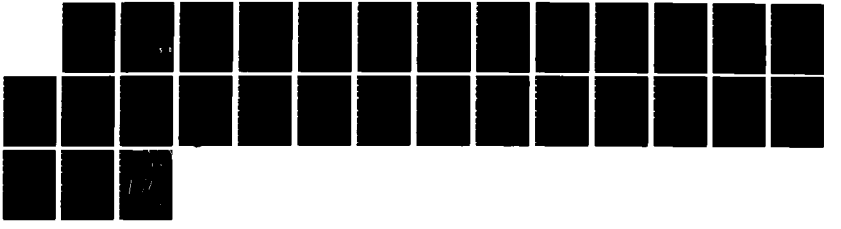
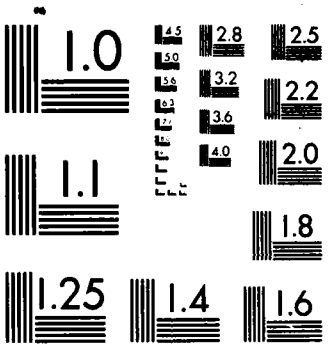
AD-A166 239 CLUSTER-MODEL CALCULATION OF RAMAN INTENSITY FOR VIBRATION OF CO ADSORBED ON COPPER(U) CALIFORNIA UNIV SANTA BARBARA QUANTUM INST J WU ET AL. FEB 86 TR-2 1/1

UNCLASSIFIED N00014-81-K-0598 F/G 7/4 NL





SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 2	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): CLUSTER-MODEL CALCUATION OF RAMAN INTENSITY FOR VIBRATION OF CO ADSORBED ON COPPER	5. TYPE OF REPORT & PERIOD COVERED: Annual Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Ji-An Wu, Horia Metiu and Bernard Kirtman	8. CONTRACT OR GRANT NUMBER(s): N00014-81-K-0598
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of California, Quantum Institute, Santa Barbara, CA 93106	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 056-766/4-21-81 (472)
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, Code: 612A: DKB, Arlington, VA 22217	12. REPORT DATE: February 1986
	13. NUMBER OF PAGES: 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): Office of Naval Research Detachment Pasadena, 1030 East Green Street, Pasadena, CA 91105	15. SECURITY CLASS. (of this report): unclassified/unlimited
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

This document has been approved for public release and sale; its distribution is unlimited.

18. SUPPLEMENTARY NOTES

Accepted: Surface Science

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

spectroscopy, chemical, electromagnetic

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The discovery of surface enhanced Raman spectroscopy has inspired a large body of work which has been summarized in several recent review articles. While much has been learned about various enhancement sources there is still disagreement regarding the proportion in which different factors contribute to the observed Raman cross section. Even though it is difficult to include all the opinions in a broad classification, it is fair to say that the main debate is centered around the relative importance of "chemical" versus "electromagnetic" (EM) enhancement factors.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF 014-6601

unclassified/unlimited
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0598

Task No. NR 056-766/4-21-81 (472)

Technical Report No. 2

CLUSTER-MODEL CALCULATION OF RAMAN INTENSITY FOR VIBRATION OF CO ADSORBED ON COPPER

by

Ji-An Wu, Bernard Kirtman and Horia Metiu

Surface Sci., accepted (1985)

University of California
Department of Chemistry
Santa Barbara, CA 93106

CLUSTER-MODEL CALCULATION OF RAMAN INTENSITY FOR VIBRATION OF CO ADSORBED ON COPPER

Ji-An Wu*, Horia Metiu and Bernard Kirtman

Department of Chemistry
University of California
Santa Barbara, California 93106

*Permanent Address:
Institute of Semiconductors
Chinese Academy of Sciences
Beijing (Pekin) China

I. INTRODUCTION

The discovery of surface enhanced Raman spectroscopy[1] has inspired a large body of work which has been summarized in several recent review articles.[2-8] While much has been learned about various enhancement sources there is still disagreement regarding the proportion in which different factors contribute to the observed Raman cross section. Even though it is difficult to include all the opinions in a broad classification, it is fair to say that the main debate is centered around the relative importance of "chemical" versus "electromagnetic" (EM) enhancement factors.

