Effects of Rotational-Symmetry Breaking on Physisorption of Ortho- and Para-H_2 on Ag(111)

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Quantum-state-selective thermal desorption of H_2 weakly physisorbed on Ag(111) demonstrates significantly different desorption features between the nuclear-spin modifications. An energy shift due to the rotational-symmetry breaking induced by an anisotropic interaction affects not only the enthalpy but also the entropy of adsorption. The preexponential factor for desorption of the ortho-H_2 is about three times as large as that of the para-H_2. The entropy difference indicates a perpendicular orientation preference of anisotropic physisorption potential, which also suggests the importance of partial hybridization interaction for weak physisorption.

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The van der Waals (vdW) interaction is ubiquitous in nature and fundamentally important for atoms and molecules in proximity to surfaces [1–3]. This long-range dispersive attraction in competition with the short-range repulsion forms a weak physisorption potential [4,5]. The potential can be anisotropic, and the anisotropic term of the potential brings about rotational-symmetry breaking of ad molecules. Whereas the rotational motion for classical molecules is described by vibrational motion of molecular axis around the equilibrium orientation to surfaces [6,7], the quantum molecule of hydrogen, which has large kinetic energy of rotation, retains its rotational motion even in the anisotropic potential resulting in the lifting of the rotational-state degeneracy [5,7–9].

Due to the symmetry with respect to the permutation of the nuclei, the rotational quantum number (J) of H_2 is correlated to the quantum number of the total nuclear spin (I), i.e. the rotational levels with even and odd J belong to the para ($I = 0$) and ortho ($I = 1$) modifications, respectively [10–12]. A crucial consequence due to the rotational-symmetry breaking for molecular hydrogen is dependence of physisorption properties on the nuclear-spin state including the physisorption energy and rotational partition function, which has been applied for nuclear-spin isomer separation. An essential question still under debate in this fundamental and extremely weakly physisorbed system is orientational preference and its underlying mechanism.

In the conventional theory for physisorption on noble-metal surfaces [4,5], the attractive and repulsive parts of the interaction are described by the vdW interaction and the Pauli repulsion, respectively, which leads to slight preference of parallel orientation to the surface. Previous experimental studies with electron energy loss spectroscopy [9,13–16] and molecular beam scattering [17,18] have revealed that molecular hydrogen physisorbed on smooth metal surfaces such as Ag(111) and Cu(100) behaves as a nearly free rotator. While these previous experiments supported a slight parallel-orientation preference [16–18], Wilzén *et al.* suggested a possibility of perpendicular-orientation preference [19]. In combination with the calculation on the basis of the second-order perturbation, they suggested the importance of partial hybridization interaction between the surface free electron and the unoccupied molecular orbital [19]. Moreover, recent *ab initio* calculations with multireference configuration interaction have shown significant preference of perpendicular orientation of H_2 to the surface [20,21] in contrast to the commonly accepted theory. The anisotropic potential and resultant orientation preference of molecular hydrogen are thus apparently controversial, and further sophisticated experiments are strongly required.

Motivated by these studies, we adopted rotational-state-resolved temperature programmed desorption (TPD) capable of probing the kinetics of H_2 on surfaces including both the adsorption enthalpy and entropy. As the anisotropic potential couples the molecular rotation with the external stretch relative to the surface, J dependence of the center-of-mass motion reflects the anisotropic potential energy surface. On the basis of the experimental data, we discuss that the anisotropic potential of H_2 prefers perpendicular orientation on Ag(111).

