no evidence for any density waves in the runs reported here. The icosahedral broken symmetry that does appear refers to a different order parameter. Our results do bear some resemblance to ideas of Hoare,[12] based on packing units with an icosahedral symmetry. Hoare argued that the size of these "amorphons" would grow in supercooled liquids until self-limited near the glass transition by frustration effects. The nonzero $\overline{Q}_{6m}$ order parameter reported here does not require literal icosahedral packing clusters; it measures a statistically defined average correlation between bond angles. Although it is tempting to associate the orientational correlation length $\xi_6(T^*)$ with an amorphon size, Fig. 3 seems more consistent with a large increase well *above* the molecular-dynamics glass "transition" at $T_g^* \approx 0.25-0.34$.[7] If long-range bond orientational order really sets in below T_c^*, it does seem reasonable that the equilibrium order parameter cannot go above a certain maximum value less than unity, because of frustration or "blocking" associated with the icosahedral symmetry. One might expect lengthy relaxation times prior to the order parameter reaching its maximal value at an instrinsic glass transition temperature T_0.

A more detailed account of these and other investigations, including studies of pressure and quench rate dependence, and an analysis of random packing models will be given elsewhere.

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[1] D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).

[2] *Ordering in Two Dimensions*, edited by S. K. Sinha (North-Holland, Amsterdam, 1981).

[3] R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. 46, 1135 (1981).

[4] D. R. Nelson and J. Toner, Phys. Rev. B 24, 363 (1981).

[5] F. C. Frank, Proc. Roy. Soc. London 215A, 43 (1952).

[6] We use Lennard-Jones temperatures $T^* = k_B T/\epsilon$ and densities $\rho^* = \rho\sigma^3$.

[7] C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1981), Vol. 48.

[8] See, e.g., S. Goshen, D. Mukamel, and S. Strikman, Solid State Commun. 9, 649 (1971).

[9] P. Steinhardt, D. R. Nelson, and M. Ronchetti, to be published.

[10] D. Frenkel and J. P. McTague, Phys. Rev. Lett. 42, 1632 (1979).

[11] S. A. Alexander and J. P. McTague, Phys. Rev. Lett. 41, 702 (1978).

[12] M. R. Hoare, Ann. N. Y. Acad. Sci. 279, 186 (1976).

Photon-Stimulated Desorption due to Multielectron Excitations in Chemisorbed Molecules: CO on Ni(100)

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The O^+ ion yield above the O(1*s*) absorption threshold (*K* edge) from CO on Ni(100) is found to deviate significantly from the absorption coefficient. It exhibits a delayed onset by more than 20 eV with a broad maximum more than 100 eV above the threshold. This indicates the dominance of multielectron excitations over Auger deexcitation as the bond-breaking step for O^+ desorption from chemisorbed CO molecules. Fine structure in the O^+ yield around 50 eV above threshold is assigned to a resonant shake-off process.

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Photon-stimulated ion desorption (PSID) from surfaces has been shown to offer great potential for the elucidation of the electronic structure[1-3] and bond geometry[4,5] of adsorbate complexes which are of vital interest for the understanding of surface chemistry and crystallography. This potential of PSID has been established on the assumption of the general validity of the Knotek-

Feibelman (KF) model[6] which links the PSID yield to bond-breaking Auger transitions filling the primary core hole of a surface atom, i.e., to the surface absorption coefficient. However, even within this simple model, the factors which govern the ion desorption probability for different adsorbate complexes are far from being entirely understood. In order for PSID to develop into a reliable tool for the investigation of general problems in surface chemistry and crystallography it is of fundamental importance to first understand the desorption process itself. The key issue is the understanding of the *intra-atomic* processes which lead to the production of valence holes following photon excitation of a core electron and of the *interatomic* charge transfer (reneutralization) in response to this excitation.

