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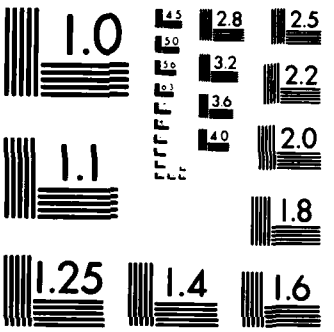

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Recently it has been proposed based on thermal desorption, electron spectroscopy and work function measurements that extremely small pores and cavities in silver films deposited at temperatures below 150K are the location of active sites for surface enhanced Raman scattering. The experiment reported here is an attempt to demonstrate in a more direct way that these cavities are responsible for the observed enhanced Raman scattering. It is shown that by filling these cavities with Xe atoms the enhancement effect on deposited pyridine can be dramatically reduced. Originator-supplied Keywords:

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# THE EFFECT OF XE UNDERLAYERS ON THE SURFACE ENHANCED RAMAN SCATTERING OF PYRIDINE ON COLD SILVER

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**ABSTRACT:** Recently it has been proposed based on thermal desorption, electron spectroscopy and work function measurements that extremely small pores and cavities in silver films deposited at temperatures below 150K are the location of active sites for surface enhanced Raman scattering. The experiment reported here is an attempt to demonstrate in a more direct way that these cavities are responsible for the observed enhanced Raman scattering. It is shown that by filling these cavities with Xe atoms the enhancement effect on deposited pyridine can be dramatically reduced.

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There are essentially three types of vacuum deposited Ag films which exhibit SERS: films deposited on cold substrates,[1,2] films deposited on microscopically rough surfaces[3] and extremely thin Ag island films.[4] Experiments on the latter two indicate that long range electromagnetic effects can lead to significant enhancement in the Raman scattering process. This was most clearly seen in experiments in which the silver surfaces were prepared in vacuum with controlled roughness.[5-9] There are, however, some unique aspects connected with the SERS of coldly deposited Ag films.[1,2,10-12] The most striking of these is that the coldly deposited films lose their ability to exhibit SERS once the films are warmed to room temperature.

Recently it has been proposed that the SERS takes place with molecules inside cavities and pores that are known to be present in these coldly deposited silver films.[13,14] This proposal, however, was essentially based on indirect evidence, *i.e.*, the behavior of Xe atoms or pyridine adsorbed on the surface of the coldly deposited silver films, seen by various surface analytical techniques, coincided remarkably well with a number of SERS properties seen on these films, and the fact that computations on sinusoidal gratings with short periodicity and large amplitude demonstrated that higher fields could exist in the regions of the grooves.

The present work is an attempt to establish a more direct connection between the cavity site concept and the SERS phenomenon. One of the puzzling behavior of the coldly deposited silver films is what we call the low temperature anneal.[12,15] Briefly, when approximately one monolayer of pyridine is deposited at temperatures below 10K the SERS effect tends to be small; however on warming the intensity increases irreversibly until the temperature is about 70K. At the time this effect was first observed, this observation did not seem to agree with the idea of electromagnetic

resonance effects due to protrusive roughness and indicated some sort of SERS active sites. It was concluded that rather than the silver atoms the pyridine molecules are mobile at 70K, *i.e.*, moved to or reoriented themselves at the active sites.[12] The concept of a cavity as the location of the active sites has several advantages and the experiments described here test whether it would be possible to fill the cavity with a non-Raman scattering entity such as Xe before depositing the pyridine and to see its effect on SERS.

The UHV system and the Raman spectroscopy apparatus used in these experiments are identical to those described previously.[16,17] A 12mm×12mm sapphire substrate was used in combination with a mechanism capable of masking part of the substrate for producing different surface coverages on different parts of the substrate. The deposition of Ag, Xe and pyridine was monitored with a quartz microbalance. A 100 mW beam of the 18837 $cm^{-1}$ Kr ion laser line was used for the primary beam and the Raman spectrometer was set for about 4 $cm^{-1}$ resolution.

