The torsional–rotational spectral structure of ethanol molecules adsorbed on polycrystalline silver substrate

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Abstract. A laser photoacoustic spectrometer (LPAS) using a branch-tunable carbon dioxide laser source and a piezoelectric transducer as a detector was employed to study the adsorption of ethanol on a polycrystalline silver surface at 108 K. The strength of bonding between adsorbate and substrate was found to lie between physisorption and chemisorption according to the values of heat of adsorption (33.2 kJ mol^{-1}, 38.8 kJ mol^{-1}, 39.5 kJ mol^{-1} and 44.2 kJ mol^{-1}, obtained by thermal-desorption spectroscopy). A fine spectral structure of seven peaks was obtained in the region of 1045–1054 cm^{-1}, which bears striking resemblance to that obtained by Fourier-transform infrared spectroscopy for gaseous ethanol. Taking into consideration the results of the thermal-desorption study, which suggests weak bonding between ethanol and the silver surface, this fine spectral structure was attributed to the internal torsional rotation of the ethanol adsorbates. To our knowledge, this work is the first report on a torsional–rotational fine spectral structure of ethanol adsorbate on a silver surface. Thus our findings show that torsional–rotational structure exists not only in free molecules as in the gas phase, but also in the adsorbate phase. The set-up used in this experiment was capable of providing 1 cm^{-1} fine spectral resolution at 1 L exposure sensitivity. The LPAS technique developed here has potential for studying other systems as well.

1. Introduction

Several techniques are available to study the vibrational spectrum of adsorbed molecules on metal surface. High-resolution electron energy-loss spectroscopy (HREELS) [1, 2] and infrared reflection absorption spectroscopy (IRAS) [3, 4] are two prominent ones. The former suffers from low resolution (although it is termed high resolution) even though its sensitivity is high. The latter exhibits both high resolution and sensitivity. However, it involves the use of a double/triple monochromator and therefore is quite expensive. On the other hand, the application of photoacoustic spectroscopy (PAS) (using a conventional infrared or Fourier-transform infrared (FTIR) instrument) to study the vibrational spectrum of adsorbed molecules has become a standard technique in recent years. Earlier on, some authors, including one of us, employed a laser as a light source and developed the laser photoacoustic spectroscopy (LPAS) technique [5–7], which obtained some interesting results. The present work is an attempt to improve the resolution and sensitivity of the LPAS technique by means of a branch-tunable carbon dioxide laser beam as light source (spectral range 931.6–1084.6 cm^{-1}) and a piezoelectric transducer (PZT) as a detector, to study the C–O vibrational mode of the ethanol molecule adsorbed on a polycrystalline silver substrate (the C–O stretching vibrational mode of gaseous ethanol molecules is in the vicinity of 1050 cm^{-1}, which falls in the range of

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a carbon dioxide laser). With the advantages of the narrow bandwidth of the laser probe and the high sensitivity of the PZT, it was expected that fine spectral features of ethanol molecules adsorbed on a silver surface might be explored by this LPAS technique. Beside, as the laser beam, with narrow bandwidth, is fully resonant with the vibrational mode excitation of adsorbed ethanol molecules, the rotational structure of a vibrational spectrum, if it exists, might possible be observed. This observation is due to the side-effects which normally exist in electron spectroscopy, being negligibly small.

Rotational spectra of ethanol in the gas phase obtained by Raman and microwave spectroscopy have been reported by several authors [8–13]. Assignment of some rotational and torsional–rotational transitions of *gauche* and *trans* ethanol conformers were made. Solid ethanol spectra in the far-infrared region were also reported [14]. However, there is no *report to date on the rotational spectrum of adsorbed ethanol molecules on a polycrystalline* silver surface. It appears therefore profitable to study the adsorption of ethanol on a silver surface from different points of view.

The structure of the ethanol molecule is shown in figure 1. The distances and angles are as follows [15]: CH = 1.11 Å, OH = 0.95 Å, CC = 1.54 Å, CO = 1.42 Å, ∠HCO = ∠CCO = ∠HCH = 109° 28′, ∠COH = 110°. For a free ethanol molecule the methyl, methlene, and hydroxyl groups can rotate freely. These are internal torsional rotations relative to the main frame C–C–O.

