

THEORY OF PENNING IONIZATION OF ADSORBED CO  
BY METASTABLE HELIUM ( $2^1S$ ,  $2^3S$ )-BEAMS\*

Sheng-Wei Wang† and G. Ertl  
Institut für Physikalische Chemie  
der Universität München, W. Germany

ABSTRACT

Theoretical analysis of Surface Penning Ionization (SPI) is reported and applied to the process  $He^* + CO \rightarrow He + CO^+ + e^-$  for CO molecules adsorbed on a Pd(111) surface. Potential curves, ionization rates, and angular distributions of the emitted electrons are calculated. The results exhibit the extreme surface sensitivity of SPI and indicate its usefulness in studying the electronic and geometrical properties of adsorbates.

(Submitted to Surf. Sci. Letters)

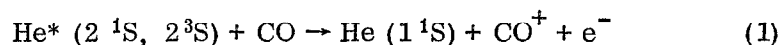
---

\* Work supported in part by the Department of Energy under contract number DE-AC03-76SF00515 and the Alexander von Humboldt Foundation.

† Alexander von Humboldt Postdoctoral Fellow, 1977-1978.

Present address: Stanford Linear Accelerator Center, P. O. Box 4349,  
Bin 74, Stanford, CA 94305, USA

Recently Conrad et al. [1] reported on electron emission from a CO-covered Pd(111) surface initiated by the collision of metastable excited He\* atoms. The emission spectra exhibit peaks at electron kinetic energies of  $E_{\vec{K}} \sim 7.3$  eV and  $E_{\vec{K}} \sim 4.8$  eV for the singlet state ( $2^1S$ ) of He\*; with the helium triplet state ( $2^3S$ ) these peaks are shifted down by 0.8 eV. These features were identified as being caused by excitation of the CO ( $5\sigma + 1\pi$ )- and  $4\sigma$ -orbitals, respectively, through an Auger deexcitation (also called Penning ionization) process:



However, it was not clear then whether the physical source of the very strong electron emission near threshold was the INS mechanism or "true" secondaries due to SPI. As this is one of the important aspects involved in the development of this new surface spectroscopy, a question has been raised [2]: In the case of photoemission, photons penetrate the surface several layers deep and the ionized electrons on their way out of the surface can be engaged in inelastic collision events in a cascade fashion, thus creating strong secondary electrons (Fig. 2a, Ref. 1). Since in the case of SPI electron emission occurs at the outmost layer, is it plausible that the two relatively weak peaks in the emission spectrum are associated with the intense emissions near the threshold? This question will be answered via a detailed theoretical analysis of the emitted electron angular distributions.

In this paper we present the first theoretical analysis of surface Penning ionization (SPI) for CO molecules chemisorbed on a surface at low collision energy ( $\lesssim 0.1$  eV) of the He\* ( $2^1S$ ,  $2^3S$ )-beams. Potential energy curves of the collision partners, as well as ionization rates and angular distributions of the emitted electrons, have been investigated at various impact geometries,

assuming CO standing straight up on the surface with the carbon atom attached to the surface.

At sufficiently low collision energies, the electronic transition of (1) can be treated within the Born-Oppenheimer (adiabatic) approximation. For each fixed helium-oxygen internuclear separation  $\vec{R}$  (the origin of  $\vec{R}$  is the oxygen nucleus), the initial electronic state of He\*-OC is actually imbedded in the continuum of the states of He-OC<sup>+</sup> + e<sup>-</sup>, and the excited He\* (excitation energy E\* = 20.6 eV for 2 <sup>1</sup>S and 19.8 eV for 2 <sup>3</sup>S) is energetic enough to ionize electrons from the highest occupied levels of CO. If V<sub>i</sub> and V<sub>f</sub> denote the interaction energies of the initial and final state collision partners, then the kinetic energy E $_{\vec{K}}$ ( $\vec{R}$ ) of the emitted electron can be approximated in the effective one-electron theory as

