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Determination of the molecular symmetry of acetylene on Ni(001) by electron-impact scattering

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Angle-dependent electron-energy-loss measurements of acetylene on Ni(001) are used to deduce molecular symmetry on the surface by consideration of selection rules for vibrational excitation by impact scattering. Chemisorbed acetylene has C_2 symmetry with a mirror plane along $\langle 110 \rangle$ and a molecular plane tilted relative to the surface.

Electron-energy-loss spectroscopy (EELS) is a powerful method for studying vibrations of adsorbed species with the potential of exciting all the modes by dipole and impact scattering mechanisms.¹ The vibrational interaction via the dipole mechanism takes place with the electron far from the surface. On the other hand, electrons that lose energy by impact scattering interact locally with the adsorbate-substrate complex and can provide additional symmetry and geometric information. This capability was shown in impact scattering calculations by Tong *et al.*² for CO/Ni(011), which found two types of symmetry selection rules which can be used to obtain local symmetry and bond site information. One rule has been applied to determine the polarization of a parallel mode of atomic hydrogen on W(110) (Ref. 3) using off-specular collection. In the present work, we vary the crystal azimuth with respect to the scattering plane and use both symmetry rules to determine the local symmetry of acetylene on Ni(001) at $\cong 170$ K.

A new EELS spectrometer capable of detecting scattered electrons in and out of the incidence plane is used. In addition to the variable analyzer motion, the sample manipulator allows the crystal to be rotated about its normal to vary the alignment of surface principle axes with respect to the plane of incidence. The experiments discussed here consider in-plane scattering which is required to apply the selection rules; the angle of incidence is 65° from the surface normal. The resolution is set between 5–8 meV. *In situ* low-energy-electron diffraction (LEED) and Auger electron spectroscopy (AES) are further used to characterize surface order and cleanliness. The surface is cleaned by repeated cycles of Ar ion sputtering and annealing; the chamber is ion pumped

during experiments and the working pressure is $< 1.3 \times 10^{-8}$ Pa. The accuracy of the crystal azimuthal alignment with respect to the scattering plane is estimated to be within $\cong 2^\circ$ by LEED. The crystal azimuthal angle is defined as follows: $\phi_x = 0^\circ$ when $\langle 010 \rangle$ -type mirror planes are both \parallel and \perp to the scattering plane and $\phi_x = 45^\circ$ when $\langle 110 \rangle$ -type mirror planes are both \parallel and \perp to the scattering plane.

Figure 1(a) compares EELS spectra taken on-specular ($\theta_i = \theta_s = 65^\circ$) and 30° off-specular for a 2-L ($1 \text{ L} = 10^{-6}$ torr sec) exposure of C_2H_2 on Ni(001) at $\cong 170$ K for $\phi_x = 0^\circ$. The polar angle dependence of the loss intensities indicate that the 117- and 362-meV losses are impact excited; the 92-, 100-, and 162-meV losses are largely dipole excited; and the 180-meV loss is weakly dipole excited. The 140-meV loss appears to be mostly impact excited. A weak loss feature observed at 60–65 meV is tentatively assigned to a metal-carbon mode. The 162-meV loss corresponds to the CC stretching mode as found in previous EELS work.⁴ The 362-meV loss is straightforwardly assigned to the symmetric and asymmetric CH stretching models, $\nu_{CH \text{ sym}}$ and $\nu_{CH \text{ asym}}$, respectively, which are not sufficiently split to be resolved. The frequency shifts of ν_{CC} and ν_{CH} from the gas phase acetylene values⁵ imply a strong orbital rehybridization ($sp^{2.6}$) and a *cis*-distorted molecular species.^{6(a)} LEED observations in the course of these experiments show a weak, diffuse $c(2 \times 2)$ structure for < 10 -L exposures. This implies that ordered domains of two orthogonally oriented structures coexist. Further assignments will be made using the impact scattering selection rules which are discussed below together with the surface selection rule for dipole scattering.

