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OFFICE OF NAVAL RESEARCH  
Contract N00014-75-C-0949  
Task No. NR 392-012  
TECHNICAL REPORT NO. 78-01

Calculation of Energy Spectra for ESD of  $H^+$  From  $H_2$   
Adsorbed on Tungsten  
In  
Surface Science

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20 April 1978

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REPORT DOCUMENTATION PAGE		HEAD INSTRUCTION REPORT COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Calculations of Energy Spectra for ESD of $H^+$ From $H_2$ Adsorbed on Tungsten		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) R. Janow and N. Tzour		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Physics, The City College New York, NY 10031		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0949
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research 715 Broadway New York, NY 10003		12. REPORT DATE April 20, 1978
		13. NUMBER OF PAGES 17 (22/190)
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited		18. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 24 TR-78-01      22 20 Apr 78		
18. SUPPLEMENTARY NOTES Surface Science 10 Richard Janow Narkis/Tzour		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electron desorption, chemisorption, Tungsten Hydrogen		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We calculate the kinetic energy distribution of $H^+$ ions desorbed from tungsten surfaces via ESD. Our calculations produce energy spectra consistent with experimental observation for several plausible atomic adsorption sites.		

CALCULATION OF ENERGY SPECTRA FOR ESD OF  $H^+$  FROM  $H_2$   
ADSORBED ON TUNGSTEN\*

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ABSTRACT

We calculate the kinetic energy distribution of  $H^+$  ions desorbed from tungsten surfaces via ESD. Our calculations produce energy spectra consistent with experimental observation for several plausible atomic adsorption sites.

\*Research Sponsored by the U.S. office of Naval Research under  
ONR contract No. N00014-75-C-0949

Electron Stimulated Desorption is a phenomenon in which a beam of low energy electrons (100 - 500 e.v.) impinges on an adsorbate covered surface, causing the ejection of ions or neutral particles. Ion yields, ESD total cross sections, and energy distributions have been found experimentally for a variety of adsorbate-substrate combinations. Most recently, angular dependent patterns of strongly focussed ion impact spots have been observed, whose geometry may reflect the substrate unit cell structure.<sup>1-3</sup> ESD data provide important clues to the chemisorption geometry and insight into the character of surface interactions. Several recent review articles exist.<sup>4-7</sup>

A phenomenological model of the ESD process in one dimension was suggested<sup>8,9</sup> by Gomer, Menzel, and Redhead, (GMR). This multistep model pictures adsorbate atoms to be promoted via Franck-Condon transitions from a bound vibrational level to an excited anti-bonding state, which may dissociate with the emission of an ion.

This paper presents a first principles calculation of the kinetic energy distribution for  $H^+$  ions desorbed from tungsten surfaces via ESD. Here we amplify previous work, which focussed primarily on the angular dependence in  $O^+$  emission.<sup>10,11</sup> A kinetic theory applying to ESD in three dimensions was formulated in our earlier work from first principles using a generalization of the GMR picture. Ions were assumed to move classically, with their dynamics governed by an adparticle-surface effective potential. Bond healing reneutralization mechanisms may cause ions to be recaptured.

These may desorb as neutrals, if their history as ions provides sufficient kinetic energy. The electronic transitions involved in ionization and quenching (reneutralization) necessitate quantum mechanical descriptions of these processes.

This study of  $H_2/W$  is prompted by our recent findings for  $O^+$  desorbed from  $O_2/W$ . We calculated ESD Ion Angular Distributions and energy spectra, using simple models for the interaction of  $O^+$  with the surface. Despite the crudity of the model potential employed, rough agreement of calculated peak ion energies with experiment should have been obtained, if a ground state surface generates the potential relevant to emission dynamics.

Experimental determination of the  $\beta_1$  state (high coverage)  $O^+$  energy peak yields 8.8 e.v., and a large spectral width which contrast sharply with the prediction of our model for  $O^+$ . Strong focussing effects and the main features observed in ESDIAD's were, however, replicated in our earlier work for several speculative oxygen adsorption geometries. We are currently investigating the hypothesis that either molecular adsorption or long lived excited states on the surface may explain the ESD spectrum of  $O^+$ .