The substrate was prepared by first depositing a silver island film on a substrate at 100°C. The substrate was then cooled to 70K and about 400Å of Ag was deposited at a rate of about 2 Å/sec. The substrate was then cooled below 10K and, at first, a monolayer (ML: by this we mean the amount equivalent to a monolayer on a flat surface) of Xe was deposited while the left half of the substrate was masked. This was then followed by a deposition of 2 ML of Xe with the bottom half of the substrate masked. The result was that the substrate now had four different quadrants; one with no Xe, and the other three with the equivalent of 1, 2 and 3 ML of Xe as shown in in the inset of Figure 1. The substrate was then warmed to about 60K which is below the temperature for appreciable sublimation of physisorbed Xe. The purpose of this step was to make sure that the Xe atoms had enough thermal energy to migrate into the cavities.

The substrate was then cooled once more below 10K for a final deposition of approximately one monolayer of pyridine over the entire substrate so that the same amount of pyridine was condensed on each quadrant. The time from the deposition of Ag on the cold substrate to the deposition of pyridine was kept as short as possible, in practice about 30 minutes, in order to reduce contamination of the substrate. The background pressure during this procedure was $10^{-9}$ Torr.

The Raman spectrum of each quadrant was taken immediately after the deposition of pyridine. Typical spectra spanning the two ring mode vibrations (975 $cm^{-1}$ to 1075 $cm^{-1}$) of the pyridine is shown in Figure 1. The quadrant without any Xe clearly showed the characteristic vibration of pyridine, but the quadrants with Xe underlayers gave considerably reduced signals with those of two and three Xe layers almost undetectable. This is consistent with the earlier estimate that it takes about 2 monolayers of Xe to fill the cavities.[14]

In the subsequent Raman measurements the substrate was shielded from the laser beam while it was warmed to an annealing temperature $T_a$, kept there for about three minutes and then cooled down at least 20K below $T_a$ for the Raman measurement. The purpose of this was to minimize the heating effects due to the laser. The anneal temperature $T_a$ was increased in steps. The effect of the low temperature anneal was seen with the quadrant without the Xe. The pyridine signals are the strongest of all quadrants and grew slowly with increase in temperature. This is in accord with the low temperature anneal results reported earlier. The peaks due to the quadrants with Xe underlayers remained relatively unchanged up to about 40K. The spectra taken after an anneal at $T_a$=55K are shown in Figure 2. The considerable increase in peak intensities of the pyridine with no Xe underlayer can be seen but note that the peaks of pyridine with 2

and 3 Xe under layers are beginning to increase. We attribute this to the increased mobility of Xe and pyridine with temperature allowing interchange of the two species to begin.

When the $T_a$ is increased beyond 70K we see dramatic increases in peaks for all four quadrant. See Figure 3. Certain structural changes begin to take place at this stage. One such changes is the beginning of appreciable sublimation of the physisorbed Xe, even out of the pores.[18] Another change might involve the atomic scale movement of surface Ag atoms due to the thawing out of some of the instability that was frozen into the film when the silver film was deposited at 70K. Also with increasing temperature the pyridine molecules are steadily being drawn into the pores while the Xe atoms escape from the surface. Figure 3 shows the spectra taken from all four quadrants for $T_a$=130K. This is just below the temperature where appreciable sublimation of pyridine can take place. Note that the ordinate scale is changed from those of Figure 2 indicating the remarkable increase in the enhancement that has now taken place. The effect of what we call the high temperature anneal[11,12] is clearly dominating the change. This is starting to take place at a lower temperature than previously reported[12] because the Ag film was deposited this time at a considerably lower temperature 70K in contrast to 150K. The behavior described above is summarized in Figure 4 in which the peak height of the symmetric ring mode vibrational band measured from the background as baseline is plotted against the annealing temperature $T_a$.

