Suppression of nonresonant background in coherent picosecond active Raman spectroscopy of molecular gases

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Picosecond active Raman spectra were obtained for gaseous ammonia using frequency-tunable pulses. The totally symmetric vibration of the ammonia molecule at 3334 cm^{-1} was excited. It was found experimentally that a delay of a test pulse made it possible to suppress a signal due to a nonresonant susceptibility, whose presence restricted potential applications of active Raman spectroscopy.

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1. We shall report the results of coherent active Raman spectroscopy (CARS) of gaseous ammonia in which the sensitivity of the CARS method was improved by using picosecond pump pulses and test pulses delayed relative to the excitation.

2. An important application of the CARS method is fast and local determination of the concentrations of various molecules. One of the main obstacles to increasing the sensitivity of the method in the case of small amounts of molecules is the presence of a background signal associated with the four-photon interactions due to the nonresonant electronic nonlinearity.[1,2] Various methods for removing the nonresonant background, for example, the polarization technique, have been suggested for cw CARS.[3] In the case of pulsed CARS one can use the difference between the dephasing times of the molecular vibrations T_2 and of the electron nonlinearity τ_{el} ($\tau_{el} \ll T_2$). If the duration of the pump pulses obeys $\tau_{el} \ll \tau_p < T_2$, a delay of a test pulse rela-

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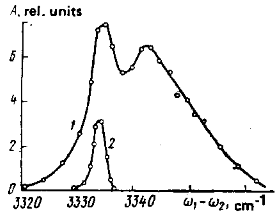

FIG. 1. Picosecond CARS spectra of ammonia at 45 Torr in the absence (1) and presence (2) of delay of a test pulse by 200 psec relative to the exciting pulses.

tive to an excitation pulse by a time exceeding τ_p can remove the nonresonant background before the resonant signal disappears.

The effects associated with such a delay of a test pulse can be observed using a nondegenerate CARS configuration in which a test pulse differs in frequency from the excitation pulses. In the only (known to the authors) investigation of picosecond CARS in gases,[4] concerned with gaseous nitrogen, the configuration used has been degenerate, so that the effects under discussion could not have been observed.

3. Apparatus used to apply picosecond CARS to gaseous ammonia consisted of a YAG : Nd^{3+} laser with passive mode locking, a system for separating a single picosecond pulse, three amplifiers, a parametric oscillator containing two lithium niobate crystals arranged in series, and a system of prisms and mirrors ensuring both collinear injection of radiation of three frequencies into an ammonia cell and delay of a test pulse. The radiation entering the cell was focused at its center by a lens with a focal length of 155 mm. One of the excitation pulses represented radiation of the garnet laser ($\lambda = 1.06\ \mu$) of 5 mJ energy; the second excitation pulse was in the form of radiation from the parametric oscillator tunable in the range 1.4–4 μ and having an energy of ~0.3 mJ; the test pulse was the second harmonic ($\lambda = 0.53\ \mu$) of energy 4 mJ. The duration of the garnet laser pulses was 35 psec.

Tuning of the parametric oscillator to the wavelength 1.6 μ excited the totally symmetric vibration of the ammonia molecule at 3334 cm^{-1}. The radiation of the anti-Stokes frequency emerging from the cell was focused on a slit of a diffraction spectrograph. The spectrum of the signal was recorded by an FÉU-39 photomultiplier with a slit in front of its cathode. The resolution of the spectrum was 1 cm^{-1}.

The photomultiplier signal together with a signal from a pyroelectric detector measuring the energy of the parametric oscillator reached the inputs of analog-digital converters. Digital data from the converter outputs were applied to a 15 VSM-5 minicomputer, which averaged the CARS signals when the energy of the parametric oscillator pulses was within the required range.

4. Curve 1 in Fig. 1 is the spectrum of the signal obtained at an ammonia pressure of 45 Torr when the test pulse delay was zero. Clearly, for zero delay, the resonant signal was observed against a background due to the nonresonant susceptibility. The spectral width of this background was 30 cm^{-1} and it was equal to the line width of the parametric oscillator in the investigated wavelength range. The main contribution to the nonresonant susceptibility was made by the glass walls of the cell. The intensities of the resonant and nonresonant signals were equalized by shifting the central frequency of the parametric oscillator away from resonance.

Additional measurements of the resonant signal in the case when the central frequency of the parametric resonator was tuned to resonance and of the nonresonant signal in the absence of ammonia indicated that the ratio of the energies of the resonant and nonresonant signals, amounting to 10^2 for zero delay of the test pulse, increased to 10^6 when the delay was 100 psec. Further increase of this ratio on increase in the delay of the test pulse could not be recorded because the nonresonant signal became less than the noise in the recording system.

Measurements of the spectral profile of the resonant signal obtained for various delays of the test pulse confirmed that it was coherent.

5. Our experiments established that the sensitivity of the CARS method in detection of small amounts of molecules could be increased considerably by employing picosecond pump pulses and delaying a test pulse relative to the excitation. The ratio of the energies of the resonant and nonresonant signals was increased by a factor of 10^4. A picosecond parametric oscillator with a tunable excitation frequency was used for the first time in CARS.

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