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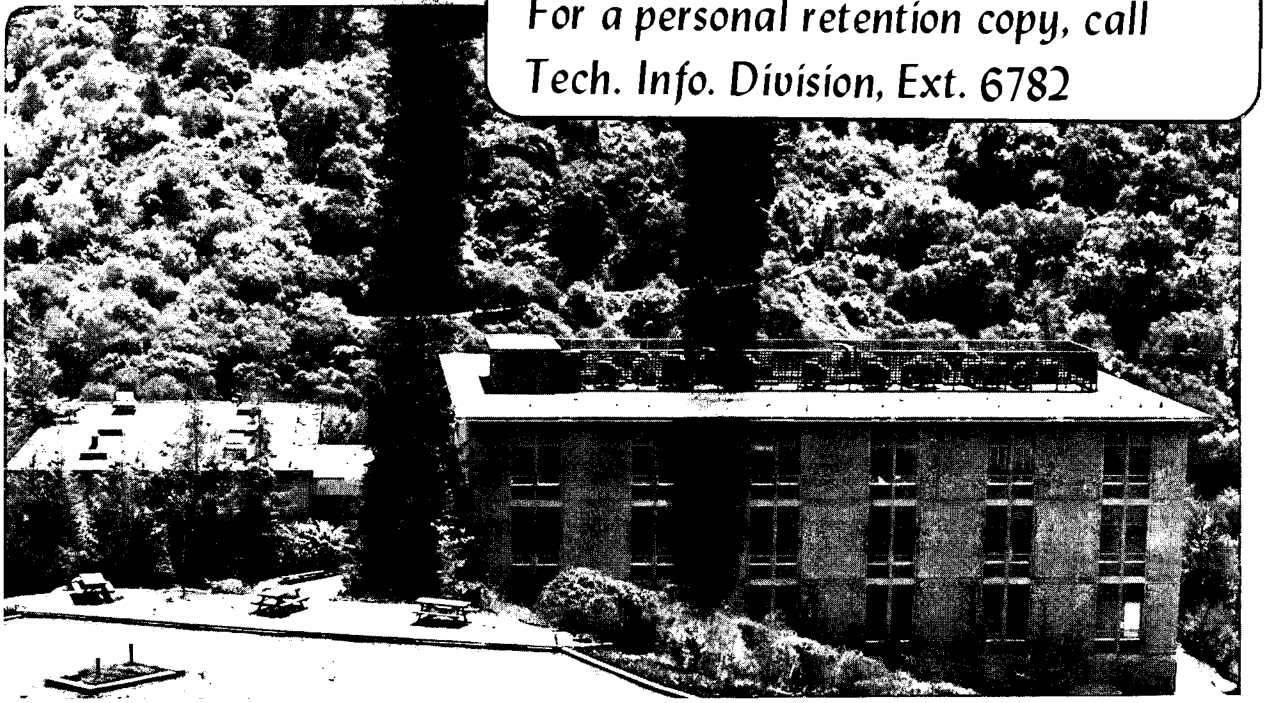

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ABSTRACT

Formaldehyde photopredissociation was studied under collisionless conditions by the technique of crossed laser and molecular beams. Detection of the molecular product CO after excitation of H_2CO near the S_1 origin gives strong support to the sequential coupling model for fast nonradiative decay of S_1 states through broadened S_0 levels to the continuum. For H_2CO excitation at 283.9 nm, formation of the radical product HCO dominates dissociation to molecular products by at least one order of magnitude.

I. INTRODUCTION

The mechanism of formaldehyde photodissociation has been the subject of extensive experimental and theoretical work.[1] Formaldehyde is large enough to have interestingly complex photochemistry; a detailed understanding of this molecule could prove useful as a prototype for the photochemistry of small polyatomics. Formaldehyde is small enough for *ab initio* calculations and can serve as a testing ground for theoretical investigations. In particular, its small size permits *a priori* calculations of radiationless transition rates for comparison to quantum-state resolved experiments. In addition, formaldehyde plays important roles in combustion,[2] polluted atmospheres,[3] and laser isotope separation.[4]

The overall photodissociation process of interest is

$$\begin{aligned} H_2CO + h\nu(280 - 355\ \text{nm}) &\rightarrow H_2CO\ (S_1,v) \\ H_2CO\ (S_1,v) &\rightarrow H_2 + CO \\ &\rightarrow H + HCO, \end{aligned}$$

but this simple representation belies the complexity of the dynamics.

The absorption spectrum of the formaldehyde $\tilde{A}\ {}^1A_2 \leftarrow \tilde{X}\ {}^1A_1$ transition is well understood; individual rotational lines can be resolved and assigned for many vibrational bands.[5] S_1 does not correlate with the ground state products of either channel (Fig. 1), so dissociation at the energies of interest can only occur via a radiationless transition to S_0

or T_1. Although ground state H_2CO is almost isoenergetic with the molecular products H_2 + CO, recent <u>ab initio</u> calculations of the S_0 surface[6 - 8] indicate that the top of the barrier between the two is within a few kcal/mole of the S_1 origin. Photochemical quantum yield studies[9] also indicate a barrier in this region. The threshold for radical formation is well established: photochemical[9 - 11] and thermochemical[12] determinations agree, and <u>ab initio</u> calculations[6, 13] show no barrier in the exit channel for radical dissociation on the S_0 surface. The spectrum of T_1 near its origin is also well studied.[5] Several discrete, diatomic-like S_1 - T_1 perturbations have been observed and assigned in higher vibronic bands.[14] T_1 can dissociate to ground state radicals over a barrier.[13] The S_1 and T_1 origins, the threshold for radical formation, the top of the barrier for dissociation to molecules on the S_0 surface and possibly that for dissociation to radicals on the T_1 surface are all close in energy, as shown in Fig. 1. Thus the number of available pathways can complicate the photodissociation mechanism.

Collision-free decay rates of single rovibronic levels near the S_1 origin vary over two orders of magnitude with little systematic dependence on rotational quantum numbers.[15, 16] A sequential coupling model has been proposed[15a] in which S_1 levels decay via a "lumpy continuum" comprised of S_0 levels broadened by dissociation of S_0 to H_2 + CO. S_0 formaldehyde is estimated to have only ~ 10 vibrational states per cm^{-1}

at these energies, so the fast irreversible nonradiative decay observed requires the dissociation continuum as the final state. The energies involved may be less than the barrier to dissociation on the S_0 surface,[6] but calculated tunneling rates through this barrier provide a reasonable magnitude of S_0 level broadening.[17] Tunneling also provides one possible rationale for the higher photochemical threshold observed for D_2CO.[9] The sequential coupling model is supported by the dramatic changes in decay rate observed as energy resonances are tuned with a Stark field,[15b] but no experimental observation of collision-free dissociation has previously been made.

