# Photodissociating trimethylamine at 193 nm to probe dynamics at a conical intersection and to calibrate detection efficiency of radical products

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This paper reports crossed laser-molecular beam scattering experiments measuring the photofragment velocities and product branching in the photodissociation of trimethylamine  $(N(CH_3)_3)$  at 193 nm. We have observed two primary N–CH<sub>3</sub> bond fission channels that ultimately produce different nitrogen-containing species,  $CH_3+N(CH_3)_2(\tilde{X}^2B_1)$ ;  $CH_3+N(CH_3)_2^* \rightarrow CH_3 + CH_2NCH_3+H$ . The data also indicate that a third minor channel may contribute to the dissociation dynamics,  $CH_3+N(CH_3)_2^{\dagger} \rightarrow CH_3+NC_2H_4+H_2$ . The experiments show that ground state N(CH<sub>3</sub>)<sub>2</sub> radicals are formed in the photodissociation, in sharp contrast to the exclusive production of NH<sub>2</sub> ( $\tilde{A}^2A_1$ ) in a similar molecule, methylamine. We discuss how this results from the differing dynamics through the  $S_1-S_0$  conical intersection in the exit channel in these two dissociating amines. We also use the photodissociation results to calibrate the mass spectrometric sensitivity at the m/e = 15 daughter ion for methyl radicals vs N(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>NCH<sub>3</sub> products. This provides the only necessary calibration to determine an absolute branching ratio in any system producing a methyl radical in one reaction channel and N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ) or CH<sub>2</sub>NCH<sub>3</sub> in other reaction channels. (© 1999 American Institute of Physics. [S0021-9606(99)01734-1]

### **I. INTRODUCTION**

These experiments on trimethylamine serve two purposes. First, trimethylamine  $(N(CH_3)_3)$  provides a model system to test how the nuclear dynamics influences whether a reaction proceeds adiabatically or whether electronically nonadiabatic effects alter the branching between product channels. Second, the photodissociation to  $CH_3+N(CH_3)_2$  allows us to calibrate the relative sensitivity of mass spectrometric detection of these polyatomic radicals, species important in combustion and other processes. This calibration allows us to determine absolute branching ratios in any unimolecular or bimolecular reaction that forms  $CH_3$  in one product channel and  $N(CH_3)_2$  in another, without having to resort to unreliable semiempirical estimates of the ionization cross sections of the radicals nor to prohibitively difficult measurements of their daughter ion cracking patterns.

Ammonia<sup>1,2</sup> and its methyl-substituted derivatives<sup>3</sup> have been studied as examples of molecules containing a conical intersection along the dissociation reaction coordinate. The first singlet excited state of ammonia (accessed via an  $n \rightarrow 3s$  Rydberg transition) is predissociated by an  $n \rightarrow \sigma^*$ state, leading to fission of the N–H bond. In this exit channel, the wave function encounters a conical intersection, which influences whether ground or excited state NH<sub>2</sub> products will be formed. In planar geometries along the N–H bond fission coordinate, the  $\tilde{A}$  state of NH<sub>3</sub> touches the ground state potential energy surface, so molecules dissociating with near-planar geometries can form ground state NH<sub>2</sub> radical products via an electronically nonadiabatic transition to the ground state potential energy surface near the conical intersection. In bent geometries, however, the splitting between the  $S_1$  surface and the ground state of ammonia is larger. Because of this, dissociative trajectories sampling largely bent geometries dissociate adiabatically on the  $S_1$ potential energy surface and form NH<sub>2</sub> radicals in the  $\tilde{A}$ state. Thus, by preparing an amine in its  $\tilde{A}$  state and determining the branching ratio into formation of ground and electronically excited NR<sub>2</sub> radicals, one can study the nonadiabatic effects brought about by a conical intersection.

Experiments on the photodissociation of ammonia  $(NH_3)$  accessing the first excited singlet state showed the production of ground-state amidogen radicals,

$$NH_3 + h\nu(n \rightarrow 3s) \rightarrow NH_2(\tilde{X}^2B_1) + H,$$

to be the dominant dissociation channel.<sup>1,4</sup> (Electronically excited amidogen was found to contribute from 10% to 30% to the N–H bond fission pathway,<sup>1</sup> depending on the amount of excess energy following N–H bond fission.) Upon substitution of a methyl group for one hydrogen to give methylamine (CH<sub>3</sub>NH<sub>2</sub>), excited state amidogen radicals were formed exclusively,

$$CH_3NH_2 + h\nu(n \rightarrow 3s) \rightarrow NH_2(\tilde{A}^2A_1) + CH_3$$

and no evidence of ground state  $NH_2$  radicals was found.<sup>3</sup> We explain these results below, and then detail how the electronic adiabaticity in the photodissociation of trimethylamine is influenced by the nuclear dynamics in the region of a conical intersection.

Our previous experiments on methylamine excited to its  $S_1$  surface demonstrated the influence of NH<sub>2</sub> wagging motion in the excited state on the dissociation to NH<sub>2</sub>( $\tilde{A}^2A_1$ ) radicals.<sup>3</sup> In amines, the equilibrium geometry of the ground

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state is nonplanar about the nitrogen, whereas it is planar in the  $S_1$  state. The Franck–Condon transition thus induces NH<sub>2</sub> wagging motion (or NR<sub>3</sub> umbrella motion) on the excited state surface, resulting in a large amplitude of the scattering wave function at highly nonplanar geometries. Here we see that these nuclear dynamics prevent the wave function from being "funneled down" to the ground state surface, by avoiding near-planar geometries where nonadiabatic dynamics caused by the conical intersection are important. In methylamine, the NH<sub>2</sub> wagging motion is evident both in the  $n \rightarrow 3s$  Rydberg absorption band and in resonance Raman experiments exciting into this  $n \rightarrow 3s$  transition.<sup>3</sup> (In ammonia, although NH<sub>3</sub> umbrella motion also occurs, the high velocity along the N-H bond fission coordinate presumably allows the dynamics to traverse the conical intersection diabatically, thus accessing the ground state potential surface.)

Studying the photodissociation dynamics of trimethylamine (N(CH<sub>3</sub>)<sub>3</sub>) offers a key opportunity to probe how the nuclear dynamics influence whether or not a conical intersection is traversed adiabatically. In methylamine, the NH<sub>2</sub> wag is observed to dominate the dynamics of the molecule as the C–N bond breaks, decreasing the amplitude of the scattering wave function near planar geometries, where it could nonadiabatically hop to the ground state potential to produce NH<sub>2</sub> ( $\tilde{X}^2B_1$ ). In trimethylamine, the density of vibrational states is much higher, so intramolecular vibrational energy redistribution (IVR) of population out of the N(CH<sub>3</sub>)<sub>3</sub> umbrella motion could allow the scattering wave function to access geometries near the conical intersection and result in an increased fraction of NR<sub>2</sub> ( $\tilde{X}^2B_1$ ) products compared with that observed in methylamine.

