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Surface-Enhanced Raman Spectroscopy as a Probe of Adsorbate-Surface Bonding: Benzene and Monosubstituted Benzenes Adsorbed at Gold Electrodes

by

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SURFACE-ENHANCED RAMAN SPECTROSCOPY AS A PROBE OF ADSORBATE-SURFACE BONDING: BENZENE AND MONOSUBSTITUTED BENZENES ADSORBED AT GOLD ELECTRODES

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ABSTRACT

Surface-enhanced Raman spectra of benzene and eight monosubstituted benzenes adsorbed at gold electrodes have been examined in order to probe the nature of adsorbate-surface bonding for simple aromatic molecules. Benzene appears to adsorb flat via π adsorbate-surface interactions as evidenced by the significant (20-30/cm) downshifts in the symmetric ring breathing mode (ν_1) and the absence of other ring modes in the SER spectra. Similar results were obtained using gold surfaces prepared by electroplating or anodic-cathodic potential sweeps in chloride, although much more stable SERS was obtained by using the latter procedure. The ring substituents $-CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$, -Cl, -Br, -CN, $-NO_2$, -COOH and -CHO were chosen so to provide steric perturbations or alternative binding modes to the metal surface. With the alkyl, benzoate, and aldehyde substituents, small yet significant (ca. 5-15/cm) decreases in the ν_{12} and ν_{18a} characteristic ring modes along with band broadening were observed upon adsorption, consistent with attachment via the benzene ring. For the halogen substituents, smaller such downshifts were obtained along with the appearance of low-frequency modes associated with halogen-surface vibrations, indicating the role of substituent bonding in the adsorption. For the nitro and nitro substituents, the ring modes were unaltered in frequency or bandshape upon adsorption while intense internal substituent modes were observed. The frequency shifts obtained for the latter modes along with the appearance of substituent-surface vibrational bands indicate that surface binding occurs entirely via the substituent rather than the benzene ring. Studies with deuterium-labelled adsorbates indicate that the adsorption-description kinetics were rapid on the time scale required to obtain the surface Raman spectra.

A major application of vibrational spectroscopies at metal surfaces is to gain information on the nature of adsorbate-surface interactions from differences in the form of the spectra, especially frequencies and bandshapes, for species in bulk and interfacial environments. A potentially valuable such technique, especially at electrochemical interfaces, is surface-enhanced Raman scattering (SERS).[1] Although limited to polycrystalline, mildly roughened, surfaces (most prominently at silver, copper and gold) absolute spectra can rapidly be obtained with high resolution ($\sim 1\ cm^{-1}$) over wide frequency ranges, enabling a variety of vibrational bands associated with internal and absorbate-surface modes to readily be detected.

We have recently reported a straightforward procedure by which gold surfaces can be prepared so to yield extremely stable as well as intense SER spectra for a miscellany of adsorbates.[2] In particular, stable SER spectra can be obtained at gold for adsorbates such as oxyanions,[2] ethylene,[3] carbon monoxide,[4] etc., that yield weak or even undetectable signals at the traditionally preeminent SERS metal, silver.[2] This is attributed in part to a greater stability of the SERS-active sites (probably large metal clusters[1a]) at gold, so that their survival does not require the presence of high adsorbate coverages as appears to be the case at silver.[1a,5]

We report here a study of potential-dependent SERS for benzene adsorbed at gold-aqueous interfaces. Benzene is of interest in view of its simple symmetric structure, and the likely involvement of π orbitals in the surface bonding. The influence of metal-benzene π bonding upon the vibrational spectra has been examined for bulk-phase arene complexes.[6] A number of vibrational studies of benzene adsorbed at metal surfaces have been reported.[7,8] These include several SERS studies,[8] although only one[8e] refers to an electrochemical environment. This latter observation (benzene SERS at

silver electrodes[8e]), is perhaps questionable since several laboratories, including our own, have been unable to duplicate it.[9]

We also summarize SER spectra for nine monosubstituted benzenes, C_6H_5X, where X = $-CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$, -Cl, -Br, -CN, $-NO_2$, $-COO^-$, and -CHO. These substituents were chosen so to alter the adsorption stereochemistry and/or to provide possible alternative binding sites to the metal surface. The results demonstrate the value of SERS for ascertaining the mode of attachment of molecules to electrode surfaces. A companion paper[10] examines such adsorbate-surface interactions for alkenes and alkynes at gold electrodes on the basis of their SER spectra.

EXPERIMENTAL

The electrochemical cells and the laser Raman system used for the SERS measurements have been described in detail elsewhere.[11] Raman excitation was provided by a Spectra Physics Model 165 Kr^+ laser operated at 647.1 nm, the scattered light being collected by means of a SPEX Model 1403 scanning double monochromator. The gold electrode, although stationary, was of rotating disk construction (Pine Instruments Co.), consisting of a 0.2 cm radius disk sheathed in 0.6 cm radius Teflon. It was mechanically polished successively with 1.0 and 0.3 μm alumina immediately before use. Electrode roughening, so to yield SERS-active gold, was accomplished as described in ref. 2, involving a succession (20-25) of potential sweep oxidation-reduction cycles at 500 mV sec^{-1} in 0.1 M KCl from -300 to 1100 mV versus the saturated calomel electrode (s.c.e.).

Benzene and the monosubstituted benzenes were obtained as either reagent or "Gold Label" grades from Aldrich Co. Water was purified by means of a Milli Q system (Millipore Corp.). All electrode potentials are quoted versus the s.c.e., and all measurements were made at room temperature, 23 ± 1°C.

RESULTS AND DISCUSSION

(a) Benzene

Following electrochemical roughening by means of oxidation-reduction cycles in 0.1 M KCl as described above,[2] the gold electrode was rinsed thoroughly and transferred into the electrochemical SERS cell containing only supporting electrolyte, usually 0.1-1.0 M H_2SO_4 or 0.1 M Na_2SO_4. The acidic medium enabled potentials, E, as positive as 1100 mV to be examined prior to oxide film formation, whereas hydrogen evolution did not occur in the neutral medium until around -800 mV. The SER spectra in both electrolytes exhibited a weak band at 185 cm^{-1}, for E $\geq$ -300 mV, attributed to a sulfate-surface stretching mode,[2] which increased in intensity with increasing positive potentials, as expected from the greater sulfate specific adsorption under these conditions. Additional weak broad bands around 1500-1600 cm^{-1} and 2960 cm^{-1} were often observed, probably due to adsorption of organic impurities (cf. silver surfaces, ref. 12). These bands, however, could essentially be eliminated by further water purification by means of multiple distillations from alkaline permanganate.

Addition of a few mM of benzene, so to produce a near-saturated solution, yielded an additional well-defined band around 965-975 cm^{-1}. A typical set of potential-dependent SER spectra, from -500 to 700 mV vs s.c.e. in the 900-1050 cm^{-1} region are shown in Fig. 1. While a single peak at 972-975 cm^{-1} was observed for E < -300 mV, at more positive potentials a pair of peaks at about 975 and 965 cm^{-1} were obtained. The integrated intensity of both peaks reached a maximum around 200 mV. Similar results were obtained using acidic and neutral sulfate media, and in perchlorate and fluoride supporting electrolytes. No other features in the SER spectra clearly attributable to benzene were observed.

Given that the frequency of the 965-975 cm^{-1} SERS feature is close to that for the intense symmetric ring breathing mode (Wilson mode ν_1) in the normal Raman (NR) spectrum of liquid benzene, 992 cm^{-1}, together with the absence of other strong bands in either the NR or infrared spectra of benzene in this region,[13] it is reasonable to attribute it to the ν_1 mode of adsorbed benzene. The surface coverage, θ, of benzene at gold under comparable conditions has been estimated to be relatively high, $\theta \geq 0.2$, having a broad maximum centered around 300 mV.[14] This is roughly in accordance with the potential dependence of the SERS intensities (Fig. 1). The dependence of the SERS intensity upon the bulk benzene concentration in 0.5 M H_2SO_4 was also examined, along with the corresponding differential capacitance (C_d) - potential curves for the gold surface. The SERS intensities increased and the C_d values progressively decreased with increasing benzene concentration up to ca. 2 mM but remained independent of concentration above this point, indicating the onset of saturation coverages in the ca. 0 to 300 mV region.

