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TECHNICAL PROGRESS REPORT

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Submitted by:	Aron Kuppermann Aron Kuppermann Principal Investigator Professor of Chemical Physics California Institute of Technology

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TECHNICAL PROGRESS REPORT

1 July 1972 - 30 June 1973

Aron Kuppermann

Publications:

CALT-767P4-96	"Electron Impact Excitation of H_2O," S. Trajmar, W. Williams, and A. Kuppermann, J. Chem. Phys. 58, 2521 (1973). Submitted to AEC herewith.
CALT-767P4-97	"Exact Quantum Mechanical Reaction Probabilities and Rate Constants for the Isotopic Collinear $H + H_2$ Reactions," D. G. Truhlar, A. Kuppermann, and J. T. Adams, J. Chem. Phys., in press. Submitted to AEC herewith.
CALT-767P4-98	"Selection Rules and Quasi Selection Rules in Three-Body Exchange Reactions," Michael Baer, submitted to Chem. Phys. Letters. Submitted to AEC herewith.
CALT-767P4-99	"Comparison of Semi-Classical Exact Quantum and Quasi-Classical Reactive Transition Probabilities for the Collinear $H + H_2$ Reaction," J. M. Bowman and Aron Kuppermann, Chem. Phys. Lett. 19, 166 (1973). Submitted to AEC herewith.
CALT-767P4-100	"Intermolecular Potentials for Polyatomic Molecules from Crossed Molecular Beam Experiments," R.J. Gordon, M. C. Coggiola, and A. Kuppermann. Abstract of paper to be presented at the Fourth International Symposium on Molecular Beams, Cannes, France, July 9 to 12, 1973. Submitted to AEC herewith.
CALT-767P4-101	"Quantum Initial Conditions in Quasi-Classical Trajectory Calculations," J. M. Bowman, G. C. Schatz, and A. Kuppermann, Chem. Phys. Lett. 19, 21 (1973). Submitted to AEC herewith.
CALT-767P4-102	"Time Delays and Resonances in the $H + H_2$ Exchange Reaction," George C. Schatz and Aron Kuppermann. Abstract of paper presented at the American Physical Society Mtg, San Diego, California, March, 1973. Submitted to AEC herewith.

CALT-767P4-103	"Electronic Spectroscopy of 1,3-Butadiene by Electron Impact," Oren A. Mosher, Wayne M. Flicker, and Aron Kuppermann. Abstract of paper presented at the American Physical Society Meeting, San Diego, California, March 1973. Submitted to AEC herewith.
CALT-767P4-104	"Description of Molecular Elastic Scattering by Central Field Potentials," M. J. Coggiola, Robert J. Gordon and Aron Kuppermann. Abstract of paper presented at the American Physical Society Meeting, San Diego, California, March 1973. Submitted to AEC herewith.
CALT-767P4-105	"Comparison of Semi-Classical, Exact Quantum and Quasi-Classical Reactive Transition Probabilities for the Collinear H + H_2 Reaction," Joel M. Bowman and Aron Kupperman. Abstract of paper presented at the American Physical Society Meeting, San Diego, California, March 1973. Submitted to AEC herewith.
CALT-767P4-106	"Quantum and Quasi-Classical Reaction Probabilities for the Collinear F + H_2 Reaction," George C. Schatz, Joel M. Bowman and Aron Kuppermann. Abstract of paper presented at the American Physical Society Meeting, San Diego, California, March 1973. Submitted to AEC herewith.
CALT-767P4-107	"A Direct Test of the Vibrationally Adiabatic Theory of Chemical Reactions," J. M. Bowman, Aron Kuppermann, J. T. Adams. and Donald G. Truhlar, submitted to Chem. Phys. Letters, 20, 229 (1973). Submitted to AEC herewith.
CALT-767P4-108	"Triplet States in 1,3-Butadiene," Oren A. Mosher, Wayne M. Flicker, and Aron Kuppermann, Chem. Phys. Lett. 19, 332 (1973). Submitted to AEC herewith.
CALT-767P4-109	"Use of Central-Field Potentials for Describing $H_2(D_2)$ Elastic Scattering by Other Molecules, M. J. Coggiola, R. J. Gordon and Aron Kuppermann, accepted for publication in Chem. Phys. Letters. Submitted to AEC herewith.
CALT-767P4-110	"Large Quantum Effects in the Collinear F + H_2 → FH + H Reaction," George C. Schatz, Joel M. Bowman, and Aron Kuppermann, J. Chem. Phys. 58, 4023 (1973). Submitted to AEC herewith.

CALT-767P4-111	"Electronic Spectroscopy of 1,3-Butadiene by Electron Impact," Oren A. Mosher, Wayne M. Flicker, and Aron Kuppermann, submitted to J. Chem. Phys. Submitted to AEC herewith.
CALT-767P4-112	"Central Field Intermolecular potentials from the Differential Elastic Scattering of $H_2(D_2)$ by Other Molecules," A. Kuppermann, R. J. Gordon, and M. J. Coggiola. Paper presented at the General Discussion on Molecular Beam Scattering, University College London, Faraday Division, Chemical Society, 16-18 April 1973, to appear in Vol. 55 of Discussions of that division. Submitted to AEC herewith.
CALT-767P4-113	"Quantum Dynamics of Chemical Reactions," Aron Kuppermann. Abstract of seminar presented at the Department of Chemistry, Ohio State University, Columbus, Ohio, 2 March 1973. Submitted to AEC herewith.
CALT-767P4-114	"Quantum Effects in Chemical Reactions," Aron Kuppermann. Abstract of seminar presented at the Department of Chemistry, Indiana University, Bloomington, Indiana, 28 February 1973. Submitted to AEC herewith.
CALT-767P4-115	"The Role of Direct and Resonant (Compound State) Processes and of their Interferences in the Quantum Dynamics of the Collinear $H + H_2$ Exchange Reaction," George C. Schatz and Aron Kuppermann, J. Chem. Phys., in press. Submitted to AEC herewith.
CALT-767P4-116	"Semi-Classical S Matrix Theory of Reactive and Non-Reactive Atom-Molecule Collisions," J. M. Bowman and Aron Kuppermann, submitted to Chem. Phys. Submitted to AEC herewith.
CALT-767P4-117	"Comparison of Boundary-Value and Initial-Value Methods for the Accurate Quantum-Mechanical Solution of the Collinear Reactive Scattering Problem," D. J. Diestler, D. G. Truhlar, and Aron Kuppermann, Chem. Phys. Lett. 13, 1 (1972). Submitted to AEC herewith.
CALT-767P4-118	"Quantum, Quasi-Classical and Semi-Classical Reaction Probabilities for the Collinear $F + H_2 \rightarrow FH + H$ Reaction," G.C. Schatz, J.M. Bowman, and Aron Kuppermann. Abstract of paper to be given at the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Beograd, Yugoslavia, 16-20 July 1973. Submitted to AEC herewith.

CALT-767P4-119	"Description of H_2 and D_2 Scattering off Other Molecules by Central Field Potentials," M. J. Coggiola, Robert J. Gordon, and Aron Kuppermann. Abstract of paper to be presented at the Eighth International Conference on Physics of Electronic and Atomic Collisions, Beograd, Yugoslavia, 16-20 July 1973. Submitted to AEC herewith.
CALT-767P4-120	"Time Delays, Phase Behavior and Resonances in the Collinear $H + H_2$ Exchange Reaction," G. C. Schatz and Aron Kuppermann. Abstract of paper to be presented at the Eighth International Conference on Physics of Electronic and Atomic Collisions, Beograd, Yugoslavia, 16-20 July 1973. Submitted to AEC herewith.
CALT-767P4-121	"Streamlines of Probability Current Density and Tunneling Fractions for the Collinear $H + H_2 \rightarrow H_2 + H$ Reaction," John T. Adams and Aron Kuppermann. Abstract of paper to be presented at the Eighth International Conference on Physics of Electronic and Atomic Collisions, Beograd, Yugoslavia, 16-20 July 1973. Submitted to AEC herewith.
CALT-767P4-122	"Quantum Effects in Chemical Reactions," Aron Kuppermann. Abstract of symposium paper to be presented at ACS Kinetics Symposium, Chicago, 27-28 August 1973. Submitted to AEC herewith.
CALT-767P4-123	"Studies in Chemical Dynamics and Radiation Chemistry," Technical Progress Report, 1 July 1972 through 30 June 1973. Submitted to AEC herewith.

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INDEX

1. SCIENTIFIC PROGRESS

1.1 Low Energy Electron Scattering. Low energy electron impact is quite effective in causing atomic and molecular transitions which are optically forbidden. Electronic states of molecules which cannot be reached from the ground state by optically allowed transitions play nevertheless an important role in understanding the structure and dynamics of molecules. For example, triplet excited states of molecules which have singlet ground states have in general quite different structural parameters and potential energy surfaces. The measurement of the corresponding excitation energies furnishes some information about these differences and is useful in testing out the validity of approximate quantum mechanical calculations of these quantities. In addition, the chemical properties of these triplet states are different from those of the ground state and are of importance in understanding the chemical effects of systems in which low energy electrons are present, such as in radiation chemistry and in electrical discharges. In these systems, triplet states can be formed either by direct electron impact excitation or by ion-electron recombination. Finally, triplet states are also important in understanding sensitized photochemical reactions in which a spin-allowed electronic excitation is produced in a sensitizer molecule (whose ground state is a singlet) by absorption of light. This molecule then may undergo intersystem crossing to a triplet state which can transfer its triplet excitation to a sensitized molecule. The latter then undergoes chemical reactions characteristic of a triplet state.

In order to investigate these optically forbidden states, an apparatus to measure the energy and angular dependence of the differential cross sections for electrons scattered by molecules has been designed, constructed, and put into operation. The details of its construction and operation are given in previous technical reports and in a thesis by James K. Rice.

Since the last technical report, the studies on 1-2 butadiene were completed by thoroughly analyzing with the aid of computer programs designed to remove noise spikes, subtract background, average the data over neighboring channels and plot them, locate the position of peaks and of significant slope breaks in the spectra, deconvolute overlapping bands which have significantly different angular distributions, and calculate the integrated areas under spectral bands before or after deconvolution. Two papers were prepared on this butadiene work. One, a short preliminary communication, which appeared in Chem. Phys. Letters and another one, quite lengthy and detailed, being submitted for publication in J. Chem. Phys. Both these papers are attached as a part of the present report (Report Codes CALT-767P4-108 and CALT-767P4-111). In addition, this work was presented at the March 1973 meeting of the American Physical Society in San Diego, California.

The apparatus is usually submitted to repeated bake-outs. This is necessary in order to clean up the critical field-producing surfaces. Small extents of dielectric deposits on them produce sufficiently strong electric field distortions to strongly affect the trajectory of the low energy (as low as 1.5eV) electrons moving through the machine, which appreciably deteriorates the sensitivity and resolution of the apparatus. The cumulative affect of these repeated bake-outs is to produce a misalignment of critical internal components of the apparatus, requiring frequent and time-consuming realignment operations. In order to minimize these effects, we subjected the apparatus to an extensive modification. One of the important changes was the introduction of accurate locating pins, so as to make the apparatus self-aligning. In addition, we introduced Burndy snap-on connectors for the electrical connections. The electron gun was replaced by a more sophisticated one to produce better collimation of the electron beam incident on the electron monochromator. Both 2-inch center diameter spherical energy analyzers, which had been somewhat corroded over the years, were replaced by aluminum ones designed for better location accuracy and lower residual magnetic fields. Many of the electron optical lenses were rebuilt to permit easier access and facilitate future changes. Finally, in order to decrease the spectrometer bake-out temperature and frequency, a separate vacuum furnace was designed, built and put into operation which permits a bake-out of internal spectrometer components to 350 °C. All such components are baked in this oven before being introduced into the spectrometer.

The modifications above took several months. After they were completed, the instrument was put back into operation and checked out. It was then used to study five molecules: ammonia, allene, azomethane, NO and propyne. The results reported below on these molecules are preliminary, and based on a visual analysis of the raw spectra. They will be subjected to a more careful computer analysis in the next few months.