Note that the experimental energy distribution for ESD of  $H^+$  from  $H_2/W$  peaks at 1.7 ev. for high coverage on polycrystalline material.<sup>12</sup> This lies in the range expected with a ground state surface model. Attention is therefore restricted here to calculating the  $H^+$  spectrum, inasmuch as it provides a critical test of the GMR picture of ESD employed in previous work. The detailed calculations closely parallel those discussed in Ref. 10.

Reasonable values were adopted for some of the phenomenological parameters required.

A three dimensional model for the anti-bonding  $H^+$  - W surface potential was constructed for W(100), W(111), and W(110), in the manner described in earlier work<sup>10</sup>. Here  $H^+$  ions are assumed to respond to a time independent potential field which we approximate by the sum of unperturbed tungsten atom Hartree potentials, plus an image contribution. The corresponding force governs ionic motion following dissociation from the surface.

Experimental evidence indicates that  $H_2$  adsorbs on W in atomic form - with recent experimental confirmation. At high coverage ( 2 atoms/unit cell) the characteristic vibration energy is 135 Mev, contrasting sharply with that expected for molecular vibrations.

We approximated the ground state potential for Hydrogen atoms by three dimensional parabolic wells at each of several test adsorption sites, using spring constants matched to the experimentally determined vibration frequencies.

At 300° K., the ground state vibration level spacing is large compared to the thermal energy. Hence, adsorbed hydrogen atoms are assumed to vibrate in the zero point harmonic oscillator state. H atoms ionized by electron impact are represented by a minimum uncertainty wave packet corresponding to a classical Gaussian distribution of the form:

$$P_i^0(\vec{r}, \vec{v}) = \prod_{i=1}^3 \left[ (2\pi p_i \nu_i)^{-1} e^{-v_i^2/2\nu_i^2} e^{-(r_i-b_i)^2/2p_i^2} \right] \quad (1)$$

Here  $b$  locates the adsorption sites. The widths in atomic units are given by

$$p_i = (2m\omega_i)^{-1/2} ; \quad v_i = (\omega_i/2m)^{1/2} \quad (2)$$

The parameters used in this calculation yield  $p_i \approx .24 a_0$ . The finite width in velocity space was included but has negligible effect.

We limited our calculation to the shape of ion energy distributions, which are obtained by folding the ion-solid potential  $E_2$  against the ground state distribution. Fig. 1 provides a one dimensional illustration, with gaussian shape of  $P_1^0$  skewed to form a high energy tail in the spectrum, due to variation in the slope of  $E_2$ . The spectral shape will also be modulated by the ion survival probability against reneutralization. In the present calculation, reneutralization effects are taken to be independent of initial position, as is the ionization cross section. The parameters required to construct realistic models of reneutralization are not yet known.

This (GMR) interpretation of kinetic energy spectra is a good description of ESD only if the substrate remains in its ground state during ion propagation, which is assumed here, or if the potential is produced by substrate excitations whose lifetimes are long compared to ion flight times. If the cross section to produce surface excitations is large enough, with the decay lifetime comparable to the time of flight, another width mechanism may contribute via competition between the relaxation and

reneutralization lifetimes. Inelastic recoil involving substrate and adsorbate atoms may also widen the ion spectra. This mechanism however should not be significant for light ions.

It was necessary to calculate  $H^+$  desorption spectra for each of the W(100), W(111), and W(110) faces, inasmuch as the polycrystalline sample used by Nishijima and Propst<sup>12</sup> had an unknown mixture of faces. We calculated spectra for hydrogen atoms adsorbed at each of several highly symmetric points on each unit surface cell. Experimental ESJAD spot patterns for  $H^+$  on W(100) support this symmetric choice of sites.<sup>2</sup>

Fig. 2 summarizes numerical results for each of the tungsten faces studied. For comparison, we have plotted the  $H^+$  experimental spectrum normalized to the same scale. The low energy portion of this spectrum appears gaussian, while above the peak at 1.7 ev one finds a tail, having an algebraic appearance, and an apparent cutoff at about 7 ev. It is interesting to point out that the experimental spectrum for  $O^+$  desorption from W, in particular, as well as those for some other systems studied experimentally peak at significantly higher energies, and do not display a pronounced tail.

On each surface studied, we find calculated spectra which closely mimic the experimental one in width, peak ion energy, and in the presence of a tail.

