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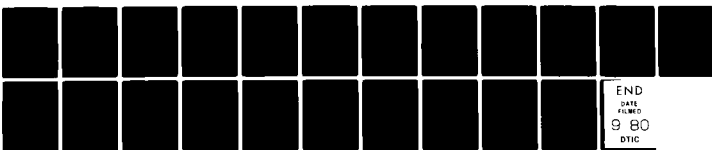
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VIBRATIONAL FREQUENCIES OF HALOGEN ATOMS ADSORBED ON SILVER MET--ETC(U)
JUL 80 H NICHOLS, R M HEXTER N00014-77-C-0209

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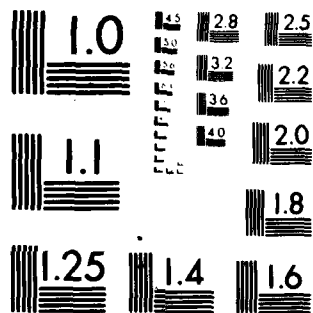
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Vibrational Frequencies of Halogen Atoms
Adsorbed on Silver Metal Surfaces

by

Henry Nichols and Robert M. Hexter

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VIBRATIONAL FREQUENCIES OF HALOGEN ATOMS
ADSORBED ON SILVER METAL SURFACES

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ABSTRACT

The vibrational frequencies of halogens adsorbed on Ag(100) are calculated. The frequency of a single adsorbed atom vibration perpendicular to the surface is obtained from AgX ($X = F, Cl, Br, I$) crystal frequencies. Interaction between dipoles consisting of the effective charge on the adsorbed atom and its induced image charge produces a coverage dependent frequency. The effective charge on the adsorbed atom is assumed to be 1.0 e, while the electronic polarizability of the real-plus-image atom system is assumed to be twice the electronic polarizability of X^- . At full coverage, the calculated frequencies for the $k = 0$ modes are 437, 241, 150, and 113 cm^{-1} respectively for $X = F, Cl, Br, I$, which compare well with experimental values, and these frequencies are assigned to external vibrational modes of halogen atoms adsorbed on silver.

INTRODUCTION

Enhanced Raman scattering by molecules adsorbed on metal surfaces has now been reported for a relatively large number of molecules, and for a growing number of metals.¹⁻¹⁶ It appears that Raman scattering intensities from metal-surface adsorbed molecules can be as much as 10^5 - 10^6 times greater than that expected from the number of molecules on the surface and normal inelastic scattering cross sections.^{4,10} It is also quite clear that, in order to observe this enhancement of intensity, the metal surface must be roughened,¹⁷ and the theoretical basis for this requirement has been discussed by several authors.^{18,19} Experimental roughening procedures have included mechanical abrasion followed by ion sputtering,²⁰ electrochemical cycling,²¹ photochemical cycling,¹⁷ and controlled vacuum deposition of metal islands.²² In the case of electrochemical preparations, cycling is not mandatory; Bergman has used a procedure in which a positive potential of approximately 0.5V (relative to SCE) is applied to a silver electrode in aqueous alkali fluoride; the electrode is then removed from solution while it is still under potentiostatic control.²³

Bergman and co-workers have used radiochemical techniques to determine the amount of CN^- adsorbed on Ag surfaces.⁷ They found the coverage to be on the order of a monolayer. Only in this case is the intensity enhancement by a factor of $\sim 10^6$ firmly established. A similar study, designed to determine the amount of pyridine adsorbed

on a silver electrode, indicated that this amount corresponded to 10-100 monolayers of pyridine.²⁴ Part of the Raman intensity observed with adsorbed pyridine may therefore be due to this increased coverage.

