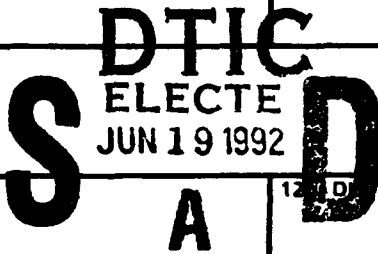


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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 6/1/92	3. REPORT TYPE AND DATES COVERED Interim/Technical		
4. TITLE AND SUBTITLE High resolution electron energy loss spectroscopy of CO co-adsorbed with cyanogen (C ₂ N ₂) on Pt(111): Dielectric screening of dipole scattered modes		5. FUNDING NUMBERS PE 4134002 C N00014-87-K-0257 P00001		
6. AUTHOR(S) Quanyin Gao and John C. Hemminger				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Institute for Surface and Interface Science, and Department of Chemistry University of California, Irvine Irvine, California 92717				
8. PERFORMING ORGANIZATION REPORT NUMBER 33		9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division, Code: 1113PS 800 N. Quincy Street Arlington, VA 22217-5000		
10. SPONSORING / MONITORING AGENCY REPORT NUMBER		11. SUPPLEMENTARY NOTES Submitted to <u>Surface Science</u>		
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: Distribution unlimited				
12b. DISTRIBUTION CODE		13. ABSTRACT (Maximum 200 words) We have investigated the effects of the co-adsorption of CO with cyanogen on the vibrational spectrum of the CO as determined by high resolution electron energy loss spectroscopy. Since cyanogen is easily polarizable (polarizability ~53Å ³), we expected that the intensities of the CO vibrational spectra would be substantially modified by dipole screening effects. The linear CO stretching mode of on-top bonded CO is strongly screened by co-adsorbed C ₂ N ₂ . However, the CO stretching mode of bridge bonded CO is not strongly effected. The effect which we observe for on-top bonded CO is consistent with a dipole screening mechanism with a polarizability for the co-adsorbed C ₂ N ₂ of ~41Å ³ in reasonable agreement with the known polarizability of C ₂ N ₂ . It is known that cyanogen adsorbs on Pt(111) in two bonding states referred to in the literature as the α-state, and the β-state of cyanogen. The dipole screening of the CO vibrations is entirely due to the α-state of the co-adsorbed cyanogen.		
14. SUBJECT TERMS Vibrational spectroscopy, HREELS, dipole screening, platinum, CO, C ₂ N ₂		15. NUMBER OF PAGES 16		
16. PRICE CODE		17. SECURITY CLASSIFICATION OF REPORT Unclassified		
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		
20. LIMITATION OF ABSTRACT SAR				

OFFICE OF NAVAL RESEARCH

Contract N00014-90-J-1180

R&T Code 413q003----01

Technical Report No. 33

High Resolution Electron Energy Loss Spectroscopy of CO Co-Adsorbed with
Cyanogen (C_2N_2) on Pt(111): Dielectric Screening of Dipole Scattered Modes

by

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Submitted to Surface Science

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June 1, 1992

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ABSTRACT

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High Resolution Electron Energy Loss Spectroscopy of CO Co-Adsorbed
with Cyanogen (C_2N_2) on Pt(111): Dielectric Screening of Dipole
Scattered Modes

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Abstract

We have investigated the effects of the co-adsorption of CO with cyanogen on the vibrational spectrum of the CO as determined by high resolution electron energy loss spectroscopy. Since cyanogen is easily polarizable (polarizability $\sim 53\text{\AA}^3$), we expected that the intensities of the CO vibrational spectra would be substantially modified by dipole screening effects. The linear CO stretching mode of on-top bonded CO is strongly screened by co-adsorbed C_2N_2 . However, the CO stretching mode of bridge bonded CO is not strongly effected. The effect which we observe for on-top bonded CO is consistent with a dipole screening mechanism with a polarizability for the co-adsorbed C_2N_2 of $\sim 41\text{\AA}^3$ in reasonable agreement with the known polarizability of C_2N_2 . It is known that cyanogen adsorbs on Pt(111) in two bonding states referred to in the literature as the α -state, and the β -state of cyanogen. The dipole screening of the CO vibrations is entirely due to the α -state of the co-adsorbed cyanogen.

1. Introduction

Vibrational spectroscopies, such as Fourier transform reflection absorption infrared spectroscopy (FTRAIRS) and high resolution electron energy loss spectroscopy (HREELS), have been widely applied to the study of surface reaction systems. The reaction intermediate and reaction paths are usually proposed based upon the observed vibrational characteristics of surface species [1-4]. It has become increasingly important to extract not only the qualitative information from these vibrational spectra but also the quantitative information, which requires the analysis of vibrational peak intensity.

Recently, several experimental results using FTRAIRS have indicated the presence of dielectric screening effect caused by the co-adsorbates [5-6]. This reminds people of being more careful with the analysis of vibrational band intensity, especially for coadsorption system. This also raise the question of to what extent the vibrational band of interest be screened by the coadsorbate, and of the possibility of predicting such effect based on the known information of the free molecules.

The interest to study co-adsorption of CO with C_2N_2 are stimulated by the following considerations. (i) We want to know whether this dielectric screening will affect the dipole scattering

modes monitored by HREELS as that has been observed for FTIRAS. These modes have the same metal surface selection rule for both HREELS and FTIRAS. (ii) We would like to know for the CO+C₂N₂ co-adsorption system, whether both linear and bridge CO stretching bands are equally screened by the co-adsorbed C₂N₂. (iii) We like to see whether both α and β adsorption states of C₂N₂ have similar screening effect.

