Spectroscopy of two-photon transitions in C_2H_4 using the degenerate four-photon interaction method

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Two-photon resonances with the overtone modes ν_7 and ν_8 of C_2H_4 are investigated by the degenerate four-photon interaction (DFI) method in an amplitude-polarization variant. The spectrum of multiphoton absorption (MPA) on the lines of the P branch of the (00°1–10°0) band of the CO_2 laser is interpreted.

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1. The importance of the spectroscopy of overtones of molecular vibrations has greatly increased in recent years in connection with investigations of multiphoton excitation of molecules.[1]

Traditional spectroscopic methods are not effective, since the intensities of the corresponding transitions on the overtone, allowed due to anharmonicity, are low.

The proposed method of active spectroscopy, which is based on the degenerate four-photon interaction, has the advantage that its nonlinear susceptibility $\chi^{(3)}(\omega_c:\omega, \omega, -\omega)$ is related only to vibrational transitions that are allowed in the harmonic oscillator approximation, ensuring a high signal level.

2. In the DFI process, three waves are mixed (frequencies ω) and, in addition, if two of them (pumping) are oriented opposite to one another, then synchronous signal generation is realized in the form of a reversal of the wave front of the third (probe) wave.

DFI can be used for spectroscopy of IR active molecular vibrations and for their first overtones, since the cubic susceptibility of this process has resonances at these vibrational levels. In addition, the nature of the resonance (single- or two-photon) is determined from a comparison of DFI spectra measured at different angles between the polarizations of the pumping and probing waves.

The possibility of such a transition stems from the fact that for DFI, where frequency conversion ($\omega_c = \omega$) does not occur, in addition to the usual (for parametric processes) mechanism for generating the signal wave, which is related to phasing of the resonance vibrations of molecules, there exists a characteristic mechanism.[2] It is based on the formation of an index of refraction grating due to the change in the population difference of the single-photon transition in the field of the standing wave formed by the interference of the pump $\mathbf{E}_H$ and probe $\mathbf{E}_{\pi p}$ waves. Scattering of the other pumping wave by this lattice leads to the appearance of a signal wave propagating in a direction opposite to the probing wave.

For crossed polarization, $\mathbf{E}_H$ and $\mathbf{E}_{\pi p}$ no longer interfere, excluding the contribution of this mechanism to the signal. For this reason, the appearance of new peaks

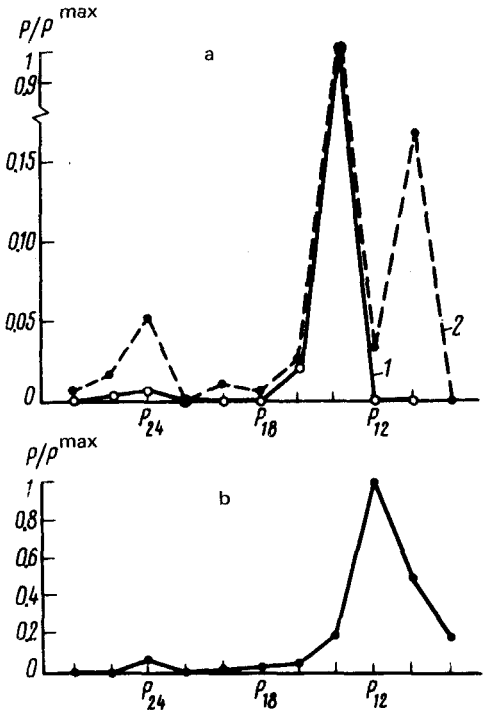

FIG. 1. a) Frequency dependences of DFI powers in C_2H_4 with orthogonal (1) and coinciding (2) polarizations of pumping and probing waves. The gas pressure is 20 and 30 Torr, respectively; b) frequency dependence of TH power with C_2H_4 pressure of 40 Torr.

accompanying the transition from the DFI spectrum with orthogonal polarization of pumping and probing waves ($P_\perp(\omega)$) to the spectrum with coinciding polarizations of these waves ($P_\parallel(\omega)$) is due to single-photon resonances, while all of the remaining peaks in the dependences $P_\perp(\omega)$ and $P_\parallel(\omega)$ are related to two-photon transitions.

3. The experimental dependences of the DFI power in C_2H_4, measured on lines of the P branches of the (001) band of the CO_2 laser are shown in Fig. 1a. They were obtained in a cell having a length of 2 cm with countermoving pumping waves and a small (3.5°) angle between the pumping and probing waves. The DFI signal was recorded with a cooled Ge-Au photoresistor on an oscillograph with a memory. In order to separate the signal wave from the background illumination at the same frequency, the spatial coherence of the signal wave was used, while its separation from the pumping wave was based on the difference in their directions of propagation.

4. It follows from a comparison of the experimental dependences $P_\perp(\omega)$ and $P_\parallel(\omega)$ that two-photon resonances with $2\nu_7$ and $2\nu_8$ are localized on the lines P_{14}, P_{16}, and P_{24}, P_{26}, closer to P_{14} and P_{24}, respectively, while single-photon resonances are localized on P_{10} and P_{12}.

5. This interpretation of the spectra is confirmed by investigations of the dependences of the ratio $P_\perp/P_\parallel$ on the C_2H_4 pressure or buffer gas pressure (Ar) in extra-

and intraresonator variants of the process. They showed the different nature of the saturation of $P_\perp$ and $P_\parallel$ in a strong field. This is attributed to the fact that the signal $P_\perp$ is determined by two-photon resonances, while $P_\parallel$ is likewise determined by single-photon resonances.

The DFI spectrum shown in Fig. 1a for mutually orthogonal polarizations of the pumping and probing waves is obtained by placing the cell with C_2H_4 in a TEA CO_2 laser resonator, which provided conditions for saturation of single-photon transitions at the frequencies under study.

A control experiment in SF_6, where according to Ref. 2, a two-photon resonance is achieved on P_{16}, showed that under the conditions realized in the present work the spectrum of the $P_\perp$ signal reflects two-photon transitions.

6. There is considerable interest in the use of DFI to identify three-photon resonances in the spectrum of the third harmonic. The third harmonic (TH) of the CO_2 laser, because of the resonances with overtones of the modes ν_7 and ν_8, was recorded in C_2H_4 (Fig. 1b). The maximum of the TH on P_{12}, where the $P_\perp$ DFI signal is missing, which means that there are no two-photon resonances, can be attributed to the three-photon resonances with 3ν.

The information obtained with the help of DFI on the overtone frequencies permits an interpretation of the spectrum of multiphoton absorption in C_2H_4. MPA maxima[1] are due to two-photon (P_{14}, P_{26}) and three-photon (P_{10}) resonances with $2\nu_7$, $2\nu_8$, and 3ν, respectively. We note that these lines also exhibit an appreciable single-photon absorption, which is favorable for accumulating molecular energy and decreasing the efficiency of parameteric processes. For this reason, there is some difference between the frequencies of the maxima in MPA and TH spectra. The three-photon nature of the resonance on P_{12} and P_{10} explains the tendency for displacement of the MPA maximum toward P_{10} with increasing intensity of the exciting field.

7. In conclusion we emphasize that the dependence of the cubic susceptibility of DFI on the dipole moments of transitions allowed in the harmonic approximation only determines the possibility of using DFI for spectroscopy of weakly anharmonic vibrations, demonstrated in this work for the example of the ν_7 mode of C_2H_4. This feature also provides a large $\chi^{(3)}$ and makes this a promising method with the use of continuous lasers.[4]

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