Recent experiments carried out by Smardjewski and co-workers indicated that only those molecules immediately adjacent to a silver surface exhibit enhanced Raman scattering.²⁰ While these authors studied pyridine adsorbed on silver in ultrahigh vacuum (UHV), their apparatus did not have any capability of surface characterization. However, a more recent investigation by Zwemer, Shank and Rowe, in which surface characterization by Auger electron spectroscopy (AES) was carried out on the same system, has demonstrated that the scattered intensity decreases continuously with the distance from the surface,²⁵ in agreement with the recent theoretical advances.¹⁹ While there is an inherent difficulty in the use of AES to determine coverage because of the electron beam-induced damage of adsorbed molecular films, essentially the same Raman scattering intensity vs. coverage plots have been obtained using AES²⁵ as with a measurement of the change of Ag surface work function in the low dose region.²⁶

Raman spectra of pyridine adsorbed on silver following electrochemical roughening in aqueous KCl solutions manifest a strong band at $\sim 240 \text{ cm}^{-1}$. This band has been attributed by Creighton et al. to the Ag-N stretching motion of adsorbed pyridine.²⁷ However, Raman spectra of pyridine adsorbed on silver under UHV conditions are missing this band.²⁰ Furthermore, this band is observed in the spectrum of light scattered by a silver surface which has been electrochemically roughened in a pyridine-free aqueous chloride solution, and other low frequency bands take the place of the one at 240 cm^{-1} when the electrolyte is changed.²⁸ Finally, M-N stretching frequencies in metal amine complexes

generally lie in the $400\text{--}500\text{ cm}^{-1}$ region, except for divalent metals.²⁹

Evans, Albrecht, Ullevig and Hexter have characterized a silver electrode surface before and after electrochemical cycling using secondary ion mass spectroscopy, Auger electron spectroscopy and scanning electron microscopy.³⁰ They found that the reformed Ag surface was quite clean, except for Cl contamination, the origin of which was KCl in the electrochemical solution. The Cl was easily removed by ion sputtering, and it was shown to be contained in a AgCl layer on the surface.

In the present work, the vibrational frequencies of halogen atoms adsorbed on Ag(100) are calculated, in order to assess the assignment of the observed low frequency bands to vibrational motion of these adsorbed species.

MODEL SYSTEM

LEED studies by Zanazzi and Jona show that Cl adsorbed on Ag(100) surface has a $C(2 \times 2)$ structure in which each Cl atom is bonded to four Ag surface atoms.³¹ This structure, having one molecule per two-dimensional unit cell, is used as a model system here for all adsorbed atoms. Only the symmetric stretching mode perpendicular to the surface is considered for adsorbed X ($X = F, Cl, Br, I$), and the substrate is assumed to be a perfect electrical conductor. Now a charge located at a distance d above the surface of a perfect electrical conductor will induce an image charge at a distance d below the surface of the substrate.³² The image charge will then have the same magnitude, but opposite sign, as the adsorbed charge and, in addition, the same

polarizability.

We have recently presented a molecular dipole model appropriate for the internal optic modes of surface adsorbed molecules.³³ This model includes the interaction between the dipoles in the adsorbed layer and the image dipoles in the substrate. The present investigation, which is applied to external optic modes involving motions of the entire adsorbed species with respect to the surface, assumes that only one layer of dipoles is present. These dipoles consist of the real-plus-image charges, and they are treated as point dipoles.

The potential energy of surface adsorbed X is the sum of two contributions, a static surface field term and a dipolar coupling term. According to Mandel and Mazur,³⁴ this may be written as

$$2V = \mathbf{q}_s^+ \mathbf{\omega}_0^2 \mathbf{q}_s + \boldsymbol{\mu}^+ \mathbf{T} (\mathbf{I} + \alpha \mathbf{T})^{-1} \boldsymbol{\mu} \quad (1)$$

where $\mathbf{q}_s$ is an N-dimensional vector of the mass-weighted displacement coordinates of the N atoms adsorbed on the surface, $\mathbf{\omega}_0^2$ is a diagonal matrix of the squared static surface field frequencies, $\boldsymbol{\mu}$ is a 3N-dimensional vector of the dipoles associated with the adsorbed X atoms, $\mathbf{I}$ is a 3N x 3N identity matrix, α is a 3N x 3N electronic polarizability matrix, and $\mathbf{T}$ is a 3N x 3N dipole field propagation tensor with elements

$$\begin{aligned} T_{\tau\tau'} &= 1/r_{\tau\tau'}^3 \text{ if } \tau \neq \tau' \\ &= 0 \quad \tau = \tau' \end{aligned}$$

where $r_{\tau\tau'}$ is the distance between atoms τ and τ' . Expanding the

dipoles in terms of the coordinates q_s

$$\mu = \mu_0 + (\partial\mu/\partial q_s) q_s + \dots \quad (2)$$

and substituting the terms linear in q_s for μ in (1), the potential energy may be written in quadratic terms as

$$2V = q_s \omega_0^2 q_s + q_s^+ \sum_{\tau} (I_{\tau} + \sum_{\tau'} q_{\tau'}^T)^{-1} q_s (\partial\mu/\partial q_s)^2 \quad (3)$$

