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Photodissociation of 2-Bromoethanol  
and 2-Chloroethanol at 193 nm

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**Abstract**

2-bromoethanol and 2-chloroethanol were photodissociated in a molecular beam at 193 nm. Only one primary reaction channel was observed, elimination of the halogen atom, with an average translational energy release of 33 kcal/mol. In the case of 2-bromoethanol, some of the  $C_2H_4OH$  partner fragment survived and some underwent secondary dissociation to produce  $C_2H_4$  and OH. The surviving  $C_2H_4OH$  contained up to 43 kcal/mol of internal energy, far more than the expected  $C_2H_4-OH$  bond energy of ~28 kcal/mol. The initial C-Br recoil occurs with a large exit impact parameter and leaves most of the internal energy in  $C_2H_4OH$  rotation, creating rotationally metastable fragments. The angular distributions of the secondary  $C_2H_4$  and OH products were strongly forward-backward peaked with respect to the primary ( $C_2H_4OH$ ) velocity vector, consistent with the decay of a long-lived complex in which the total angular momentum is perpendicular to the velocity vector and mainly carried away as orbital angular momentum. This effect is

analogous to that observed in the decay of similar long-lived complexes in crossed molecular beams experiments.

## Introduction

The 2-haloethanols are among the simpler molecules with an intramolecular hydrogen bond. Their photodissociation behavior is of interest for several reasons. There now exists a large body of information on the photodissociation of halogen containing compounds,<sup>1-4</sup> and in this case the hydrogen bond to the halogen atom may alter the dissociation dynamics. A likely photoproduct is  $C_2H_4OH$ , the primary product in the reaction of OH and ethylene at low temperatures.<sup>5</sup> If subsequent decay of  $C_2H_4OH$  could be observed through secondary dissociation to  $C_2H_4$  and OH, an improved value of the heat of formation of the  $C_2H_4OH$  radical could be obtained, in the same way that the C-Cl bond strength in  $C_2H_4Cl$  was determined.<sup>2</sup> If not, the photodissociation of 2-bromoethanol might be an efficient source of  $C_2H_4OH$  radicals.

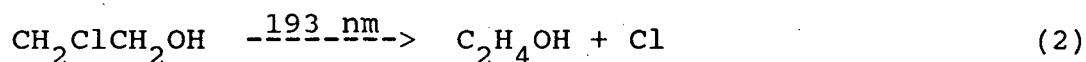
The reaction of OH and ethylene has been studied by Tully in a series of gas cell experiments, using laser induced fluorescence (LIF) to monitor the OH.<sup>6</sup> At low temperatures ( $\leq 500$  K) reaction (1)



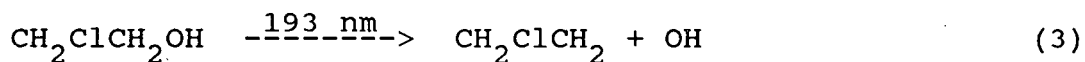
is thought to be the only important channel leading to consumption of OH. The subsequent decay of this adduct occurs slowly and has not been measured. Between 500 and 650 K equilibrium between the forward and reverse reactions is established on a

millisecond timescale and the measured disappearance rate decreases by more than a factor of 15.<sup>6</sup> Only at higher temperatures does H atom abstraction begin to compete effectively with addition.

In an attempt to measure the kinetics of the reverse reaction, Tully dissociated 2-chloroethanol at 193 nm, expecting to see reaction (2)



which produces the "adduct" photolytically. The approach to equilibrium could then be observed from the opposite direction. Unexpectedly, there was a large, immediate rise in the OH signal, which peaked at ~1.5 msec and then began to fall.<sup>7</sup> This could be from several sources, and did not appear to be from equilibration on a much faster timescale than the 100 nsec resolution of the experiment. One possibility was that part of the signal was due to the dissociation of 2-chloroethanol in reaction (3),

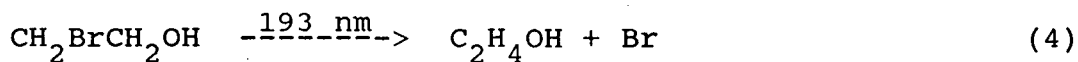


which produces OH directly. This is not implausible, as 193 nm is at the red edge of the first peak in the absorption spectrum of 2-chloroethanol. This transition is thought to be centered on the C-Cl bond, but the threshold for absorption by the R-O-H

group will also be nearby. It is more likely that the initial step in reaction (2) leaves enough internal energy in the  $C_2H_4OH$  for it to fall apart through the reverse of reaction (1) before it has a chance to become thermalized. With a C-Cl bond energy of  $\sim 80$  kcal/mol, a photon energy of 148 kcal/mol, and an adduct stability of  $\sim 28$  kcal/mol with respect to ethylene and OH,<sup>8</sup> a substantial amount of energy must be released into translation for the  $C_2H_4OH$  to be formed below its dissociation limit.

To elucidate this matter, we performed molecular beam photodissociation experiments on 2-chloroethanol at 193 nm to determine the primary photochemical pathways and the translational energy release. Because 2-chloroethanol absorbs very weakly, only reaction (2) could be observed and the only fragment which could be detected with good signal-to-noise (S/N) was  $Cl^+$ . This was sufficient to provide the translational energy distribution ( $P(E_T)$ ) for reaction (2) and thus the internal energy of the  $C_2H_4OH$  fragment. As suspected, large amounts of internal energy were found to remain in the  $C_2H_4OH$ .

In order to further investigate the reaction dynamics of this system, we also photodissociated 2-bromoethanol under similar conditions. The absorption cross-section is much larger and all the fragments could be observed. The only primary channel occurring was reaction (4),





which is analogous to the similar reaction of 2-chloroethanol. Some of the  $C_2H_4OH$  adduct survived and some underwent secondary dissociation through reaction (5).



The angular distribution of the secondary products of this reaction was strongly forward-backward peaked with respect to the primary  $C_2H_4OH$  velocity vector, indicating that the angular momentum of the  $C_2H_4OH$  is perpendicular to its velocity vector and mainly carried away as orbital angular momentum of the secondary products, similar to that observed in the decay of certain long-lived complexes in crossed-beams reactive scattering experiments.

### Experimental

The photodissociation experiments were performed on a crossed laser-molecular beam apparatus, which has been previously described in detail.<sup>9</sup> Briefly, a molecular beam is crossed by a laser and the photodissociation products are detected with a quadrupole mass spectrometer. The molecular beam source is rotatable to allow data collection at angles of 0 to 90°. The detector signal is monitored with a multichannel scaler to allow time-of-flight (TOF) measurements of the velocity distributions of the neutral products.

