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TITLE: DETAILED QUANTUM TRANSITION STATE THEORY.
APPLICATION TO COLLINEAR REACTIONS

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SUBMITTED TO: Proceedings of the CECAM Workshop on
Reactive Scattering in Orsay, France
in the summer of 1977. May 15 July 7, 1977.

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DETAILED QUANTUM TRANSITION STATE THEORY.

APPLICATION TO COLLINEAR REACTIONS

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ABSTRACT

THE APPLICABILITY OF THE DETAILED QUANTUM TRANSITION STATE THEORY (DQTST) OF LIGHT AND SICZEK (J. CHEM. PHYS. 64, 1907 (1976)) IS INVESTIGATED FOR SEVERAL COLLINEAR SYSTEMS. WE CONSIDER THE EFFECTS OF BOUNDARY CONDITIONS AND THE PLACEMENT OF THE TRANSITION STATE SURFACE ON THE DQTST PREDICTIONS. IT IS SHOWN THAT THE RELIABILITY OF DQTST IS NOT SIMPLY CORRELATED WITH ANY PROPERTY OF THE REACTION PATH PROFILE (BARRIER HEIGHT OR REACTION EXOTHERMICITY); FEATURES OF THE POTENTIAL ENERGY SURFACE ASSOCIATED WITH OTHER DEGREES OF FREEDOM MUST ALSO BE CONSIDERED.

I. INTRODUCTION

THE ACCURATE SOLUTION OF THE THREE DIMENSIONAL QUANTUM REACTIVE SCATTERING PROBLEM IS VIRTUALLY INTRACTABLE FOR ALL BUT THE SIMPLEST ATOM-DIATOM SYSTEMS DUE TO THE LARGE NUMBER OF COUPLED CHANNELS WHICH MUST BE TREATED. RECENTLY, LIGHT AND SICZEK (%1) DESCRIBED A METHOD FOR OBTAINING THE TOTAL REACTION PROBABILITY FROM SPECIFIED QUANTUM STATES OF REACTANTS WITHOUT HAVING TO EXPLICITLY FOLLOW THE SCATTERING DYNAMICS OF PRODUCTS. THIS METHOD COMBINES A FULL QUANTUM SCATTERING TREATMENT FOR REACTANT DYNAMICS WITH A TRANSITION STATE THEORY ASSUMPTION FOR THE PRODUCT DYNAMICS. THIS TRANSITION STATE THEORY ASSUMPTION IS APPLIED TO THE EXACT NUMERICAL SOLUTION OF SCHROEDINGER'S EQUATION ON A SURFACE IN THE INTERACTION REGION. BOUNDARY CONDITIONS ARE APPLIED ON THIS SURFACE SO THAT ANY FLUX REACHING THIS SURFACE IS ASSUMED TO BE PURELY REACTIVE (OUTGOING TOWARDS PRODUCTS), AND THE DETAILED DYNAMICS FOR THIS FLUX IS FOLLOWED NO FURTHER. THIS DETAILED QUANTUM TRANSITION STATE THEORY (DQTST) APPEARS AT FIRST TO BE IDEALLY SUITED TO HIGHLY EXOTHERMIC REACTIONS, FOR WHICH THE OUTGOING FLUX ASSUMPTION SEEMS INTUITIVELY VALID SO LONG AS THE TRANSITION STATE SURFACE (TSS) IS POSITIONED TOWARDS THE DOWNHILL SIDE OF THE REACTION. IF RELIABLE, IT IS CONCEIVABLE THAT MANY FULLY QUANTUM MECHANICAL THREE DIMENSIONAL REACTIVE SCATTERING CALCULATIONS WITHIN THE DQTST FRAMEWORK WILL BECOME TRACTABLE. SUCH CALCULATIONS WOULD REQUIRE A FULL DYNAMICAL TREATMENT OF A RELATIVELY SMALL NUMBER OF REACTANT CHANNELS (AT LOW RELATIVE KINETIC ENERGY), BUT WOULD STILL PROVIDE IMPORTANT INFORMATION

ABOUT THE TOTAL REACTION PROBABILITY FROM EACH INITIAL STATE OF REACTANTS.

IN APPLYING DQTST TO THE PLANAR H+H₂ REACTION, LIGHT AND SICZEK (%1) REPORT ENCOURAGING RESULTS FOR TOTAL REACTION PROBABILITIES FROM SPECIFIC ROTATIONAL STATES OF REACTANTS. THIS CALCULATION INCLUDES ONLY ONE VIBRATIONAL STATE IN THE CLOSE COUPLING EXPANSION OF THE SCATTERING WAVEFUNCTION, AND AS SUCH DOES NOT DIRECTLY INVESTIGATE THE IMPORTANCE OF VIBRATIONAL DEGREES OF FREEDOM TO THE PERFORMANCE OF DQTST. A TEST OF THE PERFORMANCE OF DQTST REQUIRES A COMPARISON OF THE DQTST PREDICTIONS WITH EXACT CALCULATIONS. SINCE EXACT CALCULATIONS FOR THREE DIMENSIONAL EXOTHERMIC REACTIONS WITH SEVERAL VIBRATIONAL (AND HENCE MANY ROTATIONAL) STATES ARE SOMEWHAT OVERLY AMBITIOUS PROJECTS AT THIS TIME, WE HAVE APPLIED DQTST TO SEVERAL REACTIVE SYSTEMS WITHIN THE COLLINEAR APPROXIMATION. THE COLLINEAR APPROXIMATION SHOULD PROVIDE A RELIABLE INSIGHT INTO THE IMPORTANCE OF VIBRATIONAL DEGREES OF FREEDOM. WE WILL REPORT HERE UPON THE PERFORMANCE OF DQTST FOR THE COLLINEAR H₃, FH₂, HF₂, AND HEH₂₊ SYSTEMS.

IN THE NEXT SECTION (SECTION II), WE REVIEW THE DQTST METHOD AND DESCRIBE IN DETAIL HOW IT IS APPLIED TO THE COLLINEAR REACTIVE SCATTERING PROBLEM. IN SECTION III WE PRESENT RESULTS FOR THE METHOD AS APPLIED TO THE FOUR COLLINEAR SYSTEMS MENTIONED ABOVE. SECTION IV CONCLUDES WITH A DISCUSSION OF THE RESULTS.

II. THE DQTST METHOD

THE DQTST METHOD OPERATES BY SOLVING EXACTLY THE SCHRODINGER EQUATION FROM ASYMPTOTIC CONFIGURATIONS OF REACTANTS UP TO A TRANSITION STATE SURFACE (TSS) IN THE INTERACTION REGION WHERE BOUNDARY CONDITIONS APPROPRIATE TO DQTST ARE APPLIED. IF THE TSS IS CHOSEN TO BE LOCATED IN THE ASYMPTOTIC PRODUCT REGION OF CONFIGURATION SPACE, EXACT SCATTERING INFORMATION WILL BE OBTAINED FROM SPECIFIC REACTANT STATES TO SPECIFIC PRODUCT STATES. BY PLACING THE TSS IN THE STRONG INTERACTION REGION, WE NO LONGER EXPECT AN ACCURATE DESCRIPTION OF THE SCATTERING DYNAMICS TO SPECIFIC STATES OF PRODUCTS, BUT RATHER WE SEEK TO DETERMINE ACCURATELY ONLY THE TOTAL REACTION PROBABILITY FROM SPECIFIC REACTANT STATES. OF COURSE, ONE OF THE QUESTIONS WE WOULD LIKE TO ANSWER HERE IS HOW THE PLACEMENT OF THE TSS IS RELATED TO THE SHAPE OF THE POTENTIAL ENERGY SURFACE UNDER CONSIDERATION AND THE LEVEL OF ACCURACY TO BE EXPECTED IN THE DQTST RESULTS.

A. COLLINEAR REACTIVE SCATTERING

FOR THE SOLUTION OF THE CLOSE COUPLED EQUATIONS FOR THE COLLINEAR REACTIVE PROBLEM, WE REFER THE READER TO AN EARLIER PUBLICATION (2) FOR A DETAILED PRESENTATION. THE NOTATION USED HERE FOLLOWS THAT OF REFERENCE 2, WHICH WE SHALL REFER TO AS PAPER I HENCEFORTH. BRIEFLY, CONFIGURATION SPACE IS DIVIDED INTO TWO ARRANGEMENT CHANNEL SUBSPACES BY MEANS OF A MATCHING SURFACE (LABELLED M IN FIG.1). THE ARRANGEMENT CHANNEL α

REFERS TO REACTANT CONFIGURATIONS ($A + BC$) AND THE ARRANGEMENT CHANNEL γ REFERS TO PRODUCT CONFIGURATIONS ($AB + C$). IN EACH ARRANGEMENT CHANNEL WE DEFINE A NATURAL COLLISION COORDINATE SYSTEM (u,v) , WHERE u IS A TRANSLATIONAL COORDINATE AND v IS A LOCAL VIBRATIONAL COORDINATE. AS REACTION PROGRESSES TOWARDS ASYMPTOTIC CONFIGURATIONS, u AND v TRANSFORM SMOOTHLY TO R AND r , WHICH ARE RESPECTIVELY THE MASS SCALED ATOM-DIATOM SEPARATION COORDINATE AND THE MASS SCALED INTERNUCLEAR SEPARATION COORDINATE OF THE DIATOM.

THE CLOSE COUPLED EQUATIONS FOR REACTIVE SCATTERING ARE SOLVED BY THE R-MATRIX PROPAGATION METHOD DESCRIBED IN PAPER I. EACH ARRANGEMENT CHANNEL IS SUBDIVIDED INTO SMALL SECTORS, AND IN EACH SECTOR THE WIGNER R-MATRIX IS DETERMINED ANALYTICALLY. THE SECTOR R-MATRICES ARE THEN ASSEMBLED RECURSIVELY, USING EQUATIONS DETERMINED ORIGINALLY BY ZVIJAC AND LIGHT (23), TO GIVE A GLOBAL R-MATRIX. THE SCATTERING MATRIX (S-MATRIX) IS DETERMINED FROM THE GLOBAL R-MATRIX AND THE APPROPRIATE BOUNDARY CONDITIONS.

IN EACH SECTOR, THE WAVEFUNCTION IS EXPANDED IN VIBRATION-TRANSLATION STATES,

$$\Psi(u,v) = \eta^{+1/2} \sum_{n=1}^N f_n(u) \phi_n(v,i) \quad (31)$$

WHERE THE $\eta^{1/2}$ FACTORIZATION (4) IS CHOSEN TO GIVE A HERMITIAN INTERACTION MATRIX, AND THE LOCAL VIBRATIONAL EXPANSION BASIS IS A PRIMITIVE SET OF HARMONIC OSCILLATOR STATES CHOSEN TO BE CONVENIENT FOR THE ITH SECTOR. CLOSE COUPLED EQUATIONS FOR THE TRANSLATIONAL FUNCTIONS $f_n(\omega)$ ARE THEN OBTAINED

$$\frac{d^2}{du^2} \underline{\underline{f}}(u) = \underline{\underline{D}}^{(i)} \underline{\underline{f}}(u) \quad (32)$$

WHERE THE INTERACTION MATRIX $\underline{\underline{D}}^{(i)}$ IS ~~THE~~ GIVEN IN PAPER I,

$$D_{nn'}^{(i)} = \frac{3}{4\Omega^2} \delta_{nn'} + \frac{2\mu}{h^2} \left\langle \phi_n | \eta^2 \left\{ V - V^0 + \frac{\varepsilon_n + \varepsilon_{n'}}{2} - E \right\} \right| \phi_{n'} \rangle \quad (33)$$

A TRANSFORMATION TO A CONTRACTED SET OF VIBRATIONAL BASIS FUNCTIONS IS THEN PERFORMED BY DIAGONALIZING THE INTERACTION MATRIX. THE EIGENVECTORS OF $\underline{\underline{D}}^{(i)}$ DEFINE A NEW VIBRATIONAL BASIS $\{x\}$ AND A SET OF ASSOCIATED TRANSLATIONAL FUNCTIONS $\{g\}$, WHERE

$$\chi_n^{(i)}(v) = \sum_{n'=1}^N T_{n'n}^{(i)} \phi_{n'}(v; i) , \quad n=1, \dots, P \quad (\$4)$$

$$g_n^{(i)}(u) = \sum_{n'=1}^N T_{n'n}^{(i)} f_{n'}(u) , \quad n=1, \dots, P \quad (\$5)$$

AND

$$\left(\underline{T}^{(i)} \right)^T \underline{D}^{(i)} \underline{T}^{(i)} = \underline{\lambda}^2(i) = \text{diagonal.} \quad (\$6)$$

where \underline{A}^T is the transpose of \underline{A} .

THE (NOW UNCOUPLED) TRANSFORMED EQUATIONS AND WAVEFUNCTION MATCHING CONDITIONS ARE SATISFIED BY THE R-MATRIX RECURSION EQUATIONS. A GLOBAL R-MATRIX SPANNING CONFIGURATION SPACE FROM ASYMPTOTIC REACTANTS (SURFACE A IN FIG. 1) TO THE TSS IS ASSEMBLED; THIS R-MATRIX SATISFIES THE RELATION

$$\begin{bmatrix} g_A \\ g_{TSS} \end{bmatrix} = \begin{bmatrix} R_1 & R_2 \\ R_3 & R_4 \end{bmatrix} \begin{bmatrix} g'_A \\ +g'_{TSS} \end{bmatrix} \quad (87)$$

WHERE THE PLUS SIGN IN Eq(?) INDICATES THAT THE DERIVATIVES OF THE TRANSLATIONAL FUNCTIONS ARE ALWAYS TAKEN TOWARDS LARGER VALUES OF THE COORDINATE U. BOUNDARY CONDITIONS ARE APPLIED TO THE GLOBAL R-MATRIX DEFINED IN Eq(?), ACCORDING TO THE PROCEDURES DISCUSSED BELOW.