Translationally symmetrized normal coordinates, Q_k , are related to the molecular coordinates, q_s , by the transformation

$$Q_{\tau} = \sum_{\tau'} X_{\tau\tau'} q_s$$

where $X_{k\tau} = (1/N)^{1/2} \exp[-ik \cdot \chi(\tau)]$, k is the wavevector, and $\chi(\tau)$ is the position vector of unit cell τ . Using the matrix X_{τ} , the potential energy may then be written as

$$2V = Q_{\tau}^+ \omega_0^2 Q_{\tau} + Q_{\tau}^+ \sum_{\tau'} S_{\tau\tau'} (I_{\tau} + \sum_{\tau''} q_{\tau''}^T)^{-1} Q_{\tau} (\partial\mu/\partial q_s)^2 \quad (5)$$

where $S_{\tau} = \sum_{\tau'} X_{\tau}^T X_{\tau'}^{-1}$. The lattice sum matrix, S_{τ} , is block-diagonal in k , but only $k = 0$ will be considered here. In addition, only the dipole moment components perpendicular to the surface are considered. The present treatment is analogous to that presented by Decius for dipolar coupling in three-dimensional crystals.³⁵

In order to achieve rapid convergence, the two-dimensional lattice sum may be calculated by the procedure developed by DeWette and

Schacher.³⁶ This procedure requires translational symmetry. At full coverage, the adsorbed atoms may form a two-dimensional lattice; however, this probably is not the case at intermediate coverage. One method of obtaining lattice sums at intermediate coverage is to treat the adsorbed atoms as though they always form a two-dimensional lattice with a coverage dependent "effective" lattice constant, $a(\chi)$, given by

$$a(\chi) = a_0 \chi^{-1/2}$$

where a_0 is the full coverage lattice constant and χ is the coverage fraction. The lattice sums at intermediate coverages are then given by

$$S(\chi) = \chi^{3/2} S^0$$

where S^0 is the full coverage lattice sum. This method has been used by Schmidt and Gomer,³⁷ Delanaye and co-workers,³⁸ and by Muscat and Newns.³⁹

A second method of obtaining lattice sums at intermediate coverage is to multiply the full coverage lattice sum by the coverage fraction. This method has been used by Mahan and Lucas⁴⁰ and by Bennett.⁴¹ These two methods were compared by Nichols and Hexter in an application of a dipolar coupling model to carbon monoxide adsorbed on platinum.³³ The latter method, in which $S(\chi) = \chi S^0$, was shown to be preferable, and it is used here.

The displacement coordinate, q_s , is defined here to be the displacement perpendicular to the surface of the adsorbed atom during the course of a vibration. The image atom is displaced in the opposite

direction, thereby doubling the charge displacement with respect to the displacement of the adatom. The dipole moment derivative is then $\partial\mu/\partial q_s = 2 e' m_x^{-1/2}$, where e' is the charge on X after adsorption and m_x is the mass of X. Substituting χS^0 for S in (4), the vibrational frequency of the surface adsorbed X is given by

$$\omega^2 = \omega_o^2 + \chi S^0 (I + \alpha \chi S^0)^{-1} \frac{4e'^2}{4\pi^2 c^2 m_{cl}} \quad (5)$$

where the factor $1/4\pi^2 c^2$ is included for unit conversion to cm^{-2} .

STATIC SURFACE FIELD FREQUENCY

The vibrational frequency, ω_o , of an adsorbed atom in the absence of dipolar coupling is not known. If internal optic modes are considered, such as the C-O stretching motion of adsorbed CO, then the surface isolation frequency will be lower than the static surface field frequency, as a result of the dipolar coupling of the adsorbed dipole with its own image. In the present treatment, there is only one layer of dipoles so that the static surface field frequency, ω_o , is equal to the frequency the adsorbed atom would have in the limit of dilute coverage. An approximate value of ω_o determined from AgX single crystal frequencies will be used here.