The beams were prepared by seeding 2-bromoethanol or 2-chloroethanol in helium and expanding the mixture into the source chamber through a .125 mm nozzle. The 2-bromoethanol was held in a bubbler at 46 °C, where it has a vapor pressure of about 4 Torr, with a total pressure of 145 Torr. Great care was taken to eliminate bromoethanol dimers, by heating the nozzle to 180 °C. Formation of dimers was found to readily occur at lower nozzle temperatures, no doubt from the stability derived from the pair of intermolecular hydrogen bonds which can form. The mean velocity of the beam was  $1.2 \times 10^5$  cm/sec with a FWHM spread of 10%. The 2-chloroethanol was kept at 40°C (P = 16 Torr) in the bubbler, with a total stagnation pressure of 130 Torr. The nozzle was heated to 115 °C to give a beam velocity of  $1.1 \times 10^5$  cm/sec with a spread of 12%. It is expected that there were some dimers in the 2-chloroethanol beam, but they did not obscure the single fast peak observed in the TOF spectra.

A Lambda-Physik 103 MSC excimer laser was used with ArF at 193 nm, and focused to a 2 x 5 mm spot at the intersection of the laser and the molecular beam. The laser was unpolarized unless otherwise noted. For measurements with polarized light, approximately 97% polarization was obtained with a pile-of-plates polarizer consisting of 10 UV-grade quartz plates at Brewster's angle.

## Results and Analysis

Very strong signal was detected at a mass-to-charge ratio ( $m/e$ ) of 79 and 81 in the photodissociation of 2-bromoethanol. As shown in fig. 1, there was only a single relatively fast peak in the  $m/e = 79$  TOF spectra, which is due to Br atoms produced in reaction (4). The data were fit using forward convolution techniques<sup>10</sup> to find the  $P(E_T)$  for this channel, which is shown in fig. 2 (upper curve). The  $P(E_T)$  peaks at 33 kcal/mol and releases an average of 33.8 kcal/mol into translation.

The partner fragment from reaction (4),  $C_2H_4OH$ , was detected at  $m/e = 17, 25-27, 29, 31, 43, \text{ and } 45$ . The fast edge of the  $C_2H_4OH$  signal, shown in fig. 3, can be fit with the same  $P(E_T)$ , showing that these two fragments are both from reaction (4). However, there is considerable signal missing from the slow side of the  $m/e = 31$  spectra in fig. 3, based on the  $P(E_T)$  for reaction (4). This is just from the fact that some of the slower  $C_2H_4OH$  is formed with internal energy above its dissociation limit and undergoes secondary dissociation through reaction (5). The  $P(E_T)$  which fit the surviving  $C_2H_4OH$  is shown as the lower curve in fig. 2, and peaks at 36 kcal/mol with an average translational energy release of 36.1 kcal/mol.

The  $P(E_T)$  derived from the Br atoms is the true  $P(E_T)$  for reaction (4), since Br cannot undergo any kind of secondary process. The difference between the two  $P(E_T)$ 's in fig. 2 (shown as the cross-hatched area) represents the primary  $P(E_T)$ .

for those  $C_2H_4OH$  radicals which undergo secondary dissociation. The two  $P(E_T)$ 's are identical on their fast sides, but begin to diverge at 39 kcal/mol. The  $P(E_T)$  for surviving  $C_2H_4OH$  does not drop to zero until 27 kcal/mol, indicating that some of the  $C_2H_4OH$  survives and some dissociates over a range of about 12 kcal/mol. This is strong evidence that both the  $^2P_{1/2}$  and  $^2P_{3/2}$  states (hereafter referred to as  $Br^*$  and  $Br$ , respectively) of  $Br$  are formed, since the spin-orbit splitting in  $Br$  is about 11 kcal/mol.

The  $m/e = 29, 31, 43,$  and  $45$  data were all identical (the best  $S/N$  was at  $m/e = 31$ ), showing a single peak, but at lower masses there was evidence of the secondary dissociation products of  $C_2H_4OH$ . TOF spectra with signal from reactions (4) and (5) at  $m/e = 17$  and  $26$  are shown in fig. 4. A simple 2-dimensional velocity diagram analysis showed that these were consistent through momentum conservation with  $OH$  and  $C_2H_4$  from reaction (4). Actually fitting these data was considerably more complicated, however. The primary  $P(E_T)$  used corresponded to the difference between the two  $P(E_T)$ 's in fig. 2. It was quickly found that no simple secondary  $P(E_T)$  could match the peaks in the TOF spectra, especially those at longer times than the primary photodissociation signal. This is a consequence of the extensive "smearing out" in secondary dissociation, where all combinations of primary and secondary velocities and angles (in plane as well as out-of-plane) are averaged over. The molecular beam and the detector axis (which intersect at the

point where the laser beam also crosses) form a plane, and any primary dissociation out of that plane is not detected. For secondary dissociation, however, the primary step can be out-of-plane and the secondary step can bring the fragment back into the plane; for a fragment to be detected only its resultant velocity vector need be in the plane. Thus, any structure in the data is easily wiped out, and one would expect a single broad peak in the secondary TOF spectrum.

The secondary dissociation data strongly suggested forward-backward peaking with respect to the initial c.m. velocity vector of the primary product, since it is otherwise impossible to get secondary peaks both at shorter and longer times than the primary peak. With an isotropic angular distribution, the calculated secondary signal has only a single peak appearing slightly faster than the primary signal. The two peaks were reproduced using a strongly forward-backward peaked secondary angular distribution to fit the data, as shown in fig. 5. This peaking in the secondary angular distribution is due to the fact that the Br departs with a large exit impact parameter and the  $C_2H_4OH$  is left highly rotationally excited, with its angular momentum vector perpendicular to the velocity vector, as will be discussed later.

Since the  $C_2H_4OH$  dissociated with a  $\sim 20$  kcal/mol range of internal energies and released a large amount of energy into translation, the primary and secondary  $P(E_T)$ 's are correlated. Not surprisingly, since the total energy is conserved, using a

single secondary  $P(E_T)$  for all dissociating primary products with various initial velocities, both fragments could not be fit simultaneously. This was resolved by using a secondary  $P(E_T)$  of the form loosely related to that expected from a statistical theory of unimolecular decomposition

$$P(E_T) = a(E_T - b)^r (E_{\text{tot}} - E_T)^w \quad (6)$$

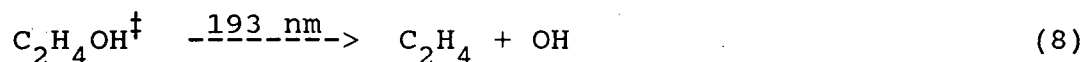
where  $a$  is a normalization constant,  $b$ ,  $r$ , and  $w$  are fitting parameters corresponding in an ideal case to a barrier height, the dimensionality of the reaction coordinate, and the number of active modes, respectively. In practice, except for  $b$ , it is doubtful that they have much physical significance at all.  $E_{\text{tot}}$  is the total excess energy available to the secondary products, calculated from the equation

$$E_{\text{tot}} = h\nu - \Delta H_1 - \Delta H_2 - E_T(1) \quad (7)$$

where  $\Delta H_1$  and  $\Delta H_2$  are the endothermicities of the primary and secondary reactions, and  $E_T(1)$  is the energy released into translation in the primary reaction. The data analysis program steps along  $E_T(1)$  and creates a new secondary  $P(E_T)$  at each available energy. This conserves energy properly and correctly normalizes the  $P(E_T)$ 's. In theory,  $r$  and  $w$  should perhaps change as function of  $E_{\text{tot}}$ , but this was not found to be necessary. With a total available energy for translation in

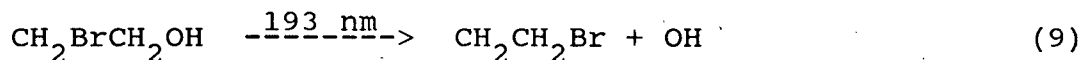
reactions (4) and (5) of 54 kcal/mol, the data could be fit with  $b = 6$ ,  $r = 1$ , and  $w = 1.5$ . This released a peak energy of between 9 and 18 kcal/mol into translation in the secondary step, depending on the energy release in the primary process.