The two kinds of effects can be defined semi-quantitatively by examining various terms appearing in the expression for the intensity of Raman scattering by a molecule located near a solid surface.[9] A source of light of frequency ω producing an electric field $E_o(\vec{r},\omega)$ in vacuum, will generate a different field $E_1(\vec{r};\omega) = \overleftrightarrow{R}(\vec{r};\omega)\cdot\vec{E}_o(\vec{r};\omega)$, if a solid surface is present. When a molecule is placed at $\vec{r}$ it will interact with $\vec{E}_1$ and acquire a Raman dipole[4,5] given by

$$\vec{\mu} = Q \frac{\partial \overleftrightarrow{\alpha}}{\partial Q} \cdot \overleftrightarrow{R}(\vec{r};\omega)\cdot\vec{E}_o(\vec{r};\omega) \qquad (I.1)$$

Here Q is the amplitude of the normal mode of interest and $\overleftrightarrow{\alpha}$ is the polarizability tensor of the molecule. The electric field $\vec{E}$ of the radiation emitted by this dipole can be written as

$$\vec{E}(\vec{r}';\omega-\omega_v) = \overleftrightarrow{G}\cdot\vec{\mu} = Q\overleftrightarrow{G}\cdot\frac{\partial \overleftrightarrow{\alpha}}{\partial Q}\cdot\overleftrightarrow{R}(\vec{r};\omega)\cdot\vec{E}_o(\vec{r};\omega) \qquad (I.2)$$

where $\vec{r}'$ is the position of the detector and $\overleftrightarrow{G}$ is the electromagnetic Green's function[4-5] for a dipole oscillating near a surface. The Raman intensity, I, corresponding to Eq. (2) is proportional to $|\vec{E}(\vec{r}';\omega-\omega_v)|^2$.

Equation (2) permits a simple classification of the total enhancement into terms involving different mechanisms: the enhancement of $\overleftrightarrow{G}$ and $\overleftrightarrow{R}$ is usually electromagnetic, while that of

$\partial\overleftrightarrow{\alpha}/\partial Q$ is "chemical". Large enhancements of $\overleftrightarrow{G}$ and $\overleftrightarrow{R}$ can be achieved[10] by using surface shapes and materials which permit the incident light and the emitting dipole to excite the electromagnetic resonances (e.g. plasmons) of the solid. Moderate off-resonance enhancements of $\overleftrightarrow{G}$ and $\overleftrightarrow{R}$ can also be obtained by using high surface curvatures[10c], or the mutual polarization of two solids located next to each other.[10e] Many examples of this kind of enhancement are described in refs. 2,4,6-8 and especially in ref. 5. An additional electromagnetic effect is caused by the coupling of the emitting dipole to its image field, which shortens the lifetime of the emitting state[6,11] and depresses the intensity of the resonant Raman signal.[12]

The magnitude of the electromagnetic effects is estimated by solving the "phenomenological" Maxwell equations under a number of assumptions. Unfortunately these assumptions are inaccurate[13,14] and their use leads to errors whose magnitude cannot be adequately estimated. This, together with the fact that in working with rough surfaces it is extremely difficult to control surface structure (which strongly influences the EM effects), makes it difficult to assess how much of the observed enhancement is due to electromagnetic effects and how much to chemical ones. Nevertheless a broad survey[5] of various spectroscopic probes on a great variety of surfaces shows that the electromagnetic theory is in qualitative agreement with many experimental observations. Furthermore, some of the most careful studies in the SERS literature, carried out by Murray and Bodoff[15], Mullins and Campion[16] seem to indicate that the chemical effects are small.

However not all molecules are alike, and a large number of studies have pointed out behavior at variance with the qualitative predictions of the EM theory[17]. The extent to which these studies are conclusive is still debated, and a large number of theoretical models[17-28] have been used to suggest possible sources of chemical enhancement, and to estimate its magnitude.

The majority of these proposals are summarized by Fig. 1 which schematically represents the Raman process for an adsorbed diatomic molecule. The incident photon of frequency ω excites an electron from the ground state $|0\rangle$ into the state $|i\rangle$; this electron moves through the solid, excites the "local phonon" (e.g. the diatomic's vibrational stretching mode) and is scattered into the state $|j\rangle$; subsequently the electron decays into the ground state and emits a Raman photon. The total emission is obtained by adding up all such processes occurring at all the points A, B and C in the system, for all the electrons that can participate without violating the conservation laws or the Pauli principle.

To say that an accurate calculation of this process is extremely difficult is an understatement.[29,30] Thus, the existing models, including the one to be presented here, have had to resort to severe approximations. This makes them conceptually useful, but limits their predictive power and reliability.

The diagram in Fig. 1 allows us to classify these models into two groups. One group relies on the fact that the electron lines (i.e., the one-electron Green's functions) have energy denominators which lead to resonant Raman signals when the incident laser or the emitted light match an electronic transition in the molecule-solid system. Since the excited electron must interact with the local phonon a substantial enhancement of the Raman signal can come only from transitions involving electrons (hence orbitals) which are located near the molecule. Because of this constraint the models involve either a new charge transfer (CT) state created by chemisorption,[19,20] or the excitation of "metal electrons" into empty "molecular" orbitals.[21,23,27] The detection of a CT state in the very carefully controlled EELS experiments of Avouris and Demuth[37] gives plausibility to the idea that a resonant enhancement of the signal can play a role in SERS. Unfortunately, no detailed Raman measurement has been made on that system at a frequency that would excite the CT state. It is conceivable that a small

transition dipole derivative and/or the broadening of the state by energy transfer to the surface[12] may substantially depress the resonant Raman signal and result in a small enhancement.

