

Photoemission Line Shapes of Adsorbates: Conclusions from the Analysis of Vibration-Resolved N_2 Spectra

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Physisorbed N_2 on Ni(111) has been studied by uv photoemission using rare-gas spacer layers. For $1\pi_u$ ionization, vibrational fine structure has been resolved experimentally and analyzed in detail. The line shape of the electronic levels *cannot* be described by simple broadening of the corresponding gas-phase spectrum. Nearly no Lorentzian lifetime broadening could be observed; rather the vibrational peaks have a Gaussian line shape (narrowest FWHM, 0.21 eV). The observed peculiarities can be understood within a hopping model taking into account the deexcitation of the ionized molecule by hole transfer to neighbors.

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The origin of the broadening of photoemission line shapes is one of the fundamental questions in solid-state and surface analysis. If the various contributions were known in detail or could be derived by careful analysis, one could get additional information about the systems studied. However, in many cases, in particular for most adsorbates, rather broad lines are observed whose analysis is difficult or impossible. Thus many spectral details that are observable in high-resolution data of isolated (i.e., gas-phase) molecules or atoms are lost when these are condensed or adsorbed on a surface. The major contribution to this so-called "solid-state broadening effect" is generally believed to be of Lorentzian type, i.e., to be due to a reduction of the hole lifetime in the photoemission final state upon adsorption. Various other contributions, apart from the obvious instrumental effects, have been suggested, such as coupling to vibrations, substrate phonons, adsorbate dipoles, electron-hole excitations, variation of the local potential because of site inhomogeneities, variation of screening due to vibrations or different adsorption sites, etc.¹⁻³ Experimentally none of these contributions could yet be isolated or excluded,³⁻⁶ and often, in particular for adsorbed molecules, these contributions are insufficient to explain the whole line-width.

Therefore, we have started a detailed investigation by choosing an adsorbate model system, for which the influence of the metallic substrate can stepwise be reduced by spacer monolayers of inert rare-gas atoms like Xe and Ar. As adsorbate the relatively inert molecule N_2 has been taken because of the large separation of the vibrational levels of its uv-photoemission-spectroscopy (UPS) peaks, which turned out to be important for the analysis. It is well known that uv-photoemission spectra of molecules in the gas phase show a characteristic "splitting" of the valence levels due to vibrational excitation of the ionic final state. This fine structure is sensitive to the bonding character of the ionized orbital and

allows one to derive details of the intramolecular potential.⁷ In general, this information is lost in the adsorbate phase due to the above-mentioned broadening effect. The smallest ever reported broadening of adsorbate photoemission peaks was found for the $1\pi_g$ level of O_2 physisorbed on graphite.⁶ But also for this system the width of ~ 0.3 eV was still larger than the vibrational splitting of 0.22 eV, and hence a detailed line-shape analysis was impossible.

In the present example, N_2 on Ni(111), we were able to reduce the overall broadening to 0.21 eV as compared to the vibrational splitting of the $1\pi_u$ ionized state of 0.22 eV by utilizing a homogeneous monolayer of Xe as spacer for reduction of the substrate influence. Hence, more details can be directly derived from the original data, and more reliable information can be obtained by a numerical line-shape analysis. The results are surprising in many respects. They show that in general even the line shapes of physisorbates cannot generally be described by simple convolution of gas-phase data with some broadening function, but that the deexcitation process must be taken into account. Since suitable theoretical predictions are presently missing, we suggest a hopping model which enables a good description of our experimental results. The remaining general broadening is found to be mainly Gaussian. Lorentzian lifetime broadening can definitely be excluded as a major contribution. These results are believed to be important not only for the interpretation of UPS spectra from such weakly bound molecular layers but also for a general understanding of electron spectroscopies.