It has been established earlier that coldly deposited silver films are porous and when Xe is deposited on such silver films thicker than about 100Å, about 1.5 ML of Xe are absorbed into the pores of the film.[14] Therefore when only one ML of Xe is deposited most of the surface region is bare. Pyridine molecules which are deposited on top of this

would certainly have easy access to any SERS active sites other than those within the pores and a small fraction may find room in the pores. When 2 ML of Xe is predeposited the pores are completely filled but a large fraction of the nonporous surface is bare. However with a 3 ML deposit of Xe the entire surface is covered with at least 1 ML of Xe. If SERS active sites consist of atomic scale protrusive configurations such as adatoms or larger clusters of silver atoms,[19,20] they will not be covered by a monolayer of Xe. It could even be argued that the Xe atoms will facilitate the migration of the pyridine molecules to the tips of such active sites.

The results of these experiments are completely consistent with the proposal that the relevant SERS active sites for the pyridine molecules are within the pores. They indicate that atomic scale protrusions and adatoms which are likely to be abundant on the surface of these coldly deposited films do not play a dominant role in the SERS by themselves.

The history of SERS points to a complex phenomenon consisting of a number of possible mechanisms with each experimental situation emphasizing some subset of all the possible mechanisms. It should be emphatically pointed out that the proposal of the cavity site model for SERS does not necessarily exclude the possibility of other mechanisms in SERS, such as chemical interactions including charge transfer mechanisms.[21] Within the pores and cavities it is very probable that some of the surface metal atoms are chemically more active than atoms of low index crystallographic surfaces. Molecules within the pores can be coordinated to the pore surface in many ways. That large scale roughness of the order 1000Å also contributes to the SERS of coldly deposited silver films is seen in the comparison of cold silver films with and without an island silver film underlayer.[12] We conclude that for coldly deposited Ag

films and pyridine molecules the case for cavity sites as an important factor has been strengthened.

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## REFERENCE


1. T. H. Wood and M. V. Klein, *J. Vac. Sci. Technol.* **16**, 459 (1979).
2. R. R. Smardzewski, R. J. Colton and J. S. Murday, *Chem. Phys. Letters* **68**, 53 (1979).
3. J. C. Tsang and J. Kirtley, *Solid State Commun.* **30**, 617 (1979).
4. C. Y. Chen, E. Burstein and S. Lundquist, *Solid State Commun.* **32**, 63 (1979).
5. J. E. Rowe, C. V. Shank, D. A. Zwemer and C. A. Murray, *Phys. Rev. Letters* **44**, 1770 (1980).
6. P. N. Sanda, J. M. Warlaumont, J. E. Demuth, J. C. Tsang, K. Christmann and J. A. Bradley, *Phys. Rev. Letters* **45**, 1519 (1980).
7. A. Girlando, J. G. Gordon II, D. Heitmann, M. R. Philpott, H. Seki and J. D. Swalen, *Surf. Sci.* **101**, 417 (1980).
8. C. A. Murray, D. L. Allara and M. Rhinewine, *Phys. Rev. Letters* **46**, 57 (1981).
9. P. F. Liao, J. G. Bergman, D. C. Chemla, A. Wokaun, J. Melngailis, A. M. Hawryluk and N. P. Economou, *Chem. Phys. Letters* **82**, 355 (1981).
10. I. Pockrand and A. Otto, *Solid State Commun.* **37**, 109 (1981).
11. I. Pockrand and A. Otto, *Solid State Commun.* **38**, 1159 (1981).
12. H. Seki, *J. Chem. Phys.* **76**, 4412 (1982).
13. H. Seki and T. J. Chuang, *Chem. Phys. Letters* **100**, 393 (1983).
14. V. E. Albano, S. Daiser, G. Ertl, R. Miranda, K. Wandelt and N. Garcia, *Phys. Rev. Letters* **51**, 2314 (1983).
15. H. Seki, *Solid State Commun.* **42**, 695 (1982).
16. H. Seki and U. Itoh, *J. Chem. Phys.* **72**, 2166 (1980).
17. H. Seki and M. R. Philpott, *J. Chem. Phys.* **73**, 5376 (1980).
18. V. E. Albano, S. Daiser, R. Miranda and K. Wandelt, *Surf. Science* (to be published).

19. J. Billmann, G. Kovacs, A. Otto, *Surf. Sci.* 92, 153 (1980).

20. A. Otto, I. Pockrand, J. Billmann and C. Pettenkofer in "Surface Enhanced Raman Scattering," Ed. by R. K. Chang and T. E. Furtak (Plenum Press, 1981).

