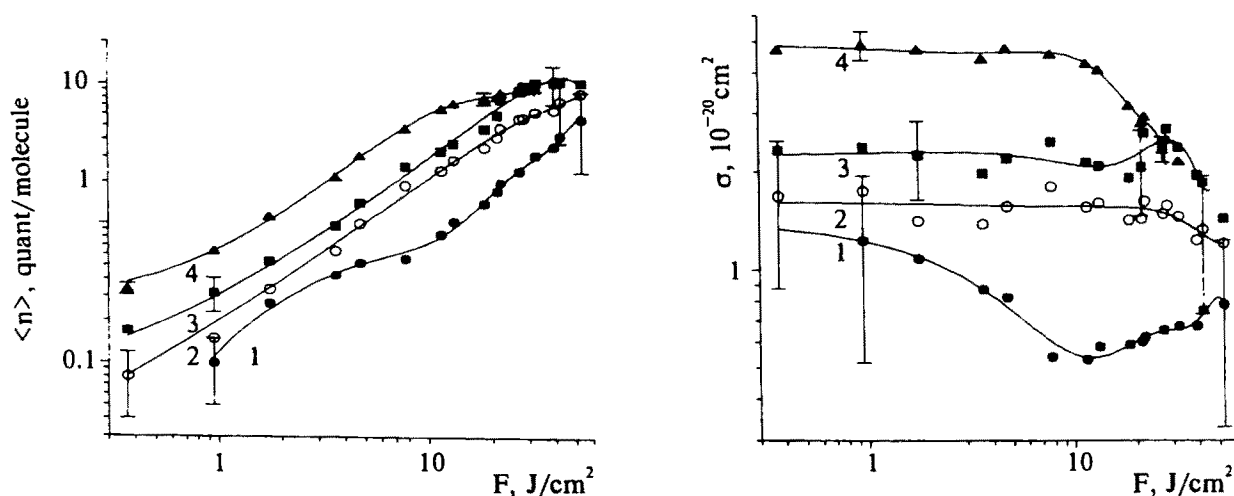


Fig. 2. Average number of quanta $\langle n \rangle$ absorbed by a CH_3OH molecule as a function of the fluence F of a YSGG:Cr:Er laser at the CH_3OH pressure P : 1) 1.5 torr; 2) 3 torr; 3) 5 torr; 4) 12 torr.

Fig. 3. Absorption cross section σ as a function of the fluence F of a YSGG:Cr:Er laser for MPE of CH_3OH molecules at the pressure P : 1) 1.5 torr; 2) 3 torr; 3) 5 torr; 4) 12 torr.

which provided a fluence of 55–110 J/cm^2 at a pulse energy of 20–40 mJ. In the case of a lens with $f = 70$ mm, the fluence was up to 1 kJ/cm^2 .

The signal from the OAD was fed to an oscilloscope of the type S9-8a. The OAD was placed in a gas cell with NaCl windows separated by 16.2 cm. The detector was placed in a side cavity at a distance of 3 cm apart from the laser beam. The signal from the waist region was selected by means of apertures separated by 0.8 cm from each other. The laser radiation was focused by a lens $f = 130$ mm and attenuated by standard optical glass filters. The OAD was calibrated by means of direct calorimetry. In performing the calibration, a previously observed [10] dependence of the OA signal on the beam radius r in the excitation region was taken into account. For this purpose, the signal from the OAD was measured as a function of r for a fixed fluence by employing apertures with various diameters.

The relative error of the measurements that is related to the statistical straggling of the OAD signal (Figs. 2 and 3) was better than 10%. However, upon reducing the gas pressure the error of absolute calibration increased because at low absorption the energy absorbed in the cell was comparable to the statistical straggling of the pulse energy. Thus, the shapes of the curves are statistically reliable, whereas their positions along the y axis are determined with an error that is indicated in Figs. 2 and 3.

3. Measurement Results and Discussion

Multiphoton excitation of CH_3OH molecules by radiation of the YSGG:Cr:Er laser was studied under both collisionless (1.5 torr) and collisional (5, 7, and 12 torr) conditions.

