

## Covalent Bonding of CN to the Pt(111) Surface

W. Daum and F. Dederichs

*Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich, D-52425 Jülich, Germany*

J. E. Müller

*Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, D-52425 Jülich, Germany*

(Received 10 June 1997)

We present a vibrational study of the CN/Pt(111) system immersed in acetonitrile, using optical sum-frequency generation. Frequencies of  $2073\text{ cm}^{-1}$  (on-top) and  $1861\text{ cm}^{-1}$  (hollow), distinctly above and below that of the isolated molecule, demonstrate a covalent CN-metal bond. Cluster calculations show that the strengthening and weakening of the C-N bond at the on-top and hollow sites is due to a surface-induced depletion of the antibonding  $4\sigma$  and bonding  $1\pi$  orbitals, respectively. We illustrate our results with a comparison to the reference CO/Pt(111) system. [S0031-9007(97)05125-9]

PACS numbers: 68.45.Kg, 71.15.Fv, 82.65.My

The cyanide (CN) molecule has the peculiar property that its internal bond is strengthened when it binds to metal and nonmetal atoms, a feature for which no conclusive explanation has been presented so far. The strengthening of the C-N bond was revealed by vibration spectroscopy showing stretching vibration frequencies above the value of the isolated molecule. It was observed in metal-CN complexes such as  $[\text{Pt}(\text{CN})_4]^{2-}$  [1], as well as in studies of CN adsorption on various metal electrode surfaces in aqueous electrolytes [2]. Available theories describe the CN-metal bonding as dominantly ionic [3,4] and ascribe the intramolecular bond strengthening to a charge transfer from the  $5\sigma$  orbital of the  $\text{CN}^-$  ion towards the metal atom [1]. In this Letter we develop a new model for the CN-metal bond, which we apply to the CN/Pt(111) system. In particular, we show that the CN-metal bond is dominantly covalent and that the weakly antibonding  $5\sigma$  orbital is not responsible for the observed frequency shifts. Using optical sum-frequency generation (SFG) we measured the stretching vibration frequencies of CN adsorbed on a Pt(111) surface in a liquid ambient. We observed two different CN species in our vibration spectra with frequencies distinctly above and below that of the isolated molecule, corresponding to strengthened and weakened internal bonds, respectively, which clearly demonstrates the covalent character of the CN-metal bonds. In order to aid in the interpretation of the results we performed total-energy cluster calculations using the local density approximation for exchange and correlation, and a localized muffin-tin orbital (MTO) basis [5] with  $s$ ,  $p$ , and  $d$  functions in all atoms. The calculations permit us to assign the high-frequency (low-frequency) vibration to CN adsorbed at the on-top (hollow) site, and to show that the bond strengthening (weakening) is due to a surface-induced depletion of the antibonding  $4\sigma$  (bonding  $1\pi$ ) CN orbital. For comparison, we also present our experimental and theoretical results for the reference CO/Pt(111) system.

CN was adsorbed on the Pt(111) surface by a new procedure involving high-temperature dissociation of acetonitrile ( $\text{CH}_3\text{CN}$ ) [6], which enabled us to study energetically less favorable adsorption sites. A (111)-oriented Pt single crystal surface was cleaned by flame annealing and, still being red hot, exposed to the vapor above liquid acetonitrile. After cooling down to room temperature the crystal was immersed without potential control into the liquid, where the CN-covered Pt surface remained stable for several hours. SFG and cyclic voltammetry experiments with the same adsorption procedure but with an aqueous electrolyte containing acetonitrile allowed us to unambiguously identify CN as the adsorbate [6]. The CO/Pt(111) surface was prepared in an aqueous electrolyte (0.1 M  $\text{HClO}_4$ ) by bubbling CO through the liquid [7]. For SFG we mixed tunable picosecond infrared pulses from an optical parametric amplifier with laser pulses of  $0.53\text{ }\mu\text{m}$  at the Pt/liquid interface. All beams including the sum-frequency photon beam were  $p$  polarized. To minimize absorption of the infrared laser power we allowed only a thin ( $\sim 1\text{ }\mu\text{m}$ ) layer of liquid between the surface and a prismatic  $\text{CaF}_2$  laser window. SFG in a ZnS reference sample was used to correct the spectra for power fluctuations of the laser system.