$$E_{\vec{K}}(\vec{R}) = E^* - E_j + (V_i(\vec{R}) - V_f(\vec{R})), \quad (2)$$

where j denotes the levels (4σ, 5σ, and 1π<sub>x,y</sub> orbitals of CO) from which the ejected electrons originate and E<sub>j</sub> is the effective binding energy (including orbital binding energy shift and width upon chemisorption and relaxation energy shift upon ionization) of these electrons in the absence of He\*. The E<sub>j</sub>'s are taken from the corresponding photoemission experiments, i. e., 15.7 eV for 4σ and 12.8 eV for (5σ + 1π) levels [3]. The last term in Eq. (2) is required to fulfill the energy conservation for the electronic transition involved and gives an additional width to the energy distribution of the emitted electrons. Further broadening can result from vibrational final states, but its calculation will not be attempted here. V<sub>i</sub> and V<sub>f</sub> are calculated by using a density-functional formalism [4] within the local-spin-density approximation [5] for the exchange-correlation energies. The wave functions of He\*, He, and CO are taken from Burke et al. [6] and Brion and Moser [7]. No spherical

approximations have been made throughout the whole calculations. The depth of  $V_i$  is found to be very small (Fig. 1) and variations of  $V_f$  for the various kinds of final state are also negligible (i. e.,  $< 0.1$  eV) at He\*-OC separations where the electronic transition takes place. The resulting width of less than 0.1 eV of the electron energy distribution is in qualitative agreement with measurements with gaseous CO [8], and indicates a 'hard core' type collision process. More recent gas phase experiments indicate that the potential minimum of  $V_i$  has an even smaller depth of only a few meV [9].

The classical turning point  $R_c$  has  $R_c(2^1S) > R_c(2^3S)$  and  $R_c(\text{normal incidence}) > R_c(\text{off-normal incidence})$ , as a consequence of size ( $2^1S > 2^3S$ ) and the anisotropy of the electron density distribution of the CO molecule.

The transition amplitude for (1) can be written in its lowest-order approximation as

$$\begin{aligned} T_{E_{\vec{K}}, i}(\vec{R}) = & \int \psi_i(1) \psi_{2S}^{\text{He}^*}(2) \cdot \frac{1}{r_{12}} \cdot \left( \psi_{1S}^{\text{He}}(2) \psi_{E_{\vec{K}}}(1) \right)^* d1d2 \\ & + \int \psi_i(1) \psi_{2S}^{\text{He}^*}(2) \cdot \frac{1}{r_{12}} \cdot \left( \psi_{1S}^{\text{He}}(1) \psi_{E_{\vec{K}}}(2) \right)^* d1d2 \end{aligned} \quad (3)$$

where the first term represents the direct Coulomb interaction of the initial and final state orbitals and the second term is the exchange interaction. For singlet He\* both terms are calculated and the exchange term dominates. This has also been observed on the basis of results in gas phase experimental data [10]. For triplet He\* only the exchange term is allowed. Coulomb wave functions (with Coulomb phase shifts) were used, centered at the oxygen atom for the continuum orbitals  $\psi_{E_{\vec{K}}}$  and partial wave expansions with angular momentum up to  $l = 7$ . The ionization rate  $\Gamma(\vec{R})$  was then calculated via the Golden Rule formula [11]:

$$\Gamma(\vec{R}) = 2\pi\rho_{E_{\vec{K}}} \int |T_{E_{\vec{K}}, i}(\vec{R})|^2 d\hat{K} \quad (4)$$