From the OAD signal we calculated, by a conventional procedure, the average number of quanta $\langle n \rangle$ absorbed by a molecule and the absorption cross section $\sigma = \langle n \rangle h\nu / F$, where $h\nu = 7.3 \cdot 10^{-20}$ J is the energy of a quantum of the YSGG:Cr:Er laser. The dependences of $\langle n \rangle$ and σ on the laser fluence for the YSGG:Cr:Er laser are shown in Figs. 2 and 3, respectively. The parameters b and $K/h\nu$ calculated by the

TABLE 1. Parameters $K/h\nu$ and b of multiphoton absorption for experimentally measured dependences of the number of quanta absorbed by a molecule $\langle n \rangle = KF^{1+b}/h\nu$ on the fluence F at various CH_3OH pressures

Laser	P , torr (collisions per pulse)	$K/h\nu$, 10^{-2}	b	F , J/cm^2
YSGG:Cr:Er	1.5 (0.65)	4.6 ± 2.7	0.21 ± 0.03	7-53
	3 (1.3)	22 ± 11	-0.02 ± 0.03	0.95-53
	5 (2.15)	19 ± 5	0.13 ± 0.02	0.37-22
	7 (3.0)	52 ± 10	-0.22 ± 0.03	0.37-22
	12 (5.16)	100 ± 10	-0.25 ± 0.03	0.37-12

TABLE 2. Multiphoton absorption parameters $K/h\nu$ and b of the dependences of $\langle n \rangle = KF^{1+b}/h\nu$ on the laser fluence F at various CH_3OH pressures obtained for an HF laser and a OPO in [4] and [5], respectively

Laser	P , torr (collisions per pulse)	$K/h\nu$, 10^{-2}	b	F , J/cm^2
HF	0.033 (0.07)	0.65 ± 0.05	-0.34 ± 0.05	0.7-48
	0.39 (0.8)	4.4 ± 0.1	-0.17 ± 0.01	0.04-39
	0.51 (1.0)	7.4 ± 0.3	-0.23 ± 0.03	0.03-40
	5.08 (10.8)	21 ± 3.0	-0.02 ± 0.02	0.01-32
OPO	1.00 (0.07)	7.5	0.00	0.04-4

least-squares method from the equations

$$\sigma = KF^b; \quad (1)$$

$$\langle n \rangle = \frac{1}{h\nu} KF^{1+b} \quad (2)$$

for the experimentally measured dependences of $\langle n \rangle$ and σ on F are presented in Table 1.

Figures 4 and 5 and Table 2 present similar dependences and coefficients for the case of an HF laser ($\tau_p = 300$ ns, $F = 0.04 - 50$ J/cm^2) and a OPO ($\tau_p = 10$ ns, $F = 0.04 - 4$ J/cm^2) taken from [5] and [6], respectively, where τ_p is the duration of the generated pulses.

The dependences shown in Figs. 4 and 5 and a comparison of Tables 1 and 2 show prove for the higher efficiency of MPE of CH_3OH molecules excited by the YSGG:Cr:Er laser as compared to the HF laser, which is manifested in the greater number of absorbed quanta for the same fluence and number of collisions per pulse and in the greater slope (the exponent $1 + b$) of the dependence of $\langle n \rangle$ on F under collisionless conditions.

Considerable MPE efficiency (as compared to the HF laser) was also observed under the action of broadband OPO radiation. In [5], this trend was explained by anharmonic interaction of a radiatively excited mode with the rest of the modes of the vibrational reservoir. Within the framework of the suggested model it