The photodissociation of trimethylamine at 193 nm was previously investigated by Kawasaki and co-workers.<sup>5</sup> They fit their data to one N-CH<sub>3</sub> bond fission channel, in which only 13% of the available energy following N-C bond fission is partitioned to relative translation. This amount is far less than that observed following ammonia excitation,<sup>1</sup> in spite of the much larger excess energy available for partitioning in the former molecule (73.5 kcal/mol in trimethylamine vs 39.5 kcal/mol in ammonia). Such small amounts of translational energy following trimethylamine photodissociation mean formation of products with high internal energy, perhaps  $N(CH_3)_2(\tilde{A}^2A_1)$ , although Kawasaki et al. considered the quantum yield of this channel to be very small. We originally undertook the present study as a means of determining an absolute branching ratio for the dissociation channels in *N*,*N*-dimethylformamide;<sup>6</sup> our results on trimethylamine photodissociation were, however, so different than those obtained by Kawasaki et al. that we report them here.

We now review recent work on the absorption and fluorescence spectra of the alkylated amines to help clarify what states are accessed at each wavelength and subsequent internal conversion processes. Traditionally, the absorption spectra of substituted amines have been discussed by comparison with ammonia,<sup>7,8</sup> but recent work shows that the transitions have not been accurately assigned.<sup>9</sup> By analogy with ammonia, the singlet states in the Franck–Condon region were assigned as arising from an  $n \rightarrow 3s$  Rydberg transition ( $S_1$ ), an  $n \rightarrow 3p$  Rydberg transition (S<sub>2</sub>), and a higher lying valence  $n \rightarrow \sigma^*$  transition. The  $n \rightarrow \sigma^*$  state predissociates the  $S_1$  state along the dissociation coordinate. While these assignments are in accord with the observed ammonia absorption spectrum and have been successfully used for many years to explain experimental results from other amines, recent calculations by Taylor et al. show that the electronic character, energetic spacing, and number of these electronic states changes upon alkyl substitution.<sup>9</sup> Significant Rydberg character on the carbon atoms contributes to several lowlying states. These calculations have identified three dominant transitions that contribute in the spectral region of interest. They are all Rydberg in character, and are labeled by Taylor *et al.*<sup>9</sup> as 3s-b, 3s-d, and 3p (where all transitions originate from the nonbonding orbital on nitrogen and b and *d* represent "bonding" and "dissociative" in his notation). Excitation of trimethylamine at 193 nm likely excites the 3s-d state in the Franck–Condon region, the  $S_2$  state. Internal conversion to the  $S_1(3s-b)$  potential energy surface then occurs before dissociation, as indicated in other work described below.

Many experiments have examined the  $S_2$  state of trimethylamine, the state accessed by 193 nm excitation. Experiments by Kawasaki and co-workers detected fluorescence from trimethylamine around 300 nm following excitation of the molecule at 193 nm.<sup>5</sup> This fluorescence spectrum is very similar to that obtained following direct excitation of trimethylamine to its lowest  $n \rightarrow 3s$  Rydberg state  $(S_1)$ ,<sup>10</sup> and was therefore assigned to fluorescence from  $S_1 \rightarrow S_0$ . Thus, the dissociation of trimethylamine excited at 193 nm proceeds by fast internal conversion from the  $S_2$ state to the  $S_1$  state, with subsequent dynamics occurring from the  $S_1$  surface. Two studies have observed fluorescence from  $S_1$  to  $S_0$  following excitation to the  $S_1$  state and at excitation energies where the  $S_2$  and  $S_1$  absorptions overlap.<sup>10,11</sup> The authors of these papers reach different conclusions about the distribution of population in vibrational levels of the  $S_1$  state, but in spite of these conflicting interpretations, both studies concur that rapid internal conversion from the  $S_2$  to the  $S_1$  state occurs. Because of the similarity of fluorescence spectra over the range of excitation wavelengths, it seems reasonable to assume that the  $S_2 \rightarrow S_1$  internal conversion is occurring near the Franck-Condon region. Thus, the molecules, whether accessing the  $S_1$  state optically or via internal conversion from the  $S_2$  surface, begin their dissociation dynamics in the quasi-bound region of the  $S_1$ potential. This  $S_1$  surface is the analog of the state accessed in the 222 nm excitation of methylamine discussed above.

This study focuses on the photodissociation dynamics of trimethylamine following 193 nm excitation. In particular, we wish to test the influence of the conical intersection mentioned above on the photodissociation dynamics of this molecule. The experiments thus determine the amount of  $N(CH_3)_2(\tilde{X}^2B_1)$  formed after internal conversion to the  $S_1$  surface. The experiments also calibrate the relative sensitivity to the  $N(CH_3)_2$  products and their momentum-matched  $CH_3$  partners at  $CH_3^+$  in our mass spectrometer. We show how this calibration allows us to determine absolute branch-

ing ratios for forming these products in competing reactions in other systems.

### **II. EXPERIMENT AND CALCULATION METHODS**

In these experiments, we photodissociate trimethylamine molecules with unpolarized 193 nm light and detect the resulting neutral photofragment recoil distributions with a crossed laser-molecular beam apparatus.<sup>12</sup> The dissociation products are detected following electron bombardment ionization (at several possible parent and daughter ion fragments) as a function of their times of arrival with respect to the dissociating laser pulse. We could not probe any possible contributions from C–H bond fission in these experiments as the heavy  $CH_2N(CH_3)_2$  product would be energetically constrained to have a small recoil velocity, so is only detectable very close to the molecular beam axis.

A 5% mixture of trimethylamine in helium was obtained from Matheson Gas Products. The mixture was expanded through a 0.12 mm diameter nozzle heated to approximately 200 °C, with a stagnation pressure of 300 Torr. The low percentage mixture and high nozzle temperature were required to prevent formation of trimethylamine clusters (a problem well-addressed in the literature).<sup>9,13</sup> The high nozzle temperature also reduced clogging of the nozzle orifice. We measured the temperature using a chromel alumel thermocouple, calibrated using a helium beam time of flight. To measure the velocity of the parent molecular beam *in situ*, we rotated the molecular beam source to point into the detector and raised a chopper wheel into the beam. The mean peak beam velocity was  $1.73 \times 10^5$  cm/s with a full width at half-maximum (FWHM) of 17%.

After photodissociation with a pulsed excimer laser, neutral dissociation products scatter from the crossing point of the laser and the molecular beam with velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted during dissociation. Fragments scattered into the  $1.5^{\circ}$  acceptance angle of the detector travel 44.4 cm and are ionized by 200 eV electron bombardment. After mass selection with a quadrupole mass filter, the ions are counted with a Daly detector and recorded with a multichannel scaler with respect to their time-of-flight (TOF) from the interaction region after the dissociating laser pulse. Forward convolution fitting of the TOF spectrum (taking into account the ion flight time) determines the distribution of energies released to relative product translation in the dissociation. The plane defined by the molecular beam and the detector axis is perpendicular to the direction of laser propagation, and molecular beam source angles are given here with respect to the detector axis.