where  $\rho_{E_{\vec{K}}}$  is the density of states of the continuum levels.  $\Gamma(\vec{R})$  is peaked at the classical turning point and decays roughly exponentially for larger separations (Fig. 2). Therefore, the electron emission properties can essentially be determined at the classical turning point. Contrary to the photoemission case where the overlap occurs throughout the surface region, in SPI the overlap is confined to the outermost part of the surface atoms. Therefore, Fig. 2 is obtained by calculating only the oxygen part of the overlap integral  $S_1$  (in Eq. (5)). In this case,  $S_1$  for the  $5\sigma$  orbital is larger than that for the  $4\sigma$  orbital. This seems to explain why the  $5\sigma$  orbital can contribute more than the  $4\sigma$  orbital, as has been observed in [1]. It has also been observed that this was the case in the gas phase experiment [8]. The contribution due to the carbon atom will be included and discussed in a future publication. The angular distributions of the emitted electrons of (4) can be calculated with T approximated for both singlet and triplet He\* as

$$T_{E_{\vec{K}}, i}(\vec{R}) \sim (S_1 \cdot S_2) / R \quad (5)$$

where

$$S_1 = \int \psi_i(1) (\psi_{1S}^{\text{He}}(1))^* d1$$

$$S_2 = \int \psi_{2S}^{\text{He}^*}(2) (\psi_{E_{\vec{K}}}^*(2))^* d2$$

This arises from the first term in the bipolar expansion of  $r_{12}^{-1}$ .

Our approximation is closely related to that of Ebding and Niehaus [12] except that in their formulation an unknown proportionality constant is left over and later the equation is used as the basis for their semiempirical analysis of the emitted electron angular distributions. Both approximations recognize that the main contributions to the exchange integral come from the region where the overlaps of the orbitals have considerable values. The first overlap integral  $S_1$

represents the initial state effects which depend on the type of CO orbitals involved and the incident beam angle  $\theta_{\text{He}^*}$ ,  $\phi_{\text{He}^*}$  ( $\theta$  is defined with respect to the CO molecular axis and points outward from the metal,  $\phi = 0$  is defined along the  $\text{He}^*$  incident direction). This integral is a smooth function of  $\theta_{\text{He}^*}$ : for example  $S_1 = 0$  at  $\theta_{\text{He}^*} = 0$  for  $\pi$  orbitals due to symmetry and increases in magnitude as  $\theta_{\text{He}^*}$  varies (only the direct term of (3) contributes to T in this case). The "angular pattern" of the emitted electrons is determined by the joint effect of  $S_1$  and the second overlap integral  $S_2$ , which represents the final state effect. The resulting angular pattern from excitation of the  $5\sigma$ -level with  $\text{He}^* 2^1\text{S}$  at normal incidence and with an impact parameter  $b = 0$  is reproduced in Fig. 3a. It shows variations due to interference of partial waves included in the final state continuum wave functions. The complete angular pattern to be compared with experiment is obtained by evaluating for a given angle of incidence Eq. (5) for various impact parameters  $b$  at the respective turning points as illustrated by Fig. 3b and by subsequent averaging over the allowed values for  $b$ . For this purpose the  $c4\times 2$ -CO/Pd(111) overlayer geometry with a mutual separation of  $6.04 a_0$  between neighboring CO molecules was considered. The resulting angular distributions of the electrons emitted from the CO levels by singlet  $\text{He}^*$  atoms at different angles of incidence are reproduced in Fig. 4. At normal incidence, strong emission backwards toward the incident beam direction is obtained, which casts shadows in the forward beam direction. At off-normal incidence, these shadow effects are preserved, although to a lesser extent. Such effects have also been reported for gas phase experiments [13].