The other chemical enhancement mechanism invokes the fact that the polarizability of the metal-molecule system might be much larger than that of the molecule alone, since (qualitatively speaking) some of the metal's electrons which can scatter from the local mode have much higher polarizability than the electrons bound to the molecule. This idea is at the basis of Otto's proposal[13,17] for the role of atoms in SERS. A version of it, the modulated reflectance model, was discussed by Maniv and Metiu.[18]

In the present paper we examine theoretically the idea that metal atoms on a solid surface might increase the Raman polarizability of the molecules adsorbed on them. To estimate the order of magnitude of this increase we use ab-initio Hartree-Fock calculations for a CO molecule adsorbed on Cu. This method permits us to do a better job in computing the detailed local binding properties than the Newns - Anderson Hamiltonian or the jellium RPA calculations that have been used in prior work. Unfortunately, the large number of electrons severely limits our ability to deal with the effects of the extended solid. The following strategy was, therefore, employed. Noting that atomic hydrogen like Cu contains a single S electron outside of a core we calculated the properties (primarily bonding, but also the core-hole states of H_nCuCO clusters and compared them with the results of Cu_5CO ab-initio Hartree-Fock calculations[31], as well as with the experimental results for CO adsorbed on Cu surfaces. It turns out that the linear H-Cu-CO complex reproduces the properties mentioned above reasonably well. Therefore one hopes that the polarizability derivative of the complex with respect to the C-O stretch will also agree reasonably well with experiments for CO bonded to a Cu atom adsorbed on a Cu surface (i.e. the adatom model). We do not expect, of course, to obtain the correct electromagnetic properties of the surface but this is not

a handicap since we are only interested in the local modification of the polarizability derivative caused by the chemical bonding. Thus, this calculation is especially relevant to Otto's atom model.[3,17]

The main result is that $\partial\alpha^{zz}/\partial R_{CO}$ where z is along the CuCO axis and R_{CO} is the C-O bond distance, is increased by the binding of CO to Cu by a factor of ~2. This gives a Raman intensity enhancement of ~4. Careful experiments[16] give for this quantity an order of magnitude of ~6, or of less than 10. The experiments were not carried on the CO/Cu system and we mention them here only to indicate that we are in general agreement with the order of magnitude obtained from data taken and analyzed with great care.

It should be observed that without adding hydrogen the CuCO complex, by itself, gives results which are qualitatively different from those of CO chemisorbed in an on-top site. The hydrogren atom attracts electrons from the Cu core and this allows the Cu atom to bind more strongly to CO as it does in the real system. By carefully choosing the cluster it may be possible to accomplish a similar simplification for studying chemisorption properties of other molecules and/or other sites on a Cu surface.

II. CLUSTER MODEL

As noted in the Introduction Bagus and Seel[31] (BS) have previously used a cluster model to calculate the adsorption properties of CO on Cu(100). They considered the case of on-top binding, which is appropriate for CO in a C(2x2) overlayer structure,[32,33] and placed the Cu atom which binds to CO at the apex of a Cu_5 square pyramid. The four Cu atoms in the base of the pyramid represent the nearest neighbors in the second layer of the (100) copper surface.

Since the electronic configuration for atomic Cu consists of a single s electron outside of closed shells we thought it might be possible to simplify the BS model without significant loss of accuracy by substituting hydrogens for the nearest neighbor Cu atoms. However, trial calculations on CuH_4 showed that there was excessive charge transfer (~0.56e) from the hydrogens to the central Cu. Further examination revealed (see Sec. III) that this charge transfer occurred, in large part, into the 4p Cu orbitals of π character which suggested replacing the four atom square by a single H atom on the symmetry axis. Indeed, upon doing so, the charge transfer was reduced to ~0.06e, a reasonable value for a neutral or quasi-neutral metal surface.[34]

Of course, the small total charge transfer is just one criterion that the simplified HCuCO cluster model should satisfy. It also ought to reproduce other properties of CO binding to Cu, particularly the Cu-C equilbrium bond length and the Cu-C bond energy. As we will see in Sec. III HCuCO does quite well for both of these properties. In fact, compared to experiment[32,35] it gives a better binding energy than the BS model which underestimates it.

For calculations of the C-O bond polarizability derivative it is important that the valence molecular orbitals primarily localized on CO be accurately described. Again, we will see in the next section that the orbitals obtained from our model are in close agreement with the corresponding Cu_5CO orbitals.

III. COMPUTATIONS

All of the electronic structure calculations reported in this paper were carried out by the ab initio Hartree-Fock self consisent field method using the HONDO5 program.[36] For open shell systems the orbitals were unrestricted, for closed shell systems they were taken to be doubly-occupied.