The best agreement on each face is found for the hydrogen adsorption sites directly over a surface layer tungsten atom. We

speculate that these may have filled in the high coverage situation which produced the experimental results.

Note that the five fold coordinated site A' on W(100) also produces a spectrum peaking near 1.7 ev. This, however, is sharply peaked, exhibiting no significant trace of a tail. Site A' has been suggested for the low coverage  $\beta_2$  phase of  $H_2/W(100)$ . Several mechanisms discussed below might contribute to broadening the spectrum.

Reneutralization is a strong process in this system, as evidenced by the small ESD cross section for  $H^+$ , and by the known large magnitude of isotope effects. Depending on realistic values of several parameters, reneutralization may cause broadening and skewing of the spectra in Fig. 2 to either higher or lower energy. The one-dimensional limit of our kinetic theory, together with a simple model, furnishes an illustration.

First impose a Born-Mayer form for the  $H^+ - W$  potential:

$$E(z) = V_0 e^{-\alpha(z-b)} \quad (3)$$

For the  $H^+$  reneutralization rate assume:

$$Q(z) = Q_0 e^{-\beta(z-b)} \quad (4)$$

Here  $b$  is the chemisorption site coordinate.

Apart from a normalization constant, the resulting spectrum is

$$F(\epsilon) \propto \epsilon^{-1} \exp\left[-\frac{1}{2}(\ln \epsilon/x)^2\right] \exp\left[-\frac{Q_0}{\alpha} \left(\frac{mT}{2V_0}\right)^{1/2} \left(\frac{\Gamma(R)}{\Gamma(R+\frac{1}{2})}\right) \epsilon^{R-\frac{1}{2}}\right] \quad (5)$$

Here  $\epsilon = E/V_0$  ;  $\chi = d/(2mw)^{1/2}$  , all in atomic units.

The second exponential expresses modulation of the spectrum due to quenching, with the ratio  $R = \beta/\alpha$  of the ranges providing a measure of competing effects associated with quenching. It is reasonable to expect  $R$  of order unity, since the ranges of both  $Q$  and  $E$  depend on the tails of wave functions of the solid which extend into the vacuum.

A priori, fast ions might be assumed to have the lowest probability to be reneutralized. On the other hand, fast ions are those created closest to the surface, and which, interact most strongly with substrate electrons increasing the quenching probability. The sense in which the resulting energy spectrum is skewed is strongly model dependent. For  $R=1/2$ , quenching is uniform but for  $R > 1/2$  the relative intensity of spectral tails present in Fig 2 would be reduced. The opposite effect occurs for long range quenching, defined here by validity of the condition  $R < 1/2$ .

Experimental ESD spectra for  $D^+$  from  $D_2/W$  might be useful in establishing reneutralization effects, due to mass dependence in the exponent above. The vibrational states, however, possess complicating mass dependence. The prominent tails in some of the calculated  $H^+$  spectra in Fig. 2 can be attributed to the large amplitude of zero point motion for light particles. Fig. 3 shows calculated  $D^+$  spectra, which shows considerable narrowing compared to their counterparts in Fig. 2.

Note that higher order processes which involve surface excitations are possible contributors to the  $H^+$  spectrum in the region near its cutoff above 7 e.v. The limiting energy is given by the  $H^+ - W^+$  Coulomb repulsion, which is about 8 ev for  $3.3a_0$  separation. Somewhat lower energies are expected for high rydberg surface states. Some preliminary calculations, using a delta function model for the vibrational state distribution show that finite width spectra can be produced via competition between the surface state lifetime and the reneutralization rate. A site such as A' might produce a broadened spectrum via such processes. Another process possibly contributing to the broadening makes use of coupling between translational states of the ions and vibrations in the surface. Significant energy loss would result from the creation of such multiphonon final states.

To summarize, these results for ESD of  $H^+$  from  $H_2/W$  support the theoretical picture of ESD proposed by GMR and formalized in our previous work. Despite the crudity of models used, this calculation produces energy spectra consistent with experiment for several surfaces and plausible atomic adsorption sites. In particular, our model  $H^+ - W$  potential, in which the surface remains free of excitation, provides a qualitatively correct description for ESD of  $H^+$  from  $H_2/W$ . The lack of experimental data about ESD cross sections and reneutralization effects prohibits us from making definitive statements which would select the dominant surfaces and adsorption sites contributing to the experimental  $H^+$  spectrum.