In all cases rather strong emission occurs into the direction from which the incident  $\text{He}^*$  hits the CO molecule. However, in the experiment this range is not accessible, but rather electrons on the other side of the surface normal

are collected, where only weaker intensities are emitted. A high fraction of produced electrons is emitted into the solid, where they may lose their energy by colliding with metallic electrons. Subsequent secondary electron emission will then occur. These findings may explain the strong secondary electron emission observed in the experiment (see Fig. 2b, c of Ref. 1) at low kinetic energies. Moreover, the theory predicts a smooth decrease in emission intensity as the emission polar angle varies by about 20–30° away from the surface normal towards the specular directions for off-normal incident angles ( $\theta_i = 35^\circ$ ,  $55^\circ$ , and  $70^\circ$  cases in Fig. 4). These findings correlate well with preliminary experimental results [14]. Calculations have also been carried out for a tilted CO ( $35^\circ$  with respect to surface normal) at  $35^\circ$  incident beam angle; the results (not shown in Fig. 4) indicate substantial differences within these angle ranges. A consequent analysis of such data may yield information on the orientation of the molecular axis on the surface.

Fruitful discussions with H. Conrad, G. Doyen, H. Haberland, J. Küppers, and M. A. Van Hove are gratefully acknowledged. Financial support was obtained from the Alexander von Humboldt Foundation and the U.S. Department of Energy.

REFERENCES

- [1] H. Conrad, G. Ertl, J. Küppers, S. W. Wang, K. Gérard, and H. Haberland, Phys. Rev. Lett. 42 (1979) 1082.
- [2] H. D. Hagstrum, private communication.
- [3] T. Gustafsson, E. W. Plummer, D. E. Eastman, and J. L. Freeouf, Solid State Commun. 17 (1975) 391.
- [4] S. W. Wang and W. H. Weinberg, Surf. Sci. 77 (1978) 14.
- [5] O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B 10 (1974) 1319.
- [6] P. G. Burke, J. W. Cooper, and S. Ormonde, Phys. Rev. 183 (1969) 245.
- [7] H. Brion and C. Moser, J. Chem. Phys. 32 (1960) 1194.
- [8] H. Hotop and A. Niehaus, Int. J. Mass Spectrosc. and Ion Phys. 5 (1970) 415.
- [9] H. Haberland, personal communication.
- [10] H. Hotop and A. Niehaus, Z. Phys. 228 (1969) 68.
- [11] W. H. Miller, J. Chem. Phys. 52 (1970) 3563.
- [12] T. Ebding and A. Niehaus, Z. Phys. 270 (1974) 43.
- [13] H. Hotop and A. Niehaus, Chem. Phys. Lett. 8 (1971) 497.
- [14] H. Conrad, G. Ertl, J. Küppers, and H. Haberland, in preparation.



FIGURE CAPTIONS

1. Interaction energy curves between final state (a-d) and initial state (e-h) collision partners. The classical turning points at 6.4, 5.7, 4.8, and 4.5 a. u. for the various initial state collision configurations are indicated. 66 meV is the mean kinetic energy of the impinging He\* beam at 300 K.
2. Ionization rate  $\Gamma(R)$  as a function of internuclear separation for He\*  $2^1S$ -OC head-on collision at normal incidence.
3. (a) Angular distribution for electrons emitted from the  $5\sigma$ -orbital by He\* singlet head-on impact ( $b=0$ ) at normal incidence ( $\theta_i = 0$ ).  
(b) Illustration of classical turning points at various impact parameters for normal incidence.
4. Angular distributions of electrons emitted from the various CO levels after averaging over impact geometries for  $\theta_i = 0^\circ, 35^\circ, 55^\circ, \text{ and } 70^\circ$ . Broken lines indicate the directions of the impinging He\* atoms. The z-axis indicates the surface normal and points outward away from the surface.