The diatomic frequency, ω_d , of an AgX molecule in single crystal AgX is taken to be that frequency the molecule would have in the absence of dipolar coupling within the crystal. According to Fox and Hexter,⁴² ω_d is given by

$$\omega_d = 2^{-1/2} \left[\omega_t + \frac{8\pi}{9} \frac{p^2}{a_o^3} \right] \quad (6)$$

for the face centered cubic structure found for AgF, AgCl, AgBr, and AgI (phase III). ω_t is the transverse optic mode frequency in the single crystal, p is magnitude of the transition dipole moment, and a_0 is the lattice constant. ω_d will be used as an initial starting frequency for X bonded to only one Ag surface atom.

The quadratic potential energy, V_d , of diatomic AgX is partitioned into the sum of two contributions, V_k and V_e . That is,

$$V_d = V_k + V_e \quad (7)$$

where

$$V_k = \frac{1}{2} \omega_d^2 q_d^2 - \frac{e_o^2}{b}$$

where q_d is a mass-weighted diatomic displacement coordinate, b is the AgX crystal bond distance, and e_o is the charge on the X atom in the crystal. The second term in (7) contains the electrostatic contribution to the vibrational potential energy. V_k then corresponds to the non-electrostatic, or valence, contribution. Expanding V_e in terms of q_d , (7) may be expressed in quadratic terms as

$$V_k = \frac{1}{2} \omega_d^2 q_d^2 - \frac{e_o^2 q_d^2}{\bar{m}_{AgX} b^3} \quad (8)$$

where $\bar{m}_{AgX}$ is the reduced mass of AgX.

Inclusion of the image charge allows the potential energy, V_s , of the real-plus-image system to be written as

$$V_s = 4V_k + \frac{e'^2}{2d} \quad (9)$$

where d is the distance of the X atom to the surface. The valence contribution to the potential energy of diatomic AgX is approximated here to be the same for each of the four AgX bonds of surface adsorbed X; hence, the factor of 4 in (9). Expanding (9) in terms of q_s , the potential energy may be expressed in quadratic terms as

$$V_s = 4 \left[\frac{1}{2} \omega_d^2 - \frac{e_o^2}{\bar{m}_{AgX} b^3} \right] \frac{\bar{m}_{AgX}}{m_X} \cos^2 \theta q_s^2 + \frac{e_s'^2 q_s^2}{2m_X d^3} \quad (10)$$

where $\cos \theta$ is the angle between an AgX bond and the surface normal. The static surface field frequency, ω_o , is then found to be

$$\omega_o^2 = 8 \left[\frac{1}{2} \omega_d^2 - \frac{e_o^2}{\bar{m}_{AgX} b^3} \right] \frac{\bar{m}_{AgX}}{m_X} \cos^2 \theta + \frac{e_s'^2}{m_X d^3} \quad (11)$$

APPLICATION TO Cl/Ag (100)

Crystalline AgCl has the face centered cubic structure, with four molecules per unit cell and a lattice constant of $5.547 \text{ \AA}$.⁴³ Jones and co-workers have reported the Restrahl frequency of single crystal AgCl to be 103 cm^{-1} and the dipole moment derivative to be $51.3 \text{ cm}^{3/2} \text{ sec}^{-1}$.⁴⁴ Substituting these values into (6) gives the diatomic frequency $\omega_d = 77.1 \text{ cm}^{-1}$. The motion of the atoms in the crystal responsible for this frequency is primarily the AgCl stretch along the body diagonal having an equilibrium bond distance, $b = 4.80 \text{ \AA}$. This value of b and the effective charge, $e_o = 0.71 e$, reported by Jones and co-workers⁴⁴ for Cl in crystal AgCl is substituted into (8) to give $V_k = 2304 q_d^2$.

The adsorbed Cl is assumed to form four equivalent bonds with the surface Ag atoms with a bond distance of $2.77 \text{ \AA}$, identical to that found in single crystal AgCl. The angle between an AgCl bond and the surface normal is then 47.3° . Since the distance of the Cl nucleus to the surface is not known, the Cl atom is assumed to be a sphere with a radius equal to its ionic radius, $1.8 \text{ \AA}$,⁴⁵ in contact with the surface. The value of d in (11) is then $1.8 \text{ \AA}$, thus producing a static surface field frequency of 159 cm^{-1} with an effective charge of $e' = 1.0 e$.

