

Hopping of the Photohole during Photoemission from Physisorbed N₂: The Influence of Band Formation on Vibrational Excitation

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N₂ physisorbed on top of a Xe spacer layer on Ag(111) and Pd(111) has been studied by angle-resolved and polarization-dependent UV photoemission. The N₂ 1 π_u valence level exhibits a vibrational fine structure due to two multiplets corresponding to the ionic (N₂⁺) and neutral (N₂) states. The neutral-state multiplet is explained through hopping of the photohole during photoemission. We show that its intensity is stronger for emission from the in-plane component of 1 π_u , than for the perpendicular one. This is due to a larger lateral overlap in the former case, as concluded by the observed band formation.

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The linewidth in photoemission is a fundamental and still largely unsolved problem in surface physics. Generally, there are several processes in the condensed state which can reduce the lifetime of the photohole and thus contribute to the broadening compared to the gas phase. Important contributions to the linewidth may arise from coupling of the photohole to excitations in the solid (electron-hole pairs or phonons), phonon sidebands, or site inhomogeneities [1-3].

A characteristic feature of photoemission spectra of molecules in the gas phase is the splitting of the valence levels into a multiplet of peaks due to vibrational excitation in the ionic final state of the photoemission process [4]. The vibrational multiplet is normally not resolved for adsorbed molecules. In the case of physisorbed molecules the interaction of the photohole with the solid is considerably weakened, but phonon-sideband excitation or site inhomogeneities can still contribute to the broadening [2,3]. The first vibration-resolved photoemission spectrum of an adsorbed molecule was reported for the 1 π_g level of O₂ physisorbed on graphite [5]. Another example has been shown by Höfer, Breitschäfer, and Umbach, who adsorbed N₂ on top of Xe physisorbed on the Ni(111) surface [6]. The effect of the spacer Xe layer is to further reduce the influence of the substrate.

Höfer, Breitschäfer, and Umbach showed that the line shape of the 1 π_u level of physisorbed N₂ cannot be reproduced by just convoluting the gas-phase data with an appropriate broadening function. Instead they had to include both the vibrational-excited states of N₂⁺ as well as those of N₂. A hole created by the photoemission process in the gas phase is necessarily localized on the ionized molecule for an "infinite" time, whereas in the physisorbed phase it can be filled by electron transfer from a neighboring molecule. This hopping process is characterized by a time constant τ_h . If τ_h is of the same order of magnitude as the vibrational period in the ionic state of the N₂ molecule, then the final state of the photoemission process is composed of vibrationally excited states of the ionic $A^2\Pi_u$ state (frequency=224 meV) [4] and of vibrational-excited states of the neutral $X^1\Sigma_g^+$ state (fre-

quency=289 meV) [6,7].

If the model of Höfer, Breitschäfer, and Umbach is correct, one expects the strength of the N₂ contribution to vary with the lateral interaction of the N₂ 1 π_u orbitals, which, on the other hand, gives rise to two-dimensional band formation. In order to test this prediction, we performed an angle-resolved and polarization-dependent investigation of a N₂ monolayer separated by a Xe spacer layer from Ag(111) and Pd(111) surfaces. We have found a strong variation of the contributions from the two N₂⁺ and N₂ multiplets with the lateral interaction. Our finding supports the model of Höfer, Breitschäfer, and Umbach and improves the understanding of this new broadening mechanism in photoemission from adsorbed molecules.

