Lifetime Broadening of Excited Pyrazine Adsorbed on Ag(111)

J. E. Demuth and Ph. Avouris
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 6 May 1981)

High-resolution electron-energy-loss spectroscopy has been used to study the vibrational broadening in the ${}^1B_{2u}(\pi,\pi^*)$ excited state of pyrazine adsorbed on Ag(111). Strong lifetime broadening of ~100 mV for the first and ~20 mV for the second pyrazine layers are determined. These lifetimes are in reasonable agreement with those predicted by classical theory.

PACS numbers: 73.20.Hb, 34.50.Ez, 79.20.Kz

We present the first high-resolution electron-energy-loss study of the electronic excitations of an adsorbed molecule which resolves excited-state vibrational structure. In particular, we have studied the loss spectra of pyrazine in monolayer and multiple layers on a Ag(111) surface. From the broadening of the vibronic levels of the ${}^1B_{2u}(\pi,\pi^*)$ state of pyrazine as a function of surface-layer thickness, we determine the reduction of the excited-state lifetime associated with energy transfer to the metallic surface. The lifetime of the molecules directly adsorbed on the metal surface has thus been determined for the first time. Our results surprisingly indicate lifetimes comparable to those predicted by classical electromagnetic theory.[1] Other recent studies have either been unable to study this small-distance regime[2] or have found anomalously long lifetimes.[3] Thus, our results are important not only to test present theories of energy transfer to surfaces,[1,4] an important consideration in sputtering or photoinduced surface reactions, but also for the application of high-resolution or time-resolved excited-state laser spectroscopies to study adsorbed molecules and surface reactions. We conclude that such methods will be of limited use to study chemisorption or adsorbed species directly on metal surfaces due to the severe lifetime broadening which occurs.

The measurements were performed in a UHV system (typical operating pressures of $< 1\times 10^{-10}$ Torr) equipped with a hemispherical-deflector-based electron monochromator and energy analyzer described elsewhere.[5] This spectrometer has a fixed scattering angle of 90° and collects a well-defined (~0.2-mm-diam), collimated electron beam (< 1°) reflected from the sample. Both single sweep and multichannel analysis of the pulse counted signal were performed. The sample, which was cooled to 140 K, could be rotated to observe both specular ($\theta_{\rm in}=\theta_{\rm out}$) and off-specular ($\theta_{\rm in}\neq\theta_{\rm out}$) scattering events in the plane of incidence. Beam energies up to 20 eV were used with a resolution (full width at half maximum of the specular beam) of between 10 and 30 meV. Pyrazine dosing was done via the ambient. The ion gauge readings reported here are uncorrected.

In Fig. 1 we show the electron-loss spectra as a function of increasing pyrazine exposure in langmuirs (1 L = 10^{-6} Torr s) to the clean Ag(111) surface at $T = 140$ K. For clean Ag(111) we observe a silver plasmon at 3.85 eV,[6] which shifts to lower energies upon adsorption. The features at ~4.8, 6.5, and 7.8 eV agree well with the excitation maxima to the ${}^1B_{2u}$, ${}^1B_{1u}$, and ${}^1B_{2u}+{}^1B_{1u}$ excited states of gaseous pyrazine,[7,8] respectively. The new, low–energy-onset feature begin-

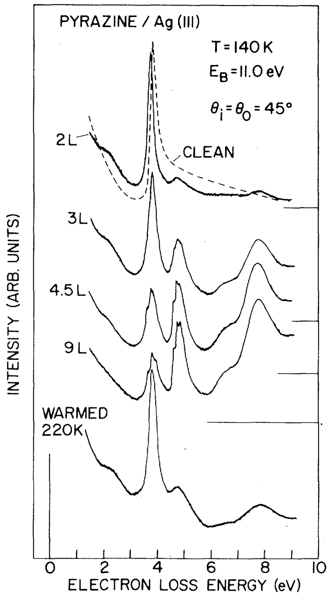

FIG. 1. Electronic-energy-loss spectra for clean Ag(111) and as a function of pyrazine exposure. Specular scattering conditions are used with an elastic beam full width at half maximum of 30 mV.