Thermal-desorption spectroscopy (TDS) was also employed in this work to provide auxiliary information about the nature of bonding between ethanol and the silver surface. Four different adsorption states were observed, leading to the conclusion that the adsorption was just between physisorption and chemisorption, i.e. a rather weak bonding existed between ethanol and the silver surface.

2. Experiments

2.1. Laser photoacoustic spectroscopy (LPAS)

In an ultra-high-vacuum (UHV) environment ($\sim 10^{-10}$ Torr) obtained by using a large sputtering ion pump, a commercial pure polycrystalline silver plate, pressed and polished in Fudan University, was cooled down to 108 K by a liquid nitrogen cold finger and then exposed to ethanol molecules, which were fed into the chamber through a feeding syringe. The ethanol was analytically pure. Before adsorption, the silver surface was bombarded repeatedly by an argon-ion sputtering gun for cleaning and it was then checked by Auger analysis that there was no carbon, oxygen, or sulphur left on the surface. Also the residual gas consisted almost exclusively of atomic mass numbers 2 and 28 as determined by a quadrupole mass spectrometer. A single mode CW carbon dioxide laser, which can be tuned by a grating in the range between 931.6 and 1084.6 cm^{-1}, was used. The laser was linearly polarized. The laser intensity was normalized with the help of an additional piezoelectric *disc of the same model as the LPAS signal detector in order to reduce the influence of strong* periodic fluctuations of the laser beam intensity. The infrared laser beam, incident at 75° to the normal of the silver substrate of the sample, was about 3 mm in diameter. The silver substrate acted not only as a catalytic specimen but also a reflector to suppress the giant photoacoustic background induced by the detector itself. This laser beam was modulated by a stable mechanical chopper and was allowed to enter the vacuum chamber through a window of ZnSe with infrared anti-reflection coating on both surfaces.

In this work we focused our attention on the region around 1050 cm^{-1} as we had found in our preliminary experiments that there was some interesting fine spectral structure in
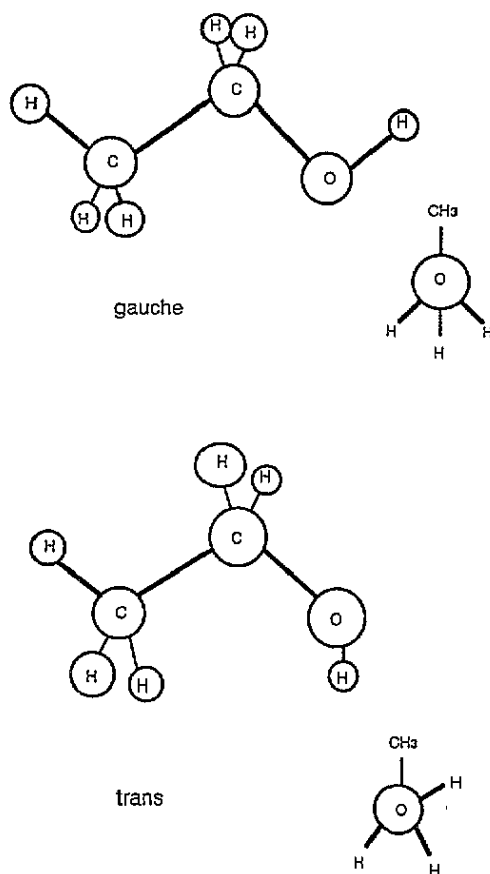
Figure 1. A model of the structure of the ethanol molecule: the *gauche* and *trans* conformers of ethanol.

the C–O stretching vibrational mode of ethanol adsorbates. To obtain a spectrum, we did not follow the usual practice of measuring the LPAS signal while scanning over a certain frequency range. Rather, we fixed the frequency at a preset value and monitored the LPAS signal as a function of exposure time (under a fixed pressure of 4.5×10^{-8} Torr). In a very limited spectral region of only 9 cm^{-1} (from 1045 to 1054 cm^{-1}), 20 laser lines were available according to the branch-tunable carbon dioxide laser output. By measuring the LPAS signal for 20 different laser lines, it was possible to compose spectra at different exposure quantities. The exposure quantity was varied from 1 L (Langmuir, 1 L = 1×10^{-6} Torr s) to 30 L. Some of these LPAS vibrational spectra of adsorbed ethanol on a silver surface are shown in figure 2. The results were reproducible.

