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VIBRATIONAL SPECTROSCOPY WITH ANGLE-DEPENDENT EELS:
ACETYLENE CHEMISORPTION ON Pd(111)

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SURFACE VIBRATIONAL SPECTROSCOPY WITH ANGLE-DEPENDENT EELS:

ACETYLENE CHEMISORPTION ON PD(111)

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Abstract

High resolution electron energy loss measurements and LEED observations for normal and deuterated acetylene chemisorbed on Pd(111) are reported. Analysis of specular and off-specular energy loss data permits classification of the vibrational modes in terms of long-range dipole and short-range impact scattering mechanisms. Impact scattering intensities are found to be relatively strong for some modes and comparable in strength to intensities of dipole-excited modes. The vibrational data indicates that chemisorbed acetylene is strongly rehybridized ($\sim sp^{2.5}$), in approximate agreement with earlier photoemission work. Comparison is made to vibrational assignments for C_2H_2 chemisorbed on Ni(111) and Pt(111) as well as relevant model compounds. A surface bonding geometry is proposed which involves acetylene coordination at threefold sites on the Pd surface in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.

I. Introduction

A popular theme in modern surface science investigations has been the study of atomic and molecular adsorption on single crystal surfaces under well-defined experimental conditions. Such systems may provide important insight and information on various aspects of catalyzed surface reactions¹. A major area of investigation has been hydrocarbon adsorption and reactivity on transition metal surfaces, and a wide variety of surface sensitive techniques have been applied to these studies including ultraviolet photoemission spectroscopy (UPS), low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (EELS)². In this paper we present and interpret angle-dependent EELS results for the vibrational spectra of acetylene (C_2H_2) chemisorbed on Pd(111) at low temperature (~150K). We find that the chemisorbed acetylene molecule is strongly rehybridized, and we postulate a model surface bonding geometry. Relevant to our work here we cite recent photoemission³ and EELS⁴⁻⁷ work for C_2H_2 chemisorption on (111) surfaces of Ni, Pd, Pt and Rh.

A critical aspect of EELS vibrational analysis has involved the electron energy loss mechanism. It is now recognized that in addition to a long-range dipole scattering mechanism the short-range "impact" scattering mechanism is important as well. Dipole scattering theory showed that the scattering is strongly peaked in the direction of specular reflection and that only modes which have a dynamic dipole moment perpendicular to the surface may be observed on specular (surface dipole selection rule)⁸. However, with the initial observation of off-specular impact scattering for H on W(100)⁹ and more recent studies on hydrocarbons^{5,10}, the importance of impact scattering has become increasingly apparent. Impact scattering is dominant in the gas phase¹¹ due to various resonance processes. Such resonances have been reported very recently

for several physisorbed molecules¹². A theoretical framework to treat several important aspects of surface impact scattering has been developed by Tong, Li, and Mills¹³. In the present work we present a rather detailed angular analysis of the energy loss spectra for chemisorbed C_2H_2 and C_2D_2 , allowing an approximate classification of modes excited by dipole and impact mechanisms. Only by such analysis can symmetry arguments based on the surface dipole selection rule be applied with confidence.

II. Experimental

The experimental apparatus consisted of an ion-pumped stainless-steel vacuum system (base pressure $\sim 1 \times 10^{-10}$ Torr) equipped for EELS, LEED, Auger spectroscopy, ion-sputtering and quadrupole mass spectrometry. Liquid nitrogen cooling was used to obtain a nominal sample temperature of 150K in these experiments. The preparation and cleaning of the Pd(111) sample and sample dosing have been previously described¹⁰. Purified C_2H_2 (99.6%) from Matheson and C_2D_2 (99%) from Merck and Co. were used in these measurements and were examined mass spectroscopically. Precautions were taken against acetone impurity in the C_2H_2 by passing the gas through a dry-ice cooled molecular sieve trap. Sample exposures cited here have been corrected for ion-gauge sensitivity.

The high-resolution electron spectrometer has been described earlier¹⁴. In these experiments the resolution (FWHM) of the elastic beam varied between 10 and 12 meV (~ 80 - 100 cm^{-1}) at count rates of $\sim 10^5$ Hz. Care was taken that this resolution and analyzer transmission was essentially maintained over the entire spectral range (0- 3200 cm^{-1}). Spectra were obtained by digital scanning and data acquisition with an LSI-11 microcomputer, except for initial spectrometer tuneup which employed X-Y recorder display of the ratemeter output versus analyzer slit voltage.

Off-specular measurements were performed by rotation of the sample about an axis perpendicular to the plane of electron beam incidence, while holding the angle between the monochromator and analyzer fixed. The angular FWHM of the elastic beam was found to be approximately 4° by this procedure. For the condition of specular beam analysis the incident beam angle was 65° from the surface normal.