A suitable CGTO minimum basis set for describing the 3d transition series has been developed by Tatewaki and Huzinaga.[37] They used a contraction of three Gaussians to represent the s and p orbitals but found that a fourth GTO was required to give an accurate atomic 3d orbital energy. This contracted minimum basis will be referred to as SET A. It turns out, however, that one cannot achieve sufficient binding of Cu to CO unless a 4p polarization function is added to the basis. To this end we adapted the 4p orbital obtained by Wachters[38] for the $3d^{10}4p$ configuration of atomic Cu. Instead of eleven Gaussian functions only the three with largest coefficients were retained and these were then contracted and scaled leading to basis set B. In order to test the convergence of our calculations still a third set (SET C) was constructed by making a 1/1/1 split of the 4s orbital and a 3/1 split of the 3d.

Three different contracted Gaussian bases were chosen for the CO moiety as well. The first (SET 1) was the minimum 3G set of Tavouktsoglou and Huzinaga[39] the second (SET 2) was Dunning's[40] double zeta [4s2p] contraction, and the third a [5s4p] set (SET 3) which resulted from splitting of Dunning's orbitals.[41] There are, all together, 9 possible combinations of Cu and CO basis functions which may be uniquely designated A1, ..., C3. Finally, for the hydrogen atom we employed the standard Hehre, Stewart and Pople[42] STO-3G basis function.

In order to investigate the CO basis we have determined a number of properties for the free CO molecule most of which are shown in Tables I and II. From the tables it is apparent that, although SET 1 is inadequate, SETS 2 and 3 reproduce with good accuracy the results of experiment and/or better calculations as

far as the equilibrium bond length, axial polarizability α_{zz}, and Mulliken gross populations are concerned.

The error in the dipole moment of CO compared to experiment is a well-known[43] consequence of the Hartree-Fock approximation. Evidently, the consequences are not as serious for the polarizability nor, we assume, the polarizability derivative. The polarizability was obtained by finite perturbation theory[44] using a quadratic fit to the energies found for an applied field equal to -0.01, 0.00, +0.01 a.u. As a check the dipole moment determined by fitting agreed with the directly computed value (at F=0) to within ±.002 a.u.

By comparing basis sets 2 and 3 in Table I we get an indication that our calculations may be reasonably well converged with respect to basis set size. However, it is hazardous to draw conclusions in this regard as one can see from the polarizability resuts of McLean and Yoshimine[45] and Huo[46] quoted in the table.

Our initial test of the Cu basis was carried out on the CuH_4 cluster. We noticed immediately that there was considerable charge transfer from the hydrogens to Cu. As an example, the Mulliken gross populations for set B are presented in Table III. Clearly, the negative charge on Cu (0.56e) is much too large for a neutral or quasi-neutral Cu surface. compared to the $d^{10}s^1$ free atom it is evident that the additional electronic charge has gone into the 4p orbitals. The π-like 4p's ($4p_x$,$4p_y$) alone can account for almost the entire deviation from neutrality. Thus, as noted earlier, we were persuaded to substitute a single H atom on the symmetry axis for the H_4 group. Upon doing so the $4p_x$ and $4p_y$ populations fell essentially to zero which was expected and the charge on Cu was reduced to 0.06 as desired. It should be observed that the H of CuH is considerably less positive than the H's of CuH_4 showing that the effect is not simply due to having only 1/4 as many H atoms.

One might wonder whether the last remaining H atom can be eliminated as well. In fact it must be retained for otherwise CO does not bind to Cu, at least in calculations with the basis sets

used here.[47] In order to see whether the HCuCO model adequately remedies this deficiency we did preliminary computations employing the A1 and B1 bases. Only the Cu-C distance was varied, the C-O and Cu-H bond lengths were fixed at the equilibrium minimum basis set value[48] for the free molecules. The binding parameters that were found are compared in Table IV with those of BS and experiment. Without 4p orbitals in the Cu basis (SET A1) the binding is too weak. Once such polarization functions are included (SET B1) the results are quite satisfactory although the excellent agreement with experiment may be partly fortuitous. A Mulliken gross population analysis of the three highest valence orbitals derived from free CO (Cf. Table V) - carried out for SET B2 - further demonstrates the similarity between the BS model and ours as far as the CuCO entity is concerned.

IV. RESULTS AND DISCUSSION

Our final results for the HCuCO cluster model of CO adsorbed on Cu(100) are reported in Tables VI and VII. The former table pertains particularly to the properties of the Cu-C bond, the latter to the C-O bond. In both cases the B2 and C2 basis sets were employed along with a Cu-H bond length fixed at 2.709 a.u. The latter distance is the equilibrium value for the free molecule in the minimum basis. This is close to the experimental result[49] of 2.765 a.u. and we would not expect it to change much with enlarging the basis set or forming the HCuCO cluster. We also tested this calculation to insure that the polarizability derivative we seek, $\delta\alpha_{zz}/\delta R_{C-O}$, is insensitive to small variations in R_{Cu-H}.