At very fast times in the  $m/e = 17$  and 26 TOF spectra there is signal which cannot be from the secondary dissociation of  $C_2H_4OH$  with only one photon. It is likely from the secondary photodissociation of  $C_2H_4OH$  in reaction (8), where the



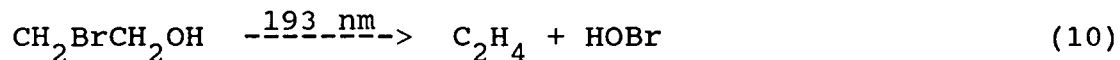
$C_2H_4OH^\dagger$  from reaction (4) has a wide range of internal energies. Power dependence measurements showed that the  $Br^+$  signal was linear with laser power and that the primary reaction is a one-photon process. Little power dependence data were taken at  $m/e = 17$  and 26, but they seemed to show that the fastest signal changed in relative size with respect to the main peaks, consistent with what one would expect for reaction (8).

There was no evidence of any other reactions. No signal was observed at  $m/e = 93$  ( $CH_2Br^+$ ) or any higher mass, showing that there was no such reaction analogous to (3) as (9) occurring.



Signal from  $HOBr$  was also checked for to ensure that there was

no contribution from reaction (10). The strongest evidence,



however, is the single, momentum-matched peaks in the  $m/e = 29$ , 31, 43, 45, 79, and 81 TOF spectra. If any other primary reaction were occurring it would certainly produce additional signal at one or more of these fragments.

Polarization measurements were made of the signal from Br, since it provides a complete picture of the primary photodissociation reaction. Data were taken with the laser horizontally and vertically polarized (with respect to the detector) at 20° and 40°. These laboratory angles include a wide range of c.m. recoil angles and any anisotropy effects should be obvious. Between horizontal and vertical polarization, the signal levels changed less than 1% and the shapes of the TOF spectra were absolutely identical, indicating that reaction (4) is completely isotropic.

Signal from the photodissociation of 2-chloroethanol could only be observed at  $m/e = 35$  ( $\text{Cl}^+$ ). The shape of the peak, shown in fig. 6 (top), is quite similar to that of  $\text{Br}^+$ , and is likely to be solely from reaction (2). The  $P(E_T)$  which fits this data also peaks at 33 kcal/mol and is shown in fig. 6 (bottom). Very weak signal could be observed at a few masses corresponding to the  $\text{C}_2\text{H}_4\text{OH}$  fragment, but it was insufficient for any kind of analysis.



## Discussion

A. Energy Release and Primary Dissociation Dynamics. In the photodissociation of 2-bromoethanol, only one primary reaction channel was observed, loss of Br through reaction (4). A large amount of the available energy was released into translation and the  $P(E_T)$  peaked far from zero. The photon energy at 193 nm is 148 kcal/mol and assuming a C-Br bond energy of 68 kcal/mol,<sup>11</sup> the total available energy is about 81 kcal/mol, including 1 or 2 kcal/mol from vibrational energy in the molecule which is not relaxed in the supersonic expansion. Of this, an average of 33.8 kcal/mol or 42% appears in translation. In comparison, in the photodissociation of 1,2-C<sub>2</sub>F<sub>4</sub>BrI at 193 nm, where one reaction channel involved breaking a C-Br bond of approximately equal strength, an average of only 25 kcal/mol was released into translation.<sup>3</sup> Presumably this is mainly due to the greater number of low frequency vibrational modes in the C<sub>2</sub>F<sub>4</sub>I product.

In neither case could the production of different spin-orbit states of Br (Br\* is higher than Br by 10.54 kcal/mol) be distinguished. The translational energy distributions are too broad to resolve the two states, unlike in the photodissociation of similar molecules containing C-I bonds, where the much higher spin-orbit splitting of the I atoms (21.7 kcal/mol) allowed the two different states to be resolved in TOF spectra.<sup>2,4</sup>

The large release of translational energy reflected in the  $P(E_T)$  is suggestive of a direct dissociation from a repulsive excited electronic state. This is consistent with previous interpretations of excitation at 193 nm as being an  $(\sigma^* \leftarrow n)$  transition on the C-Br bond,<sup>3</sup> which is directly repulsive and has a lifetime of less than a picosecond. Therefore it is surprising that no anisotropy effects were observed in dissociation with polarized light. The photodissociation of 1,2- $C_2F_4BrI$  was found to have a strongly parallel polarization dependence,<sup>3</sup> with an anisotropy parameter of 1.85, close to the limiting value of 2 for a purely parallel dissociation.<sup>12</sup> It is unlikely that this lack of anisotropy in the photodissociation of 2-bromoethanol is due to a long dissociation lifetime, since the initial excitation should still be a directly repulsive transition localized on the C-Br bond. Rather, because of the intramolecular OH-Br hydrogen bonding, as the molecule dissociates it may undergo large geometrical rearrangements and dissociate with a wide range of impact parameters, thus wiping out any anisotropy in the dissociation. It is also possible that the initial transition may have both parallel and perpendicular components.

2-bromoethanol and 2-chloroethanol exist in the gas phase as intramolecularly hydrogen-bonded monomers in the gauche conformation.<sup>13</sup> The XCOO dihedral angles ( $X = Cl, Br$ ) are both close to  $64^\circ$ , with the hydroxyl proton-X bond lengths about 0.5 Å less than the sum of the atomic van der Waals radii,<sup>13</sup>

indicating a strong interaction. Experimental studies and theoretical calculations have indicated that this structure is about 2 kcal/mol more stable than the trans configuration,<sup>14</sup> where the halogen and the OH are on opposite sides. In a supersonic expansion, essentially all the molecules should be in the gauche conformation, though there is also the possibility of forming dimers with two intermolecular hydrogen bonds.