Photochemical product studies have been done *under conditions where collisions are involved in the decay of* S_1. Photochemical quantum yields for the molecular and radical channels have been measured at pressures > 5 Torr.[9 - 11] The kinetics of CO formation after H_2CO photolysis at 337 nm have been studied by absorption of individual rotational lines from a CO laser.[18, 19] CO ($J \approx 10$) was produced slowly compared to the S_1 decay, and at a rate proportional to pressure for the pressure range of 0.1 - 5 Torr. Extrapolation of the data to zero pressure gave a CO appearance rate of $0.0 \pm 0.26\ \mu s^{-1}$, in contrast to the prompt H_2CO dissociation required by the theory for collision-free nonradiative decay.

The crucial test for the sequential coupling model is clearly the direct observation of dissociation products in the absence of collisions. This paper reports the results of an experiment designed to provide this test using the technique of crossed laser and molecular beams. Dissociation via both the molecular and radical channels does indeed occur without collisions; angular and translational energy distributions of the dissociation products are presented.

II. EXPERIMENTAL

The molecular beam apparatus used for the photofragmentation studies has been described in detail elsewhere.[20] The laser and molecular beams crossed at 90 degrees, and dissociation fragments were detected by an electron bombardment quadrupole mass spectrometer which could be rotated in the plane of the beams.

A Quanta-Ray YAG-pumped dye laser and wavelength extension system were used in these experiments. For studies of the molecular channel of formaldehyde photodissociation, ~ 1 mJ of tunable uv between 338 and 353 nm was obtained by summing the visible output from Coumarin 500 (Exciton) with 1.06 μm YAG fundamental in a KDP crystal. Etalons were used in both the YAG and dye lasers, and the uv linewidth was ≤ 0.25 cm^{-1} as estimated from the width of the narrowest lines in a gas phase fluorescence excitation spectrum of H_2CO (Doppler width = 0.06 cm^{-1} at 300 K). Fluorescence from an external gas cell containing ~ 1 Torr of H_2CO was used as a wavelength reference, as described by Weisshaar.[15a] Individual rotational lines were easily assigned using high resolution spectral data from Ramsay.[21] For studies of the radical channel of H_2CO dissociation, ~ 3 mJ of 284 nm light with a linewidth of ~ 2 cm^{-1} (no etalons) were obtained by frequency doubling the output from Rh 6G (Exciton). In this wavelength range the H_2CO spectrum is not well understood, precluding detailed rotational assignments. The laser entered and exited the molecular beam apparatus via quartz Brewster angle windows. For the molecular channel studies the laser beam (3 mm diameter) was double passed through the formaldehyde beam. At the shorter wavelength, experiments done with the laser unfocused (10 mm diameter, 2 passes) and focused on the interaction region (1 mm diameter, 1 pass) gave qualitatively identical results. The focused configuration was generally used because of somewhat better signal. The laser repetition rate was 10 Hz, and the uv pulse length was ~ 4 ns.

The formaldehyde beam was made by heating paraformaldehyde powder (Matheson) in an oil bath to ~ 90 C with helium flowing over it. A fritted glass disk was usually used to trap any particles being carried in the gas stream, and a dry-ice/isopropanol bath trapped any water or trioxane formed during the depolymerization. Two hundred Torr of the mixture of 10% H_2CO in helium was expanded through a 0.23 mm diameter glass nozzle. A 0.76 mm diameter skimmer was located 7.5 mm from the nozzle. Mass spectrometric analysis of the resulting beam was done by chopping the beam, measuring the signal level with the beam on and off, and taking the difference. No evidence was seen for the presence of dimers (< 0.1%) or trimers (< 1.0%) in the beam (the limits given represent the statistical noise), nor for impurities in the beam in the mass range 37 to 59 amu. The velocity distribution of the beam was obtained by the time-of-flight (TOF) method. The average beam speed was measured to be 1.27×10^5 cm/s and the full-width-half-maximum (FWHM) velocity spread was ~ 10%. The rotational temperature of the H_2CO beam was between 30 and 60 K, as estimated from fluorescence excitation spectra.[22] Three stages of differential pumping, two skimmers, and a final defining slit gave sufficient spatial definition to the beam to allow CO product detection 8° from the H_2CO beam. The distance from the nozzle to the interaction region was 8 cm, and the pressure in the main chamber was ~ 3×10^{-7} Torr with the beam on. With the resolution of the quadrupole set at FWHM = 1 amu and with the detector at 10°, the mass 28 background was ~ 7.5×10^5 counts/s with the beam on, and 6.0×10^5 counts/s with the beam off, giving 30 background counts during the 50 μs time interval for signal acquisition after each laser pulse. Velocity spectra of the product at a given detector angle were obtained from analysis of the flight time of the product from the interaction region to the ionizer located 21 cm away. The spatial width of the molecular beam at the interaction region was 3 mm. The detector has three defining slits which geometrically limit detection to signal originating in a 3 mm by 3 mm region about the collision center. The velocity of the H_2CO molecules will remove them from the detector viewing region in approximately 3 μsec. The experiment thus measures dissociation events which occur within 3 μsec of the laser pulse.

The signal from the detector was amplified, processed by a pulse-height discriminator, then sent to a 256 channel scaler used for TOF measurements. A photodiode provided a trigger pulse for the multichannel scaler, and an LSI-11 computer handled data acquisition and signal averaging.

III. RESULTS AND ANALYSIS

A. Molecular Dissociation near the S_1 Origin

The photodissociation of formaldehyde to H_2 + CO was studied for individual rotational states in the 2^14^1 and 4^1 vibrational bands (339 and 353 nm, respectively). Figure 2 shows time-of-flight (TOF) measurements of the CO product at four laboratory angles for excitation of the $rQ_1(3)E$ and $rQ_1(4)O$[23] rotational lines in the 2^14^1 band of H_2CO (29515.2 cm^{-1}), which overlap within the bandwidth of the laser. The measured lifetime for these states was short (48 ns),[22] hence non-radiative decay is expected to be the dominant decay mechanism. The 2^14^1 band was used for the angular distribution data because the signal intensity was twice that of the 4^1 band. There was no signal in the mass 28 TOF spectrum when the laser was tuned out of resonance with a formaldehyde absorption line, nor when either the laser or the molecular beam was blocked. No TOF signal for masses 29 or 30 was observed, and TOF spectra for the 4^1 and 2^14^1 bands were superimposable within the experimental error. After two hours of counting at each angle, the integrated signal intensities at the four laboratory angles 10°, 15°, 25°, 35° were the same to within 11%. Since the recoil velocity of CO is comparable to the H_2CO velocity (see Fig. 3), this suggests that the center-of-mass (CM) product angular distribution is also nearly isotropic. This was confirmed when an excellent fit to the data was obtained using an isotropic CM angular distribution. The data shown in Fig. 2 are the results of 2 hours of counting at 10, 15 and 25°, and 8 hours at 35°.