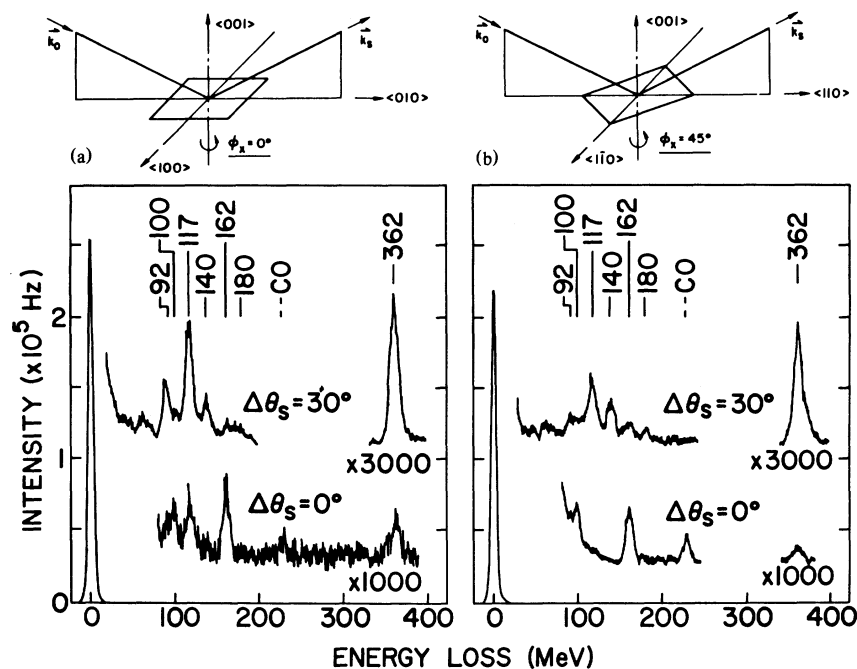


FIG. 1. EELS spectra for acetylene adsorbed on Ni(001) at $\cong 170$ K. Angle of incidence = 65° , impact energy $\cong 5$ eV, specular and in-plane off-specular collection. (a) Scattering plane aligned along $\langle 010 \rangle$; (b) scattering plane aligned along $\langle 110 \rangle$.

In order to apply the mirror symmetry selection rules for the impact scattering modes, the crystal azimuth was varied with respect to the scattering plane (ϕ_x) between the nonequivalent mirror planes of the clean crystal for specular (and off-specular) scattering conditions. EELS spectra for analogous spectrometer collection geometries as in Fig. 1(a) but with the crystal aligned with $\phi_x = 45^\circ$ are presented in Fig. 1(b). The principle difference is that the 117-meV loss is markedly attenuated for $\phi_x = 45^\circ$ (there appears to be a slight diminution of the 362-meV loss also). This type of azimuthal behavior for the 117-meV loss has not been observed previously for a molecular species and the interpretation of the data using the observation in the focus of this paper. No new modes are observed for azimuthal alignments between the two crystal mirror planes. The attenuation of a loss upon crystal azimuthal rotation cannot occur for long-range dipole scattering (specular collection) and verifies the fact that the 117-meV mode is impact excited. For large acetylene exposures this azimuthal angle-dependent attenuation was not observed.

The selection rules are considered in more detail for the interpretation of the azimuthal behavior of EELS loss intensities. These rules predict the following:

(1) An impact-excited mode that is odd with respect to reflection about a mirror plane which is parallel to the scattering plane will not be observed

for any polar collection angle.

(2) An impact-excited mode that is odd with respect to reflection about a mirror plane which is perpendicular to the scattering plane will not be observed for specular collection. (Rotation symmetry about an axis \perp to the surface is a sufficient condition for attenuation on-specular but does not apply here.⁷) The derivation is based on time-reversal invariance for incoming and outgoing waves in the *elastic approximation* which is considered to be valid for most EELS experiments where the loss energy is a small fraction of the impact energy.

Interference maxima and minima can occur independent of symmetry considerations at different impact energies as was shown in the multiple-scattering calculation for CO/Ni(001) (Ref. 2). However, it is observed in the present case that the azimuthal attenuation of the 117-meV loss occurs for various impact energies between $\cong 3.5$ and $\cong 10$ eV.⁸ This, together with the aforementioned coverage-dependent behavior, supports the conclusion that the attenuation of the 117-meV loss at $\phi_x = 45^\circ$ is associated with a symmetry effect.