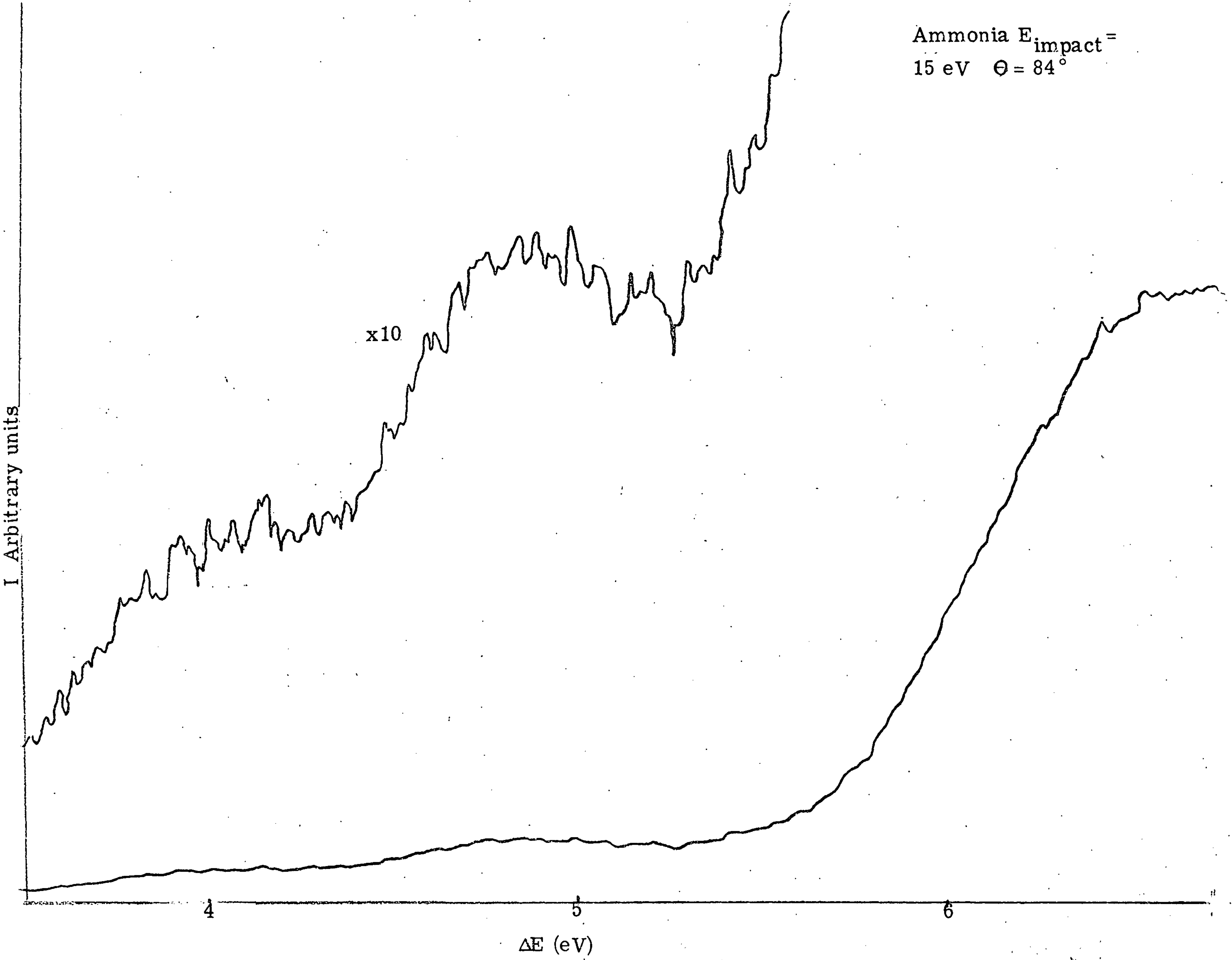
The studies on ammonia were done at an impact energy of 15eV and scattering angles of 1°, 5°, 15°, 30°, 50°, 60°, 70° and 84°, and at 20 eV and 85°. Three vibrationally excited bands were observed at 0.43, 0.85

and 1.24 eV (±0.02 eV) energy loss, corresponding to v'' = 1, 2, and 3 of the D_3 normal vibration of the ground electronic state $\tilde{X}^1A_1$ (IR spectroscopy places v'' = 1 at 0.427 eV). Twelve vibronic bands (v′ = 0 to v′ = 11) of the $\tilde{X}^1A_1 \rightarrow A^1A_2''$ band system have been observed. This is the lowest excited (singlet) state which has been observed in ammonia and it is the only one for which the assignment is commonly considered to be definite.

Two extremely weak transitions have been observed at 3.95 ± 0.1 eV and 4.75 ± 0.1 eV. The angular dependence of their intensities, as well as their energy dependence indicate a probable triplet state assignment for the two excited states. If these assignments are correct, this would be the first time that triplet electronic states have been identified in ammonia. A tracing of a raw spectrum at an impact energy of 15 eV and scattering angle of 84° is shown in Figure 1, showing these states, very clearly. We are very interested in the relationship between them and the 4.4 eV state we have previously observed in water, as reported in past technical progress reports and in the attached reprint (Report Code CALT-767P4-96). We will continue to investigate ammonia further.

We have studied allene (propadiene) at impact energies of 20 eV and 40 eV and scattering angles of 8°, 15°, 22.5°, 30°, 45°, 60°, 70° and 80°, and at 60 eV and 15° and 70°. We have observed a vibrationally excited state of the ground electronic state. In Figure 2 we show a tracing of a raw spectrum at 40 eV impact energy and 45° scattering angle. The absorption in the 4 to 5.5 eV region corresponds to two triplet states, peaking approximately at 4.3 and 4.8 eV respectively. Their triplet character was established from the angular and energy dependence of their intensities, in the usual manner.

Figure 1


Ammonia E_{impact} =
15 eV Θ = 84°
x10
I Arbitrary units
4
5
6
ΔE (eV)

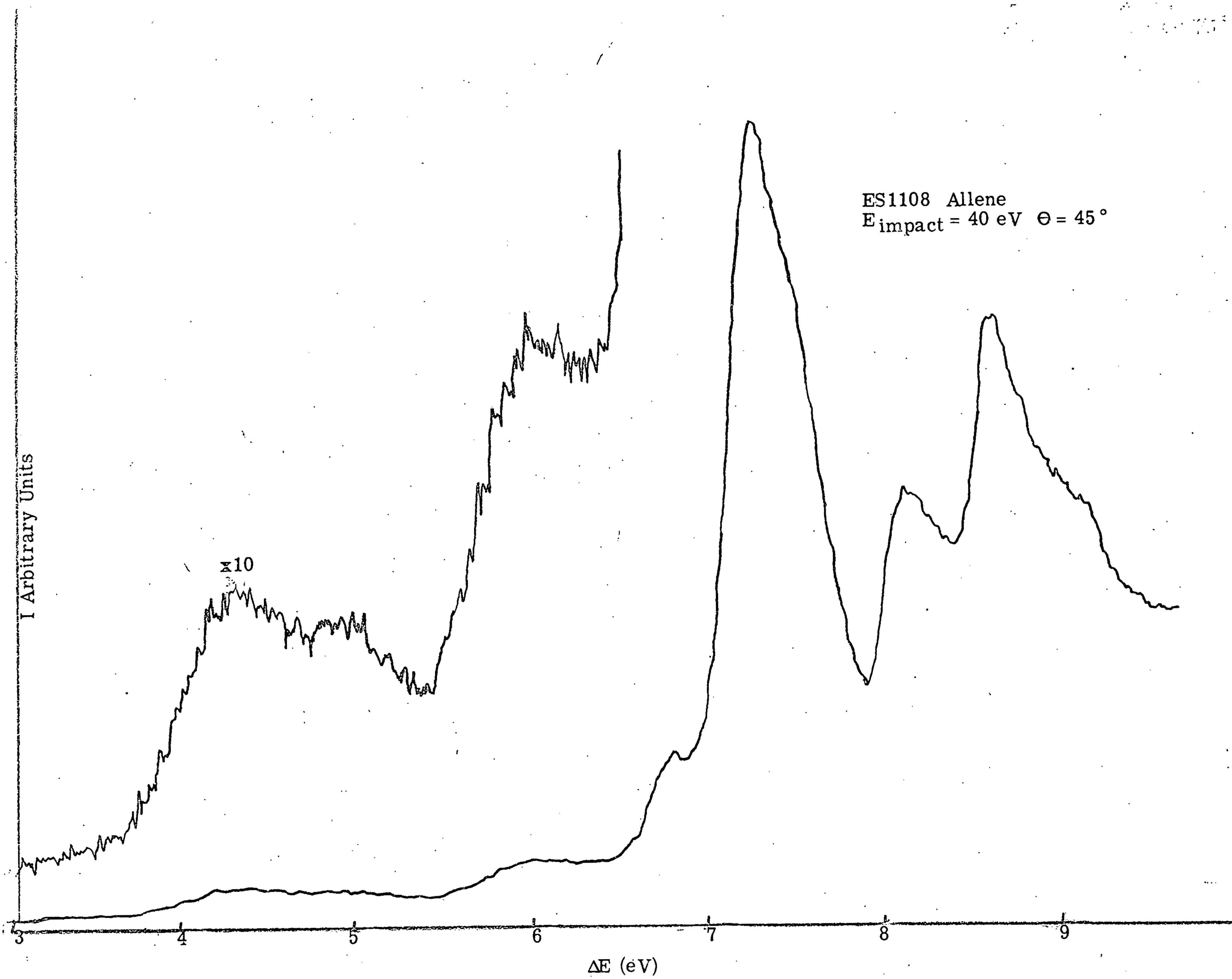

ES1108 Allene
E impact = 40 eV Θ = 45°
x10
I Arbitrary Units
ΔE (eV)
3
4
5
6
7
8
9