Jaswal and Sharma reported $2.85 \text{ \AA}^3$ as the electronic polarizability of Cl^- .⁴⁶ Twice this value is used here for the electronic polarizability of the real-plus-image atom system. Fig. 1 shows the calculated frequency vs. coverage curve for the Cl/Ag(100) system, using (5). At full coverage, the calculated frequency is 241 cm^{-1} .

APPLICATION TO Br/Ag (100)

The lattice constant of the face-centered-cubic AgBr crystal is $5.775 \text{ \AA}$.⁴³ Jones and co-workers⁴⁴ reported the Restrahl frequency as 80.1 cm^{-1} and the effective charge on Br as $e_o = 0.71 e$, which gives a dipole moment derivative of $38.5 \text{ cm}^{3/2} \text{ sec}^{-1}$. The diatomic frequency is then $\omega_d = 59.3 \text{ cm}^{-1}$ using (6). Taking $b = 5.00 \text{ \AA}$, $\theta = 44.8^\circ$, and $e' = 1.0 e$, the static surface field frequency is 100 cm^{-1} . The electronic radius of Br^- and the electronic polarizability are $1.95 \text{ \AA}^3$ ⁴⁵ and $4.09 \text{ \AA}^3$,⁴⁶ respectively. Application of (5) gives the frequency vs. coverage curve shown in Fig. 1. A broad band centered at $170 - 176 \text{ cm}^{-1}$ has been observed by Pemble when KBr is

used as the electrolyte for electrochemical roughening of a silver surface.²⁸ The full coverage frequency is calculated here to be 150 cm^{-1} .

APPLICATION TO F/Ag (100)

AgF crystallizes in the face-centered-cubic lattice with a lattice constant of $4.936 \text{ \AA}$ reported by Bottger and Geddes.⁴⁷ In an infrared study of AgF films, these authors also reported the transverse optic mode frequency as 170 cm^{-1} and, in addition, the effective charge on the F ions was determined to be 0.89 e. The diatomic frequency is then $\omega_d = 130 \text{ cm}^{-1}$. Using $\theta = 55.6^\circ$ and an ionic radius of $1.33 \text{ \AA}$,⁴⁵ the static surface field frequency is 316.8 cm^{-1} . The polarizability of F^- , $\alpha_{\text{F}^-} = 0.858 \text{ \AA}^3$, gives a full coverage frequency of 437 cm^{-1} . Fig. 1 shows the frequency vs. coverage curve predicted by (5). Since AgF is water soluble, electrochemical roughening of Ag in aqueous KF does not yield an adsorbed fluorine layer.

APPLICATION TO I/Ag (100)

AgI has six different crystal structures. The phase diagram shows that there are two structures stable at 25° C and one atmosphere.⁴⁸ These are the hexagonal wurtzite structure, AgI (II), and a cubic zincblende form, AgI (II'). At 25° C and a pressure of $\sim 4 \text{ Kb}$, a face-centered-cubic form, AgI (III), is stable. Jacobs reported a lattice constant of $6.06 \text{ \AA}$ for AgI (III).⁴⁹ Hanson et al. reported

Raman spectra of several phases of AgI, and assigned the LO frequency as $105 \pm 10 \text{ cm}^{-1}$ for AgI (III). Using the Lyddane-Sachs-Teller relationship and the optical constants reported by Bottger and Geddes, the TO frequency is expected to be 88 cm^{-1} . These same authors give $e_o = 0.61 e$ as the effective charge on I. These values give a diatomic frequency of 63.1 cm^{-1} for AgI. Using the ionic radius of I^- , $2.15 \text{ \AA}$, the electronic polarizability $\alpha_{\text{I}^-} = 6.45 \text{ \AA}^3$, $\theta = 42^\circ$, and $e' = 1.0 e$, the static surface field frequency is found from (11) to be 82 cm^{-1} . The full coverage of frequency determined from (5) is 113 cm^{-1} , which agrees favorably with the band at 110 cm^{-1} observed by Pemble when the silver surface is electrochemically roughened in aqueous KI. Fig. 1 gives the frequency vs. coverage curve for this system.