2. Experimental Section

All our experiments are performed in a UHV chamber equipped with Auger, LEED, quadrupole mass spectrometer and ion gun on the first level and HREELS on the second level. The base pressure of the chamber is 1×10^{-10} torr. The HREEL spectrometer is from LK technology Inc. with double monochromator and rotatable single analyzer. In our experiment the resolution is 26 cm⁻¹ for the FWHM of the elastic peak confirmed by Gaussian profile fitting and counting rate is about $\sim 10^5$ counts/sec at this resolution. Each digitized scan has a step size of 5 cm⁻¹. A whole scan of a HREEL spectrum is from -200 cm⁻¹ to 3500 cm⁻¹.

The carbon monoxide (CO) and cyanogen (C₂N₂) are from Matheson with a purity of 99.5% and of 98.5%, respectively. All adsorptions are performed by back filling the chamber with a leaking valve to a desired pressure (usually $\sim 10^{-8}$ torr) and the amount of adsorption is controlled by varying exposing time.

3. Results

3.1 HREELS of 0.1L CO with C₂N₂ co-adsorption.

A series of HREELS are recorded after adsorbing 0.1L CO at 170K, then co-adsorbing C₂N₂. At 170K, adsorption of 0.1L CO on Pt(111) resulted a spectrum shown in figure 1a. Two strong peaks are observed at 2062 and 468 cm⁻¹ which can be assigned to linear CO stretching mode (ν_{CO}) and Pt-CO stretching mode ($\nu_{\text{Pt-C}}$)[7]. After co-adsorption of 0.1L C₂N₂ at 170K, an additional peak is observed at 918 cm⁻¹ which can be attributed to the C-C stretching mode (ν_{CC}) of the adsorbed C₂N₂ molecules (figure 1b)[8-11]. With 0.4L co-adsorbed C₂N₂, three more peaks are observed at 290, 360 and 618 cm⁻¹ (figure 1c). The 290 cm⁻¹ and 360 cm⁻¹ peaks are tentatively attributed to the cyanogen-Pt substrate stretching mode for α adsorption and β adsorption state of cyanogen molecules, respectively. The 618 cm⁻¹ peak is assigned to the bending mode of CCN group (δ_{CCN}) of C₂N₂ molecules [12]. Further co-adsorption of C₂N₂ to 0.85L leads to new peaks at 508 and 2200 cm⁻¹ (figure 1d). The 508 cm⁻¹ peak is assigned to the asymmetric bending (γ_a) of C₂N₂ molecules [9-11] and the 2200 cm⁻¹ is a typical CN stretching mode (ν_{CN}) [13-14]. Severe intensity damping for ν_{CO} mode are observed with further co-adsorption of C₂N₂ (figure 1e,f).

3.2 Annealing

The νCO intensity is fully recovered after heating the crystal to 390K (figure 1g) indicating that the relative intensity reduction for νCO mode is not a result of replacing CO by C_2N_2 adsorption. This annealing temperature is high enough to desorb α adsorption state of the C_2N_2 molecules while maintaining CO adsorption. This is further explained in the following TDS results of $\text{CO}+\text{C}_2\text{N}_2$. The linear CO stretching peak intensity relative to the elastic peak is plotted in figure 2 as a function of C_2N_2 coverage. A slight increase in linear CO relative intensity with initial small amount of C_2N_2 adsorption are observed which may be caused by background CO adsorption during HREELS data collection. Further adsorption of C_2N_2 results in reduction of the linear CO relative intensity.

3.3 Thermal Desorption of $\text{CO} + \text{C}_2\text{N}_2/\text{Pt}(111)$

The thermal desorption spectra of 0.1L CO (mass 28 amu) co-adsorbed with 3L C_2N_2 (mass 52 amu) are shown in figure 3. The C_2N_2 TDS results clearly indicate two desorption peaks at $\sim 260\text{K}$ and $\sim 680\text{K}$ which have been assigned as α and β adsorption state of C_2N_2 on Pt(111) [8,15]. The CO desorption peak is at $\sim 430\text{K}$. It is obvious that our previous HREELS result (fig. 1g) with heating $\text{CO}+\text{C}_2\text{N}_2$ system to 390K will desorb the α adsorption state of C_2N_2 and retain the surface CO and β adsorption state of C_2N_2 .

3.4 HREELS results of 1L CO with C_2N_2 co-adsorption.

Only linear CO species is present for the previous HREELS results with 0.1L CO coverage. To study the possible dielectric screening effect on bridge CO species, 1L CO are adsorbed on Pt(111). The HREEL spectrum indicates that at this coverage, both linear and bridge CO species are present on the surface. This is shown in figure 4a where energy loss peaks at 2065, 1836, 468 and 350 cm^{-1} are observed. These peaks are attributed to linear CO stretching (ν_{CO}), bridge CO stretching (ν_{CO}), carbon to platinum substrate stretching for linear CO species ($\nu_{\text{Pt-CO}}$) and symmetric stretching of carbon to platinum for bridge CO species ($\nu_{\text{s Pt-C-Pt}}$), respectively [7]. Co-adsorption of 0.5L C_2N_2 on this CO pre-covered surface results in a spectrum shown in figure 4b. Four additional peaks from C_2N_2 are observed at 275, 365, 633 and 916 cm^{-1} . These peaks are tentatively attributed to α state C_2N_2 to Pt substrate stretching ($\nu_{\alpha} \text{C}_2\text{N}_2\text{-Pt}$), β state C_2N_2 to Pt substrate stretching ($\nu_{\beta} \text{C}_2\text{N}_2\text{-Pt}$), CCN bending δ_{CCN} and CC stretching (ν_{CC}) mode, respectively [8-12]. After co-adsorbing 1.5L C_2N_2 (figure 4c) the relative intensity of the linear CO peak is reduced by a factor of ~ 2 indicated by a spectrum amplification factor change from previous 150 to 300. A new peak from C_2N_2 adsorption is observed at 1603 cm^{-1} which is attributed to C=N stretching mode [14] of β state C_2N_2 . Further co-adsorption of C_2N_2 results in additional intensity reduction for linear CO and increase in intensity for bridge CO as shown in figure 4d and 4e.