The experiments were performed at a base pressure of 3×10^{-11} mbar in a modified VG ESCA III chamber, equipped with standard facilities for x-ray photoemission spectroscopy and monochromatized UPS and with a quadrupole mass spectrometer for temperature-programmed desorption. The experimental resolution for uv-photoemission He I spectra ($h\nu = 21.22$ eV) was 0.09

eV. Sample cooling to ≤ 20 K was achieved with a He-flow cryostat. The composed layers were prepared by exposing the clean Ni(111) surface to $> 10^{15}$ Ar or Xe atoms/cm² through a capillary-array beam doser. After thermal desorption of multilayer Ar or Xe atoms a homogeneous rare-gas monolayer was obtained, which was subsequently exposed to 1.2×10^{15} N₂ molecules/cm² ($= 3.1$ langmuirs). The N₂ monolayer on top of the rare-gas monolayer was again obtained by thermal desorption of multilayer N₂ (desorption temperature $T_{\max} = 28$ K). N₂ desorption spectra taken after completion of UPS measurements showed only one sharp peak at $T_{\max} = 31$ K, indicating that no intermixing between the layers occurs. For the preparation procedure a microprocessor-controlled heating facility was required for optimum reproducibility and precise temperature control.

In Fig. 1, HeI spectra of N₂ adsorbed on different underlayers (a)–(c) and of isolated⁷ N₂ (d) are compared. The gas-phase spectrum (d) shows a pronounced vibrational splitting of the UPS peaks, especially of that of the bonding $1\pi_u$ orbital. The peak width (FWHM ≤ 0.05 eV) is limited in this case by experi-

mental resolution.⁷ Without a rare-gas spacer layer (a) the adsorption of N₂ on Ni(111) leads to an ordered mixture of a chemisorbed (cs-N₂) and a physisorbed (ps-N₂) species for the saturated monolayer.⁸ While the chemisorption bond of the cs-N₂ species to the metal results in a complete rearrangement of its outer valence orbitals, the three peaks in the spectrum of the ps-N₂ species correspond to the $2\sigma_u$, $1\pi_u$, and $3\sigma_g$ orbitals also seen for isolated N₂.⁸ Relative peak separations and relative peak intensities are very similar in the gas phase (d) and the physisorbed state (a), but the peaks of ps-N₂ show a large common broadening of > 0.3 eV. Thus the vibrational splitting observed for the gas-phase data is unresolved.

The overall broadening is significantly reduced if N₂ is physisorbed on a monatomic rare-gas spacer layer [Figs. 1(b) and 1(c)]. In the case of N₂/Xe/Ni(111) individual vibrational states of the $1\pi_u$ peak, corresponding to the $A^2\Pi_u$ state of N₂⁺, are clearly resolved (c). The spectrum of N₂/Ar/Ni(111) represents an intermediate case; the $1\pi_u$ peak does not display distinct vibrational states but its shape unambiguously reflects the corresponding vibrational structure.

We have analyzed the line shape of the $1\pi_u$ peak in great detail using different model functions. If the photoemission process is fast compared to all other excitations ("sudden approximation"), the line shape of a peak corresponding to photoemission from a certain orbital is determined by the overlap integral of the initial-state and final-state wave functions $|\langle \Psi_i | \Psi_f \rangle|^2$. Separating the electronic wave functions $|\varphi\rangle$ and the core functions $|\psi\rangle$, $|\Psi_i\rangle = |\varphi_i\rangle |\psi_0\rangle$, $|\Psi_f\rangle = |\varphi_f\rangle |\psi_n^+\rangle$ (Born-Oppenheimer approximation), the energy distribution of the photoelectrons is given by

$$j(E) \propto |\Delta_{fi}|^2 \sum_{n=0}^{\infty} |\langle \psi_0 | \psi_n^+ \rangle|^2 \delta(E + E_n^+ - \hbar\omega). \quad (1)$$

In general, the variation of the optical matrix element $\Delta_{fi} = \langle \varphi_f | \mathbf{A} \cdot \mathbf{P} | \varphi_i \rangle$ can be neglected over the vibrational-band width (~ 1 eV) of one electronic state. Thus the intensity of the n th vibrational peak with energy E_n^+ is directly proportional to the Franck-Condon (FC) factor $|\langle \psi_0 | \psi_n^+ \rangle|^2$.