DISCUSSION

There have been several approximations used in the calculated frequency vs. coverage curves. These are:

1. The silver substrate is treated as a perfect electrical conductor with an "effective surface" located below the adsorbed nucleus at a distance equal to the ionic radius of X^- . Schmidt and Gomer increased the distance of the adsorbed atom to the surface in order to account for the dipole moment implied by the decrease in the work function of tungsten observed when potassium is adsorbed on tungsten.³⁷ In this case, the dipole moment arises from the charge on the adsorbed atom and its classical image charge. The change in the work function is then attributed to this layer of dipoles. Gomer and Swanson then assumed that classical image theory is valid if the surface is recessed by an amount equal to

the Fermi-Thomas screening length of the metal.⁵² Newns has shown that this procedure is an approximation for the linearized Fermi-Thomas theory.⁵³ In light of the estimates of parameters used in this work, it does not seem productive to pursue more accurate atom-surface distances.

2. The electronic polarizability, α , of the real-plus-image atom is twice the electronic polarizability of X^- . If this value is decreased, the dipolar shift term in (5) will increase so that the frequency of the adsorbed atoms will be greater at full coverage.

3. The effective charge, e' , on the atom after adsorption is 1.0 e. If the true effective charge is less than the 1.0 e used here, the calculated static surface field frequency, ω_0 , would be smaller. The effective charge is also a factor in the dipolar coupling term in (11), leading to a further decrease in the calculated full coverage frequency with decreasing e' .

4. The static field frequency, ω_0 , depends upon the valence potential energy, V_k , of the Ag-X surface bonds, and V_k has been approximated to be the same as that associated with the stretching mode of diatomic AgX along the body diagonal of single AgX. In addition, V_k is assumed to be the same for each of the Ag-X surface bonds. The validity of this approximation is difficult to ascertain.

5. The reduced mass associated with the vibration of a surface adsorbed atom should be very nearly the mass of the adsorbed atom. Using the mass of the adsorbed atom, as was done here, assumes that the surface silver atoms move in conjunction with

the bulk substrate. This approximation should be more valid for the less massive adatoms, F and Cl, than for Br and I, whose masses are comparable to that of an Ag atom. Both ω_0 and the calculated full coverage frequency would be greater if the reduced mass were less than the mass of the adatom.

There are only three parameters, ω_0 , e' , and α , in (5) which relate the vibrational frequency of the adsorbed atoms to the coverage. It is instructive to examine the effect of errors in each of these parameters on the full coverage frequency calculated from (5). If ω_0 is assigned an error of $\pm 10\%$, then the full coverage frequencies are 437 ± 23 , 241 ± 11 , 150 ± 7 , and $113 \pm 6 \text{ cm}^{-1}$, respectively for $X = \text{F, Cl, Br, I}$. An error of $\pm 10\%$ in e' yields the full coverage frequencies 437 ± 21 , 241 ± 14 , 150 ± 8 , and $113 \pm 5 \text{ cm}^{-1}$, respectively for $X = \text{F, Cl, Br, I}$. A $\pm 10\%$ error in α gives 437 ± 2 , 241 ± 3 , 150 ± 2 , and $113 \pm 2 \text{ cm}^{-1}$, respectively for $X = \text{F, Cl, Br, I}$.

The calculated frequencies of 241 and 113 cm^{-1} , respectively, for Cl/Ag(100) and I/Ag(100) at full coverage, are very close to the frequencies of 240 cm^{-1} found in Raman studies where KCl was used as an electrolyte²⁷ and the frequency of 110 cm^{-1} attributed to I/Ag .²⁸ The calculated full coverage frequency of Br/Ag(100) is 20 cm^{-1} lower than the observed frequency, 170 cm^{-1} , of adsorbed Br .²⁸ AgF is soluble so that an experimental frequency is unavailable. While the frequencies determined here should be viewed as approximate, they do indicate that the assignment of the observed low frequency modes to adsorbed halogens is completely reasonable. Raman spectra of CO and CN^- adsorbed on Ag manifest strong lines at 150 and 226 cm^{-1} , respectively,^{54,6} which are probably also due to the same kinds of external modes we have

modeled in the present investigation. Taken together with the results of the surface characterization studies,³⁰ the assignment of the observed low frequencies to such external modes is quite definite.

