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**PRODUCTION AND PHOTODISSOCIATION OF  $\text{CCl}_3$   
RADICALS IN A MOLECULAR BEAM**

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**Production and Photodissociation of  $\text{CCl}_3$   
Radicals in a Molecular Beam**

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**Abstract**

We have produced a pulsed supersonic beam of  $\text{CCl}_3$  radicals by photolyzing  $\text{CCl}_4$  at 193 nm inside a teflon nozzle. The radicals were thermalized by a buffer gas, then expanded out the end of the nozzle. Cold  $\text{CCl}_3$  radicals were photodissociated at 308 nm and the product velocity distributions were measured by time-resolved mass spectrometry. Only one primary reaction was observed,  $\text{CCl}_3 \rightarrow \text{CCl}_2 + \text{Cl}$ , with an average kinetic energy release of 13 kcal/mol. Some of the  $\text{CCl}_2$  absorbed a second photon to produce  $\text{CCl} + \text{Cl}$ .

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## Introduction

There has long been great interest in the properties and reactions of polyatomic radicals.<sup>1</sup> These open-shell species are key intermediates in combustion, atmospheric chemistry, and many other reactions. Because of their generally high reactivity, they tend to be transient species and must usually be produced directly prior to study.

Much effort has been directed toward producing radicals,<sup>2</sup> in order to elucidate their structures, reactivities, and other properties. In previous molecular beam photofragmentation experiments, we have found evidence of the secondary photodissociation of primary radical fragments, such as  $C_2H$  (from acetylene)  $\rightarrow C_2 + H$ ,<sup>3</sup> and with  $CH_2BrI$ .<sup>4</sup> Because the initial radical fragments are typically formed with a wide range of angles, velocities, and internal energies (in sharp contrast to a well-collimated molecular beam), the information obtainable on the secondary dissociation dynamics is limited. It would be a considerable improvement to photodissociate internally cold radicals directly in a molecular beam, where they would start with a narrow (and measurable) velocity and angular distribution. In addition to photodissociation, this source could be used for spectroscopy or other experiments.

Several groups have previously worked on the production of radicals in a supersonic beam. Smalley and coworkers developed a radical source attached to the end of a pulsed valve.<sup>5</sup> Gas from the pulsed valve travels down a narrow channel intersected by a

transverse hole and then expands out the end. At a fixed delay after the valve opens, a laser beam passes through the transverse hole, producing radicals from a precursor molecule. The radicals are rapidly thermalized by collisions with a buffer gas and then cooled in a supersonic expansion. The transverse hole allowed some of the radicals to escape out the sides, but this was estimated to be a minor loss.<sup>6</sup> With this source, spectra of methylene and methoxy radicals, as well as methoxy complexed with argon, were obtained.<sup>5</sup>

In a similar way, Andresen et al. constructed a two-stage source of OH radicals, using a quartz tube mounted to the end of a pulsed valve.<sup>7</sup> A UV laser beam crosses the tube, producing OH from  $\text{HNO}_3$  or  $\text{H}_2\text{O}_2$ . The OH radicals were used to characterize the supersonic expansion process and for inelastic scattering experiments.<sup>7</sup> Sappey and Weisshaar used a source of this type for spectroscopy experiments but found it difficult to produce polyatomic radicals.<sup>8</sup> Miller and coworkers have also generated radicals in a jet, by crossing a supersonic expansion with an electron beam or a laser.<sup>9</sup>

For the high number densities needed in photodissociation experiments which measure fragment velocity and angular distributions, we found it necessary to confine the initial photolysis products before the expansion. We observed that for polyatomic radicals, a quartz assembly, using either a tube or a square channel constructed of quartz plates, tended to accumulate deposits, ultimately either blocking the laser beam or

shattering. Our final source design was essentially the same as that of Smalley and coworkers,<sup>5</sup> but used a pulsed valve with higher throughput.

