LOW-ENERGY ELECTRON SCATTERING BY MOLECULES ADSORBED ON METAL SURFACES

Z. Lenac
"Rudjer Bošković" Institute, 41001 Zagreb, Croatia,
Yugoslavia

M. Šunjić*
Institute of Physics, University of Zagreb, 41001 Zagreb,
Croatia, Yugoslavia

Scattering cross section

High-resolution electron energy loss spectroscopy of molecules adsorbed on metal surfaces has recently been the subject of extensive investigations$^{1-10)}$. This method is capable of giving important information on the structure and bonding of adsorbates. In many cases, adsorbed molecules of very low concentration can be treated as dipoles in the first approximation. We may assume the following: (i) The molecule is described as a point dipole oscillating harmonically with frequency ω_0; it is placed at z_0 above the metal surface and couples to the electron by the electron-dipole interaction. (ii) The molecule is screened by the metal through the classical image term. (iii) Above the metal surface (z>0) the electron wave function is represented as a "reflected plane wave":

$$\psi^{\pm}_{\vec{Q}}(\vec{r}) = e^{i\vec{\kappa}\vec{\rho}}(e^{\mp ikz} + R(\vec{Q})e^{\mp i2\delta(\vec{Q})}\; e^{\pm ikz}) \qquad (1)$$

Here (+,-) refer to the incoming and outgoing state, respectively. $\vec{Q}=(\vec{\kappa},\pm k\hat{z}_0)$ is the free-electron wave vector divided into a parallel ($\vec{\kappa}$) and a normal (k>0) component. R^2 is the reflectivity and δ is the phase shift for surface potential scattering in the specular direction.

The differential cross section in the first Born approximation is simply defined as the ratio of the one-loss to no-loss line:

$$\frac{d\sigma}{d\Omega'} = \frac{1}{R^2 S_{eff}} \left(\frac{E'}{E}\right)^{1/2} \frac{m}{M} \frac{e^2}{E\cdot\hbar\omega_0} \left(\frac{d\mu}{ds}\right)^2 \cdot |f(\vec{Q},\vec{Q}')|^2 \qquad (2)$$

where the scattering amplitude describing the angular

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[*] Also at the "Rudjer Bošković" Institute, Zagreb, Croatia, Yugoslavia.

dependence of the scattered electrons is

$$f(\vec{Q},\vec{Q}') = \frac{\Omega}{4\pi} \langle \psi^{-}_{\vec{Q}'} | \frac{\hat{\mu}_o \vec{r}}{r^3} | \psi^{+}_{\vec{Q}} \rangle \ . \qquad (3)$$

The wave vector $\vec{Q}$ ($\vec{Q}'$) of the incoming (outgoing) electron with energy E ($E' = E - \hbar\omega_o$) forms an angle θ (θ') with the surface normal; m is the electron mass, M the vibrator reduced mass and s the vibrator normal coordinate. $\vec{\mu} = \mu\hat{\mu}_o$ is the dipole moment of the real and image dipole and it generally contains both the parallel ($\vec{\mu}_{\parallel}$) and the normal ($\vec{\mu}_{\perp}$) component. $S_{eff} = S \cos\theta$ is the effective normalization area, where S is the metal surface per one adsorbed molecule. The factor K^2 normalizes the spectrum (2) per one elastically reflected electron in the specular direction.

Results

Insertion of (1) into (3) gives four terms contributing to f, as shown schematically in fig. 1. The first term represents the scattering from the dipole, with zero surface reflectivity and no phase change. For the corresponding gas-phase case, this term gives a cross section peaked in the forward direction, and it contributes little in the forward direction of observation. This is also valid for the fourth term ($\sim RR'$).

The second (third) term proportional to R (R') represents the electron-dipole scattering after (before) reflection on the surface, with phase change δ (δ'). The scattering peak is in the specular direction. These terms contribute most of the inelastic spectrum; they diverge for elastic scattering, leading to $\sigma_{el} \sim R^2$, as expected.

Apart from the usual interference between the four terms

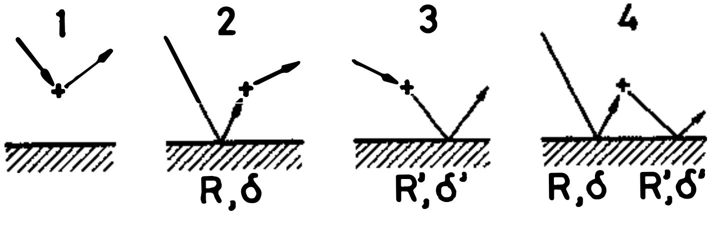

Fig.1. The four contributions to the scattering amplitude. Abbreviations: $R=R(\vec{Q})$, $R'=R(\vec{Q}')$, $\delta=\delta(\vec{Q})$, $\delta'=\delta(\vec{Q}')$.

in Fig. 1 there is also the interference between the normal and parallel dipole scattering. However, for randomly oriented dipole there is no such interference effect. The same holds in the limit $R=R'=1$.