III. Results

EELS spectra and LEED patterns have been examined as a function of C_2H_2 exposure over a range of 0.5-2.0 L (1L= 10^{-6} Torr-sec) at $T=150K$. In Figure 1 we show the EELS vibrational spectra as a function of exposure for C_2H_2 in the specular direction. Features attributed to the C_2H_2 adsorbate occur at 500, 673, 872, 1034, 1402, and 2992 cm^{-1} as well as a small, broad peak due to CO impurity near 1800 cm^{-1} . As shown in Figure 1 we find that the spectral intensities saturate near 1.5 L exposure, and we find no evidence for a significant change in the adsorbate over the exposure range examined. One notes, however, some changes in relative intensities of the loss peaks as a function of coverage.

LEED observations parallel the EELS data in the sense that a weak $(\sqrt{3} \times \sqrt{3})R 30^\circ$ diffraction pattern is seen at 0.5 L exposure which grows in intensity up to 1.5-2.0 L exposure. This pattern was readily visible but the fractional-order spots were diffuse, indicative of relatively small domains of ordered C_2H_2 . We also note, but do not discuss in detail here, that warming of the adsorbate to $\sim 200K$ results in irreversible changes in the EELS spectra and is accompanied by disordering of the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ LEED pattern. Warming the C_2H_2 adsorbate to 300K leads to at least partial conversion of C_2H_2 to the ethylidyne ($\rightarrow C-CH_3$) molecule¹⁰. Details of the thermal evolution of C_2H_2 and C_2H_4 on Pd(111) will be discussed elsewhere¹⁵.

The results illustrated in Figure 1 and our LEED observations indicate that the C_2H_2 overlayer is fully developed at approximately 1.5 L exposure. Most

spectra were taken at this exposure because of the relatively intense loss features. We present here spectra taken at an electron beam impact energy of $E_0 = 3.8$ eV, which was found to give relatively high elastic and inelastic count rates. We have also examined the impact energy dependence of the energy loss features¹⁶, but we do not discuss this aspect in detail here. We note, however, that marked changes in relative intensities of certain loss features occur as a function of electron beam energy, consistent with the differing excitation mechanisms of dipole and impact scattering discussed below.

We now turn to discussion of specular and off-specular EELS data. The off-specular data is important for two reasons: (i) it may provide symmetry information on the adsorbate by identifying those loss features which are dipole-enhanced and those which are predominantly impact excited; (ii) weaker loss features, not readily apparent on specular, may often be resolved off-specular. In the present study over 30 complete spectra were obtained for each of the adsorbates C_2H_2 and C_2D_2 in an angular range of -15° to $+15^\circ$ from the specular beam direction. In Figures 2-3 we illustrate representative specular and off-specular data for C_2H_2 and C_2D_2 . In Figure 2 for C_2H_2 we note the relative intensity change between the peaks at 673 cm^{-1} and 872 cm^{-1} and the relative change in strength of the 2992 cm^{-1} loss. These relative intensity changes are mimicked in the C_2D_2 spectra (Figure 3) for the corresponding loss features at 511 cm^{-1} , 621 cm^{-1} , and 2249 cm^{-1} . We note that the C_2D_2 spectra are somewhat complicated by the presence of a small amount of C_2H_2 as confirmed by a weak loss peak near 3000 cm^{-1} (CH stretch). Although such C_2H_2 may possibly be formed by HD exchange from residual surface hydrogen we believe it more likely to arise from C_2H_2 background impurity during sample exposure to C_2D_2 . In Figure 3 we identify only those spectral features which we were able to clearly attribute to C_2D_2 by analysis of a large number of spectra.

The results of the off-specular analysis are summarized in Figure 4. Here we show absolute intensities measured for the principal C_2H_2 and C_2D_2 loss features as a function of angle from specular. The interpretation of these angular profiles is based on the result that vibrational modes which are dipole-enhanced should exhibit a strongly pronounced specular lobe of narrow angular width⁸. The actual angular width in our experiments is approximately governed by the (instrumental) width of the elastic beam, shown in the top panel of Figure 4. Vibrational modes which exhibit broad angular behavior are attributed to a short range impact scattering mechanism. We emphasize that these arguments do not imply that modes which are allowed by the surface dipole selection rule will always exhibit strong dipole enhancements. In some cases the dynamic dipole moment may be sufficiently small that impact scattering contributions dominate¹⁷.

Based on the above arguments we determine from Figure 4 that for C_2H_2 the modes at 673 cm^{-1} (CH bend) and 1402 cm^{-1} (CC stretch) are dipole enhanced. We also note that the modes of the deuterated species closely resemble the corresponding C_2H_2 modes both in angular behavior and in absolute intensity. Such a correspondence was also used to advantage by Ibach and Lehwald for C_2H_2 on Ni(111).⁵ We further identify the modes at 872 cm^{-1} (621 cm^{-1}) and 2992 cm^{-1} (2249 cm^{-1}) as being impact excited. These modes exhibit a much broader angular behavior than the dipole-enhanced modes, the mode at 2992 cm^{-1} (CH stretch) being essentially flat¹⁸. Because of a slight peaking on specular one may argue for some dipole enhancement of the 872 cm^{-1} (621 cm^{-1}) mode but such behavior is permissible for impact scattering as well. Finally, we mention that additional weaker loss peaks were found at 500 cm^{-1} and 1034 cm^{-1} for C_2H_2 and tentatively identified ca. 850 cm^{-1} for C_2D_2 , but reliable angular data for these low intensity modes was not obtainable. In Table 1 we summarize the observed

frequencies for C_2H_2 and C_2D_2 , the dominant excitation mechanisms, and the probable mode assignments discussed in Section IV.