It is interesting to compare the present SER spectra with other vibrational spectra for adsorbed benzene and organometallic benzene species. Moskovits and DiLella have observed SERS for benzene on silver films at low temperatures.[8a] Although several IR-, as well as Raman-, active modes were detected, the ν_1 mode was by far the most intense. Only a small downshift, 10 cm^{-1}, of the ν_1 frequency from the bulk-phase value was observed, and even smaller (≤ 5 cm^{-1}) shifts were seen for the other internal benzene modes.[8a] Similarly small frequency shifts in ν_1 for adsorbed benzene have also been seen for unenhanced surface Raman spectra at silver[7f] and for (apparent) SERS at nickel and platinum clusters.[8b,c] Somewhat larger vibrational shifts for several other ring modes were nevertheless seen in the last study; these are compatible[8b] with those seen for electron energy loss spectra (EELS) for benzene adsorbed on Pt(III).[7a] The ν_1 mode is not observed in EELS of adsorbed benzene.[7a,b,d,e] This is presumably due to a surface selection rule prohibiting the observation of modes in EELS that

involve vibrations parallel to the surface; indeed a flat orientation for adsorbed benzene is consistent with most vibrational and structural data for benzene at metal-gas interfaces.[7a-e]

The mild (15-25 cm^{-1}) downshift in ν_1 seen here for benzene SERS at gold is, however, reasonable on the basis of a flat adsorbate orientation since the anticipated back donation of electron density from the metal surface to benzene π^* antibonding orbitals should significantly decrease the frequency of modes, such as ν_1, that involve C-C stretching. Substantial downshifts in the frequencies of C=C and C≡C stretching modes have been seen for alkenes and alkynes adsorbed at these metals.[3,10] (See the companion paper[10] for further details.) This interpretation for the downshift of ν_1 for adsorbed benzene at gold is also compatible with the comparable frequency shifts seen for coordinated benzene in π-bonded arene complexes.[6,15]

The appearance of a clearly resolved pair of ν_1 bands in Fig. 1 suggests that there are at least two bonding geometries, possibly associated with distinct types of surface sites yielding differing adsorbate-surface interactions. Indeed, a similarly resolved pair of peaks have been seen for the C=C stretch and symmetric CH_2 bending modes for SERS of adsorbed ethylene at gold electrodes.[3] Competitive adsorption with halide ions can be instructive in this regard.[3] The addition of 0.1 M NaCl had essentially no effect upon the benzene SER spectra in Fig. 1 even though chloride specific adsorption occured as sensed by the appearance of the characteristic 260 cm^{-1} chloride-surface stretching mode.[2] Addition of 20 mM NaBr, however, resulted in the virtual disappearance of the 977 cm^{-1} band at more positive potentials. Nevertheless, the 965 cm^{-1} band remained essentially unaffected even in the face of strong Br^- adsorption as sensed via the dominant appearance of the 165 cm^{-1} bromide-surface stretching mode.[2] This suggests that the 965 cm^{-1} band is associated with the more "tightly bound" benzene,

as might be expected. An additional band, however, appeared at 1027 cm^{-1} upon bromide addition. This might be due to bromobenzene formed by a surface-catalyzed reaction between adsorbed benzene and bromide (*vide infra*). Alternatively, this band could be due to the ν_{18a} (C-H deformation) mode: although Raman-inactive for benzene itself this mode may become allowed (as for monosubstituted benzenes,[13] *vide infra*), if the adsorbed benzene is tilted in the presence of adsorbed bromide so to lower its symmetry.

Surface-enhanced Raman spectra for benzene were also measured at roughened gold surfaces prepared using the method described by Busby and Creighton,[16] involving ex-situ electroplating from 5 mM $AuCl_3$ on to a polished gold surface at -150 mV. The objective was to compare the intensity and stability of the SER spectra to those obtained using our usual procedure[2] based on ex-situ potential cycling. The typical conditions for optimal SERS intensities for the electroplating and potential cycling methods were ascertained to be the passage of 350 mC cm^{-2} electrodeposition charge (cf. ref. 16), and between 20 and 25 oxidation-reduction cycles, respectively. Although the electroplating procedure initially yielded ν_1 band intensities for adsorbed benzene that were significantly (ca. 20-30%) higher than those obtained using the potential cycling method, the former signals decayed gradually with time, whereas the latter signals remained essentially constant over extended periods (several hours) at a given potential. Thus after one hour, for example, the signal intensities at 0 mV obtained following gold electroplating had decayed to about 50% of those observed following potential cycling. Interestingly, the electroplated surfaces yielded only one, somewhat broader, ν_1 band centered at 970 cm^{-1}, rather than the resolved pair of bands around this frequency that are characteristic of the surfaces roughened with the potential-cycling procedure (Fig. 1).

(b) Alkyl Monosubstituted Benzenes

Given that the SER spectra for benzene at gold are consistent with a flat adsorbate orientation, it is of interest to ascertain to what extent the adsorbate-surface interactions are perturbed by the addition of ring substituents. Alkyl groups are of interest in view of their inertness and the possibility of inducing steric constraints on the surface bonding geometry.

Figures 2 and 3 show typical SER spectra for adsorbed toluene and t-butylbenzene, respectively, in comparison with the corresponding NR spectra of the pure liquids. The former were obtained for alkylbenzene-saturated 0.5 M H_2SO_4 solutions. The spectra are presented over the frequency range, ca. 700-1300 cm^{-1}, within which the major SERS bands occur. For toluene, four such bands are clearly identified, at 781, 991, 1020, and 1204 cm^{-1} in the SER spectra, which are matched with NR bands at 786, 1003, 1030, and 1211 cm^{-1} (Figure 2). These bands are assigned[13] to the ν_1, ν_{12}, and ν_{18a} ring modes (Wilson number notation), and to a ring-methyl stretch, ν_{C-CH_3}, respectively. Note that the strongest feature in both the tolune SER and NR spectra is the ring breathing mode ν_{12}, rather than the totally symmetric mode ν_1 which dominates the benzene Raman spectra. (The ν_{12} and ν_{18a} modes are both inactive for the latter molecule.)

Similar features are obtained in the t-butylbenzene spectra (Figure 3), except that a number of additional SERS as well as NR bands are obtained, mostly associated with internal substituent modes.[13] Most of these bands are downshifted only slightly (< 5 cm^{-1}) in the SER spectra from the NR values, yet the ring modes, especially ν_{12} and ν_{18a}, are again significantly downshifted, to 989 and 1025 cm^{-1} from 1003 and 1034 cm^{-1} (Figure 3). As for benzene, neither alkylbenzene yielded clearly detectable C-H stretching vibrations in the SER spectra.

Similar results were also obtained for iso-propylbenzene, the ν_{12} and ν_{18a} modes shifting from 1003 and 1030 cm^{-1} in the NR to 989 and 1020 cm^{-1} in the SER spectra. The potential dependence of the SER intensities for all three alkylbenzenes was similar to that for benzene, exhibiting a broad maximum around 100 mV. The peak frequencies exhibited little or no dependence upon potential within the region ca. -500 to 700 mV. Especially at positive potentials (≥ 0 mV) low-frequency shoulders appear on the ν_{12} peak (Figs. 2,3), somewhat reminiscent of the form of the benzene ν_1 band (Fig. 1).

Taken together, these findings are suggestive of a flat (or similar) orientation of the alkylbenzene ring as for benzene, again involving adsorbate-surface π interactions, although in view of the smaller frequency downshifts these may be weaker than for benzene itself.

