

Title	Normal mode analysis of surface adsorbed and coordinated pyridine molecule
Author(s)	Mizutani, G.; Ushioda, S.
Citation	Journal of Chemical Physics, 91(1): 598-602
Issue Date	1989-07-01
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/4544
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Description	

Normal mode analysis of surface adsorbed and coordinated pyridine molecule

G. Mizutani and S. Ushioda

Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Sendai 980, Japan

(Received 8 August 1988; accepted 1 March 1989)

We have carried out a normal mode analysis of the molecular vibrations of pyridine adsorbed on silver surfaces or coordinated to various molecules and ions. There are two types of bonding that result in distinct shift patterns of the normal mode frequencies upon adsorption or coordination. "Metal ion-type bonding" is characterized by a strong pyridine-substrate bond which results in large frequency shifts, while "halogen-type bonding" causes comparatively smaller shifts due to weaker bonding. Adsorption on silver surfaces corresponds to weak halogen-type bonding, and the major cause of the observed frequency shift is the electron transfer (back donation) into the aromatic ring upon adsorption.

I. INTRODUCTION

Vibrational spectroscopy is one of the important methods of investigating the site and orientation of surface adsorbed molecules as well as the dynamics of adsorbate-substrate interactions. To obtain the vibrational spectra of adsorbates, one may use electron energy loss spectroscopy (EELS), infrared absorption and reflection spectroscopy (IRARS), or Raman spectroscopy (RS).¹ The relevant information one obtains by these methods are the frequency, linewidth, and selection rules of various molecular vibration modes. Changes in these quantities upon adsorption reflect the structure of the adsorption site and the strengths of bonding, and in extreme cases some of the vibrational modes may even disappear due to dissociation.²

In this paper we focus on the frequency shift of normal modes of the pyridine molecule upon adsorption on metal surfaces. The vibrational modes of adsorbed pyridine have been investigated extensively, particularly in connection with the surface enhanced Raman scattering (SERS) phenomena.³ In its Raman spectra the totally symmetric ring breathing mode (ν_1) at 992 cm^{-1} (for free molecules) shifts about 12 to 1004 cm^{-1} while the trigonal breathing mode (ν_{12}) at 1032 cm^{-1} shows no frequency shift.⁴ This is an interesting observation that deserves close analysis, but to our knowledge there has been no careful study of the frequency shift of the normal modes of pyridine upon adsorption. The observed difference in the behavior of the two modes must arise from the different motional patterns and the change in the spring constants of specific bonds upon adsorption. The change in spring constants is in turn caused by redistribution of bond charges in the molecule and the consequent change in the bond order. Thus from a normal mode analysis we may expect to gain information not only on the change in the spring constants but also on the electron density distribution of adsorbed molecules.

The main purpose of this paper is to explain the different behavior of the ν_1 and ν_{12} modes of pyridine in particular, and more generally to understand the pattern of frequency shifts of normal modes when a molecule is adsorbed. Coordination of molecules to ions is similar to adsorption, and it affects the normal mode frequencies by causing redistribu-

tion of electrons among different bonds. Thus we will consider coordinated pyridine along with the adsorbed species.

This paper is organized in the following fashion. In Sec. II we review some of the known facts about the frequency shift of the normal modes of pyridine upon adsorption and coordination, and in Sec. III we discuss fitting of the force constants in the normal mode analysis. Section IV contains the results of the analysis and the discussion of the results as well as their implications on the bonding mechanism.

II. REVIEW OF EXPERIMENTAL DATA

In Fig. 1 we reproduce the Raman spectra of adsorbed pyridine on a well-defined (100) surface of Ag in UHV.⁴ The ν_1 mode, which is seen at 992 cm^{-1} for gaseous pyridine, shifts its frequency to 1004 cm^{-1} for about a monolayer coverage (10 L), while the ν_{12} mode, which is seen at 1032 cm^{-1} for gaseous pyridine, remains at the original frequency for all coverages. These are the spectra that originally drew our attention to this problem. In Table I we summarize the frequency shifts of Raman and IR lines of molecular vibrations of adsorbed and coordinated pyridine. Only the A_1 modes are listed, because they are the ones that are strongly affected by coordination or adsorption. The table contains data for pyridine adsorbed on Ag surfaces, pyridine-metal compound complexes, pyridine-halogen complexes, and pyridine-water complex. For the Ag-adsorbed species we list two sets of data for rough surfaces by Van Duyne⁵ and by Yamada,⁶ and two sets of data for smooth surfaces by Udagawa *et al.*⁴ and by Campion *et al.*⁷ The data for the coordinated species with metal compounds are taken from the work by Goldstein *et al.*^{8,9} and Akyüz *et al.*¹⁰ The data by Goldstein *et al.* are for $2(\text{pyridine})\text{CuCl}_2$ and those by Akyüz *et al.* are for copper tetranickelate complexes. The data for halogen molecules are from the work by Haque and Wood.^{8,11} Those for water is from Stidham and DiLella.^{8,12}