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### FIGURE CAPTIONS

Fig. 1 The qualitative behavior of effective potentials for ionic ESD, as functions of  $z$  coordinate.  $V_0$  is the chemisorption energy. The  $z$  coordinate of the adsorption site is 'b'. The metal + adsorbate system in its ground state is designated by  $(M + A)$ . An anti-bonding potential leading to ionic ESD is denoted  $(M + A^+)$ . The substrate here is free of excitation. The dashed line  $(M^* + A^+)$  suggests the behavior of the effective potential for an ion interacting with the excited substrate. The asymptotic energy difference is  $V_I$ , the atomic ionization potential, if both incident and ejected electrons are Auger emitted to the vacuum.

Fig. 2 a, b, c, calculated ion energy distributions for ESD of  $H^+$  from  $H_2$  on W(100) W(111), and W(110). All spectra are normalized to unity, with energies given in electron volts. The broken curve shows experimental results of Nishijima & Propst<sup>12</sup>. On each surface, highly symmetric sites were chosen for calculation, as shown by Insets for each surface geometry, with  $3.3 a_0$  taken to be the W-H bond length. On W(100) site A' is five-fold coordinated, site E is a two-fold coordinated bridge site, and sites A, D are singly coordinated. ON W(111) all sites are singly coordinated  $3.3 a_0$  above W atoms. On W(110), sites B, C are bridge sites, site D is three-fold coordinated to

surface layer W atoms and site A is singly coordinated over the surface.

Fig. 3 Calculated spectra for ESD of  $D^+$  from tungsten. Here, spectra for the sites directly over surface tungsten atoms are shown.