(c) Chloro- and Bromobenzene

Given that chloride and bromide ions bind strongly to gold electrodes and can be detected in the SER spectra from their characteristic adsorbate-surface vibrations around 265 and 185 cm^{-1}, respectively, it is of interest to ascertain if chlorine and bromine aromatic substituents can provide surface anchors for benzene rings. Figure 4 shows potential-dependent SER spectra in the 150-350 cm^{-1} and 900-1100 cm^{-1} regions obtained for 0.1 M KCl saturated with bromobenzene. The ν_{12} and ν_{18a} modes appear at 998 and 1028 cm^{-1}, shifted only slightly from the NR values of 1002 and 1023 cm^{-1}. The ν_1 mode appears in the NR spectrum[13b] at 1072 cm^{-1}, so that the SERS feature at 1065 cm^{-1} can reasonably be assigned to this mode.

Since these downshifts in ν_{12} and ν_{18a} (4-5 cm^{-1}) are somewhat smaller than for the alkylbenzenes (10-15 cm^{-1}), it appears that the benzene ring-surface interactions are even weaker for bromobenzene as a result of surface attachment via bromine. Support for this notion is deduced from the

low-frequency region (Fig. 4). Aside from the band around 260 cm^{-1}, due to adsorbed chloride ions, a peak around 175-180 cm^{-1} appears at more positive potentials. The latter feature is ascribed to adsorbed bromine since it is close to the frequency, 185 cm^{-1}, for adsorbed bromide at gold.[2] Chloride rather than sulfate supporting electrolyte was employed due to interference from the 180 cm^{-1} band seen for adsorbed sulfate (*vide supra*). Some spectra were obtained in 0.1 M NaF so to minimise any influence of anion coadsorption. Similar spectra resulted, except of course for the absence of the 260 cm^{-1} band. The SERS intensities were found to be independent of the bulk bromobenzene concentration even down at 0.2 mM, suggesting the presence of saturation coverages under these conditions. Markedly lower, yet concentration-independent differential capacitance values were obtained from ca. 350 to -400 mV upon the addition of bromobenzene under these conditions in 0.1 M KCl media.

The SER spectra of perdeuterated bromobenzene, C_6D_5Br, as well as hexadeuterated benzene were also examined to further check the spectral assignments and particularly as a means of studying the rapidity of surface exchange. As expected, significant downshifts in the frequencies of the various ring modes were obtained for the deuterated analogs in the SER as well as the NR spectra. For example, the ν_{12} SERS band for bromobenzene shifts from 998 to 960 cm^{-1} upon deuteration. The ν_1 SERS bands for benzene shift from ca. 977 and 965 cm^{-1} to 928 and 920 cm^{-1}, to be compared with the NR shift from 992 to 946 cm^{-1}. A weak SERS band around 3050 cm^{-1} for bromobenzene was confirmed as arising from C-H vibrations from the large downshift to 2285 cm^{-1} seen upon deuteration.

The rapid injection of 1 mM C_6D_5Br to a solution already containing 1 mM C_6H_5Br in 0.1 M NaF yielded a 50% decrease in the 998 cm^{-1} band intensity and the

appearance of an equal intensity 960 cm^{-1} band. That this change was almost complete during the time (ca. 60 secs) required to record the SERS bands indicates that the adsorption-desorption kinetics are rapid on this time scale. Similar results were also obtained for surface exchange measurements with C_6H_6 and C_6D_6.

Adsorbed chlorobenzene yielded similar SER spectra as for bromobenzene in that a band at 240-250 cm^{-1}, assigned to chlorine-surface stretching, appeared at potentials positive of 100 mV in sulfate media. The ν_{12}, ν_{18a}, and ν_1 bands in the SER spectra of chlorobenzene, at 996, 1015, and 1076 cm^{-1}, are nonetheless downshifted more significantly (ca. 5-10 cm^{-1}) from the corresponding NR bands at 1002, 1026, and 1086 cm^{-1}, respectively, than is seen for bromobenzene. This is suggestive of a stronger benzene ring-surface interaction for chlorobenzene than for bromobenzene, which might be anticipated from the larger bromine atom constraining the benzene ring to tilt further from a flat orientation. In view of the small frequency shifts involved for both adsorbates, however, these interpretations are only speculative.

(d) Benzonitrile and Acrylonitrile

In order to further explore the possibility that ring substituents can act as surface anchoring groups, providing alternative as well as additional binding sites to the aromatic ring itself we examined potential-dependent SERS for benzonitrile (i.e., cyanobenzene). Besides the anticipated strong surface binding ability of the cyano nitrogen, this system is of particular interest since the frequency of the C-N stretching mode, ν_{CN}, is known from

bulk complexation studies to provide a sensitive monitor of the mode of nitrile coordination.[17]

Figure 5 shows potential-dependent SER spectra for 20 mM benzonitrile in 1 M H_2SO_4 at -200, 400, and 1000 mV. Several features are worthy of note. A broad feature around 2240-2260 cm^{-1} is observed, attributable to ν_{CN}. The ν_{CN} frequency is shifted to higher values compared with that in the NR spectrum, 2230 cm^{-1}, to an extent which increases with increasing positive potential. By analogy with metal ion coordination, this frequency shift is indicative of σ bonding of the nitrile nitrogen to the metal surface.[17] Also indicative of such nitrogen binding is the appearance of a band around 250-260 cm^{-1} at more positive potentials (Fig. 5), since bands in this region are both expected and observed for other coordinated cyan groups that bind to the surface via the nitrogen atom.[18]

The frequencies of the SERS ring modes are also consistent with this picture. Thus the ν_{12} and ν_{18a} vibrations occur at 1000-1003 and 1030-1035 cm^{-1} in the SER spectra, close to (although slightly larger than) the NR values of 1001 and 1024 cm^{-1}, respectively, even though a shoulder to ν_{12} around 990 cm^{-1} is also seen (Fig. 5) as for other substituted benzenes (Figs. 2-4). A prominent SERS band at 1596 cm^{-1} was also observed, along with weaker bands at 1175-1185 and 1195-1205 cm^{-1}. These bands correspond to ν_{18a}, ν_{9a} (CH deformation) and ring combination modes, respectively, having NR counterparts at 1598, 1178, and 1195 cm^{-1}.[13,20] This near-identity of the SER and NR ring mode frequencies suggests that the benzene ring is not attached directly to the metal surface, but is bound via the nitrile substituent. Some influence upon the ring vibrational frequencies might still be expected from an inductive effect via the nitrile bridge, even if the benzene ring is entirely pendant. This accounts for the slight upshift in the ring frequencies upon adsorption, increasingly so at more positive potentials where

the nitrile-surface σ bonding becomes progressively stronger as evidenced by the marked increase in the ν_{CN} frequency. In addition to the anticipated downshifts in the ring modes a flat orientation for adsorbed benzonitrile would presumably be accompanied by a "sideways" CN-surface π bond, which would yield a marked downshift in the ν_{CN} frequency.[17] That the opposite is observed on both counts argues pervasively for the presence of a "vertical", rather than flat, orientation for adsorbed benzonitrile, especially at more positive potentials. A significant fraction of the adsorbed benzonitrile may nonetheless assume a flat orientation at more negative potentials, as evidenced by the appearance of a low-frequency shoulder on the ν_{12} and ν_{18a} modes for E ≤ 400 mV (Fig. 4). This is consistent with electrostatic considerations since the vertical orientation involves the electronegative nitrile group directed towards the metal surface, which is clearly most favorable at positive electrode charges.

Also of significance in this regard is the observation of a C-H stretching band around 3060-3070 cm^{-1} (Fig. 5). While similar SERS bands are detected for other monosubstituted benzenes, these are very weak and usually are observable only at more negative potentials. Given such aromatic C-H stretching bands are typically intense in the NR spectra, on the basis of surface selection rules their very low SERS intensity may well be associated with a flat ring orientation. The more intense SERS C-H band for benzonitrile is therefore also consistent with a different orientation for this adsorbate.