B. DQTST BOUNDARY CONDITIONS

IN ACCORDANCE WITH THE TRANSITION STATE ASSUMPTIONS, WE WISH TO APPLY BOUNDARY CONDITIONS SPECIFYING ONLY OUTGOING (REACTIVE) FLUX ON THE TSS. IN PRINCIPLE, WE DO NOT CARE HOW THE OUTGOING FLUX IS DISTRIBUTED AMONG THE CHANNELS DEFINED BY THE LOCAL HAMILTONIAN ON THE TSS, SINCE ANY UNITARY TRANSFORMATION AMONG OPEN CHANNELS DEFINED ON THE TSS WILL PRESERVE THE TOTAL FLUX PASSING THROUGH THE SURFACE. HOWEVER, WE DO WANT THE BOUNDARY CONDITIONS ON THE TSS TO TAKE A FORM SUCH THAT THE DQTST CALCULATIONS ARE GUARANTEED TO REPRODUCE EXACT CALCULATIONS AS THE TSS IS MOVED TOWARDS ASYMPTOTIC PRODUCT CONFIGURATIONS. WE WOULD ALSO LIKE TO IMPOSE BOUNDARY CONDITIONS ON THE TSS WHICH DISTURB THE SCATTERING DYNAMICS AS LITTLE AS POSSIBLE. AS WE SHALL SEE LATER, THERE IS NO COMPLETELY SATISFACTORY WAY TO ACCOMPLISH THIS SECOND OBJECTIVE.

The boundary conditions ~~represented~~ ^{for} the DOTST method
 are similar to those encountered in standard reactive
 scattering problems. The DOTST boundary conditions differ from
 the exact situation in the definition of the asymptotic
 Hamiltonian for the outgoing product states. The asymptotic
 reactant Hamiltonian is, in terms of the mass weighted
 separation coordinates R_α and r_α ,

$$H(R_\alpha, r_\alpha) = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\alpha^2} + \frac{\partial^2}{\partial r_\alpha^2} \right) + V_\alpha^\circ(r_\alpha) \quad (\$8)$$

WHERE THE ASYMPTOTIC POTENTIAL IS

$$V_\alpha^\circ(r_\alpha) = \lim_{R_\alpha \rightarrow \infty} V(R_\alpha, r_\alpha) \quad (\$9)$$

THE ASYMPTOTIC PRODUCT HAMILTONIAN HAS IDENTICALLY THE SAME
 FORM AS ABOVE, EXCEPT THAT THE CHANNEL ARRANGEMENT LABEL α IS
 REPLACED BY THE PRODUCT LABEL γ . THE PRODUCT COORDINATES
 ARE RELATED TO THE REACTANT COORDINATES BY THE MASS DEFINED
 ROTATION ANGLE ξ_p ($2, 25$), WHERE

$$\begin{bmatrix} r_\alpha \\ R_\alpha \end{bmatrix} = \begin{bmatrix} \cos \xi_\beta & -\sin \xi_\beta \\ \sin \xi_\beta & \cos \xi_\beta \end{bmatrix} \begin{bmatrix} r_\alpha \\ R_\alpha \end{bmatrix} \quad (\$10)$$

ON THE TSS, THE LOCAL NATURAL COLLISION COORDINATES (u, v) DEFINE MOTION PERPENDICULAR TO THE TSS (u) AND IN THE TSS (v). THESE COORDINATES ARE RELATED TO THE ASYMPTOTIC REACTANT COORDINATES BY A TRANSFORMATION SIMILAR TO Eq(10), WITH AN ANGLE OF ROTATION INTERMEDIATE IN VALUE BETWEEN ZERO AND THE REACTANT TO PRODUCT TRANSFORMATION ANGLE ξ_β DEFINED ABOVE. SO THAT THE DDTST BOUNDARY CONDITIONS ARE GUARANTEED TO EVOLVE INTO THE EXACT CONDITIONS AS THE TSS IS MOVED TOWARDS PRODUCTS, WE DEFINE THE HAMILTONIAN ON THE TSS AS

$$H_{TSS}(u, v) = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2} \right) + V_{TSS}(v) \quad (\$11)$$

WHERE THE LOCAL VIBRATIONAL POTENTIAL IS

$$V_{TSS}(v) = V(u_{TSS}, v) \quad (\$12)$$

IN THIS FASHION, THE SCATTERING WAVEFUNCTION FOR VALUES OF u

Beyond the TSS is

$$\Psi_n(u,v) = \sum_{n'=1}^{N_{\text{open}}^{\gamma}} \tilde{\chi}_{n'}^{(f)}(v) \exp(i\tilde{k}_{n'} u) S_{nn'}^{\gamma\alpha} (k_n/\tilde{k}_{n'})^{1/2}$$

$$+ \sum_{n'=N_{\text{open}}^{\gamma}+1}^P \tilde{\chi}_{n'}^{(f)}(v) A_{nn'} \exp(-|\tilde{k}_{n'}|u) \quad (\$13)$$

WHERE THE INTERNAL STATES $\tilde{\chi}_{n'}^{(f)}$ ARE EIGENFUNCTIONS OF THE LOCAL VIBRATIONAL POTENTIAL.

DIFFICULTIES IN APPLYING DOTST BOUNDARY CONDITIONS ARISE IN SPECIFYING THE CHANNEL MOMENTA $\tilde{k}_{n'}$ OF Eq(13) ASSOCIATED WITH THE INTERNAL STATES $\tilde{\chi}_{n'}^{(f)}$. IF DOTST BOUNDARY CONDITIONS ARE TO EVOLVE INTO THE PROPER ONES ASYMPTOTICALLY, ONLY TWO CHOICES ARE POSSIBLE, AND THERE ARE DEFINITE PROBLEMS WITH EITHER CHOICE. THE FIRST LOGICAL CHOICE IS TO USE CHANNEL MOMENTA APPROPRIATE TO THE EIGENVALUES OF THE LOCAL INTERNAL STATES AND THE TOTAL SCATTERING ENERGY. HOWEVER, THIS CHOICE PRODUCES UNDESIRABLE RESULTS NEAR THRESHOLD FOR REACTIONS WITH A BARRIER IF THE TSS IS LOCATED TOO NEAR THE BARRIER. IN THIS CASE, IT MAY HAPPEN THAT ALL THE LOCAL CHANNELS WILL BE CLOSED, CAUSING DOTST TO PREDICT NO FLUX THROUGH THE TSS AT ALL (ONLY LOCALLY OPEN CHANNELS CAN CARRY FLUX). THE OTHER BOUNDARY CONDITION CHOICE IS TO USE THE ASYMPTOTIC CHANNEL MOMENTA. IN THIS APPROACH, FLUX TUNNELING THROUGH A BARRIER IS ALLOWED TO

PENETRATE AND AN IMPROVED DQST PERFORMANCE AT THRESHOLD IS OBTAINED. THIS SECOND CHOICE HAS DRAWBACKS ALSO. FOR MANY REACTIVE SYSTEMS, THERE ARE MORE CHANNELS OPEN LOCALLY AT THE TSS THAN THERE ARE ASYMPTOTICALLY. THESE ADDITIONAL LOCAL CHANNELS MAY BE QUITE SUBSTANTIALLY POPULATED, BUT THE USE OF FINAL CHANNEL MOMENTA FORCES THE FLUX IN THESE CHANNELS BACK ACROSS THE TSS AND RESULTS IN DQST UNDERESTIMATING THE ACTUAL TOTAL REACTION PROBABILITIES. BOTH BOUNDARY CONDITION CHOICES WERE INVESTIGATED BY LIGHT AND SICZEK (21) FOR THE PLANAR H + H₂ SYSTEM, AND EACH PROVIDED PREDICTIONS OF COMPARABLE ACCURACY. WE WILL PRESENT RESULTS FOR BOTH TYPES OF BOUNDARY CONDITIONS HERE.

KEEPING THE COMMENTS ABOVE IN MIND, WE NOW PROCEED TO DISCUSS HOW THE BOUNDARY CONDITIONS OF Eq(13) ARE APPLIED, IN MATRIX FORM, TO THE FINAL GLOBAL R-MATRIX OF Eq(7). GENERALLY, THE TSS LIES IN THE POLAR COORDINATE REGION OF THE Y ARRANGEMENT CHANNEL, AND YET THE FINAL HAMILTONIAN Eq(11) HAS A FORM APPROPRIATE TO THE PRODUCT CARTESIAN TYPE COORDINATES (ONLY ROTATED). FOR THIS REASON, A POLAR-CARTESIAN MATCHING PROCEDURE IS PERFORMED ON THE R-MATRIX BEFORE BOUNDARY CONDITIONS ARE APPLIED. THIS PROCEDURE IS REQUIRED BECAUSE THE OUTGOING FLUX ASSUMPTION ON THE TSS IMPLIES THAT PRODUCT STREAMLINES WILL BE PERPENDICULAR TO THE TSS (SEE FIG.1). THEREFORE, IN THE LAST PROPAGATION SECTOR, THE POLAR-CARTESIAN MATCHING PROCEDURE GIVES A NEW R-MATRIX \tilde{R} , WHERE

$$\begin{bmatrix} \underline{\underline{R}}_1 & \underline{\underline{R}}_2 \\ \underline{\underline{R}}_3 & \underline{\underline{R}}_4 \end{bmatrix} = \begin{bmatrix} \underline{\underline{R}}_1 & \underline{\underline{R}}_2 \underline{\underline{C}} \\ \underline{\underline{C}} \underline{\underline{R}}_3 & \underline{\underline{C}} \underline{\underline{R}}_4 \underline{\underline{C}} \end{bmatrix} \quad (\$14)$$

AND $\underline{\underline{C}}$ IS THE SYMMETRIC MATRIX

$$C_{nn'} = \left\langle \tilde{\chi}_n^{(f)} \left| \eta^{\frac{1}{2}} \right| \chi_{n'}^{(f)} \right\rangle \quad (\$15)$$

THE SECTOR INDEX F IN Eq(15) REFERS TO THE FINAL SECTOR IN ARRANGEMENT CHANNEL γ WHOSE OUTER BOUNDARY IS THE TSS. THE VIBRATIONAL BASIS FUNCTIONS $\chi_{n'}^{(f)}$ IN Eq(14) ARE THOSE APPROPRIATE TO THE POLAR REPRESENTATION OF THE WAVEFUNCTION IN THE FINAL SECTOR $\gamma^{(f)}$ (IN WHICH THE INTERACTION IS DIAGONAL), WHEREAS THE BASIS $\tilde{\chi}_n$ IS APPROPRIATE TO A CARTESIAN REPRESENTATION OF THE WAVEFUNCTION IN WHICH THE CURVATURE TERMS IN THE COUPLING MATRIX ARE SET TO ZERO. THE CARTESIAN BASIS $\underline{\underline{D}}^{(f)}$ DIAGONALIZES THE COUPLING MATRIX IN THE FINAL SECTOR WHEN $m = 1$ IN Eq(3).

BOUNDARY CONDITIONS FOR THE DOTST METHOD ARE APPLIED TO THE R-MATRIX $\underline{\underline{R}}$ OF Eq(14) TO GIVE THE S-MATRIX, WHERE

$$\underline{k}^{-\frac{1}{2}} \underline{S} \underline{k}^{\frac{1}{2}} = \underline{\underline{W}}^{-1} \underline{\underline{W}}^* \quad (\$16)$$

$$\underline{\underline{W}} = \begin{bmatrix} \tilde{R}_1 O_\alpha' - O_\alpha & \tilde{R}_2 O_\gamma' \\ \tilde{R}_3 O_\alpha' & \tilde{R}_4 O_\gamma' - O_\gamma \end{bmatrix} \quad (\$17)$$

WHERE \underline{k} IS A DIAGONAL MATRIX OF ASYMPTOTIC CHANNEL MOMENTA
AND

$$(O_\nu)_{nn'} = \begin{cases} S_{nn'} \exp(i k_n^\nu R_\nu^\infty), & \text{channel } n \text{ open} \\ S_{nn'} \exp(-i k_n^\nu |R_\nu^\infty|), & \text{channel } n \text{ closed} \end{cases} \quad (\$18)$$

$\nu = \alpha, \gamma$

THE CHANNEL MOMENTA k_n^α ARE THOSE APPROPRIATE FOR ASYMPTOTIC REACTANTS, AND AS DISCUSSED EARLIER, THE CHANNEL MOMENTA k_n^γ ARE CHOSEN EITHER TO BE THOSE APPROPRIATE TO THE LOCAL OR

FINAL PRODUCT VIBRATIONAL EIGENSTATES. IN CHANNEL α , R_α^∞ IS THE VALUE OF THE REACTANT ATOM-MOLECULE SEPARATION ON SURFACE A IN FIG. 1; AND IN CHANNEL γ , R_γ^∞ IS THE VALUE OF THE PRODUCT ATOM-MOLECULE SEPARATION ON THE TSS. HOWEVER, IN THE POLAR REGION OF THE PRODUCT CONFIGURATION SPACE, R_γ^∞ IS NOT CONSTANT ON THE TSS AND THE VALUE OF R_γ^∞ ON THE REACTION PATH IS USED. THIS PROCEDURE HAS THE EFFECT OF INTRODUCING AN ARBITRARY (AND UNIMPORTANT FOR DOTST) PHASE FACTOR IN THE REACTIVE S-MATRIX ELEMENTS.