In closing this section we emphasize two aspects of the angular-dependent EELS data not discussed above. First, although we have identified certain modes as being "dipole enhanced" we note that these modes also have significant contributions from non-dipole (impact) mechanisms. For example, if we make the rough approximation that the intensities from two mechanisms are simply additive and, furthermore, that the impact scattering is independent of angle we may estimate the relative strength of the two mechanisms. We find by this very rough calculation that each of the modes at 1402 cm^{-1} (ν_{CC}) and 673 cm^{-1} (ρ_{CH}) derive ~85% of their intensity on specular from dipole scattering. Secondly, we point out the considerable relative strength of the impact excited modes, even on specular. The modes at 872 cm^{-1} and 2992 cm^{-1} for C_2H_2 are perhaps the strongest impact excited modes (in a relative sense) yet observed for a chemisorbed molecule. Other examples have been reported for hydrocarbons, especially for ν_{CH} modes^{5,10}.

IV. Discussion

In this section we discuss the vibrational mode assignments for C_2H_2 chemisorbed on Pd(111) and compare to other spectroscopic information on this system, relevant molecular analogues and corresponding data for Ni(111) and Pt(111). We note that a rather extensive ultraviolet photoemission study of C_2H_2 and C_2H_4 was carried out by Demuth³ on (111) surfaces of Ni, Pd, and Pt whereas EELS vibrational data was reported for Ni and Pt by Demuth, Ibach, and Lehwald⁴⁻⁶. Felter and Weinberg¹⁹ have recently summarized various aspects of the photoemission and EELS work on Ni and Pt and have discussed appropriate chemisorption models.

The vibrational mode assignments given in Table I for C_2H_2 on Pd(111) are based on deuteration shifts, angular variation of the loss intensities and comparison to relevant molecular analogues. The presence of the ν_{CH} mode at 2992 cm^{-1} and the ν_{CC} mode at 1402 cm^{-1} confirms that the molecular geometry is strongly distorted from the free (sp hybridized) C_2H_2 ground state. By comparison with gas phase hybridization data²⁰ on the ν_{C-H} and ν_{C-C} frequencies we conclude that the C_2H_2 molecule is approximately $sp^{2.5}$ hybridized with a C-C bond length of $1.42 \pm 0.03\text{ \AA}$. This geometry is in reasonable agreement with the estimated C-C bond length of $1.34\text{--}1.39\text{ \AA}$ given by Demuth³ on the basis of an approximate photoemission analysis. However, the photoemission analysis was unable by itself to rule out a class of weakly distorted acetylene structures³.

Although we may safely conclude that the molecular geometry for C_2H_2 on Pd(111) is strongly distorted, further conclusions on surface geometry are speculative and rely heavily on comparison to model compounds, such as organometallic complexes. However, these compounds rarely serve as ideal models and vibrational data is frequently sparse. To our knowledge, the most relevant compound for C_2H_2 for which vibrational analysis is available is $C_2H_2(Co)_2(CO)_6$.²¹ In this compound the C-C bond length is estimated as $1.37\text{--}1.39\text{ \AA}$, the acetylene probably adopting a μ -bridging geometry²¹. It is also of interest to compare to vibrational frequencies of electronically excited states of C_2H_2 ²², as emphasized recently by Felter and Weinberg¹⁹. In Table 2 we summarize relevant vibrational data on these systems as well as EELS chemisorption work. Since the most complete (angular-dependent) EELS analyses are available for Ni⁵ and Pd we rely most heavily on these comparisons. The ν_{CC} and ν_{CH} frequencies clearly indicate a stronger molecular distortion for the case of Ni($-sp^{2.7}$). However, we find a remarkable similarity between the reported frequencies and isotopic shifts for the δ_{CH} and ρ_{CH} ²³ bending modes for C_2H_2 on Pd(111) and Ni(111). This may suggest a similar surface bonding

geometry for C_2H_2 on the two surfaces. We also note favorable correspondence between certain vibrations for C_2H_2 on Pd(111) and the excited (1A_u) state of acetylene. (The trans-bent 1A_u state is probably not favored for chemisorption but the cis-bent excited state is expected to have similar frequencies¹⁹.) Excellent correspondence in the ν_{CC} frequencies for $C_2H_2/Pd(111)$ and the di-cobalt complex is evident but the ν_{CH} modes are $\sim 100\text{ cm}^{-1}$ higher in the complex. We take this as some evidence that the chemisorbed acetylene is somewhat more distorted on the Pd(111) surface than in the di-cobalt complex and is coordinated to more metal atoms.