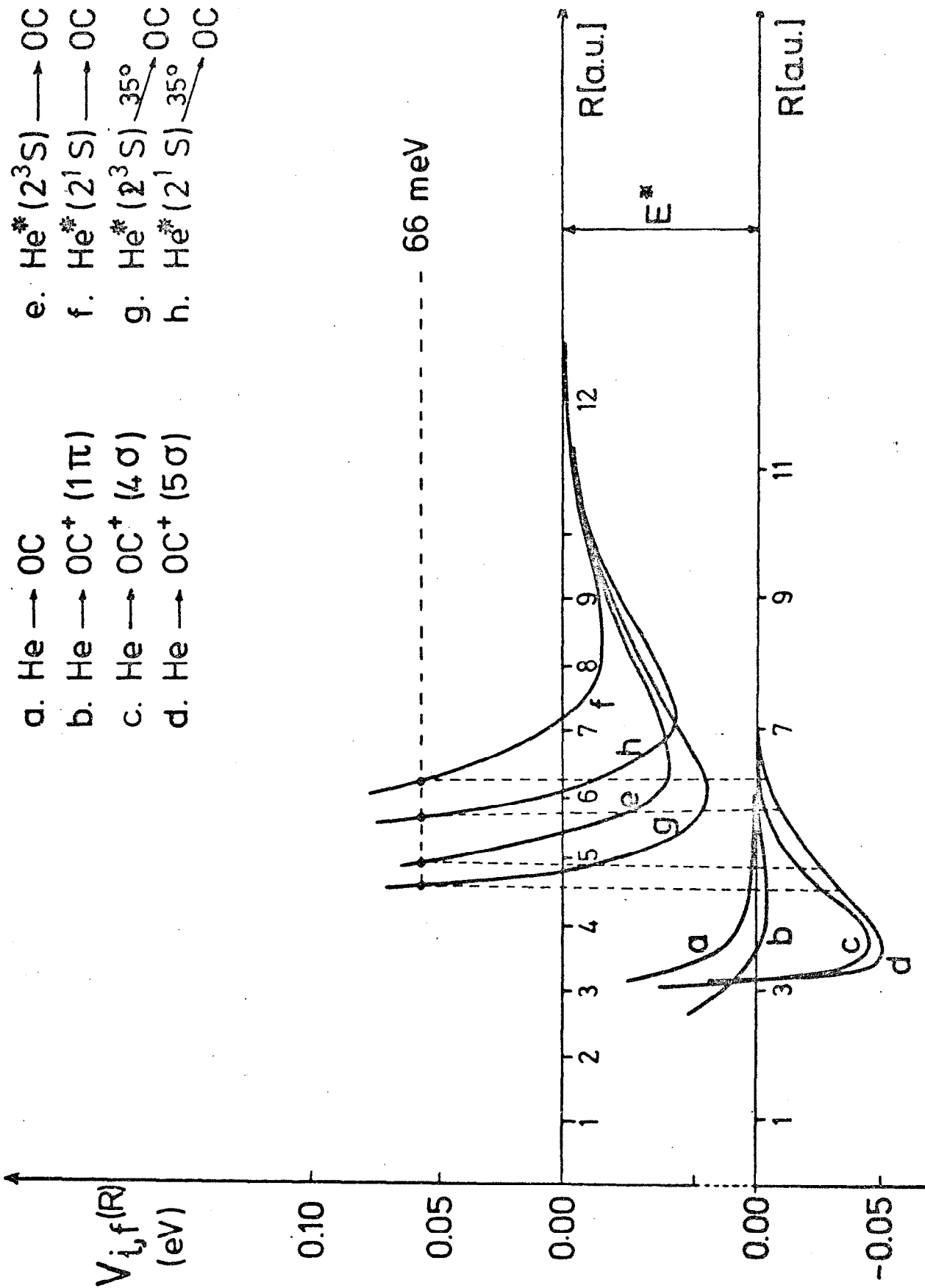


Fig. 1