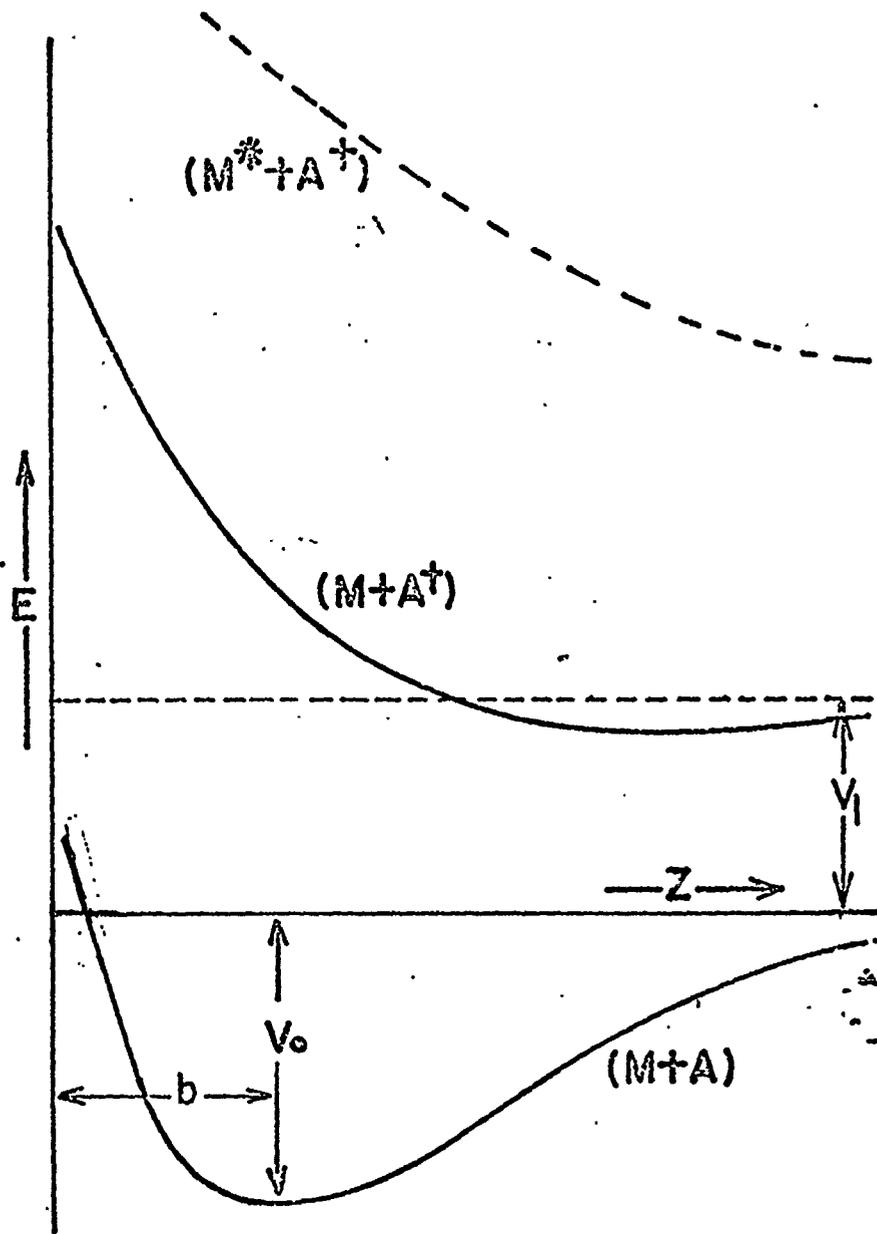


FIG. 1

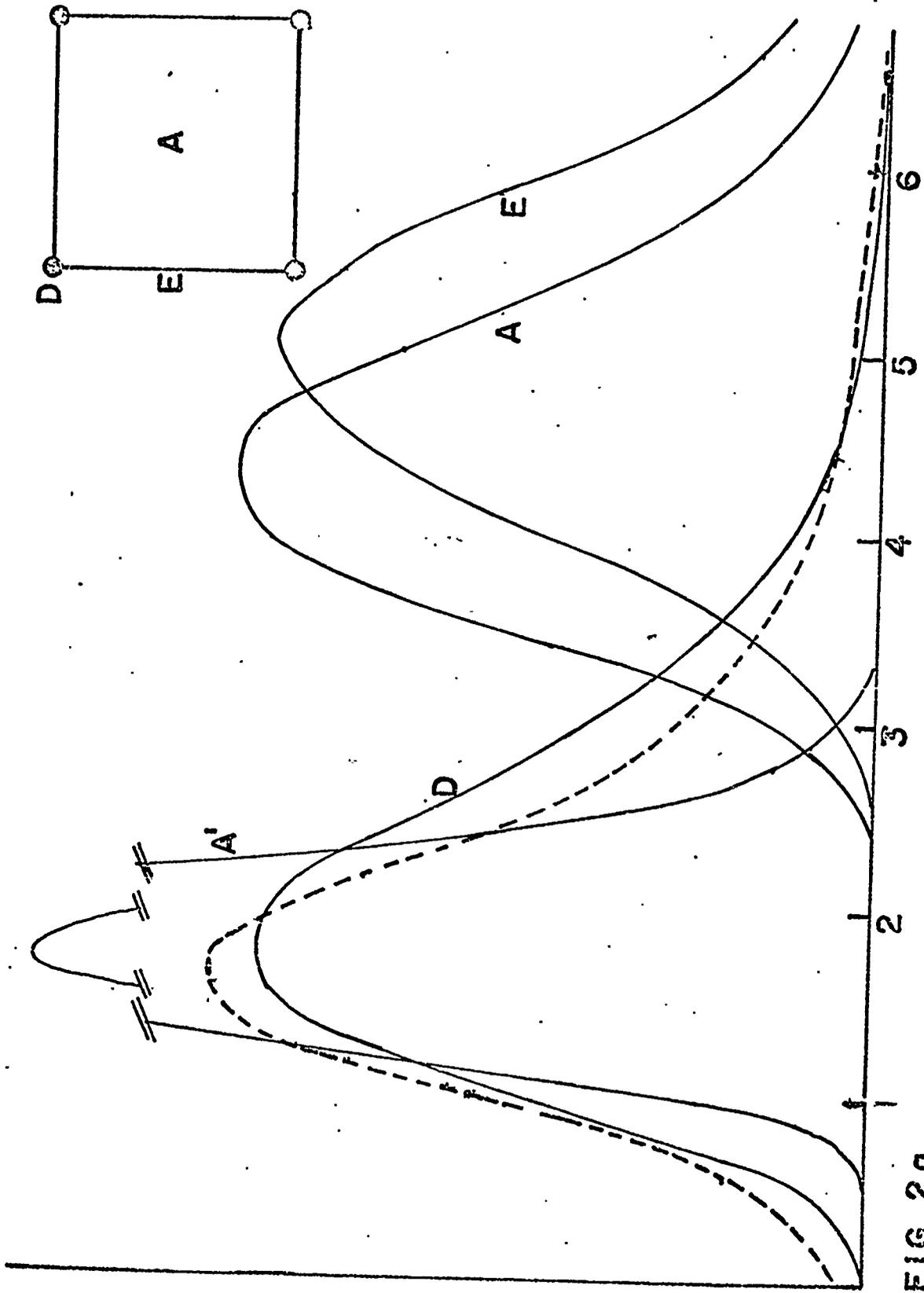