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base operating pressure below 2×10^{-8} Pa. The Ag(111) single-crystal substrate was cleaned by cycles of Ar^+ bombardment at 500 eV and annealing at 800 K for 1 min. The Auger-electron spectra revealed that the substrate was chemically clean with no trace of oxygen contaminants and the low-energy electron diffraction showed a sharp 1×1 pattern with low background. Undesirable surface defects such as vacancies and steps on the Ag(111) were evaluated to be less than 2% [6]. After cleaning, the sample was cooled to 10 K by a liquid-He transfer type cryostat and exposed to normal-H_2 introduced with a flux-controlled doser [6,22], where the hydrogen dosage is described as the Langmuir unit ($1\ \mathrm{L} = 1.33 \times 10^{-4}\ \mathrm{Pa \cdot s}$). The sample temperature was measured by a calibrated type E thermocouple. About 30 s after the dosage the sample was heated to 30 K by radiation from a W filament behind the sample at a heating rate of 2.5 K/s to induce thermal desorption of H_2. TPD spectra of physisorbed H_2 were taken using either a differentially-pumped quadrupole mass spectrometer (QMS, $m/e = 2$) through an aperture of 4 mm in diameter [6] or a specific H_2-$Q(J)$ transition of the $(2+1)$ resonance-enhanced multiphoton ionization (REMPI) via the $E, F^1\Sigma_g^+$ state [11,12,23] for the rotational-state-selective detection.

Figure 1(a) shows QMS-TPD spectra at various H_2 dosages. At 0.5 L dosage, the desorption signal is observed at 12–28 K with a peak temperature of ~17 K. While the TPD spectrum grows until 6.4 L without any change of the spectral shape, it saturates above 6.4 L dosage. It is worth noting that the peak temperature and spectral shape of the TPD spectrum remain unchanged within the experimental accuracy with increasing initial H_2 coverage [24], which point to the first-order desorption kinetics with the coverage-independent parameters of the activation energy for desorption (E_d) and the preexponential factor (ν) in the Polanyi-Wigner (PW) formula [25]. Such coverage-independent characteristics of the desorption parameters suggest a weak H_2-H_2 intermolecular interaction [26,27] and a negligible coupling between the in-plane and out-of-plane motion [20]. We note here that the QMS-TPD spectral shape shown in Fig. 1(a) is apparently different from that of the typical first-order desorption [28] in that the trailing side of the spectra is broader than the leading side and the entire spectral width is rather broad [29] in spite of the homogeneity of the noncorrugated Ag(111) surface [6,18,20]. We confirmed that almost the same QMS-TPD spectrum of physisorbed H_2 is also observed on a highly oriented pyrolytic graphite (HOPG) surface.

Figure 1(b) shows the REMPI-TPD spectra of $J = 0$ (p-H_2) and $J = 1$ (o-H_2) measured about 30 s after the H_2 dosage of 0.2 L with a heating rate of 2.5 K/s . No REMPI-TPD signal of $J \geq 2$ was observed. While the spectral shape of $J = 0$ is asymmetric, i.e. the trailing side is broader than the leading side, that of $J = 1$ is rather symmetric. It should be noted that the effect of ortho-para conversion on the TPD spectrum can be neglected because the conversion time is sufficiently longer than the TPD measurement time [24]. Also shown in the figure is the sum of the $J = 0$ and $J = 1$ desorption spectra and the QMS-TPD spectrum. We can recognize that the $(J = 0)+(J = 1)$ REMPI-TPD spectrum is almost identical to the QMS-TPD spectrum. This agreement is reasonable because the ortho- and para-H_2 are both in their lowest rotational states of $J = 1$ and $J = 0$ below 30 K and the QMS detects both of them without distinction [11,12]. We note here that the observed signal exclusively originates from H_2 directly desorbed from the surface: If there were H_2 desorbed from the sample holder followed by scattering from the chamber wall at 300 K, significant intensities of $J \geq 2$ would be observed, and the $(J = 0)+(J = 1)$ REMPI-TPD spectrum would deviate from the QMS-TPD spectra.