We conclude this discussion with speculation on the possible surface geometry for C_2H_2 on Pd(111). By utilizing the vibrational assignments and assigned scattering mechanisms (Table 1) one may place some restrictions on the point group symmetry of the chemisorbed acetylene. If one considers the first layer of palladium atoms only then one may have acetylene surface geometries of C_{2v} and C_2 symmetry, but the highest symmetry is C_s if second layer interactions are significant. However, in the case of C_{2v} symmetry, neither of the ρ_{CH} modes would be dipole enhanced, contrary to our EELS observations. Furthermore, the fact that one of the ρ_{CH} modes (872 cm^{-1}) is apparently not dipole enhanced, argues in favor of a geometry with C_s or C_2 symmetry. We cannot, however, rigorously rule out lower symmetry (C_1) structures since the dynamic dipole moment of the 872 cm^{-1} mode may simply be relatively small.

To summarize, we favor a structure with C_s or C_2 symmetry, and the former seems most likely if second layer interactions are significant. The strong distortion ($\sim sp^{2.5}$) and our estimated C-C bond length of 1.42 \AA is suggestive of the bonding of acetylenic ligands in trinuclear transition-metal complexes. We cite, for example, the $Os_3(CO)_{10}(C_2Ph_2)$ compound where the C-C bond length is 1.44 \AA and the molecule is symmetrically coordinated near the center of the metal

triangle²⁴. Figure 5 illustrates this suggested surface geometry for C_2H_2 in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. In this model the C-C axis lies parallel to the surface and the molecular plane of the cis-bent C_2H_2 (CCH angle -122°) is slightly tilted relative to the surface normal as indicated. This model has C_s symmetry and is consistent with the fact that the ρ_{CH} (asym.) mode does not show dipole enhancement. We also note that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure exhibits rather close-packing of the acetylene molecules as shown by the approximate Van der Waals radii²⁵. Certainly, many other models are possible including various tilted C-C axis and trans-bent configurations. More definitive analysis will require detailed normal coordinate calculations for model surface geometries.

Acknowledgements

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Table 1. Assignment of the vibrational modes, frequencies (cm^{-1}) and excitation mechanisms for C_2H_2 on Pd(111) at $T=150\text{K}$. Standard deviations of measured frequencies are generally less than 10 cm^{-1} .

<u>C_2H_2</u>	<u>C_2D_2</u>	<u>$\nu_{\text{H}}/\nu_{\text{D}}$</u>	<u>Dominant Mechanism</u>	<u>Mode Assignment</u>
2992	2249	1.33	impact	$\nu_{\text{CH}}^{\text{d}}$
1402	1359	1.03	dipole	ν_{CC}
1034	850 ^a	1.22	(c)	δ_{CH}
872	621	1.40	impact	ρ_{CH} (asym.)
673	511	1.32	dipole	ρ_{CH} (sym.)
500	(b)	--	(c)	$\nu_{\text{Pd-C}}$

^aWeak loss peak assigned to the region $840\text{--}860 \text{ cm}^{-1}$.

^bNot resolved.

^cNot determined.

^dSymmetric and asymmetric modes too close to resolve.

Table 2. Comparison of vibrational mode assignments and frequencies (cm^{-1}) for free (ground and first excited state), complexed, and chemisorbed acetylene on (111) surfaces of Ni, Pd, and Pt. Frequencies given in parentheses for deuterated molecules.

Vibrational Mode	C_2H_2^a ($1^1\Sigma_g^+$)	Excited C_2H_2^b (1^1A_u)	Complexed ^c $\text{C}_2\text{H}_2\text{Co}_2(\text{CO})_6$	Chemisorbed		
				$\text{C}_2\text{H}_2/\text{Pd}(111)$	$\text{C}_2\text{H}_2/\text{Ni}(111)^d$	$\text{C}_2\text{H}_2/\text{Pt}(111)^e$
ν_{CH} (sym.)	3374 (2701)	--	3116 (2359)	2992 (2249)	2920 (2190)	3010 (2245)
ν_{CH} (asym.)	3287 (2427)	3020 (2215)	3086 (2297)			--
ν_{CC}	1974 (1762)	1380 (1310)	1403 (1347)	1402 (1359)	1220 (1190)	1310 (1260)
δ_{CH} (sym.)	612 (505)	--	768 (602)	1034 (850)	1080 (890)	985 (730)
δ_{CH} (asym.)	729 (539)	1049 (844)	894 (751)	--	1370 (1090)	--
ρ_{CH} (sym.)	--	--	--	673 (511)	690 (540)	770 (570)
ρ_{CH} (asym.)	--	--	--	872 (621)	860 (640)	--
$\nu_{\text{M-C}}$	--	--	605 (561) 551 (520)	500 (---)	560 (---) 480 (460)	570 (---) 340 (310)

^aHerzberg, Ref. 20, ground state.

^bIngold et al., Ref. 22, first electronically excited singlet state (trans-bent).

^cIwashita et al., Ref. 21.

^dIbach and Lehwald, Ref. 5.

^eIbach and Lehwald, Ref. 6.