21. J. E. Demuth and P. N. Sanda, *Phys. Rev. Letters* 47, 57 (1981).

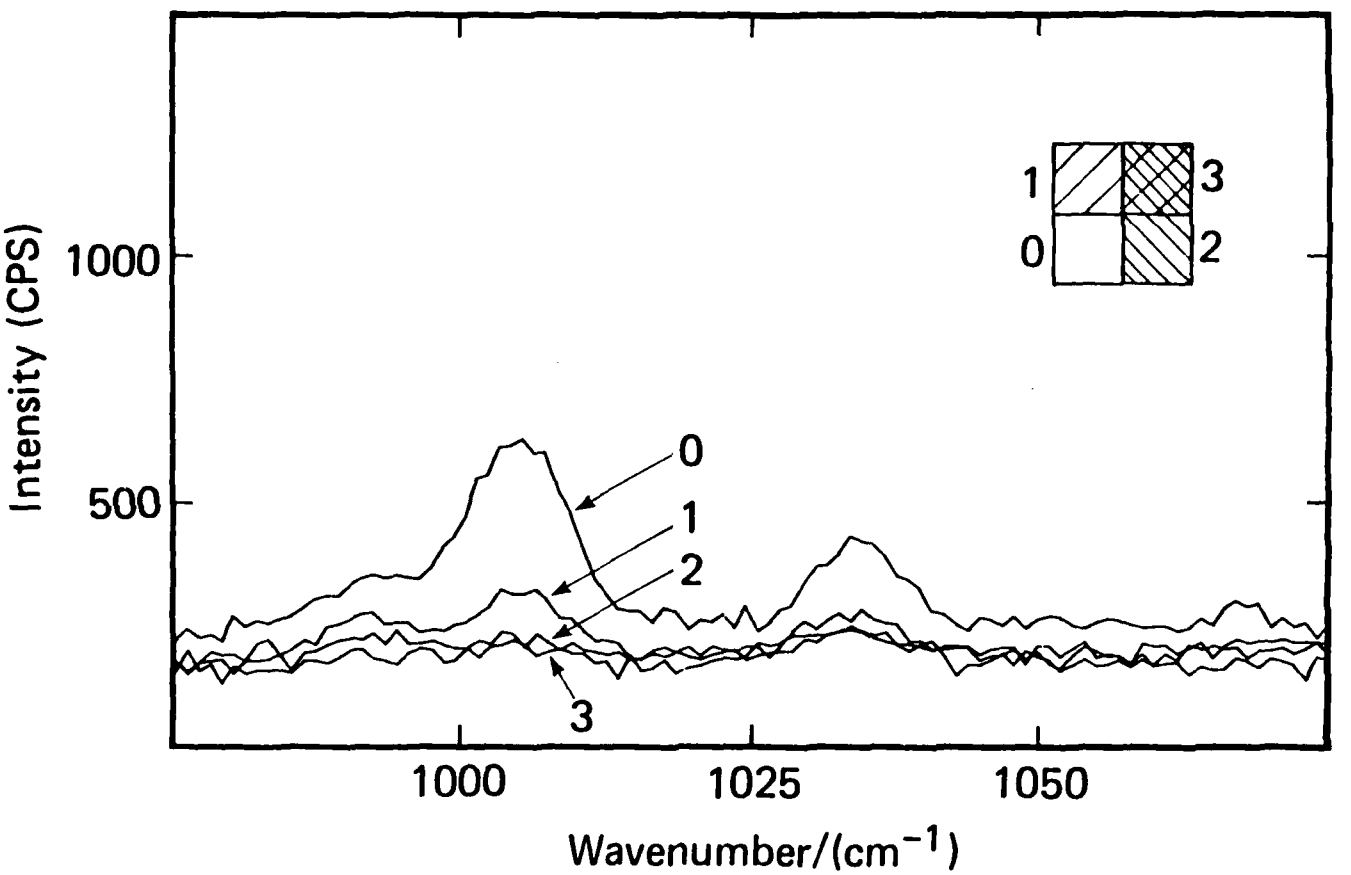


**Figure 1.** The SERS spectra of pyridine on a coldly deposited silver film taken right after pyridine deposition at T=12K. The spectrum 0 is for no Xe underlayer, spectrum 1 is for 1 monolayer equivalent of Xe underlayer, spectrum 2 is for 2 monolayer equivalent of Xe underlayer, and spectrum 3 is for 3 monolayer equivalent of Xe underlayer. The inset shows the Xe underlayer pattern on substrate.