2.2. Thermal-desorption spectroscopy (TDS)

The thermal-desorption spectrum was obtained with a quadrupole mass spectrometer (VG Masstorr F). The tungsten heating filament was placed close to the central part of the silver substrate and the thermocouple was mounted on the bottom of the silver substrate. After the chamber achieved UHV conditions and the silver surface had been cleaned and cooled down, ethanol was introduced onto the silver substrate to a certain level, say 3.3 L. The mass

spectrum of the ethanol gas was then recorded and several fragments could be identified. The mass spectrometer was then adjusted to obtain the thermal-desorption spectrum of one of the main fragments of ethanol, viz. atomic-mass number 31, with the temperature being varied from 108 K to 160 K at a heating rate γ of 1 K min^{-1}. Likewise, a thermal-desorption spectrum with similar features as that of mass 31 was obtained for another main fragment of ethanol, viz. atomic-mass number 45. Moreover, the thermal-desorption spectra obtained at different exposure quantities ranging from 3 L to 300 L were almost identical in terms of peak positions and relative intensities.

3. Results and discussion

Figure 2 is the laser photoacoustic spectrum (LPAS) of ethanol molecules adsorbed on a polycrystalline silver surface at a temperature of 108 K with the laser tuning range between 1045 cm^{-1} and 1054 cm^{-1}. Keeping the pressure at 4.5×10^{-8} Torr and by increasing the exposure time, the exposure was varied from 1 L to 30 L with a dosing rate of 0.045 L s^{-1}. The experimental curves in figure 2 correspond to 1 L, 2 L, 4 L, 6 L, and 8 L. It can be seen that the separations between the spectral peaks were not equal. It is well known that absorption in this particular wavenumber range is characteristic of a C–O stretching vibrational mode of ethanol. To confirm the identity of these fine spectral structures, a Fourier-transform infrared spectrum (FTIR, Nicolet 20SXC) for gaseous ethanol at atmospheric pressure was obtained in the same wavenumber range. Figure 3 is the FTIR transmittance spectrum and figure 4 shows its enlarged version of absorbance (inverted transmittance; only the interesting portion between the two dashed lines of figure 3 was enlarged). Comparing figure 2 with figure 4 (see also table 1), it could be seen that in the range around 1045–1054 cm^{-1} there were seven peaks in both spectra with almost identical peak positions and relative separations.

Since the intensity of the LPAS spectrum increased with exposure time and there were minor shifts in peak positions under various exposure quantities, bearing in mind that the LPAS spectrum was not obtained by the conventional scanning model, it appears very unlikely that the fine features of the LPAS spectrum owed their origin to noise. Therefore, such striking similarity between the two spectra leads one to believe that the fine spectral structure exhibited by the LPAS spectrum was the vibrational–rotational spectrum of ethanol molecules adsorbed on polycrystalline silver substrate.