As we have already noted, on a smooth silver surface the frequency of the ν_{12} mode does not shift while the ν_1 mode shifts its frequency by about 12 cm^{-1} . In contrast both modes shift their frequencies on a rough silver surface. Thus it appears that pyridine molecules adsorbed on rough and smooth silver surfaces behave differently. When we look at

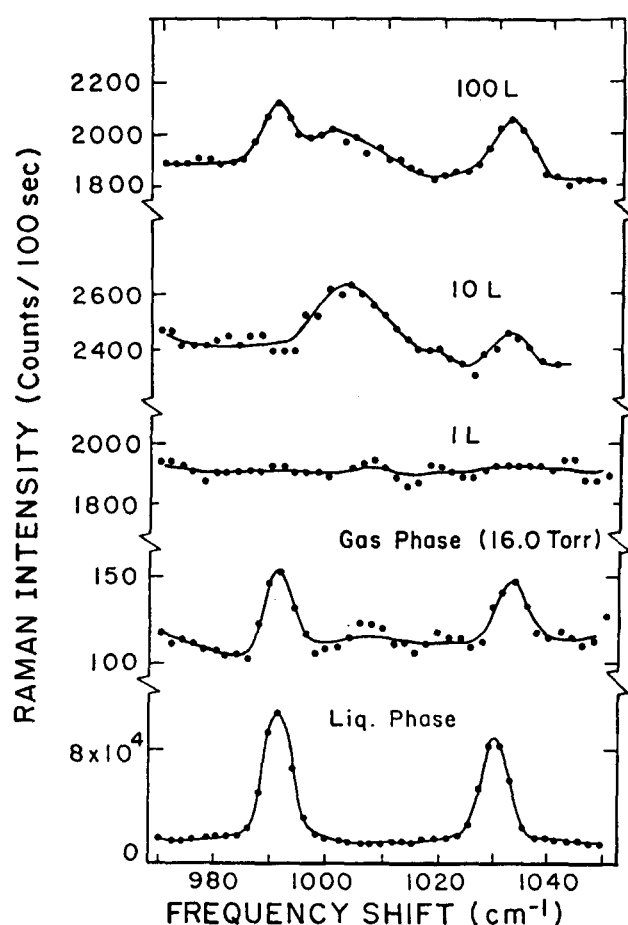


FIG. 1. Raman spectra of pyridine on a smooth Ag(100) surface for three exposures, and in the gaseous and liquid phases. (After Ref. 4.)

coordinated pyridine, we can notice a similar but more distinct difference between coordination to metal ions on one hand and to halogen and water molecules on the other; i.e., the ν_{12} mode shows a larger shift for metal ion coordination

than for coordination to halogen and water molecules. Also other modes including the low frequency modes show a similar trend for the two groups of coordinated species. There appears to be a clear difference between the two types of bonding. Thus we will distinguish them by calling them metal ion-type bonding and halogen-type bonding. From the frequency shift pattern we can classify adsorption to both rough and smooth silver surfaces as halogen-type bonding.

III. NORMAL MODE ANALYSIS

Although there are several previous calculations of the vibrational normal modes of pyridine, including a recent *a priori* calculation with anharmonic potentials,¹³ we will follow, as did Long *et al.*,¹⁴ the conventional method by Wilson with only harmonic potentials.¹⁵ Frequency shift due to force constant change is sensitive not to the model of the force fields, but rather to the symmetry or the displacement pattern of the mode in question. Thus a harmonic model is sufficient for the present purpose.