In Compiling Table VI the C-O bond length was held constant at the free molecule value determined by the SET 2 basis. Note that the binding properties, which are similar in value to our preliminary results (Cf. Table IV) remain in good agreement with experiment. The Cu-C bond polarizability derivative is quite small as may be seen by comparing the derivative for the C-O bond. We used the Cu-C equilibrium bond distances computed for this table as input to obtain the C-O bond properties given in Table VII.

α_{zz} is a nearly linear function of R_{Cu-C} and R_{C-O} in the vicinity of the equilibrium bond lengths. Hence, the specific values chosen for these parameters is not important. If R_{C-O} is increased from 2.136 to 2.256 a.u., for example, the (SET C2) polarizability derivative in Table VII changes from 16.51 to 16.80 a.u.

The differences between basis sets B2 and C2 again provide some indication of how well-converged the results are. In general, these differences are relatively small. Although the latter statement is not true for the polarizability derivative $\delta\alpha_{zz}/\delta R_{Cu-C}$; in that case the change is small on an absolute basis.

As we have already emphasized in the Introduction, our

intention was to estimate to what extent the non-resonant Raman signal for the C-O stretch is increased when CO binds to a Cu surface. An HCUCO cluster has been used to simulate the on-top binding of CO on Cu(100). The fact that our cluster reproduces the binding properties of adsorbed CO and the CO valence orbitals of pyramidal $Cu_5^{\eta}CO$ gives us hope that a correct estimate of the Raman intensity has been obtained. This is especially likely since the property sought is a local quantity. Our result is that the "chemical" enhancement is about a factor of four which is in general agreement with the few careful estimates based on experimental data.[15,16] We emphasize that the present calculation does not deal with the question of resonant enhancement.

Acknowledgement

This work was supported in part by NSF (CHE82-06130) and by the Office of Naval Research.

REFERENCES

1. D.L. Jeanmaire and R.P. Van Duyne, J. Electroanal. Chem. 84, 1 (1977); M.G. Albrecht and J.A. Creighton, J. Am. Chem. Soc. 99, 5215 (1977).

2. R.K. Chang and T.E. Furtak, Surface Enhanced Raman Scattering, (Plenum, New York, 1982).

3. (a) A. Otto, Appl. Surf. Sci. 6, 309 (1980); A. Otto in Light Scattering in Solids vol. 4, eds. M. Cardona and G. Guntherodt (Springer, New York, 1983). (b) I. Pockrand, Surface Enhanced Raman Vibrational Studies of Solid-Gas Interfaces (Springer-Verlag, Berlin, 1983).

4. H. Metiu and P. Das, Ann. Rev. Phys. Chem., 35, 507 (1984).

5. H. Metiu, Progress Surface Science, 17, 153 (1984).

6. G.W. Ford and W.H. Weber, Physics Reports 113, 197 (1984).

7. R.K. Chang and B.L. Laube, CRC Critical Reviews in Solid State and Materials Sciences, 12, 1 (1984).

8. M. Moskovits, Rev. Mod. Phys. 57, 783 (1985).

9. S. Efrima and H. Metiu, Chem. Phys. Lett. 60, 54 (1978); J. Chem. Phys. 70, 1602 2297 (1982); Israel J. Chem. 17 (1979).

10. (a) D.S. Wang, H. Chew and M. Kerker, Appl. Opt. 12, 2256 (1980); 19, 3373 (1980); (b) S.L. McCall, P.M. Platzman and P.M. Wolff, Phys. Lett. 77A, 381 (1980); (c) J.I. Gersten, J. Chem. Phys. 72, 5779 (1980); J.I. Gersten and A. Nitzan, J. Chem. Phys. 73, 3023 (1980); (d) F.J. Adrian, Chem.

Phys. Lett. 78, 45 (1981); (e) P.K. Aravind, A. Nitzan and H. Metiu Surface Sci. 110, 189(1981); P.K. Aravind, R. Rendell and H. Metiu, Chem. Phys. Lett. 85, 396 (1982); P.K. Aravind and H. Metiu, J. Phys. Chem. 86, 5076 (1982); Surface Sci. 124, 506 (1983).

11. R.R. Chance, A. Prock and R. Silbey, Adv. Chem. Phys. 37, 1 (1978).

12. S. Efrima and H. Metiu, J. Chem. Phys. 70, 1939 (1979); Surface Sci. 92, 417 (1980); F.W. King and G.C. Schatz, Chem. Phys. 38, 245 (1979).