A similar conclusion as to the orientation of adsorbed benzonitrile at gold electrodes has been reached on the basis of surface infrared data.[21] Evaluation of SERS for benzonitrile at gold under the same conditions as employed for the potential-modulated surface infrared measurements[21] (20 mM benzonitrile in 1 $\underline{M}$ H_2SO_4) yielded ν_{CN} peak frequencies that were virtually identical within

the apparent resolution of the latter technique (ca. 5 cm^{-1}). This suggests that the molecules present at SERS-active sites do not differ significantly from those sensed by the infrared probe.[22]

We also briefly examined SERS of acrylonitrile (CH_2=CH-C=N) at gold in order to ascertain if the ethylenic linkage is able to bind to the surface in the light of the apparent inability of the benzene ring to do so in the presence of the nitrile substituent. Direct attachment of alkenes to gold via the ethylene group can be diagnosed via a marked (ca. 50-100 cm^{-1}) downshift in the C=C stretching frequency, ν(C=C). An intense ν_{CN} band for adsorbed acrylonitrile was observed, shifted to higher frequency compared to the NR value (2232 cm^{-1} for liquid acrylonitrile), similar to that found for adsorbed benzonitrile. The ν_{CN} frequency at 0 mV, 2245 cm^{-1}, increased further as the potential was made more positive (e.g., 2190 cm^{-1} at 950 mV), accompanied by progressively greater band intensities. Although ν(C=C) was slightly downshifted for adsorbed compared to bulk acrylonitrile, 1594 versus 1611 cm^{-1}, respectively, this shift is much smaller than that typically obtained, ca. 70-140 cm^{-1}, for alkenes π-bonded to gold.[10] We therefore deduce that acrylonitrile is bound "end on" via a σ nitrile-surface bond, rather than by π interactions to the ethylenic and/or nitrile groups.

A different conclusion was reached for acrylonitrile adsorption at gold on the basis of surface infrared measurements involving potential modulations to around 1000 mV. A large apparent downshift (100 cm^{-1}) of ν_{CN} was observed upon adsorption, interpreted in terms of π bonding with a flat adsorbate orientation.[21] Bands having similar frequencies, around 2125 cm^{-1}, are also obtained in the SER spectra of acrylonitrile at potentials positive of 950 mV. This observation, however, is more consistent with the low-frequency ν_{CN} band being due to adsorbed cyanide formed by acrylonitrile electrooxidation, since the latter species yields almost identical SER spectra under these conditions.[19]

(e) Nitrobenzene, Benzoate, and Benzaldehyde

Given that the nitrogen-donor nitrile substituent clearly provides the preferred mode of surface attachment in competition with the benzene ring, we decided to examine monosubstituted benzenes containing oxygen-donor substituents.

Figure 6 is a comparison between a typical NR and SER spectrum for nitrobenzene. As for benzonitrile, the ν_{12} and ν_{18a} frequencies in the SER and NR spectra are virtually identical. Similarly small or negligible frequency shifts upon adsorption are seen for ν_{6b} (ring deformation), ν_{11} (out-of-plane C-H bending), ν_{8b} (ring stretch), and the C-N stretching mode at 610, 793, 1586 cm^{-1}, and 1108 cm^{-1}, respectively, in the NR spectrum.[24] However, the intense NO_2 symmetric stretching mode at 1346 cm^{-1} in the NR spectrum is broadened and shifted to 1330 cm^{-1} upon adsorption (Fig. 6). This suggests that the nitro group, rather than the benzene ring, is bound to the gold surface.

In contrast, the benzene ring modes in the SER spectra for benzoate, obtained for 5 mM $C_6H_5COO^-$ in either neutral or alkaline 0.1 M K_2SO_4, show the characteristics of the alkylbenzenes, the ν_{12} and ν_{18a} frequencies decreasing from 1005 and 1030 cm^{-1} in the NR spectrum to 990 and 1023 cm^{-1} for SERS. The symmetric CO_2 stretching mode that appears around 1395 cm^{-1} in the NR spectrum[24a] is difficult to identify in the SER spectra, although a weak band obtained around 1420 cm^{-1} may be due to this mode. Almost identical SER spectra were obtained in acidic media where the carboxylate anion will be protonated, further suggesting that this group has little influence upon the surface binding. The SERS intensity-potential dependence shows a broad maximum around 0 mV, in approximate accord with estimates of the surface coverage-potential dependence for benzoate estimated from

differential-capacitance measurements at gold.[26] It therefore appears that benzoate, unlike the nitro substituent, is unable to compete with the benzene ring in providing the preferred mode of attachment to gold surfaces. Benzaldehyde yielded very similar SER spectra to benzoate, at least with regard to the ring modes. The benzaldehyde spectra were nevertheless unusually intense. A weak SERS band around 3050 cm^{-1} could be detected, attributable to the aromatic C-H stretching vibration (*vide supra*).

In addition to shifts in frequency, it is also instructive to examine alterations in bandshape brought about by adsorption as possible diagnostic criteria for the mode of attachment. Table I summarizes such data for benzene and seven of the monosubstituted benzenes examined here, expressed as values of the full width at half maximum, FWHM, of the most easily discernable ring mode, being the ν_1 mode for benzene and ν_{12} for the monosubstituted benzenes, respectively. These data are given at several representative electrode potentials, along with the corresponding SER peak frequency, ν_{SER}, and the frequency shift encountered upon adsorption, $\Delta\nu$. The FWHM values are only approximate, having an uncertainty of 2-3 cm^{-1} in view of the need to correct for the influence of the low-frequency shoulder commonly seen on the ν_{12} SERS bands (Figs. 2-5).

Nevertheless, it is seen that the adsorbates that display negligible frequency downshifts of ν_{12} upon adsorption, benzonitrile and nitrobenzene, also yield the smallest FWHM, generally being $\leq$ 10 cm^{-1}. Indeed the FWHM values for these adsorbed molecules approach those seen in the NR spectra, as would be expected if the benzene ring interacts negligibly with the electrode surface. The significantly larger FWHM values seen for the other adsorbates is commonly observed in SERS, presumably reflecting inhomogeneous band broadening associated with interactions between the functional group and the metal surface.

The bandwidth data are therefore fully compatible with the corresponding frequency shifts seen upon adsorption, supporting the above contention that benzonitrile and nitrobenzene bind to the metal surface entirely via the substituent group, at least at positive potentials, the ring assuming a pendant position. For the other monosubstituted benzenes, both these lines of evidence indicate that the ring interacts specifically with the surface, even for the halobenzenes where the substituent is clearly also bound.

Concluding Remarks

The foregoing illustrates how SERS may be utilized to extract information on the mode of bonding of aromatic molecules to gold surfaces via a combined analysis of frequency shifts, bandshapes, and relative intensities for internal adsorbate modes and the appearance of low-frequency adsorbate-surface bands. Admittedly, the requirements of SERS limit such studies to roughened gold surfaces at present. While surface infrared techniques can yield similar information and are not limited in this manner, the advantages offered by SERS of a very wide frequency range with high intensity, resolution, and the readiness with which absolute spectra can be obtained are of crucial value.

The present results, together with those of a companion survey of aliphatic hydrocarbons at gold[3,10] form only a preliminary survey. It will clearly be important to couple such SERS measurements with further quantitative evaluation o adsorbate coverages by conventional electrochemical means, as well as with parallel surface infrared measurements. In this manner, the effects of varying both the adsorbate coverage and the physical state of the metal surface upon the vibrational spectra can be assessed in detail.

ACKNOWLEDGMENTS

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18. For example, we have observed bands around 280-290 cm^{-1} for hexacyano complexes adsorbed at gold.[19] It is worth noting in this connection that the frequency of adsorbate-surface modes, ν_{a-s}, at gold for simple anionic, as well as large polyatomic, species is primarily determined by the mass of the lead-in atom, m, so that roughly $\nu_{a-s} \propto m^{-1/2}$.[2,19] The applicability of this rule provides a useful means of identifying the bonding geometry, as in the present examples.