Figure 1 presents our SFG spectra for CN and CO adsorbed on Pt(111). The spectrum for CO (obtained at a potential of 0.02 V versus the reversible hydrogen electrode) exhibits two vibration frequencies at 2067 and  $1781\text{ cm}^{-1}$ , which are assigned to CO adsorbed at on-top and hollow sites, respectively, in accord with previous infrared studies [7,8]. For CN we observe a strong band at  $2073\text{ cm}^{-1}$  and a weaker band at  $1861\text{ cm}^{-1}$ , which must be attributed to molecules adsorbed on sites with different molecule-Pt interactions. We show below that they are also assigned to on-top and hollow sites, respectively. The dependence of the stretching vibration frequency on adsorption geometry demonstrates the involvement of the molecular orbitals in the bonding to

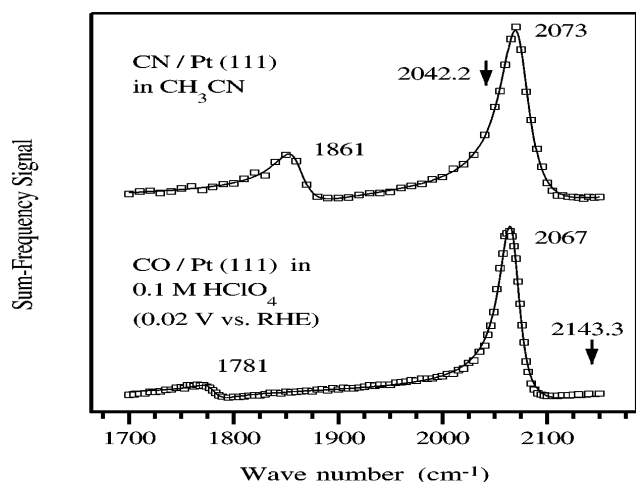


FIG. 1. Sum-frequency spectra of CN and CO adsorbed on Pt(111) in acetonitrile and in an aqueous electrolyte, respectively. The arrows indicate the frequencies of the isolated molecules.

the surface, i.e., the existence of a large covalent component in the surface bond, for both CO and CN. There are, however, important differences between the bonding properties of these two molecules. Note that the high-frequency band of CN lies  $30\text{ cm}^{-1}$  above the frequency of isolated CN ( $2042\text{ cm}^{-1}$  [9]), and  $80\text{ cm}^{-1}$  above that of  $\text{CN}^-$  ( $1991\text{ cm}^{-1}$ ; see below). This indicates a surface-induced strengthening of the C-N bond for on-top adsorption, which has no parallel in the CO/Pt(111) system where all the frequencies lie below that of the free molecule ( $2143\text{ cm}^{-1}$  [9]). Note also that the frequency difference between on-top and hollow species for CN is smaller than for CO. The CN band at  $1861\text{ cm}^{-1}$ , which corresponds to molecules with a weakened C-N bond, was not observed in previous studies where CN was adsorbed from aqueous electrolytes containing solvated  $\text{CN}^-$  ions [2]. This indicates that the on-top adsorption energy of CN is appreciably larger than the hollow one, in contrast with previous theoretical predictions for CN adsorption on the Ni(111) surface [10]. The electrolyte was shown to have no significant effect on the vibration frequencies of CO/Pt(111) [8], and we expect the same to be valid for CN/Pt(111). The electric field at the Pt/liquid interface and the dipole-dipole coupling have an influence on the frequencies, but their effects tend to cancel each other. Although the CN spectrum in Fig. 1 was measured without an externally applied potential, it is apparent that a depolarizing field due to the solvent molecules develops at the interface. For adsorbed CO the effect of this field is to decrease the frequency by about  $20\text{ cm}^{-1}$  in comparison with the uncharged Pt(111) surface [11], and we have experimental evidence suggesting that the same is also true for CN. The dipole-dipole coupling increases the frequency of on-top CO on Pt(111) by about  $20\text{ cm}^{-1}$  [12], and should also increase that of CN, although by a

smaller amount because it has a smaller dynamical dipole moment (see below).

