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Suppression of Luminescence Background in Raman Spectra by Pulsed Laser Excitation

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It has been found that excitation with nanosecond laser pulses suppresses the luminescence background in the Raman spectra of some organic compounds by factors of ten to hundred compared with ordinary cw-laser excitation. This finding may lead to a novel effective means for luminescence quenching in Raman spectroscopy.

Applications of Raman spectroscopy, especially those to biological samples, are often hindered by co-existing luminescence which tends to mask much weaker Raman signals. Several methods based on different principles including gated detection,[1)] coherent anti-Stokes Raman scattering,[2)] inverse Raman effect,[3)] and near-infrared excitation[4,5)] have been proposed to solve this problem. Up to the present time, however, no decisive solution has been obtained. In the course of our studies on the transient Raman spectra of benzophenone and its derivatives,[6)] we found that pulsed-laser excitation was effective in reducing luminescence which was emitted from trace amounts of unknown impurities. Although the mechanism of this phenomenon is not clear at present, it may be important as a new means for luminescence quenching in Raman spectroscopy. The observation on benzophenone is briefly described in this letter.

A multichannel Raman system used in the present study was described elsewhere.[7)] It consists of a Q-switched Nd:YAG laser (for pulsed excitation) or an Ar^+ laser (for cw excitation), a triple polychromator, an intensified photodiode array detector, and a minicomputer. Two different samples of benzophenone were used to clarify the origin of luminescence. Sample A was prepared according to the literature[8)] and purified by silica-gel column chromatography. No appreciable impurities were detected by infrared spectroscopy. Sample B was commercially obtained from Wako Pure Chemicals Co. and used without further purification.

The Raman spectra of Sample A in carbon tetrachloride (1 mol dm^{-3}) are shown in Fig.1, where part (a) was obtained with cw excitation (514.5 nm, $\approx$10 mW) and (b) was measured with pulsed excitation (532 nm, $\approx$10 mW average power, 5 ns pulse width, 10 Hz repetition). The detector was operated with the cw mode (no gating) in both measurements. The ordinate indicates the relative intensities measured from the absolute zero level (no baseline subtraction).

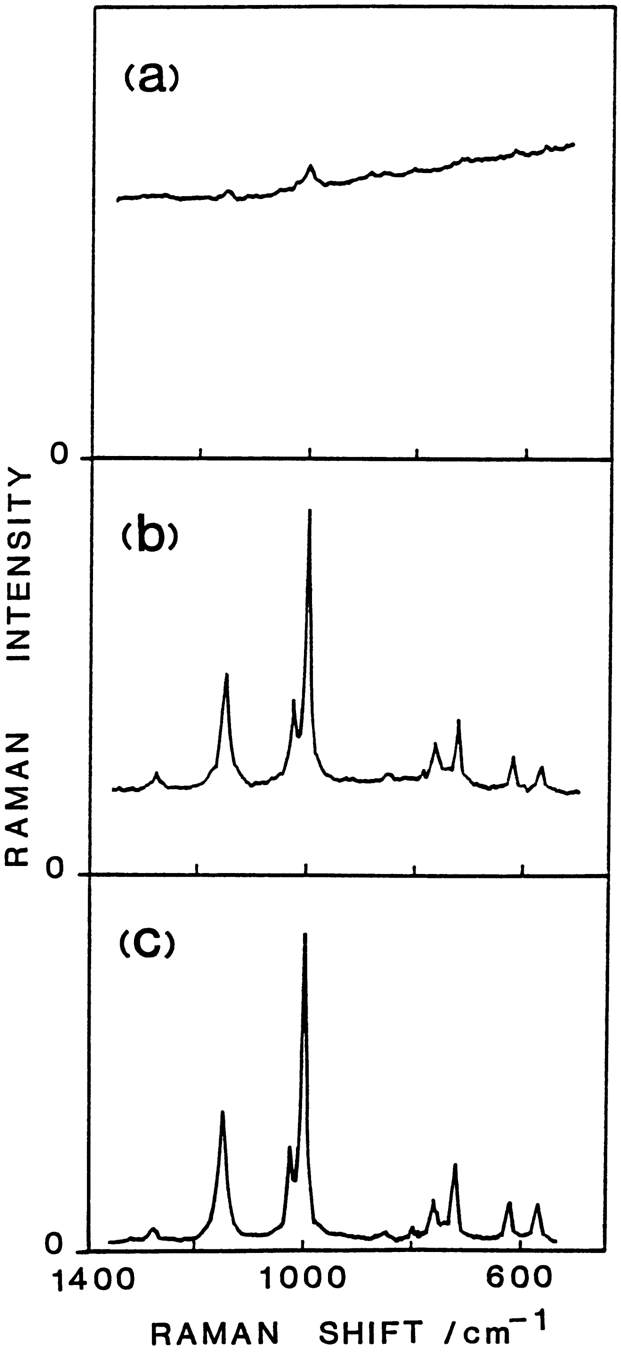

Fig.1. Raman spectra of benzophenone in carbon tetrachloride (1 mol dm^{-3}) (a) Sample A (synthesized) with cw excitation, (b) Sample A with pulsed excitation, and (c) Sample B (purchased) with cw excitation

In going from cw to pulsed excitation, the Raman to luminescence ratio increases by a factor of 33. In other words, a reduction of luminescence background by the factor of 33 was achieved only by switching the excitation from the cw mode to the pulsed. Part (c) of Fig.1 shows the Raman spectrum of Sample B obtained with cw excitation. Comparison of the spectra in Parts (a) and (c) indicates that the high luminescence background originated from trace amounts of unknown impurities in Sample A (which were not detected by infrared spectroscopy).

Elucidation of the mechanism of the luminescence quenching in the present experiment needs more detailed investigations including laser-power dependence, the effect of gating, and applications to various samples of different origins. Studies in this line is now in progress.

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