A product translational energy distribution, P(E), is obtained from the experimental time-of-flight data by calculating TOF spectra for various postulated P(E)'s, then refining the P(E)'s until a good fit to the experimental data is obtained. The computer programs used for this analysis have been described elsewhere[24] and take into account the velocity spread of the beam, the velocity dependence of the ionization efficiency of the mass spectrometer, and the Jacobian factors in the laboratory to CM coordinate transformation. The CO product translational energy distribution obtained by computer fit to the angular distribution data for the $2^1 4^1$ band is shown in Fig. 4. The error limits indicate the range over which the P(E) can be varied without adversely affecting the fit. The translational energy of the product is very high; the maximum in the distribution is at 55 kcal/mole, or 65% of the total available energy. The resolution of the machine is sufficient to separate products in different vibrational states if the rotational excitation is low,[25] and the locations where peaks for H_2 vibrational levels would fall are marked at the top of Fig. 4. No vibrational structure was seen.

B. Radical Dissociation at 283.9 nm

HCO was detected after excitation of formaldehyde at 283.9 nm, indicating that dissociation to radicals occurs without collisions. Figure 5 shows the TOF spectrum for HCO measured with the detector 8° from the molecular beam. TOF spectra observed at masses 28 and 29 were the same, indicating that most of the CO^+ detected at mass 28 is due to extensive HCO fragmentation in the ionizer. The integrated signals were within 6% (statistical σ = 12%), and all subsequent data was taken at mass 28. The HCO fragments are considerably slower than the CO products observed for excitation near the S_1 origin. This is as expected since the formation of radicals has a smaller amount of available excess energy (14 kcal/mole vs 85 kcal/mole). An angular distribution could not be measured because the HCO product is kinematically constrained to a small angle in the laboratory frame of reference by the low translational energy (see Fig. 3), and the high background from formaldehyde in the beam precludes measurements at laboratory angles less than 8°.

Figure 6 shows the P(E) that best fit the HCO TOF spectrum. An isotropic angular distribution was assumed since data at a single laboratory angle is not sensitive to the CM angular distribution, and proved adequate to fit the data. The data do not give any information about HCO fragments with less than 2 kcal/mole of translational energy, because such molecules are scattered at angles less than 8° in the laboratory frame.

Since the TOF spectrum for the radical dissociation channel was measured using mass 28, any product from the molecular product channel should also have been detected, separated in time from the HCO signal by the difference in translational energy. Experimentally, however, no evidence for any fast CO product was seen. In order to estimate the branching ratio for the dissociation, the expected signal level for the molecular product channel was calculated assuming equal production of HCO and CO, i.e. $\phi_R = \phi_M$, and using the molecular P(E) obtained in the $2^1 4^1$ band scaled to account for the increased total energy. The observed signal for the radicals was assumed to represent the total radical product, i.e. the radical P(E) was set to zero below 2 kcal/mole. This assumption provides an upper limit for the branching ratio ϕ_M/ϕ_R. Differences in the laboratory angular distribution of the two products caused by the difference in product CM velocities, and the Jacobian factor in the conversion from CM to laboratory frame of reference were taken into account in the calculation, and the result is shown in Fig. 5. The comparison between the calculated molecular signal level (dashed curve) and the experimental data indicates that $\phi_M < 0.10\ \phi_R$, since a larger ϕ_M would have resulted in a detectable product signal.

IV. DISCUSSION

A. Molecular Dissociation near the S_1 Origin

The major result of these experiments is the unequivocal detection of CO products, which confirms the $S_1 \rightarrow S_0 \rightarrow$ product coupling model for collisionless decay of S_1 formaldehyde. The observed TOF signal cannot result from the dissociation of formaldehyde dimer because no signal was seen at masses 29 or 30, and because no evidence for the presence of dimers in the beam was ever seen. The observed signal level (~ 0.3 counts/pulse) was of the order of magnitude expected from estimates of the beam density, rotational state populations, formaldehyde absorption cross section, fraction of product detected and ionizer efficiency. The similarity of the 4^1 and 2^14^1 TOF spectra is expected since these bands are separated by only 1200 cm^{-1} (4% of the total available energy), and such a small difference in total energy would not be resolvable in the product P(E) unless a change in mechanism had occurred.

The isotropic product angular distribution shows that formaldehyde dissociation occurs on a timescale long compared with rotation. The absorption band of interest is a type b transition, and the transition dipole is perpendicular to the CO bond and in the molecular plane.[5, 26] The laser was polarized in the plane of the beams, so molecules with the H - H direction parallel to the molecular beam are preferentially excited. *Ab initio* calculations of the potential energy surface indicate that the path of steepest descent from the transition state to molecular products is in the plane of the molecule.[6] Consequently, CO product from molecules in the plane of the beams at the moment of dissociation is more likely to be detected. If dissociation occurred before rotation averaged all initial orientations, the CO product distribution would show an angular dependence. The isotropic angular distribution is not unexpected since the shortest S_1 formaldehyde decay times (tens of ns)[15, 16] are considerably longer than a rotational period.

Earlier work by Houston and Moore[18] has suggested that under collisional conditions, an intermediate species may be formed. In the present experiment, only dissociation events occurring within 3 μsec after the laser pulse are detected. If any collisionless decay to another species with a lifetime greater than about 3 μsec is occurring, that species will remain in the beam undetected.

The absence of structure in the TOF spectrum could indicate that there is sufficient rotational excitation of the products to smear out structure due to vibrational excitation of the H_2 product, and/or that vibrational excitation of CO is disguising any such structure. When 55 kcal/mole is in translation, sufficient energy remains to excite H_2 to $v = 2$ or CO to $v = 4$. Although the translational energy distribution gives no direct information on the distribution of the remaining energy among the internal degrees of freedom, some possibilities are suggested by simple models. In the transition state for

H_2CO molecular dissociation calculated by Schaefer,[6] the CO (1.170 Å) and H_2 (1.246 Å) distances are longer than in the free CO (1.128 Å)and H_2 (0.7416 Å) molecules. In particular, the H - H distance in the transition state roughly corresponds to the classical turning point of $v = 3$ in H_2. If the dissociation occurs suddenly and there is no major redistribution of vibrational energy on the strongly repulsive exit channel surface, the products, particularly the H_2, should be vibrationally excited.[27, 28] This is consistent with the fact that the maximum of the P(E) roughly falls where H_2 ($v = 2$) should be. This model, however, is only qualitative since the breaking of the C - H bonds is not simultaneous. In the transition state, one C - H bond is already essentially broken ($r = 1.586$ Å, bond order = 0.2), while the other is nearly normal ($r = 1.104$ Å). Pople's[7] calculated transition state is qualitatively the same as Schaefer's, but the bond distances for the longer of the two C - H bonds and the H - H bond are somewhat greater. A very simple impulse approximation calculation,[29] treating the H_2 as a point mass and assuming that it leaves along the line connecting the H_2 center-of-mass to the C atom in Schaefer's transition state, gives CO with $J = 23$ and v(average) = 0.4 for 55 kcal/mole of product translation energy. Formaldehyde dissociation product energy distributions peaked about $H_2(v = 2, J = 3) + CO(v = 0, J = 23)$ are suggested by these simple models, but many other distributions are similarly consistent with the data.

