

Variable temperature sample cell and optical mount for laser Raman studies of adsorbed species

G. L. Schrader, Jr. and C. G. Hill, Jr.

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

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A sample cell and optical mount for use in laser Raman spectroscopic studies of adsorbed species at elevated temperatures is described. *In situ* Raman spectra of pyridine adsorbed on 60–120 mesh silica gel at room temperature, 75°C, and 150°C are reported. The cell has also been used in studies of other species adsorbed on silica, alumina, and platinum wire.

I. INTRODUCTION

In recent years a few groups have recorded the laser Raman spectra of various adsorbed species.^{1–7} Such studies provide information about the nature of the adsorbate–adsorbent interaction and are of particular interest to workers in the field of heterogeneous catalysis because of the different effects which arise in chemical and physical adsorption. The studies reported to date have involved recording the room temperature spectra of different chemical species in relatively simple sample holding devices. From the standpoint of the research worker in heterogeneous catalysis, one would like to be able to record the laser Raman spectra under *in situ* reaction conditions with a reasonable variable temperature capability. The various apparatus described by previous investigators are not suitable for such studies.

This note describes a combination batch reactor–sample holder and a sample positioning apparatus which have been used in studies of species sorbed on powdered samples. It would appear to be a relatively simple task to modify the cell to permit its use as a continuous flow reactor with operation in either a recycle or single pass mode. This work is currently in progress.

II. VARIABLE TEMPERATURE RAMAN CELL

The Raman cell for surface studies is shown in Fig. 1. The Pyrex cell is an extension of a Kovar-to-Pyrex seal. The adsorbent is placed in the central tube for bakeout and evacuation and for recording spectra. The outer tube

encloses the heating element and heat conduction fluid which are used for elevated temperature spectra. The heating circuit consists of Nichrome wire enclosed in ceramic beads; connection to an external power supply is made through tungsten leads. Mineral oil is used as the heat conduction fluid and is introduced into the annulus through the stopcocks. Laser excitation occurs via an optical flat which is sealed to the end of the tubes.

The Kovar-to-Pyrex seal is silver soldered to a stainless steel flange and is attached to an all metal bakeable valve (Granville–Phillips type C ultrahigh vacuum valve). This valve can then be connected to a conventional vacuum system for bakeout and evacuation. The gaskets used in all connections are silver plated OFHC copper. A porous stainless steel disk inserted in the inlet port of the bakeable valve prevents the adsorbent from being pulled into the vacuum system during sample preparation. The entire system can be baked out under vacuum or under a specific atmosphere at temperatures up to 450°C.

This assembly has the following advantages:

- (1) The entire assembly, rather than only a portion of the cell, can be baked out under high temperatures.
- (2) The use of an all-metal valve and the associated gaskets eliminates the presence of vacuum grease in the proximity of the cell. One of the difficulties of using Raman spectroscopy to study surfaces is the presence of fluorescence which appears as a broad band with a half-width of about

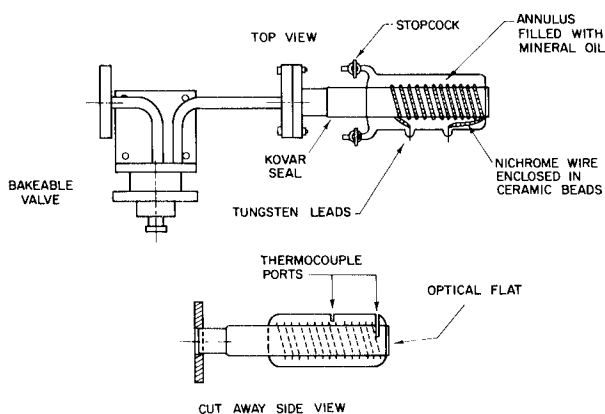


FIG. 1. Raman cell for surface studies.

