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Core-level binding-energy-shift analysis of adsorption and dissociation

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An analysis of core-level binding-energy shifts of adsorbed atoms and molecules is used to determine important thermochemical quantities which are often otherwise unmeasurable. Also presented are a new approach to interpreting adsorbate core-level spectra and a novel technique for probing adsorbed molecules in energetically unfavored orientations.

Attempts to interpret x-ray photoelectron spectra (XPS) of core levels of adsorbed atoms and molecules in terms of chemical shifts and screening shifts have played a major role in the field of surface science. However, an alternative approach can be based on the equivalent-core approximation (ECA), together with Born-Haber cycles. Such an approach has been used on gas phase molecules[1] and on metallic elements[2] to correlate thermodynamic quantities with core-level shifts, and it now appears[3] it can also be used to extract thermochemical properties which determine molecular adsorption and dissociation phenomena.

The purpose of the present work is to demonstrate that the application of this approach to adsorbed molecules and atoms provides a variety of thermochemical values such as heats of adsorption and dissociation which often cannot be measured by any other method.[4] Some such quantities, e.g., the orientational dependence of molecular heats of adsorption, are important parameters in understanding surface molecular dynamics.[5] Also, this method of analysis suggests a new conceptual approach to interpreting adsorbate core-level spectra in cases in which traditional methods are inadequate.

The work reported here was performed under ultrahigh-vacuum conditions (10^{-11} Torr) according to standard procedures.[6] Figure 1 presents XPS experimental data typical of that recorded in this work. Figure 1(a) is the spectrum of the region containing the fully screened part of the nitrogen $1s$ core-level photoemission for 0.5 monolayer (ML) of N_2 adsorbed at 100 K on Ni(100) in the $c(2\times2)$ structure. (A satellite peak at larger binding energy corresponds to incomplete screening and is off scale here.) Since the N_2 axis is perpendicular to the Ni(100) surface,[7] it is reasonable to associate the two features evident in Fig. 1(a) with the two inequivalent nitrogen atoms.[8] In Fig. 1(b), the data are resolved into a smoothly rising background and two identical Gaussian peaks having binding energies of 400.96 and 399.63 eV. According to simple, conventional analysis it would be expected that for a weakly adsorbed molecule like N_2 on Ni(100) there would be little chemical-shift difference between the two nitrogen atoms but that core-hole screened by the metal would be different and larger for the nitrogen atom closer to the surface. The nitrogen atom closer to the surface would therefore exhibit the smaller binding energy; in this case, it would be the 399.63-eV peak. However, such an analysis is misleading. The best way to see this is to view the photoemission process of Fig. 1 as a transition from a single initial state, namely N_2 on Ni(100), to either of two final states, a fully screened nitrogen $1s$ core hole on either the inner or the outer nitrogen atom. At this point, the ECA is applied to equate a nitrogen atom containing a fully screened core hole to an oxygen atom.[9] Then the ECA final states can be represented, as in Fig. 1(b), by a NO molecule bonded in either of two orientations. Assignment of the two XPS peaks to the two orientations is based on the well-known fact that NO bonds nitrogen-end down; i.e., this is the preferred or lower-energy state. Thus, the energy required to go from the initial state to the final state of lower energy must be the smaller of the two energies, or 399.63 eV. Thus the 399.63-eV peak corresponds to the outer nitrogen atom. The present analysis is clearly superior to simple chemical-shift–screening-shift arguments since it treats the photoelectron spectrum as what it really is, a group transition from the same initial state to a variety of final states.

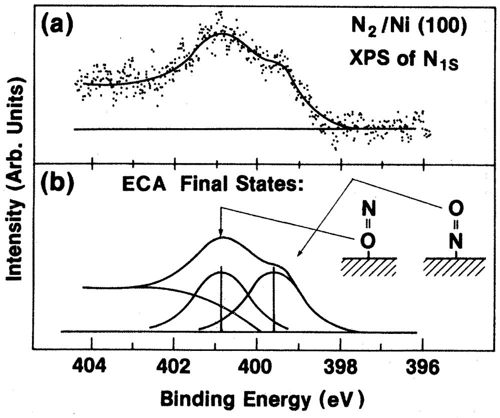

FIG. 1. The x-ray photoelectron spectrum of N_2 adsorbed on Ni(100) is presented in (a) and resolved into two peaks in (b). Also shown are the equivalent-core approximation final states.