In the dissociation of 2-bromoethanol, if the Br atom departs along the direction of the C-Br bond, the exit impact parameter will be about 1.36 Å.<sup>13</sup> Since the molecules initially have little rotational energy, the final orbital angular momentum must be approximately equal (and opposite) to the rotational angular momentum of the C<sub>2</sub>H<sub>4</sub>OH fragment,

$$L = \mu v b = -J \quad (11)$$

where  $\mu$  is the reduced mass between the two fragments,  $v$  is the relative velocity vector and  $b$  is the exit impact parameter. The peak energy release for reaction (4) is 33 kcal/mol, which corresponds to a relative velocity of  $3.1 \times 10^5$  cm/sec. With a reduced mass  $\mu = 28.8$  a.m.u., the most probable value of  $J$  will be 190. The moment of inertia of C<sub>2</sub>H<sub>4</sub>OH (about the axis perpendicular to the CCO plane) is  $7.6 \times 10^{-23}$  g·Å<sup>2</sup> which leads to a rotational energy of 38 kcal/mol. This corresponds to 89% of the available energy in rotation and translation for the production of Br, and all the energy in rotation and transla-

tion if  $\text{Br}^*$  is produced. For higher translational energies, energy conservation would be violated with an exit impact parameter of 1.36 Å. Therefore the CBr angle must widen during dissociation, giving a smaller value of  $b$  and less energy in rotation. In all cases, a large fraction of the available energy is channeled into translation and rotation, and comparatively little energy can remain as vibration in the  $\text{C}_2\text{H}_4\text{OH}$  product.

With this information, the lack of measurable anisotropy becomes more understandable. Since the 2-bromoethanol must dissociate from a range of geometries with different amounts of energy in translation and rotation in order to conserve energy and angular momentum, the anisotropy will be sharply reduced from that expected from a single dissociation geometry. The effect of the hydrogen-bonded proton is unclear, but it should exert additional torque between the Br and  $\text{C}_2\text{H}_4\text{OH}$  fragments during dissociation which would further smear out the anisotropy. The hydrogen-bonding interaction between the O-H and the Br atom could also perturb the electronic transitions on the C-Br bond, and induce additional parallel or perpendicular components.

B. Secondary dissociation. The spontaneous (without absorption of a second photon) secondary dissociation of the  $\text{C}_2\text{H}_4\text{OH}$  fragment occurs with very interesting dynamics. Since reaction (5) is endothermic by 28 kcal/mol,<sup>8</sup> unless  $\text{Br}^*$  was produced and at least 42 kcal/mol went into translation (or

53 kcal/mol in translation with Br produced) the  $C_2H_4OH$  product should be unstable with respect to  $C_2H_4$  and OH. As expected, this secondary reaction channel was observed. It was hoped that by observing the threshold for surviving  $C_2H_4OH$ , a better value for the endothermicity of reaction (5) could be obtained, similar to the work of Minton *et al.* on  $C_2H_4Cl$ .<sup>2</sup> However,  $C_2H_4OH$  with translational energies as low as 27 kcal/mol survived the  $\sim 100$   $\mu$ sec flight time to the ionizer. It is unlikely that this implies a binding energy of  $81 - 27 - 11 = 43$  kcal/mol for  $C_2H_4OH$ . A much more plausible explanation is that the high rotational energy of the  $C_2H_4OH$  fragment creates the polyatomic analogue of a centrifugal barrier to dissociation. The rotational energy cannot all be used to break the C-O bond, allowing the detection of some metastable  $C_2H_4OH$ . A simple calculation assuming a 4 Å C-O bond length at the transition state showed that 7.2 kcal/mol remained in overall rotation with  $J = 190$ . Of this, the  $C_2H_4$  accounted for 3 kcal/mol. In addition, since the primary dissociation event does not occur in a plane, some of the rotational energy will be in "prolate" motion of the  $C_2H_4OH$  ( $K > 0$ ) and will be unable to couple with the reaction coordinate or participate in the dissociation to  $C_2H_4$  and OH. Finally, there may be a slight electronic barrier to dissociation as the C=C double bond forms. This is consistent with the 5-7 kcal/mol barrier in the secondary  $P(E_T)$ .

The secondary dissociation products of  $C_2H_4OH$  showed a high degree of anisotropy in their angular distribution. The  $C_2H_4$  and OH were peaked strongly forward and backward with respect to the initial C-Br recoil direction. This would be expected for the secondary dissociation of a primary photo-product with large amounts of rotational and translational energy, which to our knowledge has not been previously observed. The initial angular momentum of the 2-bromoethanol is close to zero. As has been described, the primary reaction occurs with a large exit impact parameter, leading to high rotational excitation of the  $C_2H_4OH$  fragment. Though the primary dissociation does not occur within a planar OCCBr framework, the initial torque will be in the CCB<sub>r</sub> plane, and should lead to the rotational angular momentum being approximately perpendicular to this plane, or in other words  $\mathbf{v}$  will be perpendicular to  $\mathbf{J}$ . Secondary dissociation then occurs preferentially along a "pinwheel" perpendicular to  $\mathbf{J}$ . Since all azimuthal orientations of  $\mathbf{J}$  perpendicular to  $\mathbf{v}$  are equally likely in a beam of isotropically oriented molecules, this causes secondary signal intensity to build up preferentially along the poles, parallel and antiparallel to  $\mathbf{v}$ . This is just the photodissociation analog to the angular distribution of reaction products from the decay of long-lived complexes in reactive scattering experiments first observed by Miller, Safron, and Herschbach.<sup>15</sup> In their alkali atom-alkali halide exchange reactions, the angular momentum of the

long-lived complexes was mainly from the orbital angular momentum of the reactants and was carried away as product orbital angular momentum, giving a forward-backward peaked angular distribution.

In order to observe this forward-backward peaking, the  $C_2H_4OH$  must be long-lived with respect to the rotational period (0.24 psec with  $J = 190$ ). Since we observed metastable  $C_2H_4OH$  which survived for over 100  $\mu$ sec, some of these complexes are long-lived indeed! There is one important difference between the secondary dissociation of  $C_2H_4OH$  in this experiment and the long-lived complexes observed in crossed-beams scattering experiments. In a crossed-beams experiment, the initial beam velocities are oriented in the laboratory frame. The initial orbital angular momentum  $L$  is perpendicular to the relative velocity vector and the forward-backward scattering appears in the c.m. and laboratory angular distributions. In the photodissociation of 2-bromoethanol, the primary reaction producing  $C_2H_4OH$  is isotropic, and therefore any secondary angular distribution of  $C_2H_4$  and OH with respect to the initial Br  $C_2H_4OH$  velocity vector will still leave an isotropic c.m. angular distribution. The forward-backward peaking is with respect to the  $C_2H_4OH$  velocity vector and will instead manifest itself in the TOF spectra, with slight effects possible in the laboratory angular distribution. Instead of the broad, featureless peaks typical of isotropic secondary dissociation,<sup>3,16</sup> the signal peaks at longer and shorter times (slower

and faster lab velocities) than the primary peak from  $C_2H_4OH$ . This is because the secondary products are preferentially scattered parallel and antiparallel (forward-backward) to the initial primary recoil velocity.