The electronic structures of the isolated CN and CO molecules differ only in the respective strength of the N and O potentials, and in the occupation of the  $5\sigma$  orbital, which contains two electrons in CO, but only one in CN. The ionic  $\text{CN}^-$  molecule also has two electrons in the  $5\sigma$  orbital. However, while CO is a stable molecule, both CN and  $\text{CN}^-$  are radicals: they are stable in isolation, but they cannot exist as separate entities in the presence of even the smallest interaction with other atoms because of the position and strong dependence on occupation of the  $5\sigma$  energy. This energy is  $+1.0\text{ eV}$  for  $\text{CN}^-$  (above the vacuum level [13]) and  $-8.7\text{ eV}$  for CN (below the Fermi level of any substance), giving rise to charge transfers away from  $\text{CN}^-$  and to CN. This means that the molecule can exist only with an additional fractional charge, i.e., in interaction with other atoms. As we report below, adsorbed CN has a charge of  $0.3e$ . From the total energy as a function of the bond distance ( $R$ ) we deduce equilibrium  $R$  values of  $1.18\text{ \AA}$  for CN and  $1.14\text{ \AA}$  for CO, as well as the vibration frequencies presented in the first column of Table I. It is worth pointing out that the charging of the CN molecule produces a moderate decrease of its vibration frequency (it goes down to  $1991\text{ cm}^{-1}$  for  $\text{CN}^-$ ), which is consistent with the weak antibonding character of the  $5\sigma$  orbital. The bonding or antibonding character of the molecular orbitals was deduced by recalculating the vibration frequencies with the occupation of the orbitals changed by a small amount. We find that the  $3\sigma$  and  $1\pi$  orbitals are bonding, and the  $4\sigma$  and  $2\pi$  orbitals are antibonding, for both CN and CO. The same conclusion is obtained from the pair charges defined below. The  $\text{CN}^-$  and CO molecules exhibit linear dipole moment functions,  $\mu(R)$ , with dynamical dipoles,  $q^* = d\mu/dR$ , given by  $0.3e$  and  $0.6e$ , respectively. The dipole moment of CN, although also linear for large  $R$ , exhibits a broad minimum with  $q^* \sim 0$  at equilibrium.

To study the adsorption of CN and CO on Pt(111), we modeled a small fraction of the surface with a  $\text{Pt}_{25}$  cluster consisting of two layers: a  $\text{Pt}_{13}$  layer and a  $\text{Pt}_{12}$  layer, having at their center an on-top and a hollow site, respectively. Adsorption at the on-top site was studied by placing the molecule at the center of the  $\text{Pt}_{13}$  side of the

TABLE I. Vibration frequencies in  $\text{cm}^{-1}$  of CN and CO calculated for various adsorption geometries of a  $\text{Pt}_{25}$  cluster. The notations (|) and (–) refer to the upright and parallel orientations for the CN molecule. The experimental values are given in parentheses.

	Isolated	On-top	Bridge	Hollow
CN ( )	2063 (2042)	2150 (2073)	2000	1920 (1861)
CN (–)		1962	1929	1807
CO	2197 (2143)	2140 (2067)	1970	1880 (1781)