The data of Fig. 1 can also be used to determine heats of adsorption for NO molecules adsorbed in the orientations illustrated in Fig. 1(b). This is based on the Born-Haber cycle (two energy pathways from the same initial point to the same final point) shown in Fig. 2(a). The starting point in Fig. 2(a) is an N_2 molecule on Ni(100). The first step is N_2 desorption. The energy change for this step was measured by thermal desorption in the present work to be 11 kcal/mol. The second step is the excitation of a $1s$ electron in gas phase N_2 to the Π^* orbital. The energy for this step is 400.64 eV.[10] This transforms the molecule into the equivalent-core version of NO.[11] The other path to this same final point starts with the adsorbed N_2 molecule and

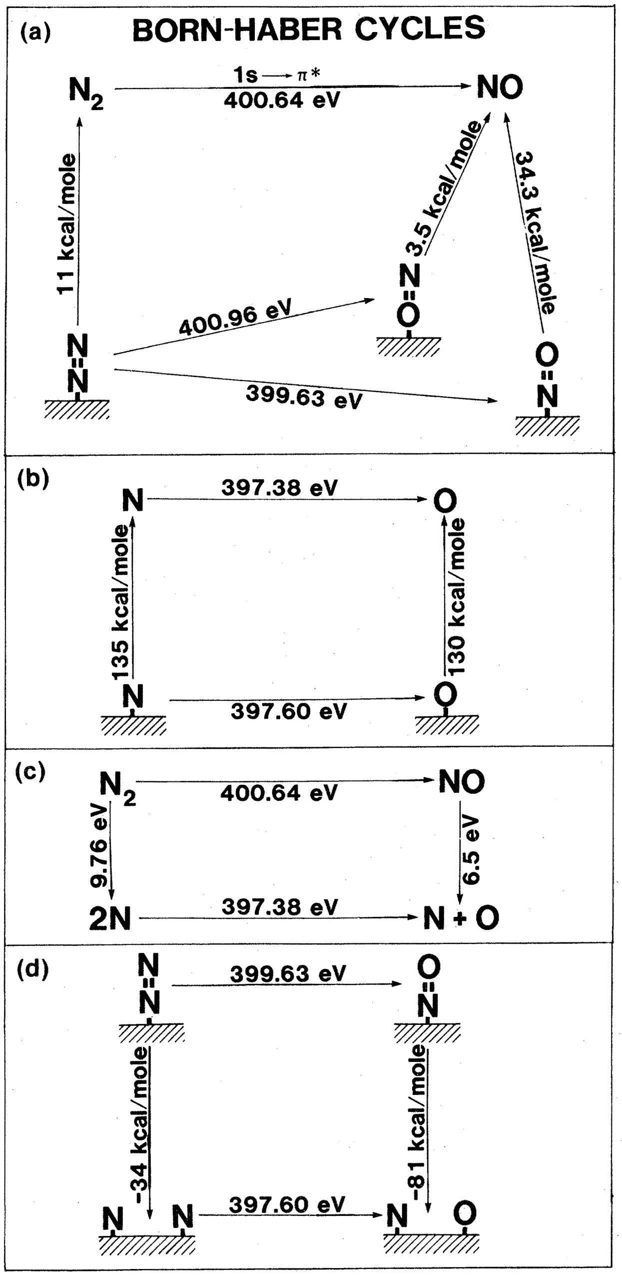

FIG. 2. The Born-Haber cycles used (a) to interpret Fig. 1, (b) for determining the heat of atomic oxygen adsorption on Ni, (c) for determining the atomic nitrogen 1*s* excitation energy, and (d) for determining the heat of dissociation of adsorbed NO.

uses the XPS result of Fig. 1 to convert it into either of the illustrated NO states.[12,13] The next step is to desorb NO from these adsorbed orientations. The energies for this step can be determined since the energies of all other steps in the Born-Haber cycle are known. The values obtained are 34.3 and 3.5 kcal/mol for NO bonded nitrogen-end down and oxygen-end down, respectively.[14] These values indicate, as expected, that NO is moderately strongly chemisorbed nitrogen-end down but physisorbed oxygen-end down. An orientational difference in heats of adsorption such as this, far from being a mere intellectual curiosity, is a key parameter required in model calculations of surface molecular dynamics.[5] Moreover, it should be noted that this is the first measurement of an orientational difference in heats of adsorption and that such a difference cannot, at present, be measured by any other method.