The experiments were performed in an UHV chamber with a base pressure of 3×10^{-11} mbar equipped with a hemispherical electrostatic energy analyzer (ADES 400, VG Scientific). The samples were cooled with liquid helium to a temperature which was low enough to allow N₂ multilayers to form, from which we estimate 20 K as an upper limit [8]. The spectra on Ag(111) were recorded at the TGM-7 (toroidal grating monochromator) beam line of BESSY (Berliner Elektronenspeicherringgesellschaft für Synchrotronstrahlung) at a photon energy $h\nu=23.0$ eV. For the measurements on Pd(111) the light source was a He discharge lamp ($h\nu=21.22$ eV) equipped with a polarizer [9]. In both cases the resolution was ≤ 0.1 eV. The monolayer coverage was determined from the distance-dependent binding-energy shift [10]. The results for N₂/Xe/Ag(111) and N₂/Xe/Pd(111) look very similar with regard to both the 1 π_u level and, most important for the following treatment, the 3 σ_g level. Hence, in the following discussion we will not differentiate between the two systems. The difference in binding energy can be reconciled with the different work functions of the two systems [$\Phi=4.0$ eV and $\Phi=4.6$ eV for N₂/Xe/Ag(111) and N₂/Xe/Pd(111), respectively].

In Fig. 1 we report spectra of the N₂ 1 π_u level in which one can clearly recognize the vibrational fine structure. Its details exhibit a marked dependence on the geometri-

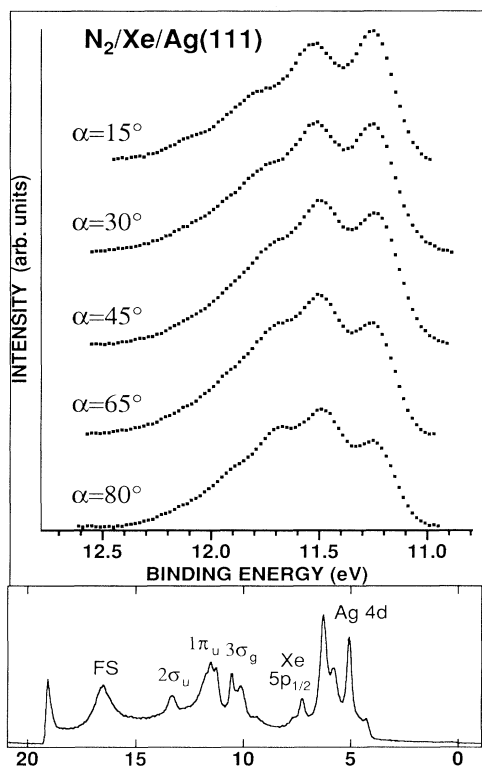


FIG. 1. Normal-emission spectra of the N_2 $1\pi_u$ level of $N_2/Xe/Ag(111)$ recorded at different incidence angles α with respect to the surface normal. A linear background has been subtracted from the measured spectra. In the inset at the bottom a spectrum is shown on an extended scale. The $2\sigma_u$, $1\pi_u$, and $3\sigma_g$ N_2 levels, together with the other features appearing in the spectrum, are indicated. A final-state (FS) peak appears at a fixed kinetic energy irrespective of the photon energy: It is due to a structure in the density of unoccupied states deriving from the N_2 $1\pi_g$ level.

cal arrangement. The peak at the lowest binding energy corresponds to an electronic transition without vibrational excitation [4] (from now on referred to as the $n=0$ peak): Its intensity monotonically grows when going from grazing incidence to near normal incidence. Another difference between the two extreme cases $\alpha=80^\circ$ and $\alpha=15^\circ$ concerns the spacing between the vibrational levels.

The curves of Fig. 1 were fitted with a superposition of two vibrational multiplets whose spacings correspond in the hopping model [6] to the stretching vibration ν^+ in the ionic $A^2\Pi_u$ and ν^0 in the ground $X^1\Sigma_g^+$ state. The intensity $I_n^{+(0)}$ of the vibrational levels $n^{+(0)}$ was assumed to obey a Poisson distribution [2,11]: $I_n^{+(0)} = \exp(-\beta_{+(0)}) (\beta_{+(0)}^n / n!)$. The single peaks were assumed to have a Gaussian line shape [6]. Parameters of the fit were the two frequencies ν^+ and ν^0 , the β_+ and β_0 parameters of the Poisson distributions, the linewidth of the Gaussian curves, the position of the $n=0$ peak, and the relative intensities of the two multiplets. An example