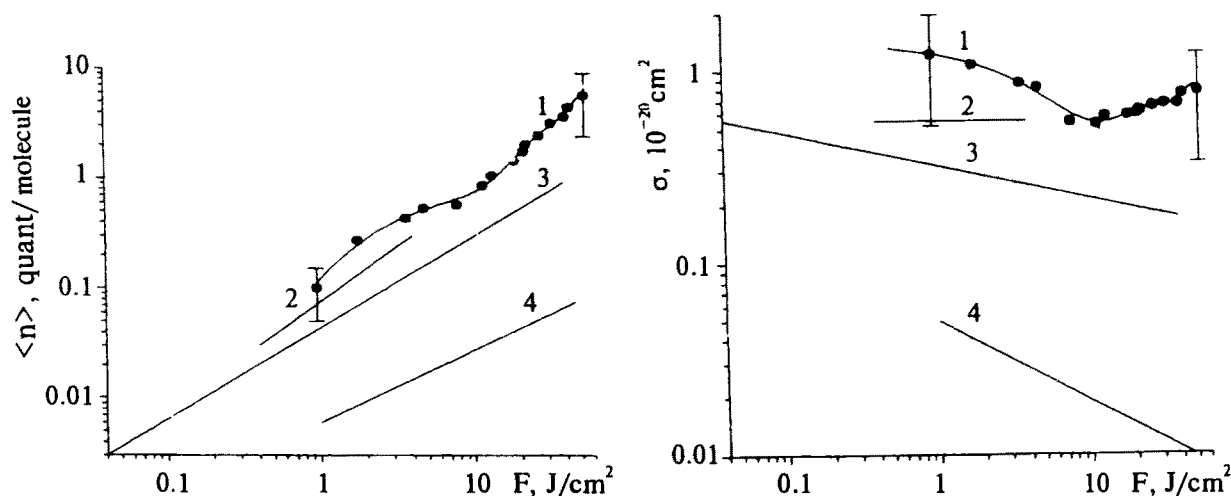


Fig. 4. Average number of quanta ($\langle n \rangle$) absorbed by a CH_3OH molecule as a function of the laser fluence F at the CH_3OH pressure P : 1) YSGG:Cr:Er laser, $P = 1.5$ torr (0.65 collision/pulse); 2) OPO [5], $P = 1$ torr (0.07 collision/pulse); 3) HF laser [4], $P = 0.39$ torr (0.8 collision/pulse); 4) HF laser [4], $P = 0.033$ torr (0.07 collision/pulse).

Fig. 5. Absorption cross section σ as a function of the fluence F for MPE of CH_3OH molecules at the pressure P : 1) YSGG:Cr:Er laser, $P = 1.5$ torr (0.65 collision/pulse); 2) OPO [5], $P = 1$ torr (0.07 collision/pulse); 3) HF laser [4], $P = 0.39$ torr (0.8 collision/pulse); 4) HF laser [4], $P = 0.033$ torr (0.07 collision/pulse).

was shown that in the case of random intermode resonances, chains of allowed transitions exist that provide absorption of a large number of quanta even in the case of strong anharmonicity. Our data indicate a higher efficiency of excitation of O–H vibrations in CH_3OH by broadband radiation at a considerably higher level of excitation of the molecule as compared to [6].

Let us now consider the reason for the greater efficiency of MPE of O–H vibrations by broadband radiation. We will consider the effect of saturation and transition to a multiphoton absorption regime in the case $p = 1.5$ torr of CH_3OH (curves 1 in Figs. 2 and 3). Saturation is observed at $F \simeq 8$ J/cm² and $\langle n \rangle \simeq 0.6$ quant/molecule. In the saturation regime, the rate of excitation $w = I\sigma/h\nu = \langle n \rangle/\tau_p$ is comparable to the rate of energy transfer per single collision $1/\tau_{\text{coll}}$. In our case, $w = 10^7$ s⁻¹. The gas-kinetic-collision-time constant in CH_3OH is 14 ns at 1 torr [5], i.e., at a pressure of 1.5 torr the frequency of collisions is $1/\tau_{\text{coll}} \sim 10^7$ s⁻¹, which coincides with the rate of excitation. A connection between the saturation effect and collisions is also shown by the fact that even in the case of rare collisions (at a pressure of 3 torr approximately 1.3 collision per pulse occur) saturation is not observed (curve 2 in Fig. 2). The most likely reason for the saturation is the “bottle-neck” effect, which is connected with the large frequency mismatch (170 cm⁻¹) of two sequential vibrational transitions, i.e., with the strong anharmonicity of O–H vibrations. Under these conditions, the “bottle-neck” effect is overcome by intermode interaction that is sensitive to the laser bandwidth and Stark broadening. The conclusion concerning the elimination of the “bottle-neck” effect by intermode interaction is based on a comparison of the frequency mismatch in the vibrational transition $1 \rightarrow 2$ ($\delta \simeq 170$ cm⁻¹) with the line width of YSGG:Cr:Er laser generation (1.2 cm⁻¹) and the field broadening caused by the Stark effect.