Figure 2(a) illustrates and defines the in-plane internal coordinates of the free pyridine molecule. We define the force constants corresponding to each internal coordinate. For stretching and bending forces we use the symbol K and H , respectively, with the corresponding internal coordinate designation added as a subscript as in K_s and H_b . Superscripts o , m , and p will be used to specify the location of the force constants at ortho, meta, and para positions in the aromatic ring. The off-diagonal force constants were not varied in our calculation, and we used the values given by Long *et al.*

To check our computer program we first compared the calculated results with those of Long *et al.*¹⁴ As can be seen in the "test program" column in Table II, we can reproduce the results of Long *et al.*¹⁴ quite well, although we had to make the C-H stretching force constant (K_s) slightly smaller than that used by Long *et al.* The mode patterns are also identical to their results. Thus, we convinced ourselves that the program is working properly.

TABLE I. The frequency shifts of the A_1 and the low frequency modes observed for adsorbed and coordinated pyridine. The frequencies in parentheses are for vibrations of bonds between two halogen atoms. The initials in "Adsorbed species on Ag" columns are R. V. = R. P. Van Duyne, H. Y. = H. Yamada, M. U. = M. Udagawa, and A. C. = A. Campion. The data by Udagawa *et al.* are for the silver (100) surface, those by Campion and Mullins with underlines are for the silver (540) surface and the rest are for the silver (111) surface.

Freq. (cm ⁻¹)	Wilson no.	Adsorbed species on Ag				Coordinated species							
		Rough surf.		Smooth surf.						In benzene			
		R. V.	H. Y.	M. U.	A. C.	Cu ²⁺	Cu ²⁺	Ni ²⁺	Ni ²⁺	I ₂	IBr	ICl	H ₂ O
3057	2	10	13				18		8				12
1582	8a	12	14			21,14	27	21	23				11
1483	19a												3.5
1217	9a	-2	-2				7		8				0.5
1068	18a						4		0	-1	-1	-1	0.5
1032	12	4	4	0	-2	10	14	10	8	-2	-1	-2	3
992	1	16	18	12	0,11	24,17	30	25,21	23	14	18	19	10
604	6a	19				41	37	28		19	13	26	12
Low freq. mode			230			268				103	134	140	
Reference		5	6	4	7	8,9	10	8,9	10	(172)	(206)	(292)	8,12

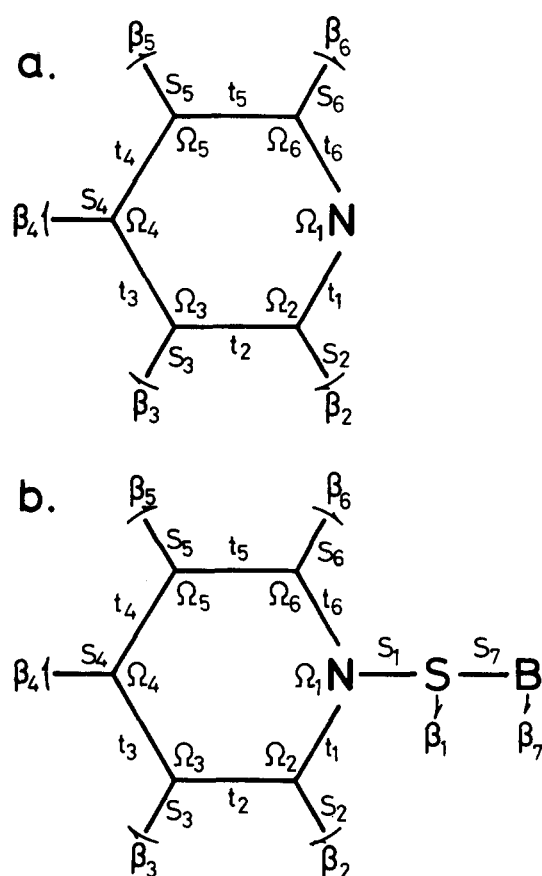


FIG. 2. The model and the in-plane normal coordinates of (a) free pyridine and (b) coordinated or adsorbed pyridine.

TABLE II. Free pyridine vibration frequencies by Long *et al.* and from this work. The third column shows the result of the test calculation for a check of the program [for configuration of Fig. 2(a)]. The fourth column shows the present results in which ν_1 , ν_{12} , and ν_{18a} modes are fitted to the experimental data, using the configuration of Fig. 2(b) with $K_s^s = 0$. Only the varied force constants are listed and those not listed in this table are the same as those by Long and Thomas (Ref. 11). For definitions of the force constants see the text.