3.5 Annealing

Annealing this 1L CO+C₂N₂ system to 390K to desorb α state C₂N₂ results in spectrum 4f. It is clearly shown that the linear CO stretching mode intensity is almost fully recovered compared to figure 4a. The bridge CO stretching mode ν_{CO} intensity is also similar to figure 4a. The vibrational peaks due to β state C₂N₂ are observed at 1288 and 1627 cm⁻¹.

The ν_{CO} mode intensity for linear CO species relative to the elastic peak is plotted in figure 5 as a function of co-adsorbed C₂N₂ dosages. A strong dielectric screening effect is observed which results in a reduction in relative intensity by a factor of ~ 3.5 .

The ν_{CO} mode intensity for bridge CO species relative to the elastic peak is shown in figure 6. It is interesting to notice that the bridge CO species intensity is not reduced by co-adsorbed C₂N₂. There is even some increase in the ν_{CO} mode intensity for bridge CO species.

4. Discussion

4.1 The C₂N₂ Co-adsorption

C₂N₂ co-adsorbate is chosen in order to study the dielectric screening effect on CO stretching mode. The reason to select such a co-adsorbate molecule is because (1) C₂N₂ free molecule has a large dielectric constant [16]. This will generate a noticeable dielectric screening effect which is shown in figure 2 and figure 5. (2) C₂N₂ adsorption on Pt(111) has been studied on Pt(111) by HREELS which

clearly indicates that there are no peaks in the CO stretching frequency region [8]. Thus, one need not worry the peak interference for the two co-adsorbed molecules in the same vibrational frequency region. (3) The TDS results has indicated two adsorption states for C_2N_2 [8,15]. α state is basically molecular adsorption of C_2N_2 with the molecular axis parallel to the metal surface [8,15] while β state is a polymerized surface C_2N_2 net work. The latter is expected to have a smaller dielectric constant in the surface normal direction due to a relative restricted electron cloud motion in that direction. Our data indeed shows that after desorbing α state of C_2N_2 , the ν_{CO} mode intensity is almost fully recovered (figure 1g and figure 4f). Thus, *the dielectric screening observed for ν_{CO} mode of linear CO species is mainly from the α state C_2N_2 .*

The C_2N_2 adsorption studies on Pt(111)[8], Pd(111) [10] and Pd (100) [10] by HREELS have indicated that upon adsorption on these surfaces, the C_2N_2 molecule is found with its NCCN axis parallel to the metal surface. In this configuration, the surface dipole selection rule will prevent the observation of ν_{CN} mode at $\sim 2200\text{ cm}^{-1}$. Our coverage dependent HREELS of C_2N_2 /Pt(111) [17] strongly support such an configuration and no ν_{CN} mode is observed just as the case on Pd(100) and Pd(111) [10]. In such an adsorption configuration, the ν_{CC} mode of C_2N_2 is also expected to be forbidden by the surface selection rule since the dynamic dipole for ν_{CC} mode is also parallel to the metal surface. However, our HREELS results indicate that this ν_{CC} mode is very strong which locates at $\sim 918\text{ cm}^{-1}$ (figure 1 and

figure 4). This can be explained by a charge transfer between the metal substrate and the adsorbed C_2N_2 molecules as the C-C bond stretches. Such an electron transfer between the adsorbed molecule and the substrate will result in a perpendicular dipole moment to the plane of metal surface, and a strong peak by dipole scattering.

The presence of β state C_2N_2 is proposed based on the TDS results where a higher temperature desorption peak is observed in addition to a low temperature peak [8,15]. Our vibrational data provides further evidence for such species. After desorbing the α state C_2N_2 , the peaks observed at 1600, 1470 (figure 1g) and 1627, 1288 (figure 4f) are clearly from the β state C_2N_2 . The peak at ~ 1600 cm^{-1} can be attributed to the C=N stretching ($\nu_{C=N}$) while the peak at 1288~1470 cm^{-1} are possibly from the C-N stretching (ν_{C-N}). Since both stretching motion is parallel to the plane of metal surface, their vibrational peak intensities are weak as observed here. The delocalization of electrons among the β state C_2N_2 polymer frame makes the C-N bond order vary between the single C-N bond and double C=N bond. The peak positions for both $\nu_{C=N}$ and ν_{C-N} modes are also expected to shift which depend on the polymerized CN frame size. A size distribution of the polymerized system will result in a broad peak as observed in figure 1g and figure 4f. The β state C_2N_2 to the substrate stretching possibly results in a peak at ~ 350 cm^{-1} . In figure 4f, the 351 cm^{-1} peak is stronger than the same peak in figure 4a which may be resulted from β state C_2N_2 to Pt substrate stretching.