The goal of the present study is to elucidate the processes which govern the ion desorption from chemisorbed *covalent molecules*. Previous studies mainly dealt with chemisorbed atoms. Furthermore, the PSID signal in these cases predominantly originated from minority species which are believed to exhibit largely *ionic* bonding character. Here, we present results for CO on Ni(100) which, from a bonding and structure point of view, is one of the best understood systems in surface science.[7] At low temperature, CO is adsorbed molecularly on the Ni(100) surface via a Ni-C bond. The present work differs from a recent study of CO on Ru(001) by Madey *et al.*[8] in that it deals with O^+ desorption following deep *core electron* excitations [O(1*s*) level; $h\nu > 500$ eV] whereas direct valence excitations still play a major role in the spectral range $h\nu < 125$ eV used by Madey *et al.*[8] The only other PSID work on a covalent adsorption system is the work on CO on W(100) by Franchy and Menzel[9] using Al $K\alpha$ radiation. However as discussed below, the results presented here are significantly different since they evoke a new desorption model while the Auger decay mechanism was believed to be operative in Ref. 9.

Our results demonstrate that for CO on Ni(100) the O^+ yield does not follow the absorption coefficient above the O K edge. Rather, the PSID yield exhibits a delayed onset by more than 20 eV and reaches a maximum more than 100 eV above the O(1*s*) threshold. This indicates that in the present case the ion desorption cannot be described by the KF model. A multielectron excitation model is proposed to account for the observed energy dependence of the ion yield. This model is also corroborated by a resonance structure in the ion yield around $h\nu = 580$ eV which is attributed to a $1\sigma \rightarrow \sigma$ shape resonance, $3\sigma \rightarrow$ continuum (or *vice versa*) double excitation. The present results have important implications for future PSID work in that they question the general potential of core-level PSID studies for surface-structure determinations. The derivation of structural information from the surface-absorption-edge fine structure (SAFS)[10] and from surface extended x-ray absorption fine structure[5] critically depends on a one-to-one correlation of the ion yield with the corresponding surface absorption coefficient. This correspondence does not exist for the system investigated here.

Experiments were carried out on the grasshopper monochromator on beam line I-1 at the Stanford Synchrotron Radiation Laboratory. The monochromator was equipped with a freshly recoated holographic grating (1200 lines/mm). The storage ring (SPEAR) was operating at 3.0 GeV with a maximum current of ~ 75 mA in four groups of four bunches. The PSID ions were detected by a channel plate assembly with use of time-of-flight mass analysis.[3] The x rays were incident on the sample at an angle of 20° from the surface. The ion yield was flux normalized by using the electron yield signal from an *in situ* coated Cu grid positioned in the beam.[11] The Ni(100) single crystal was cleaned with use of established procedures. The PSID yield spectra were taken at saturation coverage of CO at a base pressure of $< 4\times 10^{-8}$ Pa. Exposures carried out over a wide temperature range ($80\ \mathrm{K} \leq T \leq 270\ \mathrm{K}$) resulted in identical spectra.

Figure 1 shows the O^+ PSID yield from CO on Ni(100) in the range $520\ \mathrm{eV} \leq h\nu \leq 800$ eV. The O^+ yield close to the O K edge (~ 530 eV) should

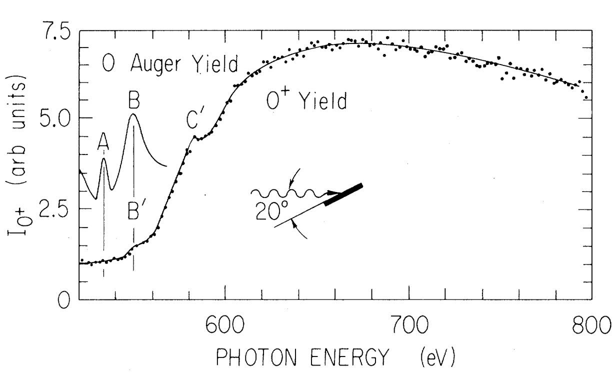

FIG. 1. O^+ PSID yield of 20-L CO on Ni(100) in comparison to the O *KLL* Auger (509 eV) yield which represents the absorption coefficient for chemisorbed CO.

