Origin of strange vibrational spectra of NO on Pt(111) surface

Hideaki Aizawa∗
Creative Research Initiative “Sousei”, Hokkaido University,
Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

Yoshitada Morikawa
Institute of Scientific and Industrial Research, Osaka University,
8-1, Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan

Shinji Tsuneyuki
Department of Physics, Graduate School of Science,
University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Katsuyuki Fukutani
Institute of Industrial Science, University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-5805, Japan

Takahisa Ohno
Computational Materials Science Center, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

(Received 10 August 2007; Accepted 22 September 2007; Published 2 October 2007)

By first-principles calculations for NO adsorbed on Pt(111) surface, we found strange behaviors of peak intensities in vibrational spectra of high-resolution electron energy loss spectroscopy (HREELS) and infrared reflection absorption spectroscopy (IRAS). For NO/Pt(111) at a high coverage, the peak intensity of fcc-hollow species is about 10 times smaller than that of atop species, although the numbers of both species on the surface are equal. By analyzing the charge density distributions, it was found that an electron transfer between the NO molecule and the surface Pt atom at the atop site takes place as the N-O bond at the fcc-hollow site vibrates, resulting in a screened dynamic dipole moment.[DOI: 10.1380/ejssnt.2007.122]

Keywords: Density functional calculations; Electron energy loss spectroscopy (EELS); Infrared reflection absorption spectroscopy (IRAS); Nitrogen Oxides; Platinum

I. INTRODUCTION

Vibrational spectroscopic techniques such as electron energy loss spectroscopy (EELS) [1] and infrared reflection absorption spectroscopy (IRAS) [2, 3] have been ubiquitously employed to characterize and identify adsorbates on solid surfaces. In particular, NO molecules on Pt surfaces have been studied extensively due to its relevance to industrial catalytic processes. However, even for simple systems of NO molecules adsorbed on the flat Pt(111) surface, the molecular arrangement and geometry have been misunderstood due to the difficulty in interpreting the observed vibrational spectra [4, 5].

For NO/Pt(111) at high coverages, for instance, it had long been believed that only the NO species adsorbed at atop sites exist on the surface, because there is only one prominent peak in the observed vibrational spectra, whose frequency corresponds to the N-O stretching vibration of the atop species [4, 5]. Recent experiments by scanning tunneling microscopy and low-energy electron diffraction analysis [6, 7] as well as first-principles calculations [8] showed, however, that fcc-hollow species also exist on the surface in addition to atop species at an NO coverage of 0.5 ML, in apparent contradiction to the vibrational data.

In the present work, we calculated vibrational spectra of HREELS and IRAS for NO/Pt(111) at a coverage of 0.5 ML, where the numbers of the fcc-hollow and atop species existent on the surface are equal. The peak intensity of the fcc-hollow species turned out to be about ten times smaller than that of the atop species, thus overlooked by the experimentalists [4, 5]. The well-known intensity transfer effect due to vibrational coupling [3] cannot explain such large difference in peak intensity. It was shown to originate from dynamic electron transfer between the adsorbate and substrate at the atop site as the N-O bond of the fcc-hollow species vibrates.

II. METHODS

The first-principles calculations were performed using the program called “STATE” (Simulation Tool for Atom TECnology) [9]. The method was based on the density-functional theory with the generalized gradient approximation to the exchange-correlation functional [10]. The one-electron wavefunctions were expanded by plane waves whose cutoff energy was 30.25 Ry. Ultrasoft pseudopotentials were employed to represent core electrons [11]. The slab model consisting of three Pt layers and one NO adlayer was used to represent the NO/Pt(111) adsorption system.
III. RESULTS AND DISCUSSIONS

The most stable structure at a coverage of 0.5 ML is shown in Fig. 1, which consists of one three-fold fcc-hollow NO species and one atop NO species in the 2×2 unit cell. In Fig. 1(b), the 2×2 unit cell is indicated by dashed lines. The NO molecule at the three-fold fcc-hollow site is perpendicular to the surface with the N-end down, while the axis of the molecule at the atop site is tilted by 52° from the surface normal. The calculated vibrational frequencies and peak intensities of the two N-O stretching modes for the structure of Fig. 1 are shown in Fig. 2, with the corresponding experimental data by HREELS for comparison [6]. In vibrational spectra of specular-mode HREELS and IRAS, peak intensities are known to be proportional to squared dynamic dipole moments. Thus the calculated peak intensities mean the squared dynamic dipole moments. Thus the calculated vibrational frequencies hereafter. The peak intensities of the fcc-hollow and atop species are 0.147 and 1.475 (in arbitrary units), respectively. Although NO molecules occupy as many fcc-hollow sites as atop sites, the fcc-hollow peak is about ten times as small as the atop peak.