The parallel C_2N_2 may change the molecular axis orientation with increasing C_2N_2 coverage especially at coverages reaching multilayer, which will result in a dipole allowed CN stretching mode. This is an expected case for figure 1 d ~ f where peaks are observed at 2200, 2175 and 2149 cm^{-1} possibly from CN triple bond stretching mode (ν_{CN}).

4.2 The CO Adsorption

In figure 1, it is noticed that the linear CO stretching frequency has increased from about 2060 cm^{-1} to ~2079 cm^{-1} as a function of co-adsorbed C_2N_2 coverage. It is also interesting to notice that peak shift for ν_{CO} mode is removed after desorbing the α state C_2N_2 (figure 1g). The possible explanation of ν_{CO} frequency change as a function of C_2N_2 coverage includes:

(1) Co-adsorbate influence on electron transfer from 5σ orbital of CO to the metal and the back donation of electron from metal into $2\pi^*$ antibonding orbital of CO. This influence may be considered as through substrate interaction. Adsorption of C_2N_2 may cause the d electrons of the metal substrate interact with C_2N_2 . As a function of C_2N_2 coverage the available d electrons of the metal substrate decrease and in turn results in a decrease in the d- π^* back donation. The ν_{CO} frequency is then expected to increase as a function of C_2N_2 coverage.

(2) The dipole-dipole coupling can also result in a increase for ν_{CO} versus C_2N_2 coverage. This effect has been theoretically treated by Scheffler [18] who concluded that an upward shift of CO frequency versus CO coverage are due essentially to dipole-dipole interactions.

(3) Adsorption site and coordination number of adsorbate change. Our results of HREELS intensity for linear and bridge bonded CO modes vs. C_2N_2 coverage (figure 5, 6) indicate that if there is an adsorption site change, it would likely be from linear on-top site to bridge site, which will results in a decrease in vibrational frequency. Thus, the upward shift in ν_{CO} frequency for linear CO can not be fully account for by the change of adsorption sites. The coordination number change may also result in frequency change, however, we do not have evidence for the presence of multiple coordinated CO on one Pt substrate atom.

4.3 The Dielectric Screening Effect

In figure 2 and figure 5 it is clearly indicated that the relative intensity of the stretching mode for linear CO has decreased as a function of co-adsorbed C_2N_2 . Here, it is important to point out that no chemical interaction are found between CO and C_2N_2 at the experimental conditions which will change CO to other chemical species. Thus, the observed intensity suppression for linear CO band

(ν_{CO}) is originated from physical cause rather than from chemical cause. Following possibilities are considered:

(1) The CO orientation change by co-adsorbed C_2N_2 via lateral interactions. If the orientation of CO changes from perpendicular to the metal surface to a tilted position, an intensity decrease is expected due to the surface dipole selection rule. From the ESDIAD study of coverage dependent CO adsorption on Pt(111), a tilt angle of ~ 6 degree is estimated for saturation CO coverage [19] from which a reduction of dipole moment of 0.5% is estimated. This amount of tilting can not account for the intensity reduction observed here (a factor of ~ 6). Thus, the CO orientation change is not a favored explanation.

(2) The "through substrate" interaction which changes the CO dynamic dipole moment. Such an interaction is possible due to the observed ν_{CO} frequency upward shift as a function of C_2N_2 coverage. However, it has been found that even with Xe co-adsorption on CO pre-adsorbed surface [5-6], the CO band intensity is considerably reduced. Since Xe adsorption is via van der Waals interaction, the modification of the CO chemical bond is negligible. Thus, we think the "through substrate" interaction may not be a major cause for CO band suppression.

(3) The co-adsorbate induced adsorption site change

The bridge CO relative intensity is found to be enhanced by co-adsorbed C_2N_2 (figure 6). There is a likely explanation that the linear CO species may have changed to bridge CO species which is induced by co-adsorption of C_2N_2 . This will result in a decrease in linear CO intensity and an increase in bridge CO intensity. While this is a possible deduction for 1L CO dosage, the result from 0.1L CO dosage (figure 1) is against this argument since no bridge CO species is observed with co-adsorption of C_2N_2 for that experiment.

(4) The co-adsorbate screening of the dynamic dipole moment of CO. Considering that the polarizability of the co-adsorbate, the local electric field at the location of CO adsorption site could be shielded. The contribution of the dipole screening effects can be estimated using the following model. Taking the CO molecules as a point dipole and the screening charge of C_2N_2 molecules as a single entity with an effective polarizability α , assuming that the electric field is normal to the surface and that polarizability tensor is diagonal in the coordinate system of the surface, the local field, with the long wavelength limit, is given by:

$$E_{loc} = E_0 - \sum_j \frac{\alpha_j E_{loc}}{r_{ij}^3} \quad (1)$$

Following Giergiel et al. [20], we get a factor γ_D , the ratio of the intensity of the local field (E_{loc}) at the adsorption site i to its value (E_0) in the absence of adjacent site j of any adsorbed molecules, expressed as:

$$\gamma_D = \frac{E_{loc}}{E_0} = (1 + C N_0^{3/2} \alpha \theta)^{-1} \quad (2)$$

where N_0 is the surface packing density (molecules/cm²) and C is a constant which only weakly depends on the type of 2D lattice (9.0366 for a square lattice and 8.8904 for a planar triangular lattice [21]). The intensity of linear CO peak relative to the elastic peak can be found from the golden-rule formula [22]:

$$\frac{I}{I_0} \propto \frac{2\pi}{\hbar^2} \sum_b |\langle b, \psi_k | H' | a, \psi_k \rangle|^2 \delta(\omega_{ba} - \omega) \quad (3)$$

where $\omega_{ba} = E_b - E_a$ is the energy needed to excite the system from vibrational state $|a\rangle$ to $|b\rangle$ and must equal the energy loss $\hbar\omega = E_k - E_{k'}$. H' is the interaction energy between the incident electron and the adsorbed molecules.

