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DESORPTION OF LARGE ORGANIC MOLECULES BY LASER-INDUCED PLASMON EXCITATION*

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INTRODUCTION

Ejection of large organic molecules from surfaces by laser-induced electronic-excited desorption has attracted considerable interest in recent years.[1,2] In addition to the importance of this effect for fundamental investigations of the ejection process, this desorption technique has been applied to the study of large, fragile molecules by mass spectrometry. In this paper, we present a new method to induce electronic excitation on the metal surface for the desorption of large organic molecules.

EXPERIMENTAL METHODS

Surface plasmons excited by a Nd:YAG laser in an attenuated-total-reflection (ATR) geometry were used to induce electronic-excited desorption of rhodamine B molecules. The second harmonic of the Nd:YAG laser beam has wavelength 532 nm and pulse width 7 ns. Rhodamine B is a dye molecule with molecular weight 479 amu, ionization potential 6.7 eV[3], and the molecular structure shown in Fig. 1.

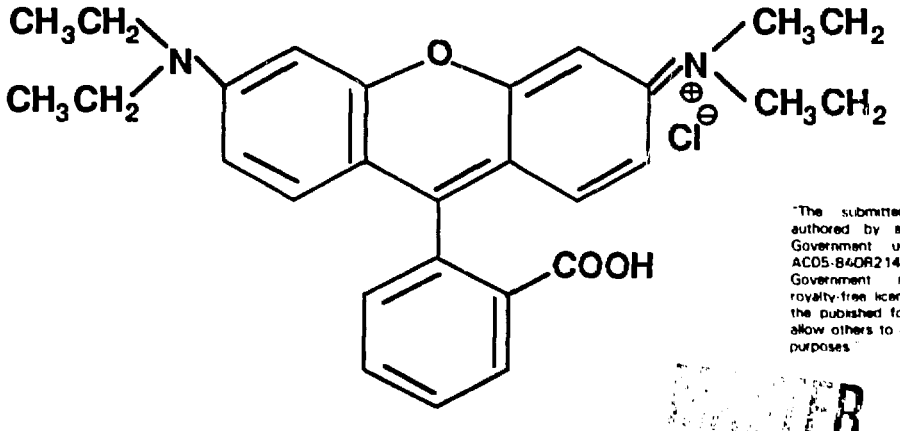

Fig. 1 Molecular structure of rhodamine B.

In our experiment, a 27 nm Al film was deposited on the base of a 45° prism in a vacuum evaporator. A rhodamine B film was next deposited on the Al film by evaporating rhodamine B powder at a very low temperature. The thickness of rhodamine B film was 80 nm. The desorbed neutrals were ionized by a XeCl laser with wavelength 308 nm and pulse width 7 ns. The signals were measured by a time-of-flight mass spectrometer (TOF-MS). The signals from the TOF-MS were recorded by a PC (80286) controlled transient digitizer. The experimental apparatus used in the desorption experiment are shown schematically in Fig. 2. By varying the delay time between the two lasers, we could obtain the delay time distributions of the desorbed neutrals. The kinetic energy distributions could then be transformed by a simple calculation.