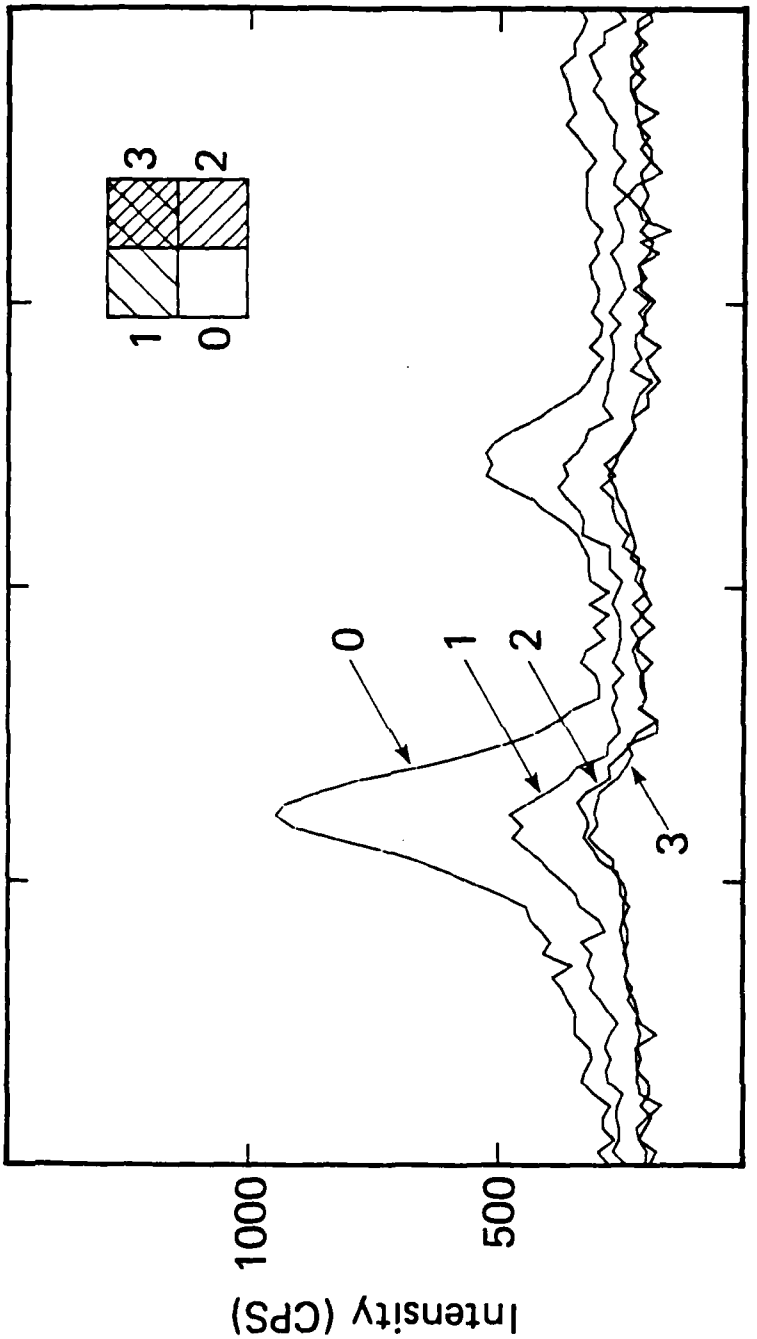


**Figure 2.** The SERS spectra of pyridine on a coldly deposited silver film after annealing at $T_a$=55K where the low temperature anneal is almost complete. Spectrum notation is as indicated in Figure 1.