THE S-MATRIX OBTAINED BY THIS PROCEDURE IS AN $(N \times N)$ MATRIX, WHERE $N = \text{NOPEN}(\alpha) + \text{NOPEN}(\gamma)$. BECAUSE NO DYNAMICS IS DETERMINED FOR THE PRODUCT CONFIGURATION SPACE, NO SIGNIFICANCE IS ATTACHED TO THE VALUES OF INDIVIDUAL S-MATRIX ELEMENTS PERTAINING TO ANY OF THE PRODUCT QUANTUM STATES. FOR EXAMPLE, IF THE S-MATRIX IS PARTITIONED

$$\underline{\underline{S}} = \begin{bmatrix} S^{\alpha\alpha} & S^{\alpha\gamma} \\ S^{\gamma\alpha} & S^{\gamma\gamma} \end{bmatrix} \quad (\$19)$$

WHERE THE MATRIX $S^{\mu\nu}$ IS DIMENSIONED $(\text{NOPEN}(\mu) \times \text{NOPEN}(\nu))$, THEN ONLY THE TWO BLOCKS $S^{\alpha\alpha}$ AND $S^{\gamma\gamma}$ ARE ANALYZED FOR THE PURPOSES OF DOTST. IN PARTICULAR, WE ARE INTERESTED IN THE

TOTAL REACTION PROBABILITIES $P_i^{\alpha+}$ FROM SPECIFIC STATES OF
REACTANTS (α), WHERE

$$P_i^{\alpha+} = \sum_{j=1}^{N_{\text{open}}} |S_{ji}^{\alpha+}|^2 \quad (\$20)$$

IN EVALUATING THE RELIABILITY OF DOTST WE SEEK TO COMPARE THE
TOTAL REACTION PROBABILITIES $P_i^{\alpha+}$ WITH THE CORRESPONDING VALUES
DETERMINED BY EXACT CALCULATIONS.

III. APPLICATION OF DQTST

THE DQTST METHOD WAS TESTED ON SEVERAL COLLINEAR REACTIVE SYSTEMS. WE STUDIED THE H₂+H REACTION ON THE PORTER-KARPLUS (%6) POTENTIAL SURFACE, THE H₂+F REACTION ON THE LEPS SURFACE DESCRIBED BY MUCKERMAN (%7) (THIS SURFACE #5), THE F₂+H REACTION ON THE SURFACE DESCRIBED BY JONATHAN, OKUDA, AND TIMLIN (%8) (SURFACE II), AND THE HeH⁺ +H REACTION ON THE DIM SURFACE OF KUNTZ (%9). THE H+H₂ REACTION IS THERMONEUTRAL AND HAS A LARGE REACTION BARRIER OF 0.40 eV, WHEREAS ALL THE OTHER SYSTEMS ARE EXOTHERMIC. BOTH THE F+H₂ REACTION (1.38eV) AND THE HeH⁺ + H REACTION (0.752eV) ARE MODERATELY EXOTHERMIC; THE F+H₂ SYSTEM PROCEEDS WITH A SMALL BARRIER (0.046 eV), WHILE THE HeH⁺⁺H REACTION PROCEEDS WITHOUT ANY BARRIER. IN CONTRAST, THE H+F₂ SYSTEM IS GREATLY EXOTHERMIC (4.50 eV) AND HAS ONLY A SMALL (0.10 eV) BARRIER. THE TOTAL REACTION PROBABILITY AS A FUNCTION OF TOTAL ENERGY WAS DETERMINED FOR EACH SYSTEM FOR TWO DIFFERENT CHOICES OF THE TSS. THESE TRANSITION STATE SURFACES ARE SHOWN IN FIG.2 FOR EACH SYSTEM, SUPERIMPOSED UPON CONTOURS OF THE POTENTIAL ENERGY SURFACES.

EXACT COLLINEAR CLOSE COUPLING CALCULATIONS HAVE BEEN REPORTED FOR ALL THE SYSTEMS TREATED HERE. THE H+H₂ SYSTEM HAS BEEN STUDIED MANY TIMES AND HAS BEEN THE SUBJECT OF MANY REVIEWS(%10). THE F+H₂ COLLINEAR REACTION WAS ORIGINALLY STUDIED BY SCHATZ, BOWMAN, AND LUPELMANN (%11); THE HeH²⁺ SYSTEM HAS BEEN STUDIED BY ADAMS (%12); AND THE H+F₂ SYSTEM HAS

BEEN STUDIED BY CONNOR, JAKUBETZ AND MANZ (%13). IN ALL CASES OUR EXACT CALCULATIONS AGREE WITH THOSE PUBLISHED PREVIOUSLY. FOR THE H+F₂ SYSTEM, WE EXTENDED OUR CALCULATIONS TO ENERGIES WHERE AS MANY AS THREE REACTANT F₂ STATES WERE OPEN. THIS IS A SOMEWHAT HIGHER ENERGY RANGE THAN REPORTED EARLIER (%13), AND BECAUSE THIS SYSTEM IS SO HIGHLY EXOTHERMIC, A REASONABLY LARGE BASIS EXPANSION IS REQUIRED TO CONVERGE THE CALCULATION.

BRIEF SUMMARY OF THE RESULTS OF THE EXACT CALCULATIONS FOR THIS SYSTEM IS SUMMARIZED IN THE APPENDIX.

No Appendix

As described in the previous section, the close coupling equations were solved using the R-matrix propagation method and a computer program now generally available (%14). Only slight modifications of this program were required to implement the DQTST method described here. The program operates as described in Paper I, except that a more flexible choice of the harmonic oscillator primitive basis is necessary to treat the H+F₂ system properly. Because this reaction is so highly exothermic, there are as many as thirteen product HF vibrational channels energetically accessible at the scattering energies we are interested in. The harmonic oscillator primitive basis described in Paper I is always chosen centered at the minimum of the local vibrational potential and characterized by a force constant chosen for the curvature of the vibrational potential at its minimum. This procedure is normally satisfactory, but for calculations requiring a very large vibrational basis, this choice of a primitive basis may be poor in describing higher vibrational states of the diatom.

Table I has only ¹⁹ integration parameters, step sizes, etc.

FOR THIS REASON, THE CENTER OF THE HARMONIC OSCILLATOR PRIMITIVE BASIS IS NOW SHIFTED TOWARDS LARGER DIATOMIC SEPARATIONS AND THE FORCE CONSTANT IS LOWERED. THIS PROCEDURE GIVES A QUITE SATISFACTORY PRIMITIVE BASIS FOR THE DESCRIPTION OF THE HIGHER EIGENSTATES OF THE POTENTIAL, AND WAS USED FOR ALL THE CALCULATIONS REPORTED HERE.

IN TABLE I WE SUMMARIZE THE ~~SHOME~~ PARAMETERS CHARACTERIZING THE CALCULATIONS REPORTED HERE.

THE RESULTS OF THESE CALCULATIONS ARE SUMMARIZED IN FIG.3, FIG.4, FIG.5, AND FIG.6. IN EACH FIGURE WE PLOT THE TOTAL REACTION PROBABILITY FROM THE GROUND STATE OF REACTANTS TO ALL FINAL STATES OF PRODUCTS. IN THE (A) PARTS OF THE FIGURES THE DQTST PREDICTIONS USING ASYMPTOTIC CHANNEL MOMENTA ARE SHOWN, AND IN THE CORRESPONDING (B) PARTS OF THE FIGURES SHOW THE DQTST RESULTS USING LOCAL CHANNEL MOMENTA. IN EACH FIGURE, THE SOLID CURVES SHOW THE EXACT TOTAL REACTION PROBABILITIES, THE DOTTED CURVES SHOW THE DOTST TOTAL REACTION PROBABILITIES FOR THE TSS PLACED AT $U = 0.1 \text{ \AA}^0$ ($1 \text{ \AA}^0 = 0.529 \times 10^{-8} \text{ cm}$), AND THE DASHED CURVE SHOWS THE DOTST RESULTS FOR THE TSS AT $U = 0.3 \text{ \AA}^0$. IN ORDER TO SIMPLIFY FUTURE REFERENCES TO THE VARIOUS CALCULATIONS, WE WILL ADOPT THE FOLLOWING NOTATION. THE CHARACTERS S1 AND S3 WILL BE USED TO REFER TO A DQTST CALCULATION WHERE THE TSS HAS BEEN PLACED AT $U = 0.1$ OR $U = 0.3 \text{ \AA}^0$, RESPECTIVELY. WE THEN APPEND THE CHARACTER A OR L TO DENOTE WHETHER ASYMPTOTIC OR LOCAL CHANNEL MOMENTA WERE EMPLOYED IN THE BOUNDARY CONDITIONS. THEREFORE, A REFERENCE TO THE S3A CALCULATION IMPLIES THE DQTST RESULTS FOR THE TSS AT 0.3 \AA^0 USING ASYMPTOTIC CHANNEL MOMENTA.

IN FIG.3 THE RESULTS FOR THE COLLINEAR H + H₂ SYSTEM ARE SHOWN. WE WILL DISCUSS THIS SYSTEM IN SOME DETAIL, BECAUSE MANY OF THE PROPERTIES OF THE DQTST APPROXIMATION WILL BECOME EVIDENT IN THIS SYSTEM AND WILL BE SEEN AGAIN FOR THE OTHER SYSTEMS TO BE CONSIDERED. USING ASYMPTOTIC CHANNEL MOMENTA, THE MOST NOTABLE DIFFERENCE BETWEEN THE EXACT AND DQTST RESULTS OCCURS NEAR E = 0.87 eV, WHERE THE EXACT CALCULATION SHOWS THE WELL KNOWN RESONANCE FOR THE H+H₂ SYSTEM. THE DQTST CALCULATIONS DO NOT SHOW THIS FEATURE FOR EITHER PLACEMENT OF THE TSS. WHEN THE TSS IS PLACED AT 0.3 Å (THE S3A CALCULATION), A BROAD FEATURE IN THE TOTAL REACTION PROBABILITY IS SEEN FROM E = .7 TO .8 eV; THERE IS NO STRUCTURE EVIDENT AT ALL IN THE DQTST RESULTS FOR THE TSS AT 0.1 Å (THE S1A CALCULATION). AT THRESHOLD ENERGIES, THE S1A RESULTS OVERESTIMATE THE TOTAL REACTION PROBABILITY, AND THEN FALL BELOW THE CORRECT RESULTS AT HIGHER ENERGIES. THE S3A RESULTS SHOW AN IMPROVED THRESHOLD BEHAVIOR, BUT STILL UNDERESTIMATE THE TOTAL REACTION PROBABILITY ABOVE THRESHOLD. THE FAILURE OF THE DQTST CALCULATIONS TO SHOW THE RESONANCE FEATURE AT E = 0.87 eV AND TO CORRECTLY PREDICT THE THRESHOLD BEHAVIOR MAY BE ATTRIBUTED TO THE FORM OF THE BOUNDARY CONDITIONS. IF THE DQTST CALCULATIONS ARE TO CORRECTLY PREDICT THE RESONANCE FEATURE, THE TSS MUST BE PLACED FAR ENOUGH TOWARDS PRODUCT CONFIGURATIONS THAT ALL FEATURES OF THE POTENTIAL ENERGY SURFACE RESPONSIBLE FOR THE RESONANCE LIE WITHIN THE TSS AND THE ASYMPTOTIC REACTANT CONFIGURATION SPACE. IN THIS CASE, IT APPEARS THAT MISSING THE RESONANCE SIMPLY INDICATES THAT THE

POTENTIAL SURFACE BEYOND THE TSS PLAYS A SIGNIFICANT PART IN THE RESONANCE. THE PROBLEMS WITH THE THRESHOLD BEHAVIOR HAVE ALREADY BEEN MENTIONED BY LIGHT AND SICZEK (%1). USING ASYMPTOTIC CHANNEL MOMENTA CAUSES THE REACTION BARRIER TO BE CHOPPED OFF AT THE TSS, AND FLUX TUNNELING THROUGH THE BARRIER IS FREQUENTLY OVERESTIMATED. THE SHORTENING OF THE BARRIER APPEARS TO BE RESPONSIBLE FOR THE OVERESTIMATION OF PROBABILITIES FOR THE S1A CALCULATION AT THRESHOLD. IN THE S3A CALCULATION, THE TSS IS FAR ENOUGH BEHIND THE REACTION BARRIER THAT TUNNELING IS MORE CORRECTLY ESTIMATED.

WE NOW TURN TO THE H + H₂ SYSTEM USING LOCAL CHANNEL MOMENTA IN THE BOUNDARY CONDITIONS. APPLYING BOTH SETS OF BOUNDARY CONDITIONS IS FREQUENTLY QUITE HELPFUL IN SEPARATING THOSE EFFECTS DIRECTLY ATTRIBUTABLE TO THE FORM OF THE BOUNDARY CONDITIONS FROM THOSE WHICH ARE INHERENTLY A PART OF THE SCATTERING SYSTEM. FOR EXAMPLE, JUST AS IN FIG.3A, NEITHER THE S1L OR S3L CALCULATIONS OF FIG.3B SHOW THE E = 0.87 eV RESONANCE STRUCTURE. THIS OBSERVATION SUPPORTS THE CLAIM THAT THE RESONANCE IS MISSED DUE TO FEATURES OF THE SYSTEM, IN THAT THE TSS HAS NOT BEEN PLACED FAR ENOUGH OUT INTO THE PRODUCT VALLEY TO ENCOMPASS ALL THE FEATURES OF THE POTENTIAL SURFACE RESPONSIBLE FOR THE RESONANCE BEHAVIOR. ON THE OTHER HAND, THRESHOLD BEHAVIOR IN DOTST CALCULATIONS APPEARS TO BE STRONGLY DEPENDENT ON THE CHOICE OF BOUNDARY CONDITIONS. THE S1L CALCULATION HAS A MISERABLE THRESHOLD BEHAVIOR, PREDICTING NO REACTION PROBABILITY AT ALL BELOW A TOTAL ENERGY OF 0.5 eV. THE FAILURE TO PREDICT ANY REACTION PROBABILITY HERE ARISES

BECAUSE THERE ARE NO CHANNELS LOCALLY OPEN AT THE TSS FOR THIS CALCULATION. BECAUSE ONLY OPEN CHANNELS CARRY FLUX, THE TOTAL REACTION PROBABILITY IS OBVIOUSLY UNDERESTIMATED. THE USE OF LOCAL CHANNEL MOMENTA MAKES THE BARRIER FOR ANY LOCALLY CLOSED CHANNEL APPEAR INFINITELY THICK. THERE ARE LOCALLY OPEN CHANNELS AVAILABLE ON THE S3 TRANSITION STATE SURFACE, AND HENCE THE S3L CALCULATION PROVIDES A MUCH MORE REASONABLE ESTIMATE OF THE TOTAL REACTION PROBABILITY AT THRESHOLD.