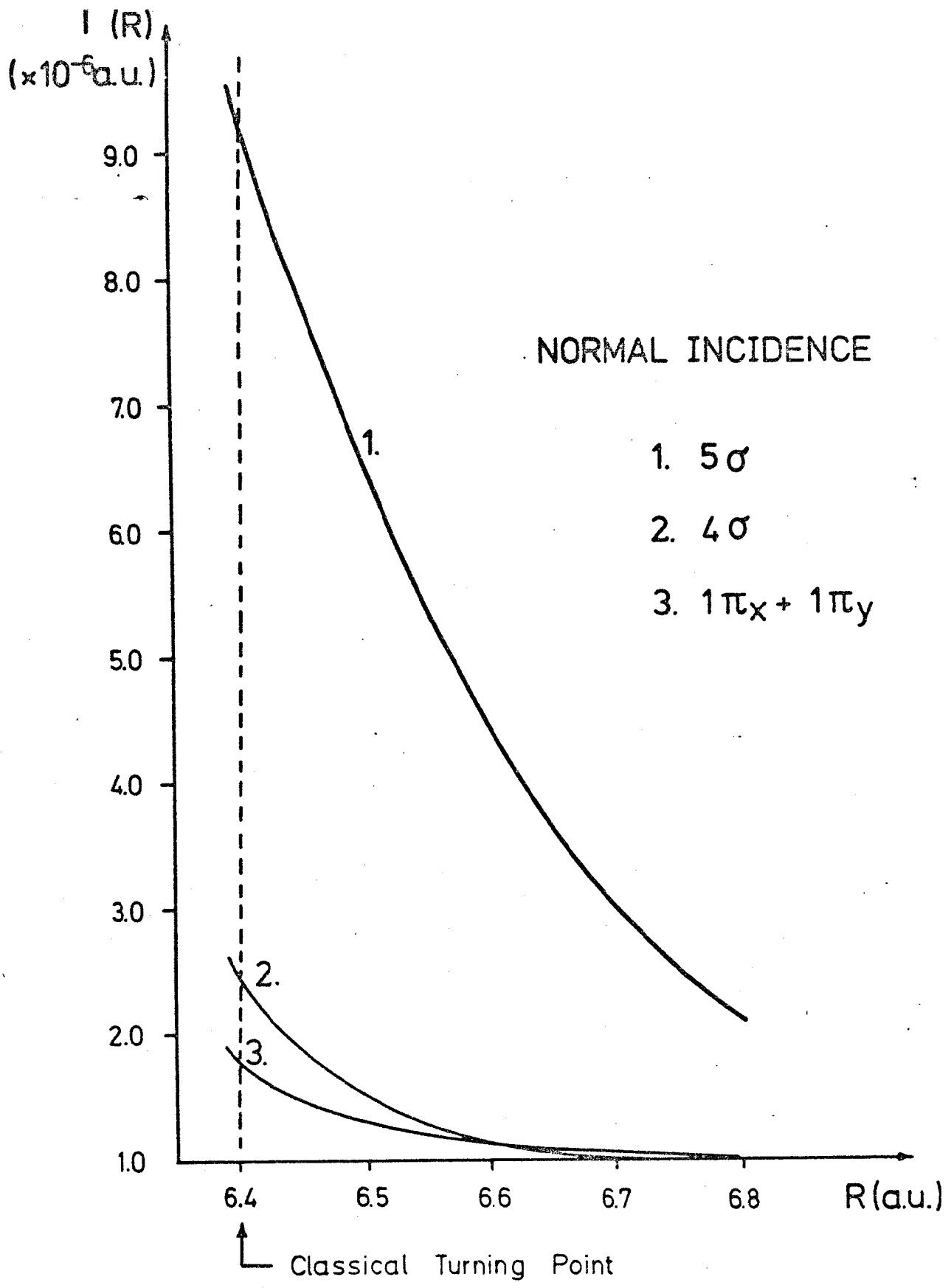


Fig. 2

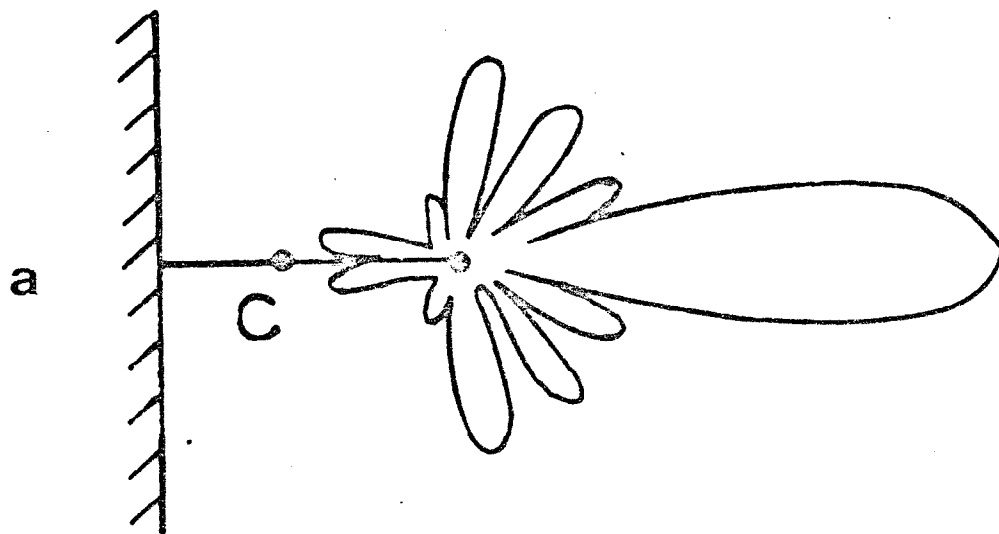