The azimuthal attenuation that is observed for the 117-meV loss is interpreted as being a direct consequence of the mirror symmetry selection rules described previously and occurs due to the particular symmetry of the adsorbate-substrate complex. This implies that (1) $\langle 110 \rangle$ is a mirror plane of the adsorbate-substrate complex, and (2) the 117-meV

mode is odd with respect to reflection about the $\langle 110 \rangle$ mirror plane. The types of molecular configurations and normal modes for the 117-meV loss that can satisfy these conditions are considered in Fig. 2 where we show several possible orientations (columns) and mode assignments (rows) from which we select one consistent with all our observations. This mode can be (a) the in-plane bending mode $\delta_{\text{CH asym}}$, with point group symmetry C_{2v} or C_s (CC axis \parallel surface); (b) the out-of-plane bending mode ρ_{CH} , with symmetry C_{2v} or C_s (CC axis \parallel surface); or (c) the out-of-plane bending mode ρ_{CH} , with symmetry C_s . Here the CC axis is tilted with respect to the surface, and the mirror plane is parallel to the CC axis.

Figure 2 also indicates whether the symmetry rules predict an intensity null for an impact-excited loss corresponding to an in-plane or an out-of-plane bending mode; the scattering direction is depicted by large arrows \parallel or \perp to mirror plane(s) of the chemisorbed complex. Due to the presence of domains, experimental observations reflect the combination of predictions for the two orthogonal scattering directions. For example, our observations on-specular imply that $\langle 110 \rangle$ is a mirror plane, and the fact that the 117-meV mode returns about 20° off-specular allows us to dismiss the arrangement of Fig. 2(b) (column 2) directly. In order to proceed with the determination of the structure, it is necessary to assign the 117-meV mode using arguments about the loss energies consistent with the symmetry information we have deduced.

The remaining mode assignments are made with comparison to optical spectroscopy studies of molecular structural analogs such as the transition-metal complex $\text{CO}_2(\text{CO})_6\text{C}_2\text{H}_2$ (Ref. 9) and dichloroethylene⁵ and to other EELS studies for chemisorbed hydrocarbons.^{6,10} Comparison to the loss energies of the out-of-plane bending modes for chemisorbed benzene on Ni(111) (Ref. 10) makes it reasonable to assign this mode as $\rho_{\text{CH asym}}$ with its counterpart $\rho_{\text{CH sym}}$ (dipole allowed) in the 92–100-meV region. This assignment is consistent with $\rho_{\text{CH sym}}$ being dipole excited where the molecular plane is tilted with respect to the surface. These considerations lead us to the tilted geometry depicted in Fig. 2(b) (column 3). This mode assignment is further supported as the 117-meV loss is similar in relative intensity for off-specular collection to the modes at 107 and 108 meV for C_2H_2 on Ni(111)^{6(b)} and Pd(111),^{6(e)} respectively, which were assigned as $\rho_{\text{CH asym}}$. Also, the amount of splitting between $\rho_{\text{CH sym}}$ and $\rho_{\text{CH asym}}$ in the present assignment is comparable in magnitude to those studies and to $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$. It is noted, however, that this molecular orientation does not agree with that deduced for room-temperature adsorption using a LEED I - V analysis.¹¹ This symmetry also predicts an attenuation of $\nu_{\text{CH asym}}$, but this

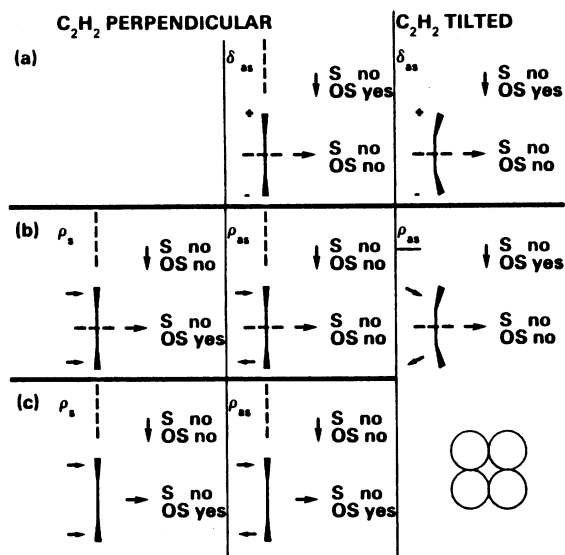


FIG. 2. Tested mode-symmetry combinations for acetylene on Ni(001). Approximate mode polarization is given by small arrows or \pm (= in/out plane of page). Dashed lines denote mirror planes; large arrows denote the direction of parallel momentum transfer. The ability to observe the particular mode for specular (S) or off-specular (OS) collection dictated by the selection rules is stated. Concluded assignment/geometry is underscored and shown with properly oriented surface unit cell at lower right.

cannot be evaluated quantitatively since $\nu_{\text{CH sym}}$ and $\nu_{\text{CH asym}}$ cannot be separately resolved.