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22. This issue arises from the probability that the molecules sensed by SERS probably constitute only a minority of the total adsorbate, being those molecules suitably close to the surface morphologies responsible for the SER effect,[1] while the infrared probe should respond to the preponderant adsorbate. The issue of the similarities and differences in corresponding surface Raman and infrared data is of current interest.[23]

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TABLE I Comparison Between Frequency Downshift of Ring Breathing Modes Absorption at Gold and Corresponding SERS Bandwidth for Benzene and Monosubstituted Benzenes

Adsorbate	Potential mv vs sce	ν_{SER} [a] cm^{-1}	$-\Delta\nu$ [b] cm^{-1}	FWHM [c] cm^{-1}
C_6H_6	500	978, 965	14, 27	14, 16
	-100	975, 964	17, 28	15, 16
$C_6H_5CH_3$	300	993	9	14
	-100	991	11	14
	-500	991	11	11
$C_6H_5C(CH_3)_3$	200	991	12	13
	-200	991	12	11
C_6H_5Cl	500	995	7	12
	100	996	6	14
	-300	997	5	15
C_6H_5Br	-100	998	4	16
	-600	998	4	17
C_6H_5CN	600	1000	0	6
	-100	999	1	10
$C_6H_5NO_2$	200	1003	1	8
	0	1003	1	10
$C_6H_5COO^-$	100	992	13	17
	-400	991	14	18

[for footnotes, see over]

Footnotes to Table I

[a]Peak frequency in SER spectra for ν_1 ring mode for benzene, ν_{12} mode for monosubstituted benzenes. (Frequency refers to major band(s), ignoring low frequency shoulders.) Experimental conditions as given in the text and figure captions.

[b]Shift in SERS peak frequency in left-hand column from corresponding normal Raman frequency for bulk-phase liquids.

[c]Full width at half peak height of SERS band, corrected for influence of low-frequency shoulders (see text).

Figure Captions

Figure 1

Comparison between symmetric ring breathing mode (ν_1) for: (A) liquid benzene at 992 cm^{-1} with: (B) corresponding SERS bands for benzene adsorbed at gold from benzene-saturated 0.5 M H_2SO_4 at -500, -100, 300, and 700 mV vs s.c.e. Laser excitation was 647.1 nm, 40 mW spot focussed to ca. 2 mm diameter on gold surface for SERS. Spectral band-pass was 5 cm^{-1}.

Figure 2

Comparison between: (A) normal Raman spectrum of liquid toluene in 700-1250 cm^{-1} region and: (B) corresponding SER spectrum for toluene adsorbed at gold at 100 mV from toluene-saturated 0.5 M H_2SO_4. Laser excitation was (A) 541.5 nm, 30 mW; (B) 647.1 nm, 70 mW; otherwise as for Figure 1.

Figure 3

Comparison between: (A) normal Raman spectrum of liquid t-butylbenzene in 700-1350 cm^{-1} region and: (B) corresponding SER spectrum for t-butylbenzene adsorbed at gold at 0 mV from butylbenzene-saturated 0.5 M H_2SO_4. Laser excitation was 647.1 nm, 80 mW; other conditions as in Figure 1.

Figure 4

SER spectra for bromobenzene adsorbed at gold at -600, -300, and -100 mV from saturated 0.1 M KCl in 150-350 cm^{-1} and 900-1100 cm^{-1} regions. Other conditions as in Figure 1.

Figure 5

SER spectra for benzonitrile adsorbed at gold at -200, 400, and 1000 mV from 1 M H_2SO_4 containing 20 mM benzonitrile, in 150-300 cm^{-1}, 900-1250 cm^{-1}, 2150-2300 cm^{-1}, and 3000-3150 cm^{-1} regions. Laser power was 30 mW; other conditions as in Figure 1.

Figure 6

Comparison between: (A) normal Raman spectrum of liquid nitrobenzene in 950-1400 cm^{-1} region, and: (B) corresponding SER spectrum for nitrobenzene adsorbed at gold at 0 mV from nitrobenzene-saturated 0.1 M Na_2SO_4. Laser power was 80 mW; other conditions as in Figure 1.

