Comments

Thermal desorption, indirect lateral interactions, and the $2\pi^*$ resonance model of CO chemisorbed on transition metals

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Gumhalter, Wandelt, and Avouris [Phys. Rev. B **37**, 8048 (1988)] have proposed a unified interpretation of a variety of experimental spectroscopic properties of chemisorbed CO on transition-metal surfaces in terms of a CO $2\pi^*$ resonance. It is pointed out here that for the strongly chemisorbed state of CO on Pt(111), independent evidence in support of the same model comes from the analysis by Joyce et al. [J. Phys. C **20**, 3381 (1987)] of the desorption measurements of Ertl, Neumann, and Streit [Surf. Sci. **64**, 393 (1977)] as a function of coverage.

By studying a variety of experimental spectroscopic features, e.g., threshold energies, level shifts, and line shapes, in terms of a CO $2\pi^*$ resonance, Gumhalter, Wandelt, and Avouris[1] have proposed a unified interpretation of such data for CO chemisorbed on transition- and noble-metal surfaces.

The purpose of this Comment is to stress that quite independent evidence in support of this same model comes from the analysis of the desorption measurements of Ertl, Neumann, and Streit[2] by Joyce et al.[3] These latter workers, in particular, set up a semiquantitative treatment of the indirect lateral interactions between CO molecules strongly chemisorbed on the (111) surface of Pt, and used the results to calculate the decrease in the desorption energy with coverage that had been observed by Ertl et al.[2]

Whereas, following pioneering work of Grimley[4] and Einstein and Schrieffer,[5] the independent studies of Flores, March, and Moore,[6] and Lau and Kohn[7] had demonstrated that an indirect interaction energy ΔE_{int} for a pair of atoms parallel to a planar metal surface would fall off with atomic separation r like r^{-5} times an oscillatory factor, in marked contrast to interactions in bulk metal[8] with inverse power r^{-3}, not r^{-5}, Joyce et al. studied the interaction between CO molecules in the $2\pi^*$ resonance model. They were able to demonstrate from their model that, with CO, the lateral interaction between parallel molecules chemisorbed on a planar surface was, at suitably large separations r,

$$\Delta E_{\text{int}}(r) \sim \beta \cos(2k_F r + \phi)/r^5 . \qquad (1)$$

Gumhalter[9] had earlier shown that the $2\pi^*$ molecular state interacts predominantly with the sp band of metal electrons, and Joyce et al.[3] noted that the underlying assumption made in deriving Eq. (1) of a spherical Fermi surface of diameter $2k_F$ was well justified therefore.

Two routes were then adopted to estimate the amplitude β and the phase ϕ in Eq. (1). The first route was via the $2\pi^*$ resonance model, in which a single parameter, denoted by V, characterized the strength of the metal surface-adsorbate interaction. For physically reasonable values of this parameter, ϕ was calculated from the model to range from 0.75 to 1.4, while the amplitude β for the same range of V varied from 0.3 to 0.8 in units 10^7 J mol^{-1}Å^5. The second route was to utilize Eq. (1), plus direct and site contributions discussed fully in Ref. 3, to extract from a least-squares fit of the experimental decrease in the desorption energy observed by Ertl et al. the values $\phi = 0.95$ and $\beta = 1 \times 10^7$ J mol^{-1}Å^5 for CO on Pt(111). Fixing V at 4 eV to obtain the phase ϕ correctly, the model of Joyce et al.[3] yielded $\beta = 0.4 \times 10^7$ J mol^{-1}Å^5, in quite reasonable accord with the experimentally extracted number.

In summary, independent evidence in support of the interpretation of spectroscopic features associated with CO chemisorbed on transition-metal surfaces is afforded by the interpretation that can be given of desorption data for CO on Pt(111), in terms of indirect lateral interactions of the form (1), with amplitude β and phase ϕ given by the $2\pi^*$ resonance model. Simpler, nonresonance models turn out to underestimate the amplitude of the indirect interaction by several orders of magnitude.

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