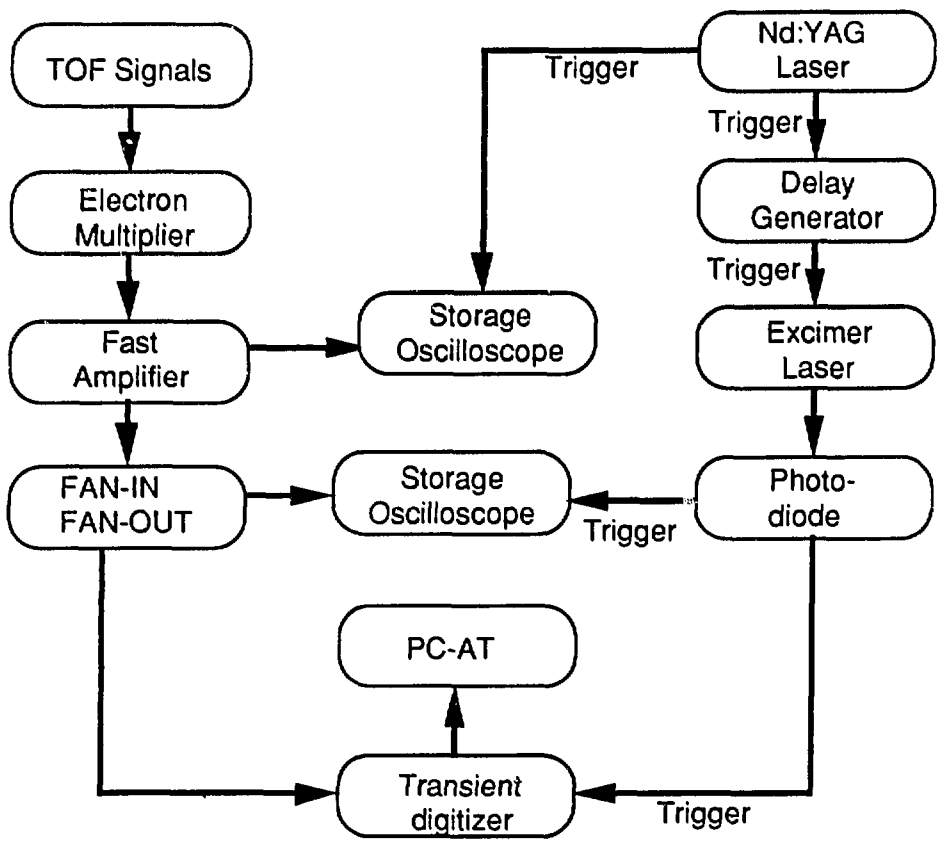

Fig. 2 The experimental apparatus.

RESULTS AND DISCUSSION

We found that at the plasmon resonance angle there were two peaks in the mass spectrum, corresponding to the masses of Al atoms and of rhodamine B

molecules. While Al has both a low energy thermal peak at 0.081 eV and a high energy peak at 0.51 eV in the kinetic energy distribution, rhodamine B has only one peak at 0.56 eV kinetic energy. Both the Al and rhodamine B high-energy signals showed peaks at photon incidence angles corresponding to the surface plasmon resonance angle (Fig. 3). The yield of fragment ions of rhodamine B was very close to the background noise and was at least an order of magnitude weaker than the yield of complete molecular ions. The thresholds for both Al and rhodamine desorption were observed at a laser fluence of about F = 80 mJ/cm^2. At laser fluences exceeding about F = 300 mJ/cm^2 the rhodamine B signal disappeared and significant fragmentation signals appeared. The maximum rhodamine B desorption yield at the plasmon resonance angle was obtained at the laser fluence F = 178 ± 5 mJ/cm^2. When the fluence was increased beyond the maximum, the magnitude of the rhodamine B peak decreased while the magnitude of the Al peak increased. Since Al atoms from the substrate film were always observed together with the rhodamine molecules, it appeared that Al atoms were desorbed over a large area. This was also evidenced by physical damage observable on the metal film.

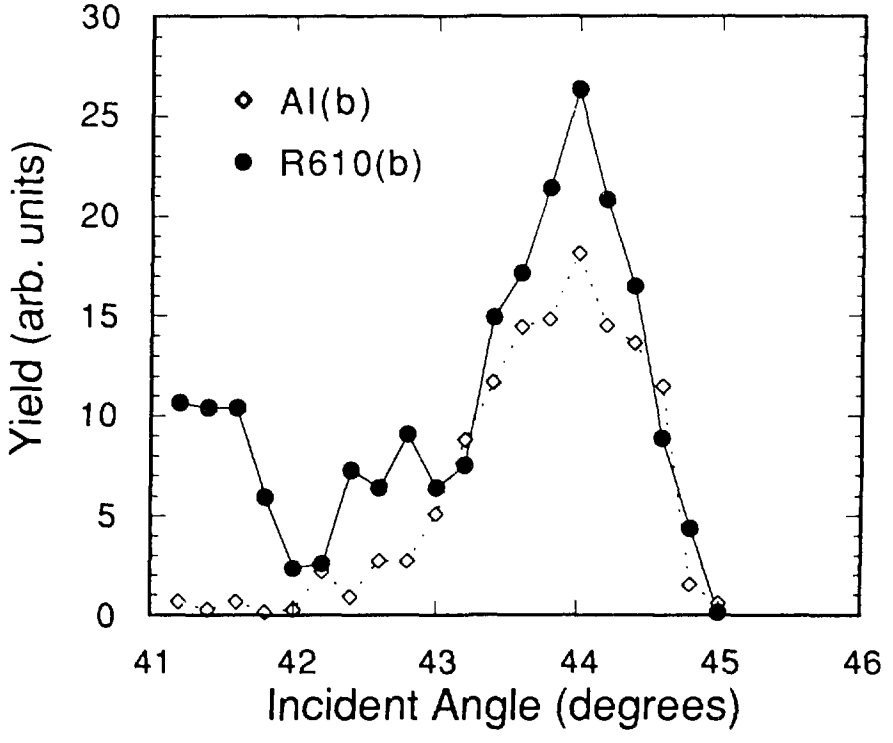

Fig. 3. Desorption yields of rhodamine B molecules and Al atoms as a function of photon angle of incidence for a laser fluence 178 mJ/cm^2.

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