IN FIG.4 THE DOTST RESULTS FOR THE F + H₂ SYSTEM ARE SHOWN. OF ALL THE SYSTEMS STUDIED HERE, THE DOTST APPROXIMATION IS WORST FOR THE F + H₂ SYSTEM. THE EXACT CALCULATION IS CHARACTERIZED BY A SUCCESSION OF SHARP RESONANCE FEATURES, NONE OF WHICH ARE SEEN IN THE DOTST RESULTS. IN BOTH THE S1A AND S1L CALCULATIONS (FIG.4A AND FIG.4B) THE TOTAL REACTION PROBABILITY RISES FROM THRESHOLD QUICKLY UP TO UNIT REACTION PROBABILITY, AND ESSENTIALLY STAYS THERE OVER THE ENTIRE ENERGY RANGE CONSIDERED. MOVING THE TSS OUT FURTHER ONLY PARTIALLY IMPROVES THE DOTST RESULTS; BOTH THE S3A AND S3L CALCULATIONS GENERALLY OVERESTIMATE THE TOTAL REACTION PROBABILITY. SINCE THE GENERAL QUALITY OF THE DOTST RESULTS FOR THIS SYSTEM ARE LESS SENSITIVE TO THE FORM OF THE DOTST BOUNDARY CONDITIONS (LOCAL VS. ASYMPTOTIC MOMENTA), WE SUSPECT THAT THE POOR PERFORMANCE OF DOTST IS RELATED DIRECTLY TO THE SHAPE OF THE F + H₂ POTENTIAL ENERGY SURFACE. WE RETURN TO THIS POINT IN THE NEXT SECTION.

IN FIG.5 THE H + F₂ SYSTEM IS STUDIED. THE EXACT TOTAL

REACTION PROBABILITY FOR THIS SYSTEM IS A VERY SMOOTH FUNCTION OF ENERGY, RISING FROM THRESHOLD NEAR $E = 4.6$ EV TO NEAR UNIT PROBABILITY NEAR $E = 4.7$ EV. THE DOTST CALCULATIONS ARE IN SUSTANTIAL AGREEMENT WITH THE EXACT RESULTS, WITH THE EXCEPTION OF THE S1A CALCULATION. IN FACT, THE BEST PERFORMANCE WE WILL SEE IN THIS PAPER FOR THE DOTST METHOD IS FOR THIS SYSTEM WHEN LOCAL CHANNEL MOMENTA ARE USED IN THE BOUNDARY CONDITIONS. IT IS NOT CLEAR WHY THE S1A REACTION PROBABILITIES ARE UNDERESTIMATED. THERE ARE ONLY THREE OR FOUR CHANNELS OPEN AT THE S1 TSS IN THIS ENERGY RANGE, WHILE THERE ARE TWELVE TO THIRTEEN CHANNELS OPEN ASYMPTOTICALLY. IN THIS CASE, APPLYING ASYMPTOTIC CHANNEL MOMENTA HAS THE EFFECT OF INSERTING A RAPID DROP IN THE POTENTIAL SURFACE TO THE FINAL ENERGETIC VALUES OF THE PRODUCTS. EXPERIMENTATION WITH OTHER FORMS FOR THE DOTST BOUNDARY CONDITIONS SUGGESTS THAT A TOO RAPID INCREASE IN THE CHANNEL MOMENTA MAY CAUSE REFLECTION FROM THE SHARP EDGE PRODUCED BY THE DROP IN THE POTENTIAL SURFACE INTRODUCED AT THE TSS. SUCH AN EDGE EFFECT MAY BE RESPONSIBLE FOR THE LOW REACTION PROBABILITIES OBSERVED IN THE S1A CALCULATION.

FINALLY, IN FIG.6 THE DOTST RESULTS FOR THE $\text{HeH}^+ + \text{H}$ SYSTEM ARE SHOWN. THIS SYSTEM DIFFERS FROM THE OTHERS IN THAT THERE IS NO REACTION BARRIER AT ALL. EXACT TRANSITION PROBABILITIES FROM SPECIFIC STATES OF REACTANTS TO SPECIFIC STATES OF PRODUCTS ARE CHARACTERIZED BY MANY SHARP RESONANCE FEATURES, AND YET THE TOTAL REACTION PROBABILITY IS A RELATIVELY SMOOTH FUNCTION OF ENERGY. BOTH THE S1A AND S3A

CALCULATIONS FOR THIS SYSTEM VERY STRONGLY UNDERESTIMATE THE TOTAL REACTION PROBABILITY. THE USE OF LOCAL BOUNDARY CONDITIONS IN THE S1L AND S3L CALCULATIONS IMPROVES THE IQTST PREDICTIONS, BUT IN NEITHER CASE ARE THE IQTST PREDICTIONS ESPECIALLY RELIABLE. THIS SYSTEM ALSO DIFFERS FROM THE OTHERS IN THAT THERE ARE SIGNIFICANTLY MORE CHANNELS OPEN AT THE TSS THAN THERE ARE IN EITHER THE ASYMPTOTIC REACTANT OR PRODUCT CHANNELS, DUE TO THE RELATIVELY DEEP WELL IN THE POTENTIAL SURFACE. AT THE ENERGY RANGE CONSIDERED HERE, THERE IS ONE OPEN REACTANT CHANNEL, FIVE ASYMPTOTICALLY OPEN PRODUCT CHANNELS, AND TEN OR ELEVEN CHANNELS OPEN AT THE TSS. THE VERY LARGE NUMBER OF CHANNELS OPEN AT THE TSS CAUSES THE S1A AND S3A CALCULATIONS TO UNDERESTIMATE THE TOTAL REACTION PROBABILITY, BECAUSE FLUX LOCALLY POPULATING THE ν GHER VIBRATIONAL STATES AT THE TSS IS FORCED BACK TO THE REACTANT CHANNEL (SINCE THESE STATES ARE ASYMPTOTICALLY CLOSED IN PRODUCTS). THIS IS AN EFFECT SIMILAR TO THE BARRIER PENETRATION PROBLEM OBSERVED IN THE H + H₂ SYSTEM PREVIOUSLY, BUT NOW WORKING IN REVERSE. IN FIG.6B, THE S1L CALCULATION APPEARS TO GIVE BETTER RESULTS THAN THE S3L CALCULATION, EVEN THOUGH THE TSS IS POSITIONED FURTHER TOWARDS PRODUCTS IN THE LATTER CASE. THE AGREEMENT IN THE S1L CALCULATION IS PROBABLY FORTUITOUS, INDICATING THAT TURBULENCE IN THE SCATTERING WAVEFUNCTION IS MOST LIKELY LOCALIZED IN THE PRODUCT REGION OF CONFIGURATION SPACE BEYOND THE S1 TSS.

IV. DISCUSSION

THE PERFORMANCE OF DQTST AS REPRESENTED IN FIGS. 3-6 IS CLEARLY VARIABLE. IN SOME CASES, SUCH AS THE H + F₂ SYSTEM, DQTST IS REMARKABLY ACCURATE; AND IN OTHER CASES, SUCH AS THE F + H₂ SYSTEM, DQTST IS UNRELIABLE. IN INTERPRETING DQTST RESULTS, IT IS NECESSARY TO CONSIDER TWO EFFECTS, THOSE CAUSED DIRECTLY BY THE FORM OF THE DQTST BOUNDARY CONDITIONS AND THOSE CAUSED BY THE POTENTIAL SURFACE BEING STUDIED. MOST TROUBLESOME ARE THOSE EFFECTS CAUSED BY THE DQTST BOUNDARY CONDITIONS, WHICH CAN GENERALLY BE EXPECTED WHENEVER THERE ARE MANY MORE OR FEWER CHANNELS OPEN AT THE TSS THAN THERE ARE ASYMPTOTICALLY IN PRODUCTS. IN EITHER CASE, AN UNFORTUNATE CHOICE OF BOUNDARY CONDITIONS WILL RESULT IN AN UNDERESTIMATION OF THE CORRECT TOTAL REACTION PROBABILITY. IN THE H + H₂ S1L CALCULATION, THE USE OF LOCAL CHANNEL MOMENTA WHERE THERE ARE NO LOCALLY OPEN CHANNELS AT THE REACTION BARRIER CAUSES THE DQTST METHOD TO PREDICT NO REACTION PROBABILITY AT ENERGIES WELL ABOVE THRESHOLD FOR THE EXACT CASE. ON THE OTHER HAND, THE USE OF ASYMPTOTIC CHANNEL MOMENTA IN THE HeH⁺ + H SYSTEM CAUSES THE TOTAL REACTION PROBABILITY TO BE UNDERESTIMATED BECAUSE THERE ARE MORE CHANNELS OPEN LOCALLY THAN THERE ARE ASYMPTOTICALLY.

IN GENERAL, WE WOULD LIKE TO APPLY BOUNDARY CONDITIONS IN

IOTST WHICH MAXIMIZE FLUX THROUGH THE TSS, SO THAT ONLY FEATURES OF THE POTENTIAL ENERGY SURFACE BEHIND THE TSS CAN CAUSE FLUX ENTERING FROM REACTANTS NOT TO REACH THE TSS. MORE WORK NEEDS TO BE DONE TO DETERMINE DIRECTLY HOW TO ENFORCE BOUNDARY CONDITIONS MAXIMIZING FLUX ACROSS THE TSS. AT FIRST THOUGHT, ONE WOULD WANT TO APPLY BOUNDARY CONDITIONS AT THE TSS SO THAT ALL CHANNELS IN THE CLOSE COUPLING EXPANSION ARE GIVEN LOCALLY POSITIVE KINETIC ENERGIES. IN THIS WAY, ANY FLUX LOCALLY POPULATING ANY CHANNEL IS GIVEN A CHANCE TO PROPAGATE ALL THE WAY TO PRODUCTS. ASIDE FROM THE ARTIFICIALITY OF THESE BOUNDARY CONDITIONS, RESULTS OBTAINED USING THEM ARE USUALLY NO BETTER THAN THOSE USING LOCAL CHANNEL MOMENTA. AS WAS MENTIONED IN THE DISCUSSION OF THE H + F₂ SYSTEM, CAUSING LOCALLY CLOSED CHANNELS TO APPEAR TO HAVE POSITIVE KINETIC ENERGIES OFTEN CREATES EDGE EFFECTS IN THE (FICTIONAL) POTENTIAL ENERGY SURFACE. THESE EDGE EFFECTS CAUSE SPURIOUS REFLECTION OF FLUX BACK TOWARDS REACTANTS.

IN SUMMARY, IT APPEARS THAT THE LOCAL CHANNEL MOMENTA CHOICE OF BOUNDARY CONDITIONS PRODUCES THE FEWEST ARTIFICIAL EFFECTS IN THE IOTST APPROXIMATION, AND IS THEREFORE THE PREFERRED CHOICE. THE ONLY SERIOUS ARTIFICIAL EFFECT USING THESE CONDITIONS OCCURS IN REACTIONS WITH A BARRIER WHEN THE TSS IS POSITIONED TOO NEAR THE TOP OF THE BARRIER, AS IN THE H + H₂ S1L CALCULATION. ALTHOUGH TUNNELING THROUGH BARRIERS IS ALLOWED BY THE OTHER FORM OF BOUNDARY CONDITIONS, EXAMINING THE H + H₂ S1A CALCULATION INDICATES THAT THE IOTST PREDICTIONS THERE ARE NOT REALLY MUCH BETTER. IN THIS CASE, THE BARRIER IS

MADE TOO THIN BY THE USE OF FINAL CHANNEL MOMENTA. USING ASYMPTOTIC CHANNEL MOMENTA ALSO CAUSES PROBLEMS WHEN THERE ARE MANY MORE OR MANY FEWER CHANNELS OPEN ASYMPTOTICALLY THAN THERE ARE LOCALLY, AS IN THE H + F2 S1A AND THE HeH⁺ + H S1A AND S3A CALCULATIONS. ARTIFICIAL PROBLEMS WITH DDTST LOCAL CHANNEL MOMENTA BOUNDARY CONDITIONS MAY BE AVOIDED BY PLACING THE TSS FAR ENOUGH BEYOND ANY REACTION BARRIER TO ACCURATELY ACCOUNT FOR TUNNELING.

THE MOST NOTABLE FAILURE OF DDTST IN PREDICTING TOTAL REACTION PROBABILITIES (ASIDE FROM ARTIFICIAL PROBLEMS DISCUSSED ABOVE) OCCURS FOR REACTIVE SYSTEMS WHICH SHOW PRONOUNCED RESONANCE FEATURES. FOR THIS REASON, THE DDTST RESULTS OBTAINED HERE WERE GENERALLY BEST FOR THE H + H₂ AND H + F₂ SYSTEMS, WHICH SHOW COMPARATIVELY LITTLE RESONANCE BEHAVIOR. DDTST RESULTS FOR THE HIGHLY RESONANT F + H₂ AND HeH⁺ + H SYSTEMS ARE CONSIDERABLY WORSE. THE FAILURE OF DDTST TO SHOW RESONANCES MUST BE ATTRIBUTED TO THE VERY NATURE OF THE DDTST TRANSITION STATE ASSUMPTION. PRESUMABLY THERE ARE FEATURES OF THE POTENTIAL ENERGY SURFACE BETWEEN THE TSS AND ASYMPTOTIC PRODUCT CONFIGURATIONS WHICH PLAY AN ESSENTIAL PART IN THE OVERALL REACTION DYNAMICS. BOTH THE F + H₂ AND HeH⁺ + H SYSTEMS ARE EXOTHERMIC (THOUGH NOT AS EXOTHERMIC AS THE H + F₂ SYSTEM), AND ALL THE SYSTEMS STUDIED HERE, EXCEPT THE HeH⁺ + H SYSTEM, HAVE A BARRIER TO REACTION. CONSIDERING THE RELATIVE PERFORMANCE OF DDTST FOR ALL THESE SYSTEMS, IT APPEARS THAT ONE CANNOT PREDICT HOW WELL DDTST WILL DO BASED SOLELY UPON PROPERTIES OF THE POTENTIAL ENERGY SURFACE RELATED TO

ENERGETICS ALONG THE REACTION PATH. FOR THIS REASON, IT APPEARS NECESSARY TO ALSO CONSIDER THE PROPERTIES OF THE POTENTIAL SURFACE PERPENDICULAR TO THE REACTION PATH.