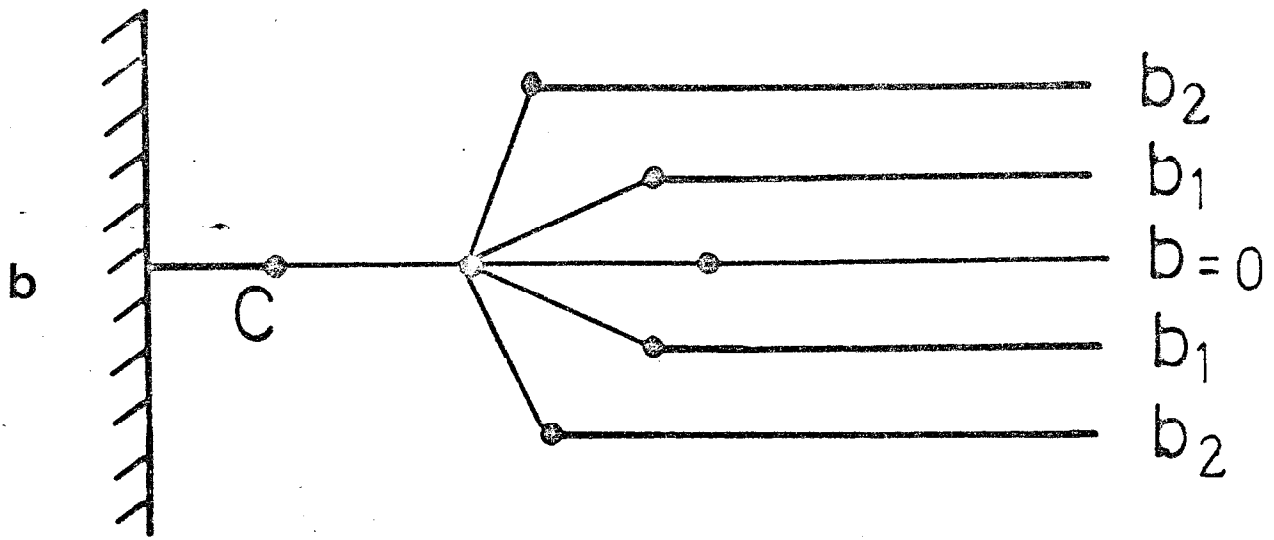