We also calculated the vibrational frequencies and peak intensities for a coverage of 0.25 ML (i.e., one NO molecule in the 2×2 unit cell), where only fcc-hollow or atop species exist on the surface. The peak intensities of the fcc-hollow and atop species were calculated to be 1.171 and 2.089, respectively.

In general, when there are two vibrational modes with near frequencies (the typical frequency difference being of the order of 10 cm⁻¹), they couple to each other to yield in-phase and out-of-phase modes. Such vibrational coupling causes the so-called intensity-transfer effect, where the intensity of the out-of-phase mode with a lower frequency is transferred to that of the in-phase mode with a higher frequency [3]. The N-O stretching frequencies of the fcc-hollow and atop species at 0.25 ML were calculated to be 1512 cm⁻¹ and 1683 cm⁻¹, respectively. The frequency difference of about 170 cm⁻¹ seems too large for the intensity-transfer effect to be significant. In order to estimate its influence on the peak intensities, we consider an imaginary situation in which fcc-hollow and atop species coexist at 0.5 ML without vibrational coupling. For the real situation with the vibrational coupling, we calculated 12 normal modes (of which only two relate to the N-O bond stretching) by diagonalizing the 12×12 Hessian matrix which is obtained by displacing each of the 12 degrees of freedom concerning the positions of the two nitrogen and two oxygen atoms in the unit cell. For the imaginary situation without the vibrational coupling, we obtained 6 normal modes each for the fcc-hollow and atop species separately by diagonalizing the 6×6 matrices. The peak intensities without the vibrational coupling were calculated to be 0.363 and 1.259 for the fcc-hollow and atop species, respectively.

The variations of the peak intensities of the fcc-hollow and atop species dependent on the NO coverage and vibrational coupling are summarized in Table 1.

| Coverage | Coupling | fcc-hollow | atop |
|----------|----------|------------|------|
| 0.25a    | No       | 1.171      | 2.089|
| 0.5b     | No       | 0.363      | 1.259|
| 0.5b     | Yes      | 0.147      | 1.475|

*Only fcc-hollow or atop species exist.
*Both fcc-hollow and atop species exist.

The corresponding vibrational spectrum by a HREELS experiment is shown for comparison [6]. The calculated intensities in the figure are normalized so that the peak around 1700 cm⁻¹ becomes as intense as the experimental one.

![FIG. 2: The vibrational frequencies and peak intensities (squared dynamic dipole moments) calculated for the structure of Fig. 1. The corresponding vibrational spectrum by a HREELS experiment is shown for comparison [6]. The calculated intensities in the figure are normalized so that the peak around 1700 cm⁻¹ becomes as intense as the experimental one.](http://www.sssj.org/ejsnt)
In order to investigate the origin of the effect induced by the increased coverage, we need to analyze the charge density distributions. Here we consider its effect on the peak intensity of the fcc-hollow species. It is proportional to the square of the dynamic dipole moment, \( \partial \mu / \partial Q \), where \( \mu \) and \( Q \) denote the dipole moment of the slab and the normal coordinate of the N-O stretching mode of the fcc-hollow species, respectively. \( \mu \) can be expressed as follows:

\[
\mu = \int \rho(r) z \, dr,
\]

with \( \rho(r) \) and \( z \) representing the charge density distribution function and the spatial coordinate normal to the surface, respectively. In numerical calculations, the partial derivative, \( \partial \mu / \partial Q \), is approximated by the difference, \( \Delta \mu / \Delta Q \). Here \( \Delta \mu \) is the change in the dipole moment when the normal coordinate is changed by a small amount, \( \Delta Q \). From Eq. (1), the dynamic dipole moment is given by

\[
\partial \mu / \partial Q \approx \int \Delta \rho(r) z \, dr / \Delta Q,
\]