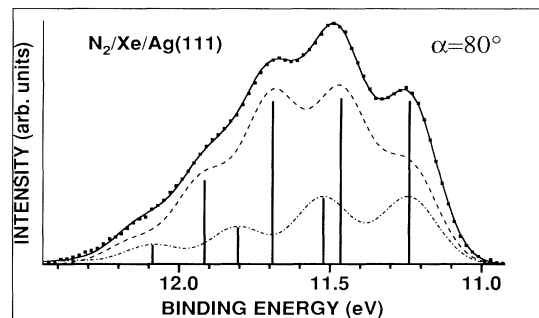


FIG. 2. Example of a fitted curve for the $1\pi_u$ level of $N_2/Xe/Ag(111)$. The incidence angle α is 80° and the emission angle θ is 0° . Position and intensity of the single vibrational levels are indicated by vertical bars. The sum of all fitted levels is indicated with a continuous line, to be compared with the measured data, which are represented by dots. The separate contributions of the two multiplets are indicated with a dashed line (ν^+ multiplet) and with a dash-dotted line (ν^0 multiplet).

of such a fit is displayed in Fig. 2. By assuming a strict Poisson distribution for the two oscillators, the quality of the fits was not as good as in Fig. 2. The required deviation from a Poisson distribution amounted to 10% or less in the case of the ν^+ vibration and up to 30% in the case of the ν^0 vibration. Regarding the vibrational excitation in the ionic $A^2\Pi_u$ state, such a deviation is also known from the gas phase [4], and depends on the geometrical arrangement [12]. The excitation of the ν^0 vibration takes place due to the evolution of the system along the potential-energy curve of the $A^2\Pi_u$ electronic state and subsequent decay to the $X^1\Sigma_g^+$ ground state. This process closely resembles the negative-ion resonance scattering mechanism of high-resolution electron-energy-loss spectroscopy [13]. If the curvature is not identical in the two potential-energy curves, a deviation from a Poisson distribution is predicted theoretically and observed experimentally [13].

The vibrational frequencies resulting from the fit range from 222 to 239 meV for the ν^+ frequency and from 271 to 284 meV for the ν^0 frequency, to be compared with 224 meV [4] and 289 meV [7] observed for the $A^2\Pi_u$ and $X^1\Sigma_g^+$ states in the gas phase. The Poisson distributions which best describe the intensity of the vibrational levels are characterized by $\beta_+ = 1.8-2.1$ and $\beta_0 = 0.7-1.0$. From these values the time constant for the hopping process can be estimated to be $\tau_h = (2-3) \times 10^{-15}$ s. In light of these results, the differences between the spectra recorded at $\alpha=80^\circ$ and $\alpha=15^\circ$ can be described as follows. The higher intensity of the $n=0$ peak and the larger vibrational spacing at $\alpha=15^\circ$ means that the oscillator that is prevalently observed in this scattering geometry is the one with the lower β parameter and with the higher vibrational frequency, that is, ν^0 . The arguments are reversed for the description of the spectrum at $\alpha=80^\circ$. This trend is actually confirmed by the results of

the fit (Fig. 3). It must be recalled that (a) the observability of the ν^0 oscillator is made possible by the occurrence of the hopping process of the photohole [6] and that (b) the spectra reported in Fig. 1 have been recorded in normal emission. Hence, the efficiency of the hopping process is greater for the $1\pi_u$ states which have the right symmetry for being observed in normal emission when the electric field of the incoming light is parallel to the surface.