Mode no.	Long and Thomas	Test program	This work
20a	3075 cm ⁻¹	3075.0 cm ⁻¹	3085.2 cm ⁻¹
13	3069	3069.2	3080.2
2	3053	3053.2	3063.6
8a	1597	1597.6	1660.7
19a	1486	1488.6	1608.8
9a	1178	1181.6	1262.4
18a	1030	1033.7	1067.8
12	1007	1008.6	1032.0
1	984	985.1	991.9
6a	605	606.0	630.0
Bond length (Å)			
C-H	1.05	1.05	1.08
C-C, C-N	1.400	1.400	1.395
Force const. (× 10 ⁵ dyn/cm)			
$K_s^{a,m,p}$	5.093	5.059	5.059
K_t^a	5.553	5.553	6.133
$K_t^{m,p}$	5.553	5.553	5.451
$H_\beta^{a,m}$	0.864	0.864	1.049
H_Ω^N	1.031	1.031	1.219

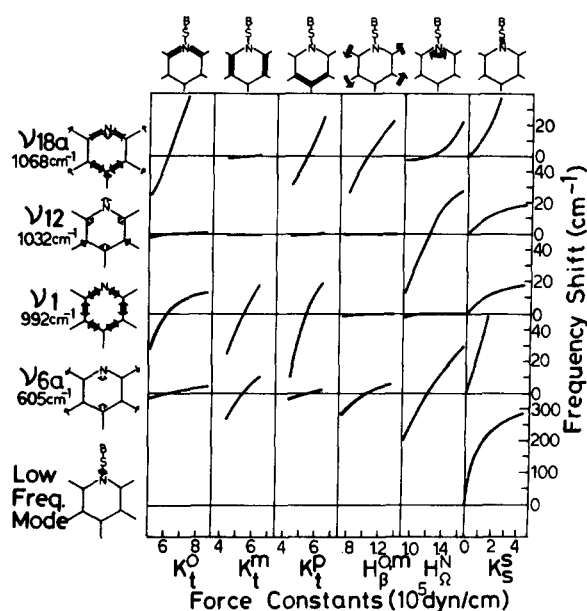


FIG. 3. The shifts of normal mode frequencies as functions of the force constants.

Figure 2(b) shows our model of the adsorbed or coordinated pyridine molecule. S is an atom of the substrate directly connected to pyridine, and B represents other atoms of the bulk or molecule. They are attached along a straight line to the nitrogen atom. We assume this model bonding geometry, because the pyridine molecule is most likely bonded to other molecules through this nitrogen atom by donating the lone pair electrons.^{8,16} We need to introduce four new internal in-plane coordinates corresponding to the new bonds; i.e., the stretching of N-S and S-B bonds (S_1 and S_7) and the bending of C-N-S and N-S-B bonds (β_1 and β_7) illustrated in Fig. 2(b).

First, we set all the force constants associated with the new bonds equal to zero and calculate the unshifted normal mode frequencies for the free molecule. The results are listed in the "this work" column of Table II. In this calculation the force constants are adjusted so that the ν_1 , ν_{12} , and ν_{18a} modes appear at 992, 1032, and 1068 cm⁻¹, respectively. $K_t^a:K_t^m:K_t^p$ ratio was taken to be 1:0.9:0.9 following Pongor *et al.*¹³ Then with the above frequencies as unshifted values in the "this work" column in Table II, we calculate the shift of the normal mode frequencies of the A_1 modes, when one of the force constants within the pyridine molecule is changed or the force constants of the N-S and S-B are introduced. There is not enough information about the bending force constants of C-N-S and N-S-B bonds, H_β^a and H_β^m ; thus we set them equal to zero throughout the calculation.

Figure 3 represents the frequency shifts of the A_1 modes against the force constant changes of different bonds in bonded pyridine molecules. On the horizontal axis we plot the values of different force constants, K_t^a , K_t^m , K_t^p , $H_\beta^{a,m}$, H_Ω^N , and K_s^s , and the vertical axis represents the corresponding frequencies of different modes indicated on the left-hand margin. The top figures illustrate the location of the respective force constants. We chose to vary these force constants,

because they are the ones most sensitively affected by coordination or adsorption. The three force constants, K_i^o , K_i^m , and K_i^p for the C–C bonds at the ortho, meta, and para positions from the nitrogen atom are sensitive to electron transfer within the ring. Similarly, the in-plane bending force constants of the C–C–H bonds, $H_\beta^o = H_\beta^m$, are sensitive to electron transfer into or out of the C–H bonds. The bending force constant of the C–N–C angle, H_α^N , is expected to be sensitive to adsorption or coordination at the N atom site. The N–S stretching force constant K_s^s representing the pyridine–substrate bonding strength was also varied in the present calculation, while the S–B force constant K_s^b was kept constant at 7×10^7 dyn/cm. The masses for S and B were set equal to the values for Cu and Cl₂, respectively, in calculating the effect of changes in K_s^s .