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17. This is seen to be the case here for the ν_{CH} modes of C_2H_2 and was observed for the ν_{CH_3} modes of (>C-CH_3) on Pd(111)¹⁰.
18. This peak is believed to consist of both symmetric and asymmetric ν_{CH} modes which lie too close to be resolved. These modes are separated by only 30 cm^{-1} in the dicobalt acetylene complex.
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Figure Captions

- Fig. 1. Electron energy loss spectra for C_2H_2 on Pd(111) as a function of C_2H_2 exposure.
- Fig. 2. Electron energy loss spectra for C_2H_2 on Pd(111) for specular and off-specular scattering.
- Fig. 3. Electron energy loss spectra for C_2D_2 on Pd(111) for specular and off-specular scattering.
- Fig. 4. Absolute intensities of energy losses as a function of the angle $\Delta\theta$ from specular for primary beam energy of 3.8 eV. Note the close similarity in angular behavior and absolute intensity for the corresponding modes of C_2H_2 and C_2D_2 .
- Fig. 5. Proposed bonding geometry for C_2H_2 on the Pd(111) surface in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. In this model the carbon atoms are located near threefold surface sites with the C-C axis parallel to the surface and the H atoms in a cis-bent configuration (C_S symmetry). Oval shaped areas are approximate regions of Van der Waals repulsion.