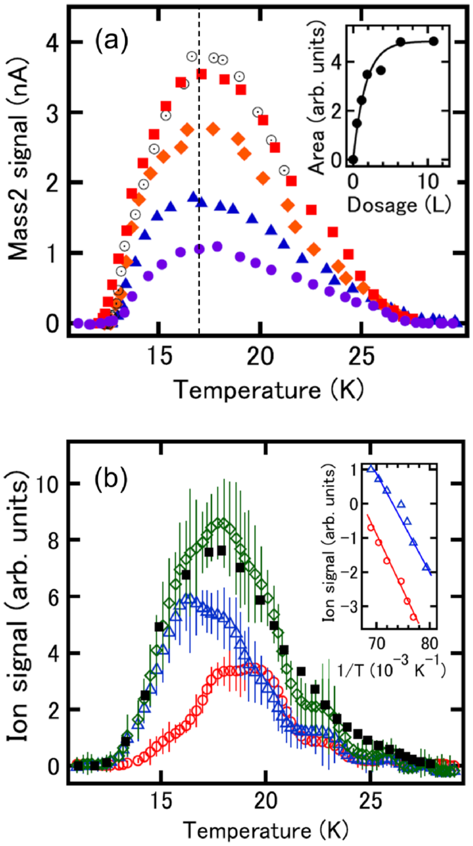

FIG. 1 (color online). (a) QMS-TPD spectra of H_2 from Ag(111) measured about 30 s after 0.5 (filled circle), 1.1 (filled triangle), 3.7 (filled diamond), 6.4 (filled square), and 10.8 L (dotted circle) dosages of normal-H_2 at 10 K with a heating rate of 2.5 K/s. The vertical dashed line at 17 K is an eye guide for the peak position. (Inset) Integrated QMS-TPD intensity as a function of the H_2 dosage. (b) REMPI-TPD spectra for $J = 0$ of para-H_2 (open triangle) and $J = 1$ of orth-H_2 (open circle) measured about 30 s after 0.2 L dosage of H_2 on Ag(111) at 10 K with a heating rate of 2.5 K/s. The plotted value is the average of some independent measurements at each data point and the error bars represent the standard deviation. The major contribution of deviation is laser fluctuations. The sum of the $J = 0$ and $J = 1$ REMPI-TPD spectrum (open diamond) and a QMS-TPD spectrum (filled square) are shown for comparison. (Inset) Arrhenius plots of the leading edge of the $J = 0$ and the $J = 1$ REMPI-TPD spectra. The solid lines are linear fits.

The inset of Fig. 1(b) shows the Arrhenius plot of the leading-edge region of the $J = 0$ and $J = 1$ desorption spectra. From the slope of linear fits, which is the so-called leading-edge analysis [30], the E_d of $J = 0$ and $J = 1$ is derived to be 26 ± 2 and 28 ± 2 meV, respectively, without any supposition of ν . The E_d for the $J = 0$ state obtained here is in agreement with the energy value for the ground state in the physisorption potential of p-H_2, 25.7 ± 0.1 meV [8]. Then, the value of ν for the $J = 0$ and $J = 1$ states can be determined from the comparison of the REMPI-TPD spectra with the simulated desorption spectra following the first-order PW equation [28]

$$-\frac{d\Theta}{dT} = \left[\frac{\nu}{\beta}\exp\left(-\frac{E_d}{k_B T}\right)\right]\Theta, \tag{1}$$

where Θ is the H_2 coverage, β the heating rate, T the substrate temperature, and k_B the Boltzmann constant. As discussed in the Supplemental Material [24], no simulated TPD spectra using constant ν values fit the entire spectrum [24]. A previous study has shown that ν can be a function of Θ and T [31]. As ν is independent of Θ from the above discussion of QMS-TPD, dependence of ν on T should be essential in the present system. Figure 2 shows the simulated desorption spectra of the $J = 0$ and $J = 1$ states using temperature-dependent ν with $\beta = 2.5$ K/s, $E_d = 26$ and 28 meV, respectively. As shown in the inset of Fig. 2, the ν's of both the $J = 0$ and $J = 1$ states at the leading-edge region are of the order of 10^8 s^{-1} and decrease monotonically to 10^6 s^{-1} with increasing temperature. Although these values are smaller than the typical frequency factor of physisorbed species ($\sim 10^{11}$ s^{-1}), a detailed study of QMS-TPD spectra for ^{3}He and ^{4}He physisorbed on Pt(111) by Niedermayer also showed ν can be of the order of 10^9 s^{-1} in the first-order thermal desorption process [25]. These experimental results thus indicate that the value of ν for weakly physisorbed light-mass species on low-corrugated surfaces tends to be smaller than the typical value for heavier physisorbates. It is worth noting here that the ν of $J = 1$ is about three times as large as that of $J = 0$. We discuss in the following the origin of such J dependence of E_d and ν based on the energy shift due to the rotational-symmetry breaking.