C. Comparison with bulk-phase kinetic studies. It is now clear that in the photodissociation of 2-bromoethanol, some of the initially formed  $C_2H_4OH$  will fall apart to  $C_2H_4$  and OH. In this experiment, about 2/3 of the  $C_2H_4OH$  adduct decomposed. Actually, if  $C_2H_4OH$  is only bound by 28 kcal/mol, there should have been even more secondary decomposition, but some of the  $C_2H_4OH$  was rotationally metastable. In a gas cell experiment, some of the rotational energy could be transformed into vibrational energy by collisions, but the nascent  $C_2H_4OH$  radicals are much more likely to simply lose energy to the bath gas. It is important to note that no OH was formed in the primary photodissociation of 2-bromoethanol, but that a small amount of  $C_2H_4OH$  underwent secondary photodissociation to produce  $C_2H_4$  and OH.

Among the surviving  $C_2H_4OH$ , the relative amounts of stable and metastable products are difficult to estimate as it is not known how much corresponds to Br and how much to spin-orbit excited  $Br^*$ , and the stability of  $C_2H_4OH$  may be incorrect. Since the difference in energy between the onset of  $C_2H_4OH$  dissociation and the point where it all dissociates is approximately the spin-orbit splitting, it is likely that both states of Br are produced. For those primary dissociation



events producing Br, almost all the  $C_2H_4OH$  should undergo secondary dissociation since about 53 kcal/mol must go into translation for the adduct to be stable. Because of the two problems just mentioned, it is difficult to reach a definite conclusion.

In the photodissociation of 2-chloroethanol to produce Cl and  $C_2H_4OH$  through reaction (2), the  $P(E_T)$  was almost identical to that for 2-bromoethanol. For Cl atoms, however, the spin-orbit splitting is only 2 kcal/mol and can almost be neglected. Assuming a C-Cl bond energy of 80 kcal/mol, the minimum translational energy for stable  $C_2H_4OH$  is  $148 - 80 - 28 = 40$  kcal/mol, or 38 kcal/mol for  $Cl^*$  formation. Therefore, the part of the  $P(E_T)$  corresponding to Cl atom production with more than 40 kcal/mol in translation must yield stable  $C_2H_4OH$ . Below 40 (or 38) kcal/mol the  $C_2H_4OH$  must be either be metastable or dissociate, unless  $C_2H_4OH$  is more strongly bound than is currently believed. Unfortunately, no partner  $C_2H_4OH$  or any secondary dissociation fragments were detected, which could have shed light on this problem.

### Conclusions

In the photodissociation of 2-bromoethanol and 2-chloroethanol at 193 nm, only one primary channel, halogen atom elimination, was observed, with a translational energy distribution peaking near 33 kcal/mol. Substantial rotational excitation in both cases resulted from the large exit impact

parameters and high recoil velocities. In the photodissociation of 2-bromoethanol, the observation of stable  $C_2H_4OH$  with as little as 27 kcal/mol in translation indicates that  $C_2H_4OH$  may be bound by up to 43 kcal/mol, or much more likely that some of the  $C_2H_4OH$  is rotationally metastable as the result of a centrifugal barrier to dissociation. The  $C_2H_4OH$  which underwent secondary dissociation producing  $C_2H_4$  and OH was found to have a strongly forward-backward peaked secondary angular distribution as a result of angular momentum constraints. This was compared to previous crossed molecular beams studies of long-lived complexes.

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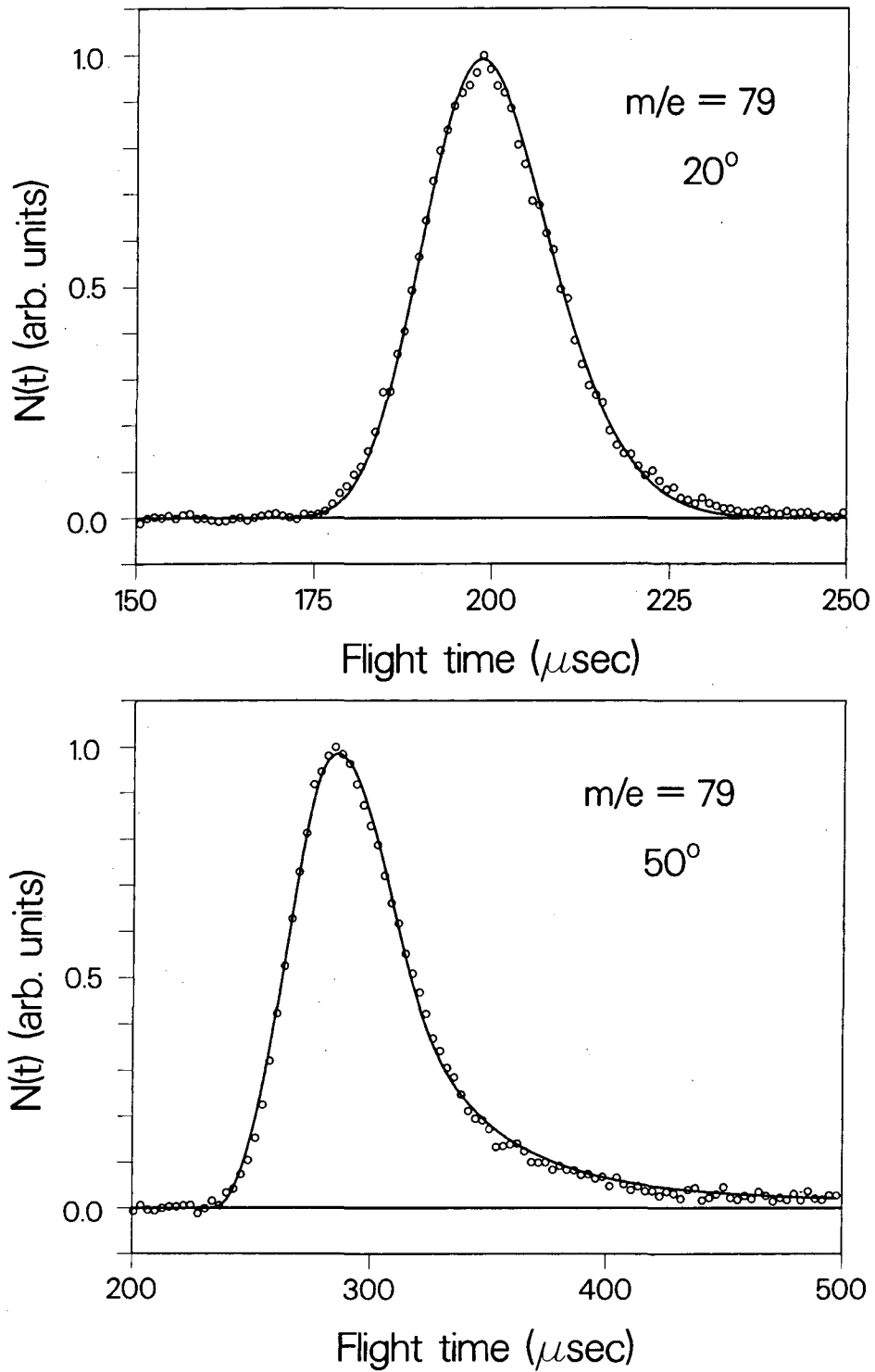
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### Figure Captions

