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The detection of electronically excited atoms and molecules by electron ejection from a metal surface[1]) has provided a means for the study of such excited species for many years[2-6]). However, published curves showing the variation in gas-phase excitation cross-sections with bombarding electron energy, for a given species, differ considerably. Some such curves, often called 'excitation functions', for the production of N_2^* by gas-phase collisions with electrons, are shown in fig. 1, together with the types of surfaces used for detection. The sharp resonant $E^3\Sigma_g^+$ state of nitrogen, first observed by Olmsted, Newton, and Street[4]), is clearly resolved in the two experiments (curves a and b) in which high resolution electron guns were used[4,5]). We have shown, by a method of delayed-coincidence counting[5]), that the photon contribution to the nitrogen excitation function is negligible in the cases[3-5]) where the crossed molecule-electron beam method is employed. The differences in the shapes, therefore, might be attributed to the different surfaces used as detectors[7]). In our experiments, an ultra-high vacuum prevailed: the curve b is for a photo-sensitive detector surface, Cs_3Sb,

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exhibiting an S-4 photoelectric response. This surface was obtained by removing the vacuum envelope of an RCA 931A photomultiplier in a detection chamber operating at ultra-high vacuum[5]).

Figure 2 shows the first differentials, for emphasis, of the nitrogen excitation function[8]) before and after deposition of cesium onto an antimony surface. The composition and photoelectric response of the cesium-coated surface are not known. It is seen that the coefficient of electron ejection does not change uniformly upon deposition of cesium, but varies with the state of electronic excitation of the molecule. In this particular case, a loosely bound cesium layer on an antimony surface, the following mechanism for the observed effect is suggested: By analogy with Penning ionization of atoms in the gas phase, the adsorbed cesium atom is ionized by the incoming excited particle: $Cs + M^* \rightarrow Cs^+ + M + e$. The free electron is drawn off the surface by an applied positive potential gradient and the yield of electrons versus excitation energy of the excited molecule will thus reflect the shape of the ionization efficiency curve for the production of Cs^+ by a Penning-like ionization process. Figure 3 shows the ionization efficiency curve of Tate and Smith[9]) for the production of Cs^+ by electron bombardment of cesium in the gas phase. There are two distinct changes in ion (or electron) yield, at respectively ~10 eV and ~15 eV , both of which could account for the shape of the curve of fig. 2(b).

Redhead has shown[10]) that the shape of the ionization efficiency curve for the production of O^+ , by electron bombardment of chemi-sorbed oxygen on molybdenum, is similar to that for the gas-phase production of O^+ from O atoms. His results also favour the interpretation of fig. 2 in terms of the above mechanism.

We conclude that, at least in the case of a cesium deposit (of unknown density) on an antimony surface, the coefficient of electron ejection varies with the excitation energy of the interacting particle. Also for this particular case, the correlation of fine structure in the excitation functions with spectroscopic states, may be erroneous because of the nonlinear variation of the coefficient of electron ejection. It is evident from this result that there is a need for more work, under conditions of ultra-high vacuum, on (i) the coefficients of electron ejection from atomically clean metal surfaces for molecules possessing different amounts of electronic potential energy, and (ii) on the effects of adsorbed molecules on the mechanism of electron ejection.

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FIGURE CAPTIONS

Fig. 1. Excitation functions for production of N_2^* by electron impact.