From Fig. 3 the effect of the force constant change is very clear. The ν_1 mode shifts when K_i^o , K_i^m , K_i^p , and K_s^s are changed, but it does not shift when H_β^o or H_α^N is changed. This is because the ν_1 mode is a symmetric C–C stretching mode. The ν_{12} mode shifts when the H_α^N and K_s^s are changed, but it does not shift when K_i^o , K_i^m , K_i^p , and H_β^o are changed. This is because the ν_{12} mode is a C–C–C, C–N–C, and C–C–N bending mode. The frequencies of ν_{18a} and ν_{6a} modes shift when the force constants are changed except in one case; i.e., the ν_{18a} mode is unaffected when K_i^m is changed. In addition the two low frequency modes emerge corresponding to the N–S and S–B stretching vibrations when these bonds are taken into account; we only show the N–S stretching mode in Fig. 3.

Table III summarizes the calculated values of the frequency shifts and the best fitting force constants for adsorption on rough and smooth Ag surfaces, and for coordination to Cu²⁺ ion, I₂, H₂O. In the table m_s and m_b are the masses of S and B atoms, respectively. ΔK_i^m is the increase in the force constant K_i^m and ΔK_s^{ave} is the increase in the stretching force constants of the five C–H bonds.

IV. DISCUSSION

As we have indicated at the beginning of this paper, the present normal mode analysis was initially motivated by the desire to understand the different shifting behaviors of the ν_1 mode and the ν_{12} mode of pyridine upon adsorption on Ag surfaces. We have found in the above analysis that the increase in the meta C–C bond strength ΔK_i^m upon coordination or adsorption is mainly responsible for these frequency shifts. This stretching force constant changes by about the same amount for both metal ion-type bonding and halogen-type bonding. Its change is due to charge transfer from the coordinated molecule or substrate to pyridine.

This effect can be understood in analogy with the electron transfer upon UV excitation of aniline.¹⁷ The aromatic ring of aniline contains excess electrons in the ground state like that of pyridine, and when aniline is excited by UV light, the excited electron is transferred to the bond between the aromatic ring and the amino radical. To counterbalance the charge, electron is supplied to the meta C–C bond of the aromatic ring. Thus the order of this bond and consequently

the force constant increases. This transformation into quinoid is certainly occurring in both adsorbed and coordinated pyridine, and this interpretation is consistent with the NMR result on the pyridine halogen complex,⁸ EELS and SERS results on adsorbed pyridine on Ag surfaces, and also a recent theoretical work.¹⁸ For adsorbed pyridine the second electron transfer has been called back donation.¹⁹

The present results shed some light on the mechanisms involved in SERS. Ueba *et al.*¹⁹ and Yamada⁶ reported that SERS of pyridine on roughened silver surfaces is mainly caused by the usual resonant Raman enhancement due to a charge transfer band created in the visible range by back donation. However, the present work suggests that back donation is not a sufficient condition for SERS to occur. According to the present analysis of the force constant K_i^m , back donation occurs even in the case of pyridine on a well-defined (540) surface of Ag where surface enhancement is not observed as reported by Campion *et al.*⁷ In order to understand this question of electron transfer theoretically, one needs to calculate the change in electronic distribution upon adsorption or coordination. We plan to carry out such calculations and see if we can reproduce the above changes in spring constants.

From the present normal mode analysis, we see that the difference between the metal ion-type bonding and halogen-type bonding originates from the difference in the force constant K_s^s between the pyridine molecule and the substrate. K_s^s is large for the metal ion-type bonding and small for the halogen-type bonding. Larger K_s^s results not only in higher pyridine–substrate stretching frequency naturally, but also in higher frequencies for all A_1 modes. A similar point for pyridine coordinated to metal compounds has already been discussed by Akyüz *et al.*,¹⁰ and the result is consistent with our analysis. This difference in K_s^s is understandable, when we consider the electrostatic properties of the molecule (ion or substrate) to which pyridine is adsorbed or coordinated. Cu²⁺ ion is electrically positive and attracts electron donor molecules. On the other hand, halogen, water, and metal substrates, which are electrostatically neutral, bond not so strongly to pyridine as does the Cu²⁺ ion.