One crucial question, however, must be answered—'In what state does the adsorbed ethanol molecule exist?'—before such an interpretation could be accepted. At 108 K, it might be expected that at a certain high value of exposure, the ethanol molecules would be condensed to form a solid film. Under such conditions, the ethanol molecules should not be able to rotate. However, as the sticking coefficient of ethanol on the silver substrate was probably well below unity, there would be less than one monolayer of ethanol adsorbate on the silver substrate even at 8 L exposure. Now, considering the bonding between ethanol and the silver substrate to be weak, as illustrated by the TDS results obtained in this work (to be described later), these rather isolated molecules, albeit 'adsorbed', might still exhibit a certain degree of rotational freedom, particularly the torsional–rotational motion mode that primarily did not involve the atom through which the ethanol was bonded to the surface. As a natural extension of this line of reasoning, it seems likely that the ethanol adsorption was either through the methylenic carbon with the internal torsional rotation of the hydroxyl group or through the oxygen atom with the internal torsional motion of the methylenic group contributing towards the fine vibrational–rotational structure of the C–O stretching
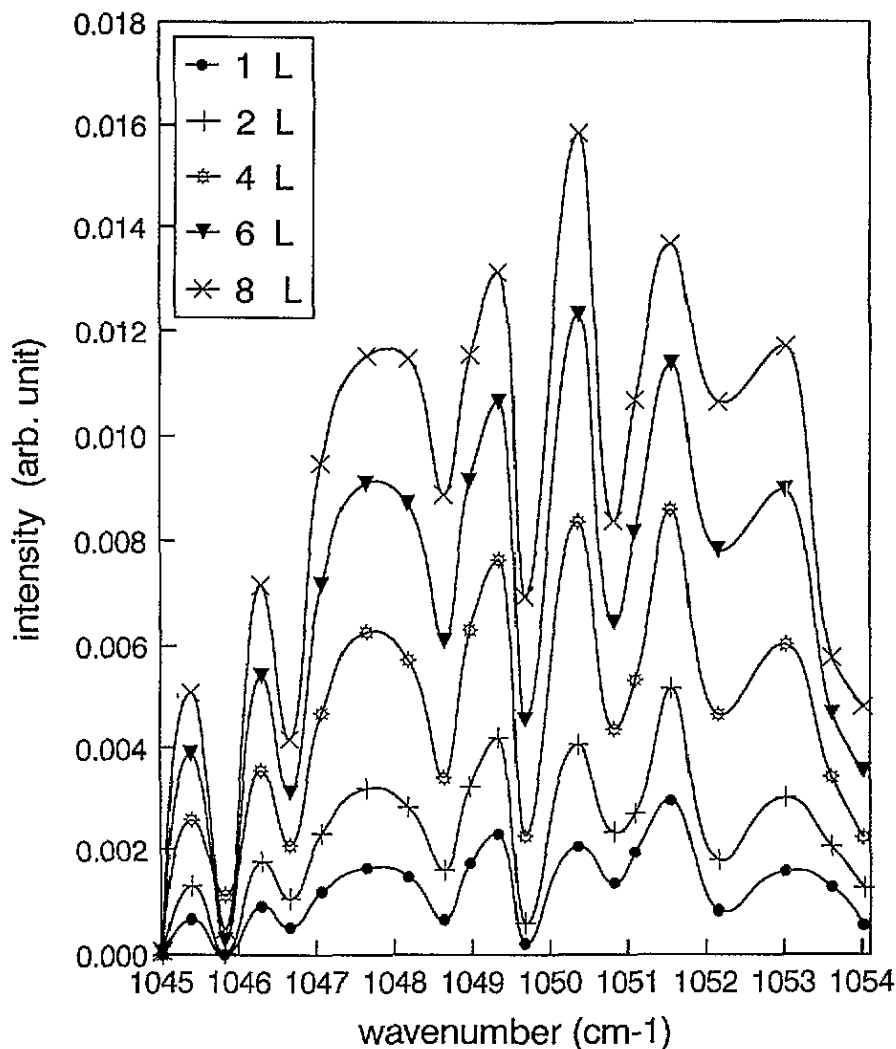
Figure 2. The laser photoacoustic spectra (LPAS) of ethanol molecules adsorbed on a polycrystalline silver surface obtained in this work. The pressure during adsorption was $p = 4.5 \times 10^{-8}$ Torr and the temperature $T = 108$ K. The exposure quantities of the experimental curves, from low exposure to high exposure, are 1 L, 2 L, 4 L, 6 L, and 8 L.

vibrational mode. At present, we are unable to differentiate between these two cases (*a priori*, both C–surface or O–surface bonding are possible [1]) or to make detailed spectral assignments although it can be said that the separations between the peaks are very similar to the internal torsional rotation of gaseous ethanol observed using microwave spectroscopy [9].