Trichloromethyl ( $\text{CCl}_3$ ) radicals have been produced by several methods, including photolysis.<sup>10-12</sup> The matrix isolation IR spectrum of  $\text{CCl}_3$  has been observed,<sup>10</sup> and though there have been somewhat conflicting reports of its electronic spectrum,<sup>11,12</sup> it definitely absorbs at longer wavelengths than  $\text{CCl}_4$ .

### **Experimental**

The experiments were conducted in a crossed molecular beams apparatus,<sup>13</sup> modified for the photodissociation of radicals as shown in fig. 1. The pulsed valve, constructed from a Physik-Instrumente piezoelectric crystal,<sup>14</sup> was mounted in a singly differentially pumped source chamber. It was crossed by the output of a Lambda-Physik excimer laser which entered through a lens in the main chamber door and passed into the source chamber through an aperture in a tube welded to the differential wall. The nozzle was constructed out of teflon to fit over the end of the pulsed valve "snout", where it was held in place with set screws. A 1.5 mm dia. channel was reamed out along the axis for the gas flow from the pulsed valve, and a 1x3 mm transverse slot was cut through the nozzle to allow the focused excimer laser to irradiate the gas pulse. After the initial photolysis, any radicals formed were thermalized before undergoing a supersonic expansion into the source chamber. The expansion was collimated by a 1.5 mm dia. conical skimmer to give a molecular beam with a

nominally 5° angular divergence. The beam was then crossed by the focused output of a second Lambda-Physik excimer laser, entering through what is normally the secondary molecular beam source. Dissociation products were detected by a rotatable mass spectrometer, and time-of-flight (TOF) spectra were recorded with a multichannel scaler.

The pulsed valve and lasers were synchronously fired in sequence, with typical delays of 200-300  $\mu$ sec between the pulsed valve and the source laser, and another 50-100  $\mu$ sec before the second laser. To measure the beam velocity, the pulsed valve and lasers were synchronized to a spinning slotted disk mounted near the interaction region of the beam and the second laser, for TOF measurements of different sections of the gas pulse. The gas mixture was obtained by bubbling He through  $\text{CCl}_4$  at 20 °C with total pressures of 200-400 Torr. The dependence of the signal and optimal delay times on backing pressure was small. Further details of the experiment may be found in ref. 15.

### Results and Analysis

With the source laser operating at 193 nm and the second laser at 308 nm, signal from the photodissociation of  $\text{CCl}_3$  was observed at mass-to-charge ratios ( $m/e$ ) of 35, 47, and 83, corresponding to  $\text{Cl}^+$ ,  $\text{CCl}^+$ , and  $\text{CCl}_2^+$ , respectively. The mass spectrometer resolution was adjusted such that at  $m/e = 83$ , both  $m/e = 82$  and 84 were transmitted as well. With both lasers off, or with only the second laser on, the TOF spectra of these ions were identical and showed only a rising peak due to gas from the

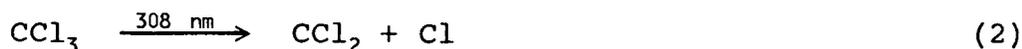
pulsed valve diffusing into the detector. With only the source laser on, this background appeared at slightly faster times, probably due to heating or shock effects from photoabsorption and photodissociation of  $\text{CCl}_4$  in the nozzle. Signal from the photodissociation of radicals was obtained by subtracting raw data with the source laser on from that with both lasers on.

This data is due to  $\text{CCl}_3$  photodissociation for the following reasons: 1) Photodissociation of  $\text{CCl}_4$  at 193 nm produces large amounts of  $\text{CCl}_3$  through the reaction<sup>15</sup>



2)  $\text{CCl}_4$  does not absorb at 308 nm,<sup>16</sup> and there was no dissociation signal with the source laser off, 3) No evidence for any larger  $\text{C}_x\text{Cl}_y$  species was found by monitoring the molecular beam at  $0^\circ$ , and 4) Signal was observed at masses corresponding to  $\text{Cl}^+$ ,  $\text{CCl}^+$ , and  $\text{CCl}_2^+$ , the neutral counterparts of which are likely photodissociation products of  $\text{CCl}_3$ , and their center-of-mass (c.m.) frame velocity distributions satisfied the requirement of conservation of momentum for pairs of fragments. Therefore the reactant was produced in the source and can only be  $\text{CCl}_3$ .