If the interaction of the N₂ molecule with its neighbors is small, the FC factors $|\langle \psi_0 | \psi_n^+ \rangle|^2$ and the vibrational energies E_n^+ of physisorbed N₂ should be very similar to those of isolated N₂, and hence the adsorbate spectrum should be equal to a broadened gas-phase spectrum. The fit shown in Fig. 2(a) for N₂ physisorbed on a Xe monolayer demonstrates that this common assumption by no means describes our data sufficiently. For the fit we have taken the relative intensities $|\langle \psi_0 | \psi_n^+ \rangle|^2$ and energies E_n^+ of the vibrational peaks from Ref. 7, and each peak was represented by the same Gaussian line shape. The synthetic spectrum was fitted with the right-hand side of the measured data (leading edge at ~ 10.5 eV). The lack of agreement between the fit and data in the left

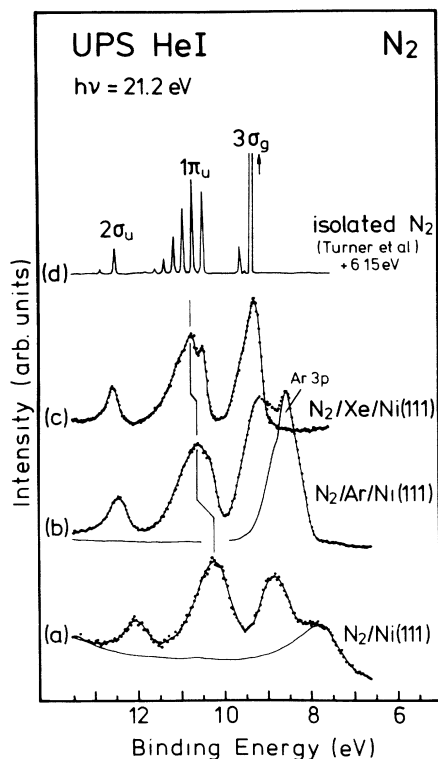


FIG. 1. Comparison of UPS HeI spectra of N₂. (a) N₂ monolayer on Ni(111) consisting of an ordered 1:1 mixture of chemisorbed and physisorbed N₂ (line represents background of pure cs-N₂ state); (b) N₂ monolayer on a monatomic Ar-spacer layer (line represents background of Ar monolayer); (c) N₂ on Xe-spacer layer; (d) isolated N₂ in the gas phase, taken from Ref. 7 and shifted by 6.15 eV to align with (c).

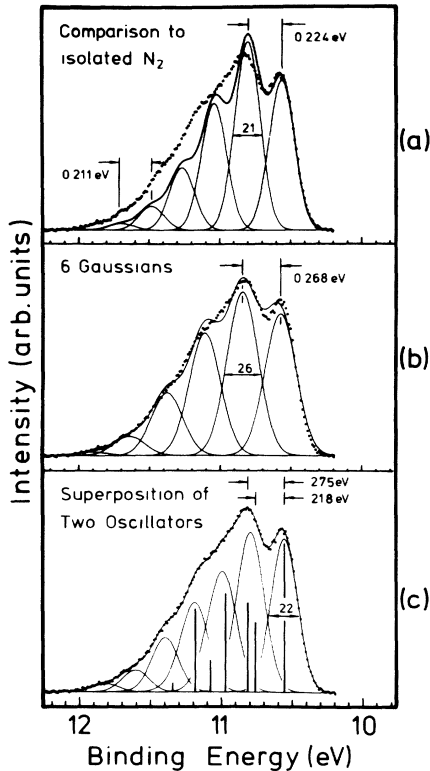


FIG. 2. Analytical fits of different model functions to the $1\pi_u$ peak of $N_2/Xe/Ni(111)$ ($A^2\Pi_u$ state of N_2). The fits (a)-(c) are explained in the text. Dots represent measured data points; lines give the fitted results. A linear background was subtracted from the spectra prior to the fitting procedure, in accordance with the experimental background [$Xe/Ni(111)$ spectrum].