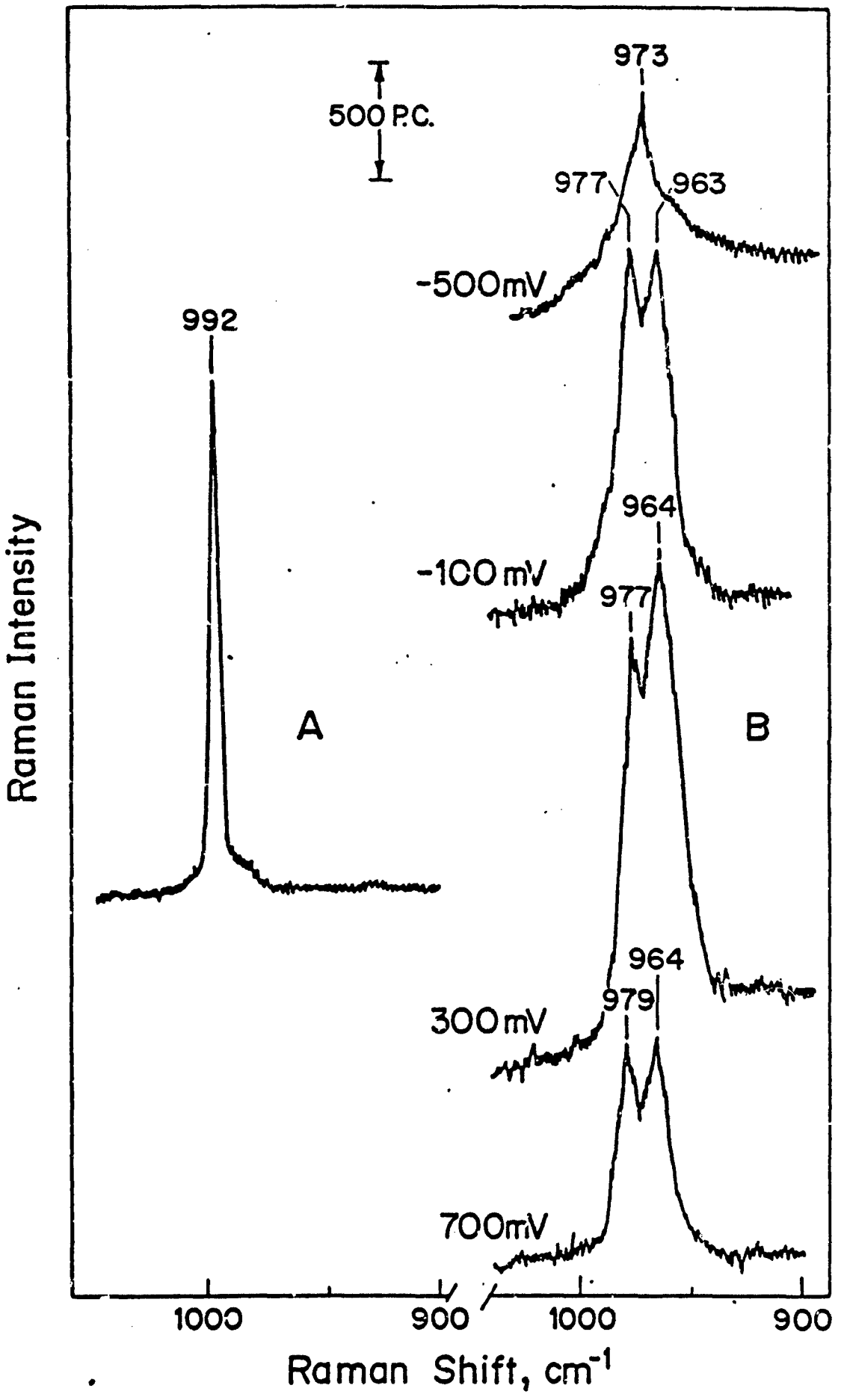


Figure 1
Gao, Weave

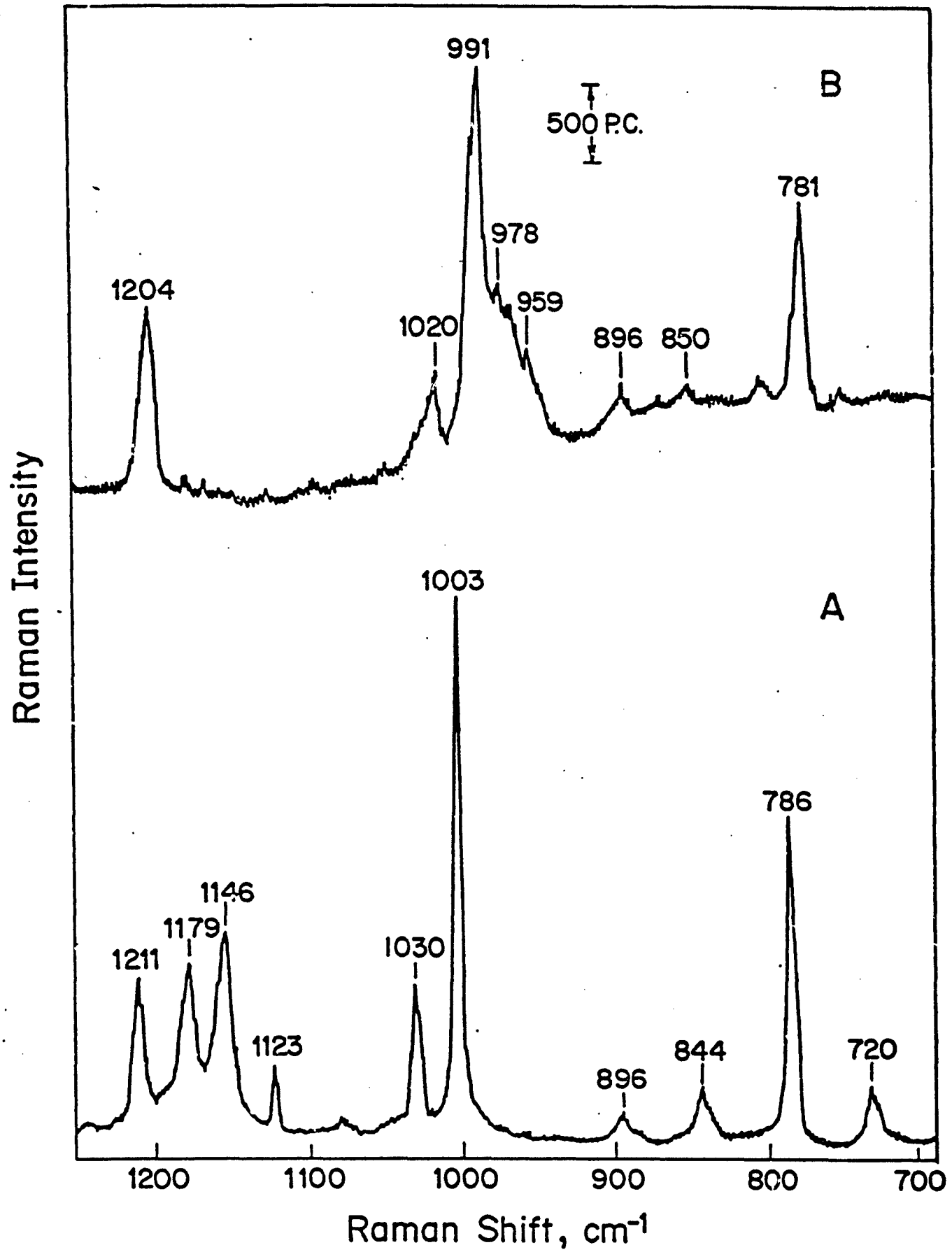
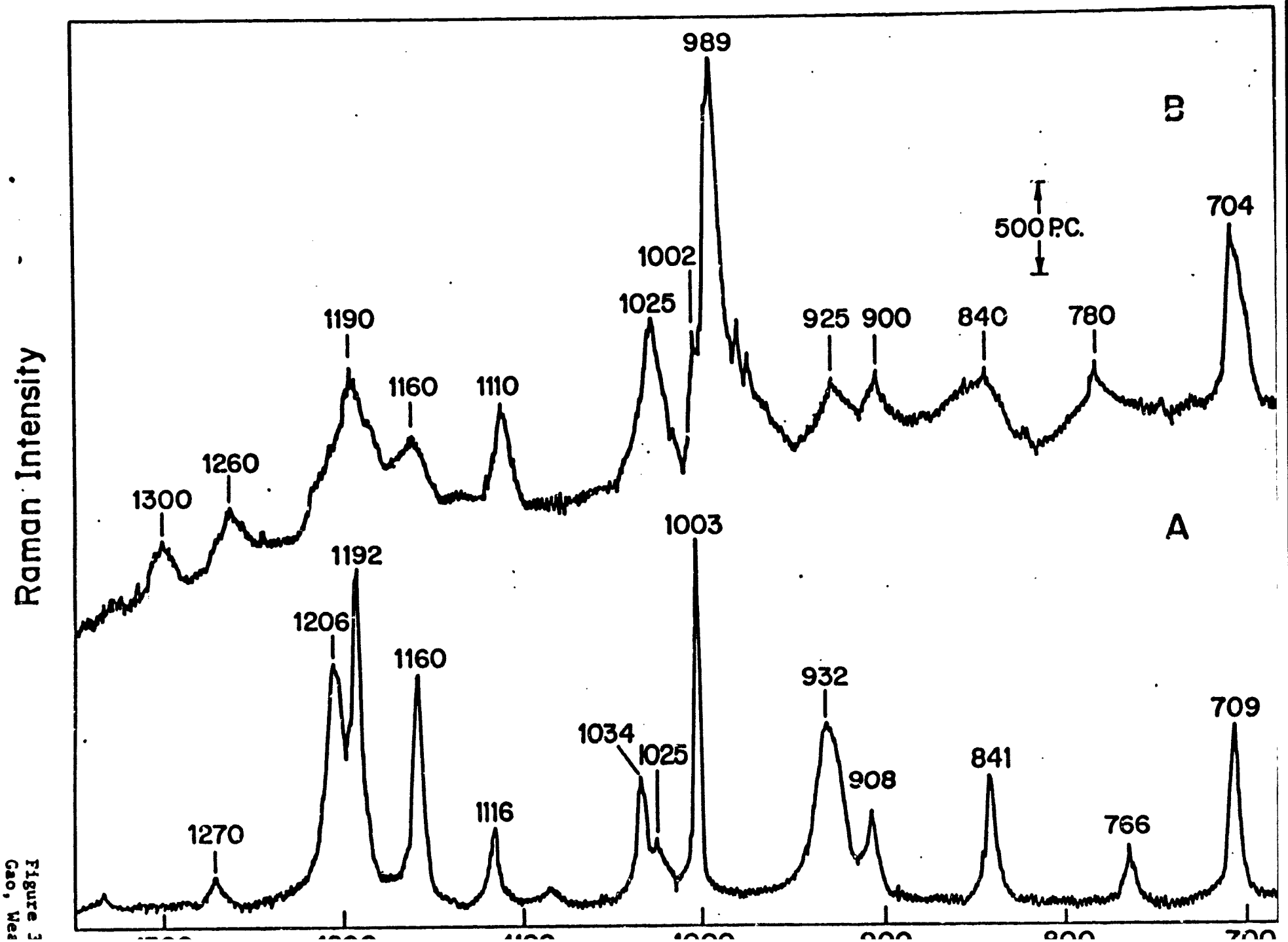