Thus, based on our results from both LPAS and TDS, we attribute the final spectral features of the LPAS spectra to the torsional rotation of either the OH group or the CH$_2$ group of the adsorbed ethanol molecules. To our knowledge, this work is the first report on a torsional–rotational fine spectral structure in a vibrational spectrum of ethanol adsorbates on a polycrystalline silver substrate at temperature around 108 K. In other words, the
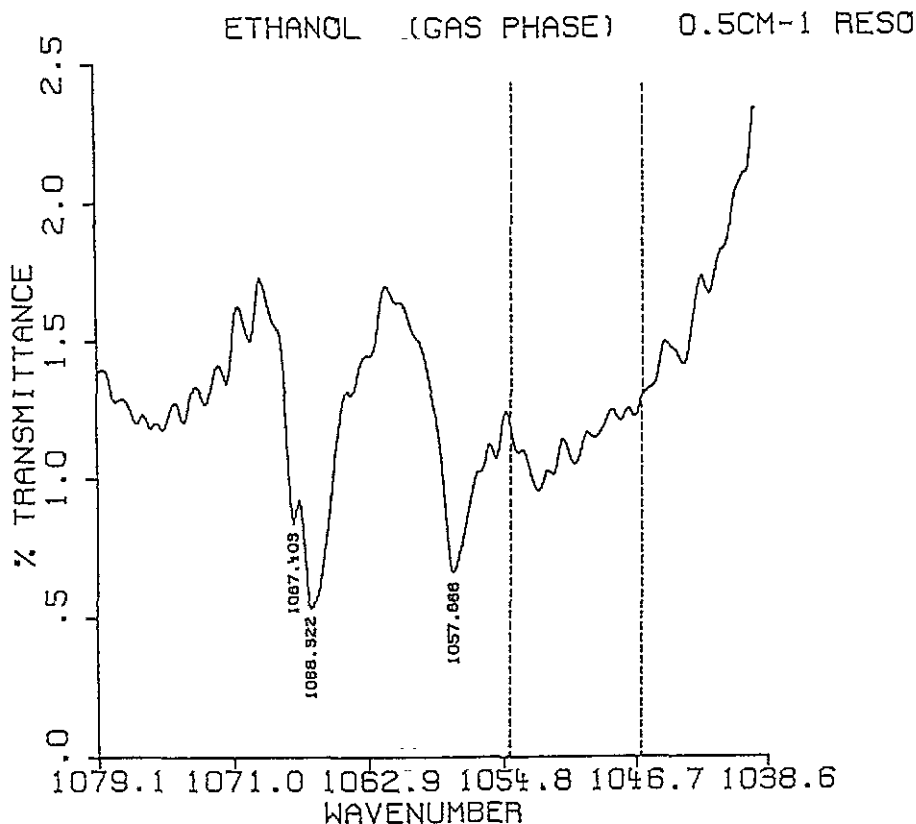
Figure 3. The FTIR transmittance spectrum of the same ethanol molecule sample in the gas phase at atmospheric pressure. The spectrum between two dashed lines was in the same spectral range as in figure 2; this was enlarged and is shown converted in figure 4.

present work had shown that internal torsional rotation could be exhibited not only by gaseous molecules, but also by adsorbed molecules. If similar findings could be confirmed for another adsorbate–adsorbent system, this might well be an area attracting the interest of surface spectroscopists in future.

We ascribe the successful observation of this fine spectral structure by LPAS to two factors: a negligible perturbation of the original adsorption due to the low quantum energy of the incident photons (a 10.6 μm carbon dioxide laser photon has energy of only 117 meV) and the narrow bandwidth of the laser beam. The latter was mainly concerned with improving exposure sensitivity and spectral resolution to the extent of 1 L and 1 cm^{-1} respectively. The former, on the other hand, might be a more fundamental contributor to the observation of the torsional–rotational behaviour of an adsorbed molecule. In any event, since the set-up of LPAS is simpler than that of infrared reflection absorption spectroscopy (IRAS), it has the potential to be developed further and to provide information complementary to that obtained from electron spectrometers.

Before we leave the discussion on LPAS, it should be noted that there were frequency shifts between LPAS and FTIR spectra of the order of 1.0–1.6 cm^{-1}. However, since we did not calibrate the two instruments by obtaining the spectra of a common substance, it is difficult to ascertain at this stage the nature of this minor frequency shift.

The TDS study on ethanol adsorbates supported the notion that ethanol molecules

Figure 4. The portion between the two dashed lines of figure 3 enlarged, indicating the relation between the absorbance and wavenumber. This spectrum of gaseous-phase ethanol was almost identical to the LPAS spectrum obtained in this work for ethanol adsorbate phase (figure 2).

Table 1. A comparison of the spectra of adsorbed ethanol (LPAS) and gaseous ethanol (FTIR). All the data are in cm^{-1}.

Adsorbed ethanol (LPAS)						
Peak position	1045.3	1046.2	1047.5	1049.2	1050.3	1051.5	1052.9
Separation	0.9	1.3	1.7	1.1	1.2	1.4

Gaseous ethanol (FTIR)						
Peak position	1046.3	1047.2	1049.0	1050.4	1051.9	1052.9	1054.2
Separation	0.9	1.8	1.4	1.5	1.0	1.3

adsorbed on a silver substrate might exhibit certain degree of rotational freedom. Figure 5 shows the TDS of ethanol at 3.3 L exposure with the fragment of atomic-mass number 31. The temperature range was 108 K to 160 K with a heating rate $\gamma = 1$ K min^{-1}. Four peaks of maximum desorption rate were found: $T_m = 113$ K, 132 K, 134 K, and 150 K.