The vibrational frequency shifts of the ν_1 and ν_{12} modes also depend on whether pyridine is adsorbed on a rough (SERS active) or smooth Ag surface (see Table I). This difference results from the difference in the force constant K_s^s for these two cases (see Table III); K_s^s is 0.57 for the rough surface and essentially zero for the smooth surface. The difference in K_s^s in turn can be attributed to the fact that a roughened surface is chemically active; a rough surface contains many high index facets which attract electrons and bond strongly, while a smooth surface of a low index face is less chemically active with small bond strength.

Now let us consider the vibrational frequency of the pyridine–substrate stretching mode for the adsorbed species on rough and smooth surfaces. For the rough surface its frequency is 230 cm^{−1} according to the Raman data by Yamada.⁶ For the smooth surface, Raman data are not available, but there are EELS data by Demuth *et al.*¹⁶ which show this mode at about 200 cm^{−1}. The calculated frequencies are

TABLE III. Calculated normal mode frequency shifts and the frequencies of the N-S and S-B bonds according to the model in Fig. 2(b). The frequencies appearing in the first column are the experimental data for free pyridine. Only the varied force constants, the mass, and the force constants due to new entities are listed. For definitions of force constants see the text. The force constants with underlines are the ones important for the present analysis.

Freq. (cm ⁻¹)	Wilson no.	Adsorbed species on Ag		Coordinated species		
		Rough surf.	Smooth surf.	Cu ²⁺	I ₂	H ₂ O
3057	2	13.0	...	18.0	...	12.0
1582	8a	39.2	34.4	36.9	28.8	18.2
1483	19a	2.4	1.2	7.3	1.9	1.5
1217	9a	8.5	7.5	11.3	6.5	4.3
1068	18a	6.0	0.7	74.7	4.8	3.9
1032	12	4.1	0.2	16.9	3.4	3.0
992	1	18.0	12.0	21.9	14.2	10.1
604	6a	20.9	7.0	93.5	16.4	13.6
N-S (S-B mode)		106.4	3.6	268.2	103.0	
<i>m_s</i> (amu)		108	108	63.5	127	1
<i>m_B</i> (amu)		10 ⁷	10 ⁷	71	127	17
<i>K_s^b</i>		20	20	7	0.91	7
<i>K_s^s</i>		0.57	0.00	3.55	0.48	0.43
ΔK_t^m		0.68	0.63	0.35	0.50	0.31
ΔK_s^{ave} ($\times 10^5$ dyn/ cm)		0.042	...	0.059	...	0.040

106.4 and 3.6 cm⁻¹ for the rough and smooth surfaces, respectively; these results are in clear disagreement with experiments. In order to explain this discrepancy between experiment and theory, we can consider additional lateral interactions between adsorbed pyridine molecules. Demuth *et al.*¹⁶ reported that there may be an attractive π_3 -nitrogen-lone-pair interaction. Through this lateral interaction the molecule is tilted from its vertical adsorption position.¹⁶ This out-of-plane force may increase the pyridine-metal stretching vibration frequency, but may have little effect on the intramolecular in-plane modes, in particular the ν_1 and ν_{12} modes. And thus the frequency of the pyridine-substrate stretching mode may be raised without increasing the in-plane intramolecular mode frequencies. If this is the case, we are underestimating the size of effective K_s^s , because we choose its value to produce proper frequencies for the intramolecular modes by combining with a well-chosen value of K_t^m .

V. CONCLUSION

We have carried out a normal mode analysis of the adsorbed and coordinated pyridine molecules. The normal mode frequencies shift upon adsorption or coordination according to two distinct patterns, which we call the metal ion-type bonding and the halogen-type bonding. For the former type, the frequency shifts are mainly caused by the introduction of a strong coordination bond between pyridine and metal ions. On the other hand, for the latter type, the frequency shifts are mainly due to the change in the force constant for meta C-C stretch in the aromatic ring. This change in the meta C-C bond strength involves electronic charge transfer just like that found in aniline excited into a quinoid-like structure by UV light. The frequency shift pattern for pyridine adsorbed on Ag surfaces corresponds to the halogen-type bonding. The difference between the rough and smooth surfaces lies in the bonding strength between the molecule and substrate, and not in the degree of back donation charge transfer.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. The authors would like to thank the late Professor H. Yamada of Kwansei Gakuin University and Dr. Y. Sasaki of Tohoku University for valuable discussions.

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