Figure
Gao, We


989
B
500 P.C.
704
1002
1025
1190
925
900
840
780
1160
1110
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1300
Raman Intensity
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1003
1192
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709
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841
908
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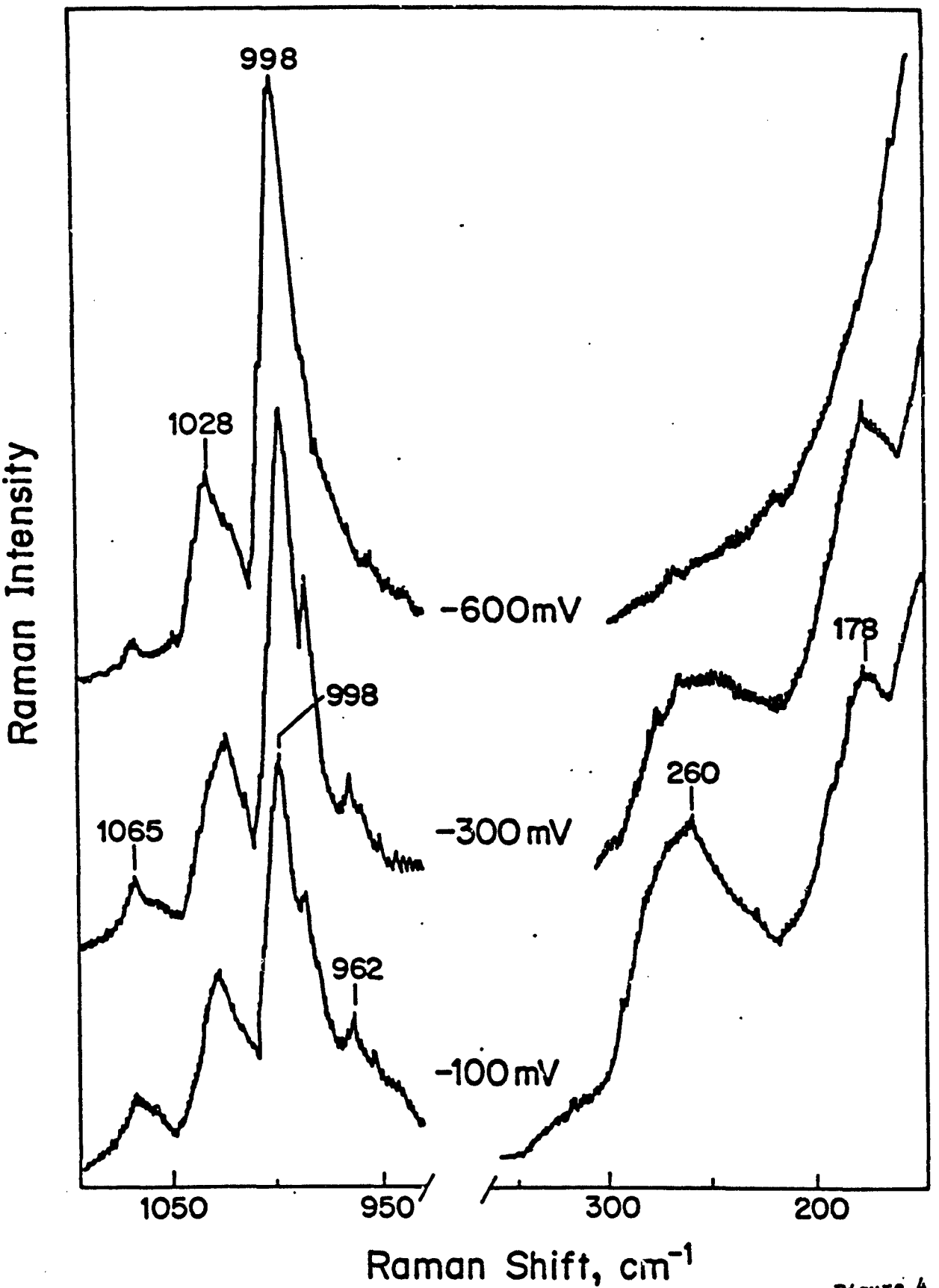