FIG. 29

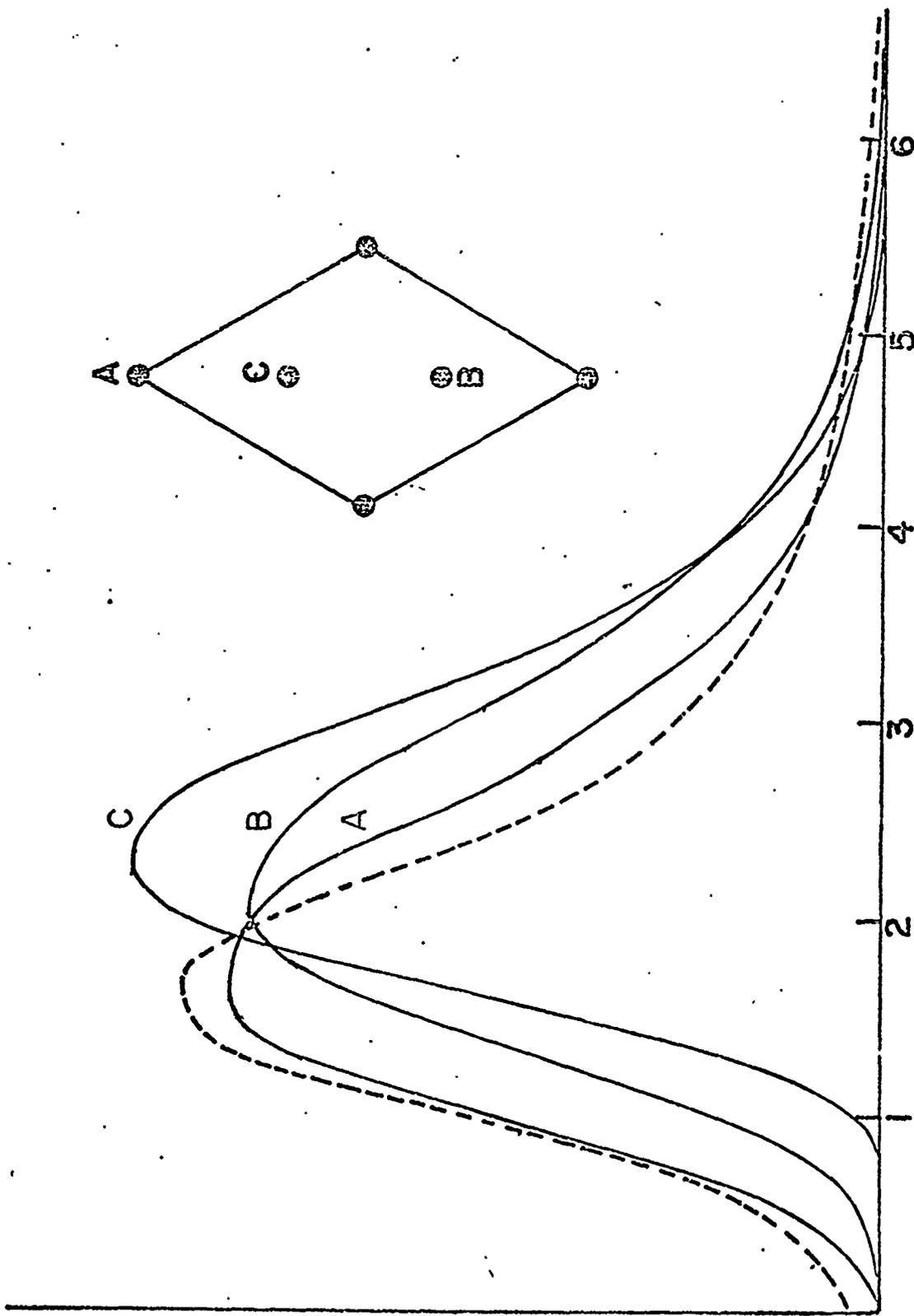