THE NATURE OF THE RESONANCE IN THE F + H₂ SYSTEM NEAR E = 1.66EV HAS BEEN STUDIED IN DETAIL BY LATHAM, McNUTT, REDMON AND WYATT(15), AND HAS BEEN SHOWN TO BE RELATED TO THE SHAPE OF THE ENERGY CORRELATION DIAGRAM FOR THE SYSTEM IN THE PRODUCT REGION OF THE POTENTIAL ENERGY SURFACE. THE ENERGY CORRELATION DIAGRAMS FOR THIS SYSTEM SHOW WELLS IN THE TRANSLATIONAL COORDINATE WHICH ARE PRODUCED BY THE BEHAVIOR OF THE LOCAL CURVATURE OF THE POTENTIAL ENERGY SURFACE PERPENDICULAR TO THE REACTION PATH. AS ONE ENTERS THE REACTION ZONE FROM REACTANTS, THE LOCAL FORCE CONSTANT DROPS FROM A VALUE REPRESENTATIVE OF THE REACTANT H₂ DIATOM TO ONE CHARACTERISTIC OF THE TRANSITION STATE GEOMETRY. LEAVING THE INTERACTION REGION AND PROGRESSING TOWARDS PRODUCTS, THE LOCAL FORCE CONSTANT INCREASES AND APPROACHES A VALUE APPROPRIATE FOR THE PRODUCT HF DIATOM. AS THE LOCAL FORCE CONSTANT INCREASES, THE VIBRATIONAL ENERGY LEVEL SPACING INCREASES MORE RAPIDLY THAN THE POTENTIAL ALONG THE REACTION PATH DECREASES. THIS EFFECT GIVES RISE TO THE TRANSLATIONAL WELLS WHICH LATHAM ET. AL. (15) HAVE DEMONSTRATED ARE RESPONSIBLE FOR THE V=0 TO V'=2 THRESHOLD RESONANCE AND THE SLOW RISE IN THE V=0 TO V'=3 REACTION PROBABILITY FOR THE F + H₂ SYSTEM.

WE MAY INTERPRET THE FAILURE OF DOTST TO SHOW RESONANCE BEHAVIOR IN THE F + H₂ SYSTEM IN THE FOLLOWING WAY. THE DOTST

METHOD RELIES ON THE TRANSITION STATE THEORY ASSUMPTION THAT FLUX CROSSING THE TSS CONTINUES ON TOWARDS ASYMPTOTIC PRODUCT CONFIGURATIONS WITHOUT ANY BACK REFLECTION. CLEARLY THEN, IF DQTST FAILS TO SHOW THIS RESONANCE BEHAVIOR, IT MUST BE DUE TO MULTIPLE CROSSINGS OF THE TSS (IN A CLASSICAL SENSE). IN THE CASE OF THE F + H₂ SYSTEM, IT APPEARS THAT THE VIBRATIONAL "SQUEEZING" OF THE POTENTIAL ENERGY SURFACE IN THE PRODUCT VALLEY IS RESPONSIBLE FOR DIRECTING FLUX ALL THE WAY BACK INTO THE REACTANT VALLEY. CLASSICALLY, ONE WOULD EXPECT TO FIND TRAJECTORIES AT THESE ENERGIES WHICH SHOW THE SYSTEM PROGRESSING ALONG TOWARDS REACTION, ENCOUNTERING THE WALL OF THE POTENTIAL SURFACE PROVIDED BY THE NARROWING OF THE VALLEY IN THE PRODUCT REGION, AND REFLECTING BACK TOWARDS REACTANTS. SIMILAR EFFECTS ARE MOST LIKELY RESPONSIBLE FOR THE RESONANCE BEHAVIOR SEEN IN THE H + H₂ AND HEH⁺ + H SYSTEMS.

IN THEIR STUDY OF THE PLANAR H + H₂ REACTION, LIGHT AND SICZEK(%) OBSERVED A QUITE SATISFACTORY PERFORMANCE OF DQTST IN PREDICTING TOTAL REACTION PROBABILITIES. IT WOULD APPEAR THAT THE REASON LIGHT AND SICZEK(%) OBSERVED SUCH GOOD BEHAVIOR FOR THE PLANAR H + H₂ CALCULATION IS IN PART AN EFFECT OF THE VIBRATIONALLY ADIABATIC NATURE OF THEIR CALCULATION. THE PORTER-KARPLUS POTENTIAL ENERGY SURFACE FOR H₃ (%) IS VIBRATIONALLY SIMILAR TO THE F + H₂ SYSTEM IN THAT THE LOCAL FORCE CONSTANT PERPENDICULAR TO REACTION IS SOFTER IN THE INTERACTION REGION THAN IT IS IN EITHER ASYMPTOTIC VALLEY. ON THE OTHER HAND, THE H + H₂ REACTION IS STRONGLY PREFERRED IN A COLLINEAR GEOMETRY, DUE TO A STRONG BENDING POTENTIAL IN THE

INTERACTION REGION. IN THIS SENSE, THE ROTATIONAL CHARACTER OF THE H₃ SURFACE IS QUITE OPPOSITE TO THE VIBRATIONAL CHARACTER. THE IDOTST TRANSITION STATE ASSUMPTION WOULD BE MUCH BETTER FOR ROTATIONAL DEGREES OF FREEDOM; IN THAT ANY FLUX WHICH MANAGES TO SQUEEZE THROUGH THE ROTATIONAL BOTTLENECK IN THE INTERACTION REGION IS NOT LIKELY TO ENCOUNTER (ROTATIONAL) FEATURES OF THE POTENTIAL SURFACE IN PRODUCT CONFIGURATIONS WHICH CAN REFLECT FLUX BACK THROUGH THE INTERACTION REGION.

ACKNOWLEDGEMENTS

THE AUTHOR ACKNOWLEDGES SEVERAL DISCUSSIONS WITH PROF. J. C. LIGHT, PROF. R. E. WYATT AND DR. R. K. NESSET AND THE HOSPITALITY OF PROF. CARL MOSER PROVIDED AT THE CECAM WORKSHOP ON REACTIVE SCATTERING IN DREAY IN THE SUMMER OF 1977, WHEN THIS WORK STARTED.

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FIGURE CAPTIONS

FIG. 1. COLLINEAR CONFIGURATION SPACE SHOWING SCHEMATICALLY THE APPLICATION OF DQTST BOUNDARY CONDITIONS. NORMAL REACTIVE SCATTERING BOUNDARY CONDITIONS ARE APPLIED WHEN SCHRODINGER'S EQUATION IS SOLVED FROM THE ASYMPTOTIC REACTANT TO ASYMPTOTIC PRODUCT REGIONS OF CONFIGURATION SPACE. IN DQTST THE SOLUTION STOPS AT THE TSS AND OUTGOING WAVE BOUNDARY CONDITIONS ARE APPLIED LOCALLY. THE PRODUCT FLUX STREAMLINES ARE PERPENDICULAR TO THE TSS. THE FINAL COORDINATES (u_f, v_f) CORRESPOND TO MOTION IN WHAT IS NORMALLY A PHYSICALLY UNREACHABLE PART OF CONFIGURATION SPACE; BUT FOR DQTST THE POTENTIAL ENERGY SURFACE CONTINUES ALONG THE u_f DIRECTION WITH A LOCAL VIBRATIONAL POTENTIAL THE SAME AS THAT ON THE TSS. AS THE TSS IS MOVED TOWARDS ASYMPTOTIC PRODUCT CONFIGURATIONS, THE DQTST PROBLEM SMOOTHLY APPROACHES THE CORRECT PHYSICAL PROBLEM. THE MATCHING SURFACE M SEPARATES THE REACTANT AND PRODUCT REGIONS OF CONFIGURATION SPACE. ALSO SHOWN ARE THE POLAR-CARTESIAN BOUNDARIES FOR THE α AND γ ARRANGEMENT CHANNELS, ORIGINATING FROM THE TURNING CENTER (TC).

FIG. 2. CONTOUR PLOTS FOR THE VARIOUS COLLINEAR SYSTEMS STUDIED HERE.

Fig 1

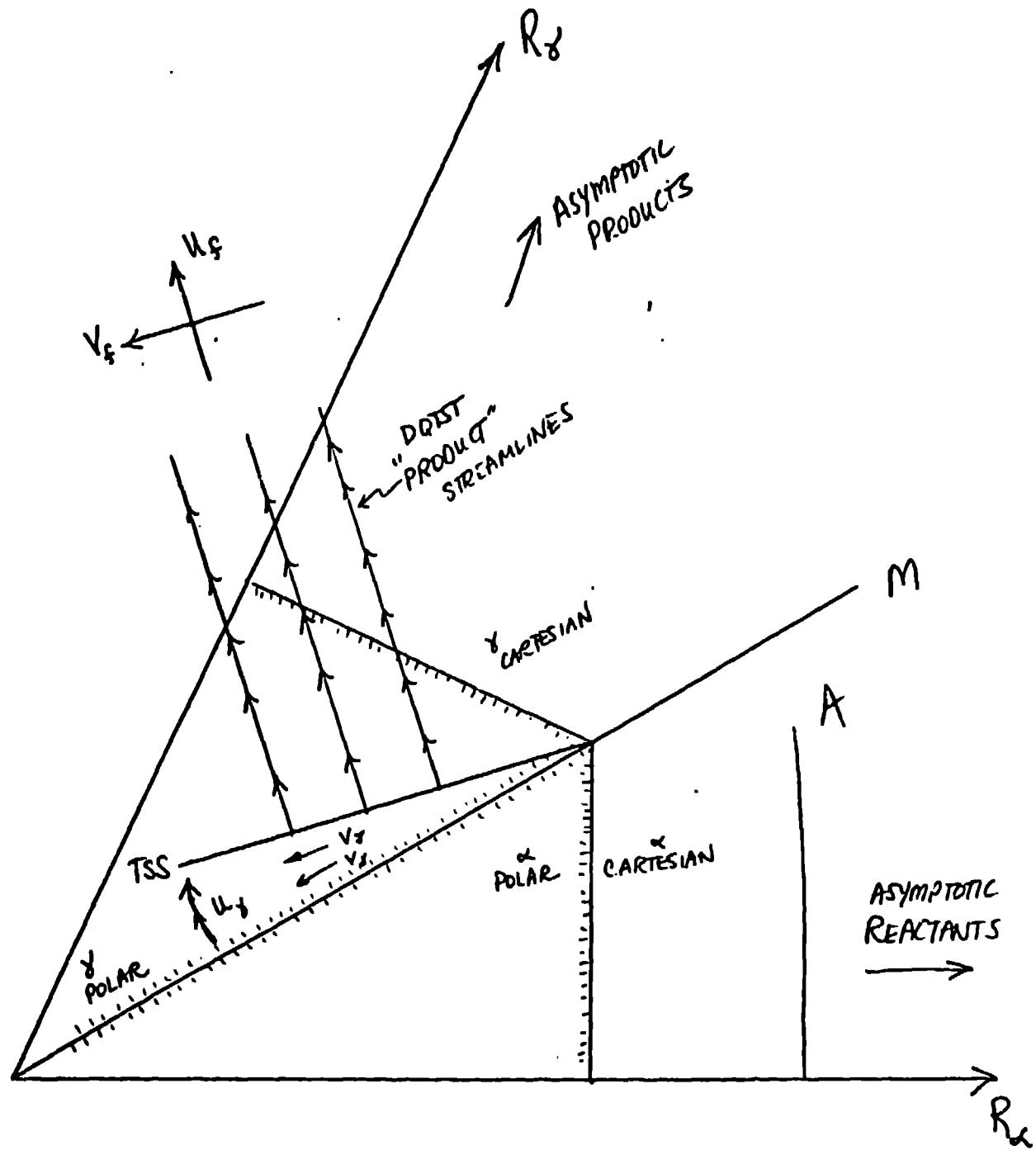
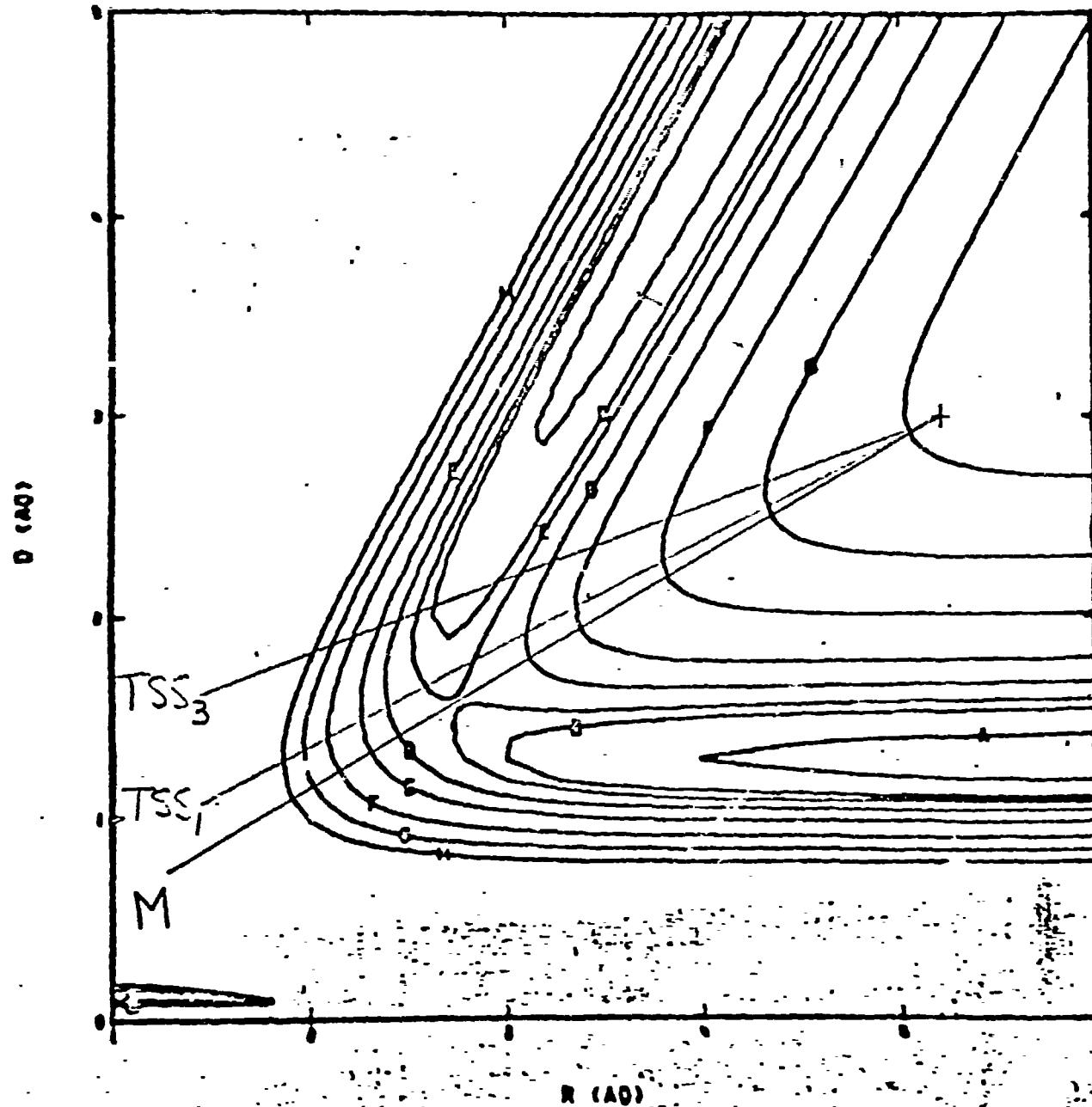