The data were fit with forward convolution techniques,<sup>3</sup> to determine the c.m. translational energy release probability distributions ( $P(E_T)$ ) for each dissociation channel. Fig. 2 shows the  $m/e = 83$  TOF spectrum, containing a single peak due to  $\text{CCl}_2$  from the reaction



The  $P(E_T)$  for reaction (2) is shown in fig. 3 and peaks at 10

kcal/mol with an average release of 13 kcal/mol into translation. In an experiment where the detector rotates in a plane containing the laser beam, there are always effects from the dissociation anisotropy, even with an unpolarized laser. The anisotropy can be expressed as

$$P(\theta) \sim (1 + \beta P_2(\cos\theta)) \quad (3)$$

where  $\beta$  is the anisotropy parameter and  $P_2(x)$  is the second Legendre polynomial.<sup>17</sup>  $\beta$  ranges from -1 (perpendicular transition) to 2 (parallel transition). Since data were taken with an unpolarized laser, the effects of anisotropy on product angular and velocity distributions were small, but a value of  $\beta = 1.0 \pm .2$  fit the data best.

The  $m/e = 47$  TOF spectrum contains two peaks, as shown in fig. 4 (top). The area under the slower peak depended linearly on the laser power while the faster peak had a quadratic power dependence. The slower peak is just from the fragmentation in the ionizer of  $\text{CCl}_2$  from reaction (2), while the faster peak is from the secondary photodissociation of  $\text{CCl}_2$  in the reaction



The production of  $\text{CCl}$  requires two photons and apparently neither step is strongly saturated. Since the  $\text{CCl}_2$  is the product of photodissociation after the supersonic expansion, it has a broad distribution of internal energies. Reaction (4) released an average of about 13 kcal/mol into translation and this energy comes from both the second photon absorbed and the initial internal energy.

The  $m/e = 35$  TOF spectrum, shown in fig. 4 (bottom), contains contributions from  $\text{CCl}_2$ ,  $\text{CCl}$ , and primary and secondary Cl atoms. There was also a sharp spike at about  $100 \mu\text{sec}$ , from the photodissociation of  $\text{Cl}_2$  in the reaction



Since the initial photolysis reaction in the source produces Cl atoms, they can recombine to form  $\text{Cl}_2$  or abstract another Cl from  $\text{CCl}_4$  or  $\text{CCl}_3$ . The  $P(E_T)$  for reaction (5) can be calculated by simply subtracting the  $\text{Cl}_2$  bond energy ( $57 \text{ kcal/mol}$ )<sup>18</sup> from the photon energy ( $93 \text{ kcal/mol}$ ). A very narrow  $P(E_T)$  centered around  $36 \text{ kcal/mol}$  fit the fast spike, indicating that it is from the photodissociation of  $\text{Cl}_2$  and that our measured beam velocity is correct. The  $m/e = 35$  TOF spectrum can be fit reasonably well assuming reactions (2), (4), and (5); since the  $P(E_T)$ 's are already determined, the only adjustable parameters are the relative heights of each curve.

### Discussion

It is clear that a pulsed photolysis source of radicals can be created with sufficient intensity to measure fragment velocity and angular distributions in molecular beam photodissociation experiments. However, there will also be other species present in the beam, chiefly undissociated precursor molecules, and perhaps the products of further chemical reactions of the fragments as well. In the photodissociation of  $\text{CCl}_4$  at  $193 \text{ nm}$  in the source, the major species was  $\text{CCl}_3$ , with some  $\text{Cl}_2$  also produced. Though difficult to measure, since  $\text{CCl}_4$  produces

essentially no parent ions in an electron bombardment ionizer,<sup>19</sup> there was certainly a large amount of undissociated  $\text{CCl}_4$ , even in the portion of the pulse with the highest concentration of radicals. This residual precursor is from two sources,  $\text{CCl}_4$  undissociated by the source laser and  $\text{CCl}_4$  "diffusing" in from segments of the molecular beam not irradiated by the laser pulse. With a strongly absorbing precursor molecule, a high buffer gas pressure (to prevent diffusion between the initial photolysis step and the supersonic expansion), and the two laser beams spatially as close as possible, it is expected that the amount of residual precursor could be reduced but never completely eliminated.