13. P.J. Feibelman, Prog. Surf. Sci. 12, 287 (1982); G. Korzeniewski, T. Maniv and H. Metiu, Chem. Phys. Lett. 73, 212 (1980); J. Chem. Phys. 76, 2697 (1982).

14. P.R. Hilton and D.W. Oxtoby, J. Chem. Phys. 72, 6346 (1980); W. Palke, Surf. Sci. 97, L331 (1980).

15. C.A. Murray and S. Bodoff, Phys. Rev. Lett. 52, 2273 (1984).

16. A. Campion and D.R. Mullins, Chem. Phys. Letters 94, 576 (1983); and D.R. Mullins and A. Campion (unpublished).

17. J. Billman, G. Kovacs and A. Otto, Surface Sci. 92, 153 (1[illegible] A. Otto, J. Timper, J. Billman, G. Kovacs and I. Pock[illegible]d [illegible]f. Sci. 92, L55 (1980).

18. T. [illegible] Metiu, Chem. Phys. Lett. 9, 305 (1980).

19. B.N[illegible] [illegible]em. Phys. Lett. 85, 561 (1981).

20. H. Ueba, [illegible] Phys. 73, 725 (1980); H. Ueba and S.

Ichimura, J. Chem. Phys. 74, 3070 (1981).

21. F.J. Adrain, J. Chem. Phys. 77, 5302 (1982).

22. K. Arya and R. Zeyher, Phys. Rev. 1324, 1852 (1981).

23. J.I. Gersten, R.L. Birke and J.R. Lombardi, Phys. Rev. Lett. 43, 147 (1979).

24. G.W. Robinson, Chem. Phys. Lett. 76, 191 (1980).

25. T.K. Lee and J.L Birman, Phys. Rev. B22, 5953, 5961 (1980); M. Philpott, J. Chem. Phys. 62, 1812 (1975).

26. S.L. McCall and P.M. Platzman, Phys. Rev. B22, 1660 (1980).

27. P.K.K. Pandey, G.C. Schatz, Chem. Phys. Lett. 88, 193 (1982); 81, 286 (1982); J. Chem. Phys. 80, 2959 (1984).

28. E. Burstein, Y.J. Chen, C.Y. Chen, S. Lundquist and E. Tossatti, Solid State Commun. 29, 567 (1979); C.Y. Chen, E. Burstein and S. Lungvist, ibid., 32, 631 (1979).

29. (a) T. Maniv and H. Metiu, Phys. Rev. B22, 4731 (1980); H. Metiu, Israel J. Chem. 22, 329 (1983). (b) A.A. Abrikosov, L.P. Gorkov and I. Ye. Dzyaloshinskii, Quantum Field Theoretical Methods in Statistical Physics, (Pergamon, New York, 1965) sec. ed. 3, p. 250.

30. A.B. Migdal, Soviet Phys. JETP 1, 996 (1958); J.R. Schrieffer, Theory of Superconductivity (W.A. Benjamin, Readings, Mass., 1964) p. 157.

31. P.S. Bagus and M. Seel, Phys. Rev. B23, 2065 (1981).

32. S. Andersson and J. B. Pendry, Phys. Rev. Lett., 43, 363 (1979).

33. S. Andersson, Surf. Sci. 89, 477 (1979).

34. See, for example, the discussion in K.S. Sohn, D.G. Dempsey, L. Kleinman, and E. Caruthers, Phys. Rev. B13, 1575 (1976).

35. J.C. Tracy, J. Chem. Phys. 56, 2748 (1972).

36. M. Dupuis, J. Rys and H.F. King, QCPE 13, 403 (1980).

37. H. Tatewaki and S. Huzinaga, J. Chem. Phys. 71, 4339 (1979).

38. A.J.H. Wachters, J. Chem. Phys. 52, 1033 (1969).

39. A.N. Tavouktsoglou and S. Huzinaga, J. Chem. Phys. 72, 1385 (1980).

40. T.H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970).

41. In going from SET 2 to SET 3 the smallest exponent functions were split out except for the s orbitals in which case it was the next to smallest exponent function.

42. W.J Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys. 51, 2657 (1969).

43. F. Grimaldi, A. Lecourt and C. Moser, Int. J. Quantum. Chem. 1S, 153 (1967).

44. J.A. Pople, J.W. McIver Jr. and N.S. Ostlund, Chem. Phys. Lett. 1, 465 (1967).

45. A.D. McLean and M. Yoshimine, J. Chem. Phys., 46, 3682 (1967).

46. W. Huo, J. Chem. Phys., 43, 624 (1965).

47. Our calculations were done for SETS A1, B1, C1 and for a C-O bond length of 2.316 a.u. which is the minimum basis equilibrium value.