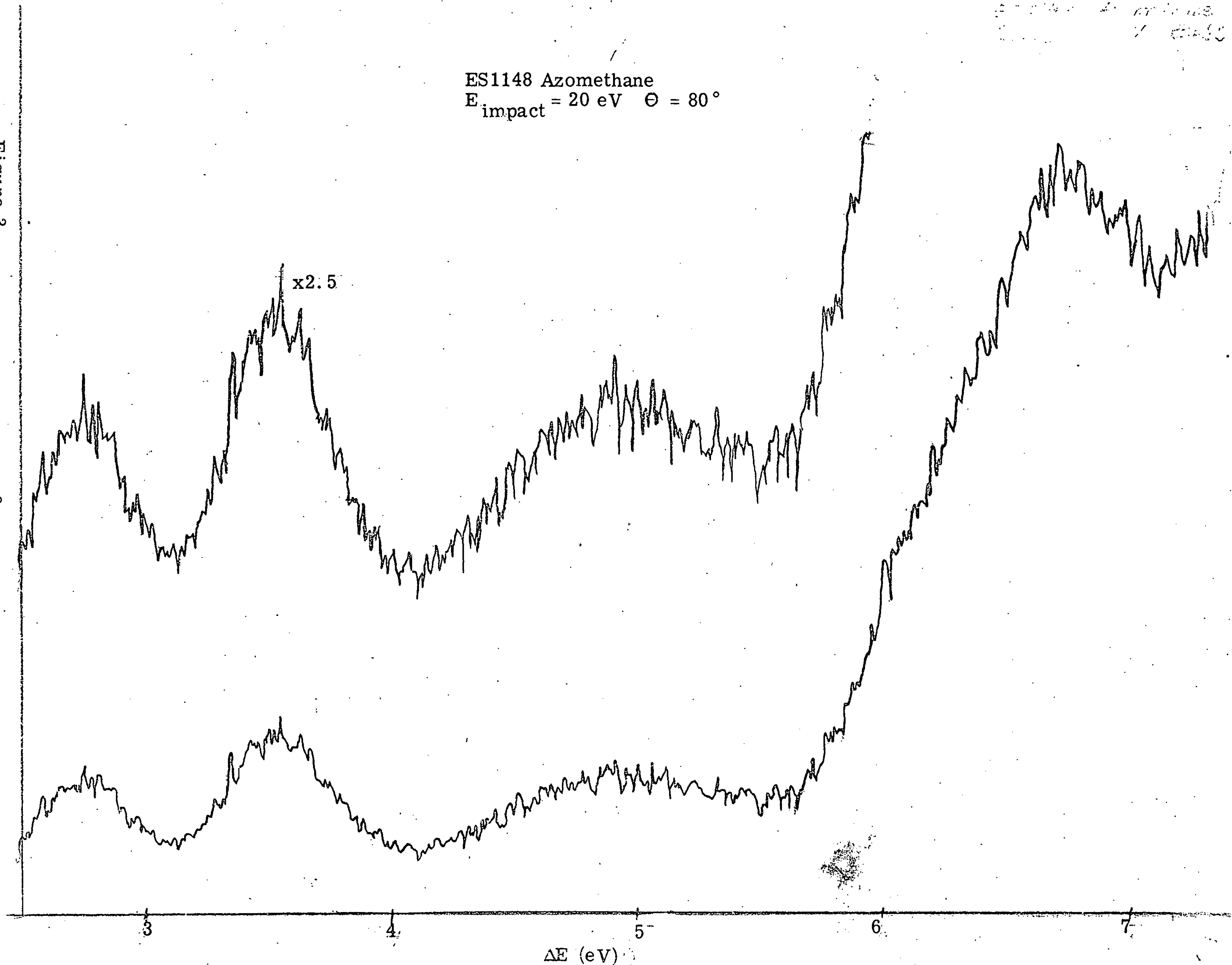
Figure 2

The second of these states has not been previously observed. The weak absorption in the 5.5 eV to 6.5 eV region corresponds to a transition peaking at about 5.95 eV. Its angular distribution is characteristic of a spin-allowed transition, and it is probably symmetry forbidden. This seems to be the first observation of a transition in this energy region. Finally, in the energy loss range of 6.5 eV to 9 eV, maxima were observed at 6.75 eV, 7.25 eV, 8.06 eV, 8.16 eV, 8.56 eV and 8.69 eV. These will be further analyzed.

Azomethane, $CH_3N_2CH_3$ was investigated at 20 eV impact energy and scattering angles of 10°, 15°, 20°, 30°, 40°, 50°, 60°, 70° and 80°. It was also studied at 40 eV and 30° and 50°. A tracing of part of the 20 eV, 80° energy loss spectrum is shown in Figure 3. We observed vibrational peaks of the ground electronic state at 0.35 eV and 0.73 eV. The maximum at 2.75 eV has an angular distribution indicative of a singlet→triplet transition. Another two maxima at 3.55 eV and 5.95 eV are observed which are spin-allowed. The first one also appears weakly in optical spectra, and is perhaps an $n \rightarrow \pi^*$ transition. The second one is probably symmetry forbidden, corresponding possibly to an A_2, A_1, or B_1 state. This seems to be the first observation of this state. Another maximum occurs at 6.75 eV, with a shoulder on its left side which could be attributed to a transition peaking at about 6 eV. If real, it is a singlet. Additional narrow Rydberg-like absorptions have been detected in the energy loss region from 8.8 eV to 9.5 eV.

Nitric oxide was studied at impact energies of 20 eV and 30 eV and scattering angles of 20° and 60°, in an attempt to detect its lowest doublet → quartet spin-forbidden transition. However, only spin allowed features were observed.

Figure 3



Propyne was studied at impact energies of 20 eV, 30 eV and 50 eV and a scattering angle of 60°. Two transitions are seen at 5.3 eV and 6.0 eV respectively, with additional peaks at 7.2 eV, 8.05 eV and 8.8 eV. The former are probably due to triplet states analogous to those we observed previously for acetylene.

As stated above, these studies are still incomplete. More extensive experiments and more elaborate treatment of the data are still required. However, from their scope it is easy to get a feeling for the extreme power of this spectroscopic technique. The significance of our observations for radiation chemistry and for the understanding of the electronic structure of the molecules studied continues to be our central motivation.

1.2 Photoelectron Spectrometry. Photoelectron spectrometry is an important tool for the determination of orbital energies of electrons and molecules. An incident beam of vacuum ultraviolet photons of energy in the range of approximately 10 to 20 eV collides with a target gas in a scattering chamber. In ordinary photoelectron spectrometry the ejected photoelectrons are usually energy analyzed at a fixed scattering angle of 90° with respect to the direction of the incident photon beam. However, there is information content in the angular distributions of photoelectrons which may be useful in the assignment of angular momentum characteristics of the orbital from which the electrons were ejected. For example, Hall and Siegel[1] found that the angular distributions of the electrons ejected from H^- and O^- by photons whose energy is from 1 to 2 eV above threshold are very different, having a $\cos^2\theta$

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[1] J. L. Hall and M. W. Siegel, J. Chem. Phys. 48, 943 (1968).

distribution for the former and a $\sin^2\theta$ distribution for the latter. Cooper and Zare[2] have attributed these differences to the fact that the ejected electron is of s-type in H^- and of p-type in O^-. Hopefully, similar differences in the photoelectrons from neutral molecules will exist and empirical rules may be found relating the angular distributions with the angular momentum or symmetry of the orbital from which the electron came. Analogous empirical rules have been found for the electron scattering case which have been extremely useful in the investigation of optically forbidden transitions in molecules as described in Section 1.1 above. Motivated by these considerations we have constructed a variable angle photoelectron spectrometer.

This instrument was used previously to make preliminary studies on argon, nitrogen, oxygen, ethylene, acetylene and ethane. The results obtained were very encouraging. They were described in last year's technical progress report and indicated that electrons ejected from different kinds of orbitals do indeed have different β parameters, where β is defined by the expression

$$\frac{d\sigma}{d\Omega} = \frac{Q}{4\pi}\left[1 - \frac{\beta}{4}(3\cos^2\theta - 1)\right]$$

Here θ is the scattering angle and $d\sigma/d\Omega$ and Q are respectively the differential and total photoionization cross sections. This expression is expected to describe the experimental data and is associated to the electric transition dipole nature of the photoionization process.

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2. J. Cooper and R. N. Zare, J. Chem. Phys. 48, 942 (1968).

A severe experimental difficulty was obvious at the time the preliminary experiments mentioned above were made. According to the expression above, $d\sigma/d\Omega$ should be symmetric around 90°, whereas we observed experimentally strong asymmetries. For example, photoionized electron intensities at 50° and 130° differed by as much as 50%. Before reliable values of β could be obtained, this asymmetry problem had to be solved. This turned out to be an extremely difficult task. We finally tracked the problem down to a much higher than expected sensitivity to relatively small residual magnetic fields. These were due to field penetrations through seams and other openings of the μ-metal shield. After demagnetizing some weld seams, fields of the order of 10 milligauss still remained inside the shield, which are still capable of producing major perturbations on the low-energy electrons as they go through the analyzer. To confirm this, we replaced the scattering chamber by an electron gun rigidly attached to the spherical electrostatic energy analyzer, and did indeed obtain a highly non-isotropic angular distribution. The detected intensity varied by a factor of 6 is the angular position of the electrostatic analyzer changed from 40° to 130°! To eliminate this problem, we constructed three pairs of square Helmholz coils, approximately 3.3 m on the side. This required about 30 km of wire. These decreased the earth's field at a position of 30 cm away from the center of the resulting cube-like structure by about a factor of 20. The μ-metal shield produces a further decrease of the maximum residual field in the critical regions of the apparatus to 0.4 milligauss. This is quite tolerable, and tests with the electron gun probe produced isotropic distributions to within 2%. Thus, the magnetic field problem was finally solved!

An additional artifact was the fact that the pressure inside the scattering box was angle-dependent. This was found out when an accurate and stable high pressure Phelps gauge was installed. The reason for this dependence is that the size of the effective slits on the walls of the scattering box are angle dependent. Once the pressure is accurately measured at each scattering angle, the effect can be corrected for numerically.

The data gathering system was further improved by installation of a high speed paper tape reader, a high speed punch and a digital multimeter which transforms analog quantities (such as lens voltages, pressure) into digital form and transmits them to the PDP-8c computer. This system was very useful in helping track down the asymmetry effects.

The apparatus has now been checked out with argon over the angular range 50° to 130° and is giving symmetric results and a correct β value. Some minor alignment problems are being corrected, and hopefully the instrument will be generating reliable data in large amounts in the near future.

1.3 Elementary Reactions by Photolysis at Variable Wavelengths.

In the last years, an apparatus was constructed in our group to study the influence of vibrational energy on the $HI^* + HI \rightarrow H_2 + I_2$ reaction. The apparatus consists of two quartz bulbs coated externally with gold and immersed in an oven. A monochromatic beam of light can photolyze one while both are filled with HI and heated simultaneously to the same temperature. The rate of the reaction in both bulbs is measured as a function of temperature for a fixed wavelength and the corresponding activation energies are determined. A difference between these would be manifestation of the effect of vibrational excitation on the reaction. The HI molecule is highly anharmonic and high vibrational states (v = 4, 5, 6) may be excited with a high enough probability to detect differences between the rates in the photolyzed and non-photolyzed bulbs. The first experiments were performed and indicated that the rate of H_2 formation in the photolyzed bulb, at about 400 °C, was slightly higher than in the non-photolyzed bulb. An analysis of the possible mechanism suggested that if the pressure at which the experiment was conducted (~500 torr) is decreased by an order of magnitude, the effect of the photolysis should increase by an order of magnitude if it is indeed due to the reaction of vibrationally excited HI molecules. At that time, the appointment of the postdoctoral fellow doing the experiments terminated and they were interrupted. An undergraduate student took over the problem, as neither a graduate student nor a research fellow were available for this purpose. After approximately a half a year, he had learned a great deal about high vacuum techniques, gas handling, pressure measurement, etc., but in the process played havoc with the apparatus which was appreciably damaged. This year two persons, a graduate student and a post-doctoral fellow inherited the experiment as a joint enterprise. The oven in which the reaction bulbs are heated was completely overhauled. It can now run at temperatures up to 800 °C, constant to within ±0.03 °C. The vacuum lines for filling the lines and handling the reaction products were completely overhauled and the accurate volumes needed for the analysis were recalibrated. Methods for handling the data appropriately were developed. The experiments should be resumed in the near future.

1.4 Collision in Crossed Molecular Beams. The work of the previous year was aimed at obtaining information concerning the effects of intermolecular potentials anisotropy on the differential elastic scattering of H_2 and D_2 by a number of diatomic and polyatomic molecules. The first phase of this work involved measuring the scattering of H_2 or D_2 hypersonic beams generated from hypersonic expansion of room temperature gas, by O_2, SF_6, NH_3, CO, and CH_4 and of D_2 by O_2, SF_6, and NH_3, and was completed during the present year. The second phase involved restudying several of these systems using cooled H_2 in order to provide information on the sensitivity of the scattering to changes in the relative collision energy. In order to accomplish this study, it was necessary to modify the primary beam source of the apparatus. This modification was accomplished by removing the existing source nozzle and replacing it by a 5 cm long tube surrounded by a stainless steel jacket which could be cooled using a liquid nitrogen flow system. In this way, the primary H_2 and D_2 gas would be cooled to ~77K before expansion through the supersonic nozzle and skimmer system. After installation, extensive tests were performed to ensure that beams of uniform energy and high intensity could be produced with the new source. Optimization of the beam by varying both the nozzle-skimmer distance and the beam driving pressure yielded a beam of sufficient quality to permit experimental measurement of cold-H_2 + SF_6 and cold H_2 + NH_3 scattering. In addition, with this added cooling capability, it was now possible to attempt to measure elastic scattering using a beam of nearly pure para-hydrogen in its lowest rotational state. Such a beam was used for the measurement of para-H_2 + SF_6 elastic scattering to compliment the experiment using cold normal-H_2 + SF_6.

The results of all these experiments were thoroughly analyzed using multi-parameter potentials of Morse-spline-Van der Waals type and specially developed computer programs. Extensive testing of these methods was carried out to ensure accurate, unbiased data reduction. As a result of these analyses, it was found that over the range of angles sampled (2°-20°) no effects of anisotropy are seen, and that excellent central field potentials can be obtained. This work was written up in the form of two papers. One (Report Code CALT-767P4-109) is in press in Chem. Phys. Letters and the other (Report Code CALT-767P4-112) is in press in the Discussions of the Faraday Division, Volume 55. It was presented at the General Discussion on Molecular Beam Scattering at University College, London, 16-18 April 1973. Since both these papers are attached to the present report, we will not discuss the results further. Suffice it, however, to say that as a result of this work it is now possible to obtain from elastic scattering experiments high-quality molecule-molecule central field potentials when one of the collision partners is H_2. Prior to this work it was feared that anisotropy effects would preclude this.