In the photodissociation of  $\text{CCl}_3$  at 308 nm, there was only one primary channel observed, reaction (2) producing  $\text{CCl}_2$  and Cl. The primary chemistry was not unexpected, but the absorption by  $\text{CCl}_3$  at 308 nm was. Several groups have observed transitions to electronically excited states in the range from 190 to 270 nm.<sup>11</sup> In another study, a band at 365 nm was attributed to the electronic absorption spectrum of  $\text{CCl}_3$ ,<sup>12</sup> but this has been suggested to be incorrect.<sup>20</sup> It is possible that the  $\text{CCl}_3$  absorption at 308 nm has some contribution from vibrational hot bands, though other researchers have observed strong vibrational cooling following photolysis in the high pressure region of a supersonic expansion.<sup>21</sup>

Reaction (2) released an average of 13 kcal/mol into translation, less than 30% of the available energy of 44-54

kcal/mol,<sup>18,22</sup> while  $\text{CCl}_4$  dissociation at 193 nm, reaction (1), released 40% of the available energy into translation.<sup>15</sup>  $\text{CCl}_3$  has a non-planar  $\text{C}_{3v}$  structure, similar to  $\text{CF}_3$ , with a Cl-C-Cl bond angle of  $116^\circ$ .<sup>10,23</sup> This low translational energy release for  $\text{CCl}_3$  is consistent with a non-planar dissociation in the loose-radical limit of the impulsive approximation. Since Cl is much heavier than C, the repulsive C-Cl bond rupture will initially release a large fraction of the available energy into C atom translational motion, and as it carries the  $\text{CCl}_2$  along, much of the initial C atom translational energy will become  $\text{CCl}_2$  internal energy. Because  $\text{CCl}_3$  dissociation is non-planar, some of this energy will end up in  $\text{CCl}_2$  rotation. In contrast,  $\text{CCl}_4$  dissociation likely occurs with a near-zero exit impact parameter and therefore exhibits a higher translational energy release.

The ground state of  $\text{CCl}_2$  is the singlet,<sup>24</sup> analogously to  $\text{CF}_2$ , with a small singlet-triplet splitting. It is likely that the singlet ground state is formed, though there is no reason why the triplet state could not be produced, or some combination of the two. The measured value of  $\beta$  does not allow any conclusions to be drawn regarding the direction of the transition dipole moment, since the observed data are the sum of contributions from two possible Cl atom spin-orbit states and two  $\text{CCl}_2$  electronic states, which would tend to smooth out any anisotropy in the angular distributions. More study is clearly required to explore the dissociation dynamics of polyatomic radicals.

In the secondary photodissociation of  $\text{CCl}_2$  radicals, reaction (4), an average of 13 kcal/mol was also released into translation. This is slightly more than the available energy at 308 nm starting with cold  $\text{CCl}_2$  radicals, and presumably the additional amount comes from internal energy already present in the nascent  $\text{CCl}_2$ . Because the  $\text{CCl}_2$  starts with a wide range of internal energies, little can be said about its dissociation dynamics, but since a large fraction of its available energy goes into translation, the dissociation likely occurs directly from an electronically excited state.

#### **Summary**

We have generated  $\text{CCl}_3$  radicals by photolysis of  $\text{CCl}_4$  at 193 nm in a pulsed radical beam source, and then dissociated the  $\text{CCl}_3$  at 308 nm. The only primary reaction channel observed was the production of  $\text{CCl}_2$  and Cl with a relatively low translational energy release. Some of the  $\text{CCl}_2$  absorbed a second photon and dissociated to CCl and Cl. In addition to  $\text{CCl}_3$  radicals and undissociated  $\text{CCl}_4$  in the beam,  $\text{Cl}_2$  was also produced, presumably from the recombination of Cl atoms in the supersonic expansion. There was no evidence for any other species produced in the source in quantities detectable with a mass spectrometer.