48. These values are 2.316 a.u. for C-O and 2.709 a.u. for Cu-H.

49. G. Herzberg, "Molecular Spectra and Molecular Structure", Vol 1, Van Nostrand, Princeton, 1950.

Table I. Comparison of calculated and experimental properties of free CO obtained for different basis sets. All quantities are in a.u.

	CGTO BASIS				
PROPERTY	SET1	SET2	SET3	MCLEAN, YOSHIMINE,[c] AND HUO	EXPERIMENT
R_e	2.316	2.153	2.127		2.132[a]
E_{HF}[b]	-1.9075	-2.6853	-2.6992	-2.7891 (-2.7860, -2.7790)	-3.377[d]
μ		-0.19	-0.23	-0.11 (-0.11, -0.063)	0.044[e]
α_{zz}		13.08	13.61	14.24 (11.88, 11.28)	17.5[f]
$(\partial\alpha_{zz}/\partial R)_e$		8.25	8.99		

a. D.H. Rank, A.H. Guenther, G.D. Saksena, J.N. Shearer and T.A. Wiggins, J. Opt. Soc. Am., 47, 686 (1957).

b. In order to obtain E_{HF} relative to the usual zero of energy, one must add -100.0000 to the values given here.

c. The three values given here are for differnt STO bases. In the order that the numbers are written they are (5s4p1d1f), (4s3p1d1f), and (4s,2p,1d,1f). For the first and third see M. Yoshimine and A.D. McLean, Int. J. Quantum Chem., 15, 313 (1967); for the second see ref. 46.

d. B.J. Ransil, Rev. Mod. Phys., 32, 245 (1960).

e. See ref. 33.

f. J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "Molecular Theory of Gases and Liquids", John Wiley and Sons, New York, 1954.

Table II. Mulliken gross populations for the three highest valence molecular orbitals of free CO as a function of basis set.

		CARBON			OXYGEN		
		SET1	SET2	BS	SET1	SET2	BS
4σ	s	0.32	0.21	0.21	0.22	0.26	0.24
	p	0.00	0.02	0.03	0.46	0.52	0.53
5σ	s	0.39	0.54	0.57	0.01	0.00	-0.01
	p	0.38	0.37	0.33	0.23	0.10	0.10
1π	p	0.26	0.23	0.23	0.74	0.77	0.77

Table III. Mulliken gross populations in CuH_4 and CuH obtained with the SET B basis.

		CuH_4	CuH	Cu
Cu	s	6.84	6.94	7.00
	ρ_σ	4.63	4.21	4.00
	ρ_π	8.53	8.00	8.00
	d_σ	1.56	1.91	2.00
	d_π	4.00	4.00	4.00
	d_δ	4.00	4.00	4.00
TOTAL		29.56	29.06	29.00
H	s	0.86	0.94	
H	s	0.86		
H	s	0.86		
H	s	0.86		

Table IV. Preliminary binding parameters for $HCuCO_3$ model of CO adsorbed on Cu(100) as compared to Cu_5CO model of BS[31] and experiments (the equilibirum distance R_e in a.u., the binding energy E_b in eV).

BINDING PROPERTY	SET A1 CuCO MODEL[a]	SET B1 CuCO MODEL[a]	Cu_5CO MODEL	EXPERIMENT
R_e	4.08	3.90	3.88	3.6 ± 0.2[b]
E_b	0.31	0.65	0.45	~ 0.7[c]

a. The C-O and Cu-H bond lengths were fixed at minimum basis set equilibrium values for the free CO and CuH molecules: $R_{CO} = 2.316$ a.u., $R_{CuH} = 2.709$ a.u.

b. See ref. 32

c. See ref. 35

Table V. Mulliken gross populations of the three highest valence molecular orbitals derived from free CO using the HCuCO and the Cu_5CO (or BS^{31}) models of CO adsorbed on Cu(100). These results are for the B2 basis set.[a]

		H(or Cu_2)[b]		Cu_1[b]		C		O	
		HCuCO	Cu_5CO	HCuCO	Cu_5CO	HCuCO	Cu_5CO	HCuCO	Cu_5CO
$\tilde{4}\sigma$	s	...	...	...	...	0.26	0.28	0.25	0.23
	p	...	...	...	...	0.03	0.04	0.47	0.45
	d	...	...	...	...	0.29	0.32	...	...
$\tilde{5}\sigma$	s	0.01	...	0.01	0.05	0.37	0.34	0.02	0.01
	p	...	...	0.01	...	0.36	0.32	0.13	0.15
	d	...	...	0.10	0.15	...	...	...	...
$\tilde{1}\pi$	p	...	...	0.01	...	0.26	0.25	0.74	0.74
	d	...	...	...	...	...	...	...	...

a. We used the bond lengths: R_{CuC} = 3.900, R_{C-O} = 2.153, and R_{Cu-H} = 2.709 a.u. The latter two are equilibrium values for the free molecules and SET 2 (CO), or SET A (CuH). Our Cu-C distance is the equilibirum SET B1 value for HCuCO.

b. Cu_1 is the copper atom on the symmetry axis; Cu_2 is the set of four nearest neighbor copper atoms in the base of the square pyramid.