Estimates of the Stark broadening $\Delta\nu$ for a YSGG:Cr:Er laser, an HF laser, and a OPO yield the following

TABLE 3. Products of MPD obtained under MPE of CH₃OH by YSGG:Cr:Er-laser radiation (with a frequency $\nu = 3704 \text{ cm}^{-1}$ and a fluence of 600 J/cm^2)

Product	Quantity, %
C ₂ H ₄	2.67
C ₂ H ₂	1.46
CH ₃ OH	61.82
Unidentified	19.79
Unidentified	14.26

values at the corresponding dipole moment of the transition $d = 0.5 \cdot 10^{-19} \text{ esu}$ [5]: 1.6 cm^{-1} in the case of a YSGG:Cr:Er laser with an intensity $I = 0.13 \text{ GW/cm}^2$; 1.9 cm^{-1} in the case of an HF laser with an intensity $I = 0.17 \text{ GW/cm}^2$ [5]; and 2.8 cm^{-1} in the case of a OPO with an intensity $I = 0.4 \text{ GW/cm}^2$ [6].

Thus, in the case of a YSGG:Cr:Er laser, neither the line width of the laser generation nor the field broadening can compensate the frequency difference, and the "bottle-neck" effect is overcome by intermode interaction. The conclusion concerning the effect of field broadening on intermode interaction in the case of MPE of O-H vibrations in CH₃OH is made based on the fact that the "bottle-neck" effect vanishes as the fluence (the intensity) of the YSGG:Cr:Er laser increases (curves 1 in Figs. 2 and 3).

Despite almost the same value of field broadening for an HF laser [5] as for a YSGG:Cr:Er laser (our experiments), the "bottle-neck" effect is not overcome for an HF laser [i.e., the absorption cross section σ does not increase with the fluence F (see Fig. 3)] under collisionless conditions even at a fluence of $\sim 50 \text{ J/cm}^2$. This provides evidence, on the one hand, for unequal influence of the line width of the laser generation and the field broadening on intermode interaction and, on the other hand, for the importance of the total "broadening" caused by both factors so that intermode interaction eventually switches off the saturation.

From Fig. 2 (curve 1) it follows that in the case of excitation of O-H vibrations in CH₃OH by YSGG:Cr:Er laser radiation, unlike an HF laser, collisionless MPD of these molecules may occur at a moderate fluence of $\sim 100 \text{ J/cm}^2$.

We carried out experiments on MPD of CH₃OH molecules by YSGG:Cr:Er-laser radiation (a fluence $F = 400$ and 600 J/cm^2) under conditions close to collisionless (a pressure of 3 torr, which corresponds to 1.3 collision/pulse). Dissociation products were recorded by means of gas chromatography. After a series of 150 pulses of the YSGG:Cr:Er laser we detected ethylene C₂H₄ among the dissociation products. After 1000 pulses ($F = 600 \text{ J/cm}^2$) of the YSGG:Cr:Er laser, acetylene and some other, unidentified products were detected in addition (see Table 3).

Thus, we achieved MPD of CH₃OH molecules by means of a YSGG:Cr:Er laser under conditions close to collisionless. For the same number of collisions per pulse and fluence, the process of MPD of CH₃OH molecules by HF-laser radiation is unlikely.

Concluding, we should note that Er solid-state lasers can operate in a mode-locking regime [11], which offers new possibilities from the viewpoint of realization of MPE and MPD in an ultrashort-pulse field, investigation of intramolecular energy transfer under IR laser excitation, and search for localized vibrational states in highly excited molecules [12]. New solid-state lasers on rare-earth ions in various crystal matrices [13] that are available now and generate efficiently in the $2.7\text{-}\mu\text{m}$ range, in addition to the YSGG:Cr:Er laser,

e.g., C₂H₅OH [14] and HCOOH, H₂CO [15], may permit investigations of nonequilibrium processes in other molecules with vibration frequencies in this region that were excited up to now by an HF laser.

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