FIG. 2b

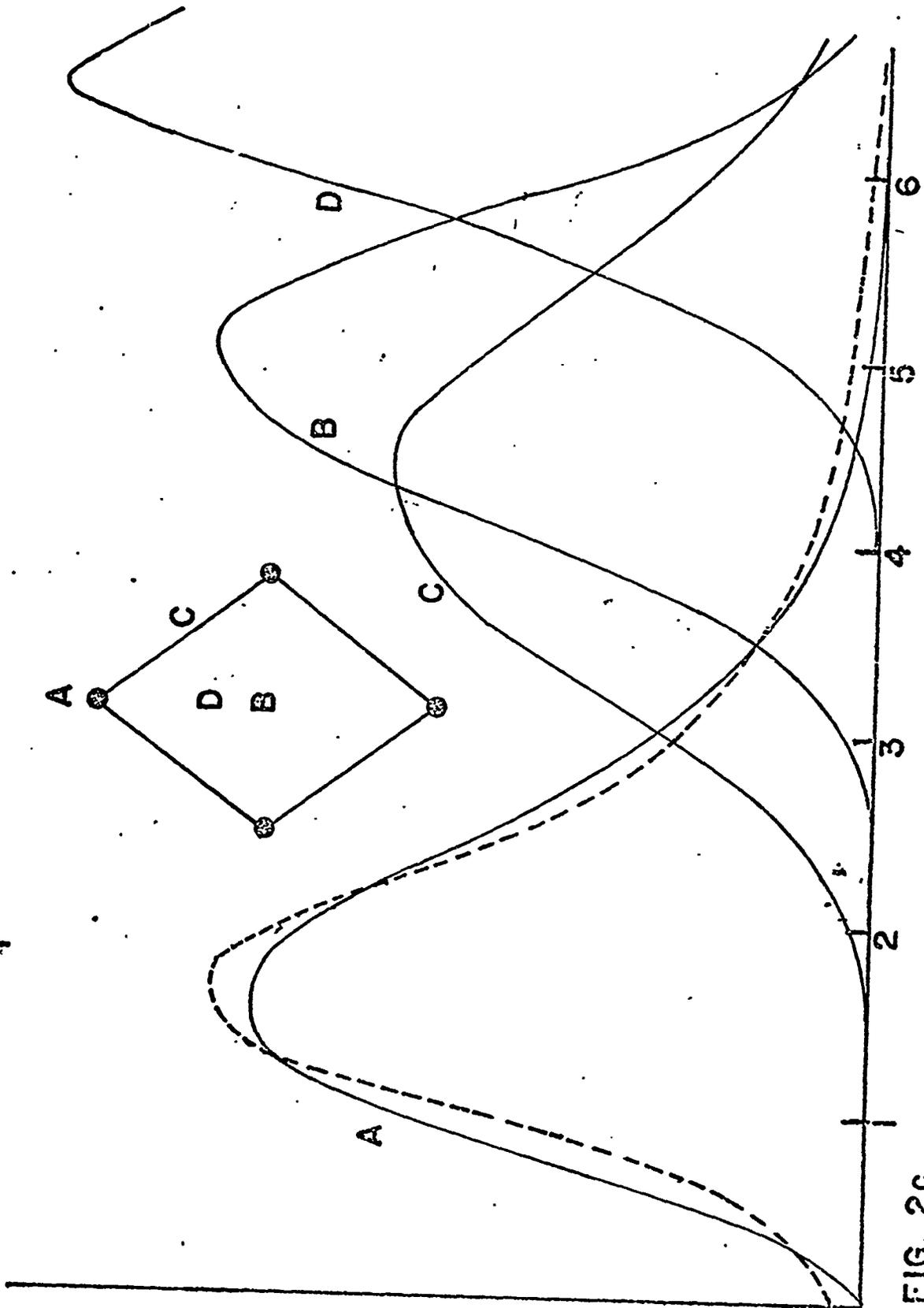


FIG. 2c

FIG. 3