ning at ~1.8 eV can be related to a metal-molecule charge-transfer excitation.[9] For these spectra we note that the incident beam energy and electron optics were adjusted such that the transmission function decreased above ~6 eV: This suppressed both the bulk plasmon[6] at 8 eV and the 7.8-eV pyrazine loss relative to the lower-energy peaks. For increasing exposures we observe the decay of the charge-transfer (CT) excitation and surface plasmon as well as the growth of the molecular excitations. The decay of the CT excitation and the first appearance of vibrational features on the ${}^1B_{2u}$ (4.8 eV) excitation for exposures above ~2.5 L signal the onset of physically adsorbed (condensed) pyrazine atop of the first layer of pyrazine. Given an estimated ion gauge correction factor of ~4, the first layer of pyrazine would have a sticking coefficient of ~$\frac{1}{2}$, which we assume for the adsorption of subsequent layers as found also for pyridine.[10] By 4.5 L exposure, i.e., ~2 layers total, well-resolved vibrational structure is observed on both the 3.8-[${}^1B_{3u}(n,\pi^*)$] and 4.8-eV peaks. Upon warming to ~220 K to desorb any condensed layers, we return to the loss spectrum characteristic of the first layer of pyrazine; i.e., pryazine adsorbed directly on the surface. Again this spectrum shows none of the expected vibrational fine structure, a point we will discuss in detail.

In considering the development of vibronic structure on the electronic excitations as a function of pyrazine spacing from the surface, we focus on the 4.8 eV [${}^1B_{2u}(\pi,\pi^*)$] excitation. In Fig. 2 we show detailed spectra of this transition for submonolayer pyrazine coverage and for multilayer coverages (~2 and ~4 layers), along with the optical absorption spectrum of gaseous pyrazine.[11] For the submonolayer spectrum, we indicate the result (solid line) of subtracting a background (dashed line) associated with the tail of the surface plasmon.

The broadening of our observed spectra relative to the optical spectra does not appear to arise from differences in bond sites and structural inhomogeneities as our vibrational-energy-loss studies (at 10 mV resolution) indicate a flat-lying molecule with the same vibrations up to a thickness of four layers. Namely, we observe strong losses from the b_{2u} out-of-plane C-H and C-C deformation modes[12] at 420 and 805 cm^{-1} while all the in-plane ir modes are strongly suppressed. From the angular dependence of this spectra we conclude that the observed vibrations (except the C-H stretch) are excited through dipole scattering. Analysis of the relative intensities of these in-plane and out-of-plane modes, as described elsewhere,[5] indicates that each of the four pyrazine layers studied lie flat to within 1.5°.[13] We thereby rule out inhomogeneous broadening as a major effect. Clearly, our experiments on a single-crystal surface will minimize such effects.

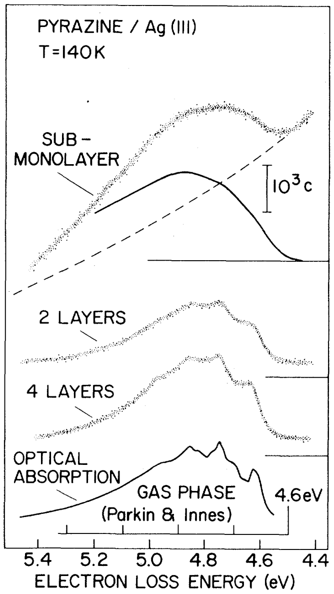

FIG. 2. Electronic-energy-loss spectra for the ${}^1B_{2u}$ state of monolayer and subsequent adsorbed layers. The optical absorption spectrum for gas-phase pyrazine (Ref. 11) is also shown.

In order to evaluate the observed broadening, we have applied Gaussian broadening to the optical spectra to account for our instrumental resolution and then Lorentzian broadening to understand the degree of lifetime broadening occurring for different pyrazine layers. The four-layer spectrum is nearly identical to what we expect if we consider our instrumental broadening alone. To match the submonolayer spectrum requires, in addition to our instrumental broadening, 100 mV of lifetime broadening. This results in the weak, broad, vibronic features on the submonolayer spectrum, which would *not* be reproduced for lifetime broadening above 140 mV. The two-layer spectrum is well reproduced by the average of the monolayer and a 15-mV lifetime broadened spectra. We point out that the severely broader features for the submonolayer spectrum are not likely caused by additionally adsorbed pyrazine in the second layer since our data-acquisition times and system pressures would only account for an extra ~0.05 monolayer. We further note that the difference in widths of the Frank-Condon envelopes of the ${}^1B_{2u}$ state between monolayer and condensed pyrazine (200 mV) is not an accurate measure but is only an approximate upper limit to the lifetime broadening for the first layer of pyrazine. Finally, we have to consider the rotational bandwidth which is present in the gas-phase optical spectrum but would not be present for condensed pyrazine. This is not accurately known: We estimate it to be ~ 10 mV and account for it in our results. Such uncertainty limits our determination of the lifetime broadening occurring for the fourth and subsequent layers. Thus the total vibronic broadening which we derive for the first monolayer, directly adsorbed on the metal, and for the second (condensed) layer of pyrazine is 100–140 mV [$(6.6-4.7)\times 10^{-15}$ s] and 20 mV (3.3×10^{-14} s), respectively.