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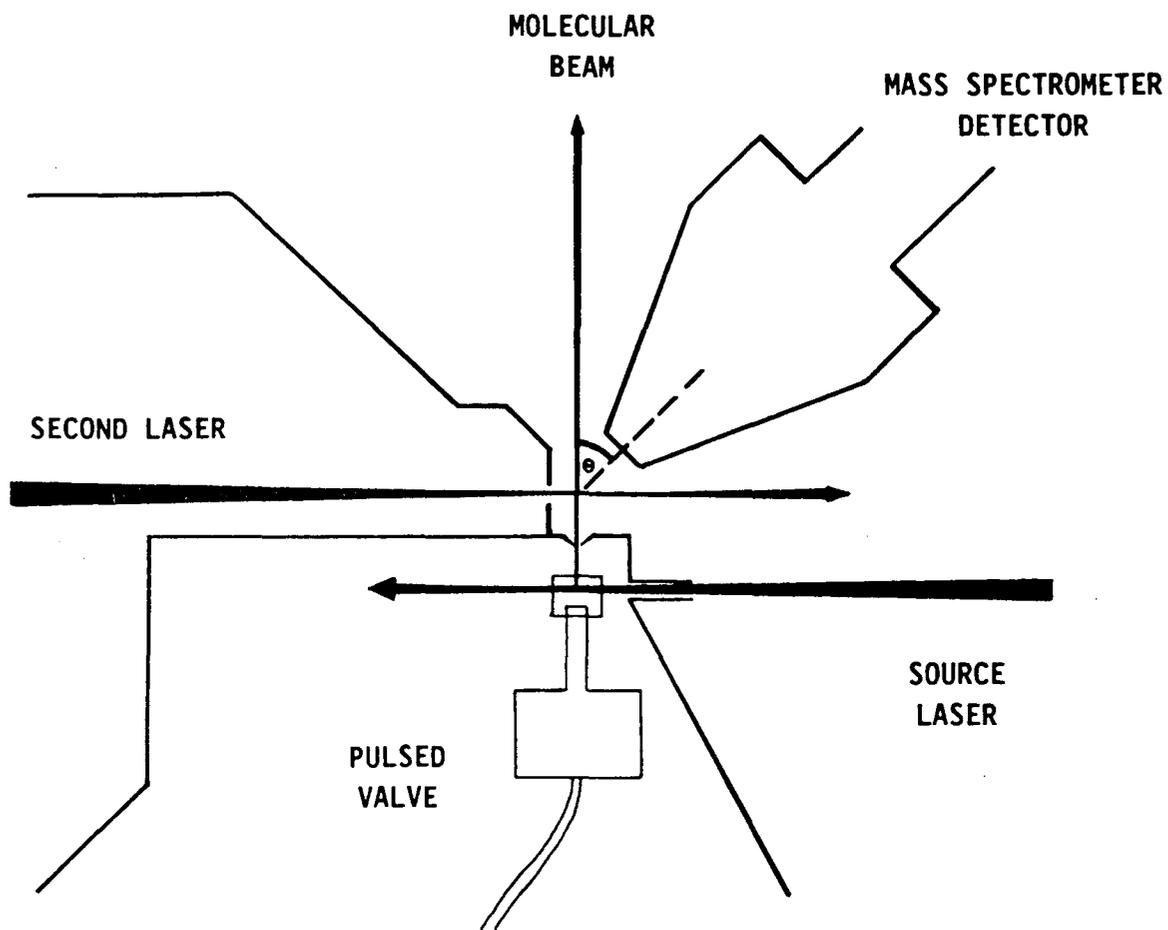