In addition to these experiments, some preliminary measurements on the elastic scattering of various molecules by water were made. To date, little information is available on the intermolecular potential parameters involving H_2O even though such information is necesssry in the description of solubility phenomena. Further experiments of this type are planned.

There is some evidence that inelastic scattering (rotational) due to non-spherical potentials manifests itself at scattering angles of 40° or larger. In order to make accurate, reliable measurements of the scattering at large angles, it is necessary to reduce the background signal in the mass spectrometer, and also to detect very low intensity scattered beams. For this purpose we have constructed and installed liquid Helium cryopump which will pump the ionizer region of the mass spectrometer, which is presently being tested. A Bendix spiraltron electron multiplier was installed to operate in parallel with the existing discrete dynode electron multiplier. It was tested out and shown to permit high efficiency counting of individual ion pulses.

In general, it is advantageous to maintain the entire mass spectrometer chamber under high vacuum at all times. To accomplish this, a remotely operated bellows driven valve has been constructed to seal the front entrance to the mass spectrometer chamber. It has been installed and checked out and is working satisfactorily. In addition, a second valve has been built which will allow the isolated spectrometer chamber to be connected with an auxilary pumping system. With these two valves, the spectrometer can be isolated prior to venting the main chamber bell jar. Once the bell jar is raised, the auxilary pumping system can be attached to the spectrometer, and the second valve opened to maintain the mass spectrometer under continuous high vacuum.

In order to measure either the product translational energy in a reactive collision, or energy transfer as a result of inelastic scattering, an analyzer of some type is needed between the scattering center and the detector. Of the several slotted disc and time-of-flight analyzers, a single disc cross correlation chopper offers the best resolution with the least beam attenuation. In order to use such a chopper, however, it is necessary to use a counting detector system. Since a counting system has now been installed, two correlation choppers have been planned. One, a large 1024 tooth wheel will be located in the primary beam chamber for beam calibration, while a smaller 256 tooth version will be placed in front of the mass spectrometer entrance. With such a system, it will be possible to detect rotational inelastic scattering of the type found at large angles due to non-spherical scattering.

The use of molecular beam techniques for reactive scattering is an important application of the technique. Among the most interesting reactions from the theoretical view point are those involving hydrogen atoms as one of the reagents. A major difficulty in doing such experiments is the production of high intensity hydrogen atoms in the chemically interesting energy range of 0.1 - 10 eV. A relatively simple method of producing an H atom beam at the lower end of the energy range is by means of thermal dissociation in a resistively heated tungsten oven. An oven of this type has been constructed, and in order to test and characterize this source, a test chamber has been constructed. This chamber is a simple stainless steel bell jar mounted over a 6-inch mercury diffusion pump. The entire chamber is bakeable and can be used for high vacuum baking of components as well as general vacuum testing. Currently, a platinum bolometer detector system is being built for use with the already operational thermal source. A second, more intense source is also being constructed in the form of an arc-heated nozzle. This source will be capable of producing H atoms with 0.1 to ~1.5 eV energy. It should produce temperatures in excess of ten thousand degrees Kelvin by means of a low voltage, high current arc. Construction of the source has been completed and will be tested in the near future in a specially designed test chamber. Plans are progressing for the internal changes in the molecular beam apparatus to accommodate the arc source. While this source is being designed primarily for hydrogen atom production, it will be a sufficiently general design to allow many noncorrosive gases to be used. With a seeding technique, heavier atoms can be produced with beam energies of up to 20 eV. The secondary beam source is being modified to permit the production of high intensity hydrogen halide beams HX (x = $C\ell$, Br, I). We plan to study reactions of the type $D + HX \rightarrow DH + X$ and $D + CH_4 \rightarrow DH + CH_3$ when these changes are complete.

1.5 Theory of Chemical Reactions and Molecular Collisions.

The theoretical activities of the group were quite extensive during the last year. They involved a series of accurate calculations of cross sections or probabilities of processes of chemical interest, for some carefully chosen simple systems. In addition, approximate model calculations were done on the same systems, in order to test the validity of simplified theories which might be applicable to more complex and realistic systems. The objective of such theoretical calculations is to help bring about a basic understanding of the molecular dynamics of chemical processes both at thermal and higher energies. Such an understanding is important for chemistry in general, but especially for radiation chemistry, which involves such a complex and interesting variety of processes many of which are very difficult to investigate by direct experimental means. In addition, we have found in the past that an interaction between theoretical and experimental work in the same group is particularly stimulating because of the cross fertilization of ideas it produces. We will now enumerate the problems which were investigated and give some of the highlights of the results obtained so far.

a) The Role of Resonances in the H + H_2 Collinear Exchange Reaction. This reaction has long served as a model for testing and developing theories of chemical dynamics[3]. One question of crucial importance regarding it (or any other chemical reaction) has been the relative importance of compound state (resonant) processes and direct processes to the reaction mechanism[4, 5]. We have studied this question by analyzing the behavior of the phases of the elements of the scattering matrix as a function of the energy of the system. Our results indicate that not only do both these kinds of processes contribute to the reaction but also that their interference plays a central role in determining the pronounced quantum oscillations of the reaction probability as a function of energy[3]. This conclusion is of crucial importance in determining the applicability of approximate methods for doing theoretical studies of chemical reactions. The currently most commonly used approximate techniques, the quasi-classical[5] and the semi-classical[6] methods, as they are presently formulated do not include these interference effects. As a result, these two methods do not reproduce the oscillations in the reaction probabilities which were obtained in the quantum results[7, 8]. Future improvements to these

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[3] D. G. Truhlar and Aron Kuppermann, J. Chem. Phys. 52, 3841 (1970); 56, 2232 (1972).

[4] S. Glasstone, K. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill (New York, 1941), Chapters 3, 4.

[5] M. Karplus, R. N. Porter and R. D. Sharma, J. Chem. Phys. 43, 3259 (1965).

[6] W. H. Miller, J. Chem. Phys. 53, 1949 (1970); 53, 3578 (1970); 54, 5386 (1970).

[7] J. M. Bowman and Aron Kuppermann, Chem. Phys. Lett. 12, 1 (1971).

[8] J. M. Bowman and Aron Kuppermann, Chem. Phys. Lett., in press.

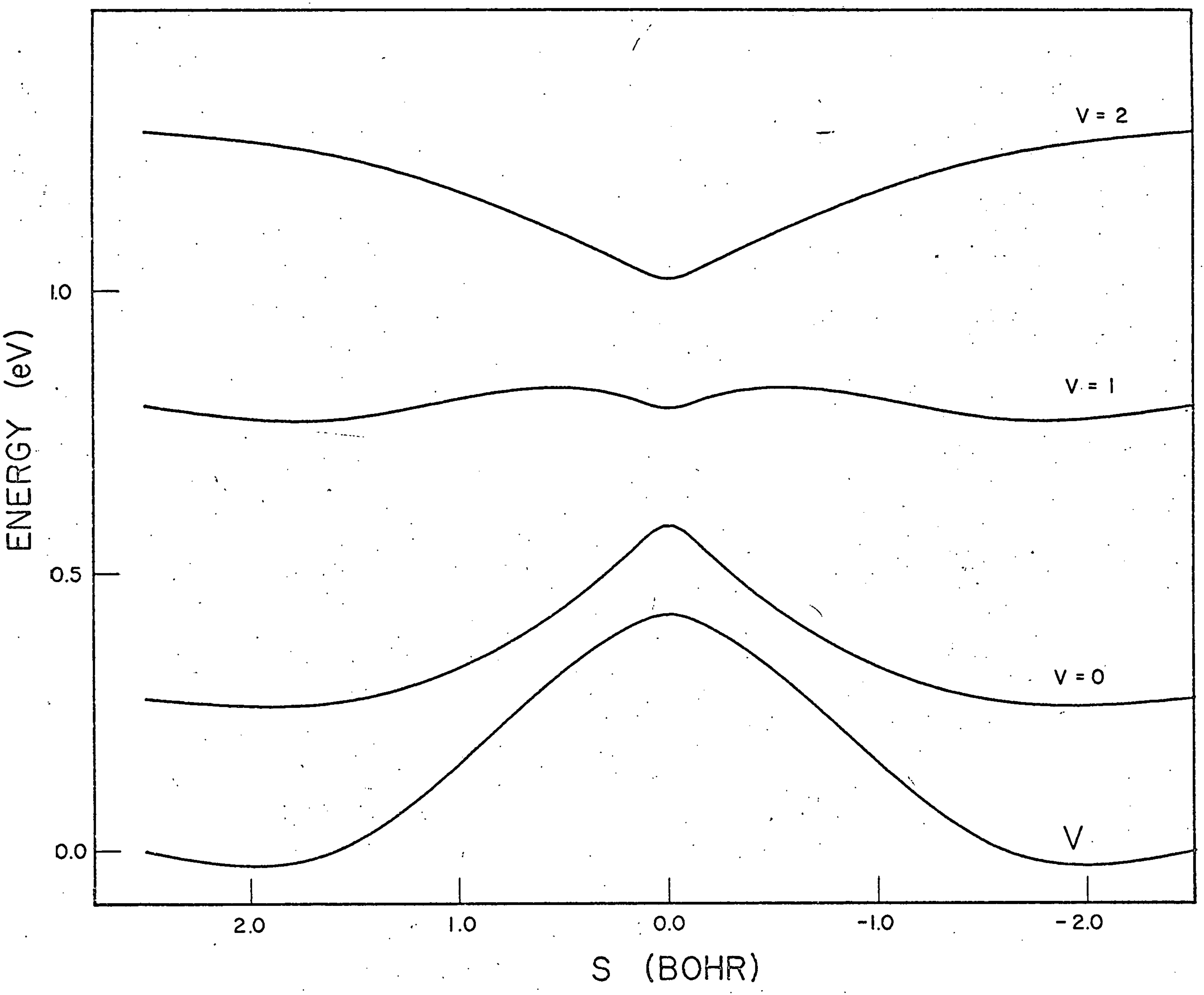
theories will have to include these effects. A preliminary paper on the results obtained will appear as a communication in J. Chem. Phys. and is attached as a part of this report (Report Code CALT-767P4-115).

The existence of these resonances may be understood on the basis of the curves shown in Figure 4. The lowest curve is the potential energy along the reaction coordinate and shows the 0.424 eV barrier associated to the potential energy surface being used. The lowest vibrationally adiabatic potential curve indicated by $v = o$ in Figure 4 has a similar shape, but the higher ones are quite different, showing wells rather than barriers at the saddle point. The $v = 2$ and higher curves are capable of supporting bound states, corresponding to quasi-bound states of H_3, which may be responsible for the resonances observed.

We are presently investigating several approaches for modifying the semi-classical theory of chemical reactions to include the effects of such resonances.

b) Classical Current Densities and Streamlines for the Collinear $H + H_2$ Exchange Reaction. We have invented a definition of current density for collinear classical chemical reaction which satisfies the correspondence principle, i.e., is the classical limit of the quantum mechanical current density. Since, as indicated in last year's technical progress report, the streamlines of probability current density indicate the regions of configuration space sampled by a chemical reaction, the corresponding classical streamlines can be used to compare quantum and classical reactions occurring on the same surface.