A signal was observed at various angles for several parent and daughter ions of the primary, neutral photoproducts; at m/e = 59 (6°, 1 M laser shots, for clusters only), 58 (6°, 500 K shots, clusters only), 43 (10°, 1 M shots; 15°, 1 M shots), 42 (10°, 500 K shots; 15°, 300 K shots), and 15 (10°, 1.5 M shots; 15°, 3 M shots; 20°, 1.5 M shots). No discernible signal was observed at m/e = 16 (10°, 250 K shots), 29 (10°, 250 K shots) or 44 (10°, 250 K shots). A small amount of signal was observed at m/e = 41 (10°, 250 K shots) and at m/e = 30 (10°, 250 K shots) but was not fit due to the poor signal to noise ratio. The strong natural background at m/e = 28 (caused by CO<sup>+</sup>) prevented collection of data at this mass. Quadrupole resolution was adjusted to roughly 1.0 amu FWHM for all masses.

A Lumonics PM-848 excimer laser filled with ArF produced the 193 nm light used to photodissociate the trimethylamine molecules. The laser beam was focussed to give an attenuated laser energy of 4 mJ/pulse in a 6 mm<sup>2</sup> spot size in the crossing region with the molecular beam.

We also include in this paper, with permission of our collaborators, one TOF spectrum recorded at the Advanced Light Source (ALS) in Berkeley.<sup>14</sup> Our study there of the photodissociation of trimethylamine at 193 nm employed photoionization in the detection, rather than 200 eV electron bombardment ionization. The ability to tune the photons to just above threshold for ionization greatly reduces the amount of dissociative ionization (cracking) in the ionizer. This enabled us to obtain a much cleaner TOF spectrum at m/e = 15 by ionizing methyl radicals at 10.5 eV. Details of these experiments will be given in a forthcoming publication;<sup>14</sup> we include this spectrum here because it contains only contributions from CH<sub>3</sub> radicals, avoiding the cracking to m/e = 15 from heavier species.

To determine the character of the excited state accessed at 193 nm, we ran a configuration interaction with single excitations (CIS) calculation with GAUSSIAN 94 using a  $6-31+G^*$  basis set of atomic orbitals.<sup>15</sup> The Hartree–Fock optimized geometry used for these calculations was taken from a paper by Taylor *et al.*,<sup>9</sup> who used a DZP basis set augmented with 3*s* Rydberg (or 3*p* Rydberg) orbitals on nitrogen and carbon atoms.

### **III. RESULTS AND ANALYSIS**

To determine the competing bond fission channels in the photodissociation of trimethylamine at 193 nm, we fit the time-of-flight (TOF) data of photofragments detected at various mass/charge ratios to translational energy distributions. Because of extensive fragmentation in our electron-bombardment ionizer, it is possible to see different daughter ions arising from the same neutral photofragment. By momentum-matching signal from heavy and light neutral partner fragments (at parent masses and at their possible daughter ions) and forward convolution fitting of our data, we are able to fit our data to three N–CH<sub>3</sub> bond fission channels. These are identified by the differing behavior of the primary N(CH<sub>3</sub>)<sub>2</sub> product as

$$N(CH_3)_3 + 193 \text{ nm} \rightarrow CH_3 + N(CH_3)_2 (\tilde{X}^2 B_1)$$
 (1)

$$\rightarrow CH_3 + N(CH_3)_2^*$$

$$\rightarrow CH_3 + H_2C = NCH_3 + H$$
 (2)

$$\rightarrow CH_3 + N(CH_3)_2^{\dagger}$$
  
$$\rightarrow CH_3 + NC_2H_4 + H_2.$$
(3)

Whether these three pathways originate from the same primary  $N(CH_3)_2$  product or from distinct dissociation dynamics will be discussed later in this paper.



FIG. 1. Experimental TOF spectra for the photodissociation of trimethylamine, taken at m/e=43, at a 10° source angle (top) and at a 15° source angle (bottom). Each spectrum represents data collected over 1 million laser shots. Open circles represent experimental data points; the total fit to these spectra (shown in a bold line) is a sum of contributions from channels shown in dashed lines. The majority of signal at this mass/charge ratio is attributed to only one nitrogen—methyl bond fission channel, fit by the slower  $P(E_T)$  in Fig. 2. [For illustrative purposes, a 7% contribution from the faster  $P(E_T)$  in Fig. 2 is included. This is the maximum allowable contribution of the fast distribution at this mass/charge ratio; scaling it higher results in overfitting the fast edge of the TOF spectra.]

#### A. Primary N–CH<sub>3</sub> bond fission

Figure 1 shows TOF spectra recorded at m/e = 43, at source angles of  $10^{\circ}$  and  $15^{\circ}$  with respect to the detector axis. We determined the photofragment translational energy distribution  $(P(E_T))$  used to fit these data by forward convolution fitting of the time-of-flight signal. The  $CH_3 - N(CH_3)_2$  bond fission channel giving the signal at mass 43 was fit with the total recoil kinetic energy distribution shown in Fig. 2 that peaks near 20 kcal/mol. We assign this signal to N-CH<sub>3</sub> bond fission because of the presence of the momentum-matched methyl fragment in the signal observed at m/e = 15 (see Fig. 3). Only the fast component (between 60 and 150  $\mu$ s flight time) of the signal observed at m/e= 15 arises from primary methyl fragments from  $N-CH_3$ bond fission; the slower component arises from cracking of the heavier dissociation partners to daughter ions of m/e= 15 in the ionizer. Signals due to  $N-CH_3$  bond fission appears at a third ion; at m/e = 42 (see Fig. 4).



FIG. 2. Translational energy distributions,  $P(E_T)$ 's used to fit the nitrogenmethyl bond dissociation pathways. The faster distribution is assigned to formation of  $CH_3 + N(CH_3)_2 (\tilde{X}^2 B_1)$ . The slower distribution is assigned to dissociation to CH<sub>3</sub>+unstable N(CH<sub>3</sub>)<sup>\*</sup> radicals, which have enough internal energy to undergo secondary bond dissociation to give CH<sub>2</sub>NCH<sub>3</sub>+H. [The slowest of these  $N(CH_3)^*_2$  radicals, containing the greatest amount of internal energy, may dissociate instead by H<sub>2</sub> elimination, giving NC<sub>2</sub>H<sub>4</sub>+H<sub>2</sub>.] See the results and analysis section for a discussion of these assignments. The fast edge of the fast  $P(E_T)$  is determined clearly by momentum-matching the CH<sub>3</sub> TOF signal to N(CH<sub>3</sub>)<sub>2</sub> signal at m/e = 42(Fig. 4), and the slow edge of the slow  $P(E_T)$  is reasonably well-determined by fitting the slow edge of the CH<sub>3</sub> signal in Fig. 5. The division of the overall  $P(E_T)$  determined from the CH<sub>3</sub> TOF spectra into contributions from stable and unstable N(CH<sub>3</sub>)<sub>2</sub> is more ambiguous because of the timeof-flight broadening affects from secondary dissociation of N(CH<sub>3</sub>)<sub>2</sub> to CH<sub>2</sub>NCH<sub>3</sub> and possibly NC<sub>2</sub>H<sub>4</sub>, as discussed in the text.

of fitting the TOF signal observed at m/e = 42 (see Fig. 4). Neither the fast edge nor the slow edge of this signal is fit by the same distribution as appears at m/e = 43. A similar predicament arises in the m/e = 15 data; the use of only the slower  $P(E_T)$  to fit the observed TOF spectra in Fig. 3 underfits the spectra both at the fast edge of the  $CH_3^+$  peak and at the fast and slow edges of the heavier cofragment peak. To fit the faster edge of the observed signal at m/e = 42, we have added an additional distribution corresponding to primary N-CH<sub>3</sub> bond fission, shown as the fast distribution in Fig. 2, peaking near 45 kcal/mol in translational energy. The assignment of this distribution to N-CH<sub>3</sub> bond fission is confirmed by the presence of momentum-matched methyl radicals observed at early arrival times in the TOF spectra at m/e = 15(Fig. 3).