Fig. 3

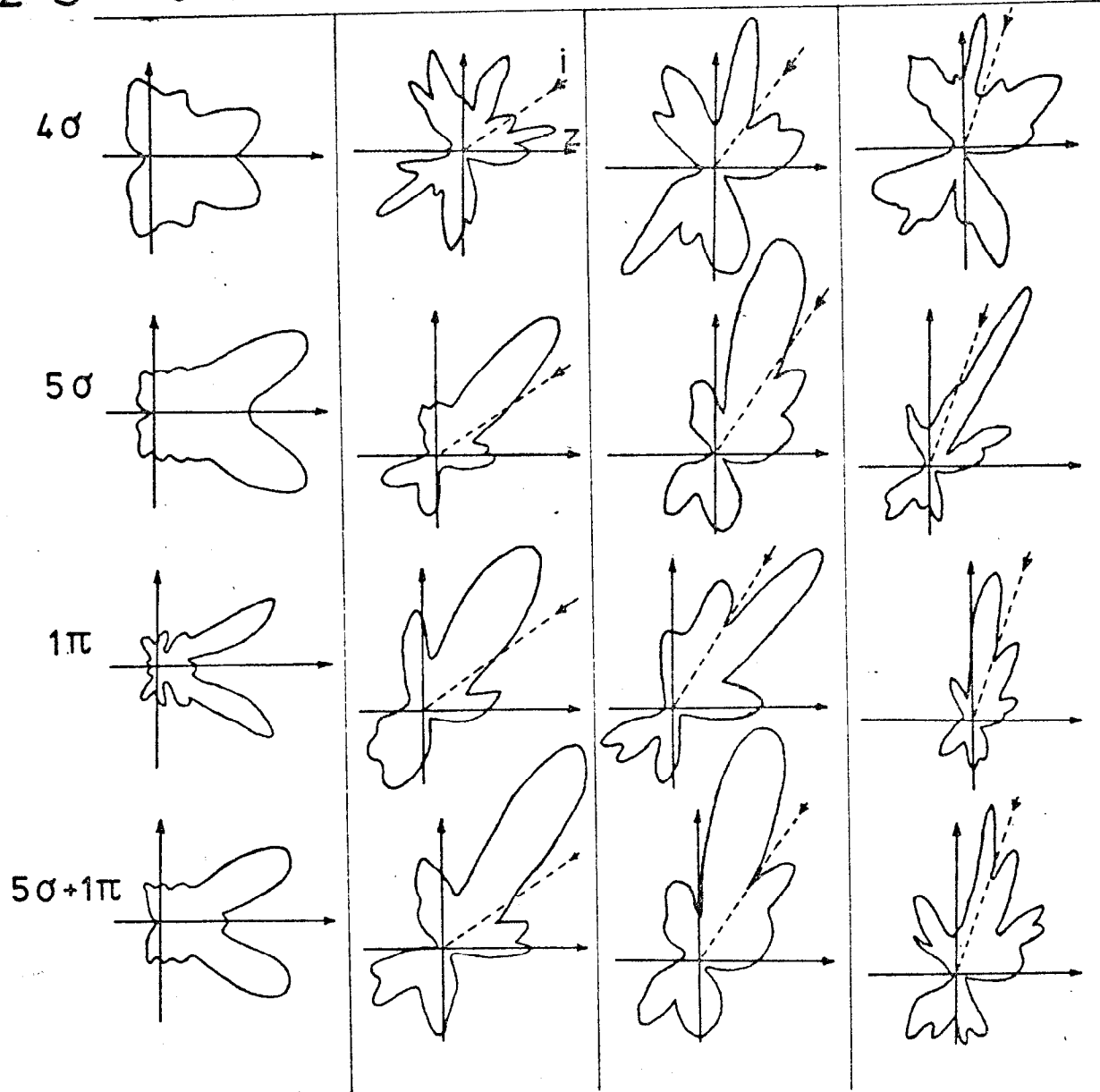
$2^1 S$  $\theta = 0^\circ$  $\theta = 35^\circ$  $\theta = 55^\circ$  $\theta = 70^\circ$ 

Fig. 4