The CO product vibrational distribution measurements of Houston and Moore[18] showed 11% of the CO in v = 1 and 2% in v = 2 for photolysis at 337 nm. For photodissociation of the analogous system HFCO, Berry[30] found < 7% of the total available energy in HF vibrational excitation. These measurements of low product vibrational energy are in qualitative agreement with the high translational energy of the present result; however, possible effects from collisional processes in these earlier studies may vitiate the comparison. If CO is indeed produced with J(avg) = 23 as implied above, the delay in the CO appearance rate observed using a CO laser (J ~ 10)[18] may be complicated by rotational relaxation. This evidence for the role of an intermediate[18] in formaldehyde dissociation may thus be compromised; CO infrared fluorescence measurements, which should be less dependent on the rotational distribution, indicate the same delay in the CO production.[19]

The product translational energy distribution obtained in this experiment will provide a good test for formaldehyde potential energy surfaces. Dynamical calculations on a good surface should give a P(E) that matches the experimental data. Such calculations would also give more reliable and detailed information on the partitioning of energy among the internal degrees of freedom than could possibly be obtained from the simple models discussed above. Handy and Carter[31] have recently developed an analytical form for the formaldehyde potential surface that should be useful in such calculations.

B. Radical Dissociation Channel

In contrast to the molecular dissociation channel, radical products have a very small fraction of the available energy in translation. This is reasonable for a unimolecular reaction with no repulsive energy release in the exit channel, if extensive energy sharing occurs among vibrational degrees of freedom. The calculations of Schaefer[6] and Morokuma[13] indeed suggest that the potential energy surface for the dissociation of S_0 formaldehyde to H + HCO does not have an exit barrier. The P(E) for such a surface would have its maximum at zero translational energy. T_1 may also be involved in radical formation, since 35220 cm^{-1} may be above the barrier for dissociation on the T_1 surface, but the present experiments give no information on this.

The present experiments indicate that dissociation to radicals is dominant over production of H_2 and CO by at least one order of magnitude at 283.9 nm. If the critical configuration for dissociation to radicals has a C - H distance 2.5 - 3 times longer than the normal C - H bond length, as suggested by *ab initio* calculations,[6] RRKM calculations give a radical dissociation rate which increases more rapidly with increasing energy than the molecular dissociation rate. Thus, it is not unreasonable that the radical channel should dominate at an energy 14 kcal/mole above the threshold for radical formation. This estimate for the molecule/radical branching ratio is not in good agreement with previous quantum yield measurements. Values of ϕ_R from 0.4 to 0.9[9 - 11] have been obtained for wavelengths between 280 and 300 nm. $\phi_M + \phi_R = 1$, so the molecule/radical branching ratios from these experiments are > 0.1. Since not all works show a smooth dependence of ϕ_R on wavelength (see Fig. 3 of Ref. 10), comparison to the present work at 283.9 nm may not be valid. The previous measurements were done at high pressures (> 5 Torr) using radical scavengers, so the discrepancy might also be attributed to the difference in pressure regime, i.e. collisonal effects.

V. CONCLUSIONS

The major conclusion of this work is that formaldehyde does indeed dissociate without collisions after excitation near the S_1 origin. This strongly supports the model derived from low pressure fluorescence decay times for S_1 decay through a lumpy continuum of S_0 levels broadened by dissociation. At higher photolysis energies, dissociation to radicals is the dominant channel and also takes place without collisions. Molecular products have a large fraction of the total available energy in translation, while the radical products have little translational energy.

The photopredissociation of formaldehyde near the S_1 origin is now quite well understood in the collisionless regime. Incorporation of collisional effects into this understanding requires further investigation.

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REFERENCES

1. W.M. Gelbart, M.L. Elert, and D.F. Heller, Chem. Rev. 80, 403 (1980), and references therein.
2. A.G. Gaydon, The Spectroscopy of Flames, 2nd Ed., (Chapman & Hall, London, and Wiley & Sons, New York, 1974).
3. J.G. Calvert, J.A. Kerr, K.L. Demerjian, and R.D. McQuigg, Science 175, 751 (1972).
4. R.E.M. Hedges, P. Ho, and C.B. Moore, Appl. Phys. 23, 25 (1980); J. Marling, J. Chem. Phys. 66, 4200 (1977); L. Mannik, G.M. Keyser, and K.B. Woodall, Chem. Phys. Lett. 65, 231 (1979).
5. D.C. Moule and A.D. Walsh, Chem. Rev. 75, 67 (1975).
6. a) J.D. Goddard and H.F. Schaefer, J. Chem. Phys. 70, 5117 (1979); b) J.D. Goddard, Y. Yamaguchi, and H.F. Schaefer, J. Chem. Phys. 75, 3459 (1981).
7. M.J. Frisch, R. Krishnan, and J.A. Pople, J. Phys. Chem. 85, 1467 (1981); L.B. Harding, H.B. Schlegel, R. Krishnan, and J.A. Pople, ibid 84, 3394 (1980).
8. G.F. Adams, G.D. Bent, R.J. Bartlett, and G.D. Purvis, J. Chem. Phys. 75, 834 (1981).
9. J.H. Clark, C.B. Moore, and N.S. Nogar, J. Chem. Phys. 68, 1264 (1978).
10. K.Y. Tang, P.W. Fairchild, and E.K.C. Lee, J. Phys. Chem. 83, 569 (1979).
11. A. Horowitz and J.G. Calvert, Int. J. Chem. Kinet. 10, 805 (1978).

12. R. Walsh and S.W. Benson, J. Am. Chem. Soc. 88, 4570 (1966); P. Warneck, Z. Naturforsch., Teil A26, 2047(1971); 29, 350 (1974).

13. D.M. Hayes and K. Morokuma, Chem. Phys. Lett. 12, 539 (1972).

14. J.C.D. Brand and C.G. Stevens, J. Chem. Phys. 58, 3331 (1973); R.E. Linder, G. Barth, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, Chem. Phys. Lett. 28, 490 (1974); F. W. Birss, D.A. Ramsay, and S.M. Till, Chem. Phys. Lett. 53, 14 (1978).

15. a) J.C. Weisshaar and C.B. Moore, J. Chem. Phys. 70, 5135 (1979); b) 72, 5415 (1980); c) J.C. Weisshaar, D.J. Bamford, E. Specht, and C.B. Moore, ibid 74, 226 (1981).

16. a) K. Shibuya, R.A. Harger, and E.K.C. Lee, J. Chem. Phys. 69, 751 (1978); b) K. Shibuya and E.K.C. Lee, ibid 69, 5558 (1978); c) K. Shibuya, P.W. Fairchild, and E.K.C. Lee, J. Chem. Phys. 75, 3397 (1981).

17. W.H. Miller, J. Am. Chem. Soc., 101, 6810 (1979); S.K. Gray, W.H. Miller, Y. Yamaguchi, and H.F. Schaefer, ibid 103, 1900 (1981).