A further discussion of this statement requires the description of the results for the $3\sigma_g$ valence state. This level exhibits, in normal emission ($k_{\parallel}=0 \text{ \AA}^{-1}$), a split of 0.4 eV (see inset of Fig. 1), which vanishes at $k_{\parallel}=0.8\text{--}0.9 \text{ \AA}^{-1}$. Such a dispersion is observed for the $3\sigma_g$ level of N_2 physisorbed on graphite and for the 5σ level of CO physisorbed on $\text{Ag}(111)$ [14]. The dispersion observed for the systems $\text{N}_2/\text{graphite}$ and $\text{CO}/\text{Ag}(111)$ can be explained with the formation of a herringbone structure. From the close resemblance of our results to the ones obtained for the quoted systems, we conclude that an in-plane oriented herringbone structure is formed also for the $\text{N}_2/\text{Xe}/\text{Ag}(111)$ and $\text{N}_2/\text{Xe}/\text{Pd}(111)$ systems. The in-plane orientation of the N_2 molecules is further corroborated by inspection of the intensity ratio I_{σ}/I_{π} of the signal from the $3\sigma_g$ and $1\pi_u$ levels in normal emission. The ratio I_{σ}/I_{π} does not exhibit any marked decrease when varying the incidence angle towards normal incidence, as would happen in the case of prevalent upright orientation [15]. The dispersion curves for a layer of N_2 molecules arranged in the herringbone structure have been calculated for the three valence levels [16]. There are four bands derived from the $1\pi_u$ level. Two bands correspond to the $1\pi_u$ levels oriented perpendicular to the plane (π_{\perp} levels) of the two N_2 molecules of the unit cell. The other two bands are derived from the $1\pi_u$ levels

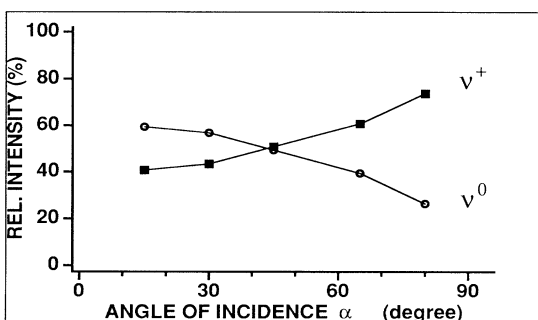


FIG. 3. Relative intensity of the vibrational multiplets forming the $1\pi_u$ level of $\text{N}_2/\text{Xe}/\text{Ag}(111)$ depending on the incidence angle α : ν^+ and ν^0 are the vibrational frequencies in the ionic $A^2\Pi_u$ state and the ground $X^1\Sigma_g^+$ state, respectively. The results refer to the normal-emission spectra of Fig. 1. The separate intensities of the two multiplets are derived by the fit procedure as displayed in Fig. 2: The intensity of the ν^+ (ν^0) multiplet is the area under the dashed (dash-dotted) line.

oriented in the plane (π_{\parallel} levels). The overlap between π_{\perp} levels of neighboring molecules is very poor, and the corresponding bands show practically no dispersion. A bigger overlap is observed for the π_{\parallel} levels, resulting in a dispersion which exhibits the typical trend characteristic of a $p_{x,y}$ -like band [17], that is, the binding energy at the $\bar{\Gamma}$ point is lower than it would be without overlap, and increases with increasing k_{\parallel} . From symmetry considerations [15], it follows that in normal emission the π_{\perp} levels can be excited only if the electric field of the incoming light has a component perpendicular to the surface, whereas a component parallel to the surface is needed to excite the π_{\parallel} levels. By comparison with the conclusions derived from Fig. 3, these selection rules state that the hopping process is much more efficient in the case of the π_{\parallel} levels than in the case of the π_{\perp} levels, that is, for those π wave functions for which the overlap with the nearest neighbors is larger.