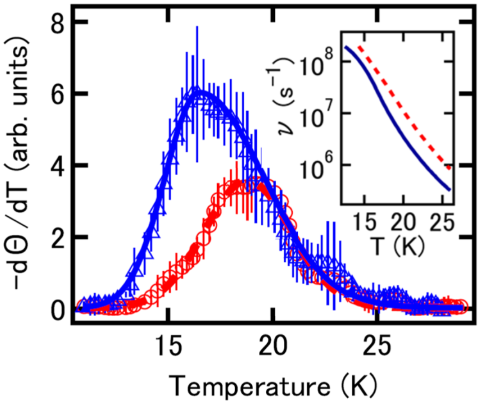

FIG. 2 (color online). Simulated TPD spectra of $J = 0$ (blue solid line) and $J = 1$ (red dashed line) with $E_d = 26$ meV for $J = 0$ and 28 meV for $J = 1$, $\beta = 2.5$ K/s, and the temperature-dependent ν shown in the inset. The REMPI-TPD spectra of $J = 0$ (open triangle) and $J = 1$ (open circle) are also shown for comparison. (Inset) Temperature-dependent ν of $J = 0$ (blue solid line) and $J = 1$ (red dashed line).

On a low-corrugated surface like Ag(111), the physisorption potential of H_2 is almost independent of φ and written as $V(z,\theta) = V_0(z) + V_2(z)P_2(\cos\theta)$, where z is the distance between the molecular center of mass and the surface, φ and θ the azimuthal (in-plane) and polar (out-of-plane) angles of the molecular axis relative to the surface, $P_2(\cos\theta)$ the second-order Legendre polynomial, $V_0(z)$ and $V_2(z)$ the isotropic and anisotropic physisorption potential, respectively [8,18]. Figure 3 shows the energy shifts of the $J = 0$ and $J = 1$ states from the free gas phase to the physisorbed phase. In an isotropic potential $V_0(z)$, both the $J = 0$ and $J = 1$ states are stabilized by the same energy $\varepsilon(n)$, where n is the quantum number of the bound state corresponding to the external stretch mode in the $V_0(z)$ potential. When the anisotropic surface field is not so large, the $V_2(z)P_2(\cos\theta)$ term can be treated as the first-order perturbation relative to the free molecular rotation in the $V_0(z)$ potential. Within the first-order perturbation, the wave function is regarded unaltered, whereas the rotational energy shift is represented by $\Delta\varepsilon(n,J,M) = \tilde{V}_2(n)\langle J,M|P_2(\cos\theta)|J,M\rangle$, where $|J,M\rangle$ is the rotational wave function written by spherical harmonics $Y_{J,M}(\theta,\varphi)$, M is the z component of J, $\tilde{V}_2(n)$ is the matrix element $\langle n|V_2(z)|n\rangle$, and $|n\rangle$ is the wave function corresponding to the n-th energy level of the external stretch in the isotropic potential, respectively. The rotational matrix element is given as [5,13]

$$\langle J,M|P_2(\cos\theta)|J,M\rangle = \frac{3}{2J+3}\left(\frac{J^2-M^2}{2J-1} - \frac{J}{3}\right). \tag{2}$$