fig 2a

CONTOURS FOR THE H H H POTENTIAL SURFACE



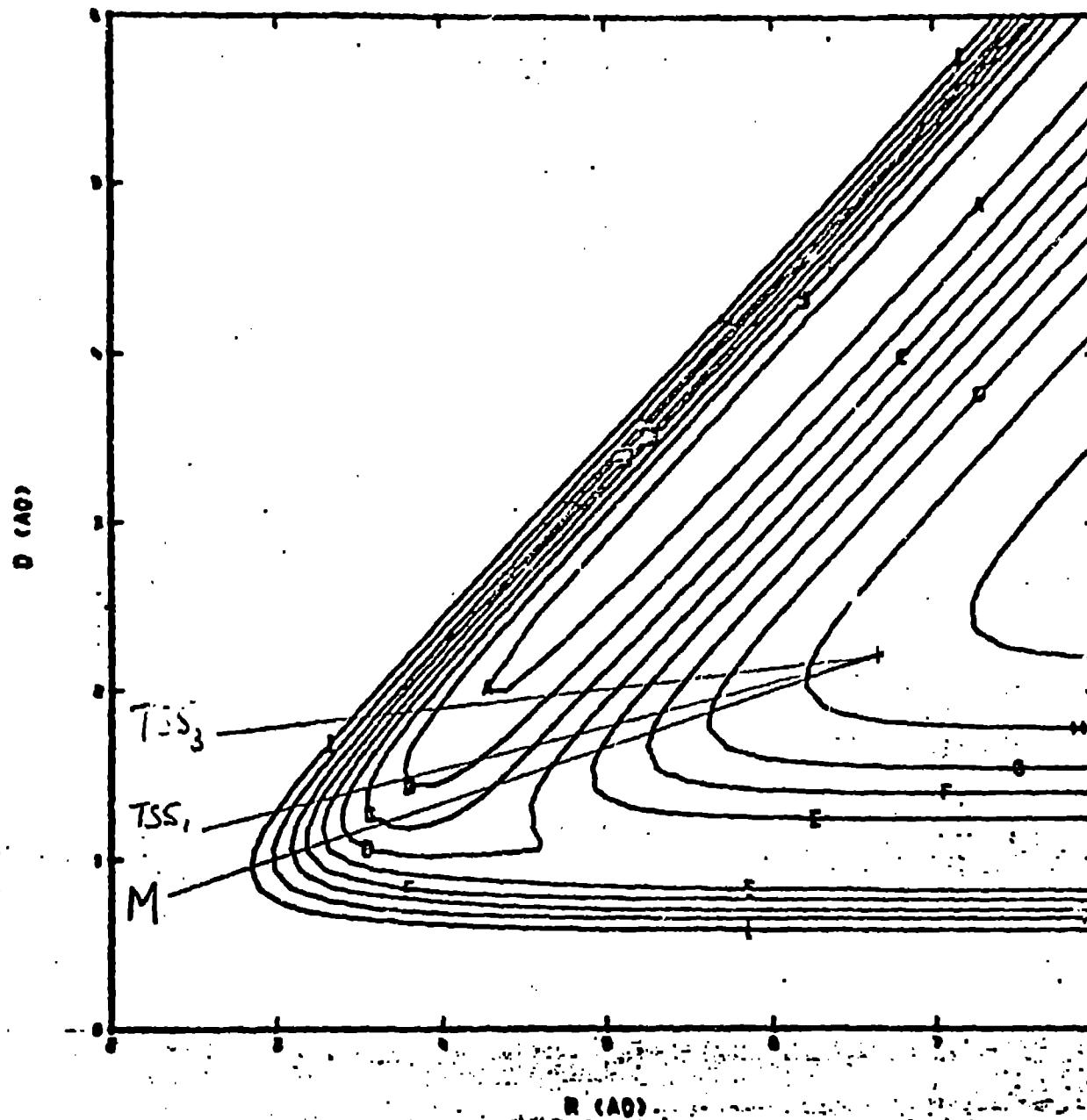
CONTOURS FOR THE H H H POTENTIAL SURFACE

IDENTIFICATION

CONTOUR VALUE

2b

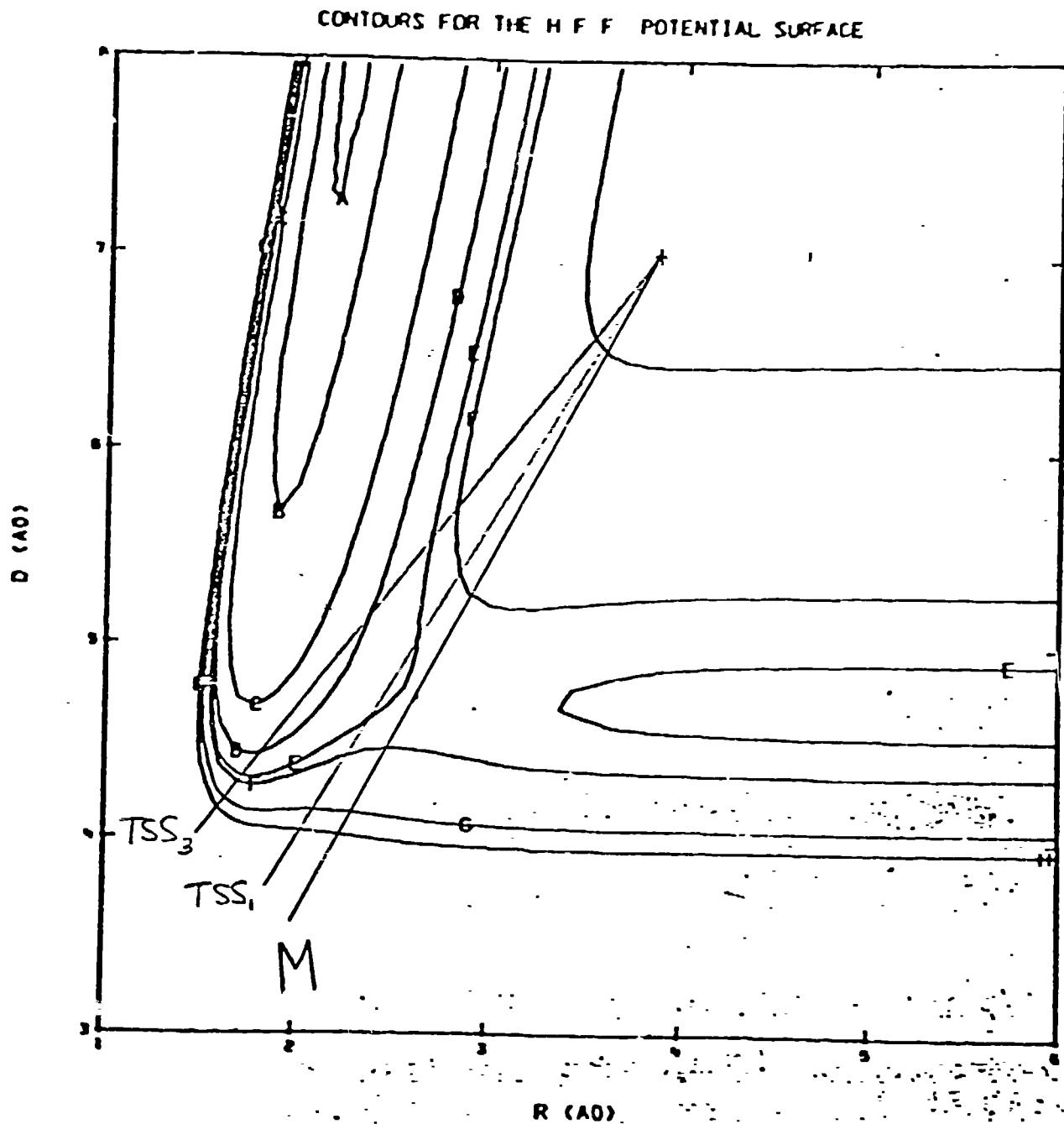
CONTOURS FOR THE F M H POTENTIAL SURFACE



CONTOURS FOR THE F M H POTENTIAL SURFACE

IDENTIFICATION	CONTOUR VALUE
A—A—A—A	.200
B—O—O—O	.600
C—C—C—C	1.000
D—D—D—D	1.400

2c

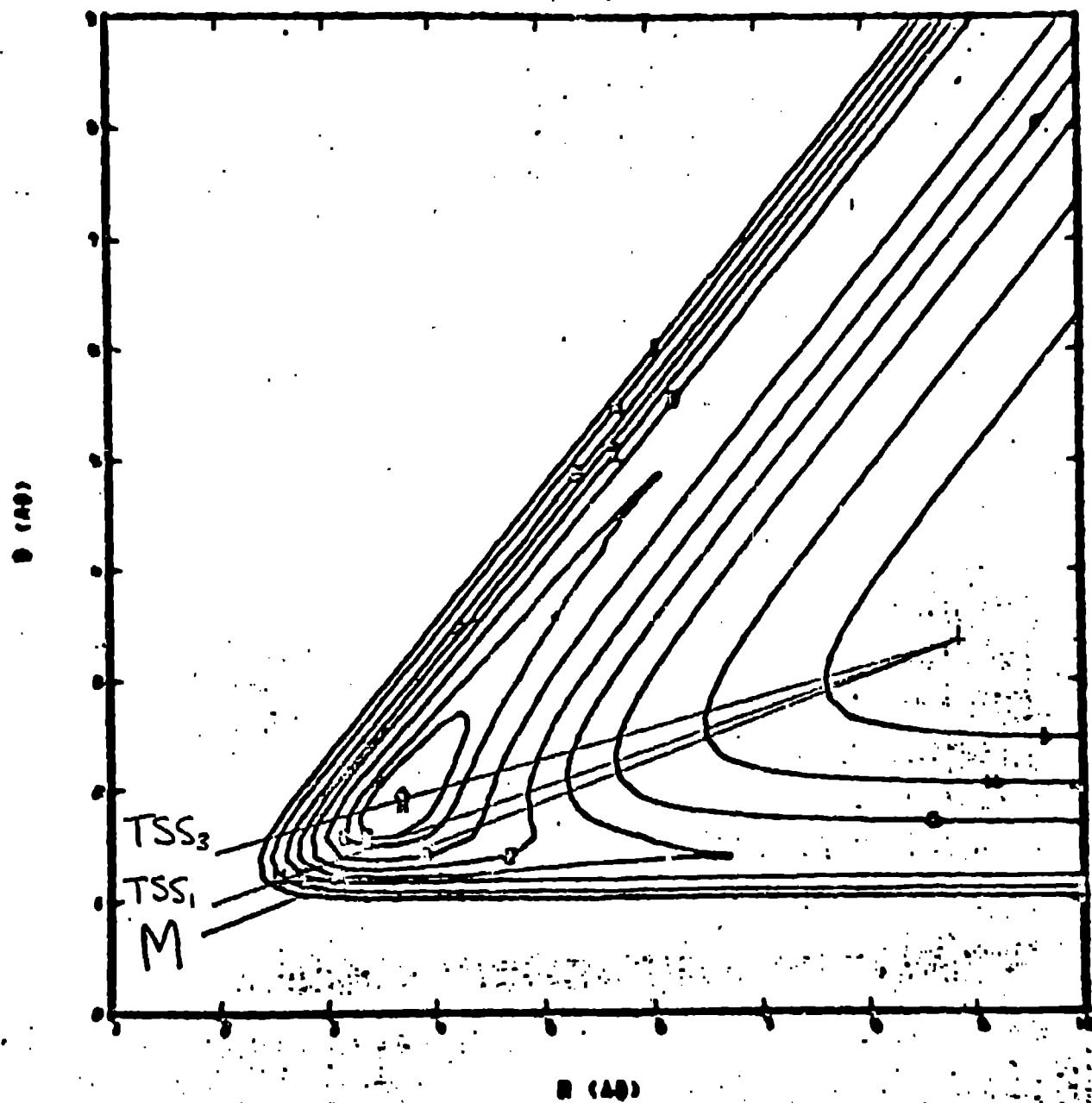


CONTOURS FOR THE H F F POTENTIAL SURFACE

IDENTIFICATION	CONTOUR VALUE
A—A—A—A	.250
B—B—B—B	1.000
C—C—C—C	> 2.00

2J.