Because we used polycrystalline silver as the substrate, the four temperatures of maximum desorption rate might be due to ethanol absorbed on different crystal planes or different surface sites on a single plane arising from defects. The well established Arrhenius relation for thermal desorption of non-dissociating adsorbates on a surface [16] is

$$Q/RT_m^2 = (\nu/\gamma) \exp(-Q/RT_m)$$

where Q is the heat of adsorption, T_m the temperature of the maximum desorption rate, γ the heating rate (1 K min^{-1}), R the gas constant, and for a first-order reaction the frequency constant $\nu = 10^{13}$ s^{-1}. These four different temperatures of maximum desorption rate correspond to the following values of heat of adsorption Q: 33.2 kJ mol^{-1}, 38.8 kJ mol^{-1}, 39.5 kJ mol^{-1}, and 44.2 kJ mol^{-1}. Usually a value of Q less than 25 kJ mol^{-1} is considered to be physisorption, and a value more than 40 kJ mol^{-1} signifies chemisorption. Therefore, although the nature of adsorption sites corresponding to each Q value cannot be identified at present, the range of Q values suggest that the adsorption of ethanol molecules on a silver
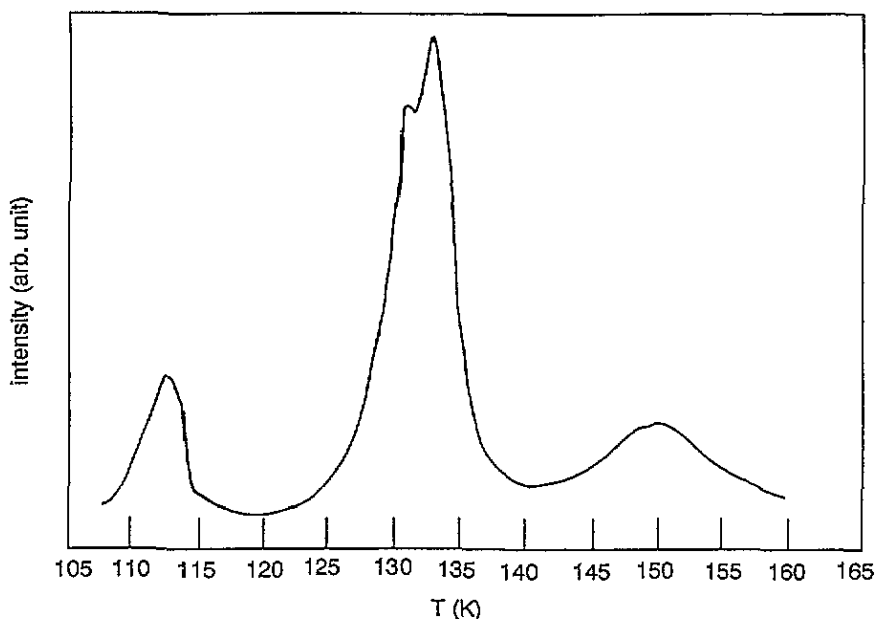
Figure 5. The TDS of ethanol adsorbates. The exposure was 3.3 L. The four peaks of maximum desorption rate were at $T_m = 113$ K, 132 K, 134 K, and 150 K. The heating rate was $\gamma = 1$ K min^{-1}.

substrate in our case could be considered to be between physisorption and chemisorption. Such weak bonding might therefore allow the adsorbate molecules to exhibit a certain degree of rotational freedom as put forward earlier.

4. Conclusions

With a branch-tunable carbon dioxide laser as light source and a PZT as detector, a laser photoacoustic spectrometer capable of rendering 1 L exposure sensitivity and 1 cm^{-1} spectral resolution was built.

Ethanol was found to be weakly adsorbed on a polycrystalline silver surface at temperature around 108 K. These weakly adsorbed molecules were capable of exhibiting internal torsional rotation behaviour as witnessed by the striking similarity between the adsorbed ethanol LPAS spectrum and the gaseous ethanol FTIR spectrum in the region around 1055 cm^{-1}.

The LPAS technique appears to be a suitable tool to explore fine spectral structure of a vibrational mode of adsorbed molecule. Further refinement of the technique as well as study on other adsorbates are called for to ascertain the findings of the present work as well as to enable the technique to be more widely applicable.

Acknowledgments

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