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## RED LUMINESCENCE OF THE AROMA OF FRUITS AT THEIR SURFACE: POSSIBLE INTERPRETATION

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An unusual luminescence upon optical excitation has been observed from above the surface of a number of common fruits and is thought to be associated with interfacial effects [1-3]. Although molecular luminescence, arising from proteins, chlorophyll and other fluorophores, is common in many biological materials, and this is the region where some chlorophyll fluorescence may be expected, we believe this emission has a different origin. It was suggested that this luminescence could be attributed to the gaseous atmosphere of organic volatiles emitted from fruits, such as alcohols, aldehydes and esters [1, 2]. However, this is not simply molecular luminescence of the volatile molecules: in our experiments, the light excitation energies (1.9-4.9 eV) are too low to transform them into excited electronic states by a single-photon process. We feel that it arises from emission involving vibrational overtones of species present in the vapours emanating from the fruit. In particular, these are likely to be associated with overtones of the highest energy vibrational modes, such as CH and OH stretch. Organic volatiles are seen to luminescence effectively when escaping through the skin of fruit (such as through a porous membrane). The role of this membrane has been examined by laser fluorimetry in model experiments for the free expansion of a vapour of a volatile compound through a nozzle [3]. Optically excited vapours of a number of organic volatiles were seen to emit red luminescence bands in 600-800 nm region under the condition of their diffusion through a nozzle. The wavelengths of these luminescence bands were close to those of the sixth C-H and the fourth O-H stretching overtones. Our results demonstrate that the natural *in vivo* processes of escaping of aroma volatiles through the skin of fruit are similar to the nonequilibrium expansion of a vapour through a nozzle. This provide a new insight into their surface phenomena and, in particular, the current vision of respiration of plants, which makes such remote detection a very generic approach and potentially an extremely powerful tool for the *in vivo* investigation not only of plants, but also animals and humans and, therefore, in biomedical applications.

### RESULTS

Fruits. Luminescence from above the surface of different fruits has been observed using either laser luminescence microscopy or a conventional spectrofluorimeter [1, 2]. The measurements were described in details in the work [1]. For example, a typical emission spectrum from an apple is shown in Figure 1-a. The spectra obtained from different fruits can be classified into two sets: 1) stronger contributions between 676 and 684 nm, and 2) relatively weak bands located around 730 and 760 nm. Further, the observed spectra were independent of excitation wavelength [2], showing that they cannot be due to the Raman effect. Alternative assignment to multi-photon processes was ruled out, since the variation of the excitation power density is accompanied by a corresponding linear variation of the luminescence intensity but does not affect the peak locations [1].

**Volatile compounds.** We have suggested in [1-3] that the emission comes from volatile components in the fruit aroma vapours. We have tested simulation of the skin of fruit in the experiment with the expansion of an aroma vapour through a single pore or nozzle (see details in [3]). Purified volatile organic compounds, such as methanol, ethanol, ethyl acetate, ethyl caprylate, acetic acid, acetone, methyl acetate and acetaldehyde (initially as liquids) have been selected as they are the most prominent components identified in the aroma of fruits [4, 5]. The spectrum from the methanol, as example, detected in the diffusion flow of methanol vapour through the pore is presented in Figure 1-a (curve-5). The spectrum is dominated by broad emission bands located around the maximum at 676 nm. Similar emission spectra were also observed on the diffusion expansion of vapours of all the aroma compounds tested, as shown in Figure 1-b. These results demonstrate the general effect of red emission and suggest the importance of a diffusion process that changes the luminescence characteristics of volatiles.