$$H' = - \sum_i \mu_i E_{loc} \quad (4)$$

where μ_i is the dipole moment operator of molecule i and E_{loc} is the local electric field at molecule i . Since $E_{loc} = \gamma_D \cdot E_0$, and $H' \propto \gamma_D \cdot E_0$, we have

$$\begin{aligned} \frac{I}{I_0} &\propto |\gamma_D E_0|^2 \\ &\propto \left(\frac{1}{1 + C N_0^{3/2} \alpha \theta} \right)^2 \end{aligned} \quad (5)$$

Figure 7 is a plot of the inverse square root of the relative intensity of linear CO mode as a function of C₂N₂ coverage [23]. From its slope we obtain an estimation of the polarizability of α state C₂N₂ molecules on Pt(111). Using Pt substrate density of 1.5×10^{15} Pt atoms/cm² [24] and $C=8.89$, we estimate the effective polarizability of C₂N₂ is on the order of 41 Å³. Considering the free C₂N₂ molecules with $\alpha \sim 53$ Å³ [16] our estimation of α is reasonable.

We feel that this dipole screening effect is a more general cause for the linear CO peak intensity suppression with co-adsorbed C₂N₂ molecules.

5. Conclusion

The present work shows that dipole scattering mode can be screened by co-adsorbed molecules. For CO+C₂N₂ system, linear CO stretching peak is strongly screened by co-adsorbed C₂N₂ while no such effect is observed for bridge CO stretching band. The screening effect is caused by α state C₂N₂ while β state C₂N₂ shows nearly no screening effect.

Acknowledgement: The authors gratefully acknowledge the financial support of this work by The Office of Naval Research and Q. Gao would like to thank Dr. J. Giergiel for helpful discussions.

Figure Captions

Fig.1 HREEL spectra on Pt(111) at 170K (a) 0.1L CO then co-adsorbed with C₂N₂ at total dosages of (b) 0.1L (c) 0.4L (d) 0.85L (e) 1.55L (f) 2.55L and (g) annealing to 390K after (f).

Fig. 2 Linear CO HREELS relative intensity (0.1L CO) versus C₂N₂ co-adsorbate dosage.

Fig. 3 Thermal desorption spectra of 0.1L CO +3L C₂N₂ adsorbed at 170K with heating rate of ~10K/sec.

Fig. 4 HREEL spectra on Pt(111) at 150K (a) 1L CO then co-adsorb C₂N₂ at total dosages of (b) 0.5L (c) 1.5L (d) 3L (e) 4.5L and (f) annealing to 390K after (e).

Fig.5 Linear CO HREELS relative intensity (1L CO) versus C₂N₂ co-adsorbate dosage.

Fig. 6 Bridge CO HREELS relative intensity (0.1L CO) versus C₂N₂ co-adsorbate dosage.

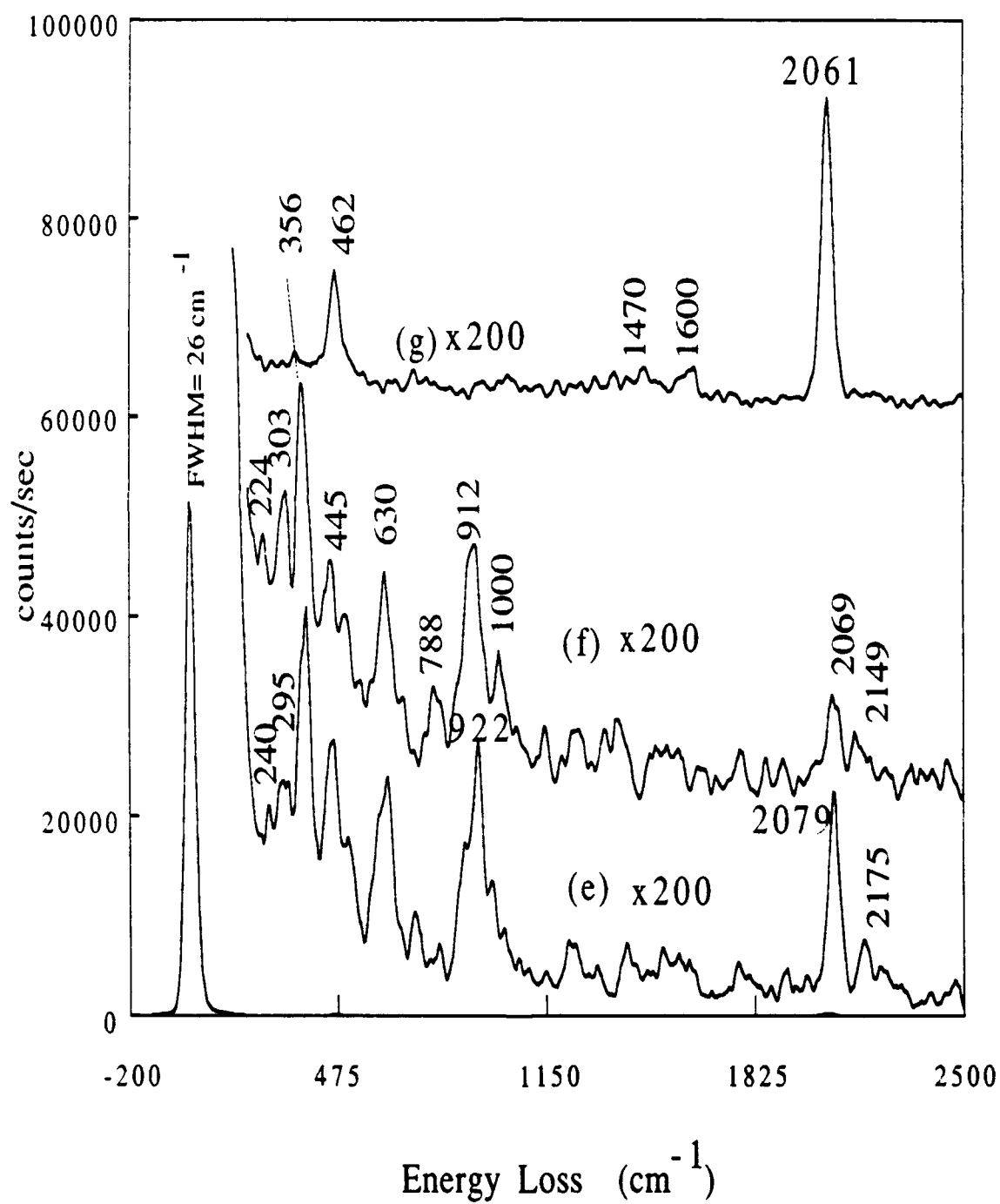
Fig.7 Reciprocal of the square root of the linear CO relative intensity (0.1L) versus the co-adsorbate C₂N₂ coverage.