We can compare our determined lifetimes to those predicted by a classical electromagnetic theory,[1] given our deduced adsorption geometry, the oscillator strength ($f = 0.1$) of the ${}^1B_{2u}$ state,[14] as well as the optical constants of Ag (Ref. 15) at 4.8 eV. Given a 2.9-Å distance for the first layer of pyrazine from the first layer of Ag atoms,[16] a 3.3-Å interlayer spacing of condensed pyrazine,[17] and an image plane at 1.95 Å from the center of the first layer of Ag atoms,[18] classical theory predicts 590 mV (1.1×10^{-15} s) and 5.5 mV (1.2×10^{-13} s) broadening (lifetimes) for the first and second layers, respectively. We expect this classical theory to overestimate the metal-molecule coupling at small distances and predict shorter lifetimes, as indicated by our results; however, the shorter than predicted lifetime for the second layer suggests the presence of additional quenching mechanisms such as electron-hole–pair excitations.[4] Although our lifetimes for the first two layers show departures from those predicted by classical theory, there is surprisingly good overall agreement which suggests that this theory can be used to predict lifetimes of adsorbed molecules on metal surfaces to within a factor of 10. This is in contrast to a recent study of the quenching of pyrazine phosphorescence on Ag (Ref. 3) which concluded that the lifetime remained almost constant below ~ 100 Å from the surface; in complete disagreement with classical theory.

In summary, we have determined the lifetimes of the ${}^1B_{2u}(\pi,\pi^*)$ excited state of pyrazine adsorbed as a monolayer and as a condensed second layer on Ag(111). The lifetimes are comparable to those predicted by classical theory. Clearly more information about energy-transfer processes in other metal/molecule systems is needed. From our results, we expect similar broadening for other allowed electronic excitations ($f = 0.1$–1) which will generally limit the usefulness of excited-state laser spectroscopies for probing the vibronic structure of similar weakly adsorbed species. Finally, we note that classical theory predicts reduced broadening for optically forbidden (e.g., spin-forbidden) excitations. Electron-scattering studies of such excitations may permit the observation of their vibronic structure and a detailed understanding of the nature of some excited states of adsorbed species.

We gratefully acknowledge J. J. Wynne for carefully reading the manuscript. This work was supported in part by the U. S. Office of Naval Research.

---

[1] R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. 37, 1 (1978), and references therein.

[2] A. Campion, A. R. Gallo, C. B. Harris, H. J. Robota, and P. M. Whitmore, Chem. Phys. Lett. 73, 447 (1980).

[3] R. Rossetti and L. E. Brus, J. Chem. Phys. 73, 572 (1980).

[4] B. N. Persson, J. Phys. C 11, 4251 (1978); B. N. J. Persson and M. Persson, Surf. Sci. 97, 609 (1980).

[5] J. E. Demuth, K. Christmann, and P. N. Sanda, Chem. Phys. Lett. 76, 201 (1980).

[6] A. Otto and E. Petri, Solid State Commun. 20, 823 (1976).

[7] K. K. Innes, J. P. Byrne, and I. G. Ross, J. Mol. Spectrosc. 14, 190 (1967).

[8] C. Fridh, L. Asbrink, B. D. Jonsson, and E. Lindholm, Int. J. Mass Spectrom. Ion Phys. 8, 101 (1972).

[9] J. E. Demuth and P. N. Sanda, Phys. Rev. Lett. 47, 57 (1981) (in this issue).

[10] P. N. Sanda, J. M. Warlaumont, J. E. Demuth, and J. C. Tsang, Phys. Rev. Lett. 45, 1519 (1980).

[11] J. E. Parkins and K. K. Innes, J. Mol. Spectrosc. 15, 407 (1965).

[12] S. Califano, G. Adembri, and G. Sbrana, Spectrochim. Acta 20, 385 (1964).

[13] Our condensed layer geometry differs from that proposed on Ni(111) where different growth conditions were used. See C. B. Harris, D. A. Zwemer, A. R. Gallo, and H. J. Robota, Surf. Sci. 85, L205 (1979).

[14] K. K. Innes, J. P. Byrne, and I. G. Ross, J. Mol. Spectrosc. 22, 125 (1967).

[15] P. B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972).

[16] This represents a reasonable distance based upon a van der Waals radius of the pyrazine molecule.

[17] C. E. Bugg, J. M. Thomas, M. Jundaralingam, and S. T. Rao, Biopolymers 10, 175 (1971).

[18] Here, we use the image plane defined in the jellium model [N. D. Lang and W. Kohn, Phys. Rev. B 7, 3541 (1973)] for Ag ($r_s = 3$).