Whereas the $(J,M) = (0,0)$ state thus shows no shift, the M degeneracy of the $J = 1$ state is lifted with an energy splitting of $(3/5)\tilde{V}_2(n)$. The $(J,M) = (1,0)$ state is stabilized to $(3/5)\tilde{V}_2(n)$ compared to the $(1, \pm 1)$ states if the sign of $\tilde{V}_2(n)$ is negative, i.e. preferred perpendicular orientation, and vice versa (Fig. 3). The E_d of p-H_2 ($J = 0$) in the ground state ($n = 0$) is given as $|\varepsilon(0)|$, while that of o-H_2 ($J = 1$) for the stable state is $|\varepsilon(0) + (2/5)\tilde{V}_2(0)|$ for $\tilde{V}_2 < 0$ and $|\varepsilon(0)\text{-}(1/5)\tilde{V}_2(0)|$ for $\tilde{V}_2 > 0$. Since E_d was 26 meV for p-H_2 ($J = 0$) and 28 meV for o-H_2 ($J = 1$) from the REMPI-TPD results, the value of $\varepsilon(0)$ is -26 meV. If we assume the sign of $\tilde{V}_2(0)$ is negative, $\tilde{V}_2(0)$ is calculated to be -5 meV, whereas $\tilde{V}_2(0)$ is $+10$ meV if $\tilde{V}_2(0)$ is positive. Although the sign of $\tilde{V}_2(0)$ cannot be uniquely determined only from the value of E_d, we discuss here that it is indeed possible if we consider the difference of ν between o-H_2 and p-H_2.

In the PW model based on the transition state theory, the preexponential factor is given by $\nu = \alpha(k_B T/h)(f_*/f_{\text{phys}})$, where α is the transmission coefficient, h the Planck constant, f_* and f_{phys} the partition functions of the activated complex (nearly isolated state) and physisorbed

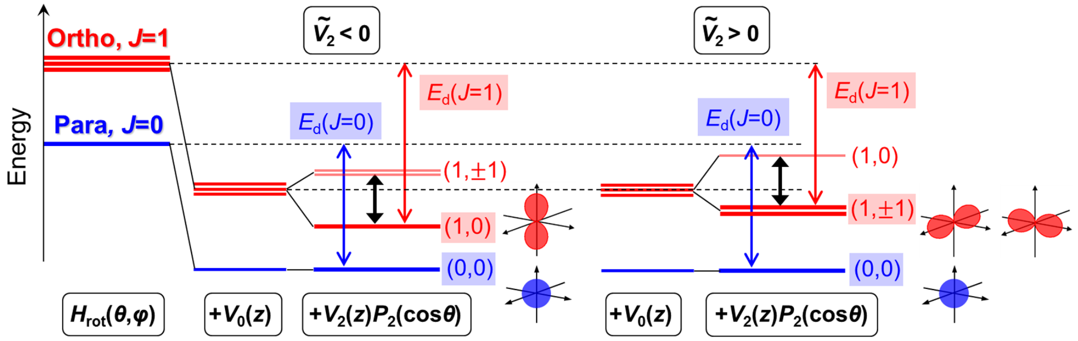

FIG. 3 (color online). Energy level diagram for $J = 0$ and $J = 1$. The number of lines in each level means the rotational degeneracy. $H_{\mathrm{rot}}(\theta, \varphi)$ represents the Hamiltonian for the rotational motion of a free rotor. Schematic illustrations show the probability distribution of the molecular axis for the respective states, $|Y_{0,0}|^2$, $|Y_{1,0}|^2$, $|Y_{1,1}|^2$, and $|Y_{1,-1}|^2$. See main text for details of the nomenclature.