Table VI. Calculated properties of Cu-C bond in HCuCO model for CO adsorbed on Cu(100). All quantities[a] are in a.u. except E_b[b] which is in eV. The fixed bond lengths are R_{C-O} = 2.153 and R_{Cu-H} = 2.709 a.u. For definition of symbols see Table I.

PROPERTY	SET B2	SET C2
R_e(Cu-C)	3.960	3.953
E_{HF}	-0.6436	-0.8132
E_b	0.78	0.79
μ	1.72	1.62
α_{zz}	29.3	31.9
$\partial\alpha_{zz}/\partial R_{Cu-C}$	1.33	0.04

a. Cf. Table I.

b. See footnote a of Table IV.

c. In order to obtain E_{HF} relative the usual zero of energy add -1745.0000 a.u.

Table VII. Calculated properties of C-O bond in HCuCO model for CO adsorbed on Cu(100). All quantities are in a.u. The fixed bond lengths are[a] R_{Cu-H} = 2.709 a.u. and[b] R_{Cu-C} = 3.960 or 3.953 a.u. The symbols are defined in the caption of Table I.

PROPERTY	SET B2	SET C2
R_e(C-O)	2.135	2.136
E^c_{HF}	-0.6437	-0.8133
μ	1.74	1.62
α_{zz}	29.0	31.6
$\partial\alpha_{zz}/\partial R_{C-O}$	15.5	16.5

a. See footnote a of Table IV.

b. Cf. Table VI.

c. Cf footnote c of Table VI.

FIGURE CAPTIONS

Fig. 1. Schematic diagram for Raman scattering by a diatomic adsorbed on a metal surface. The shape of the electron cloud is drawn approximately. Lined circles represent ion cores; wavy lines photon propagators; full lines are electron propagators, and the double line is a phonon (i.e., the stretching mode of the adsorbed diatomic molecule propagator). The energies for each propagator are noted along the lines. A more detailed description of the process is given in the text.

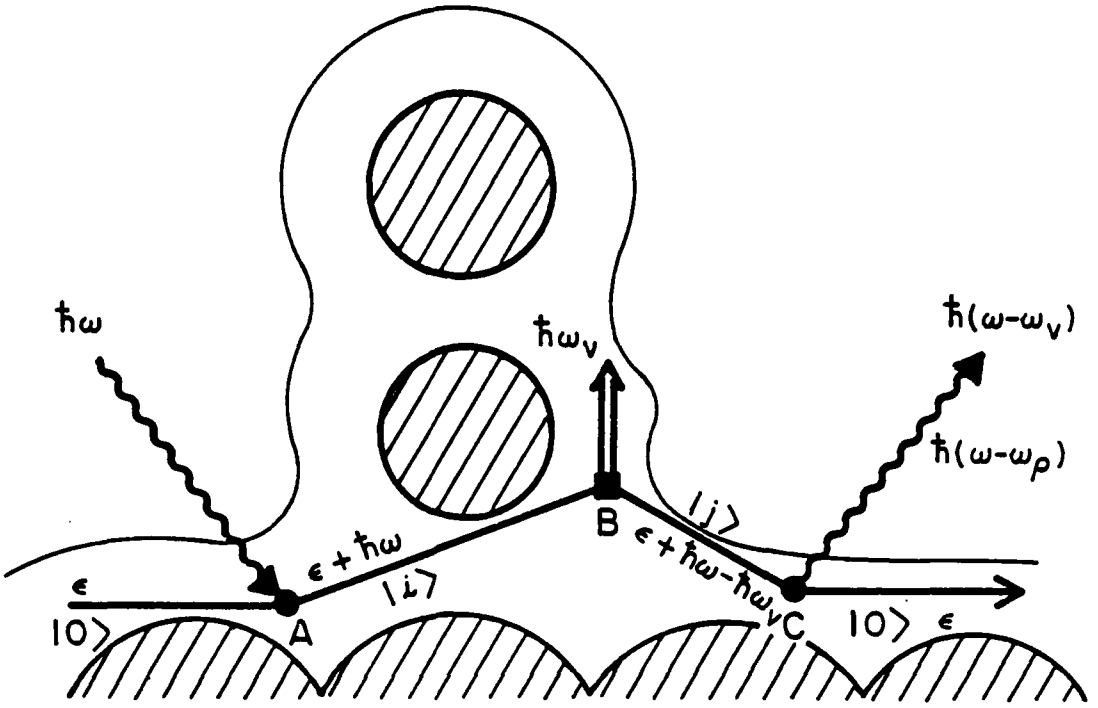


Fig. 1

END

DTIC

5-86