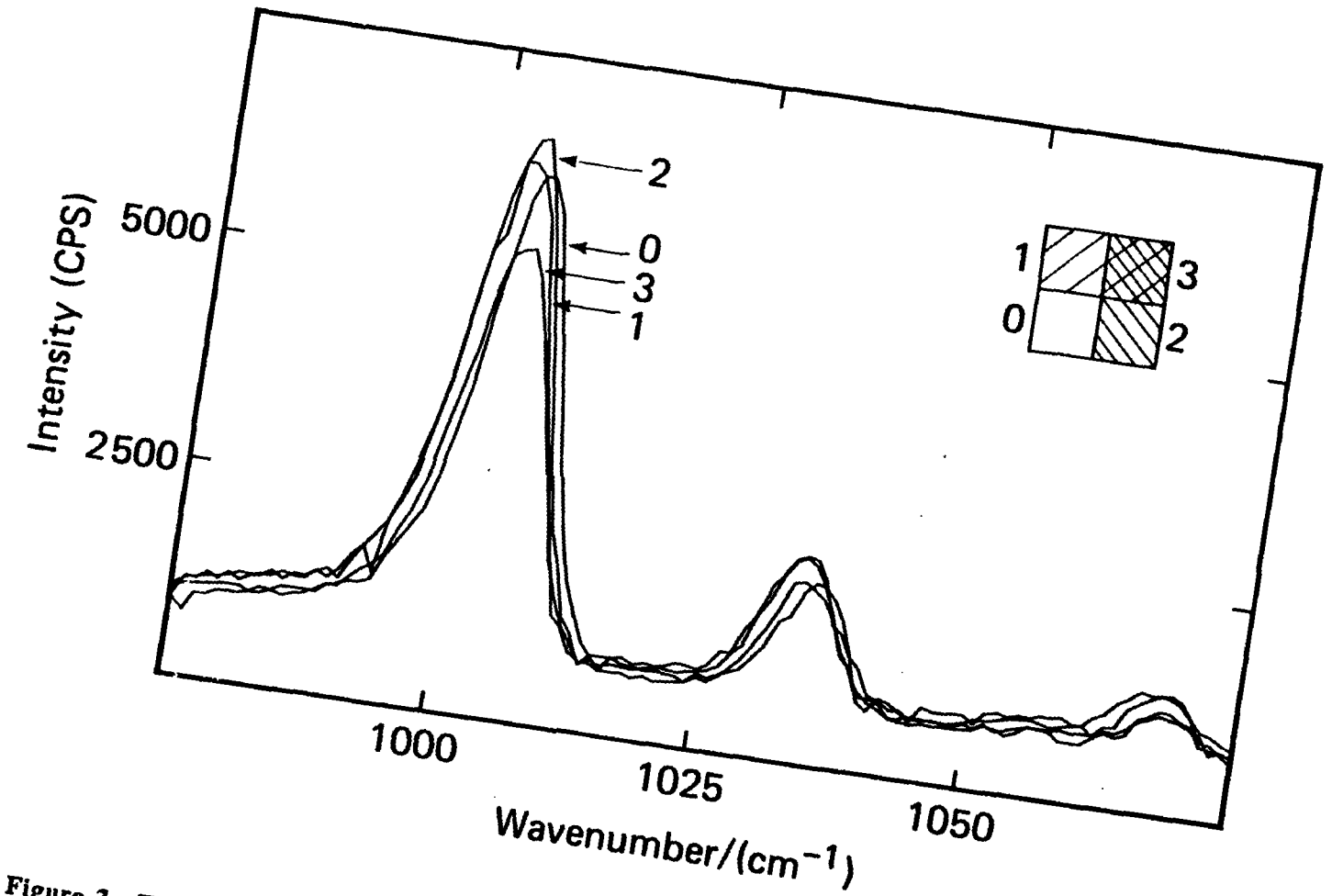


**Figure 3.** The SERS spectra of pyridine on a coldly deposited silver film after annealing at $T_a$=130K by which temperature most of the Xe has been sublimed but before any pyridine has been lost. Spectrum notation is as indicated in Figure 1.