be compared to the SAFS spectrum for the same sample[10] which is also shown in Fig. 1 for comparison. The SAFS spectrum was recorded by monitoring the O *KLL* Auger-electron yield. Peaks *A* (534 eV) and *B* (550 eV) in the SAFS spectrum correspond to transitions of a O(1*s*) (i.e., 1σ) electron to an empty 2π bound-state orbital and to a σ shape resonance, respectively. These two structures dominate the absorption spectrum in good accord with theory.[12] It is well established that the CO absorption *decreases* toward higher ($h\nu > 560$ eV) photon energy.[12,13] In contrast the O^+ PSID yield does not exhibit peak *A* and shows only a weak structure (B') at the peak-*B* position (550 eV). It steeply increases around 560 eV with a peak structure around 580 eV and reaches a broad maximum between 650 and 700 eV with a count rate of typically 200 counts/sec (which yields an estimate for the cross section of 1×10^{-22} cm^2). In addition to O^+ ions we also detected O^{2+} ions with a reduction in count rate by a factor of about 100. We did not observe any CO^+ ions in the energy range studied.

In contrast to the findings for the molecular chemisorption system CO on Ni(100) we show in Fig. 2 the O^+ PSID yield from dissociated oxygen on Ni(100). In this case the O(1*s*) absorption threshold is clearly revealed by a jump of the O^+ yield at ~532 eV with a pronounced absorption spike (width < 3 eV) just above threshold. At higher energies the ion yield exhibits a broad maximum around 650 eV with a count rate of typically 20 counts/sec. The energy dependence and count rate of the O^+ PSID yield from O on Ni(100) clearly indicates that the O^+ yield from CO on Ni(100) cannot originate from dissociated O atoms. Rather it is characteristic for molecular CO on the surface. The fact that within statistics the PSID yield was found to be independent of the CO adsorption temperature indicates that the CO-Ni bonding configuration (linear versus bridge)[15] does not play an important role in the desorption mechanism of O^+ ions around the O *K*-edge region.

The observed energy dependence of the O^+ yield from CO on Ni(100) in Fig. 1 cannot be explained by the conventional KF Auger deexcitation model. Since in the KF model the ion desorption follows an Auger cascade filling the primary O(1*s*) hole, the O^+ yield should closely mimic the absorption coefficient (i.e., the SAFS spectrum in Fig. 1). The main evidence for the failure of the KF model comes from the *delayed onset* of the O^+ PSID yield and not from discrepancies between the PSID and SAFS spectra below 560 eV. In fact we attribute peak B' in the O^+ yield to desorption proceeding via the KF mechanism. Peak *A* is not observed in the PSID yield because it corresponds to a bound-state transition. The excited but bound photoelectron will greatly enhance the reneutralization and therefore quench the ion desorption at this energy. Unfortunately, for our experimental geometry[3] low count rates prevented us from recording O^+ yield spectra at larger angles of incidence (> 20°). Such polarization-dependent studies would yield additional information since the KF mechanism is expected to give rise to a polarization-dependent edge fine structure similar to the absorption coefficient.[10]

The steep increase of the O^+ PSID yield around 560 eV indicates that another excitation channel opens up at this energy which is much more efficient for O^+ production than the conventional core-hole deexcitation channel in the KF model. We attribute this observation to the dominance of a novel desorption mechanism which involves *bond breaking via multielectron excitations*. It is well established from gas-phase work[16] that ionization of a 3σ electron in CO is most effective in causing $C + O^+$ fragmentation. This is also supported by the recent low-energy O^+ PSID study of CO on Ru(001).[8] For CO on Ni(100) the 1σ and 3σ one-electron binding energies are 531 and 29 eV, respectively.[17] Double excitation of a 1σ and a 3σ electron would require an energy which corresponds to the sum of the one-electron binding energies plus a correction for the hole-hole correlation energy. Using an equivalent-core concept (replacing C^+ by N), we can estimate the correlation-energy correction from the difference in the 3σ binding energies between CO (38.3 eV) and NO (40.6 eV) and the corresponding carbonyls and nitrosyls[14] to be of the order of 2–3 eV. Double excitation of a 1σ and a 3σ electron would thus require a photon energy in excess of 560 eV in good accord with the PSID threshold value. The probability for this 3σ shake-off process is expected to first increase with excitation energy as observed until at higher energies it has to decrease because the 1σ excitation cross section decreases. Thus the overall shape of the O^+ yield spectrum in Fig. 1 is in good qualitative agreement with the one expected from our model.