CONTOURS FOR THE NEMOH POTENTIAL SURFACE



CONTOURS FOR THE NEMOH POTENTIAL SURFACE

IDENTIFICATION	CONTOUR VALUE
-----	-0.200
-----	-0.100
-----	0.000

Fig 3a

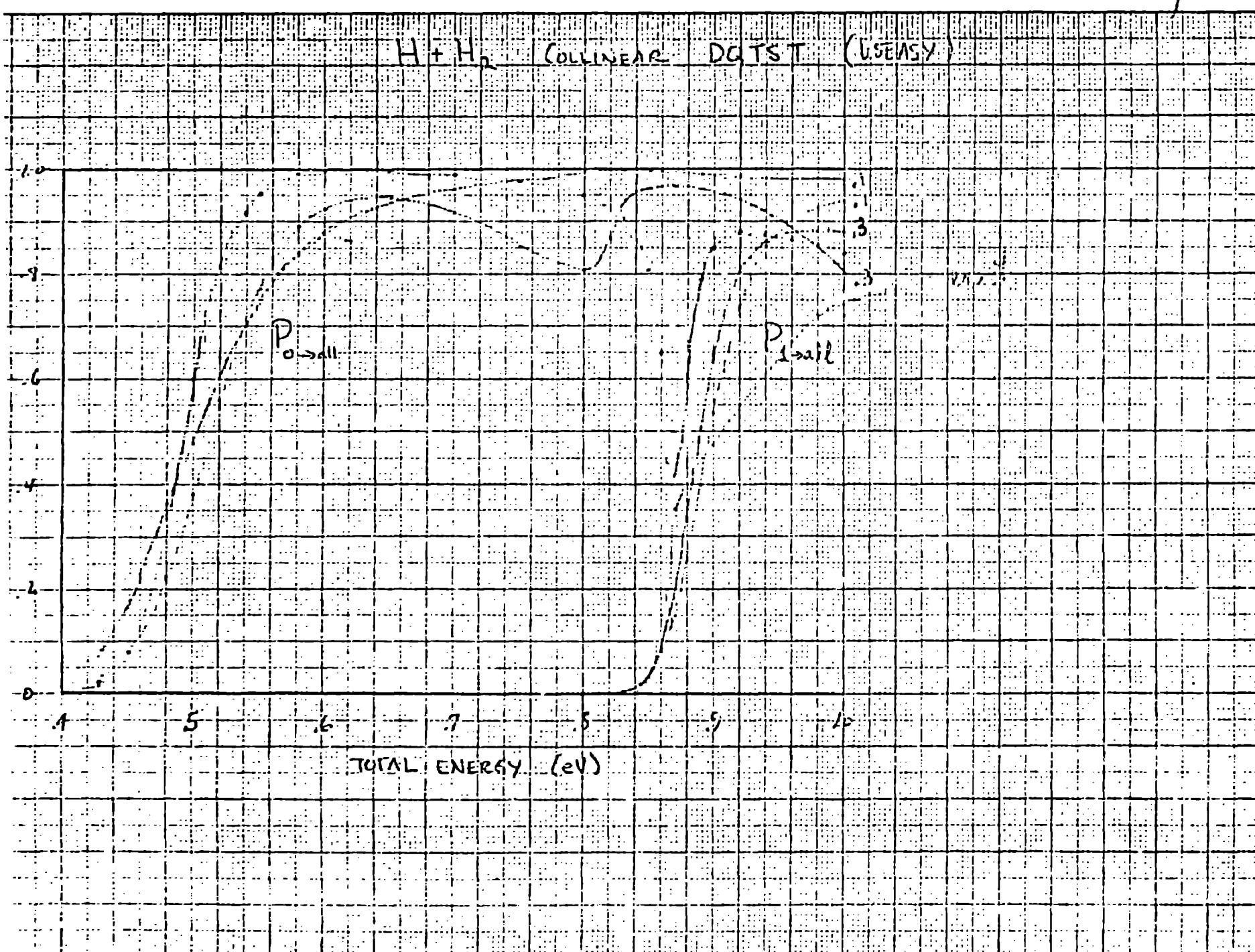


Fig 3b

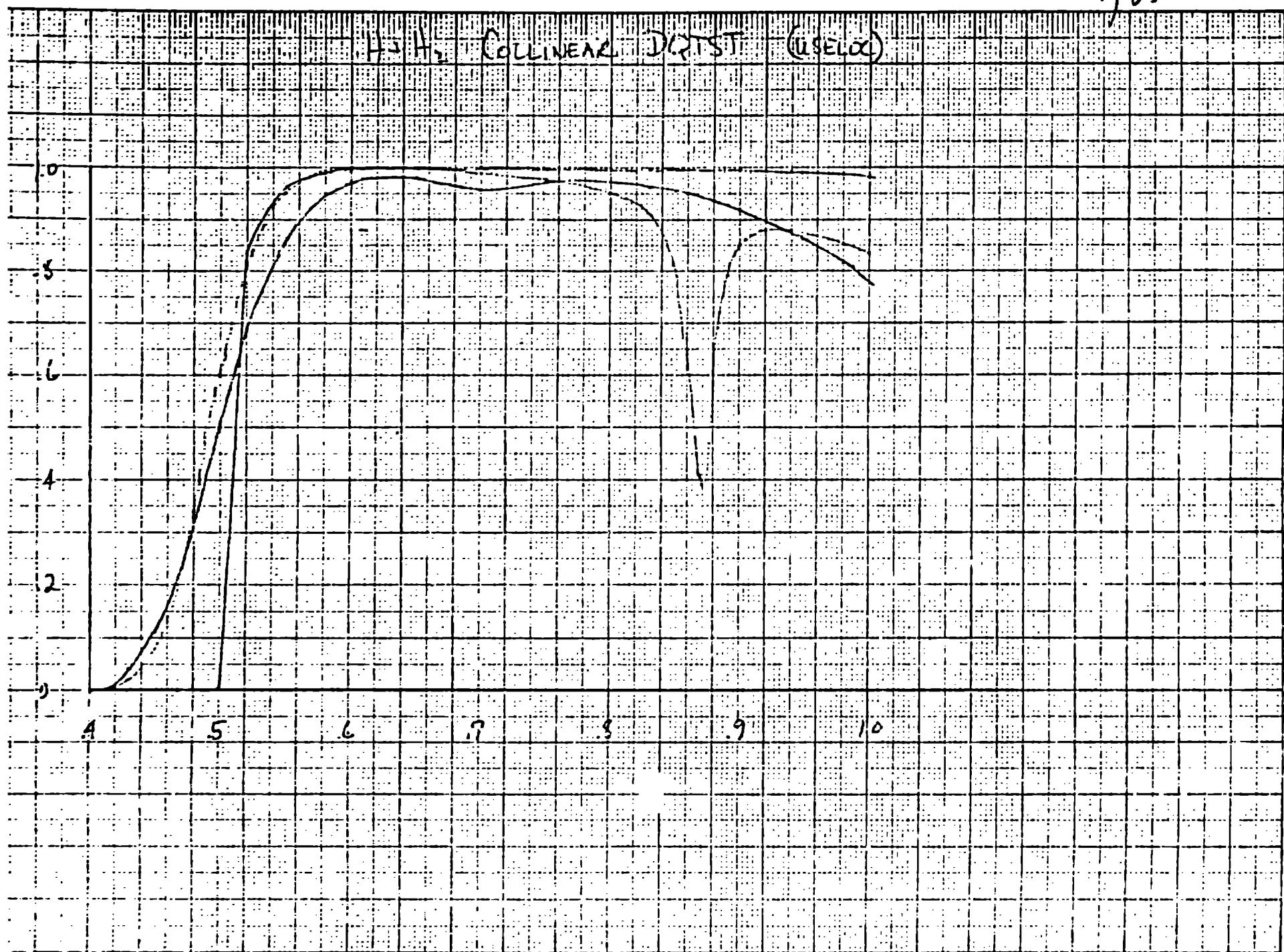


Fig 1a