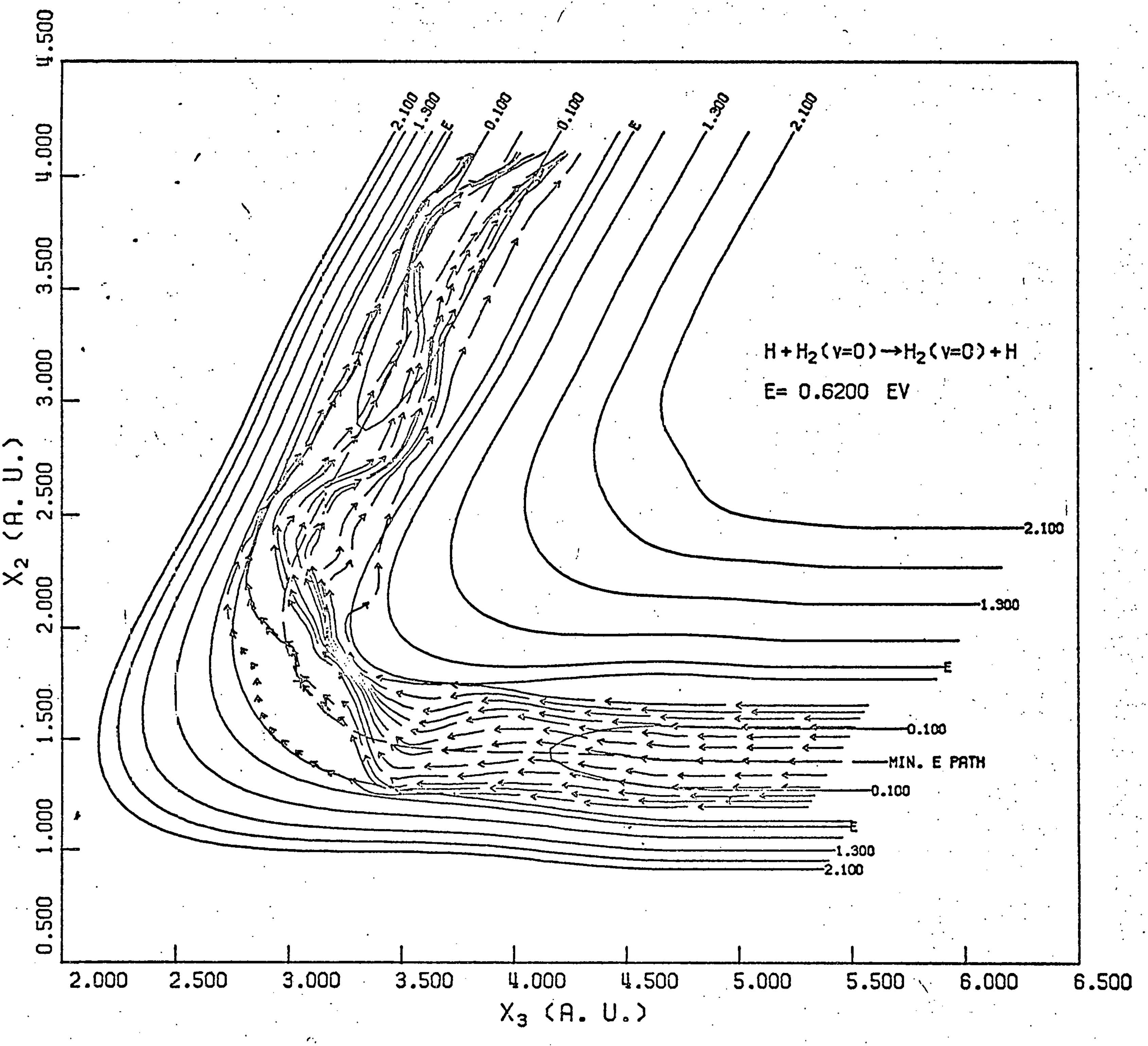
Figure 1



Let, in A + BC, x_2 be the BC internuclear distance, x_1 be the distance of A to the center of mass of BC, and x_3 be the scaled distance $(\mu_{A,\,BC}/\mu_{BC})^{\frac{1}{2}}x_1$. These coordinates were adopted for describing the quantum streamlines and are therefore used here for the classical ones also. Let us consider an infinite ensemble of classical collinear trajectories with the initial vibrational phase sampled according to the classical hamiltonian of the isolated diatonic reagent. The classical probability density ρ is defined so as to make $\rho(x_3, x_2)\, dx_3 dx_2$ equal to the ensemble probability of finding the system in the region x_3 to $x_3 + dx_3$ and x_2 to $x_2 + dx_2$ of configuration space. Let also $\underset{\sim}{v}(x_3, x_2)$ be the ensemble average velocity vector at position x_3, x_2. We define the ensemble average current density as $\underset{\sim}{j}\,(x_3, x_2) = \rho\,(x_3, x_2)\,\underset{\sim}{v}\,(x_3, x_2)$.

Using this definition (and a finite number of quasi-classical trajectories, obviously), we have calculated classical current densities and streamlines, as well as the component current density normal to transverse lines cutting the streamlines. The area under these cuts represents the product of the initial relative velocity by the reaction probability. In Figures 5 and 6 these plots are depicted at a total energy of 0.62 eV. At this energy, both the quasi-classical and quantum reaction probabilities are essentially unity. In Figures 7 and 8 we show the corresponding quantum curves. A comparison between them shows clearly that although the classical and quantum reaction probabilities at this energy are equal, the regions of configuration space sampled in the two cases are quite different. Curves of this type give great insight into the difference between classical and quantum reactive scattering.

Figure 5



H + H_2(v=0) → H_2(v=0) + H
E= 0.6200 EV
2.100
1.300
E
0.100
0.100
E
1.300
2.100
2.100
1.300
E
0.100
MIN. E PATH
0.100
E
1.300
2.100
X_2 (A. U.)
X_3 (A. U.)
0.500
1.000
1.500
2.000
2.500
3.000
3.500
4.000
4.500
2.000
2.500
3.000
3.500
4.000
4.500
5.000
5.500
6.000
6.500

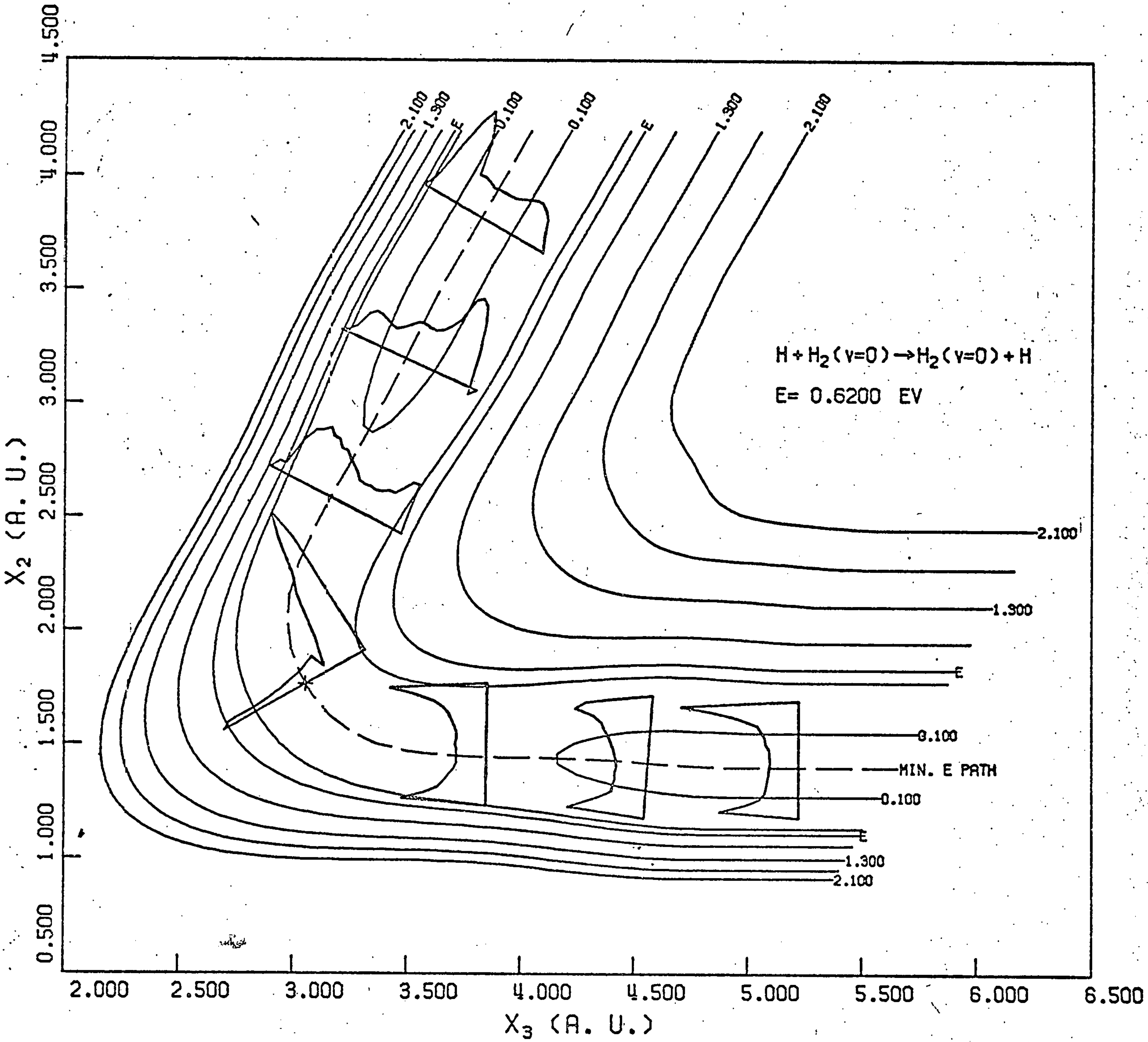
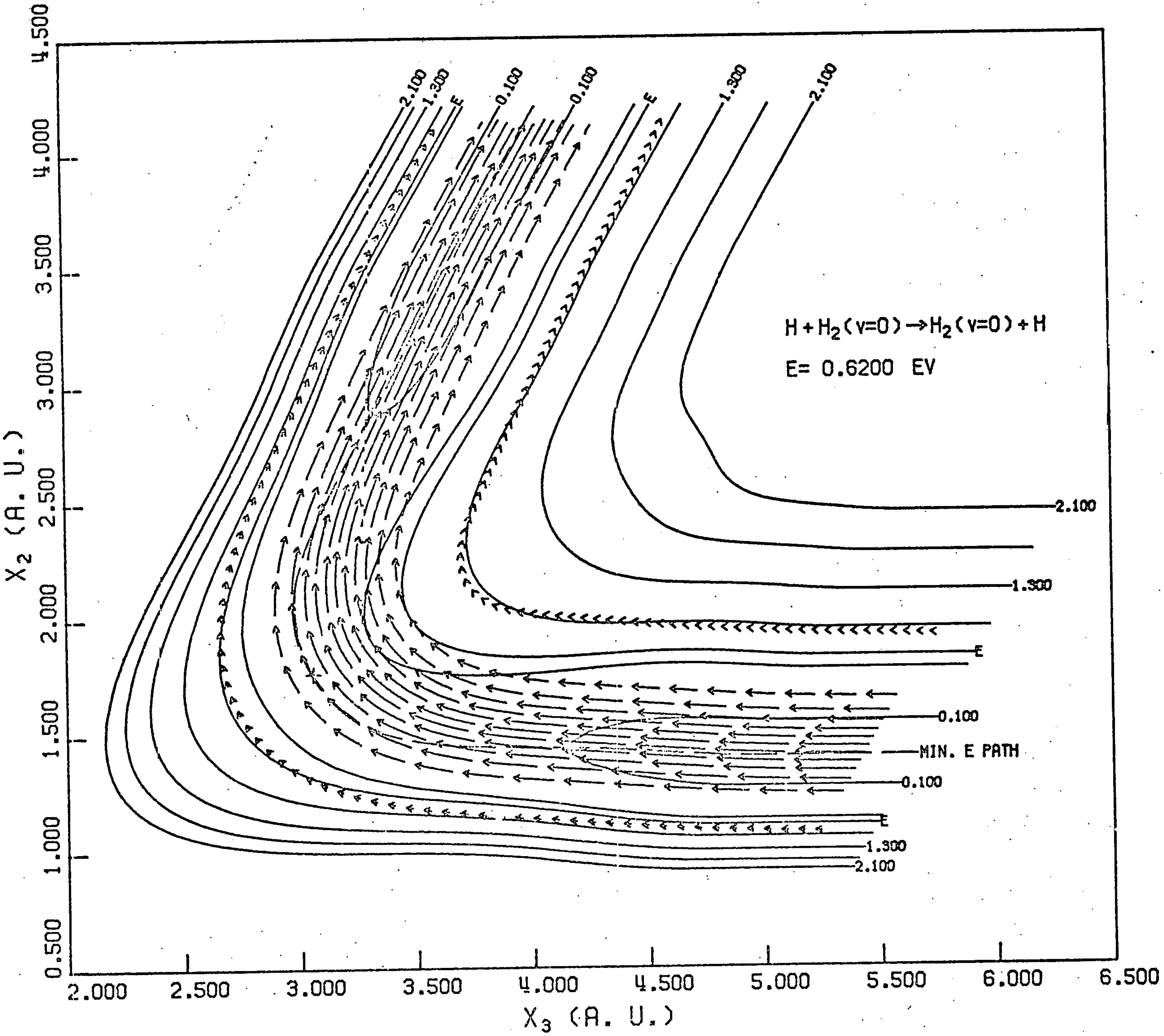