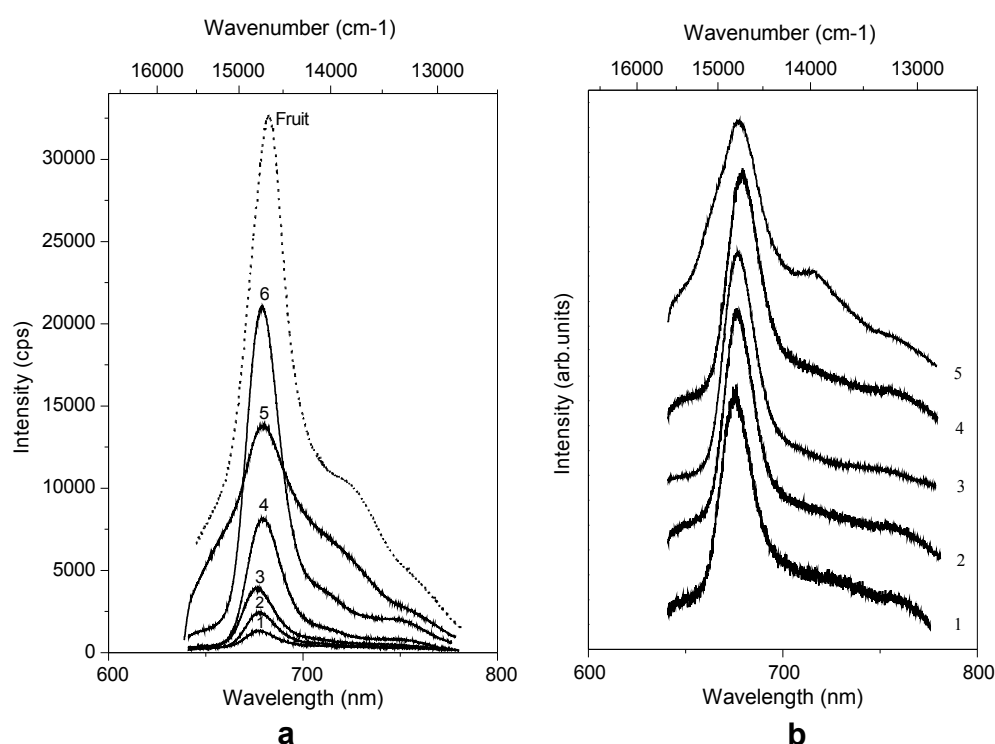


Figure 1. Luminescence spectra from diffusion flow of vapours of the aroma compounds (Renishaw-2000,  $1 \text{ cm}^{-1}$  resolution, He-Ne laser for excitation at 632.8 nm). (a) Emission intensities in a count rate per second: 1- hexanol, 2- methylbutan, 3- octanol, 4- ethanol, 5- methanol, 6- ethyl acetate, and an apple (dotted line). (b) Normalized spectra: 1- acetone, 2- methyl acetate, 3- ethyl caprylate, 4- acetaldehyde, 5- acetic acid.

## DISCUSSION

Comparing the luminescence spectra observed with fruit with those of pure samples of the potential volatile compounds involved (Figure 1-a) we can draw two conclusions: 1) these results lend support to the concept that the fruit luminescence is associated with the vapours of volatile components, 2) luminescence spectra from fruits can be considered as the superposition of relative contributions of volatiles (methanol, ethanol, etc).

Vibrational overtones. Firstly, this is not simply molecular luminescence of the volatile molecules: possible assignments to electronic states formed by a single-photon or multi-photon processes are also ruled out, as mentioned above. Since the molecules must be in their ground electronic states, it is possible to suggest that this luminescence arises from excited vibrational overtones in volatile molecules. The spectral features of aroma luminescence are similar to the overtone vibrational spectra of typical organic molecules [6-10]. These tend to be associated with the highest energy vibrational modes, such as the CH and OH stretches [6-8]. The locations of the emission bands from volatiles between 14620-14795  $\text{cm}^{-1}$  (676-684 nm) in all spectra and shoulder at 13700  $\text{cm}^{-1}$  (730 nm) from the diffusion flow of volatile vapours, as well from fruits, were close to the wavelength of a six quantum and four quantum overtones transitions of the C-H and O-H stretching vibrations, respectively. This estimation is consistent with conclusions drawn by previous reports which describe C-H and O-H stretching modes in similar compounds [9, 10].

Excitation of vibronic overtones. The first and simplest mechanism of the excitation of molecular vibrations is a selective optical absorption: absorbed photons can promote transitions to high overtone and combination states, i.e. to excited vibrations. However, no significant luminescence was observed from the equilibrated vapour of aroma [3], while the feature of luminescence of the aroma volatiles is their observation only under photoexcitation. This suggests that the emission of vibronic modes can include other processes such as partial condensation of molecules and thermal excitation of these species in the diffusion flow. Since emission from high vibrational levels implies nonequilibrium properties of the emitted vapour, it is reasonable to ask: how hot can the red emitted vapour molecules become? The overtone intensity of luminescence is proportional to the molecular population of the vibronic state involved in the transition. Using the experimental and theoretical definitions of luminescence flux per molecule, we can estimate the minimum vibronic temperature of molecules: temperatures about 1100-1400 K can be sufficient to sustain luminescence with the intensity and spectral location close to experiment. Finally, we can suggest a reasonable interpretation: i.e. that the observed red luminescence of both fruit aroma and aroma compounds most probably arise from the C-H and O-H stretching overtones and/or combination modes of the vibrational transitions in excited volatile molecules. The excitation mechanism is under discussion now and it includes the optical excitation of the expanding vapour of aroma during their partial condensation, since the heat of formation of these species can be partially converted into increasing temperature of the vibronic modes.

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