18. P.L. Houston and C.B. Moore, J. Chem. Phys. 65, 757 (1976).

19. M.B. Zughul, Ph.D. Thesis, University of California, Berkeley, 1978; Chi-ke Cheng, P. Ho, M.B. Zughul, and C.B. Moore, in preparation.

20. Y.T. Lee, J.D. McDonald, P.R. LeBreton, and D.R. Herschbach, Rev. Sci. Instru. 40, 1402 (1969).

21. D.A. Ramsay, private communication.

22. D.J. Bamford, P. Ho, Aa. S. Sudbo, and C.B. Moore, in preparation.

23. The notation $rQ_{K''}(J'')$ denotes a $\Delta K = +1$, $\Delta J = 0$ transition in absorption from the $J''K''$ ground state. O and E indicate whether $J'' + K_A'' + K_C''$ is odd or even. See also Ref. 15a.

24. Richard J. Buss, Ph.D. Thesis, University of California, Berkeley (1979).

25. R.K. Sparks, L.R. Carlson, K. Shobatake, M.L. Kowalczyk, and Y.T. Lee, J. Chem. Phys. 72, 1401 (1980).

26. G.H. Dieke and G.B. Kistiakowsky, Phys. Rev. 45, 4 (1934).

27. M.J. Berry, Chem. Phys. Lett. 29, 329 (1974).

28. R.L. Jaffe and K. Morokuma, J. Chem. Phys. 64, 4881 (1976).

29. G.E. Busch and K.R. Wilson, J. Chem. Phys. 56, 3626 (1972).

30. D.E. Klimek and M.J. Berry, Chem. Phys. Lett. 20, 141 (1973).

31. N.C. Handy and S. Carter, Chem. Phys. Lett. 79, 118 (1981).

FIGURE CAPTIONS

Figure 1. Energy level diagram for formaldehyde. The dashed lines show the correlations between bound states and continua. Approximate barrier heights shown are from *ab initio* calculations.

Figure 2. Angular distribution of CO produced by H_2CO dissociation at 339 nm. $rQ_1(3)E$ and $rQ_1(4)O$ in the $2^1 4^1$ vibronic band were excited. The solid curves are computer fits to the data for the P(E) shown in Fig. 4.

Figure 3. Newton diagram for formaldehyde dissociation. Solid line indicates product velocity in LAB frame of reference, dashed line indicates product velocity in CM frame. Angles shown are in the LAB frame.

a) indicates CM velocity for CO produced at 339 nm if all excess energy goes into product translation.

b) indicates CM velocity for HCO produced at 283.9 nm if all excess energy goes into product translation.

c) indicates HCO CM velocity for dissociation to radicals with 4 kcal/mole translational energy.

Shaded area indicates the velocity range of CO products observed at 339 nm and corresponds to the 10% height limits of the P(E) in Fig. 4.

Figure 4. Product translational energy distribution for the molecular dissociation channel derived from angular distribution data in Fig. 2. The CM angular distribution is isotropic. Shaded area indicates range for acceptable fit to data (see text). Maximum translational energies with production of vibrationally excited H_2 product are indicated at the top.

Figure 5. Mass 28 time-of-flight spectrum for HCO production at 283.9 nm. The solid curve shown is a computer fit to the data corresponding to the P(E) in Fig. 6. The dashed curve shows the calculated signal expected for molecular products if equal amounts of HCO and CO products are formed after H_2CO excitation at 283.9 nm.

Figure 6. Product translational energy distribution for radical dissociation derived from data in Fig. 5. An isotropic CM angular distribution is assumed. The data are not sensitive to the P(E) below 2 kcal/mole.

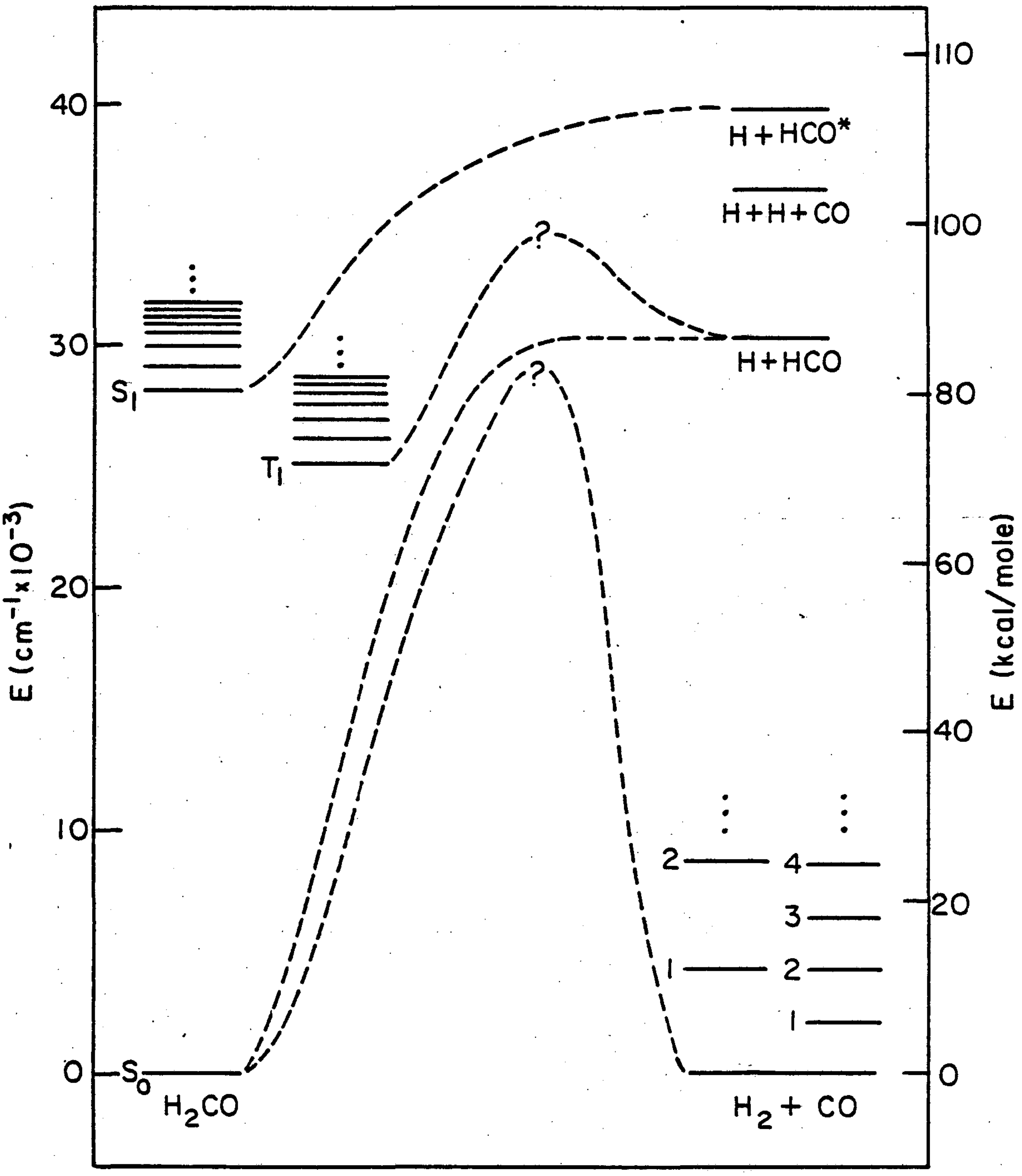

E (cm^{-1}x10^{-3})
E (kcal/mole)
40
30
20
10
0
110
100
80
60
40
20
0
H + HCO*
H+H+CO
H+HCO
S$_1$
T$_1$
S$_0$
H$_2$CO
H$_2$ + CO
?
?
2
1
4
3
2
1