complex, respectively [32]. The physisorbed H_2 behaves as two-dimensional gas freely mobile in the in-plane direction [24], and the influence of the weak physisorption on the internal stretch of H_2 and the surface phonon of Ag(111) is reasonably assumed to be negligible [20]. Hence, f_*/f_{phys} due to these degrees of freedom becomes unity for both o-H_2 and p-H_2 in a first approximation. On the other hand, the rotational partition function is different between o-H_2 and p-H_2. For H_2, the rotational partition function of the isolated state is $f_*^{\mathrm{rot}}(I) = g_I \sum_J g_J \exp\,[-BJ(J+1)/k_B T]$, and that of the nearly free rotation of the physisorbed state is $f_{\mathrm{phys}}^{\mathrm{rot}}(I) = g_I \sum_{J,|M|} g_{J,|M|} \exp[-E(I;J,|M|)/k_B T]$, where $g_I = 2I+1$, $g_J = 2J+1$, $g_{J,|M|} = 2 - \delta_{0,|M|}$, and $E(I;J,|M|)$ is the rotational energy relative to the $J = 0$ for p-H_2 ($I = 0$) and the lowest $|M|$ level of $J = 1$ for o-H_2 ($I = 1$) in the physisorbed state. By defining $F^{\mathrm{rot}}(I) \equiv f_*^{\mathrm{rot}}(I)/f_{\mathrm{phys}}^{\mathrm{rot}}(I)$, we evaluate the ratio of $F^{\mathrm{rot}}(I)$ between o-H_2 and p-H_2 ($F^{\mathrm{rot}}(1)/F^{\mathrm{rot}}(0)$). In the case of $\tilde{V}_2(0) = -5$ meV, $F^{\mathrm{rot}}(1)/F^{\mathrm{rot}}(0)$ is calculated to be about 2.3, while $F^{\mathrm{rot}}(1)/F^{\mathrm{rot}}(0)$ is about 1.5 in the case of $\tilde{V}_2(0) = +10$ meV in the temperature range of 16–23 K. The ν ratio of o-H_2 to p-H_2, i.e. $\nu(I=1)/\nu(I=0)$, between 16 and 23 K is about 2.5 from the inset of Fig. 2, which is similar to the calculated value of $F^{\mathrm{rot}}(1)/F^{\mathrm{rot}}(0) \sim 2.3$ for $\tilde{V}_2 = -5$ meV and apparently different from that of ~ 1.5 for $\tilde{V}_2(0) = +10$ meV . This result clearly indicates a perpendicular orientation preference of the anisotropic potential of H_2 on Ag(111), which is in agreement with recent theoretical studies [20,21]. It is noted that the Pauli repulsion prefers parallel orientation, and that perpendicular orientation preference originates from the attractive part of the interaction. Since a previous theoretical study predicts much smaller anisotropy for the pure vdW interaction [4], the present result of -5 meV suggests essential importance of partial hybridization interaction [19] even in this extremely weak physisorbed system. In the anisotropic potential of -5 meV, almost all (more than 97%) of the o-H_2 ($J = 1$) exist in the $M = 0$ state at 10 K and its molecular axis is out of plane, whereas the molecular axis of p-H_2 ($J = 0$) remains isotropically distributed (Fig. 3), due to the rotational quantum effect 7,27.

In summary, we have investigated the H_2 physisorption on Ag(111) at 10 K by QMS-TPD and REMPI-TPD. The coverage-independent TPD spectra showed the first-order desorption with E_d's of 28 ± 2 meV for o-H_2 ($J = 1$) and 26 ± 2 meV for p-H_2 ($J = 0$). The ν value of o-H_2 was evaluated to be about three times larger than that of p-H_2 from the REMPI-TPD results. These different desorption features between o-H_2 and p-H_2 are ascribed to the anisotropic physisorption potential where the perpendicular orientation is preferred over parallel orientation. The averaged out-of-plane potential anisotropy for the ground physisorbed state is about -5 meV, indicating that contribution of the hybridization interaction is substantial. We note from these results that the term "physisorption" so far used for weakly adsorbed H_2 may well be rephrased as "chemicalphysisorption." Finally, the anomalous temperature dependence of ν would indicate a curious behavior of the transmission coefficient α. To clarify the origin of this anomaly is apparently a challenge of the reaction rate theory and will be the subject of the future study.

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[1] P. Kisliuk, J. Phys. Chem. Solids **3**, 95 (1957).
[2] D. Li, M. H. Zhao, J. Garra, A. M. Kolpak, A. M. Rappe, D. A. Bonnell, and J. M. Vohs, Nat. Mater. **7**, 473 (2008).