Further evidence for our model comes from the position of peak C' in Fig. 1. When the $\vec{E}$ vector of the light is directed along the molecular axis excitation of electrons from a σ (e.g., 1σ or 3σ) initial state is enhanced when the final state is a σ shape resonance. In fact, peak B in the SAFS spectrum in Fig. 1 corresponds to such a $1\sigma \rightarrow \sigma$ shape resonance excitation.[10] Thus one would expect an enhancement in the O^+ yield at the photon energy where the 1σ electron is excited to the shape resonance and the 3σ electron is just ionized or *vice versa*. This should occur about 30 eV above peak B or around 580 eV in excellent agreement with the position of peak C'.

The question arises why the KF Auger deexcitation channel is so inefficient as compared to the shake-off channel. If peak B' signifies the strength of the KF channel it is seen from Fig. 1 that around 650 eV the shake-off channel is more efficient than the KF channel by more than one order of magnitude. It is known from gas-phase Auger studies of CO[18] that in fact $3\sigma \rightarrow 1\sigma$ Auger deexcitation accompanied by a valence electron (e.g., 1π) excitation is nonnegligible and one would expect $C + O^+$ fragmentation. Apparently reneutralization of the (rather deep) 3σ valence hole created in an Auger deexcitation following a single core-hole excitation must be rather effective, thus suppressing fragmentation of the molecule. In our model a multielectron excitation leaves the O atom in the CO molecule in a 1σ and 3σ hole state. Auger deexcitation following the multielectron excitation will furthermore enhance the positive charge. Since the probability that an O atom survives the desorption as a positively charged ion increases with the number of holes created during the photon excitation[19] and subsequent Auger deexcitation process, the shake-off process is more likely to result in O^+ desorption than the single core-hole excitation.

Finally we need to comment on the probability of the proposed 1σ, 3σ double excitation process. For a CO coverage of 0.7 monolayer and a flux of 1×10^9 photons/sec at $h\nu = 600$ eV we calculate a count rate of 5×10^5 O(1s) photoelectrons from tabulated cross sections.[20] Our observed count rate of 150 ions/sec then yields a ratio of about 3×10^{-4} ions per O(1s) photoelectron. This value is also a *lower* limit for the shake-off probability (i.e., if every multielectron excitation results in an O^+ ion). Note that this low value for the 3σ shake-off probability excludes the observation of the corresponding shake-off structure in a photoemission experiment but yet it dominates the ion desorption.

It is tempting to attribute the weak broad maximum in the O^+ PSID yield from atomic oxygen on Ni(100) to multielectron excitations as well. However, we believe that in this case the broad maximum is largely due to the energy dependence of the atomic O(1s) photoemission cross section as observed experimentally[21] and shown as a dashed line in Fig. 2.

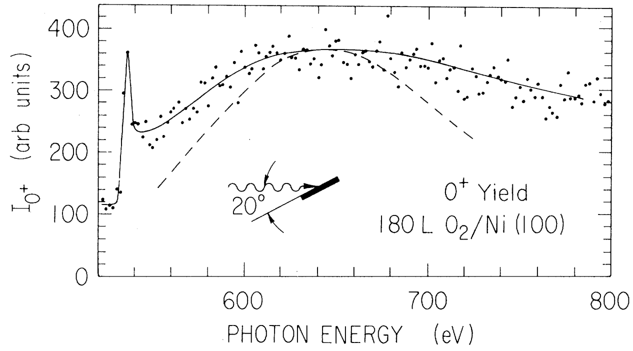

FIG. 2. O^+ PSID yield of 180-L oxygen on Ni(100). The dashed line represents the O(1s) photoemission cross section (Ref. 14).

The present results establish for the first time a novel mechanism for ion desorption following photon absorption which is shown to be dominant for CO chemisorbed on Ni(100). We have also observed similar effects for NO on Ni(100) which will be published elsewhere. This leads to the conclusion that multielectron excitations may in general dominate PSID from surfaces for adsorbate complexes with *covalent* bond character. For *ionic* bonds the KF model appears to provide an adequate description. Limitations in the use of PSID for surface-structure determinations implied by our results are pointed out.