cluster, and calculating the total energy of the cluster plus molecule as a function of the height and bond distance of the molecule. The potential energy was obtained by subtracting the energy of the Pt<sub>25</sub> cluster. The minima of the potential energy functions yield adsorption energies of 4.5 eV for CN and 2.0 eV for CO, and equilibrium C-Pt distances of 2.0 Å for both molecules. Adsorption at the bridge and hollow sites, which was studied by placing the molecule on the Pt<sub>12</sub> side of the cluster, yielded equilibrium C-Pt distances of 1.7 and 1.5 Å, respectively, for both molecules. Other geometries can be excluded for energetic reasons. We found that adsorption with the molecule parallel to the surface was unfavorable compared to the upright geometry by about 1 eV for all three adsorption sites, and that CN bonding at the on-top site via the N atom was unfavorable by 1.2 eV compared to bonding via the C atom. The latter result was also obtained in Ref. [14]. The calculated vibration frequencies of CN and CO adsorbed at different sites of the Pt<sub>25</sub> cluster are presented in Table I. Tests with smaller clusters show that these values are converged in cluster size. Note that while all the calculated frequencies of adsorbed CO are smaller than that of isolated CO, the frequency of CN adsorbed at the on-top site is larger than that of the isolated CN or CN<sup>-</sup> molecules. This description fits that of the higher experimental CN frequency, which we assign to molecules adsorbed at the on-top site. We assign the lower experimental CN frequency tentatively to the hollow site, for this leads to a uniform discrepancy between theory and experiment of 60–120 cm<sup>-1</sup> for all the frequencies of the adsorbed molecules.

The distinctive feature of the CN-metal bond is the pinning of the 5σ orbital to the Fermi level of the metal. This causes a charge transfer of about 0.3e from the surface to the molecule, and gives rise to an ionic contribution to the surface bond of 0.5 eV, which amounts to about 11% of the total adsorption energy. As a consequence of the pinning, there is an upward movement of all CN molecular orbitals by about 3 eV, and a realignment of molecular and metal energy levels. The 4σ and 1π orbitals position themselves within the energy range of the Pt 5d band, while the molecular 2π orbital moves up to about 7 eV above the Fermi level of the metal and does not take part in the surface bond, as pointed out by Bagus *et al.* [3]. This means that the CN-metal bond is due to contributions from the 1π, 4σ, and 5σ orbitals. At the bridge and hollow sites the 1π orbital has the largest contribution, while at the on-top site the 4σ and 5σ orbitals play the dominant role. The occupied 1π and 4σ orbitals lower their energies by interacting with unoccupied 5d and 6s metal states. The partially unoccupied 5σ orbital makes bonding and antibonding combinations with occupied 5d metal states, whereby the bonding combination moves downwards in energy and is fully occupied, and the antibonding combination remains

partially empty and pinned to the Fermi level. This means that the electron transfer from the metal to the molecule goes to the antibonding 5σ-5d combination. However, since there is more charge in the bonding than in the antibonding combination the net effect of the 5σ orbital is bonding to the surface. The CO-metal bond is mainly produced by the 5σ (on-top) and the 2π (bridge/hollow) orbitals. The 1π and 4σ orbitals lie too low in energy and have no appreciable interaction with Pt valence states.

To illustrate the effect of the surface on the intramolecular bond of CN adsorbed at the on-top site, we define symmetry-projected pair charges between the *i*th and *j*th atoms of the cluster [15],

$$Q_{\alpha}(i, j) = 2 \sum_{n \in \alpha} \sum_{\lambda, \lambda'} \langle \Psi_n | \chi_{i, \lambda} \rangle \langle \chi_{j, \lambda'} | \Psi_n \rangle, \quad (1)$$