Fig. 1

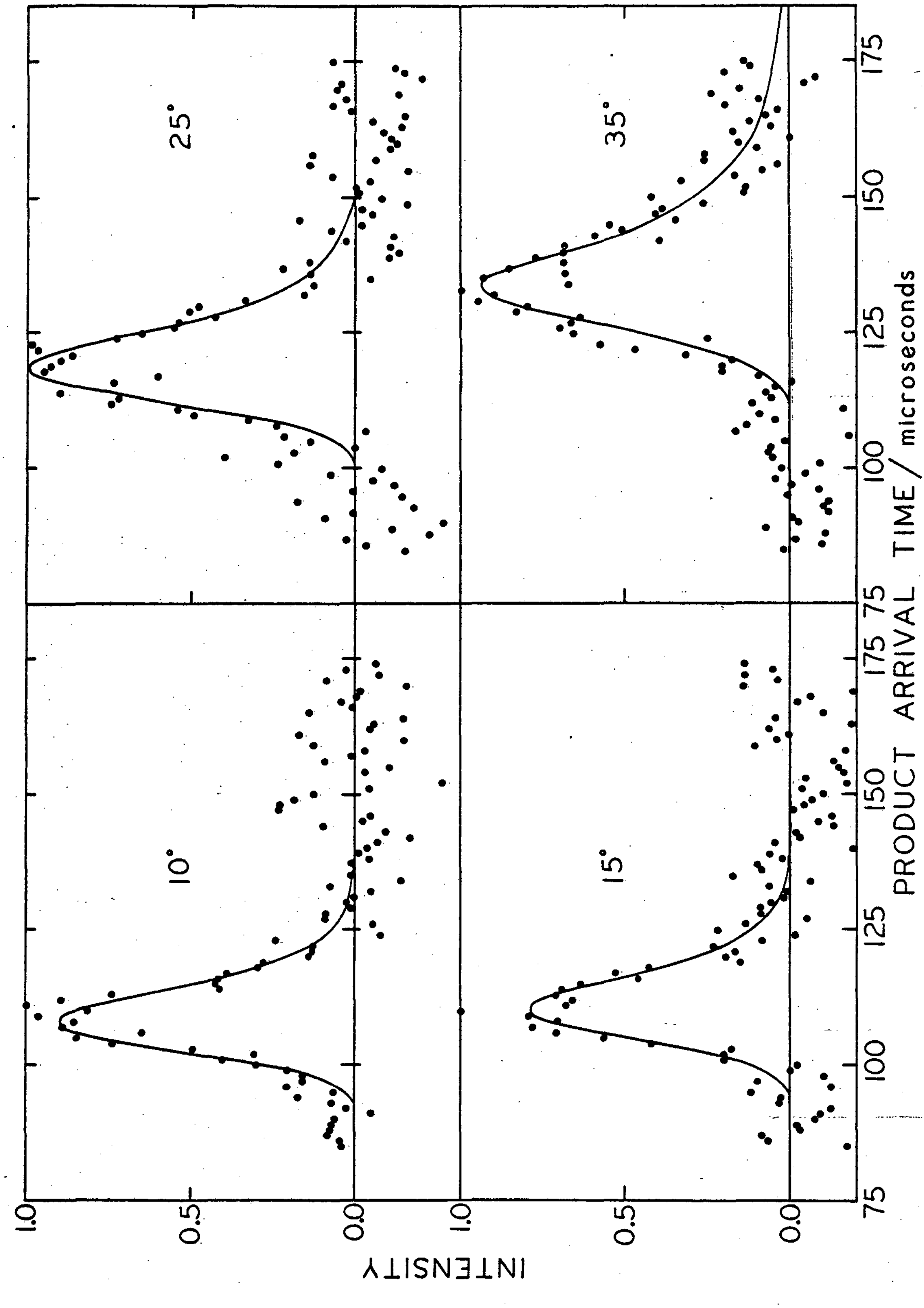

10°
25°
15°
35°
INTENSITY
1.0
0.5
0.0
1.0
0.5
0.0
PRODUCT ARRIVAL TIME / microseconds
75
100
125
150
175
75
100
125
150
175