- Fig. 1. TOF spectra of Br atoms from reaction (4) at 20° and 50° from the molecular beam. The scattered circles are the experimental data and the lines show the fits using the  $P(E_T)$  in fig. 2.
- Fig. 2. The upper curve is the  $P(E_T)$  for reaction (4), derived from the Br data shown in fig. 1. The lower curve, starting at 27 kcal/mol, represents the  $P(E_T)$  for the  $C_2H_4OH$  from reaction (4) which survives to the detector. The cross-hatched area corresponds to  $C_2H_4OH$  which underwent secondary dissociation.
- Fig. 3. TOF spectra of  $C_2H_4OH$  from reaction (4) at  $m/e = 31$  detected at 20° and 50° and fit with the  $P(E_T)$  shown as the lower curve in fig. 2.
- Fig. 4. TOF spectra of the secondary dissociation products of reaction (5). Top:  $m/e = 26$  from  $C_2H_4$  at 20°. Bottom:  $m/e = 17$  from OH at 20°. The narrow peaks near 130  $\mu$ sec are the contribution of surviving  $C_2H_4OH$  from reaction (4). The broader peaks are products of the secondary reaction (5), fit with the functional form of the  $P(E_T)$  as described in the text.
- Fig. 5. Secondary angular distribution used to fit the data shown in fig. 4 from reaction (5). 0° corresponds to the secondary velocity parallel to the velocity of the primary fragment which produced it.

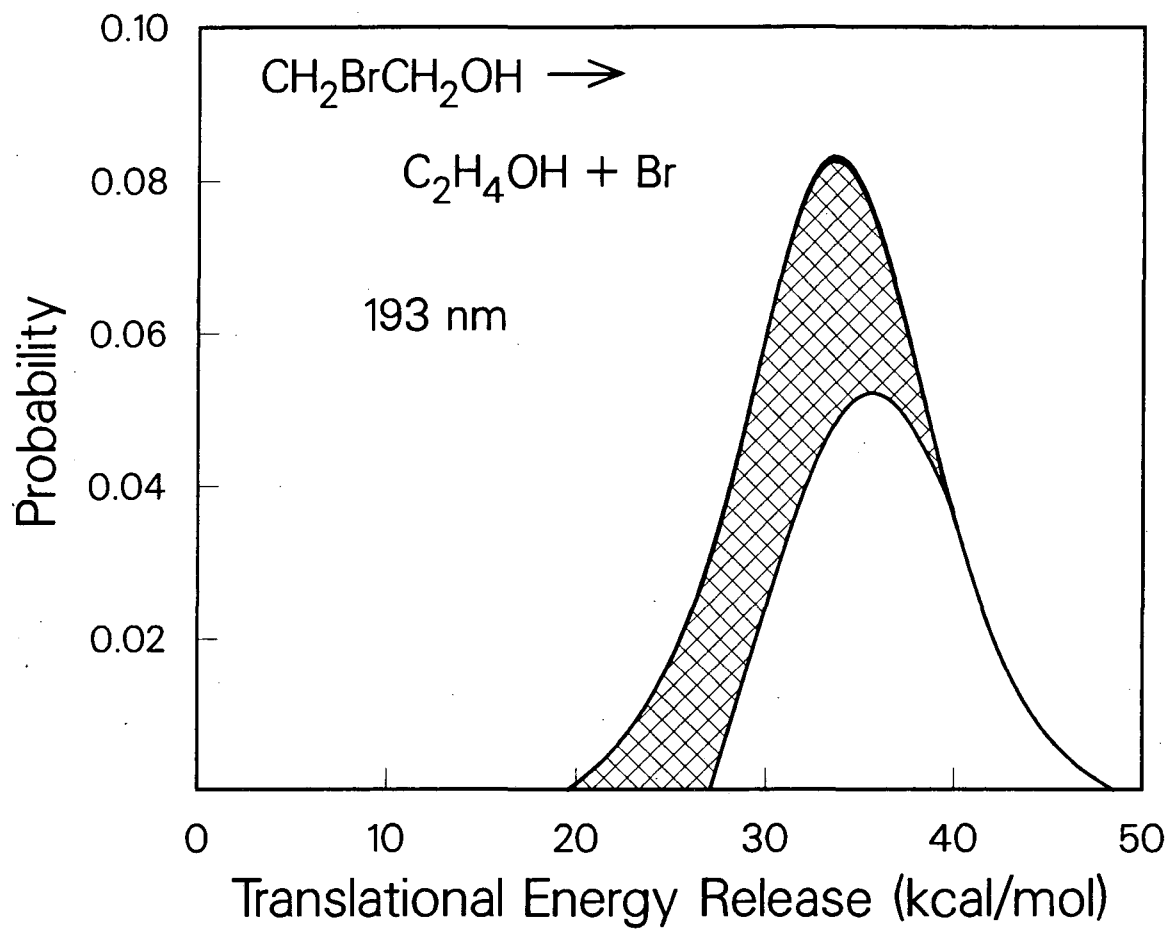
Fig. 6. Top: TOF spectrum of Cl atoms from reaction (2) at  $20^\circ$ . The data are fit with the  $P(E_T)$  shown below. Bottom:  $P(E_T)$  for reaction (2) derived from the  $m/e = 35$  data above.