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[1] M. L. Knotek, V. O. Jones, and V. Rehn, Phys. Rev. Lett. 43, 300 (1979).

[2] D. P. Woodruff, M. M. Traum, H. H. Farrell, N. V. Smith, P. D. Johnson, D. A. King, R. L. Benbow, and Z. Hurych, Phys. Rev. B 21, 5642 (1980).

[3] R. Jaeger, J. Stöhr, J. Feldhaus, S. Brennan, and D. Menzel, Phys. Rev. B 23, 2102 (1981).

[4] T. E. Madey, R. Stockbauer, J. F. van der Veen, and D. E. Eastman, Phys. Rev. Lett. 45, 187 (1980).

[5] R. Jaeger, J. Feldhaus, J. Haase, J. Stöhr, Z. Hussain, D. Menzel, and D. Norman, Phys. Rev. Lett. 45, 1870 (1980).

[6] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. 40, 964 (1978).

[7] F. J. Arlinghaus, J. G. Gay, and J. R. Smith, in *Theory of Chemisorption*, edited by J. R. Smith (Springer-Verlag, New York, 1980), p. 71, and references therein.

[8] T. E. Madey, R. Stockbauer, S. A. Flodström, J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B 23, 6847 (1981).

[9] R. Franchy and D. Menzel, Phys. Rev. Lett. 43, 865 (1979).

[10] J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler, and S. Brennan, Phys. Rev. Lett. 47, 381 (1981).

[11] J. Stöhr, R. Jaeger, J. Feldhaus, S. Brennan, D. Norman, and G. Apai, Appl. Opt. 19, 3911 (1980).

[12] J. L. Dehmer and D. Dill, J. Chem. Phys. 65, 5327 (1976).

[13] A. P. Hitchcock and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. 18, 1 (1980).

[14] E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B 18, 1673 (1978); E. W. Plummer, G. Loubriel, D. Rajoria, M. R. Albert, L. S. Sneddon, and W. R. Salaneck, J. Electron Spectrosc. Relat. Phenom. 19, 35 (1980).

[15] S. Anderson, Solid State Commun. 21, 75 (1977).

[16] G. R. Wight, M. J. Van der Wiel, and C. E. Brion, J. Phys. B 9, 675 (1976).

[17] P. R. Norton, R. L. Tapping, and J. W. Goodale, Chem. Phys. Lett. 41, 2 (1976).

[18] W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. 55, 2317 (1971).

[19] P. J. Feibelman, Surf. Sci. 102, L51 (1981).

[20] S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom 21, 285 (1981).

[21] D. H. Rosenblatt, J. G. Tobin, M. G. Manson, R. F. Davis, S. D. Kevan, D. A. Shirley, C. H. Li, and S. Y. Tong, Phys. Rev. B 23, 3828 (1981).

Pressure Measurement of Solid ^{3}He through the Magnetic Ordering Temperature

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The pressure of solid ^{3}He has been measured as a function of temperature and molar volume down to and through its nuclear ordering temperature. Pressure measurement above the ordering temperature reveals that besides the known $1/T$ term there are a significant negative term in $1/T^2$ and a positive term in $1/T^3$. The observed discontinuous change in pressure through the ordering temperature is discussed in connection with the first-order phase transition.

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Solid ^{3}He shows a peculiar nuclear magnetism because of its unique direct exchange interaction, although it has a simple nuclear spin $\frac{1}{2}$ and a bcc crystal in the low-pressure phase. The direct exchange interaction depends strongly on the lattice spacing, i.e., molar volume of solid ^{3}He. In this respect pressure measurements of solid ^{3}He have provided valuable data on the exchange interaction.[1] So far the investigated temperature range, however, has been limited to above 13 mK because of the long relaxation time. We have lowered the temperature range down to 0.47 mK, and present here the first measurements of the pressure of solid ^{3}He in that temperature range. Higher-order terms than the first-order term of $1/T$ have been observed in the pressure versus temperature relation above the ordering temperature T_N and new information on the ordering has been obtained from the pressure measurements in the ordered state.

Cooling was performed by means of adiabatic demagnetization of a copper bundle. A pulsed Pt