Fig. 2

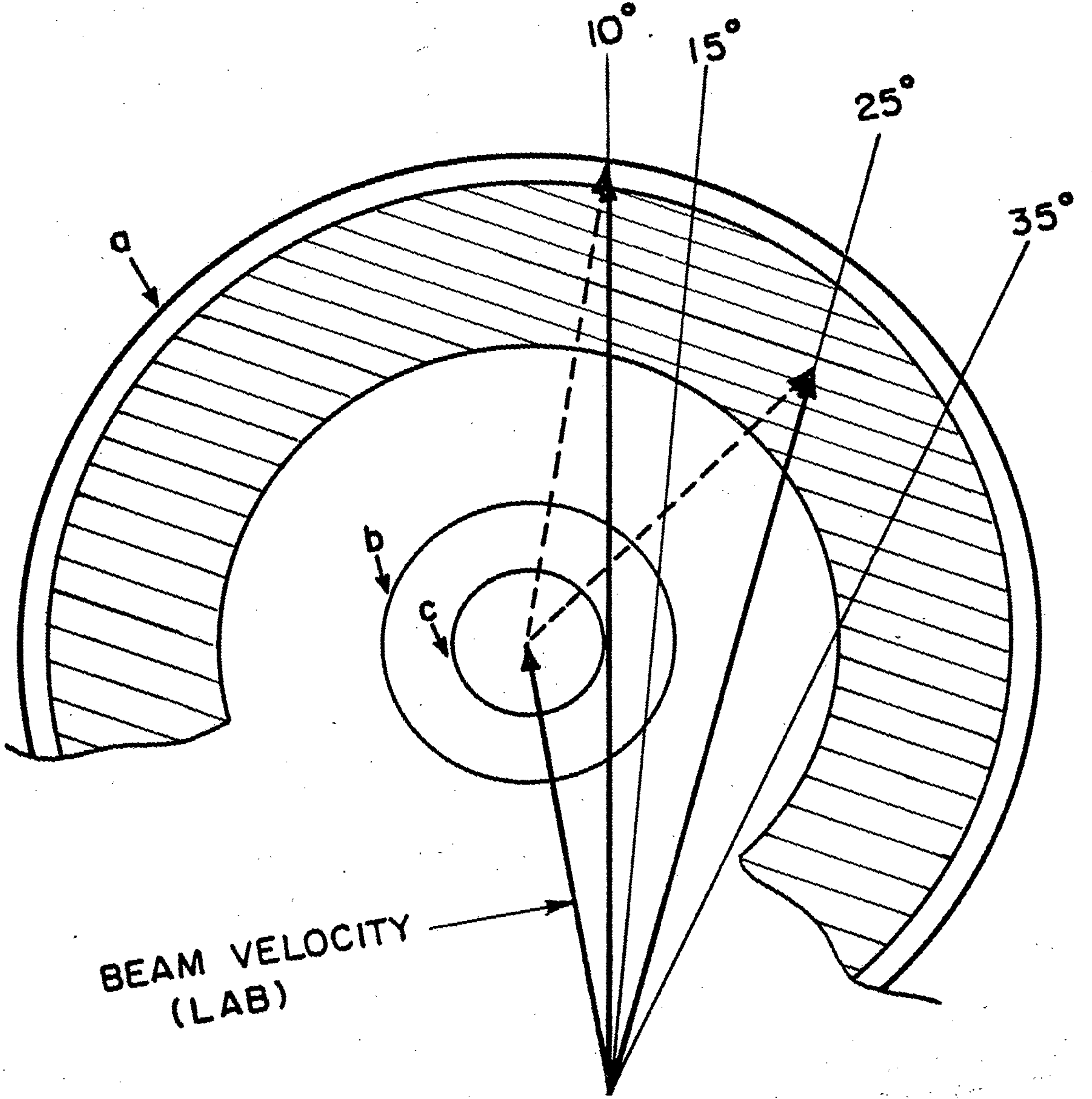
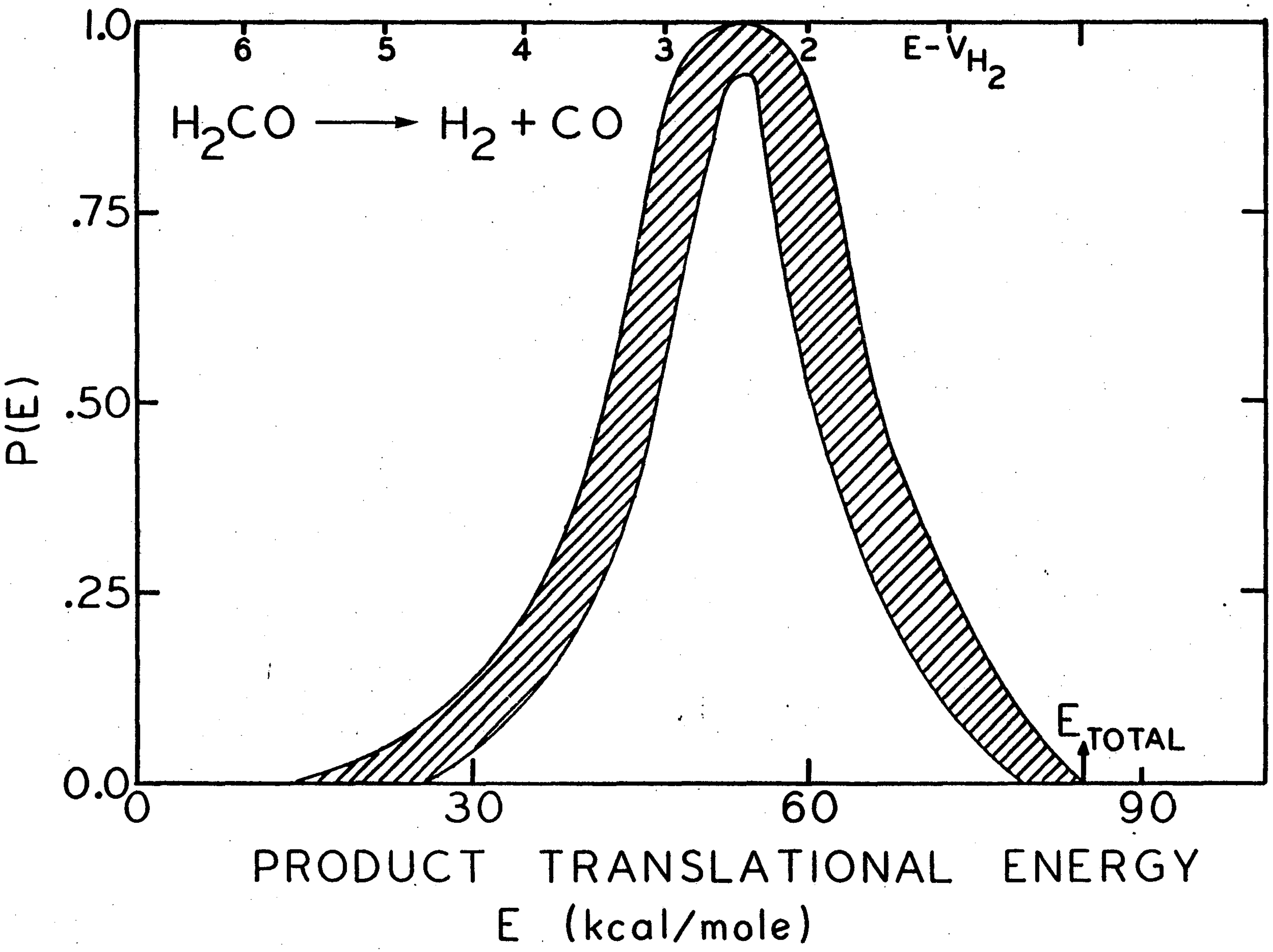


Fig. 3



1.0
.75
.50
.25
0.0
P(E)
6
5
4
3
2
E-V_{H_2}
$H_2CO \longrightarrow H_2 + CO$
E_{TOTAL}
0
30
60
90
PRODUCT TRANSLATIONAL ENERGY
E (kcal/mole)