Figure 2(b) illustrates how this approach may be applied to atomic chemisorption. The nitrogen 1*s* binding energy measured in the present work for the $c(2\times 2)$ structure of atomic nitrogen on Ni(100) is 397.60 eV. When compared with the gas phase excitation value for atomic nitrogen [derived in Fig. 2(c)] of 397.38 eV, in the context of the ECA and the Born-Haber cycle of Fig. 2(b), it is clear that the heat of adsorption of atomic nitrogen $\Delta H^{\mathrm{N}}_{\mathrm{ads}}$, must be 0.22 eV larger than that of atomic oxygen. This is significant since the heat of adsorption atomic oxygen, $\Delta H^{\mathrm{O}}_{\mathrm{ads}}$, on Ni has so far been measured only by rather crude techniques.[15] The value of $\Delta H^{\mathrm{N}}_{\mathrm{ads}}$ for Ni has, however, been determined from thermal desorption measurements to be 135 kcal/mol.[16] Since this must be 0.22 eV (=5 kcal/mol) larger than $\Delta H^{\mathrm{O}}_{\mathrm{ads}}$, we now have a new and far more reliable[14] value for $\Delta H^{\mathrm{O}}_{\mathrm{ads}}$ of 130 kcal/mol. Note that this value has not been and, in fact, cannot be determined by thermal desorption since oxygen does not desorb even at the Ni melting point. Thus, the present approach constitutes the only technique currently available for making reliable determinations of such important physical properties as $\Delta H^{\mathrm{O}}_{\mathrm{ads}}$ on Ni.

Figure 2(d) illustrates how the present approach may be used to measure heats of dissociation of adsorbed molecules that could not otherwise be determined. This case starts with the adsorbed N_2 molecule and the first step is for the heat of dissociation of adsorbed N_2, $\Delta H^{a\text{-}\mathrm{N}_2}_{\mathrm{diss}}$. The value for this quantity is just $\Delta H^{\mathrm{N}_2}_{\mathrm{ads}} + \Delta H^{g\text{-}\mathrm{N}_2}_{\mathrm{diss}} - 2\Delta H^{\mathrm{N}}_{\mathrm{ads}} = 11$ kcal/mol $+9.76$ eV $-2(135$ kcal/mol$) = -34$ kcal/mol. The next step uses the data of Fig. 2(b). Note one nitrogen atom is photoionized, and the other is a spectator. The other path to this final state is to photoionize the outer nitrogen atom, with an energy of 399.63 eV, to go to NO (as in Fig. 1) and then to dissociate the NO molecule. Since the energies associated with the other three steps are known, $\Delta H^{a\text{-}\mathrm{NO}}_{\mathrm{diss}}$ is found to be -81 kcal/mol. The minus sign means the process is exothermic. It should be noted that prior to this work, the only way available to estimate such a quantity required the use of an outdated and suspect value for $\Delta H^{\mathrm{O}}_{\mathrm{ads}}$.[15]

In conclusion, the present work demonstrates how the core-level binding-energy-shift analysis of adsorption and dissociation provides important thermodynamic quantities that often cannot be measured by any other method. It also provides a new approach to interpreting XPS peaks of adsorbates when the peak assignment is not immediately clear. Finally, it provides a novel technique for probing molecules adsorbed in configurations other than their energetically favored ones.

[1] The usefulness of this approach for gas phase molecules was first reported in W. L. Jolly and D. N. Hendrickson, J. Am. Chem. Soc. 92, 1863 (1970).

[2] Born-Haber cycles were first used with the ECA on metallic elements by J. S. Jen and T. D. Thomas, Phys. Rev. B 13, 5284 (1976), and developed more extensively by B. Johansson and N. Mårtensson, *ibid.* 21, 4427 (1980).

[3] Recent work demonstrates that when thermochemical properties of adsorbates are known or assumed in advance, the adsorbate core-level binding energies may be predicted. See M. Grunze, C. R. Brundle, and D. Tománek, Surf. Sci. 119, 133 (1982); D. Tománek, P. A. Dowben, and M. Grunze, Surf. Sci. 126, 112 (1983).

[4] An earlier attempt at this, using a quite different conceptual framework, was subject to errors (±1 eV) that were usually as large as the heats of adsorption involved. See J. Q. Broughton and D. L. Perry, J. Electron Spectrosc. Relat. Phenom. 16, 45 (1979).