Some ambiguities exist in the assignment of $\delta_{\text{CH sym}}$ and $\delta_{\text{CH asym}}$ which might be assigned at 140 and 180 meV, respectively, similar to Ni(111).^{6(b)} First, the 180-meV peak is dipole excited while $\delta_{\text{CH asym}}$ belongs to the "A" representation (i.e., not dipole allowed). Second, a 40-meV splitting is rather large considering that for the aforementioned cobalt complex a 16-meV splitting is observed. The fact that such a large splitting was observed for C_2H_2 on Ni(111) is likely due to the fact that no symmetry exists; the hydrogens are in differing local environments whereby the designation of symmetric and asymmetric modes is not formally correct. We thereby tentatively assign the 140-meV mode as being the only in-plane mode observed. If the 140-meV loss was $\delta_{\text{CH asym}}$, it should obey the azimuthal symmetry rules, which is not the case. We thereby assign this loss to $\delta_{\text{CH sym}}$ and leave the 180-meV dipole loss unassigned at this point.

The broadened loss in the 92–100-meV region could be explained by decomposition of the molecular species occurring over time possibly associated with the presence of defects on the surface. Based on earlier studies, fragmentation of the molecule under low-temperature conditions is not expected¹² but could produce a loss in this region. Such a fragment has been observed on Ni(111) and has been inter-

preted as a bending mode of a CH species.¹³ For high acetylene exposures at low temperatures the mirror symmetry is also lost and a slight shift of the 100-meV loss to lower energy is observed. This might be explained by fragmentation or a compression of the adsorbate structure. If a minority non-symmetric acetylene species coexists with the C_s species, the lack of full attenuation at $\phi_x = 45^\circ$ could be explained for lower coverages.⁸

In summary, we have applied the selection rules for impact scattering as the central consideration for the determination of adsorbate-substrate mirror planes and the assignment of the CH out-of-plane bending modes. There is a reduction of the surface symmetry upon adsorption of acetylene to C_s with a

molecular orientation such that $\langle 110 \rangle$ -type mirror planes exist for the complex. The deduction of molecular symmetry information as presented here indicates the unique ability of short-range electron scattering to probe local structure. This also provides new and complementary information for making mode assignments. It is expected that this type of analysis will have further application to molecular chemisorption studies in the future.

ACKNOWLEDGMENT

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¹H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

²S. Y. Tong, C. H. Li, and D. L. Mills, *Phys. Rev. Lett.* **44**, 407 (1980).

³G. B. Blanchet, N. J. DiNardo, and E. W. Plummer, *Surf. Sci.* **118**, 496 (1982).

⁴An off-specular spectrum of C_2H_2 on C_2D_2 on Ni(001) at $\cong 20$ -meV resolution which confirms that ν_{CC} is correctly assigned is given in W. Ho, Ph.D. thesis (University of Pennsylvania, 1979) (unpublished).

⁵G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1945), Vol. 2, p. 329.

⁶(a) J. E. Demuth and H. Ibach, *Surf. Sci.* **85**, 365 (1979); (b) H. Ibach and S. Lehwald, *J. Vac. Sci. Technol.* **18**, 625 (1981); (c) **15**, 407 (1978); (d) L. H. Dubois, D. G. Castner, and G. A. Somorjai, *J. Chem. Phys.* **72**, 5234

(1980); (e) J. Gates and L. L. Kesmodel, *ibid.* **76**, 4281 (1982).

⁷With twofold rotation symmetry the loss will not be seen on specular for any azimuthal orientation. This is not observed in the present results.

⁸The degree of attenuation, I_{45}/I_0 , is ≤ 0.25 for the low-coverage species.

⁹Yuji Iwashita, *Inorg. Chem.* **9**, 1178 (1970).

¹⁰S. Lehwald, H. Ibach, and J. E. Demuth, *Surf. Sci.* **78**, 577 (1978).

¹¹G. Casalone, M. G. Cattania, and M. Simonetta, *Surf. Sci.* **103**, L121 (1981).

¹²J. E. Demuth and D. E. Eastman, *Phys. Rev. Lett.* **32**, 1123 (1974).

¹³J. E. Demuth and H. Ibach, *Surf. Sci.* **78**, L238 (1978).