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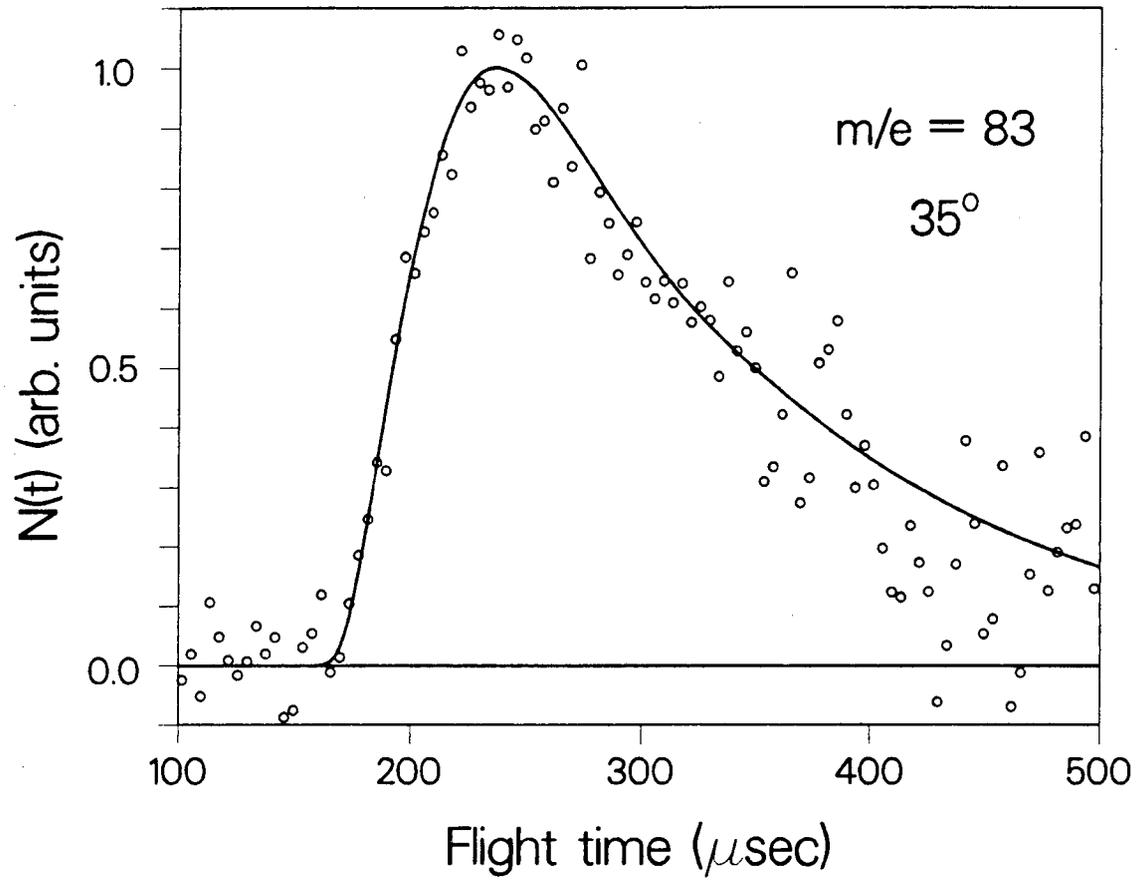
**Figure Captions**