where  $\chi_{i, \lambda}$  are MTOs centered on the *i*th atom with angular momentum  $\lambda = (l, m)$ , and the *n* summation extends over all states,  $\Psi_n$ , with symmetry  $\alpha$ . The off-diagonal term  $Q_{\alpha}(i, j)$  can be positive or negative and may be interpreted, respectively, as the bonding or antibonding charge with symmetry  $\alpha$  between the *i*th and *j*th atoms. The diagonal term  $Q_{\alpha}(i, i)$  is positive definite, and represents the charge with symmetry  $\alpha$  on the *i*th atom not involved in the bonding to other atoms. In this representation, the orbital structure of the CN-metal bond is given by the sum of the projected bonding charges between the molecule and the Pt<sub>25</sub> cluster,  $\sum_{i \in \text{CN}} \sum_{j \in \text{Pt}_{25}} Q_{\alpha}(i, j) = 0.30e, 0.09e, \text{ and } 0.05e$  for  $\alpha = 4\sigma, 1\pi, \text{ and } 5\sigma$ , respectively, which demonstrates the dominant role of the 4σ orbital in making the surface bond. The orbital character of the intramolecular C-N bond is given by the orbital-projected charges on the molecule,  $\sum_{i \in \text{CN}} \sum_j Q_{\alpha}(i, j)$ . The change in these charges induced by the surface bond is equal to  $-0.20e, -0.05e, \text{ and } +0.55e$  for the same three orbitals. This means that the 4σ and 1π orbitals act as donors; i.e., their weight on the molecule is decreased by the surface bond. In particular, the 0.2e depletion of the antibonding 4σ orbital leads to the observed strengthening of the intramolecular C-N bond. On the other hand, the 5σ orbital is an acceptor of electrons and its occupation is increased by 0.55e. However, because of its weakly antibonding character, the 5σ orbital has no appreciable effect on the strength of the C-N bond. The orbital charges add to an excess charge of 0.3e on the CN molecule, in accord with previous calculations for a PtCN molecule [14]. A similar analysis shows that at the hollow and bridge sites the CN-metal bond is dominated by a charge transfer from the bonding 1π orbital to the surface, which leads to the weakening of the C-N bond. The different behavior of the C-N bond at the on-top and bridge/hollow sites is in marked contrast with that of CO, which shows a weakening of its intramolecular bond for all geometries, as well as larger frequency differences between them. The vibration frequency of CO is determined by the amount of occupation of the strongly antibonding

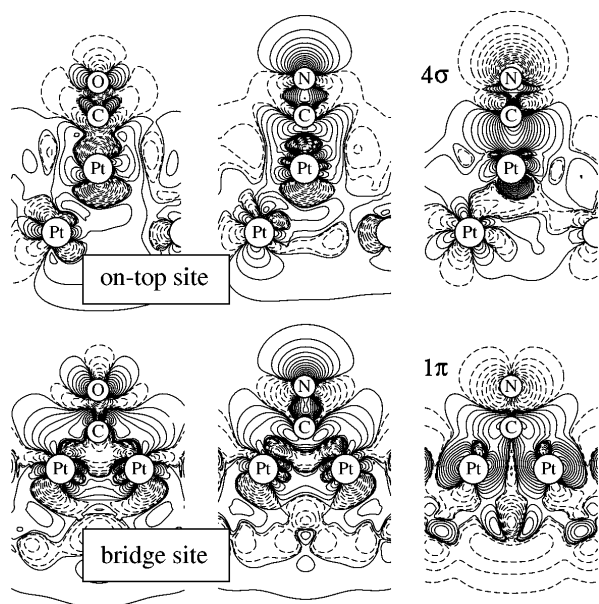


FIG. 2. Charge densities differences,  $\Delta\rho$ , induced by the adsorption of CO and CN at the on-top and bridge sites of a  $\text{Pt}_{25}$  cluster. The continuous ( $\Delta\rho > 0$ ) and dashed ( $\Delta\rho < 0$ ) contour lines represent densities given by  $2n^3 \times 10^{-4} e \text{ \AA}^{-3}$ , for  $n = -15, \dots, 15$ .

$2\pi$  orbital, which is larger at the bridge/hollow sites because of the symmetry of the environment.

The main features discussed above can be visualized in Fig. 2, which shows the redistribution of charge induced by the surface bond, as given by the charge density differences  $\Delta\rho = \rho(\text{Pt}_{25}\text{CN}) - \rho(\text{Pt}_{25}) - \rho(\text{CN})$  for CN, and similarly for CO. Note that the charge density of CN differs from that of CO in two ways: (i) there is a large transfer to the  $5\sigma$  orbital, and (ii) charge transfer to the  $2\pi$  orbital is absent. The figure also shows the charge density differences for CN adsorbed at the on-top and bridge sites, projected into the  $4\sigma$  and  $1\pi$  orbitals. These charge densities illustrate the charge transfer from these states to the metal surface, leading to the formation of the surface bond and to a strengthening (weakening) of the C-N bond at the on-top (bridge) site.