Figure 5 shows a TOF spectrum recorded at the Advanced Light Source (ALS), at m/e=15, at a 50° source angle, and using 10.5 eV photons to ionize the CH<sub>3</sub> radicals.<sup>14</sup> In this TOF spectrum, the contributions of the heavier dissociation products have been essentially eliminated, making determination of the neutral CH<sub>3</sub> TOF distribution unambiguous. The fast edge of this TOF spectrum is well fit by the fast  $P(E_T)$  (Fig. 2), and the slow edge is in excellent agreement with the slow edge of the m/e=43 signal (Fig. 1).

The energy available for translation and internal modes



FIG. 3. Experimental TOF spectra for the photodissociation of trimethylamine, collected at m/e = 15, at a 10° source angle and over 1.5 million laser shots (top), at a 15° source angle and over 3 million laser shots (middle), and at a 20° source angle and over 1.5 million laser shots (bottom). Open circles represent experimental data points; the total fit to these spectra (shown in a bold line) is a sum of contributions from channels shown in dashed lines. The fast peak arises from CH<sub>3</sub> products, while the slow peak is fit with contributions of heavier dissociation partners [N(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>NCH<sub>3</sub>], which crack to give daughter ion signal at m/e = 15 following 200 eV electron impact ionization. The slowest signal is somewhat underfit, indicating that the contributor to the slow, unfit signal at m/e = 42 in Fig. 4 may also crack to give signal at m/e = 15.

of the products can be calculated from the amount of energy put into the molecule by subtracting the amount of energy required to break the bond,

$$E_{\text{avl}} = h \nu - D_0(\text{bond})$$
  

$$\approx 148.0 - (74.6 \pm 3.0) \text{ kcal/mol}$$
  

$$\approx 73.4 \pm 3.0 \text{ kcal/mol}.$$



FIG. 4. Experimental TOF spectra for the photodissociation of trimethylamine, collected at m/e = 42, at a 10° source angle and over 500 000 laser shots (top) and at a 15° source angle and over 300 000 laser shots (bottom). Open circles represent experimental data points; the total fit to these spectra (shown in a bold line) is a sum of contributions from channels shown in dashed lines. As was found in the m/e = 15 spectra (Fig. 3), use of the two N–CH<sub>3</sub> bond fission  $P(E_T)$ 's from Fig. 2 leaves the slowest signal underfit. In the Results and Analysis section of the paper, we tentatively attribute this slowest signal for secondary dissociation of the slowest N(CH<sub>3</sub>)<sub>2</sub> radicals to H<sub>2</sub>+NC<sub>2</sub>H<sub>4</sub>. Because of the undetermined broadening of the NC<sub>2</sub>H<sub>4</sub> TOF signal relative to its primary N(CH<sub>3</sub>)<sub>2</sub> parent (due to the recoil velocity of NC<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>), we leave this slowest portion of the signal unfit.

The value we have used for  $D_0$  is a bond dissociation enthalpy, calculated using heats of formation at 298 K. [Although there are widely varying values for the heat of formation of the dimethylamidogen radical,  $N(CH_3)_2$  in the literature, the experimental value of  $33.8\pm3$  kcal/mol we have chosen comes from a more recent review article.<sup>16</sup> Note, however, that the published values for  $\Delta H_f^0$  of  $N(CH_3)_2$  and bond enthalpies in Ref. 16 are in error by 0.9 kcal/mol,<sup>17</sup> so we have made the appropriate corrections here.] The correction from bond dissociation enthalpy to energy (and from 298 K to 0 K) amounts to roughly 2-3 kcal/mol,<sup>18</sup> thus increasing by approximately 3 kcal/mol the amount of energy available for partitioning to relative product translation and internal energies. As this value is just an estimate, we leave the values as stated above with this note as to their accuracy at temperatures closer to 0 K (which better represent the conditions in a molecular beam).

# 1. Fastest products: $N(CH_3)_2 (\tilde{X}^2B_1) + CH_3$

The fastest recoiling products have been fit with a  $P(E_T)$  that extends to roughly 65 kcal/mol (see Fig. 2). Because this



FIG. 5. Experimental TOF spectra for the photodissociation of trimethylamine, collected at m/e = 15, at a 50° source angle in collaborative experiments at the Advanced Light Source in Berkeley, California (Ref. 14). Photoionization at 10.5 eV was used to detect the CH<sub>3</sub> products, virtually eliminating signal from dissociative ionization of the heavier nitrogencontaining species. Open circles represent experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from the two channels shown in dashed lines. A least-squares fitting procedure was used to determine the relative weightings of the two  $P(E_T)$ 's used to fit this spectrum, giving a ratio of 0.27:0.73 fast:slow.

distribution extends close to the limit of available energy  $(73.4 \pm 3.0 \text{ kcal/mol})$ , we assign this fast channel to formation of ground state  $N(CH_3)_2$  and  $CH_3$  products. These ground state  $N(CH_3)_2(\tilde{X}^2B_1)$  radicals do not have enough internal energy to undergo secondary dissociation (at  $E_T$ ≥44 kcal/mol) and so they arrive intact at the detector. Following 200 eV ionization, they crack to give daughter ion signal at m/e = 42 and 15 but do not appear at parent (m/e)=44). [There could be a slight contribution from  $N(CH_3)_2(\tilde{X}^2B_1)$  at m/e=43, but it must be very minor in order to avoid overfitting the fast edge of the m/e = 43 TOF spectra.] This cracking pattern following 200 eV electron impact ionization is in agreement with the cracking patterns observed from ground state N(CH<sub>3</sub>)<sub>2</sub> radicals produced by the photodissociation of dimethylformamide at 193 nm.<sup>6</sup> In recent experiments at the ALS,<sup>14</sup> we photodissociated trimethylamine at 193 nm, but used softer photoionization in the detection scheme. Even by ionizing close to threshold, we were unable to observe signal at m/e = 44, implying that the  $N(CH_3)_2^+$  ion is unstable and promptly dissociates. Recent calculations have shown the dissociation of  $N(CH_3)_2^+$  to  $NC_2H_4^+$  to be exothermic by 50 kcal/mol showing how the  $N(CH_3)_2$  can easily dissociatively ionize to give signal at  $m/e = 42.^{14}$ 

## 2. Middle translational energies: $N(CH_3)_2^* + CH_3 \rightarrow H_2C = NCH_3 + H + CH_3$

The slower recoil kinetic energy channel in Fig. 2 has a  $P(E_T)$  which extends from 0 to 45 kcal/mol and peaks near 20 kcal/mol. Our collaborative studies at the ALS have revealed that the signal at m/e=43 arises from the ionization of neutral CH<sub>2</sub>NCH<sub>3</sub>.<sup>14</sup> Thus, the primary N(CH<sub>3</sub>)<sub>2</sub> products formed from this slower distribution [whose  $P(E_T)$  has been determined from the signal at m/e=43] undergo secondary

dissociation to  $CH_2NCH_3+H$ . (The lack of any signal at m/e = 16 rules out the possibility of a molecular channel, leading to primary  $CH_4+CH_2NCH_3$  products.) Thermodynamically,<sup>16,17,19</sup>

N(CH<sub>3</sub>)<sub>2</sub>
$$\rightarrow$$
CH<sub>2</sub>NCH<sub>3</sub>+H  $\Delta H = 29.3 \pm 3.6$  kcal/mol.