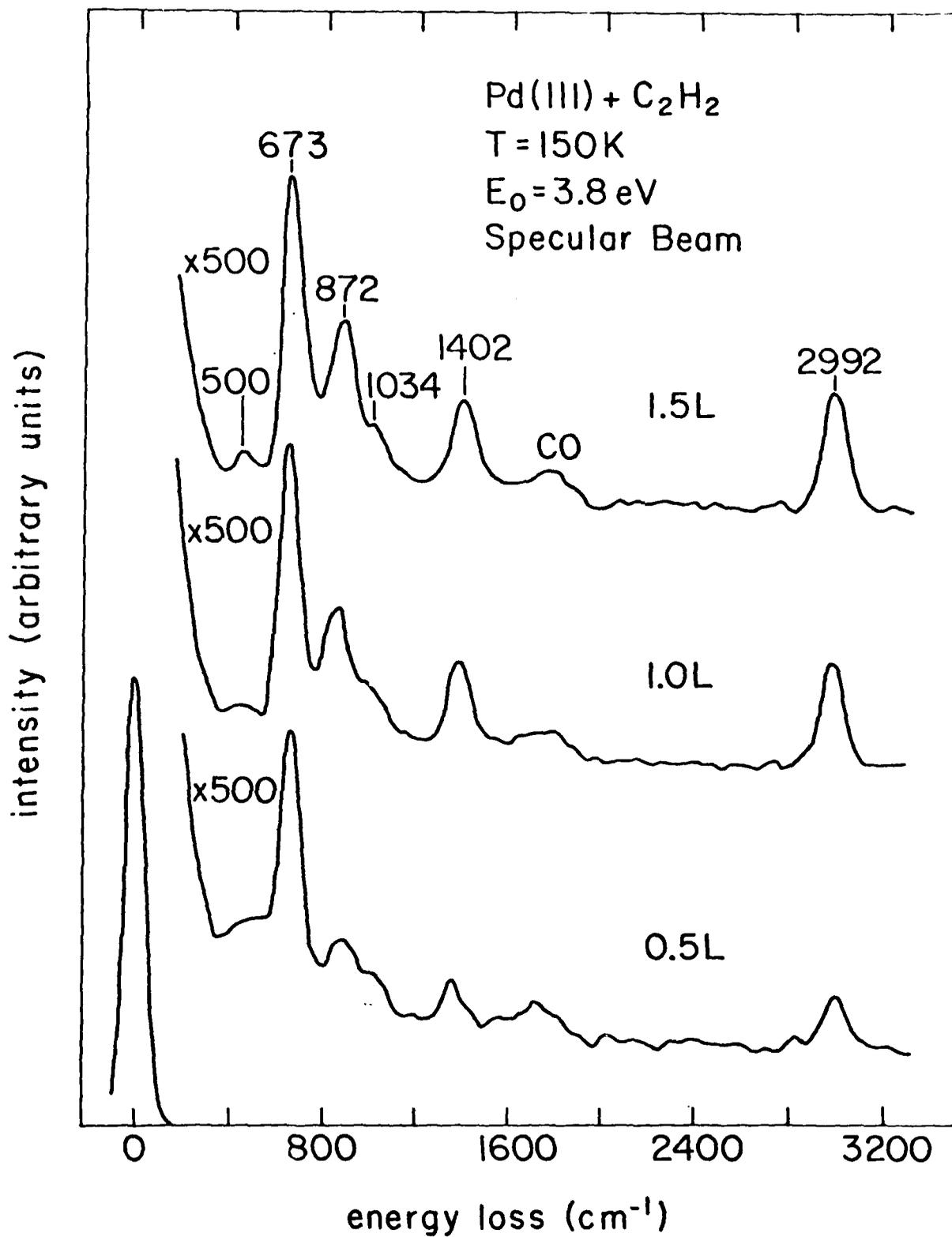


FIGURE 1

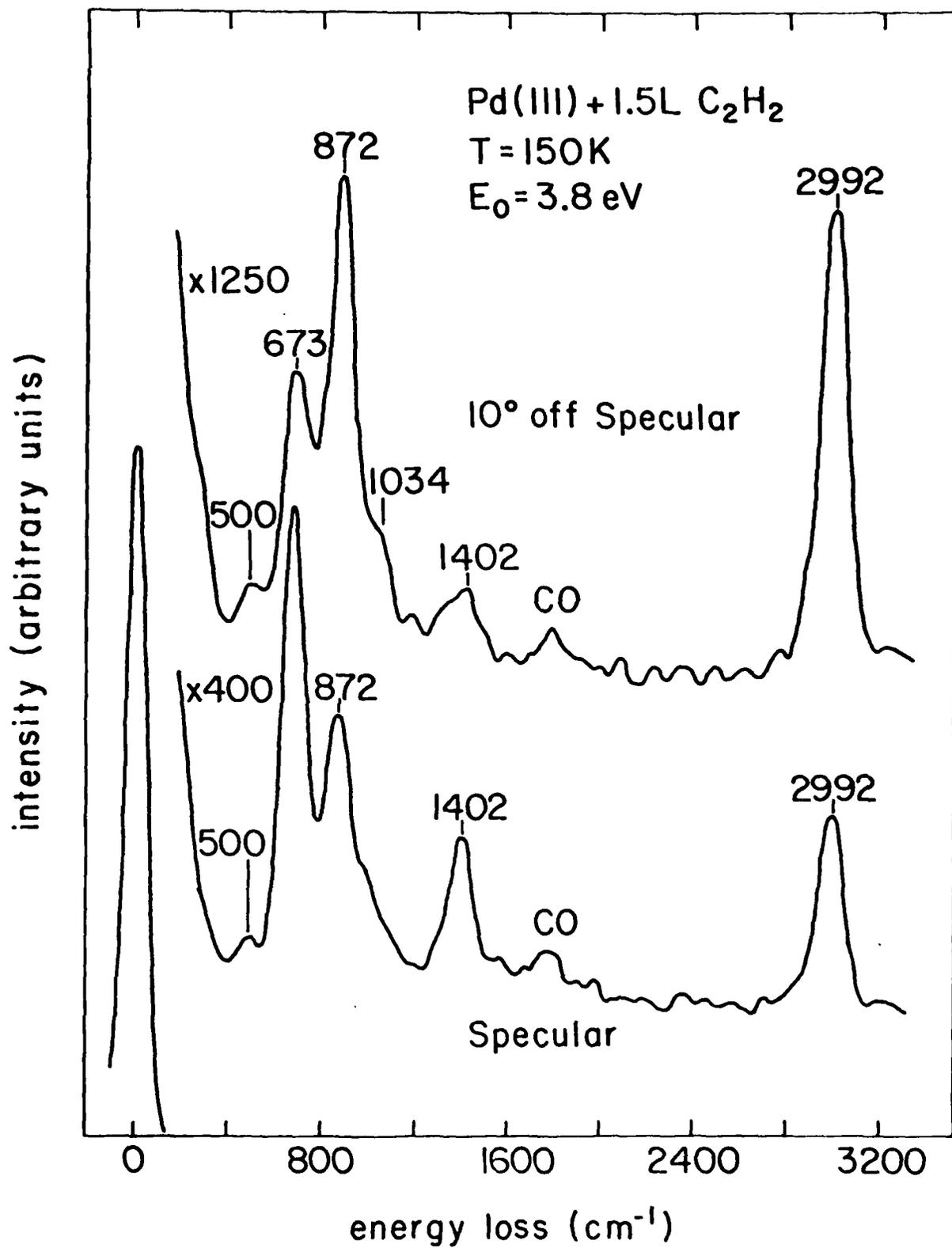


FIGURE 2