where \( \Delta \rho(r) \) is the change in the charge density distribution when the normal coordinate is changed by \( \Delta Q \). Now we take \( Q \) as the normal coordinate obtained in the imaginary calculation where the vibrational coupling to the atop species is neglected. Then the change in \( Q \) involves only the change in the atomic positions of the nitrogen and oxygen atoms of the NO molecule at the fcc-hollow site. The sign of \( \Delta Q \) is defined so that a positive value corresponds to elongation of the N-O bond. For a positive fixed \( \Delta Q \), we calculate \( \Delta \rho(r) \) for coverages of 0.25 ML (where only fcc-hollow species exist) and 0.5 ML (where fcc-hollow and atop species coexist), which we denote \( \Delta \rho_{0.25}(r) \) and \( \Delta \rho_{0.5}(r) \), respectively. As can be seen from Eq. (2), \( \Delta \rho(r) \) determines the dynamic dipole moment, and thus the peak intensity. Therefore the difference in the peak intensity between the cases of 0.25 ML (1.171) and 0.5 ML (0.363) should be reflected in the quantity \( \Delta \rho_{0.5}(r) - \Delta \rho_{0.25}(r) \). Since the contributions from the small displacements of the positive N and O ions to \( \Delta \rho_{0.25}(r) \) and \( \Delta \rho_{0.5}(r) \) cancel each other for a fixed \( \Delta Q \), \( \Delta \rho_{0.5}(r) - \Delta \rho_{0.25}(r) \) is equal to the quantity \( \Delta n_{0.5}(r) - \Delta n_{0.25}(r) \), where \( n \) denotes the electron density distribution instead of the charge density distribution. We plot this quantity in Fig. 3. The horizontal line of Fig. 3 corresponds to the long diagonal line of the unit cell (shown by a dashed line in the inset). On this line there are fcc-hollow and atop sites, whose positions are indicated by arrows. Significant changes can be seen around the NO molecule and the surface Pt atom at the atop site. Since the atop site is not occupied by NO at 0.25 ML, \( \Delta n_{0.25}(r) \) does not contribute to these changes, which originate solely from \( \Delta n_{0.5}(r) \). Then one can see that at 0.5 ML electron transfer occurs from the NO molecule to the surface Pt atom at the atop site when the N-O bond at the fcc-hollow site is elongated. Obviously, electron transfer takes place in the opposite direction when the N-O bond is shrunk.

The mechanism of how the intensity of the fcc-hollow peak is weakened is schematically shown in Fig. 4. The NO molecule in the gas phase has a permanent dipole moment in the direction from the oxygen atom to the nitrogen atom. In the adsorbed state with the N-end down, this direction is toward the surface (as opposed to the direction toward the vacuum). When the N-O bond is elongated at the fcc-hollow site, the change in the dipole moment is also toward the surface (shown by an orange arrow in Fig. 4). On the other hand, electron transfer from the NO molecule to the surface Pt atom at the atop site corresponds to the change in the dipole moment in the direction toward the vacuum (shown by a green arrow in Fig. 4). Thus the change in the dipole moment at the fcc-hollow site is screened partially by the change in the dipole moment at the atop site, resulting in a reduced dynamic dipole moment. If there is no NO molecule at the atop site, there is no way to screen the dynamic dipole moment with respect to the N-O vibration at the fcc-hollow site.
IV. CONCLUSION

In conclusion, in the vibrational spectra of NO/Pt(111), we showed why the peak of fcc-hollow species, which is prominent in the absence of atop species, is greatly diminished when atop species are present. In the presence of atop species, dynamic electron transfer at atop sites screens the dynamic dipole moment of fcc-hollow species, resulting in a greatly diminished peak. The induced electron transfer might be derived from the dipole-dipole interaction, which tends to direct one dipole opposite to the other. If this is the case, this mechanism of screening the dynamic dipole moment is expected to be operative not only for NO/Pt(111) but also for other systems, since the dipole-dipole interaction is universal.

Acknowledgments

We are grateful to Prof. K. Terakura for valuable advice. We also thank Dr. M. Matsumoto for providing us with his experimental data. The calculations were performed using the supercomputers at National Institute for Materials Science and at Institute for Solid State Physics, University of Tokyo.

[1] H. Ibach, Electron Energy Loss Spectrometers (Springer, Berlin, 1991).
[2] P. Hollins and J. Pritchard, Prog. Surf. Sci. 19, 275 (1985).
[3] P. Hollins, Surf. Sci. Rep. 16, 51 (1992).
[4] J. L. Gland and B. A. Sexton, Surf. Sci. 94, 355 (1980).
[5] B. E. Hayden, Surf. Sci. 131, 419 (1983).
[6] M. Matsumoto, K. Fukutani, T. Okano, K. Miyake, H. Shigekawa, H. Kato, H. Okuyama, and M. Kawai, Surf. Sci. 454-456, 101 (2000).
[7] M. Matsumoto, N. Tatsumi, K. Fukutani, and T. Okano, Surf. Sci. 513, 485 (2002).
[8] H. Aizawa, Y. Morikawa, S. Tsuneyuki, K. Fukutani, and T. Ohno, Surf. Sci. 514, 394 (2002).
[9] Y. Morikawa, Phys. Rev. B 63, 033405 (2001), and references therein.
[10] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[11] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).