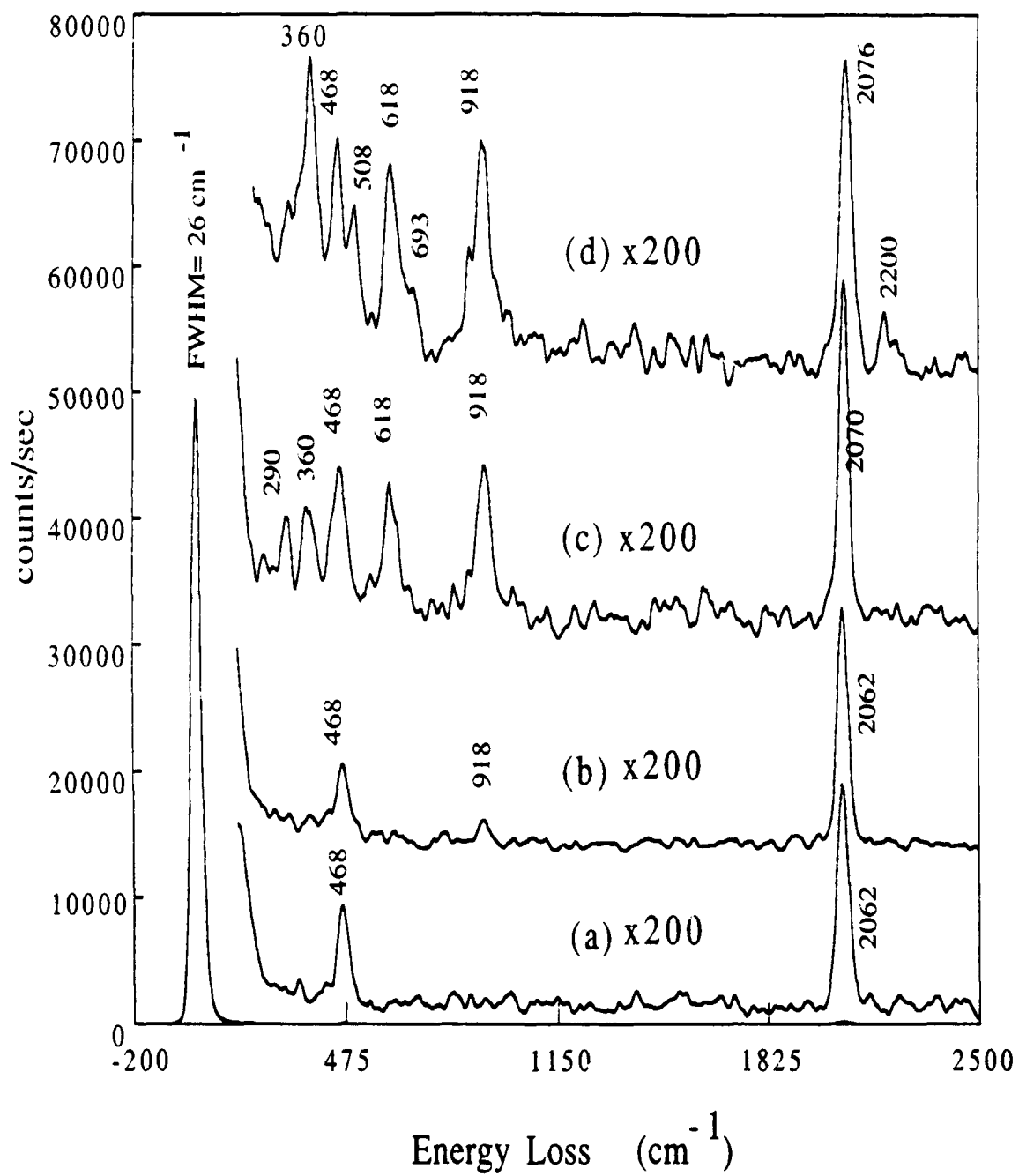
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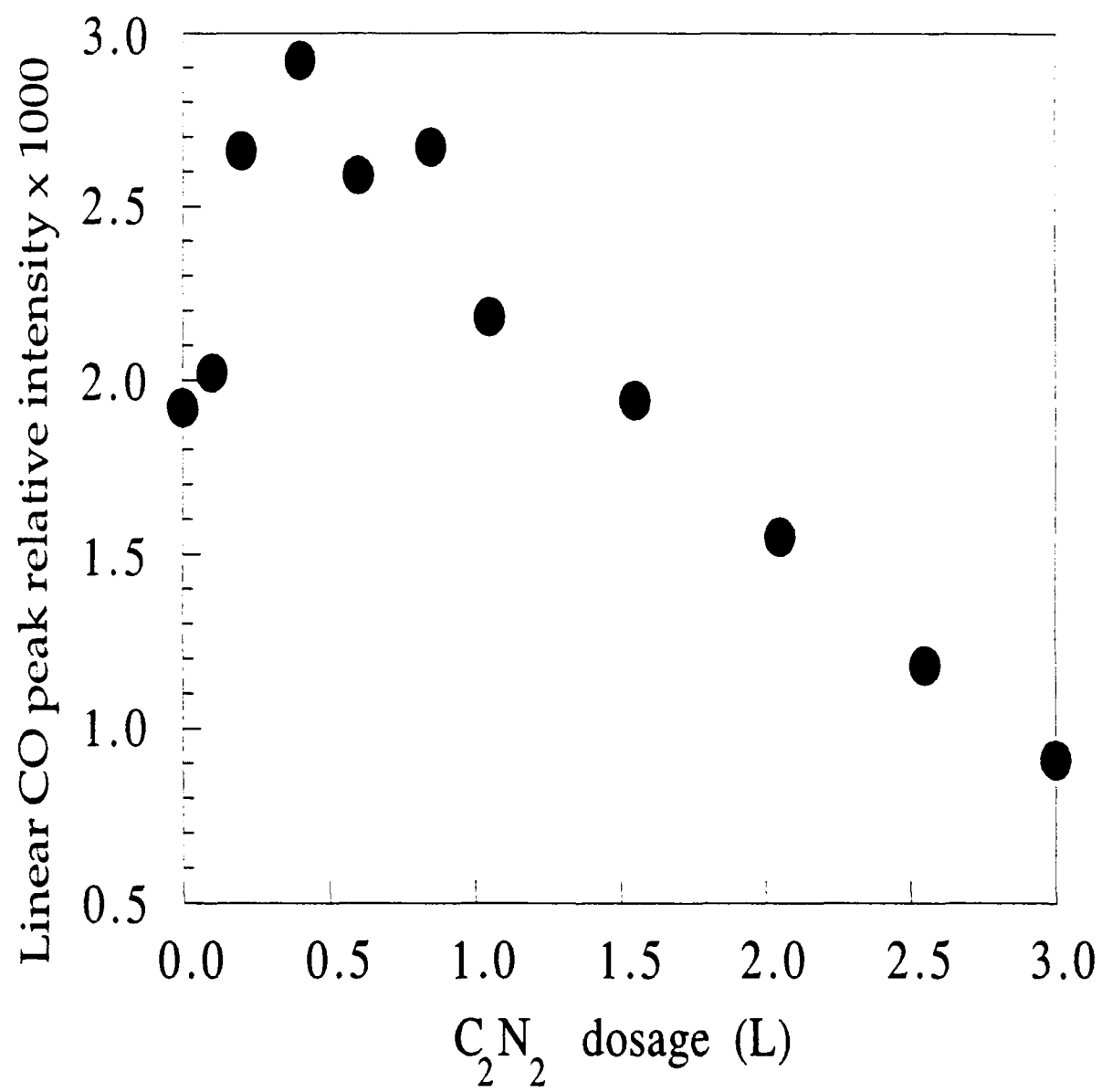