part of the spectrum of Fig. 2(a) proves the failure of this approach. Besides differences in the FC factors, a closer look gives the impression that the vibrational splitting of physisorbed N_2 is increased as compared to isolated N_2 .

The very good agreement at the leading edge of the ($n=0$) vibrational level indicates that its shape is very close to Gaussian. We have also tried Voigt functions composed of Gaussians and Lorentzians and can give an upper limit of 0.03 eV for the Lorentzian broadening of the ($n=0$) peak, independent of the subtracted background function. In contrast to common belief, we expected this result since lifetime effects resulting in a Lorentzian broadening should be of minor importance for such a weakly bound adsorbate. It is nevertheless very significant, since the surprisingly large linewidths of physisorbates have often been (at least partly) attributed to a reduced lifetime of the molecular ion caused by interaction with the metallic substrate and with adsorbate neighbors.⁴⁻⁶

In order to improve the agreement between the fit and data and to shed light on the broadening mechanism we tried a large number of fits with different combinations

of variable and fixed fit parameters representing harmonic and anharmonic (Morse) potentials. However, assuming one final-state potential, only relatively poor agreement between the fit and data can be achieved, even with a large number of variable fit parameters. The fit depicted in Fig. 2(b) is exemplary for this negative result. We assumed a harmonic oscillator with equidistant levels; Gaussian lines were used to describe the vibrational peaks and all peak intensities were varied independently. None of the parameters was related to isolated N_2 . Compared to Fig. 2(a) the agreement between the fit and data is better in the region of high vibrational levels. But the resulting peak width of 0.26 eV is obviously too large to describe the ($n=0$) peak sufficiently, whereas it is apparently still too small for the comparatively smooth course of the experimental data points above 11 eV.

A much better description of the measured spectrum is achieved by the fit shown in Fig. 2(c). This fit is based on a superposition of two oscillators, i.e., two potential curves. Using two oscillators it is possible to explain the experimental results in a simple way and to fit the data by very few parameters (only six, see below). As reason for this superposition we suggest the following model.

A valence hole created by photoionization at $t=0$ on one N_2 molecule may be filled by electron transfer ("hopping") from a neighboring N_2 molecule. If this hopping process of the hole in the two-dimensional adsorbate layer occurs with a characteristic time constant τ_h , that is, of the same order as the vibration time $\tau_{\text{vib}}=1/\omega^+$, the final-state core functions $|\psi_n^+\rangle$ of Eq. (1) are no longer stationary eigenstates of the ionic final state with infinite lifetime as in the case of isolated N_2 . Rather the wave functions $|\psi_n^+\rangle=|n;*\rangle$ must be replaced by a time-dependent description

$$|\psi^+(t)\rangle = \sum_n e^{-in\omega^+t} |n;*\rangle \langle n;*|0\rangle. \quad (2)$$

At $t=\tau_h$ the hole is switched off but the neutral molecule will not end up in the vibrational ground state $|0\rangle$. It will find itself in a vibrationally excited state $|m\rangle$ with the probability

$$P_m(\tau_h) = |\langle m|\psi^+(\tau_h)\rangle|^2 = \left| \sum_n \langle m|n;*\rangle e^{-in\omega^+\tau_h} \langle n;*|0\rangle \right|^2. \quad (3)$$

Thus the eigenstates describing the photoemission final state ψ^+ of Eq. (1) contain vibrational excitations of the ionized *as well as* of the neutral molecule. The contribution of vibrations of the neutral molecule depends on the value of the hopping time τ_h in relation to the vibration time $\tau_{\text{vib}}=1/\omega^+$. These can obviously be neglected in the two limits $\tau_h \rightarrow 0$ and $\tau_h \rightarrow \infty$ but not in the case $\tau_h \approx \tau_{\text{vib}}$.