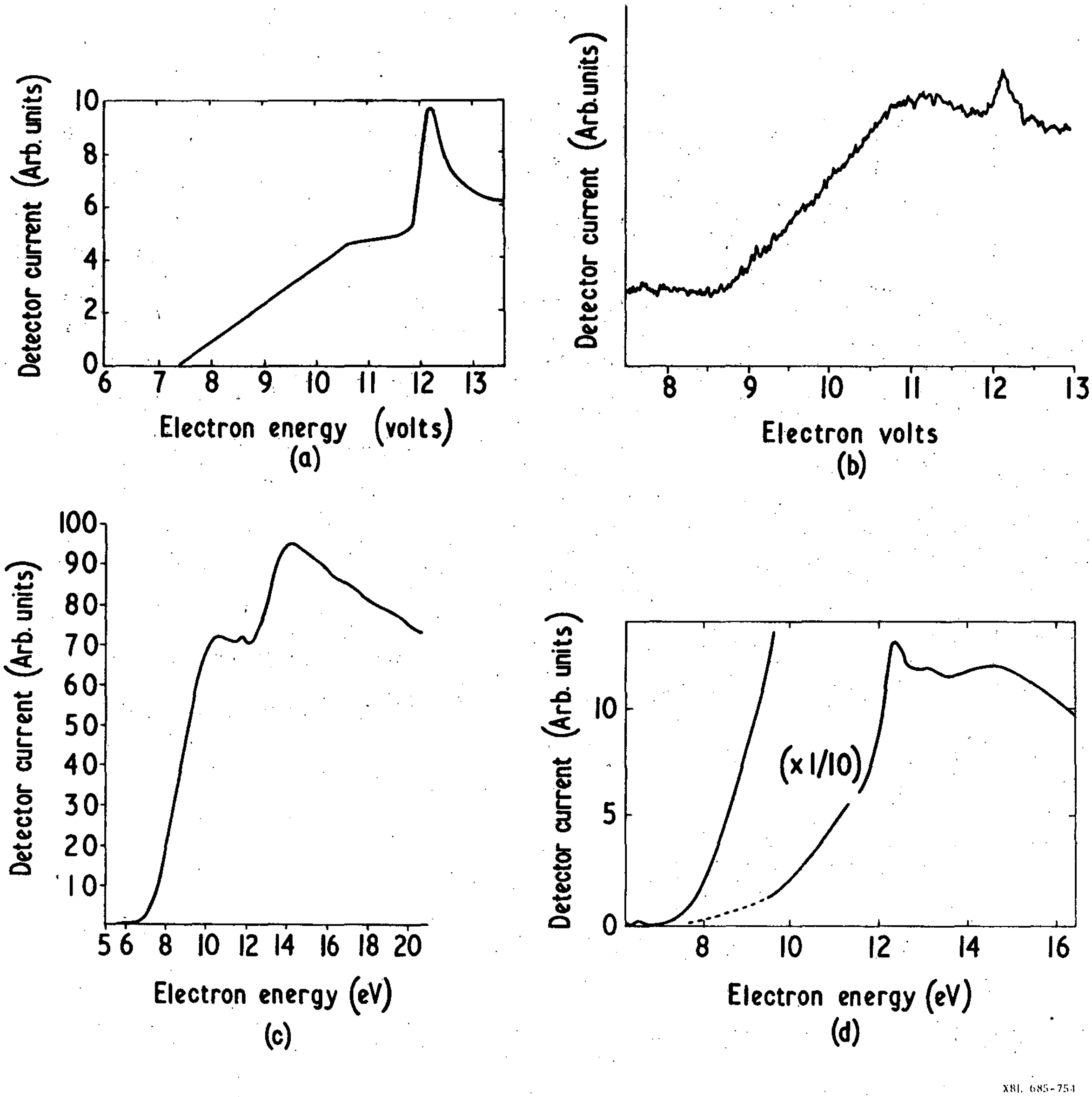
a) Ref. 4, Ag-Mg alloy surface; b) Ref. 5, Cs_3Sb surface;

c) Ref. 6, Ni surface; d) Ref. 3, Mg surface.

Fig. 2. First differentials of N_2^* excitation function.

a) Sb surface; b) Cs deposit on Sb surface; detector current in b) is 100× that in a).

Fig. 3. Ionization efficiency curve for Cs^+ (after Tate and Smith).