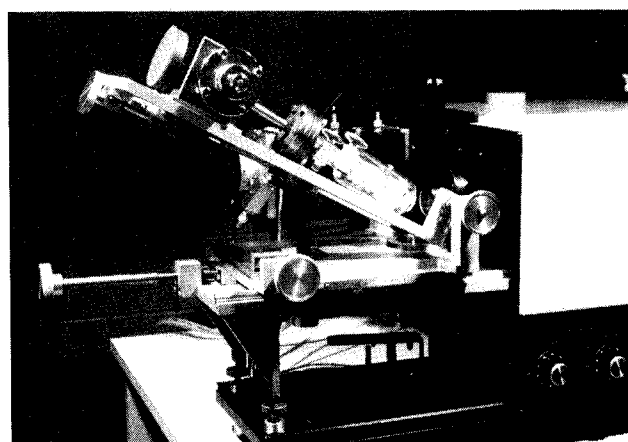


FIG. 2. Optical arrangement for data collection.

2000 cm^{-1} . This fluorescence is generally felt to be the result of strongly adsorbed traces of hydrocarbon impurities.

III. EXCITATION AND COLLECTION OPTICS

The laser Raman spectrometer employed in these studies utilized a Spex Industries model 1401 double monochromator and "third monochromator." Slit settings on the double monochromator were 250 μ , which gave a resolution of about 5 cm^{-1} at 20492 cm^{-1} . The position of the sample cell and optical mount relative to the excitation and collection optics is shown in Fig. 2. An interference filter for the 20492 cm^{-1} line of an argon laser was used for most spectra. A 16-mm microscope lens directs the laser beam onto the sample. The laser beam was defocused at the surface to increase the sample area exposed to the beam and to minimize local heating effects. An optical mount designed for use in a Spex Ramalog system is used to position the cell in the laser beam. The mounts allows for five degrees of freedom in positioning the sample: translation parallel to the laser beam, translation parallel to the spectrophotometer axis, translation perpendicular to the plane containing the spectrophotometer axis and the laser beam, rotation about an axis of the laser beam, and rotation about an axis perpendicular to the beam. Two degrees of freedom in positioning the laser beam are also available from the spectrophotometer optics. Scattered radiation is collected at 90° by an $f/1$ lens system. This system consists of a photographic closeup lens, an Astro-Berlin lens with a 35-mm effective focal length, and a telescope lens which is mounted on the Astro-Berlin lens.

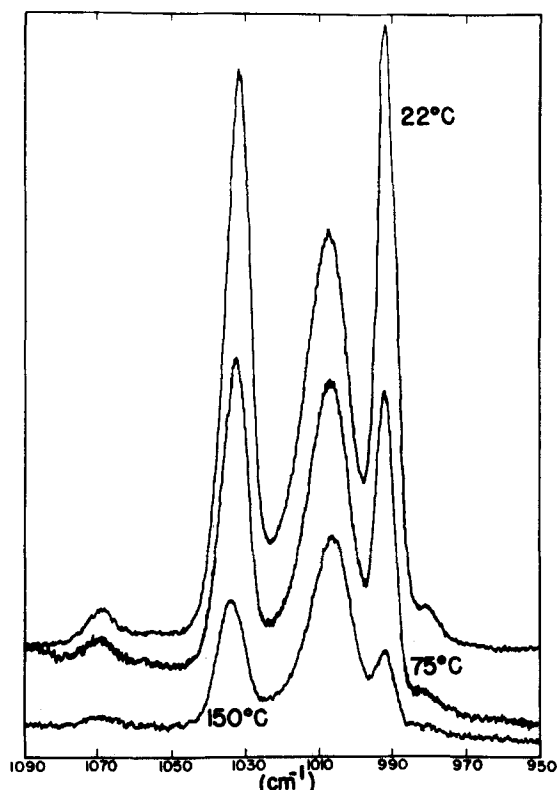


FIG. 3. Pyridine adsorbed on silica gel as a function of temperature ($^{\circ}\text{C}$). $P = 1.86 \times 10^{-2}$ bar.

TABLE I. Spectra of pyridine adsorbed on silica gel ($\Delta\nu$ in cm^{-1}). Abbreviations: h—high coverage (1.86×10^{-2} bar); l—low coverage (10^{-6} bar); br—broad.