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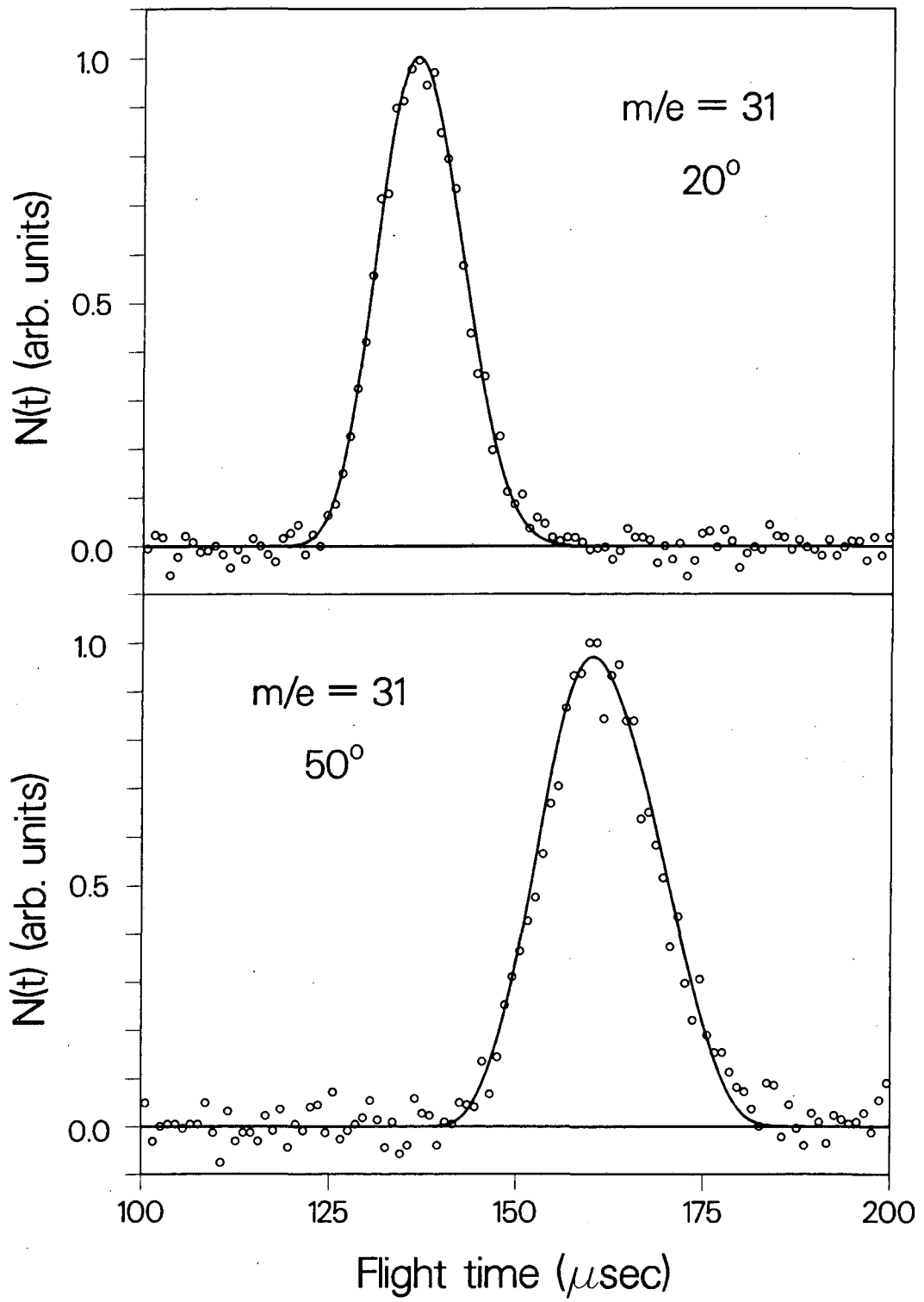
Fig. 1





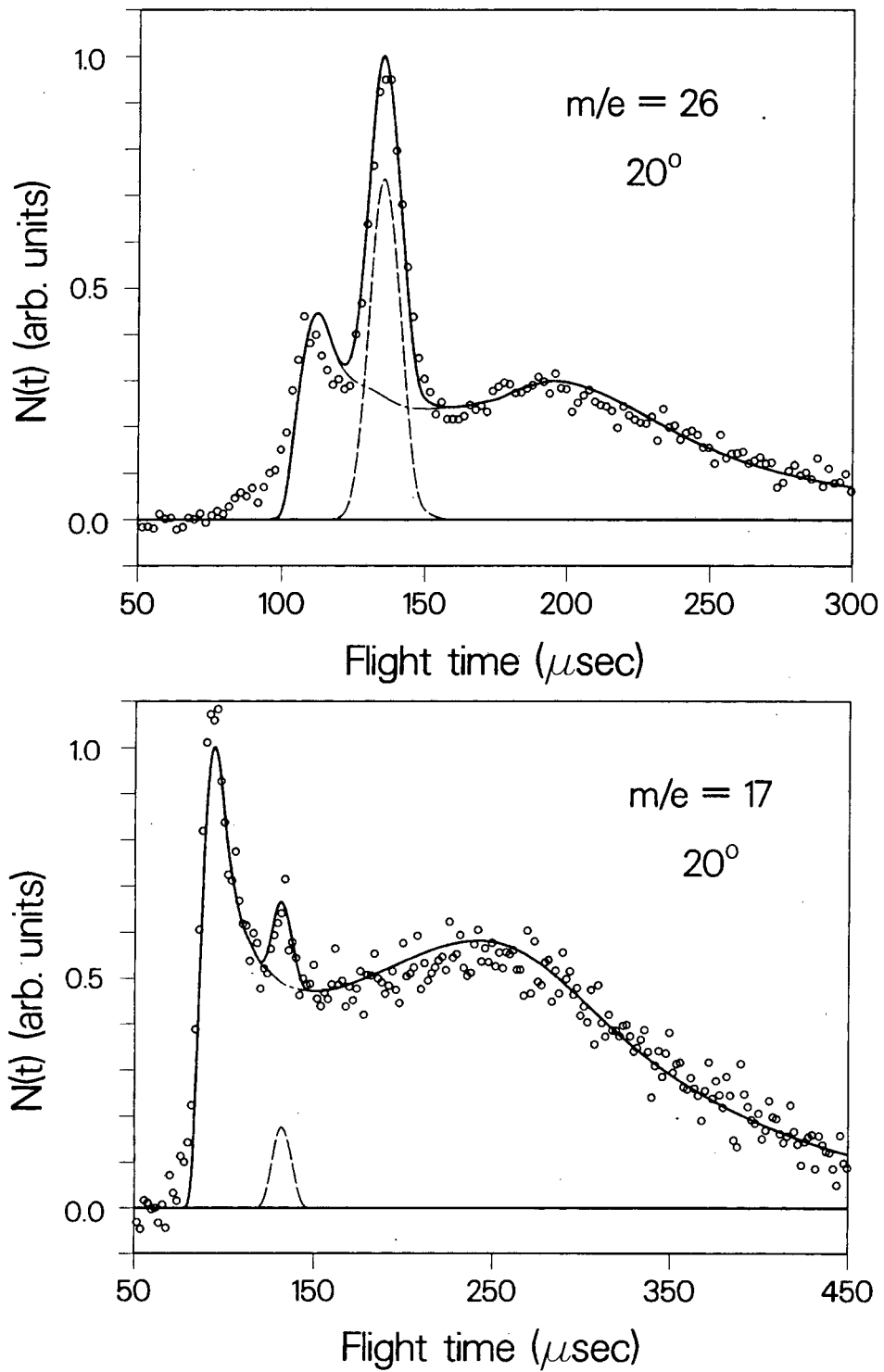
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Fig. 2