H + H_2(v=0) → H_2(v=0) + H
E= 0.6200 EV
2.100
1.300
E
0.100
0.100
E
1.300
2.100
2.100
1.300
E
0.100
MIN. E PATH
0.100
E
1.300
2.100
X_2 (A. U.)
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
X_3 (A. U.)
2.000
2.500
3.000
3.500
4.000
4.500
5.000
5.500
6.000
6.500

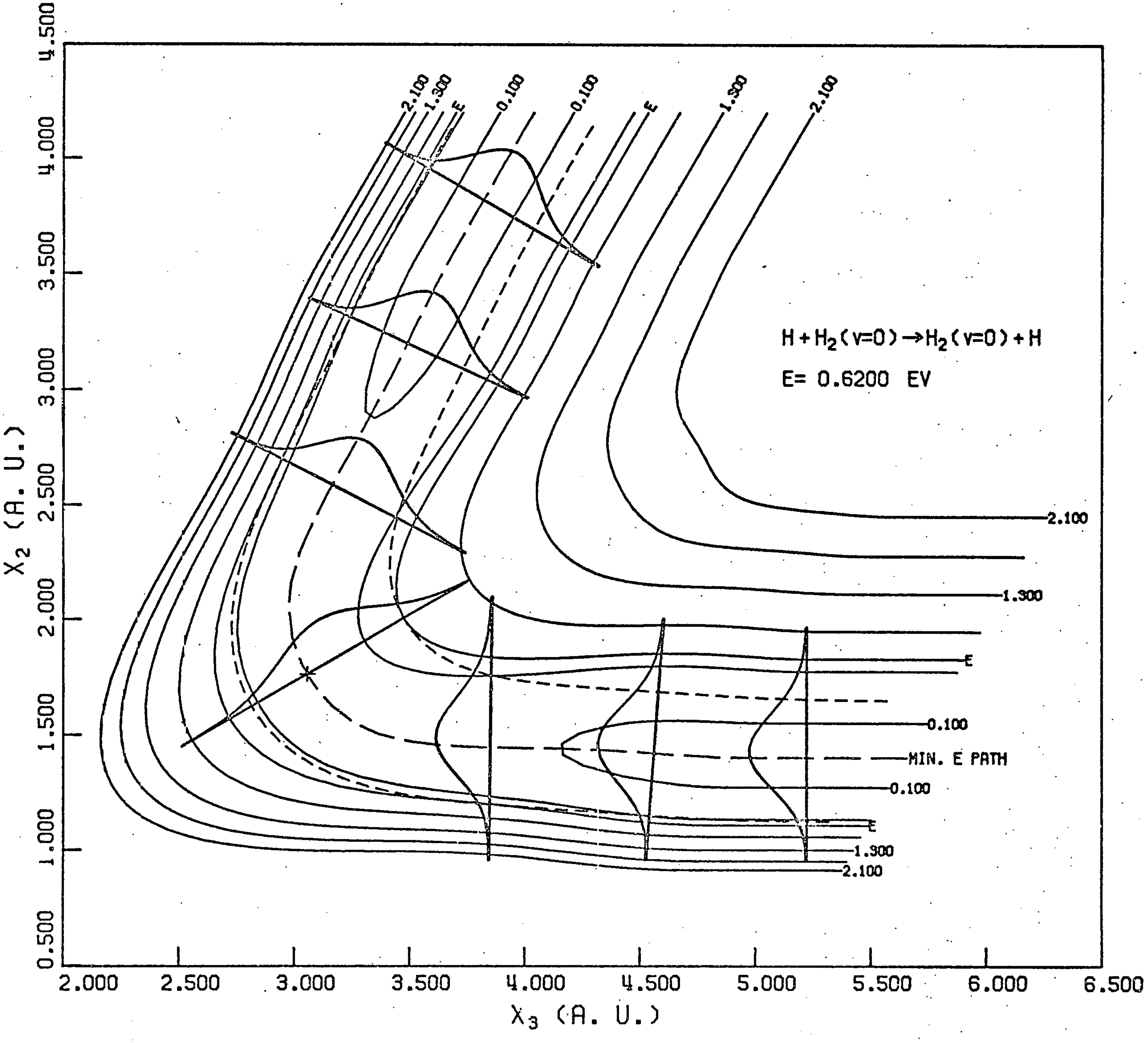
Figure 6

Figure 7



H + H_2(v=0) → H_2(v=0) + H
E= 0.6200 EV
2.100
1.300
E
0.100
0.100
E
1.300
2.100
2.100
1.300
E
0.100
MIN. E PATH
0.100
E
1.300
2.100
X_2 (A. U.)
X_3 (A. U.)
0.500
1.000
1.500
2.000
2.500
3.000
3.500
4.000
4.500
2.000
2.500
3.000
3.500
4.000
4.500
5.000
5.500
6.000
6.500

Figure 8


H + H_2(v=0) → H_2(v=0) + H
E= 0.6200 EV
2.100
1.300
E
0.100
0.100
E
1.300
2.100
2.100
1.300
E
0.100
MIN. E PATH
0.100
E
1.300
2.100
X_2 (A. U.)
X_3 (A. U.)
0.500
1.000
1.500
2.000
2.500
3.000
3.500
4.000
4.500
2.000
2.500
3.000
3.500
4.000
4.500
5.000
5.500
6.000
6.500

c) The Use of Quantum Initial Conditions in Quasi-Classical Trajectory Calculations. It has been suggested[9] that a possible way of including quantum effects in quasi-clssical trajectories (in addition to those associated with giving the reagents a quantized internal energy) was to use a quantum distribution of the initial reagent coordinates in lieu of a classical one. We have investigated this idea in detail and have shown that although very appealing it leads unfortunately to unacceptable inconsistencies. We have already published this work and this paper is attached under Report Code No. CALT-767P4-101.

d) A Direct Test of the Vibrationally Adiabatic Theory of Chemical Reactions. We included a preliminary description of this work in last year's technical progress report. This work has been completed and a paper is in press. It is attached under Report Code No. CALT-767P4-107. This study shows under what conditions the adiabatic assumption, which is the dynamical basis for the quantum form of transition state theory, is valid, and under what conditions it fails.

e) Semiclassical Theory of Chemical Reactions. Two papers have been written on this subject and are attached. One is on the formal aspects of the theory (Report Code No. CALT-767P4-116) and the other is results of the calcuations for the collinear $H + H_2$ (Report Code No. CALT-767P4-99). A more detailed one on these calculations is in final stages of preparation. In summary, for $H + H_2$ the present semi-classical approach is not capable of reproducing the correct quantum oscillations in the reaction probability versus energy curves for the $0 \rightarrow 0$ transition.

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[9] P. M. Careless and D. Hyatt, Chem. Phys. Lett. 14, 358 (1972).

f) Isotope Effects in the Quantum Collinear $H + H_2$ Exchange Reaction. This study is attached as Report Code No. CALT-767P4-97, where the accurate results are reported and a preliminary test against transition state theory is made.

g) Quantum, Quasi-Classical and Semi-Classical Reaction Probabilities for the Collinear $F + H_2 \rightarrow FH + H$, $F + D_2 \rightarrow FD + D$, $F + HD \rightarrow FH + D$ and $F + DH \rightarrow FD + H$ Reactions. Initial results of these studies were included in last year's technical progress report. Since then, a very extensive series of calculations has been made. Some of the $F + H_2$ ones have been published (Report Code No. CALT-767P4-110). A comparison between the accurate quantum and quasi-classical results indicates that there are very large quantum effects in this system, more pronounced than for the $H + H_2$ one. Figure 9 shows the quantum (solid) and quasi-classical (dashed) results for $F + H_2$ while the quantum (solid) and semi-classical (dashed dotted) results are compared in Figure 10. The corresponding quantum (solid), quasi-classical (dashed), and semi-classical (dashed dotted) results for the $F + D_2$ reaction are shown in Figures 11 and 12 respectively. As can be seen, the semi-classical results are in reasonable qualitative agreement with the quantum ones.

We have also calculated the accurate quantum probabilities for the collinear $F + HD \rightarrow FH + D$ and $F + DH \rightarrow FD + H$ reactions. The general appearance of the reaction probabilities as a function of energy are very similar to those shown in Figures 9 and 11, with the $F + HD$ curves most closely resembling the $F + H_2$ ones and the $F + DH$ ones resembling those for $F + D_2$. The most striking difference between the reactions $F + HD$ and

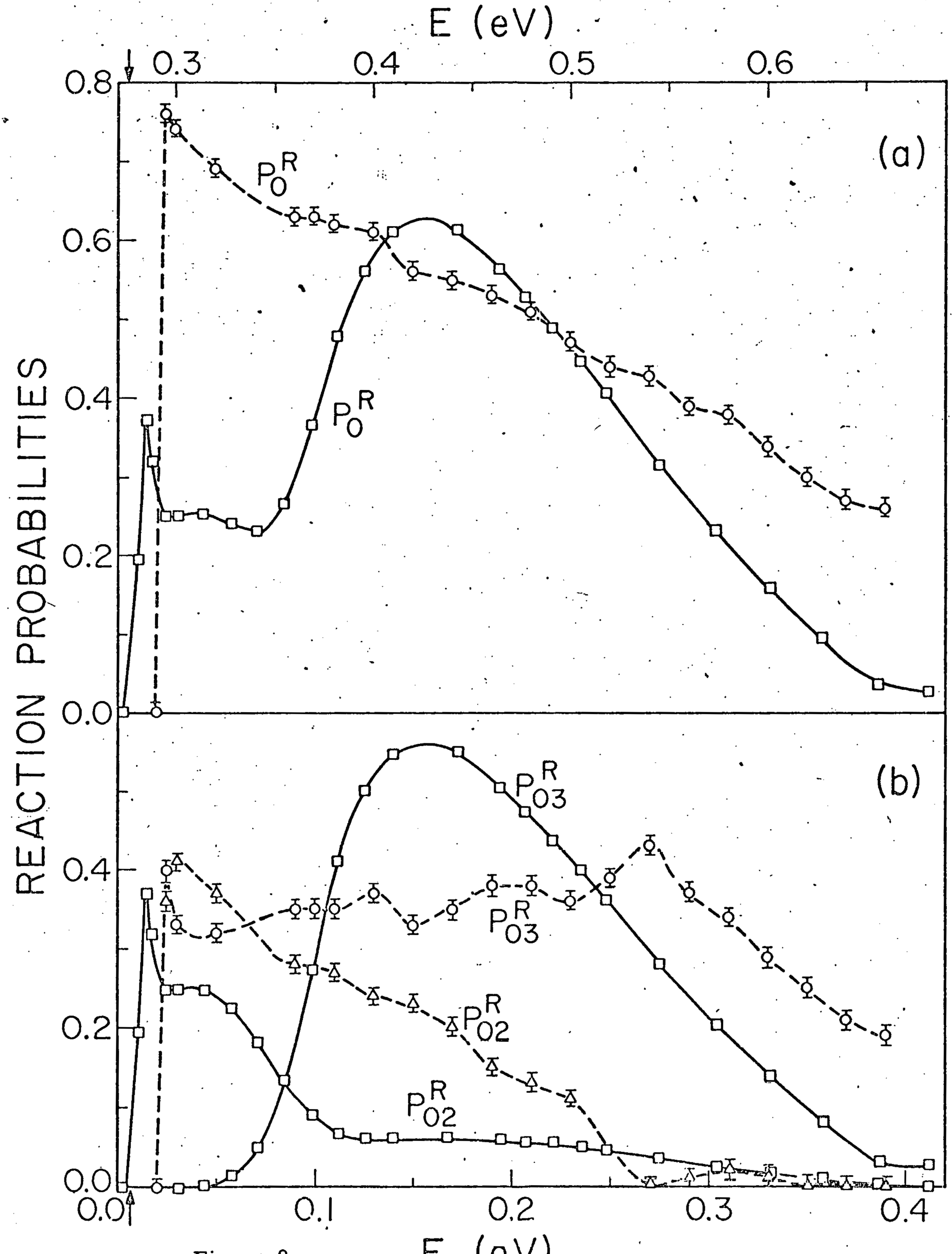

E (eV)
0.3
0.4
0.5
0.6
0.8
0.6
0.4
0.2
0.0
(a)
P_0^R
P_0^R
REACTION PROBABILITIES
(b)
P_{03}^R
P_{03}^R
P_{02}^R
P_{02}^R
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
E_0 (eV)