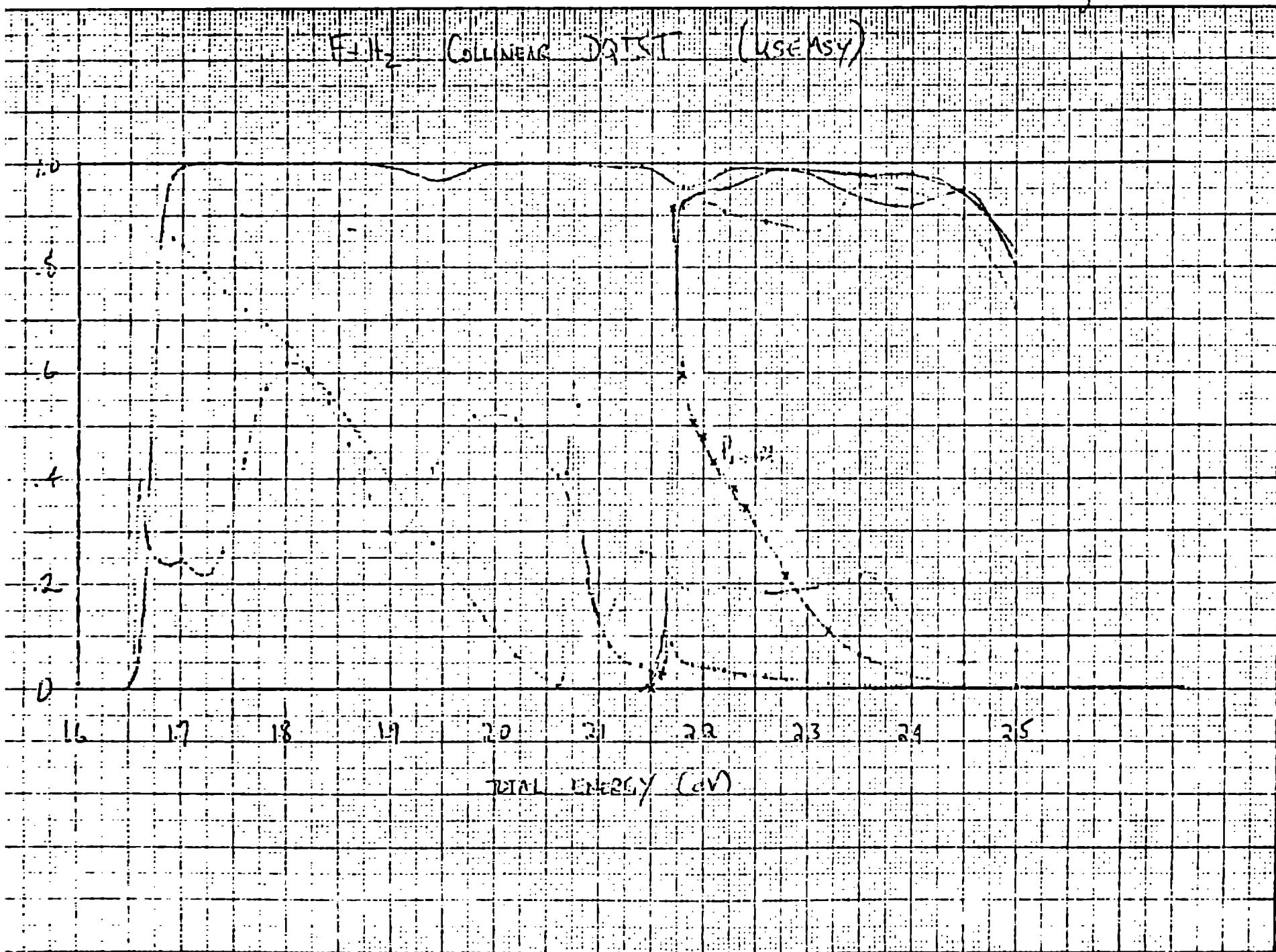


Fig 4b

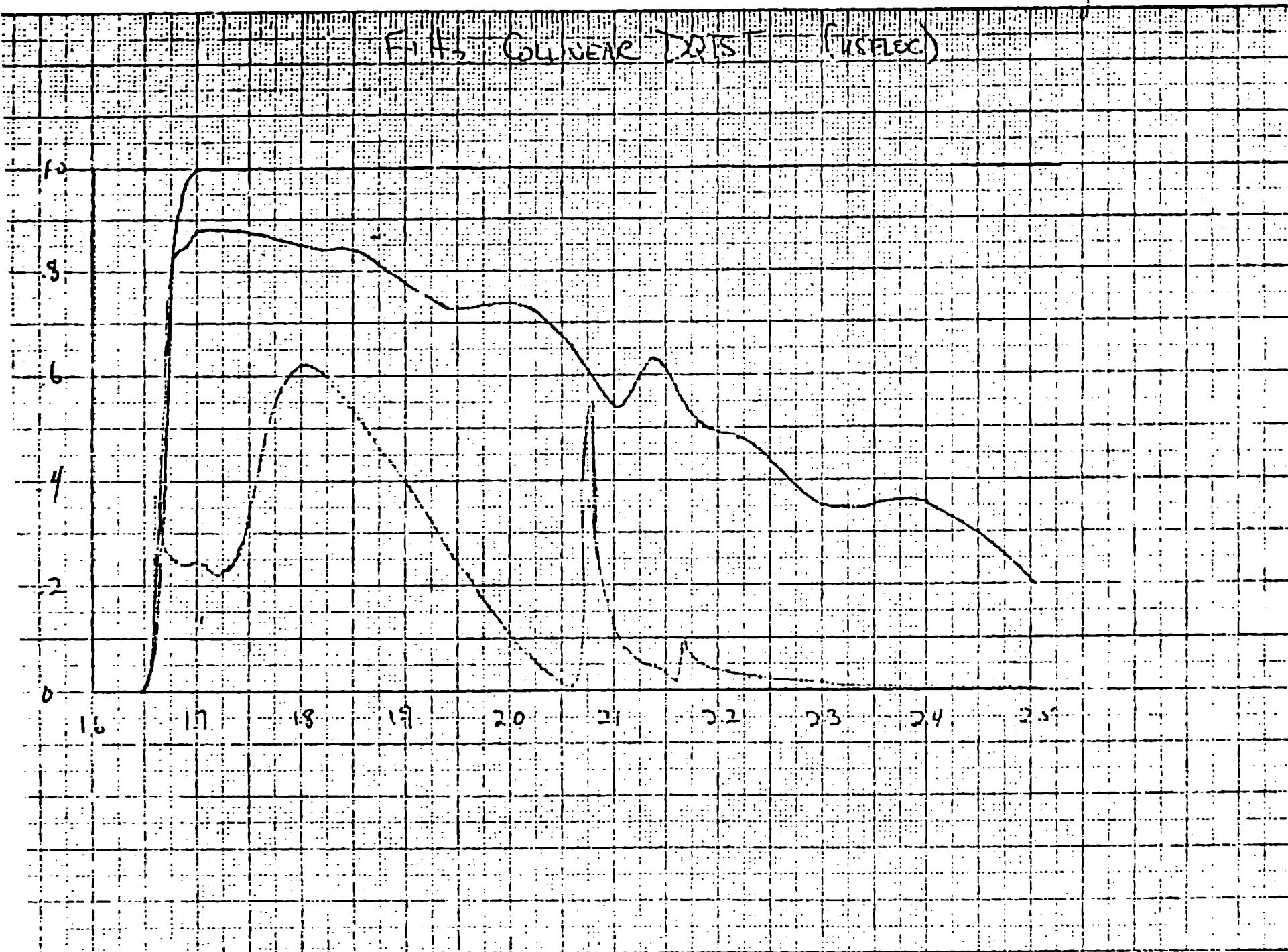


Fig 5a

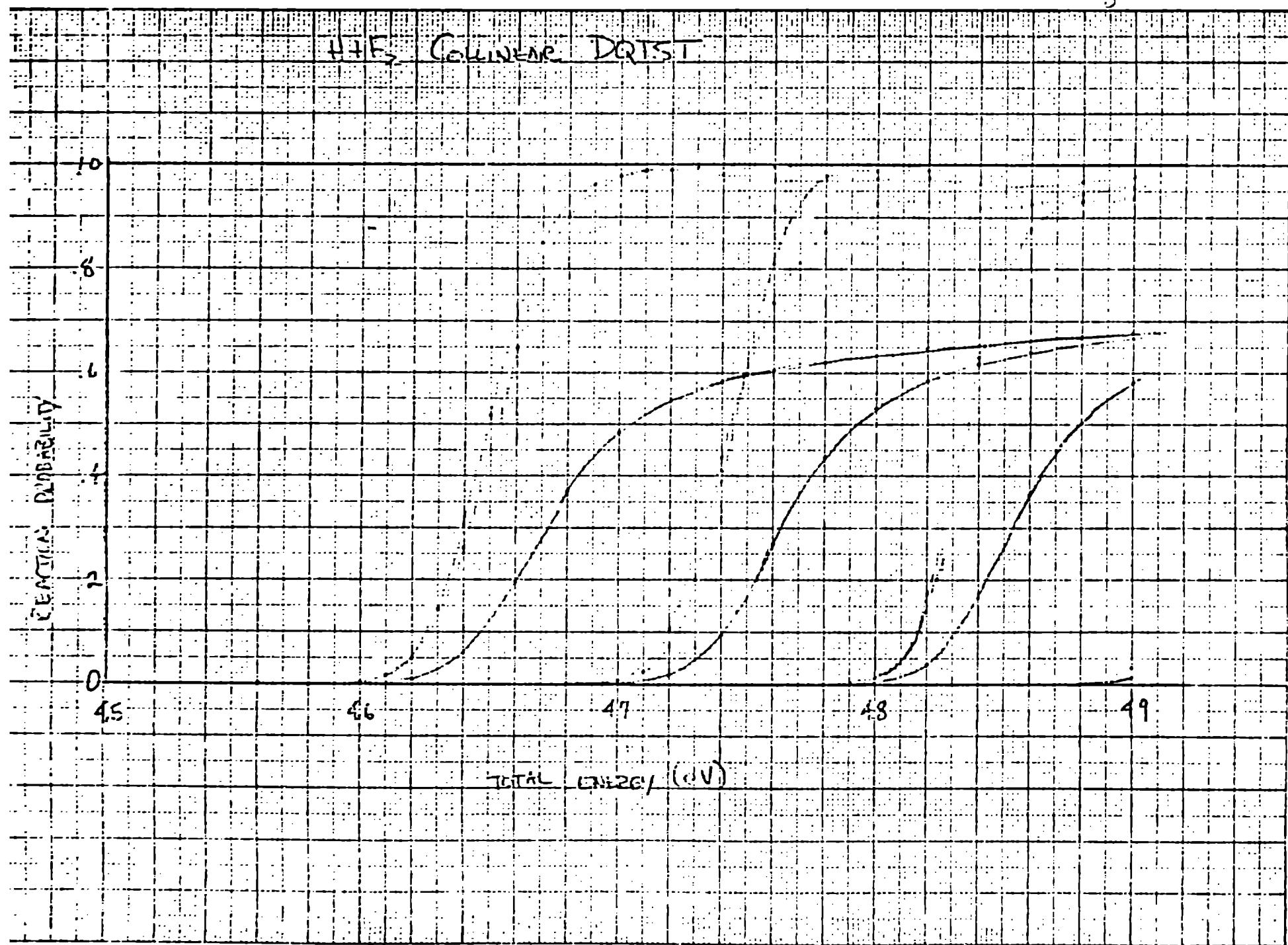


Fig 5b

44F, COLUMNAR DENSITY (SUBFACE)

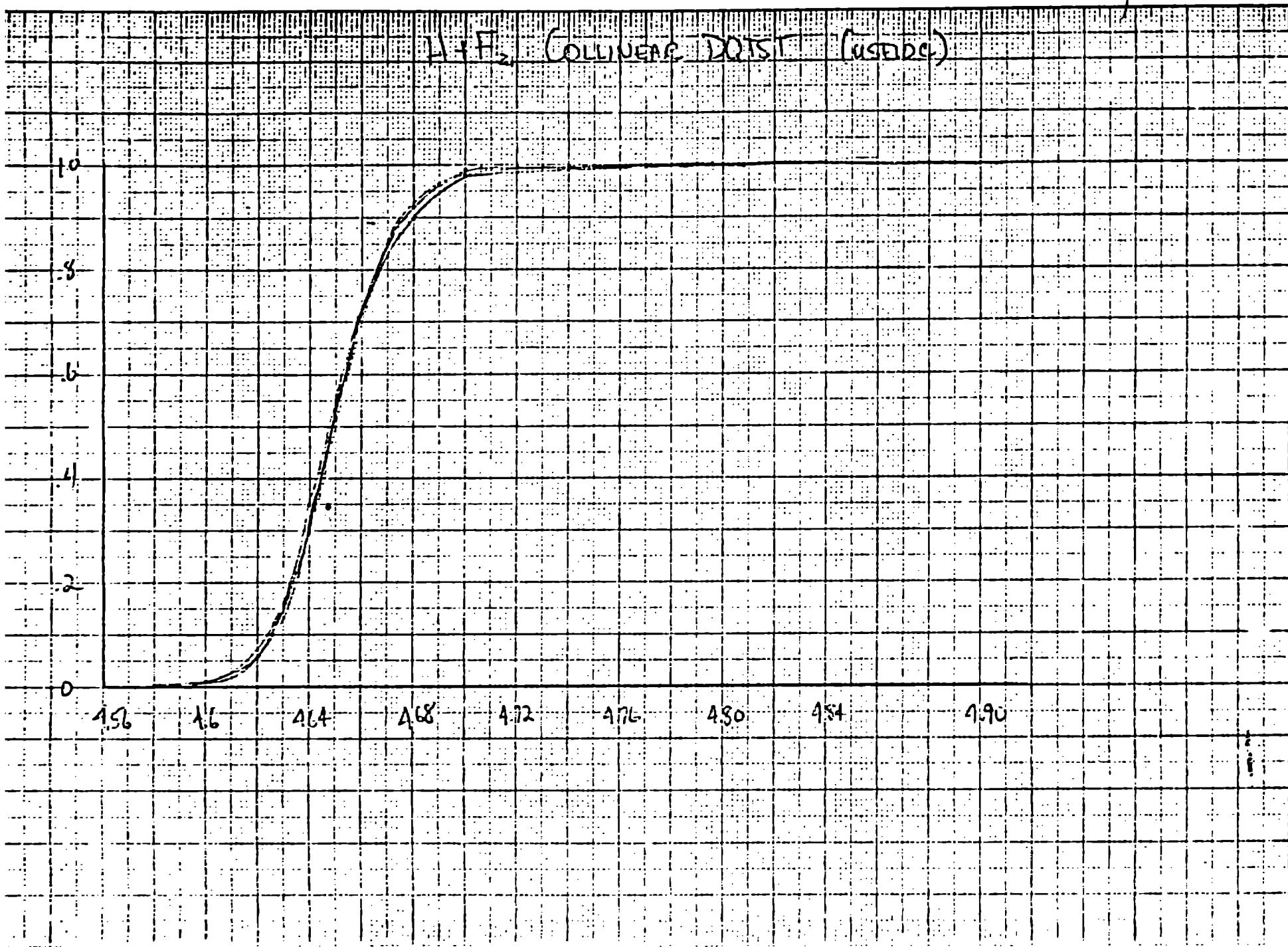


Fig 6a

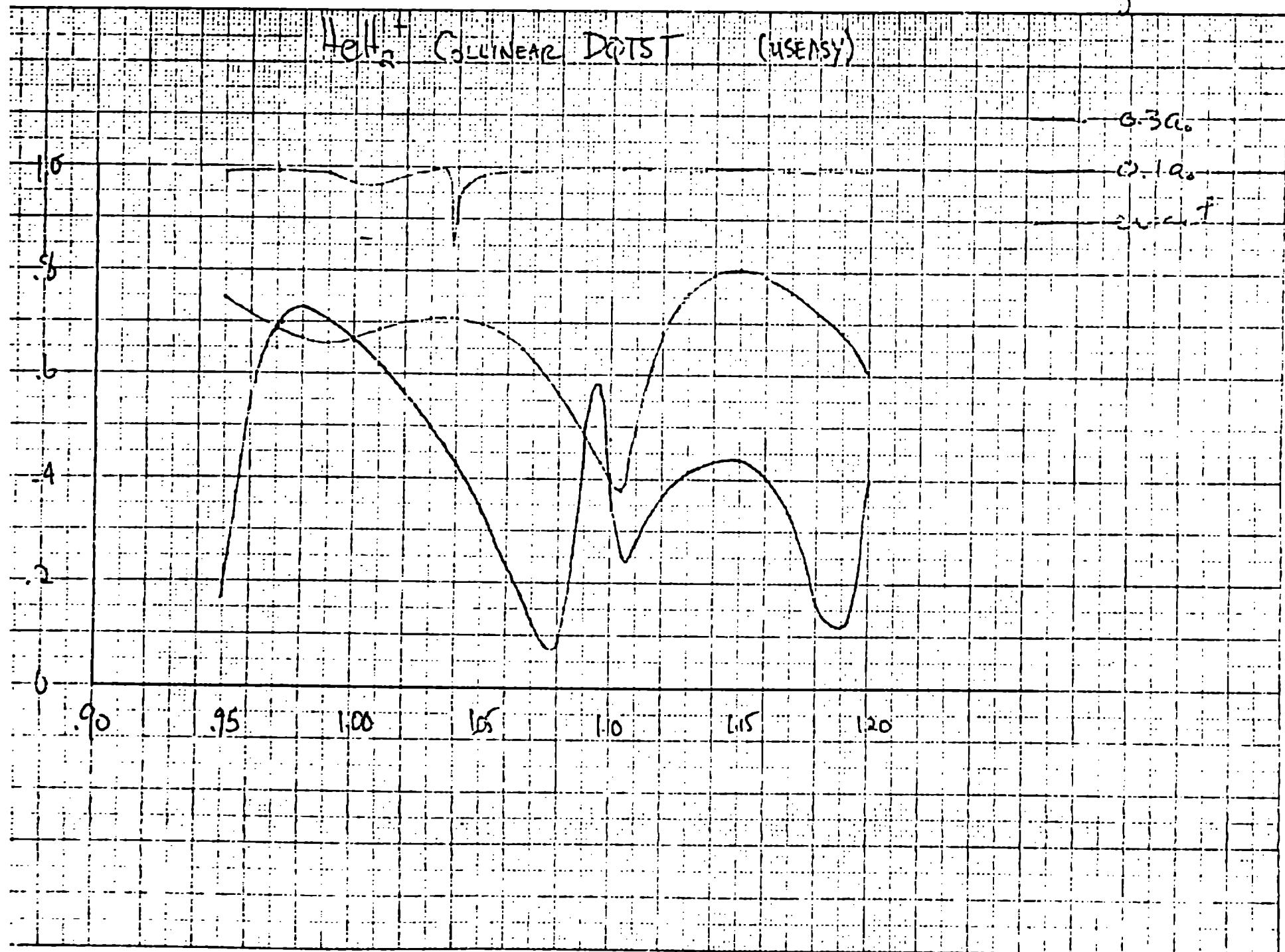


Fig 66.