Figure 4
Gao, Weaver

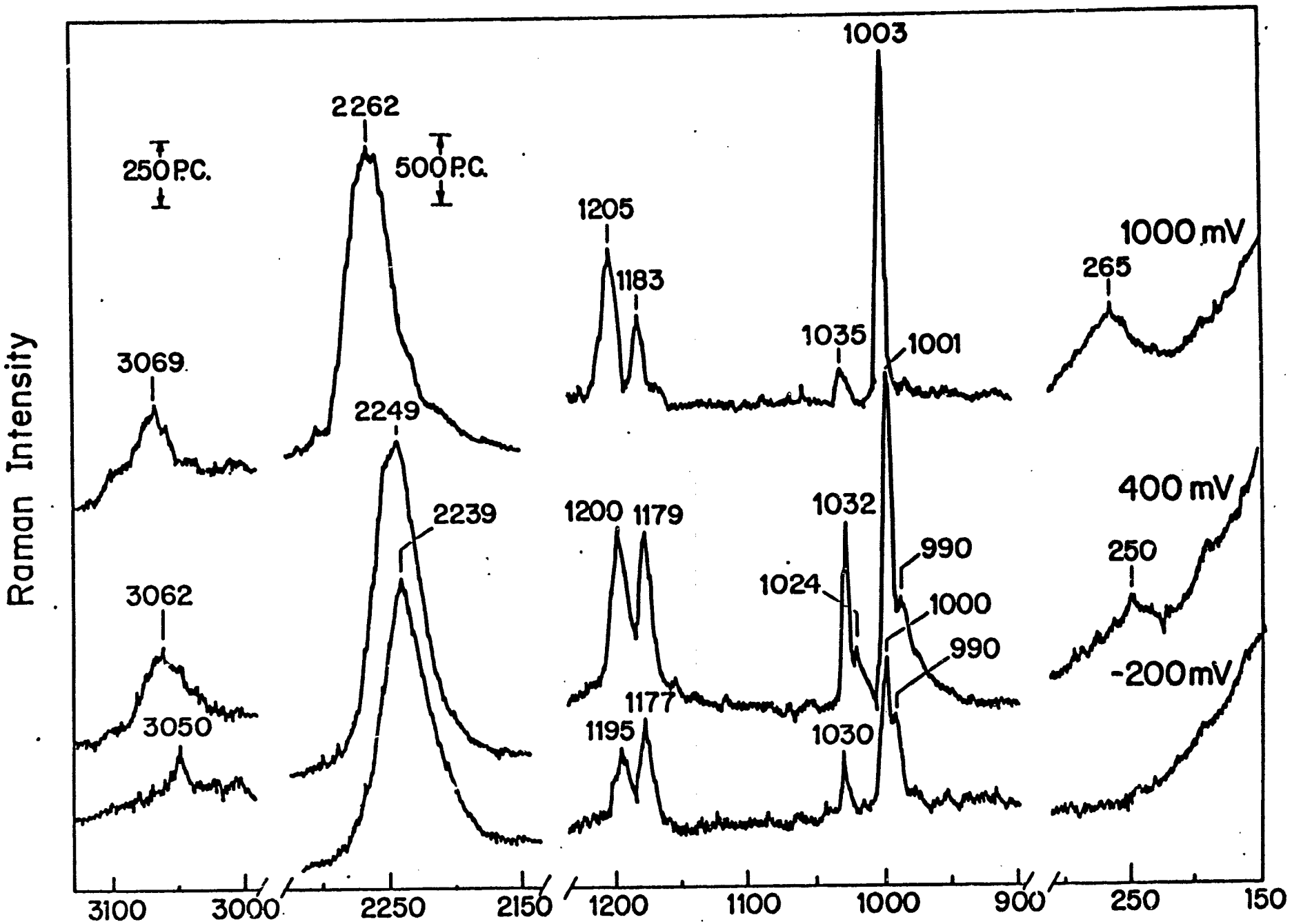

Figure 5
Gao, Weaver

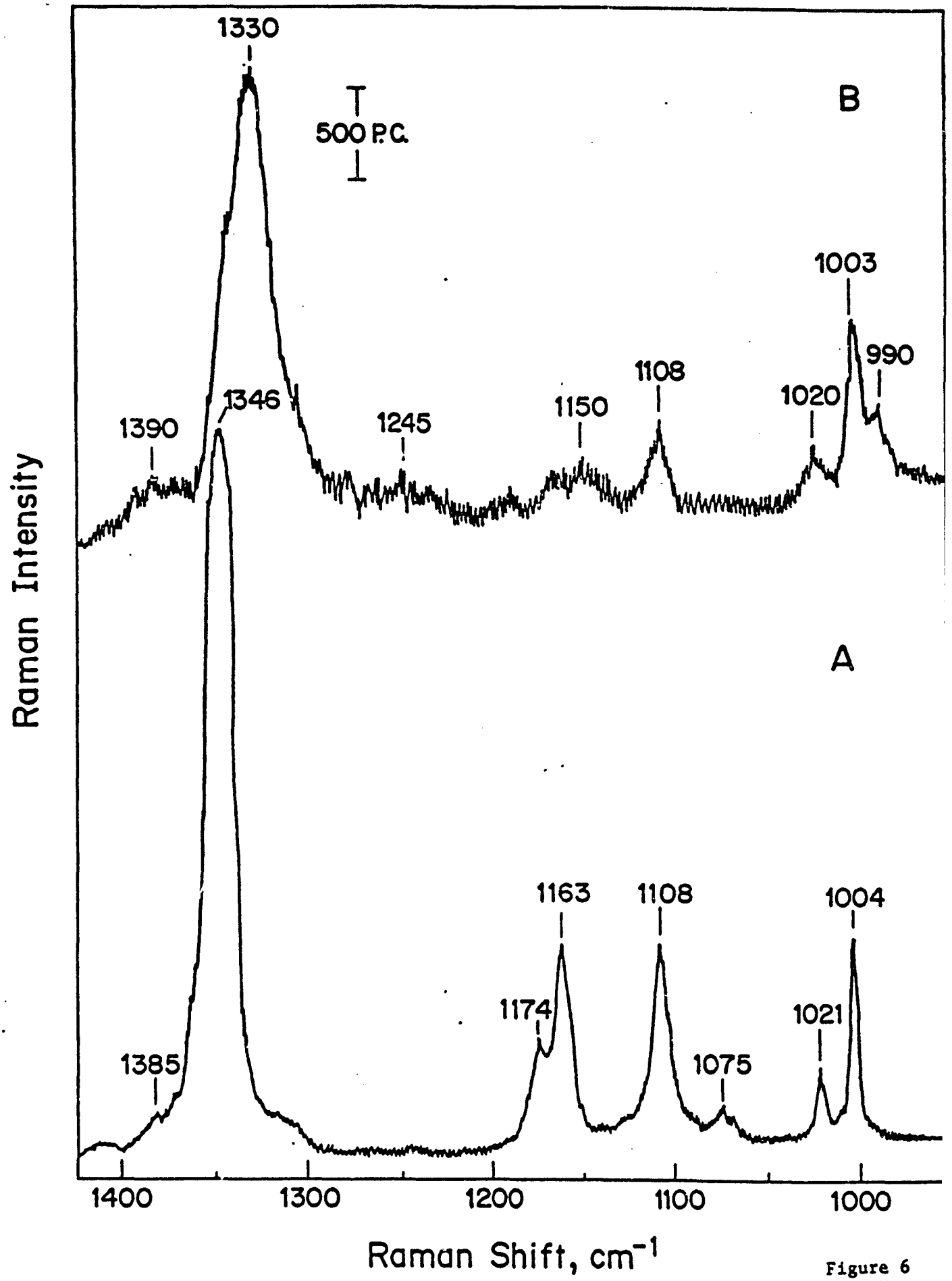

Figure 6
Gao, Weaver

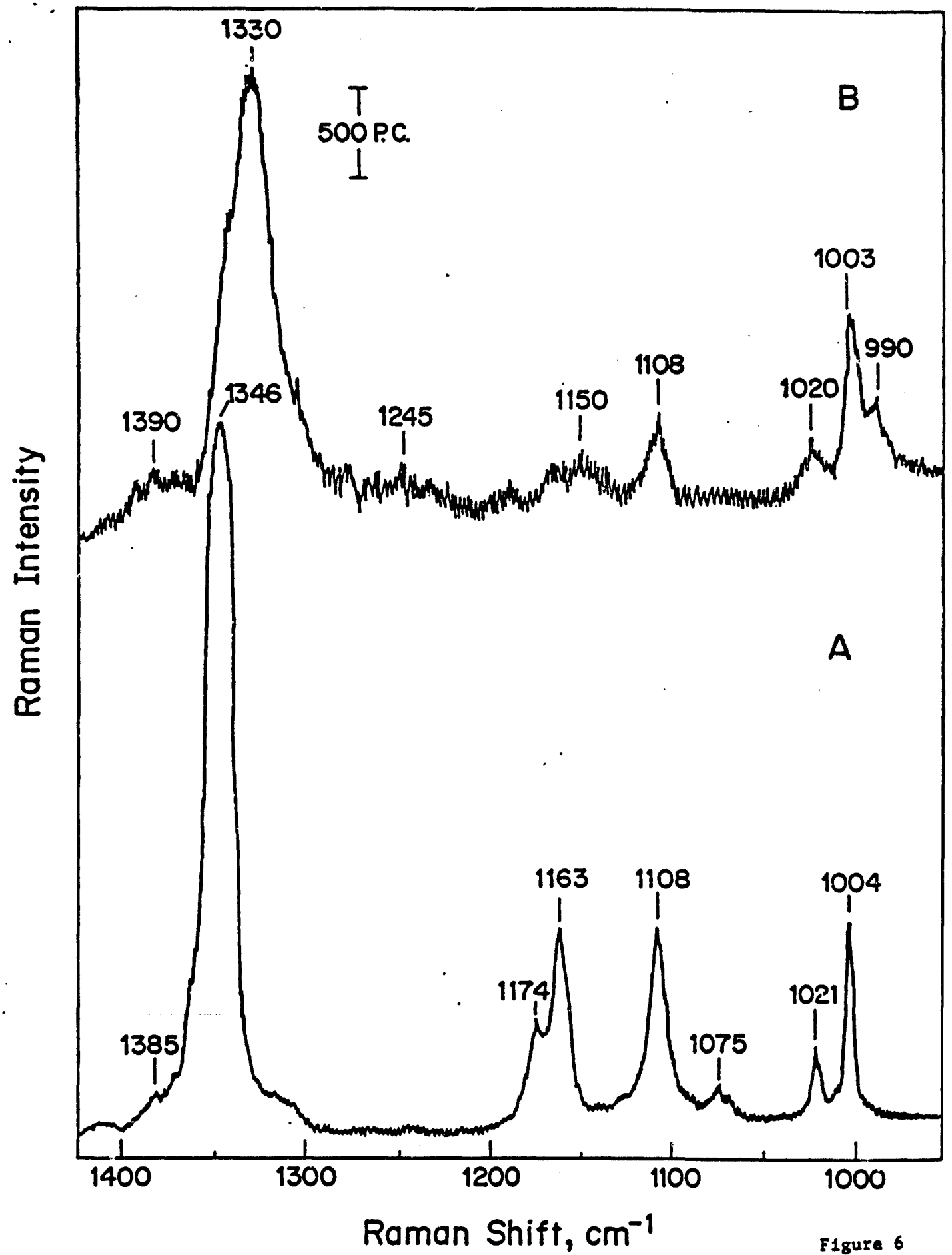

Figure 6
Gao, Weaver