Figure 9

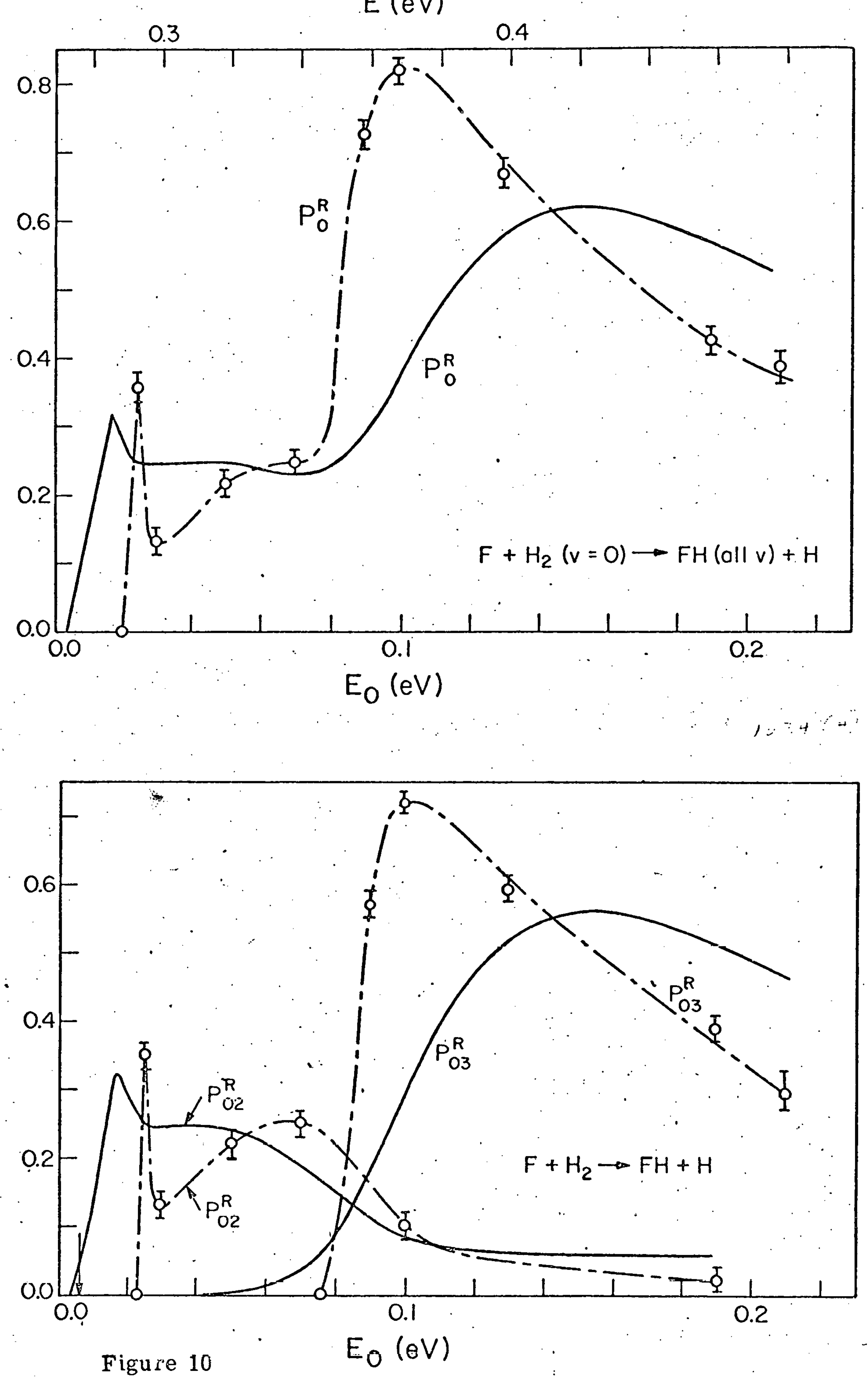
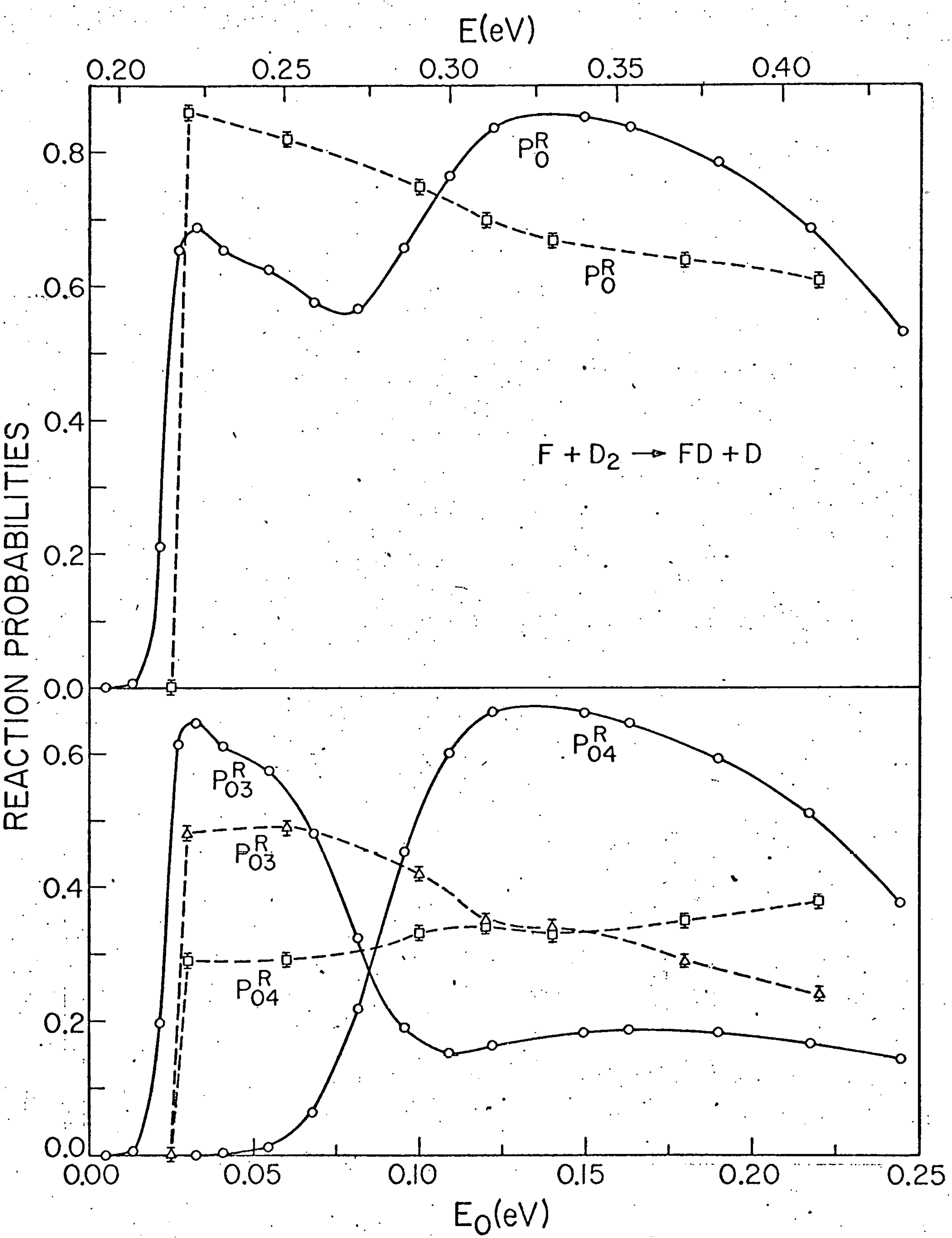

E (eV)
0.3
0.4
0.8
0.6
0.4
0.2
0.0
P_0^R
P_0^R
$F + H_2 (v = 0) \rightarrow FH (all\ v) + H$
0.0
0.1
0.2
E_0 (eV)
0.6
0.4
0.2
0.0
P_{03}^R
P_{03}^R
P_{02}^R
P_{02}^R
$F + H_2 \rightarrow FH + H$
0.0
0.1
0.2
E_0 (eV)

Figure 10



E(eV)
0.20
0.25
0.30
0.35
0.40
REACTION PROBABILITIES
0.8
0.6
0.4
0.2
0.0
P_0^R
P_0^R
$F + D_2 \rightarrow FD + D$
0.6
0.4
0.2
0.0
P_{04}^R
P_{03}^R
P_{03}^R
P_{04}^R
0.00
0.05
0.10
0.15
0.20
0.25
E_0(eV)

Figure 11

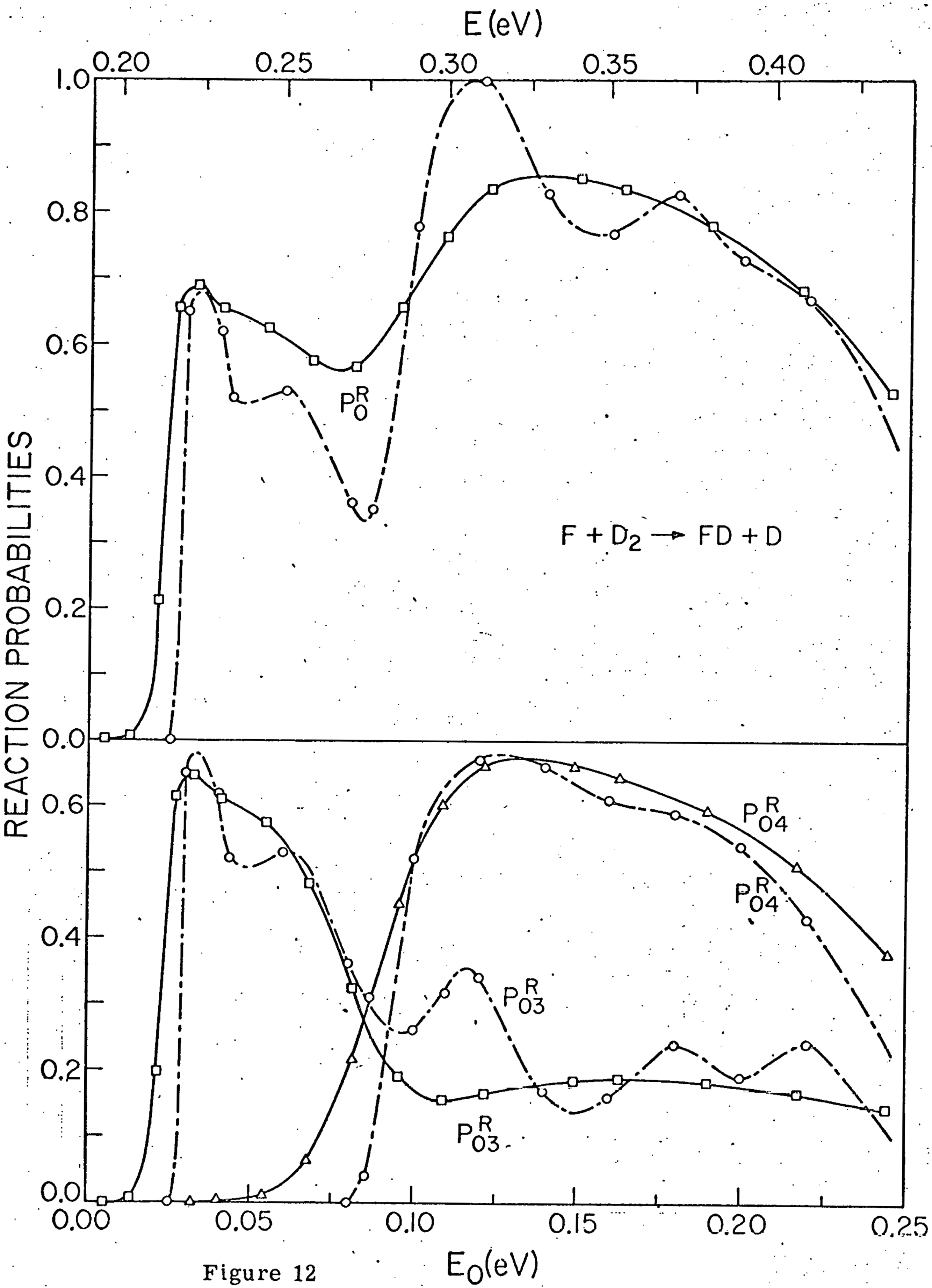

E(eV)
0.20
0.25
0.30
0.35
0.40
1.0
0.8
0.6
0.4
0.2
0.0
REACTION PROBABILITIES
P_0^R
$F + D_2 \rightarrow FD + D$
0.6
0.4
0.2
0.0
P_{04}^R
P_{04}^R
P_{03}^R
P_{03}^R
0.00
0.05
0.10
0.15
0.20
0.25
E_0(eV)