We may say that the maximum of $|f|^2$ is very close to the specular direction when the second and third term in fig. 1 dominate, i.e. for all reflectivities except for $R<<1$. The shift ε of the maximum of $|f|^2$ from the specular direction is a consequence of the momentum and energy conservation in inelastic scattering, i.e. $\varepsilon \to 0$ when $E' \to E$.

The first term dominates in the limit $R<<1$, and the scattering is rather diffuse with the maximum shifted from the specular to the horizontal direction.

Although $|f|^2$ depends strongly upon R , one can show that it is rather insensitive to the choice of δ. Let us now explain how f depends on z_o. In the limit $Qz_o << 1$, the image term gives the same contribution to $f_\perp$ as the real dipole and completely cancels $f_\parallel$. By increasing Qz_o, f starts to oscillate. In the limit $Qz_o >> 1$, the image term does not contribute to f. Furthermore, the total cross section calculated in the limit $R=R'=1$ is exactly twice larger than for the free dipole. For perfect absorption $(R=R'=0)$, the differential and total cross sections are the same as for the backward scattering from the free dipole.

The total cross section σ is obtained by integrating (2) around the specular direction and over the space angle defined by the aperture of the analyzer. Usually, $\sigma_\perp >> \sigma_\parallel$ Moreover, for elastic scattering $\sigma_\perp$ diverges for each z_o, while $\sigma_\parallel$ diverges logarithmically only in the free-dipole limit $(z_o \to \infty)$. This means that the "metal-surface selection rule" from infrared absorption is still valid for elastic electron scattering, i.e. only the normal vibration is practically excited. It may be concluded that this rule holds generally if the dipole is not too far from the surface whose reflectivity is not too low and if the excitation energy is small compared with the incoming electron energy.

Let us point out how $\sigma \sim |f|^2/R^2$ depends on R. (i) If R is not too low $(R^2 \gtrsim 0.1)$, $|f|^2$ is roughly proportional to R^2, so σ depends weakly on R. (ii) If $R^2 << 1$, then $|f|^2$ depends weakly on R, so σ becomes a strongly dependent function of R.

Discussion

Fig. 2 shows the energy dependence of the total cross section. The parameters are chosen so as to correspond to CO molecules adsorbed on a Ni surface[1,10-13].

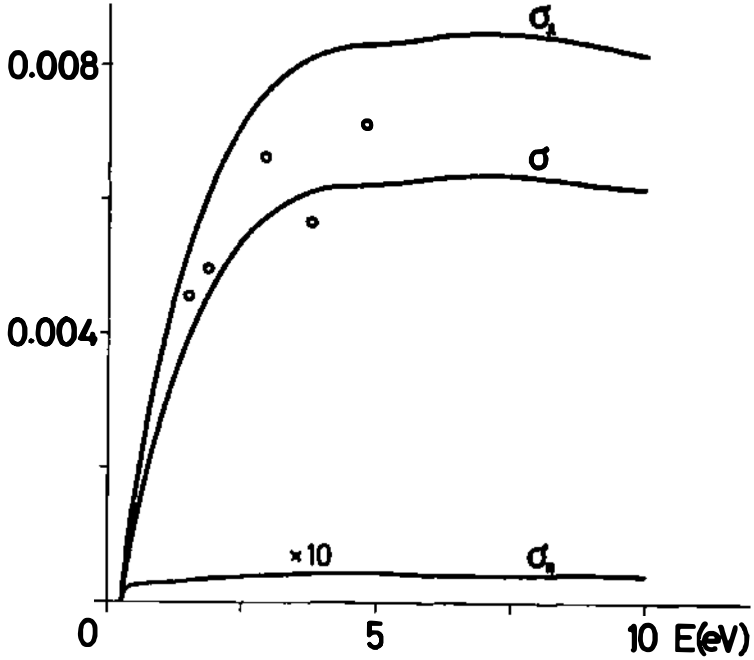

Fig.2. The total cross section σ with its normal $\sigma_\perp$ and parallel $\sigma_\parallel$ components for CO adsorbed on a Ni surface. Experimental data are represented by dots.

For experimental energies $E \gtrsim 1.4$ eV[1,14], the second and third term in Fig. 1 dominate. This means that (a) σ depends weakly on R and (b) the electron momentum transfer occurs mostly in the reflection on the surface. (a) explains the agreement of our theory with the perfect-reflectivity result[4-6], while (b) explains the agreement with the classical trajectory calculations[2,3]. The results are in good agreement with experiment, as it can be seen from Fig. 2.

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