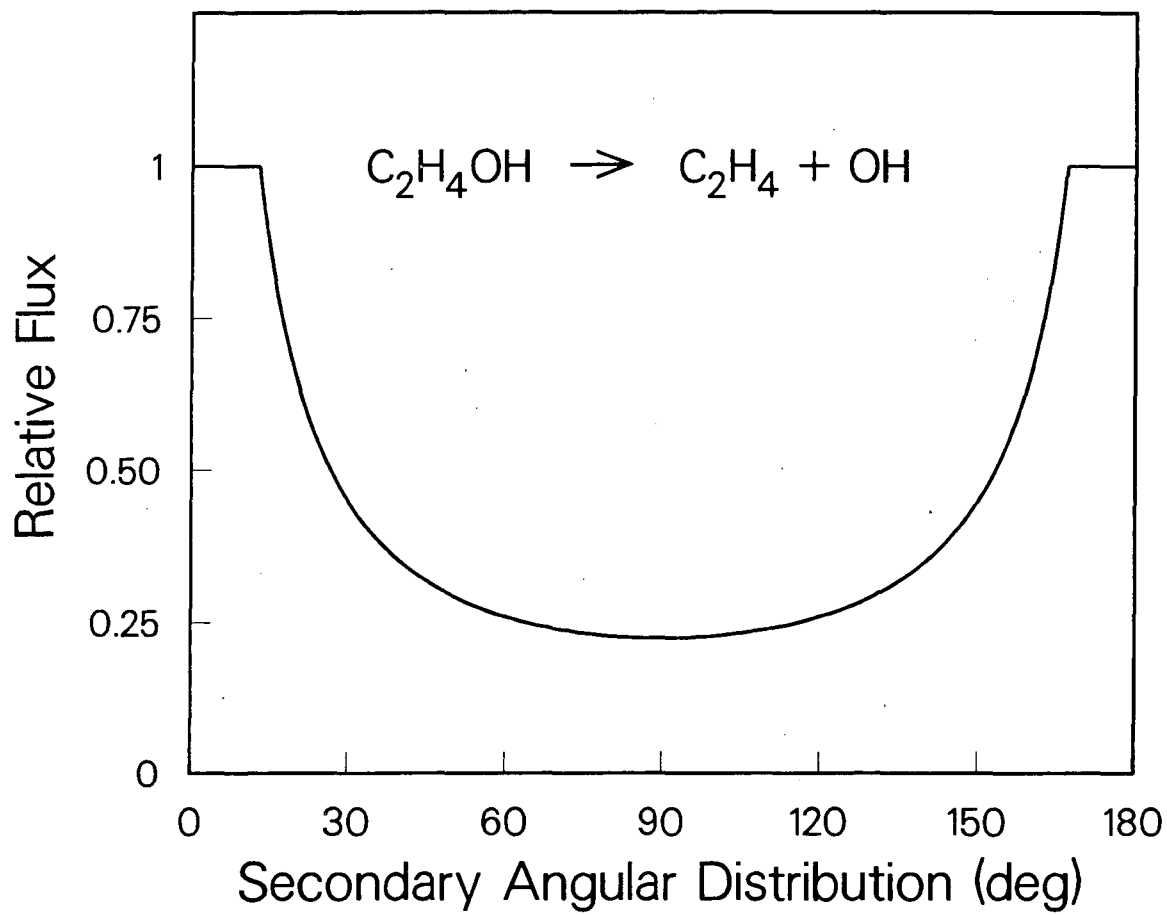
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Fig. 3



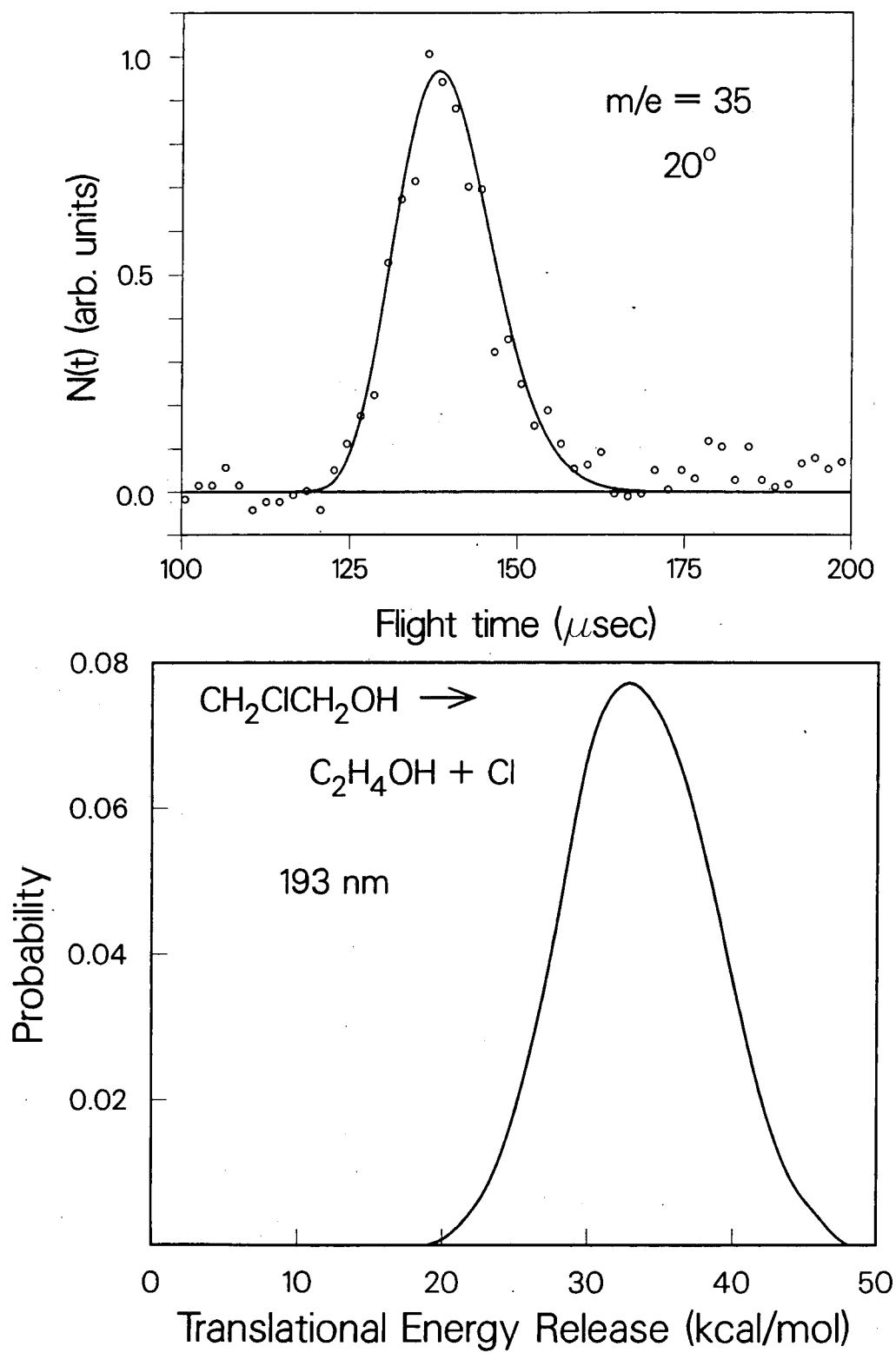
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Fig. 4



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Fig. 5



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Fig. 6

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