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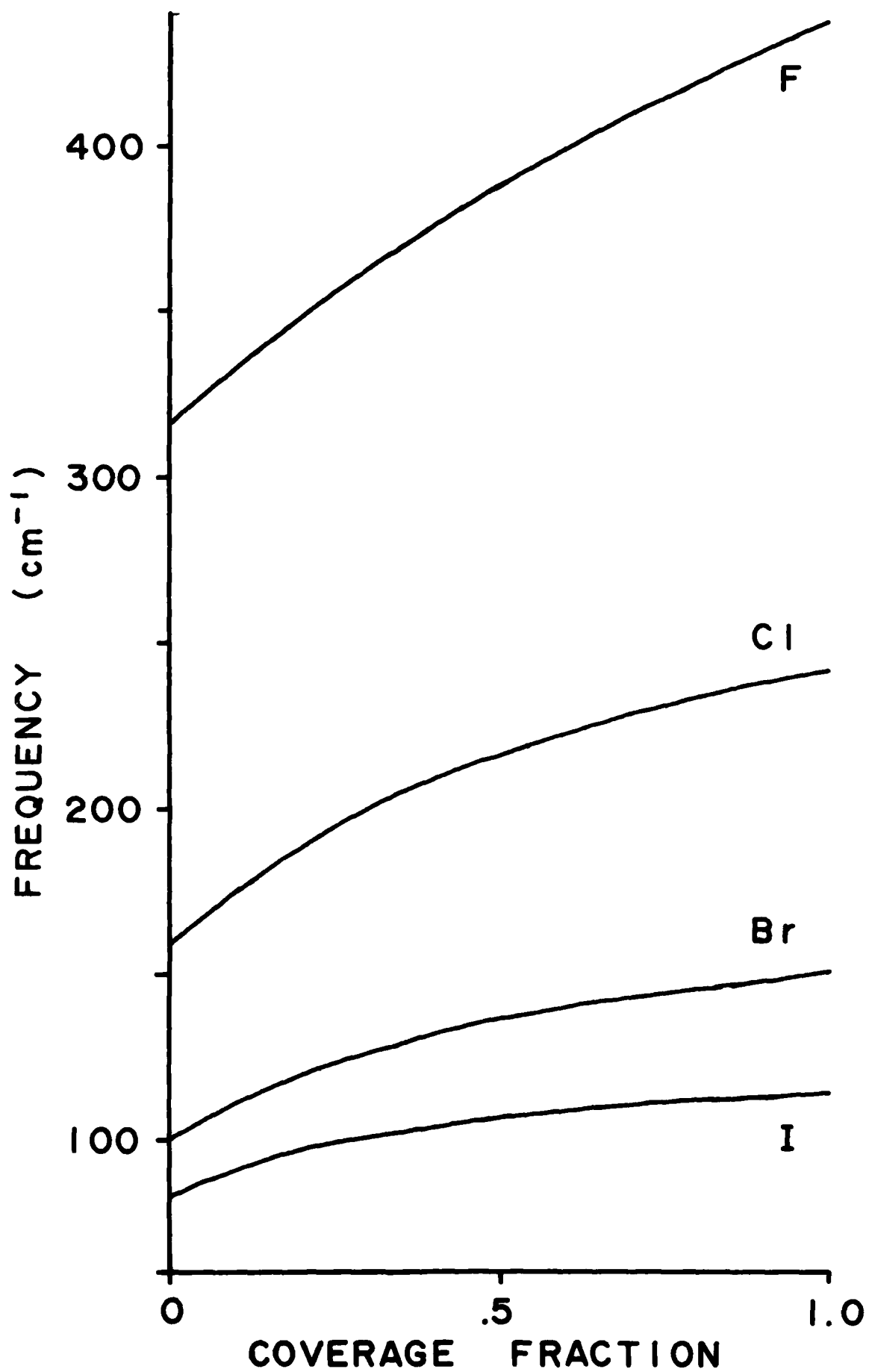
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Figure Caption

Figure 1. Calculated frequency vs. coverage curves for X/Ag(100).

X = F, Cl, Br, I.



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