1. Experimental arrangement for radical photodissociation, showing the pulsed valve in the singly differentially pumped source region, the two laser beams, and the detector. The detector could be rotated from  $0^\circ$  to approximately  $60^\circ$  in this experiment.
2.  $m/e = 83$  TOF spectrum at  $35^\circ$ . The signal is due to  $\text{CCl}_2$  from reaction (2) and is fit with the  $P(E_T)$  shown in fig. 3.
3.  $P(E_T)$  for reaction (2), derived from the data in figs. 2 and 4.
4. Top:  $m/e = 47$  TOF spectrum at  $35^\circ$ . The slower peak (— —) is from fragmentation in the ionizer of  $\text{CCl}_2$  from reaction (2), and the faster peak (— -) is from  $\text{CCl}$  produced in the secondary reaction (4). Bottom:  $m/e = 35$  TOF spectrum at  $35^\circ$ , with contributions from  $\text{CCl}_2$  (— —) and  $\text{Cl}$  (- - -) from reaction (2),  $\text{CCl}$  (— -) and  $\text{Cl}$  (— —) from the secondary reaction (4), and  $\text{Cl}$  atoms (— - - -) from reaction (5), the photodissociation of  $\text{Cl}_2$  produced in the source.



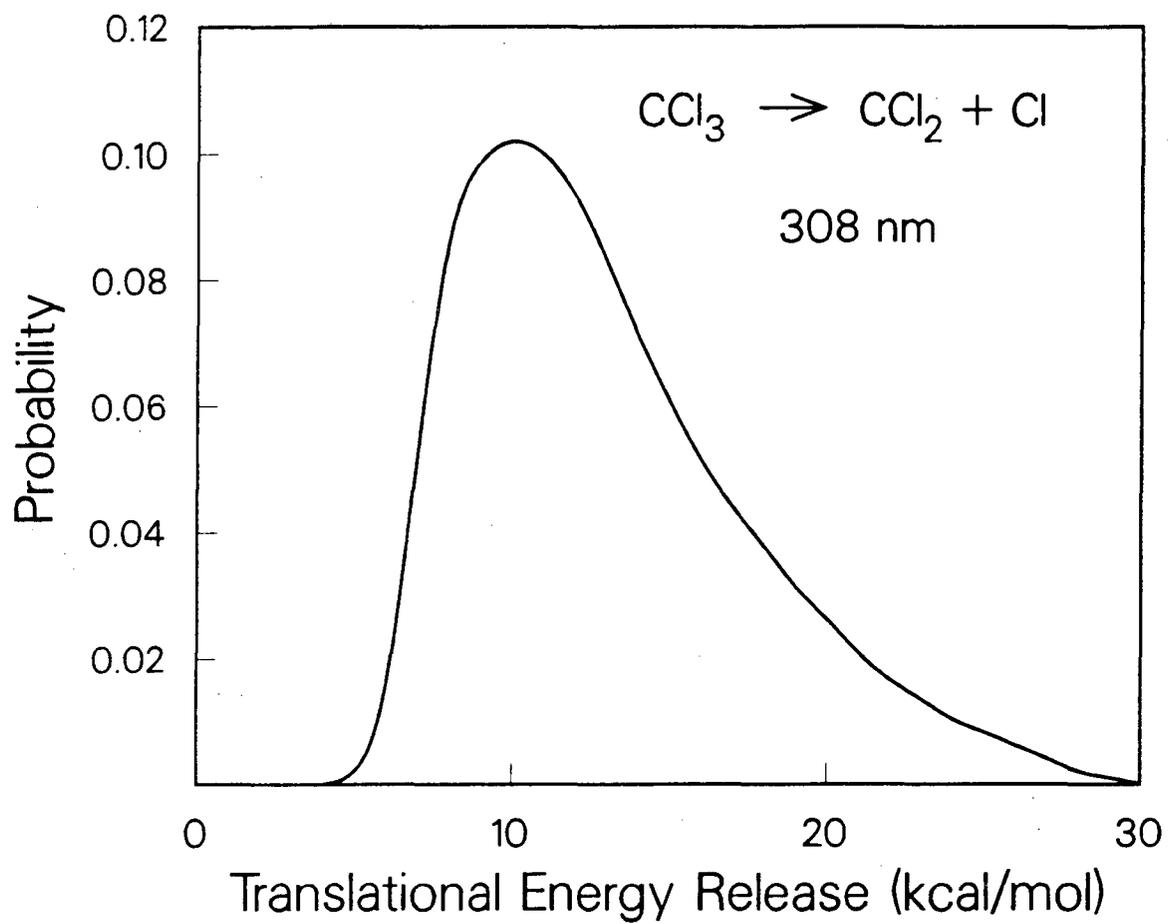
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Fig. 1