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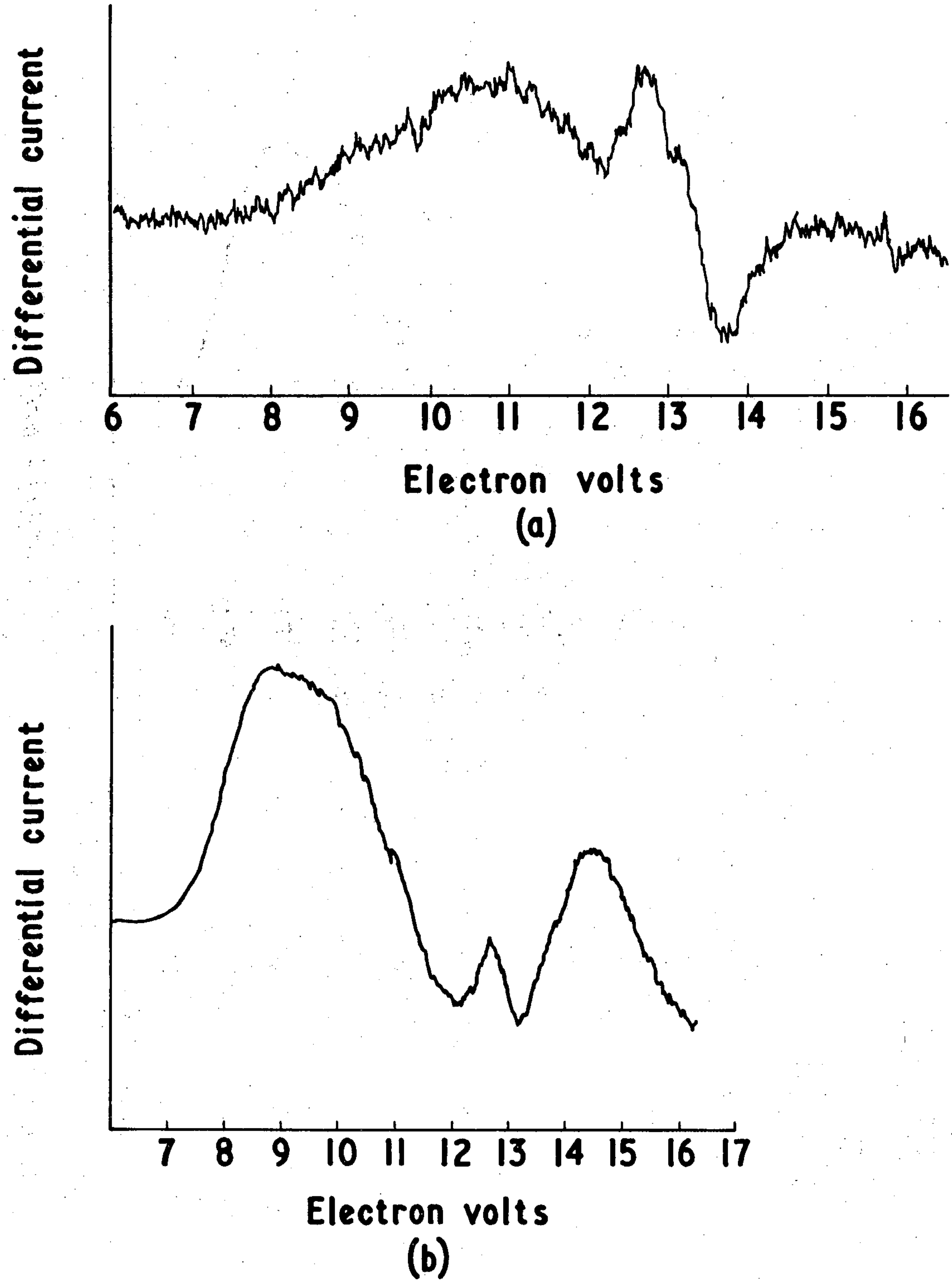