Liquid	Schrader and Hill	Relative intensity	Egerton <i>et al.</i> ⁶ (1974)	Kagel ³ (1970)
408	409 (h)	2		
604	604 (h)	4	605 (h)	604
(absent)	619 (h) 620 (l)	4	617 (h)	
653	652 (h) 654 (l)	19	655 (h)	655
711	706 (br)	1		
886	887 (h) 886 (l)	2		
942	946 (h)	2		
981	981 (h)	6		
992	991 (h)	81	991 (h)	992
(absent)	1007 (h) 1006 (l)	54	1008 (h) 1006 (l)	
1031	1032 (h) 1036 (l)	74	1032 (h) 1035 (l)	1032
1069	1069 (h) 1070 (l)	5		
1148	1151 (h) 1153 (l)	3		
1218	1218 (h) 1221 (l)		1219 (h)	1220
1483	1485 (h) 1489 (l)	3		
1575	1577 (h) 1579 (l)	15	1578 (h)	
1582	1597 (h) 1599 (l)	12	1600 (h)	
2920	2923 (h) 2926 (l)	3		
2956	2958 (h) 2964 (h) 2967 (l)	5 5		
2990	2992 (h) 3001 (h) 3006 (l)	5 5		
3057	3059 (h) shoulder 3070 (h) 3073 (l)	63	3061 (h) 3070 (l)	3061
3090				
3148	3149 (h) 3155 (l)	4		

IV. OPERATING TECHNIQUES

Sample preparation prior to contact with adsorbate begins by insertion into the cell and evacuating to 10^{-6} bar or lower for about an hour. An oxygen atmosphere of about 0.6 bar is then introduced, and the temperature of the entire assembly is raised to the desired temperature, typically 300°–400°C. Several purges of the oxygen atmosphere are performed during the 12–15 h of sample preparation. The sample is then evacuated at the desired bakeout temperature. Ultimate pressures are in the 10^{-8} – 10^{-9} bar region.

When the evacuation has been completed, the temperature is reduced, and the annulus filled with the heat conduction fluid. The temperature at which the spectrum is to be recorded is maintained by the heating element, and the adsorbate is introduced. The cell is then detached from the

vacuum system and attached to the optical mount. An incident beam angle of 70° was found to give the highest signal-to-noise ratio. A black cloth was used to cover the assembly to reduce stray radiation.

V. LASER RAMAN SPECTRUM OF PYRIDINE ON SILICA GEL

Our studies of pyridine on silica gel are consistent with those reported in the literature but differ from them in two significant respects. First we have been able to observe many more lines arising from adsorbed species than have been reported previously. Our sensitivity represents a significant improvement over those obtained by previous investigators. Second, all previous spectra have been recorded with the sample maintained at room temperature, whereas some of our spectra have been obtained at elevated temperatures.

Figure 3 is a variable temperature scan of the 950–1090 cm^{-1} region of pyridine adsorbed on silica gel (BDH chromatographic grade, 60–120 mesh, 650 m^2/g). Silica gel at the indicated temperatures was exposed to pyridine vapor for 40 min. The spectrum was then recorded while maintaining the indicated temperatures. A moderate increase in fluorescence was observed at higher temperatures.

Table I clearly indicates that significant improvements in sensitivity and signal-to-noise ratio were achieved. Many low intensity peaks not previously observed were recorded because of several improvements in instrumentation and experimental technique. Heating the silica gel under an oxygen atmosphere for several hours greatly reduces the fluorescence, as reported by previous workers.⁶ In addition, the use of an all-metal valve in the sample cell eliminated the presence of vacuum grease near the sample. Our results support the hypothesis that the fluorescence is due to traces of hydrocarbon impurities. Several other aspects of the instrumentation have also been useful in increasing the signal-to-noise ratio. Use of the optical mount was essential

for observing low intensity lines. The sample cell had to be accurately positioned for efficient excitation of the sample by the laser and for optimal collection of the scattered radiation. The use of a closeup lens substantially increased the amount of scattered radiation directed into the slits of the monochromator. Removal of the Claassen filter and the use of an interference filter for the 20492 cm^{-1} line also led to an improvement in the signal-to-noise ratio because of the increased power incident on the sample. In general, no changes were observed in the spectrum of pyridine adsorbed on silica gel for laser powers as high as 800 mW.

The results obtained with this equipment thus far indicate its potential utility for the study of adsorbed species, especially at elevated temperatures. A more detailed description of the results for the pyridine/silica gel system is being prepared for publication at a later date.⁸

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