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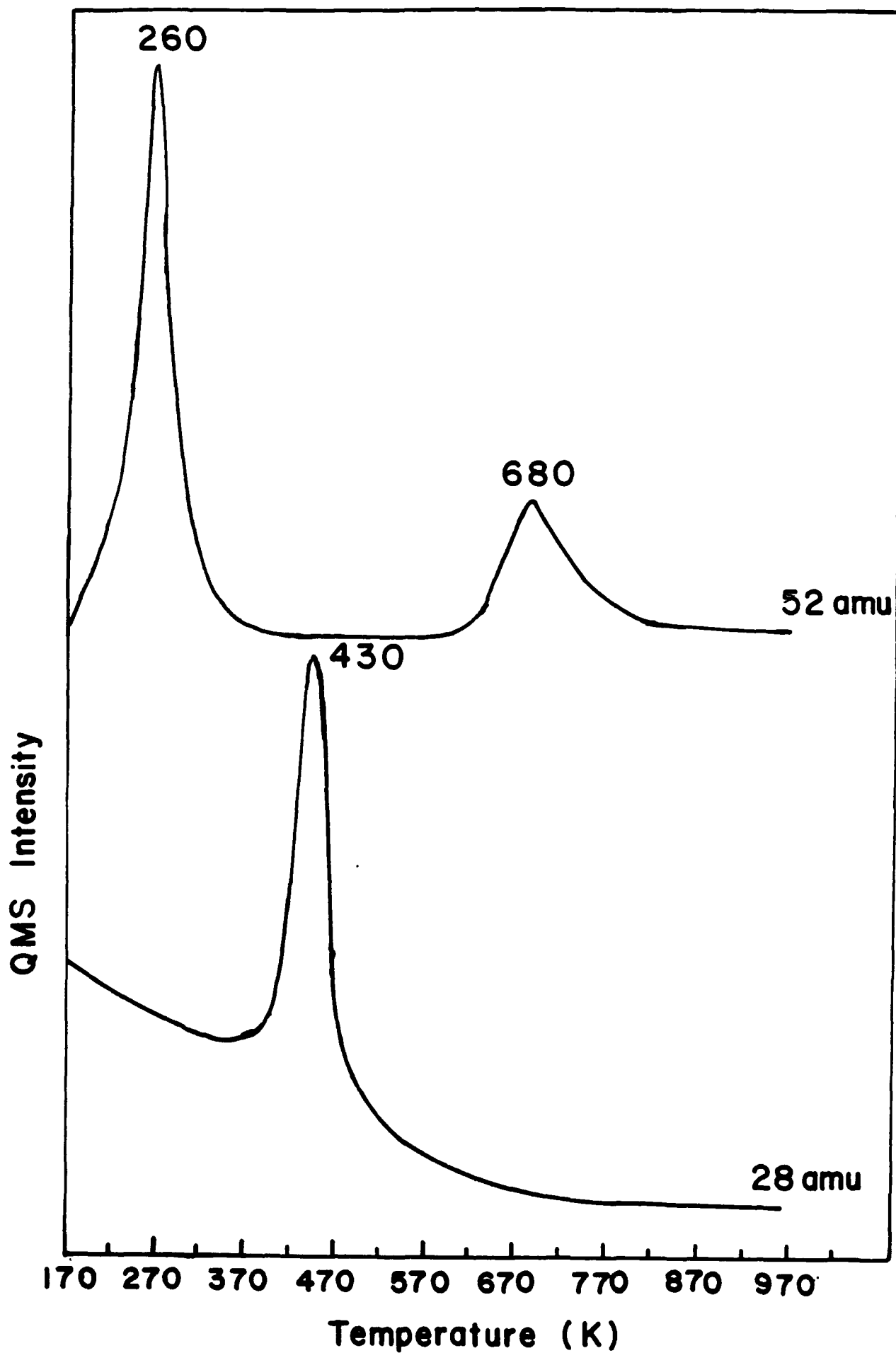
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