[3] S. Li, A. Yu, F. Toledo, Z. Han, H. Wang, H. Y. He, R. Wu, and W. Ho, Phys. Rev. Lett. **111**, 146102 (2013); F. D. Natterer, F. Patthey, and H. Brune, Phys. Rev. Lett. **111**, 175303 (2013).
[4] J. Harris and A. Liebsch, Phys. Scr. **T4**, 14 (1983); J. Harris, P. J. Feibelman, Surf. Sci. **115**, L133 (1982).
[5] P. Nordlander, C. Holmberg, and J. Harris, Surf. Sci. **152–153**, 702 (1985).
[6] Y. Kazama, M. Matsumoto, T. Sugimoto, T. Okano, and K. Fukutani, Phys. Rev. B **84**, 064128 (2011).
[7] L. Pauling, Phys. Rev. **36**, 430 (1930).
[8] C.-F. Yu, K. B. Whaley, C. S. Hogg, and S. J. Sibener, J. Chem. Phys. **83**, 4217 (1985).
[9] K. Svensson and S. Andersson, Phys. Rev. Lett. **78**, 2016 (1997).
[10] W. Heisenberg, Z. Phys. **41**, 239 (1927); D. M. Dennison, Proc. R. Soc. A **115**, 483 (1927).
[11] T. Sugimoto and K. Fukutani, Nat. Phys. **7**, 307 (2011); K. Fukutani and T. Sugimoto, Prog. Surf. Sci. **88**, 279 (2013).
[12] L. Amiaud, A. Momeni, F. Dulieu, J. H. Fillion, E. Matar, and J.-L. Lemaire, Phys. Rev. Lett. **100**, 056101 (2008).
[13] S. Andersson and J. Harris, Phys. Rev. Lett. **48**, 545 (1982).
[14] M. Gruyters and K. Jacobi, Chem. Phys. Lett. **225**, 309 (1994).
[15] K. Svensson, J. Bellman, A. Hellman, and S. Andersson, Phys. Rev. B **71**, 245402 (2005).
[16] A. J. Berlinsky, Phys. Rev. B **26**, 443 (1982).
[17] R. Schinke, V. Engel, and H. Voges, Chem. Phys. Lett. **104**, 279 (1984).
[18] K. B. Whaley, C.-F. Yu, C. S. Hogg, J. C. Light, and S. J. Sibener, J. Chem. Phys. **83**, 4235 (1985).
[19] L. Wilzén, F. Althoff, S. Andersson, and M. Persson, Phys. Rev. B **43**, 7003 (1991).
[20] Y. Kunisada, H. Nakanishi, W. A. Diño, and H. Kasai, J. Vac. Soc. Jpn. **55**, 115 (2012).
[21] G. Cilpa, M. Guitou, and G. Chambaud, Surf. Sci. **602**, 2894 (2008).
[22] T. Sugimoto, T. Okano, and K. Fukutani, J. Vac. Soc. Jpn. **52**, 141 (2009).
[23] A. E. Pomerantz, F. Ausfelder, R. N. Zare, and W. M. Huo, Can. J. Chem. **82**, 723 (2004).
[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.112.146101 for further details of experimental results and discussion.
[25] T. Niedermayer, H. Schlichting, D. Menzel, S. H. Payne, and H. J. Kreuzer, Phys. Rev. B **71**, 045427 (2005).
[26] X.-Z. Ni and L. W. Bruch, Phys. Rev. B **33**, 4584 (1986).
[27] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).
[28] J. W. Niemantsverdriet, K. Markert, and K. Wandelt, Appl. Surf. Sci. **31**, 211 (1988).
[29] W. Frieβ, H. Schlichting, and D. Menzel, Phys. Rev. Lett. **74**, 1147 (1995).
[30] J. B. Miller, H. R. Siddiqui, S. M. Gates, J. N. Russell, J. T. Yates, J. C. Tully, and M. J. Cardillo, J. Chem. Phys. **87**, 6725 (1987).
[31] H. Ibach, W. Erley, and H. Wagner, Surf. Sci. **92**, 29 (1980).
[32] D. A. King, Surf. Sci. **47**, 384 (1975).