The simplest possible representation of this hopping model is that of a superposition of two harmonic oscillators as shown in Fig. 2(c). The very good agreement be-

tween data and model is an indication for the applicability of the latter. More arguments come from the fitted results. For the fit shown in Fig. 2(c) the vibrational spacings of both oscillators were varied independently; the relative peak intensity was assumed to be a Poisson distribution for each oscillator as theoretically expected for a harmonic oscillator.⁹ The resulting Gaussian peak width of 0.21–0.22 eV fits the leading edge excellently. The *resulting* vibrational spacings of 0.218 and 0.275 eV for the two oscillators are rather close to the corresponding values of isolated N₂ in the ionic $A^2\Pi_u$ (0.224 eV) and in the neutral $X^1\Sigma_g^+$ state (0.291 eV). Note that this is a *result* of the fit based on two “unknown” oscillators which corroborates the model for the *origin* of this superposition. From Eq. (3) it can be seen that the intensity contribution of the vibrations of neutral N₂ depends on the hopping time τ_h . If this is short compared to $1/\omega^+$, higher vibrations of the neutral molecule will hardly be excited. The hopping time resulting from our best fit is 1.5×10^{-14} sec which corresponds to $0.2\tau_{\text{vib}}$.

A statistical hopping process is only possible if there is some overlap of the wave functions of neighboring molecules as must be the case in a condensed monolayer. It should be compared with a coherent description leading to a two-dimensional band structure. Using angle-resolved UPS, Schmeisser *et al.* have experimentally resolved such a band structure for the $3\sigma_g$ level of physisorbed N₂ on graphite.¹⁰ The maximum bandwidth was found to be 0.4 eV. It is very likely that the relatively broad $3\sigma_g$ peak seen in our spectra (Fig. 1) is also influenced by band formation. The overlap of the π wave functions must be much smaller, resulting in a bandwidth clearly below the experimental resolution (< 0.1 eV) of a normal UPS experiment such that neither Schmeisser *et al.*¹⁰ nor we were able to observe it directly. However, the overlap should still be large enough to allow a slow hopping at a time constant of $\sim 10^{-14}$ sec.

Finally, we should comment on the remaining general broadening of the spectrum of physisorbed N₂ as determined from the width of the ($n=0$) vibrational peak. This width increases with decreasing thickness of the rare-gas spacer layer. It is 0.21 eV in the case of the Xe layer, 0.26 eV for Ar, and 0.35 eV for N₂ physisorbed directly on the Ni(111) substrate. This broadening is most likely due to variations of the effective potential caused by site inhomogeneities and/or, more likely, by different screening contributions arising from the slow vi-

brational motion of the physisorbates perpendicular to the surface and relative to each other. It is reasonable that this effect is smallest for the Xe layer and largest for N₂ directly attached to the metal.

In summary, we have shown that the uv-photoemission spectra of N₂ adsorbed on Ni(111) reveal considerable fine structure if the influence of the substrate is reduced by rare-gas spacer layers. A detailed analysis shows that (a) the main common broadening function is dominated by a Gaussian line shape (~ 0.2 eV) with a negligible Lorentzian contribution (≤ 0.03 eV), (b) the experimental data of adsorbates, even those of very weakly bound physisorbates, cannot generally be described by a simple broadening of the respective high-resolution gas-phase data, and (c) the experimental line shape is best reproduced by superposition of two harmonic oscillators. As explanation for this finding we suggest a hopping model for the photohole which leads to a mixing of the final-state wave function with contributions from the ionic and ground states, respectively.

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