If there is no exit barrier along the dissociation coordinate (i.e., no barrier beyond that from the endoergicity), this implies that  $N(CH_3)_2$  must have 29 kcal/mol of internal energy to undergo this secondary H-atom loss. This limit of internal energy is almost identical to that calculated for the fastest-recoiling products of the slower  $P(E_T)$  distribution. Any exit barrier to H-atom loss must therefore be small; this exit barrier from  $N(CH_3)_2$  is unknown, but note that the barrier to loss of a hydrogen atom in the reaction  $C_2H_5 \rightarrow H_2C=CH_2+H$  is only on the order of a couple of kcal/mol.<sup>20,21</sup>

The CH<sub>2</sub>NCH<sub>3</sub> secondary products arising from this channel contribute to the signal at m/e = 43, 42, and 15 following our 200 eV electron impact ionization. The corresponding  $P(E_T)$  has been determined at m/e = 43, assuming this to be the only channel appearing at m/e = 43, and assuming that loss of a hydrogen atom has no effect on the velocity of  $CH_2NCH_3$  relative to its  $N(CH_3)_2$  parent. The slow edge of this signal and the slow edge of the  $CH_3^+$  signal (best seen in Fig. 5) are both well fit by this  $P(E_T)$ , determined from the m/e = 43 TOF spectrum. As mentioned in the previous subsection, the possibility of a very minor contribution to the fast edge from ground state N(CH<sub>3</sub>)<sub>2</sub> radicals cannot be excluded. The inclusion of this fast distribution would introduce some uncertainty into the fast edge of the slower  $P(E_T)$ , so the upper limit to this distribution should not be taken too quantitatively.

This experiment cannot determine the electronic state of the N(CH<sub>3</sub>)<sub>2</sub> radical before it underwent H-atom loss. The CH<sub>2</sub>NCH<sub>3</sub> molecules resulting from secondary decomposition of unstable N(CH<sub>3</sub>)<sub>2</sub><sup>\*</sup> radicals exhibit the same cracking pattern as primary N(CH<sub>3</sub>)<sub>2</sub> radicals with a similar distribution of internal energy, observed following photodissociation of dimethylformamide at 193 nm.<sup>6</sup> Thus, it is likely that in the studies of dimethylformamide, the species assigned to primary formation of N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^2A_1$ ) and said to arrive at the detector as intact N(CH<sub>3</sub>)<sub>2</sub>, underwent H-atom loss to give CH<sub>2</sub>NCH<sub>3</sub>. The compelling electronic arguments in Ref. 6 for this channel to arise from primary N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^2A_1$ ) radicals lead us to consider whether this could be the case in trimethylamine. We analyze the relevant energetics in the next paragraph.

The slower translational energy distribution extends from 0 to 45 kcal/mol (see Fig. 2). This means that the total internal energy of all of the N(CH<sub>3</sub>)<sub>2</sub> and CH<sub>3</sub> dissociation fragments from this channel is at least 73.4–45  $\approx$ 29 kcal/mol. The N(CH<sub>3</sub>)<sub>2</sub> radical has a low-lying electronic state, N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^2A_1$ ), which has been calculated to have an adiabatic excited state energy of 1.59 eV (=37 kcal/ mol), determined using the  $H^v$  (third order) *ab initio* method.<sup>6,22</sup> This value for the energy does not include zeropoint energy contributions and was calculated at globally optimized geometries obtained at a lower level of theory. Thus, it should be taken as a rough estimate of the adiabatic (minimum) energy separation between the  $\tilde{X}$  and  $\tilde{A}$  states of N(CH<sub>3</sub>)<sub>2</sub>. For an experimental estimate of the adiabatic energy separation, we use the value of  $NH_2(\Delta E_{\min}(\widetilde{A} \rightarrow \widetilde{X}))$ , which is 1.38 eV (=31.8 kcal/mol).<sup>23</sup> This value corresponds reasonably well with the limit of available energy calculated for this middle channel, where a minimum of roughly 29 kcal/mol is partitioned to internal energy of the recoiling photofragments. It is thus possible that the species that lose a H-atom in secondary dissociation are excited state  $N(CH_3)_2(\tilde{A}^2A_1)$  radicals, so long as this process is barrierless. Secondary dissociation in this scenario would be favored over fluorescence to ground state N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ), since there is no evidence for contributions from a second source of  $N(CH_3)_2$  radicals in any of the experimental data. [The short fluorescence lifetime of the electronically similar  $NH_2(\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1)$  (Ref. 4) implies that H-atom loss from  $N(CH_3)_2(\tilde{A}^2A_1)$  to form the closed-shell species  $CH_2NCH_3$ would be efficient.] Alternatively, the CH<sub>2</sub>NCH<sub>3</sub> could arise from secondary dissociation of highly internally excited  $N(CH_3)_2(\tilde{X}^2B_1)$ . With the  $P(E_T)$ 's shown in Fig. 2, this seems less likely, given the strong overlap between the two distributions. One expects less energetic overlap between formation of intact radicals [assigned to the faster  $P(E_T)$ ] and those undergoing secondary H-atom loss [assigned to the slower  $P(E_T)$ ]. While the overlap between these distributions seems necessary to fit the data at m/e = 15, note that the detailed shape of the slower  $P(E_T)$  in Fig. 2 and the fit to the data depend on the assumption that H-atom loss imparts no velocity kick to the CH<sub>2</sub>NCH<sub>3</sub> products [one of the assumptions in determining this slower  $P(E_T)$  from the m/e=43data]. If this assumption is not valid, then in Fig. 2 the  $P(E_T)$ peaking near 20 kcal/mol for primary dissociation to  $CH_3 + N(CH_3)_2$  should be narrowed to obtain the true primary  $P(E_T)$ . Without more evidence, at present we label as  $N(CH_3)_2^*$  those primary products that go on to lose a hydrogen atom, by the asterisk implying that these have a high degree of internal energy, but that we cannot definitively determine whether or not it is electronic.