Fig. 4

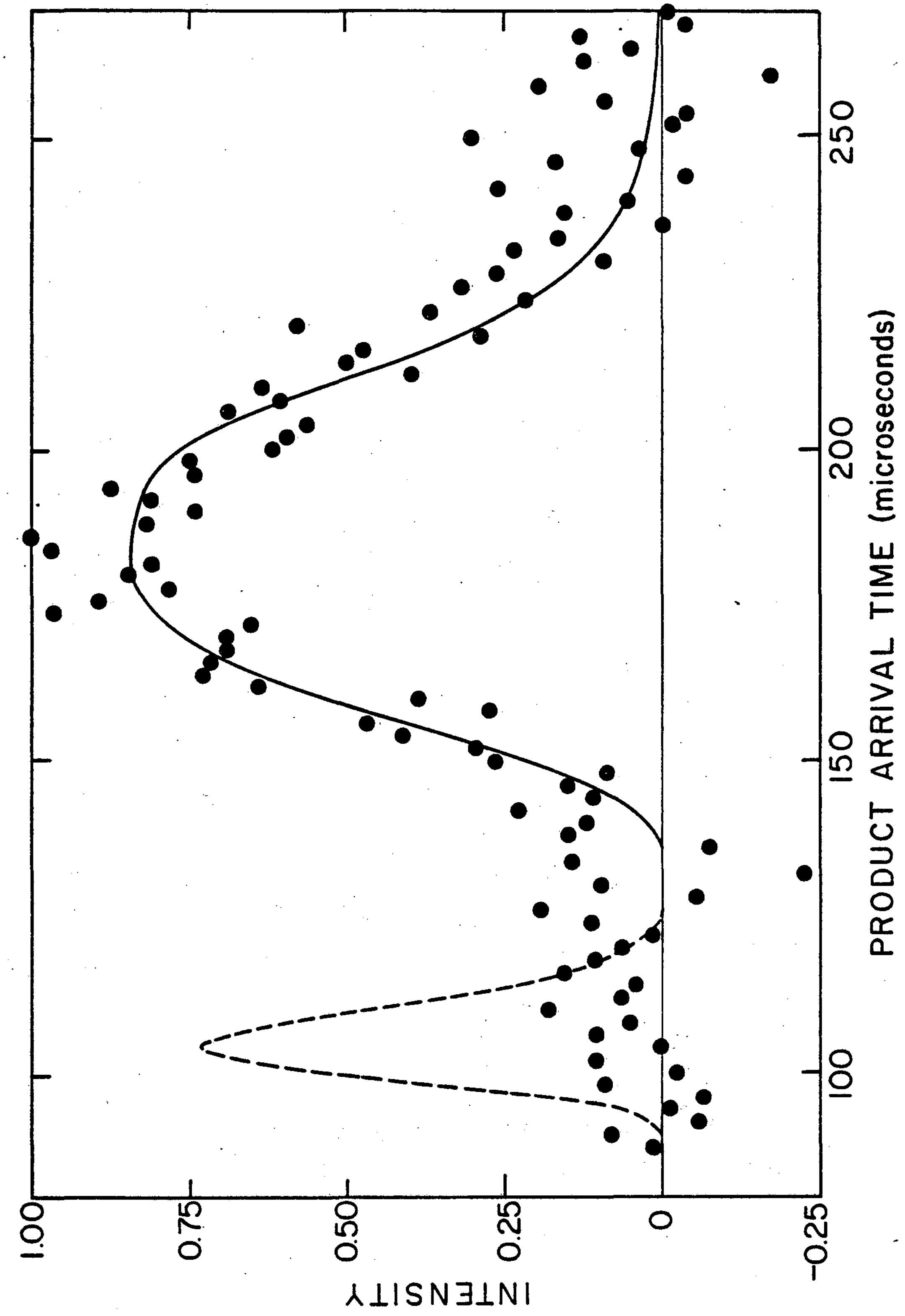
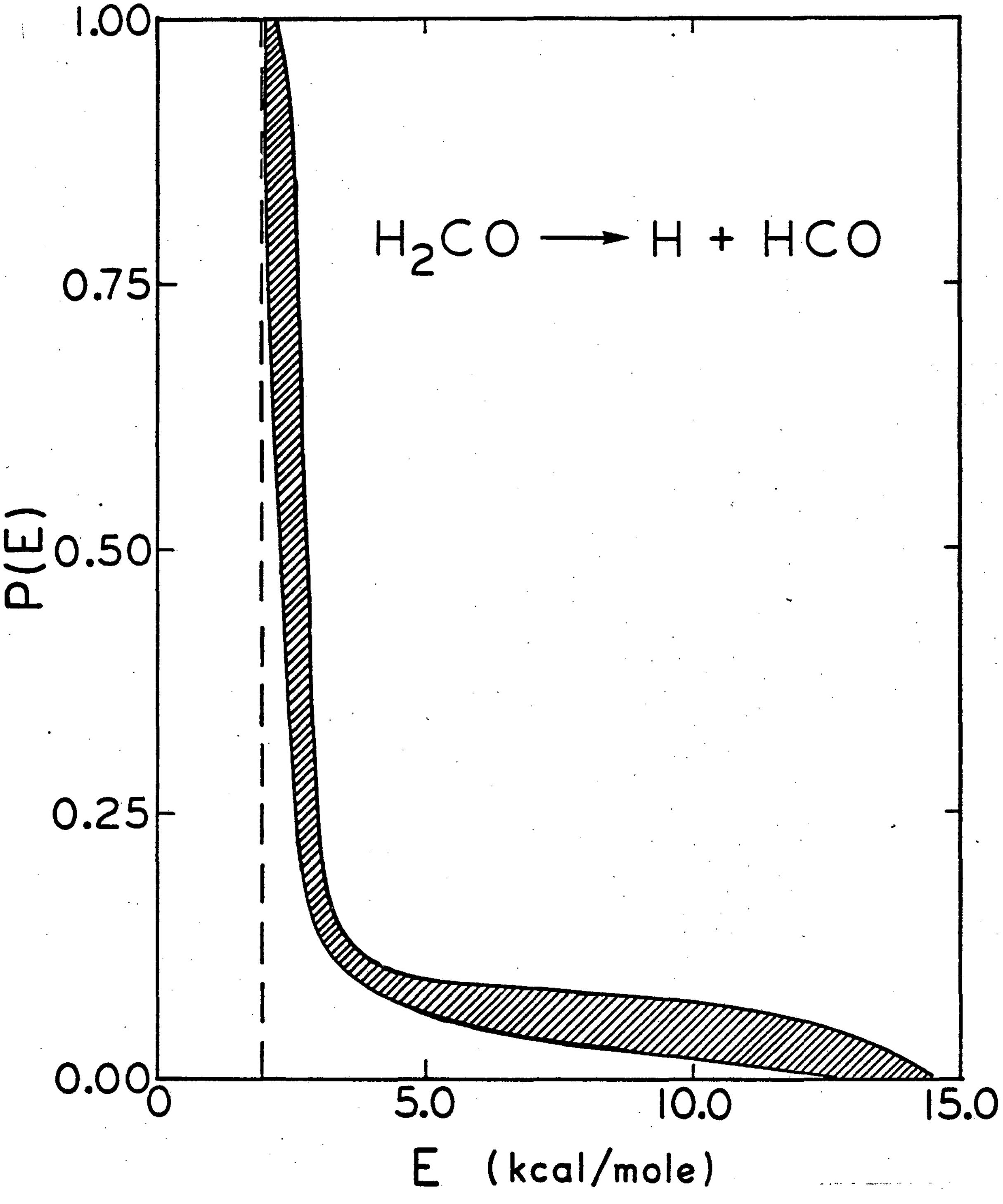

INTENSITY
1.00
0.75
0.50
0.25
0
−0.25
PRODUCT ARRIVAL TIME (microseconds)
100
150
200
250

Fig. 5



$H_2CO \longrightarrow H + HCO$
P(E)
1.00
0.75
0.50
0.25
0.00
0
5.0
10.0
15.0
E (kcal/mole)

Fig. 6

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