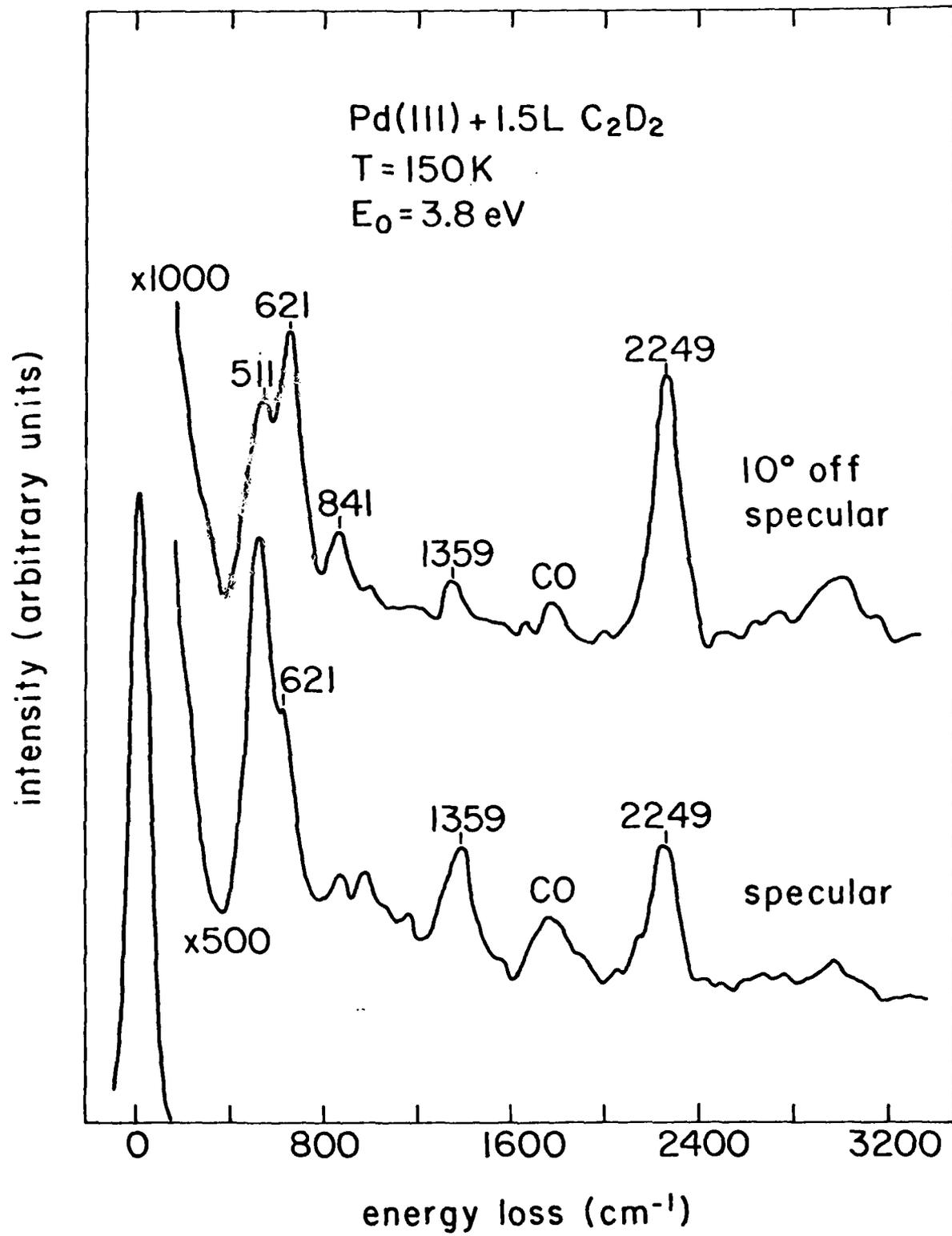


FIGURE 3

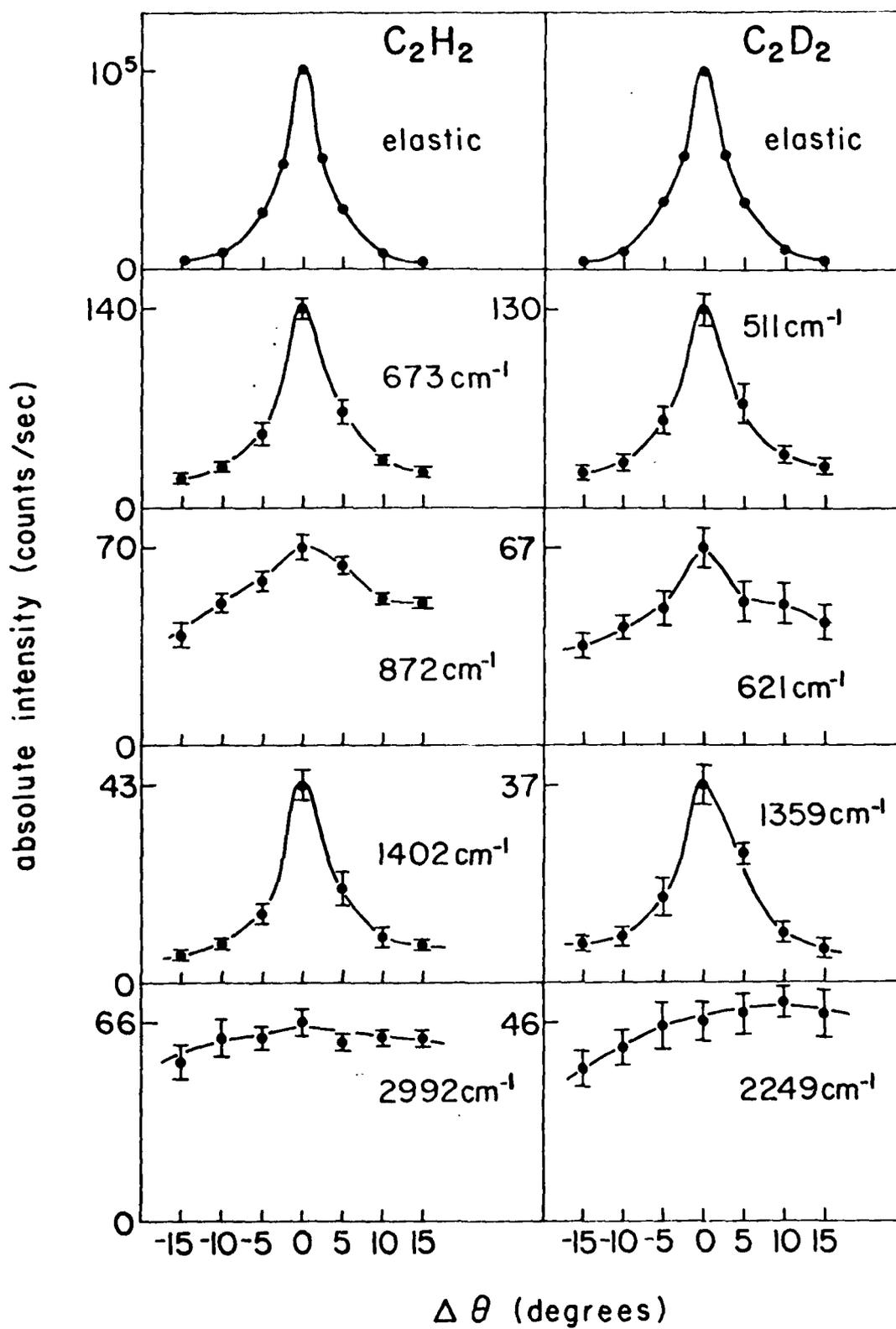


FIGURE 4