Figure 12

F + DH is the magnitude of the reaction probabilities. For F + HD the total reaction probability is generally .01 or less except at in a very narrow energy interval between 0.01 eV and 0.015 eV initial translational energy where an internal excitation resonance appears with a maximum reaction probability near unity. For F + DH, the total reaction probability exceeds 0.90 for initial translational energies between 0.05 eV and 0.25 eV. Such a pronounced difference in the quantum probabilities could result in pronounced isotope effects in the quantum three-dimensional reaction. This could be of significance for the fluorine-hydrogen chemical laser.

h) Quantum Calculations of Coplanar and Three-Dimensional Atom-Diatom Reactions. The study initiated last year has continued. The method adopted was to integrate the Schrödinger equation inwards from each of the asymptotic arrangement channel regions and to take linear combinations of the resulting solutions which match smoothly at specially chosen surfaces in configuration space. This matching procedure turned out to be particularly difficult from the conceptual viewpoint but these difficulties have now been overcome, and we are hoping to have results in the near future. In addition, two methods have been developed for doing 3-D calculations and will be programed up in the future.

i) Quantum Calculations of Electronically Non-Adiabatic Collisions. All the calculations described above refer to collisions occurring on a single potential energy surface. For many processes of interest for radiation chemistry, however, more than one such surface is involved. During the year we were involved in three studies of this kind.

The first involves the collision between two neutral atoms to produce two ions, such as $K + I \rightarrow K^+ + I^-$, in the framework of the two state approximation. The model potential used was a coulomb attraction starting at a hard sphere core for the ionic curve, and a constant potential starting at the same hard sphere core for the neutral-neutral curve. These two curves intersect each other at a crossover distance R_c and the interaction between them was assumed constant over a range around R_c and zero elsewhere. To solve this model problem accurately it was necessary to develop techniques for generating attractive coulomb wave functions for large angular momentum quantum numbers (of the order of a few thousand). After a substantial amount of effort appropriate expansions of high accuracy were obtained and used to perform calculations. It was found that the partial integral cross sections were highly oscillatory functions of the angular momentum quantum numbers, requiring a solution of the Schrödinger equation sometimes for each of several thousand angular momenta. In order to overcome this difficulty, we are investigating the behavior of the absolute value of the difference between the two eigenphaseshifts associated to each partial wave as well as of quantities associated to the eigenvectors which diagonalize the scattering and reactance matrices. Hopefully, quantities which oscillate less as a function of angular momentum will be found which will permit interpolation procedures to be used, decreasing the number of partial waves for which the coupled Schrödinger equations must be integrated. Semi-classical Stueckelberg calculations will be made for the same model potentials and its ability to predict integral and differential cross sections will be tested. As more measurements of such differential cross sections are done, it becomes more and more necessary to have available reliable methods for obtaining potential parameters from them.

A second problem we have investigated which involves two electronic potential energy curves is the scattering of 2^1S He by ground state He. There are two potential energy curves for He_2 which dissociate into this He (1^1S) + He (2^1S) configuration. One is an $A^1\Sigma^+_u$ state and the other a $C^1\Sigma^+_g$ one. Both these curves have attractive minima and a barrier at large distances. The method for obtaining cross sections for this scattering process consists of integrating the Schrödinger equation for each potential energy curve separately in order to obtain phase shifts, and then taking linear combinations of the resulting scattering amplitudes which appropriately antisymmetrize the scattering wave function. We did such calculations using recently obtained generalized valence bond curves[10]. We found that except for energies close close to the top of the barriers, approximate JWKB phase shifts differed negligibly from the accurate quantum ones. At energies above both barriers, the differential cross section oscillates very rapidly as a function of scattering angles. As the energy is decreased to below the height of the barriers, the oscillations become less rapid. Recently, Y. T. Lee and coworkers measured the differential cross section for this process at a relative translational energy of 63 meV, only a few meV above the lower of the two barriers. They found, as in our calculation, significant scattering around 90° and slow oscillations, corresponding to interference between direct and exchange processes. However, their amplitudes were much lower than the ones we have obtained. Experiments at more energies coupled with calculations of the type we have done would furnish accurate potentials curves, specially around the barriers, which could be used to test the accuracy of the generalized valance bond method and other approximate methods for calculating potential energy curves for excited diatomic systems.

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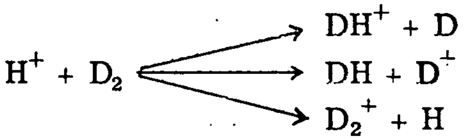
[10] S. L. Guberman and W. A. Goddard, III, Chem. Phys. Lett. <u>14</u>, 460 (1972).

Finally, a third system we are investigating corresponds to the reactions



$$H^+ + D_2 \rightarrow \begin{cases} DH^+ + D \\ DH + D^+ \\ D_2^+ + H \end{cases}$$

These reactions occur on a pair of interacting potential energy surfaces. Recently, Tully and Preston[11] calculated the cross sections for these three reactions using potentials surfaces obtained from a diatomics in molecules approach. They used quasi-classical trajectories on each surface and a Landau-Zener jumping probability between the two when the configuration space point reaches their intersection. The velocity component normal to this seam was used.

In order to test the validity of such an approach, we have initiated a program aimed at doing accurate quantum mechanical calculations of this type for collinear collisions and then surface-hoping quasi-classical calculations of the type done by Tully and Preston. The goal is to develop an understanding of the nature of chemical reactions involving more than one electronic potential energy surface.

1.6 Diffusion Kinetics in the Radiation Chemistry of Water. A paper is being written assessing the present state of this field.

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[11] J. C. Tully and R. K. Preston, J. Chem. Phys. 55, 562 (1971).

2. SCIENTIFIC AND OTHER PERSONNEL

During part or all of the last year, in addition to the project director, the following people have been associated with the project:

Dr. Robert J. Gordon, postdoctoral research fellow, molecular beams.

Dr. Michael Baer, postdoctoral research fellow, theory of chemical reactions.

Dr. Kosuke Shobatake, postdoctoral research fellow, molecular beams.

Dr. Sandor Trajmar, part-time senior research fellow.

Bjarne Andresen, visiting graduate student from the University of Copenhagen, theory of chemical reactions.

Joel M. Bowman, graduate student, theory of chemical reactions.

Johnathan A. Burke, graduate student, photochemistry.

Michael J. Coggiola, graduate student, molecular beams.

Wayne M. Flicker, graduate student, electron impact spectroscopy.

Douglas C. Mason, graduate student, photoelectron spectroscopy.

Donald M. Mintz, graduate student, photoelectron spectroscopy.

Oren A. Mosher, graduate student, electron scattering.

Robert Reiner, graduate student, molecular beams.

George Schatz, graduate student, theory of chemical reactions.

Albert Chang, programmer

John Henigman, electronics engineer, general.

William Schuelke, instrument shop head, general.

During the year, Dr. Robert J. Gordon left for the Naval Research Laboratory in Washington D. C. as a postdoctoral fellow, and has just accepted a position as an Assistant Professor in Chemistry at the University of Illinois, in Chicago. Dr. Michael Baer returned to Israel, where he now holds a joint appointment at the Soreq Nuclear Research Center and the Weizmann Institute. Dr. Kosuke Shobotake joined the group as a postdoctoral fellow, after obtaining his Ph.D. from the University of Chicago under the guidance of Profs. Stuart Rice and Yuan Lee. Mr. Bjarne Andresen, a graduate student at the University of Copenhagen, joined the group as a visitor for one year to do work on the theory of electronically non-adiabatic atomic collisions.

3. TALKS AND PUBLICATIONS

During the period covered by this report, the project director gave the following talks on different aspects of this project:

1. "Threshold Reactions of Hydrogen and Deuterium Atoms," invited talk presented at the Gordon Research Conference on Chemistry and Physics of Isotopes, Holderness School, Plymouth, New Hampshire, 25-30 June 1972.

2. "Track Structure in the Chemical Stage," invited talk presented at the Conference on Physical Mechanisms in Radiation Biology, Airlie House, Virginia, 11-15 October 1972.

3. "Cross Sections and Thresholds," invited talk presented at the Winter Course Gas Kinetics, Lake Arrowhead, California, 17-25 February 1973.

4. "Ab Initio Calculations of Cross Sections," invited talk presented at the Winter Course Gas Kinetics, Lake Arrowhead, California, 17-25 February 1973.

5. "Information Content of Scattering Wave Functions," invited talk presented at the Winter Course Gas Kinetics, Lake Arrowhead, California, 17-25 February 1973.

6. "Quantum Effects in Chemical Reactions," seminar presented at the Chemistry Department of Indiana University, Bloomington, Indiana, 28 February 1973.

7. "Quantum Dynamics of Chemical Reactions," seminar presented at the Department of Chemistry of Ohio State University, Columbus, Ohio, 2 March 1973.

8. "Central Field Intermolecular Potentials from the Differential Elastic Scattering of H_2 (D_2) by other Molecules," Aron Kuppermann, Robert Gordon, and Michael Coggiola, paper presented at the Faraday Society General Discussion on Molecular Beam Scattering, University College, London, 16-18 April 1973. Since the author was unable to attend this meeting, the paper was presented by Dr. Kosuke Shobatake.

In addition, the following talks were given by other members of the group:

9. "Time Delays and Resonances in the H + H_2 Exchange Reaction," George Schatz and Aron Kuppermann, American Physical Society Meeting, San Diego, California, 19-22 March 1973; presented by George Schatz.

10. "Electron Spectroscopy of 1, 3-Butadiene by Electron Impact," Oren Mosher, Wayne Flicker, and Aron Kuppermann, American Physical Society Meeting, San Diego, California 19-22 March 1973; presented by Oren Mosher.

11. "Description of Molecular Elastic Scattering by Central Field Potentials," M. J. Coggiola, Robert Gordon, and Aron Kuppermann, American Physical Society Meeting, San Diego, California, 19-22 March 1973; presented by M. J. Coggiola.

12. "Comparison of Semi-Classical, Exact Quantum, and Quasi-Classical Reactive Transition Probabilities for the Collinear H + H_2 Reaction," Joel Bowman and Aron Kuppermann, American Physical Society Meeting, San Diego, California, 19-22 March 1973; presented by Joel Bowman.

13. "Quantum and Quasi-Classical Reaction Probabilities for the Collinear $F + H_2 \rightarrow HF + H$ Reactions," George Schatz, Joel Bowman, and Aron Kuppermann, American Physical Society Meeting, San Diego, California, 19-22 March 1973; presented by George Schatz.

Therefore, members of the group gave a total of 13 talks at places other than Caltech about work of the project.

The list of papers submitted for publication is given following the cover sheet of this report.