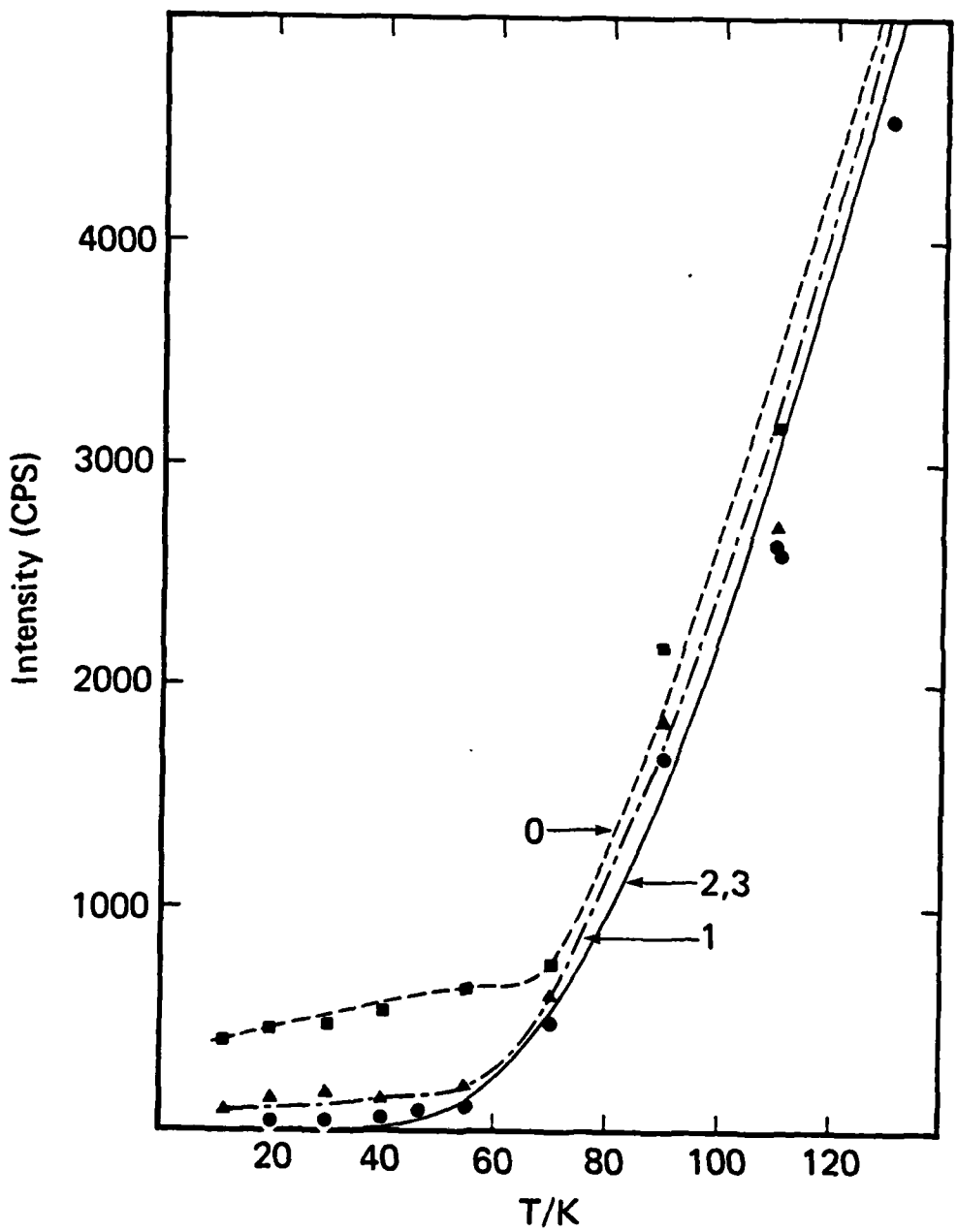


**Figure 4.** The peak height of the symmetric ring mode band of pyridine at 1003 $cm^{-1}$ as a function of the annealing temperature $T_a$.

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