# 3. Slowest translational energies: A possible $N(CH_3)_2^{\dagger} + CH_3 \rightarrow NC_2H_4 + H_2 + CH_3$ channel

As seen in Fig. 4, the slowest portion of the signal at m/e = 42 is not fit by the  $P(E_T)$ 's used to fit the CH<sub>3</sub> signal at m/e = 15. The use of just these two  $P(E_T)$ 's also unsatisfactorily fits the slow edge of the slow signal at m/e = 15 in Fig. 3. We have considered various sources of this signal, which we discuss in the following paragraphs.

One possibility for slow-arriving signal comes from photodissociation of higher-order clusters to parent, with subsequent cracking of the parent ion in the detector. We recorded a TOF spectrum at m/e = 59 (N(CH<sub>3</sub>)<sup>+</sup><sub>3</sub>), at a source angle of 6°. We observed a weak signal, but it is too slow to fit the slow edge of the TOF spectra at m/e = 42. Additionally, we took mass spectra in the experiments at the ALS,<sup>14</sup> and saw no ion signal at mass/charge ratios higher than parent. In the TOF spectra recorded at the ALS, there is also a slower component to the signal at m/e=42 not fit by the two  $P(E_T)$ 's shown in Fig. 2.<sup>14</sup> Thus, this unfit slower edge cannot be attributed to contributions from higher-order clusters in the molecular beam.

Another possibility for the slow-arriving signal arises from primary C–H bond fission in trimethylamine,

$$N(CH_3)_3 + 193 \text{ nm} \rightarrow H + CH_2 N(CH_3)_2.$$
(4)

We recorded a TOF spectrum at m/e = 58, at a 6° source angle, in order to look for slow-arriving contributions at the parent mass/charge ratio of  $CH_2N(CH_3)_2$ . The only signal we observed was fit by the same velocity distribution as the signal observed at m/e = 59 and attributed to cluster photodissociation. There was no evidence for relatively faster signal that would also contribute to the fit of the slower edge of the TOF spectrum at m/e = 42. The lack of signal that can conclusively be assigned to primary C-H bond fission does not rule out this pathway as a contributor to the dissociation dynamics. Assuming that half of the available energy following C-H bond fission goes into relative product translation (a relatively high fraction), signal corresponding to the slowly recoiling  $CH_2N(CH_3)_2$  products could be observed at a maximum laboratory source angle of 8.5°.24 There could be contributions from this channel buried under the cluster signal at m/e = 58, but it is not possible to separate the two channels with these experimental data. Additionally, in the experiments at the ALS, we saw no evidence for primary  $H_2$  elimination, as the TOF spectrum at m/e = 57 at a 5° source angle was flat.

As does  $N(CH_3)_2$  from the fastest channel, this slow product contributes to signal only at m/e = 42 and 15. Although the cracking patterns of the heavy dissociation partners are similar between this slowest channel and the fast pathway, under softer ionization conditions, the two exhibit distinct ionization onsets.<sup>14</sup> The highest mass/charge ratio at which we have observed this signal is m/e = 42. This corresponds to the parent ion signal of a radical of formula  $NC_2H_4$ which could arise from secondary dissociation of a primary  $N(CH_3)_2$  product. We tentatively assign it to formation of  $N(CH_3)_2$  that undergoes subsequent loss of molecular hydrogen, leading to a radical of formula NC<sub>2</sub>H<sub>4</sub>. Again, it is not possible to assign the primary  $N(CH_3)_2$  radical from this distribution as formed initially in its first electronically excited state or in its ground state, and we hence label it by  $N(CH_3)_2^{\dagger}$ , both to distinguish it from the  $N(CH_3)^*_2$  radical formed in the middle distribution, as well as to indicate its high degree of internal energy. This minor channel is discussed more thoroughly in Ref. 14, where it is better characterized.

# B. Calculating the relative detection efficiency of $CH_3$ and $N(CH_3)_2$ radicals

Determining a branching ratio between dissociation channels involving polyatomic radicals can be a daunting task, due to the many possible daughter ions that can result from cracking of each polyatomic parent in the electron bombardment ionizer and the difficulty of determining the ionization cross section of polyatomic radicals. One approach involves collecting data at each and every possible daughter ion and summing the contributions of all ionic species, correcting for quadrupole transmission at each mass if possible, then dividing by an estimated ionization cross section, to deduce the total amount of neutral parent prior to ionization. This is a tedious and often impractical method, especially when there are many possible daughter ions and when some of these occur at mass/charge ratios with a high natural background (e.g., at  $CO^+$ ). It further relies on having a value of the total ionization cross section, a value that for polyatomic radicals is rarely experimentally determined and so is typically estimated with one of two semiempirical methods<sup>25,26</sup> that are untested (and give differing results) for polyatomic radicals. Following the method of Kitchen et al.,<sup>27</sup> we use the fact that  $N(CH_3)_2$  and its momentummatched CH<sub>3</sub> partner are produced in a one-to-one ratio in the initial photodissociation process.<sup>28</sup> We can then calibrate the relative detection efficiency of  $CH_3$  and  $N(CH_3)_2$  (or its secondary products) at their various daughter ions without explicitly measuring the daughter ion cracking patterns or empirically estimating the total ionization cross sections.

The dissociation channels we have observed in trimethylamine produce methyl radicals in their ground electronic state. Assuming that these are formed with similar distributions of internal energy, the methyl radicals will give signal at m/e = 15 with similar efficiencies. [Note that the same relative weightings fit both the ALS data with 10.5 eV photoionization (Fig. 5) and our 200 eV electron bombardment ionization TOF spectra (Fig. 3), so, in this system, the internal energy of the CH<sub>3</sub> radicals does not strongly influence their ionization cross section.] We can thus use the relative weightings ( $r_{prob}$ 's) of the signal assigned to CH<sub>3</sub> products at m/e = 15 to obtain the branching into the two major dissociation channels in trimethylamine. (In calculating these  $r_{\rm prob}$ 's, the usual correction for kinematic factors and transit time through the electron bombardment ionizer are included.) In Figs. 3 and 5, the methyl contributions in the m/e = 15 TOF spectra are fit by a ratio of 0.27: 0.73 [faster  $P(E_T)$ : slower  $P(E_T)$  in Fig. 2]. These values for the  $r_{\text{prob}}$ 's were determined by a least-squares procedure, using the cleaner m/e = 15 data recorded at the ALS. (See Fig. 5 and Ref. 14.) The TOF spectrum shown in Fig. 5 was obtained with an ionization energy of 10.5 eV, above the ionization potential of CH<sub>3</sub>, but much lower than the onset of dissociative ionization of  $N(CH_3)_2$  (or  $CH_2NCH_3$  or  $NC_2H_4$ ) to m/e = 15. It thus does not include any contributions from the heavier partners and gives a cleaner peak from which to determine the  $r_{\text{prob}}$ 's for the CH<sub>3</sub> contributions. With the assumption of similar relative methyl ionization efficiency to give signal at m/e = 15, this gives the relative branching into these two N-CH<sub>3</sub> bond fission channels as 27%  $N(CH_3)_2(\tilde{X}^2B_1)$  and 73% unstable  $N(CH_3)_2^*$  radicals that undergo secondary dissociation to CH<sub>2</sub>NCH<sub>3</sub>+H.