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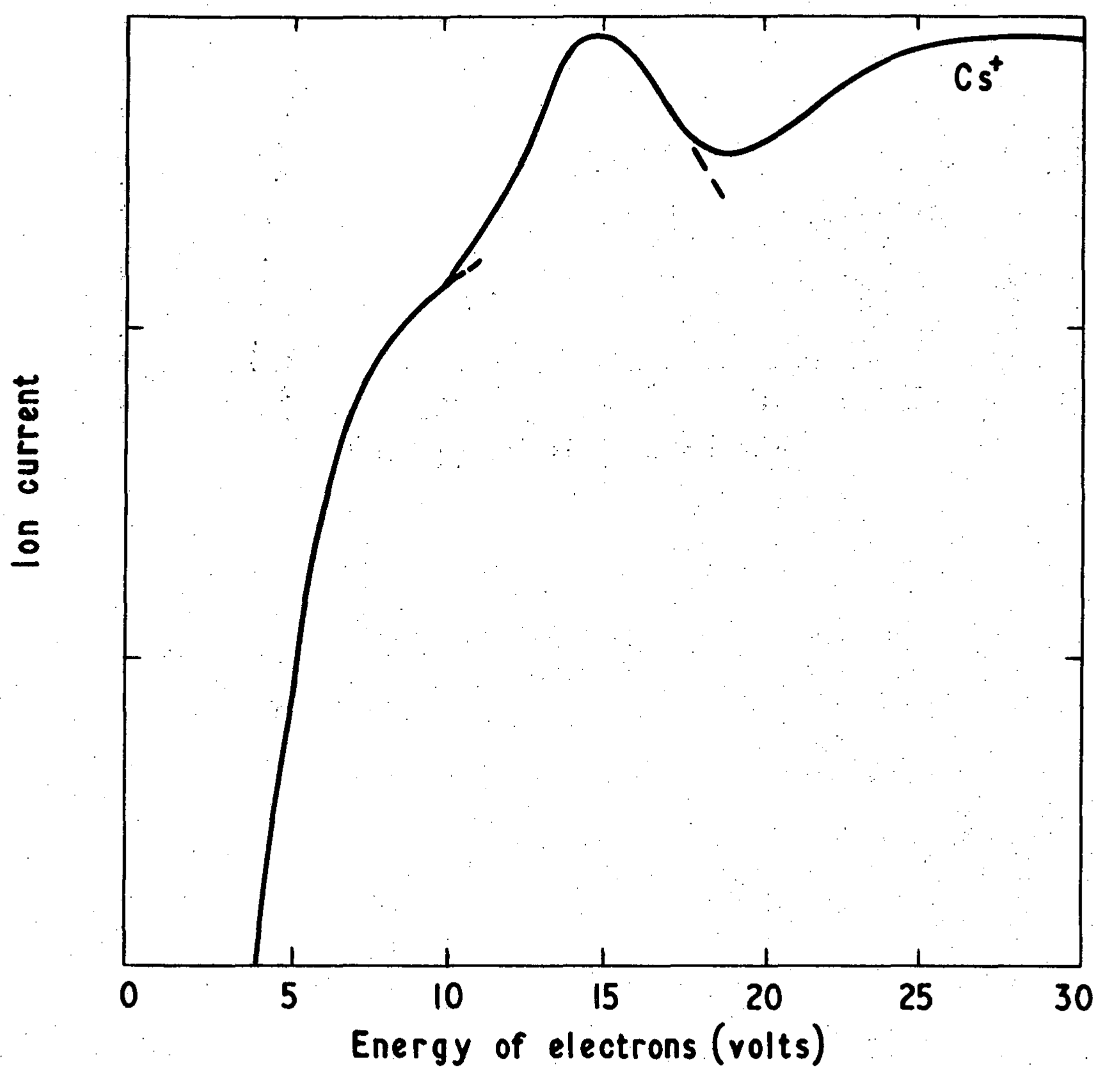

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Fig. 3. Ionization efficiency curve for Cs^+ (after Tate and Smith).