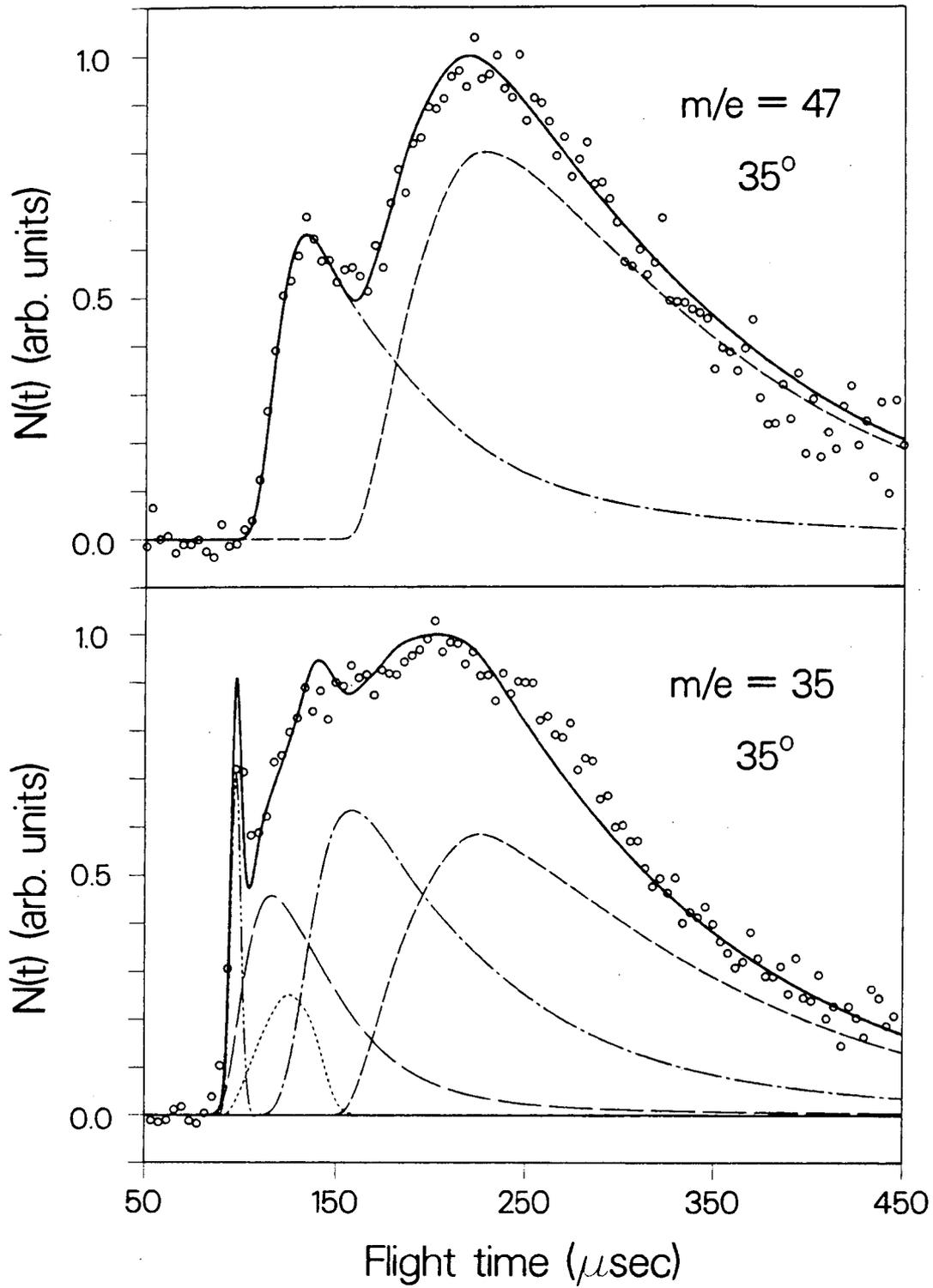
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Fig. 2



XBL 893-814

Fig. 3



XBL 893-815

Fig. 4

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