[5] J. C. Tully, Acc. Chem. Res. 14, 188 (1981).

[6] For details see W. F. Egelhoff, Jr., Appl. Surf. Sci. 11/12, 761 (1982).

[7] J. Stöhr and R. Jaeger, Phys. Rev. B 26, 4111 (1982).

[8] A similar interpretation was made for the two peaks seen for N_2 on W(110). See J. C. Fuggle and D. Menzel, in *Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces, Vienna, 1977,* edited by R. Dobrozemsky *et al.* (F. Berger, Söhne, Vienna, 1977), p. 1003. Earlier XPS work for N_2 on Ni(100) did not resolve the two structures seen in Fig. 1(a), presumably due to lower instrumental resolution. See J. C. Fuggle, E. Umbach, D. Menzel, K. Wandelt, and C. R. Brundle, Solid State Commun. 27, 65 (1978). The two peaks were resolved, however, for N_2 on Ni (110). See M. Golze, M. Grunze, R. K. Driscoll, and W. Hirsche, Appl. Surf. Sci. 6, 464 (1980).

[9] Note that they are equated only in the sense that they are expected to have essentially indistinguishable chemical properties since the core hole approximates another proton in the nucleus and the screening charge approximates another valence electron. For a fully screened deep core hole, the ECA is an excellent approximation since for valence electrons a deep core hole is almost indistinguishable from a point charge. For further details see J. B. Mann, Los Alamos Scientific Laboratory Report No. LA-3690, 1967 (National Technical Information Center, Washington, D.C.); D. A. Shirley, Chem. Phys. Lett. 16, 220 (1972); and W. F. Egelhoff, Jr., Phys. Rev. Lett. 50, 587 (1983). Furthermore it should be noted that any remaining error in the ECA will tend to cancel since the ECA is always used twice (i.e., as difference in core electron energy between gas phase N_2 and adsorbed N_2). Thus the ECA error occurs in a higher order.

[10] A. P. Hitchcock and C. E. Brion, J. Electron. Spectrosc. Relat. Phenom. 18, 1 (1980). Since spin conservation prevents the $1s \rightarrow 2p\Pi_g$ (Π^*) dipole transition from reflecting the multiplet centroid, the value in Fig. 2(a) has been corrected slightly, using the NO Rydberg series and the $1s \rightarrow 3s\sigma_g$ transition where such multiplet splitting will be negligible.

[11] The excellence of this approximation can be judged by the fact that an excited N_2 molecule with a $1s$ electron excited to the Π^* orbital has a bond length which differs from that of NO by less than 1% and vibrational excitation energies that differ by less than 0.5%. See G. C. King, F. H. Read, and M. Tronc, Chem. Phys. Lett. 52, 50 (1977).

[12] Since the XPS process is sudden with respect to molecular vibrations the nuclear coordinates are effectively frozen. This raises the question of whether the Franck-Condon factors will leave the molecule in a vibrationally excited final state. The best indications are that for a transition like $N_2 \rightarrow$ "NO" the bond length changes (≈ 0.05 Å) are so small that the transition will be to the vibrational ground state. See H. Ågren, L. Selander, J. Nordgren, C. Nordling, K. Siegbahn, and J. Muller, Chem. Phys. 37, 161 (1979).

[13] The N $1s$ binding energies are measured with respect to E_F. For the fully screened N $1s$ peak this is exactly the energy needed to turn N_2 into the ECA version of NO (the screening charge in the Π^* orbital). Thus no referencing to any vacuum level is required either in the adsorbed state or in the gas phase.

[14] The estimated uncertainty in these values of ±4 kcal/mol is due to the instrumental calibration for measurement of the absolute nitrogen $1s$ binding energies. See C. J. Powell, N. E. Erickson, and T. Jach, J. Vac. Sci. Technol. 20, 625 (1982).

[15] A value of 115 kcal/mol for $\Delta H^{0}_{\mathrm{ads}}$ is obtained from thermocalorimetry. See D. Brennan, D. O. Hayward, and B. M. W. Trapnell, Proc. R. Soc. London, Ser. A 256, 81 (1960).

[16] H. Conrad, G. Ertl, J. Kuppers, and E. E. Latta, Surf. Sci. 50, 296 (1975); Y. Sakisaka, M. Miyamura, J. Tamaki, M. Nishijima, and M. Onchi, *ibid.* 93, 327 (1980).