Under 200 eV electron impact ionization, N(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>NCH<sub>3</sub> dissociatively ionize ("crack") to give daughter ion signal at m/e=15. The observed signal at m/e=15 arises from a ratio of 1:1 N(CH<sub>3</sub>)<sub>2</sub>:CH<sub>3</sub> (or CH<sub>2</sub>NCH<sub>3</sub>:CH<sub>3</sub>) neutral products, but it is fit by a different relative probability weighting depending on the relative cracking efficiency of N(CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>NCH<sub>3</sub>, and CH<sub>3</sub> to m/e=15 (CH<sub>3</sub><sup>+</sup> or NH<sup>+</sup>).

The TOF spectra at m/e = 15 (Fig. 3) are fit by relative experimental weightings of 0.18:0.27 {N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ): its momentum matched CH<sub>3</sub>}; and 0.42:0.73 {CH<sub>2</sub>NCH<sub>3</sub>: the CH<sub>3</sub> momentum-matched to unstable N(CH<sub>3</sub>)<sub>2</sub><sup>\*</sup>}. (As discussed in the previous section, in fitting this signal, we assumed that CH<sub>2</sub>NCH<sub>3</sub> has the same velocity as the unstable CH<sub>3</sub>NCH<sub>3</sub> radicals before they lose a H atom.) The correction factors to obtain the relative amount of neutral precursor from the experimentally observed ion signal  $r_{\text{prob}}$ 's are thus N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^2B_1$ )<sub>neut</sub>=N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^2B_1$ )<sub>obs at mass 15</sub>×0.27/0.18=N(CH<sub>3</sub>)<sub>2</sub>( $\tilde{X}^2B_1$ )<sub>obs at mass 15</sub>×1.5; and N(CH<sub>3</sub>)<sub>2</sub>\*neut=CH<sub>2</sub>NCH<sub>3</sub>, obs at mass 15×0.73/0.42 = CH<sub>2</sub>NCH<sub>3</sub>, obs at mass 15×1.7. These are the calibration factors

=  $CH_2NCH_{3, obs at mass 15} \times 1.7$ . These are the canoration factors that determine the relative detection efficiency at m/e = 15 of these polyatomic nitrogen-containing species.

The  $r_{\text{prob}}$ 's of the two  $P(E_T)$ 's used to fit the slower portion of the signal at m/e = 15 following 200 eV electron bombardment ionization (Fig. 3) were determined by an iterative procedure, varying the relative contributions of the two distributions in order to obtain the "best fit" to the data. The error in these values can be estimated by fitting the data at m/e = 15 (in Fig. 3), varying the  $r_{\text{prob}}$ 's of the  $P(E_T)$ 's, in order to determine what probability weightings neither obviously overfit nor underfit particular parts of the TOF spectra. Similarly, the error in the branching ratio determination can be estimated by varying the  $r_{\text{prob}}$ 's of the  $P(E_T)$ 's in the methyl portion of the TOF spectra at m/e = 15 in Fig. 3, again to find the ranges of  $r_{\text{prob}}$ 's that give "acceptable" fits. We thus obtain a relative branching into the channels producing N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ): unstable N(CH<sub>3</sub>)<sup>\*</sup><sub>2</sub> of  $0.27 \pm 0.09 : 0.73 \pm 0.09$ and calibration factors of  $N(CH_3)_2 (\tilde{X}^2 B_1)_{neut} = N(CH_3)_2 (\tilde{X}^2 B_1)_{obs at mass 15} \times 1.5$  $\pm 0.3$ ; and N(CH<sub>3</sub>)<sup>\*</sup><sub>2 neut</sub>=CH<sub>2</sub>NCH<sub>3</sub>, <sub>obs at mass 15</sub>×1.7±0.3.

We can now use the calibrated mass spectrometric sensitivity to  $CH_3$ ,  $N(CH_3)_2$ , and  $CH_2NCH_3$  to determine the absolute branching between any channel that produces  $CH_3$ radicals and any channel that produces  $N(CH_3)_2$  radicals (or  $CH_2NCH_3$  molecules). One example, which uses this to calibrate the absolute branching ratio between the  $CH_3+HCONCH_3$  channel and the  $HCO+N(CH_3)_2$  channels from the photodissociation of dimethylformamide, is presented in the discussion.

#### C. Assignment of trimethylamine electronic states

As discussed in the Introduction, there have been varying assignments made of the transitions accessed in the ultraviolet region of the trimethylamine spectrum. We performed some basic CIS *ab initio* calculations on trimethylamine at the minimum energy geometry determined by Taylor *et al.* in their recent study of this molecule.<sup>9</sup> Although their calculations were performed at a higher level of theory than ours, we found our results to give interesting insight into the character of these transitions.

The  $S_1$  state is Rydberg in nature, containing dominantly *s* character on nitrogen with considerable density on the carbon atoms. The transition to this state is weakly allowed in the Franck–Condon region, with an oscillator strength of

0.014 in our calculations. The  $S_0 - S_2$  transition has traditionally been assigned as an n-3p Rydberg transition, in keeping with the assignments of ammonia states. As mentioned in the introduction, however, this state has been reassigned by Taylor et al. to be 3s in character. Our low-level calculations show this state to be composed of an admixture of *s* orbitals, delocalized about the nitrogen and carbon atoms (as in the  $S_1$ state). We have found this state to be the brightest one in the Franck-Condon region, with an oscillator strength of 0.138. This explains the strong intensity of this second transition in the ultraviolet absorption spectrum. There is additionally a doubly-degenerate (at  $C_{3v}$  geometries) state in this energetic region. Taylor et al. assign this state as one of 3p Rydberg character; however, our lower level calculations show this state to contain only a tiny admixture of *p*-type character on the nitrogen. The dominant Rydberg character of this state is found on the methyl groups (with no 3s Rydberg character on the nitrogen). This state lies higher in energy than the  $S_2$ state, both at the CIS (this work) and CAS-MP2 (work by Taylor et al.) levels of calculations, and has a weak oscillator strength (0.012). The large oscillator strength of the transition to the  $S_2$  state is convincing evidence that the  $S_2$  (3s-type) state is accessed in the experiments on trimethylamine at 193 nm, not the  $S_3$  (doubly-degenerate) state.

