Preliminary Note

Optically detected magnetic resonance of adsorbed species on sapphire

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Optically detected magnetic resonance spectra are reported for the aromatic pyridyl ketone 4-benzoylpyridine adsorbed on sapphire.

1. Introduction

Over the past years, much interest has been directed to the study of molecules adsorbed on surfaces, particularly because of their applicability to industrial surface chemistry. Various spectroscopic techniques have been used to characterize the interactions between the adsorbed species and the surface. Svejda and Maki first observed the optically detected magnetic resonance (ODMR) of SO_2 adsorbed on zeolite [1]. The ODMR of biacetyl adsorbed on silica has also been reported [2]. Recently, we reported the use of ODMR in the study of several aromatic ketones adsorbed on alumina [3]. Aromatic ketones were used in the study because the excited states of these molecules had been well characterized previously [3, 4].

In this preliminary note, we report what we believe is the first observation of ODMR signals from 4-benzoylpyridine (4-BZP) adsorbed on sapphire at 1.4 K.

2. Experimental details

The sapphire rods were purchased from Metro Line Industries, Inc. (Brea, CA 92621). The rod was 2 mm in diameter and 1 cm long. The 4-BZP was purchased commercially, purified by multiple crystallization and sublimation and was dissolved in chromatographic grade cyclohexane. The adsorption onto the sapphire was accomplished from a cyclohexane solution. The sample was carefully placed in a helical structure made of flattened copper wire which served as the microwave receiver. Adsorption was also performed via the vapor phase at several torrs, and the experimental results were found to be similar.

The details of the ODMR apparatus have been discussed in previous papers [5 - 7]. Briefly, the sample in the microwave helix was immersed in liquid helium and was optically pumped with a broad-banded excitation source and the surface emission was monitored with a Jarrell–Ash 1 m scanning double monochromator equipped with a thermoelectrically cooled

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photomultiplier tube. In order to achieve temperatures of about 1.4 K, the vapor above the liquid helium was pumped with two 500 l min^{-1} vacuum pumps connected in tandem. The temperature was measured using a semiconductor device. The microwave source was a Hewlett–Packard model 8350 microwave sweep oscillator. Signal averaging was performed using a Tracor–Northern instrument and the data were transferred to a Hewlett–Packard 9816 microcomputer for interactive analysis. The dynamic parameters of the depopulation process from the zero-field states were observed via the adiabatic rapid passage of the zero-field transitions as first described by Winscom and Maki [8].

3. Results and discussion

A typical adiabatic rapid passage signal is shown in Fig. 1. The results of the ODMR studies of the 4-BZP on sapphire are summarized in Table 1. In addition, the results from the previous studies on the ODMR of 4-BZP on alumina, neat 4-BZP and 4-BZP doped in benzophenone are given for purposes of comparison.

In another study we reported the effect of heavy atoms on the phosphorescent triplet state [9]. In this study, the effect of chlorine on the triplet states of chlorinated naphthalene molecules was observed. It was noted that the anisotropy in the intramolecular heavy atom effect was more evident by far than the intermolecular heavy-atom effect. This result is consistent with those observed here. There is a large increase in the perturbation along the C=O direction, represented by the significant increase in the largest of the rate constants for the phosphorescent decay. Assuming that the adsorption on the surface of the sapphire occurs via the nitrogen lone pair electrons, the effect of such an interaction on the para position could not be explained solely by a heavy-atom effect through the aromatic ring. It would appear that the interaction with the surface may involve more than just physical adsorption via the nitrogen lone pair electrons. The observation of the narrow linewidths evident from a comparision of the full width at half-maximum (FWHM) data seems to support a model in which the ad-

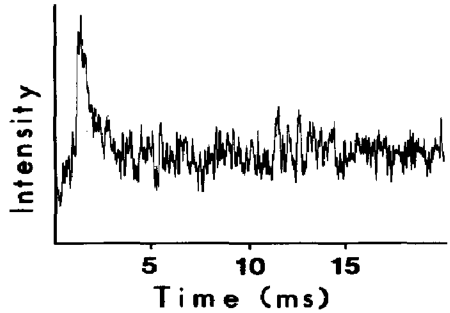

Fig. 1. Typical adiabatic rapid passage signal from 4-BZP adsorbed on sapphire. The 4345 MHz zero-field transition was swept while monitoring the phosphorescence emission. The return to the steady state population subsequent to this perturbation reflects the rate of decay from the faster of the two sublevels which were coupled by the microwave field.

TABLE 1

ODMR results for 4-BZP on alumina and on sapphire doped in benzophenone and as a neat single crystal at 1.4 K

	Zero-field splittings[a] (MHz)	*0–0* (cm^{-1})	*Rate constants* (s^{-1})
BZP on sapphire	4345 (5)	23670	1200
	3390 (10)		860
	950 (30)		40
BZP on alumina[b]	4320 (80)	23400	1700
	3285 (30)		220
	—		240
BZP neat[b]	4472 (94)	23650	1800
	3542 (100)		240
	—		900
BZP in benzophenone[b]	4033 (4)	23710	650
	3067 (3.3)		76
	—		39

[a]Values in parentheses are FWHM in megahertz.
[b]From ref. 3.

sorption is very homogeneous on the sapphire, as would be expected on a surface better defined than alumina (*cf.* Table 1). That the zero-field splittings do not differ by more than about 8% from the case of 4-BZP doped in benzophenone gives assurance that the triplet state is not greatly perturbed by the adsorption.

The fact that the 3390 MHz transition has a positive going signal for an adiabatic rapid passage experiment appears to give good confirmation that the signals being observed are not simply those of polycrystalline 4-BZP, since in the neat 4-BZP samples the same transition gave signals which showed a decrease in the phosphorescence intensity. The signals were also opposite going for the large transition, since in the neat crystal the phosphorescence intensity appeared as a negative going adiabatic rapid passage signal, whereas the intensity was positive going for the 4-BZP on sapphire.

In summary, the perturbation on the triplet sublevels is directed along the carbonyl and the plane containing the carbonyl and the two α-carbons. This fact, in addition to the observed narrow ODMR linewidths, leads to the conclusion that the 4-BZP molecules are uniformly adsorbed on the sapphire via the nitrogen on the pyridyl ring. We are currently carrying out surface analysis using Fourier transform IR methods. In addition, ODMR results of studies of other organic molecules adsorbed on sapphire will be forthcoming.

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1 P. Svejda and A. H. Maki, *Chem. Phys. Lett.*, *83* (1981) 610.
2 C. J. Sandroff, J. M. Drake and I. Y. Chan, *J. Phys. Chem.*, *89* (1985) 463.
3 D. G. Frank, K. A. Martin and A. M. Nishimura, *J. Phys. Chem.*, *88* (1984) 2961.
4 S. G. Hilburn, R. K. Power, K. A. Martin and A. M. Nishimura, *Chem. Phys. Lett.*, *98* (1983) 16.
5 K. J. Latas and A. M. Nishimura, *J. Photochem.*, *9* (1978) 577.
6 D. L. Myers, G. R. Brunk, G. Moller and A. M. Nishimura, *J. Photochem.*, *11* (1979) 249.
7 R. K. Power, K. A. Martin, D. G. Frank and A. M. Nishimura, *J. Photochem.*, *23* (1983) 335.
8 C. J. Winscom and A. H. Maki, *Chem. Phys. Lett.*, *12* (1971) 264.
9 K. J. Latas and A. M. Nishimura, *J. Phys. Chem.*, *82* (1978) 491.