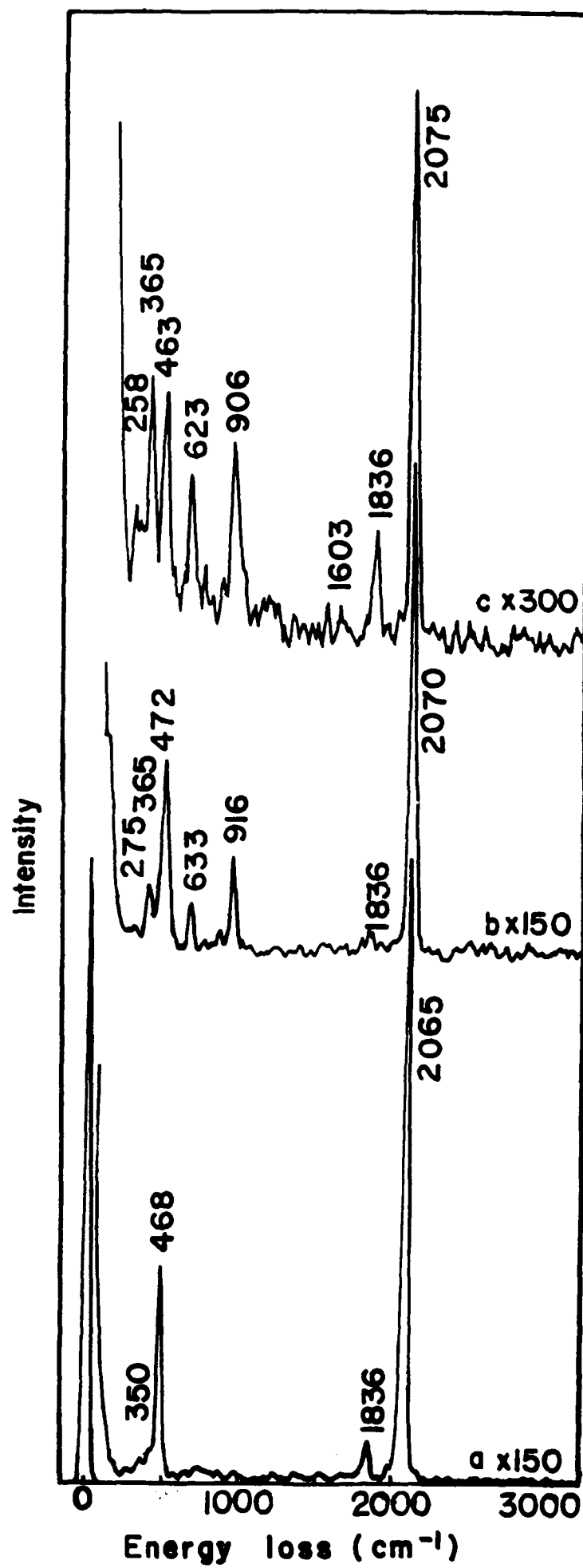
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Intensity