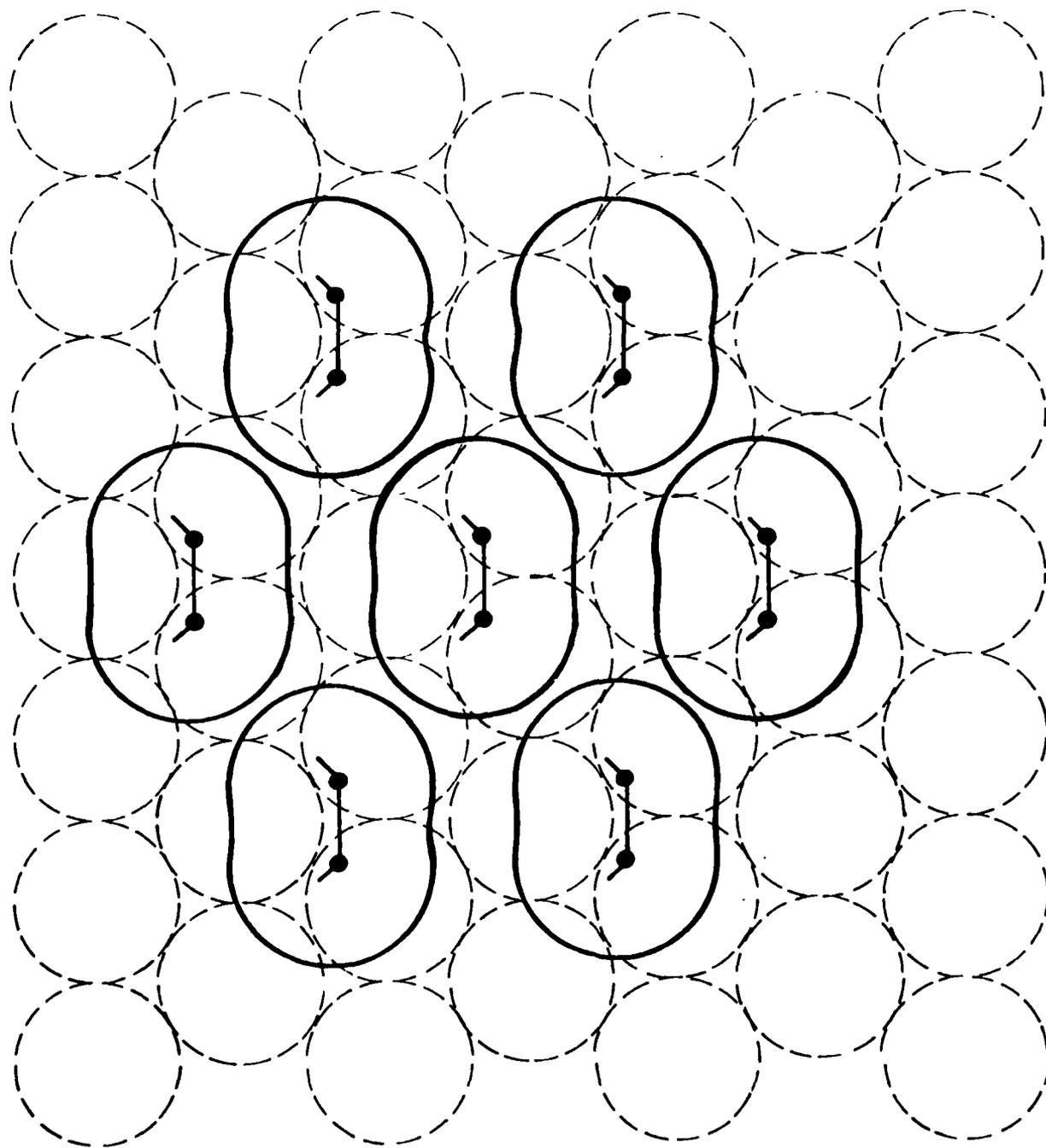


FIGURE 5

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