From the charge densities we calculated the surface dipole moment  $\mu_s = \mu(\text{Pt}_{25}\text{CN}) - \mu(\text{Pt}_{25}) - \mu(\text{CN})$ , induced by CN as a function of  $R$ , and we deduced dynamical dipole moments  $q^* = d\mu_s/dR = 0.35e$  and  $0.05e$  for the on-top and hollow sites, respectively. These values are consistent with the relative intensities of the CN spectrum in Fig. 1, confirming our on-top site assignment of the high-frequency peak. The large  $q^*$  value at the on-top site is in marked contrast with the vanishingly small dynamical dipole moment of the isolated molecule. A detailed study of the pair charges, Eq. (1), shows that it arises from a geometry-dependent charge transfer between the molecule and the surface, and that it is related

to the pinning of the surface-antibonding  $5\sigma$ - $5d$  combination discussed above. When the molecule contracts (expands) the C-Pt distance expands (contracts), and the  $5\sigma$ - $5d$  energy tends to move downwards (upwards). This tendency is compensated by a charge transfer to (from) the surface in order to keep the  $5\sigma$ - $5d$  state pinned at the Fermi level. The large distance involved in the charge transfer leads to a large  $q^*$  value. At the bridge and hollow sites there is no appreciable  $5\sigma$ - $5d$  interaction, so that the  $5\sigma$  energy and the charge transfer has only a weak dependence on geometry. For CO the dynamical dipole is insensitive to the adsorption site, and it is equal to  $q^* = 1.2e$ , which corresponds to the dynamical dipole moment of the isolated molecule plus image charge.

We conclude with a remark on the solvated  $\text{CN}^-$  ion, which also exhibits a large vibration frequency ( $2080 \text{ cm}^{-1}$  [1]), appreciably larger than our calculated frequency for isolated  $\text{CN}^-$  ( $1991 \text{ cm}^{-1}$ ). We speculate that this high frequency is not an intrinsic property of the CN group itself, but is also caused by depletion of the  $4\sigma$  orbital as a result of bonding to water molecules.

- [1] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1986).
- [2] K. A. Friedrich, W. Daum, C. Klünker, D. Knabben, U. Stimming, and H. Ibach, *Surf. Sci.* **335**, 315 (1995), and references therein.
- [3] P. S. Bagus, C. J. Nelin, W. Müller, M. R. Philpott, and H. Seki, *Phys. Rev. Lett.* **58**, 559 (1987).
- [4] C. J. Nelin, P. S. Bagus, and M. R. Philpott, *J. Chem. Phys.* **87**, 2170 (1987).
- [5] J. E. Müller, R. O. Jones, and J. Harris, *J. Chem. Phys.* **79**, 1874 (1983).
- [6] F. Dederichs and W. Daum (to be published).
- [7] F. Kitamura, M. Takahashi, and M. Ito, *Surf. Sci.* **223**, 493 (1989).
- [8] S.-C. Chang, X. Jiang, J. D. Roth, and M. J. Weaver, *J. Phys. Chem.* **95**, 5378 (1991).
- [9] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
- [10] H. Yang, T. C. Caves, and J. L. Whitten, *J. Chem. Phys.* **103**, 8756 (1995).
- [11] For CO/Pt(111) is acetonitrile without externally applied potential we find an on-top frequency of  $2075 \text{ cm}^{-1}$ , about  $20 \text{ cm}^{-1}$  lower than for the Pt/vacuum interface.
- [12] M. Tüshaus, E. Schweizer, P. Hollins, and A. M. Bradshaw, *J. Electron Spectrosc. Relat. Phenom.* **44**, 305 (1987).
- [13] A positive  $5\sigma$  energy does not contradict the stability of isolated  $\text{CN}^-$ . The electron affinity of CN (3.8 eV) is the average of the  $5\sigma$  energies with occupations 1 and 2.
- [14] J. P. Flament and M. Tadjeddine, *Chem. Phys. Lett.* **238**, 193 (1995).
- [15] R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955); see also J. E. Müller, *Surf. Sci.* **178**, 589 (1986).