The distinction between π_{\parallel} and π_{\perp} levels is demonstrated by the results of Fig. 4, which also evidence the existence of the dispersion. Using s (p) polarization and normal emission the π_{\parallel} (π_{\perp}) levels are preferentially excited which exhibit the higher (lower) efficiency of the hopping process. The extended spectra, from which only small windows are shown in Fig. 4, look actually very similar to the equivalent spectra of Fig. 1, i.e., the full curve for s light and $\theta=0^\circ$ looks like the curve for $\alpha=15^\circ$ in Fig. 1 and the full curve for p light and $\theta=0^\circ$ looks like the curve for $\alpha=65^\circ$ in Fig. 1. These symmetry considerations are mirrored in a small dispersion

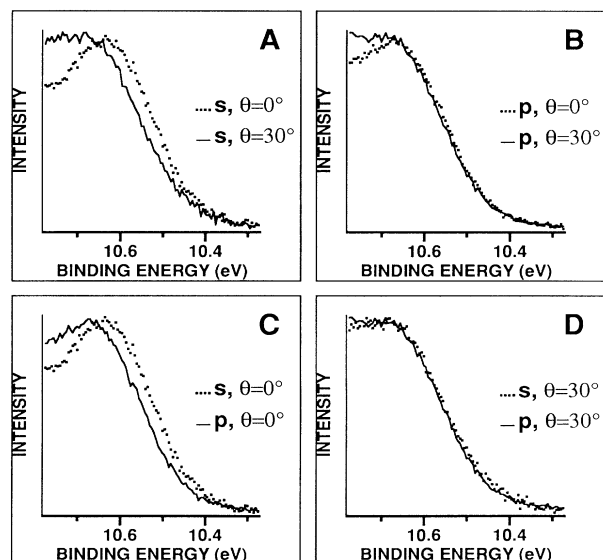


FIG. 4. Leading edge of the $1\pi_u$ level of $\text{N}_2/\text{Xe}/\text{Pd}(111)$. The angle of incidence α is fixed at 70° . Four spectra have been recorded, at normal emission ($\theta=0^\circ$) and away from it ($\theta=30^\circ$), with s - and p -polarized light. For the sake of clarity the four spectra are compared pairwise as explained in the text.

effect as explained in the following. With s polarization a lower binding energy is observed at $\theta=0^\circ$ (normal emission) than at $\theta=30^\circ$ due to the $p_{x,y}$ -like dispersion of the π_{\parallel} level [16,17] as displayed in Fig. 4(a) where a shift of about 30 meV can be observed. For the sake of completeness it must be said that at $\theta=30^\circ$ the selection rule [15] breaks down, and most probably the signal is measured from both the π_{\parallel} and π_{\perp} levels. No shift is observed for the flat band of the π_{\perp} level excited with p polarization [Fig. 4(b)]. The overlap between nearest neighbors results, at the $\bar{\Gamma}$ point, in a binding energy which for the $p_{x,y}$ -like π_{\parallel} level is lower than it would be without overlap, as is the case for the π_{\perp} level. This explains the binding-energy difference of about 30 meV between the spectra of Fig. 4(c) measured with s and p polarization. This difference is no longer observed in Fig. 4(d), due to the increased binding energy along the π_{\parallel} band apart from the $\bar{\Gamma}$ point, and to the breakdown of the selection rule at $\theta=30^\circ$ as mentioned above.

In summary, we have confirmed the recent observation [6] that the vibrational fine structure of the $1\pi_u$ level of physisorbed N_2 can be described as the superposition of two multiplets corresponding to the vibrational frequencies in the ionic (N_2^+) and in the neutral (N_2) state. The appearance of the neutral-state multiplet, which is not observed in the gas phase, can be explained by the occurrence of hopping of the photohole during the photoemission process. For the first time we have established a correlation between the efficiency of the hopping process (high intensity of the neutral-state multiplet) and the overlap between the wave functions of neighboring molecules (measurable dispersion in a two-dimensional band). Both effects are higher for the in-plane component of $1\pi_u$ than for the perpendicular one. The occurrence of two vibrational multiplets is a further mechanism for the broadening of photoemission spectra from adsorbed molecules. Our measurements contribute to the understand-

ing of this important effect.

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