### **IV. DISCUSSION**

# A. Dissociation dynamics and the effect of the conical intersection

Following internal conversion to the  $S_1$  surface, trimethylamine dissociates to form  $\tilde{X}$  state N(CH<sub>3</sub>)<sub>2</sub> products [possibly also N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{A}^2 A_1$ )]. Unlike in methylamine dissociation at 222 nm, where only  $NH_2(A^2A_1)$  is produced, a considerable fraction of the dissociating trimethylamine molecules hop from the upper  $S_1$  surface to the lower  $S_0$  surface, resulting in the observed ground state products. Clearly the dynamics through the conical intersection are playing an important role. There are two dominant factors that can influence whether an amine starting on the  $S_1$  surface is funneled to the ground state via electronically nonadiabatic transitions near the conical intersection, giving NR<sub>2</sub>( $\tilde{X}^2B_1$ ) products, or whether it instead remains on the  $S_1$  surface, producing  $NR_2(\tilde{A}^2A_1)$  radicals. One of these is the velocity of the trajectory through the avoided crossing that forms the conical intersection at planar geometries. The other is the geometry of the molecule as it traverses the avoided crossing (since the geometry determines the off-diagonal potential coupling), which may be influenced by how the molecule is prepared on the  $S_1$  surface (whether direct or accessed through internal conversion). While the larger velocity through the crossing in ammonia photodissociation to NH<sub>2</sub>+H may partly contribute to the dominance of the  $NH_2(\tilde{X}^2B_1)$  product channel, a comparison of the velocity through the crossing in trimethylamine and methylamine dissociation cannot explain why the latter produces only NR<sub>2</sub>( $\tilde{A}^2A_1$ ) while the former gives considerable  $NR_2(\tilde{X}^2B_1)$ . (This is the case whether one considers the observed recoil kinetic energy distributions or the maximum allowed recoil velocities in trimethylamine and methylamine dissociation.<sup>29</sup>) We thus consider the vibrational dynamics at the conical intersection to understand the differing branching in these molecules.

Molecules encountering the conical intersection near planar geometries experience only a weak coupling between the diabatic reactant and product electronic configurations. [At planar geometries, symmetry dictates that trajectories funnel down to produce only NR<sub>2</sub> ( $\tilde{X}^2B_1$ ) radicals, the diabatic products.] However, molecules that have considerable energy in the N(CH<sub>3</sub>)<sub>3</sub> umbrella motion (or for methylamine, NH<sub>2</sub> wag motion) traverse the avoided crossing at bent geometries, where there is a large energetic splitting between the adiabatic  $S_0$  and  $S_1$  potential energy surfaces. (This energetic splitting arises from a correspondingly large offdiagonal potential coupling between the diabatic surfaces that mix and split to form the  $S_0$  and  $S_1$  adiabats.) These latter molecules thus remain on the upper adiabat during dissociation, giving excited state NR<sub>2</sub> products. Clearly the method of preparing trimethylamine (or methylamine) on the  $S_1$  surface can affect whether energy is localized in the  $N(CH_3)_3$  umbrella motion (or the NH<sub>2</sub> wag motion), inhibiting formation of ground state products. The experiments on methylamine excited the molecule directly to the  $S_1$  surface using 222 nm light. These experiments on trimethylamine, on the other hand, initially excite the molecule to the  $S_2$ surface and populate the  $S_1$  surface indirectly via internal conversion. As discussed in the introduction, this coupling between  $S_2$  and  $S_1$  likely occurs in the neighborhood of the Franck–Condon region, such that  $S_1$  is populated in the quasibound region of the potential. Nonetheless, the time required for internal conversion allows significant intramolecular vibrational redistribution to occur. The IVR is further facilitated by the higher density of vibrational states in trimethylamine, allowing energy to flow out of the Franck-Condon excited umbrella motion into degrees of freedom which give the scattering wave function more amplitude at planar geometries. Thus, the scattering wave function in trimethylamine can sample near-planar geometries, where the probability of a nonadiabatic hop to the ground state potential is larger, producing proportionally more ground state  $N(CH_3)_2$  radicals than  $NH_2(\tilde{X}^2B_1)$  observed from the smaller methylamine molecule.

A comment should be made about the vast difference between the results of our study and those of Kawasaki *et al.*<sup>5</sup> While we have found evidence for three competing primary N–CH<sub>3</sub> bond fission channels following 193 nm excitation of trimethylamine, Kawasaki *et al.* fit their data to only one translational energy distribution, which bears little resemblance to those found in this study. Additionally, they found an average of 13% of available energy following N–CH<sub>3</sub> bond fission partitioned to relative product translation, while the 29 kcal/mol average translational energy determined from the CH<sub>3</sub> TOF spectra in our studies corresponds to 39% of available energy partitioned to product recoil. The most likely reason for these differing results is the different beam conditions used in the two studies. While ours have utilized a 5% mixture of trimethylamine seeded in helium, Kawasaki *et al.* used a neat sample of trimethylamine. Recent studies have shown that clustering of amines in supersonic expansions can be significant.<sup>9,13</sup> It is likely that the spectrum observed by Kawasaki *et al.* arises from dissociation of clusters in the beam and that monomer dissociation contributes much less significantly to their results. In order to rule out the possibility of multiphoton effects contributing to our data, we performed a power study on the TOF signal at m/e=42. We confirmed that the experiments were conducted below saturation intensity, by ensuring that the integrated signal area varied linearly with laser power under the conditions of this study.

# B. The calibration of detection efficiency to obtain branching ratios

As mentioned earlier, obtaining branching ratios between dissociation channels producing polyatomic radicals is a task fraught with difficulties. The method of detection utilized in these experiments, which involves ionizing the neutral reaction products, results in the appearance of signal at various daughter ions of the precursor. No mass spectral data is available for the vast majority of radical neutral polyatomic molecules, necessitating estimates of the ionization cross section, daughter ion cracking patterns, etc. When one wishes to calibrate the branching ratio between energeticallyallowed product channels in a quantitative manner, e.g., for the purposes of modeling combustion reactions from elementary reactions, the errors introduced in such estimates can result in large uncertainties in the relative importance of various reaction channels.

In the case of trimethylamine dissociation, we calibrated the relative detection efficiency of the polyatomic products at m/e = 15, as they all fragment to give signal at this mass. Because each N–CH<sub>3</sub> bond fission channel produces CH<sub>3</sub> and N(CH<sub>3</sub>)<sub>2</sub> radicals in a one-to-one ratio, one can calibrate the relative detection efficiency of N(CH<sub>3</sub>)<sub>2</sub> (or its secondary products) at m/e = 15 without having to measure daughter ion cracking patterns or estimate total ionization cross sections. Using this method, we have determined the correction factors (by which relative signal levels at m/e = 15 must be multiplied to correct for total ionization cross sections and daughter ion cracking probabilities) to be  $1.5\pm0.3$  for N(CH<sub>3</sub>)<sub>2</sub> ( $\tilde{X}^2B_1$ ); and  $1.7\pm0.2$  for unstable N(CH<sub>3</sub>)<sub>2</sub><sup>\*</sup> undergoing secondary dissociation to CH<sub>2</sub>NCH<sub>3</sub>, relative to CH<sub>3</sub> signal level.

These calibration factors from the trimethylamine data can give corrections for the relative sensitivity of our mass spectrometric detection to each species,  $CH_3$ ,  $N(CH_3)_2(\tilde{X}^2B_1)$ , and  $CH_2NCH_3$ , at any required daughter ion. Thus, if another reactive process of interest has two competing product channels, one that produces methyl radicals and another that produces  $N(CH_2)_2(\tilde{X}^2B_1)$  radicals, we can calibrate the branching ratios between these product channels using the relative sensitivities from our trimethylamine data, and we need only take data at one daughter ion for each species. We used preliminary estimates of these calibration factors in an earlier paper in order to determine branching ratio among dissociation channels in the

N,N-dimethylformamide.<sup>6</sup> Here we use our final values for these calibration factors and discuss in the context of the trimethylamine experiments the means by which such a calibration technique can be applied to other systems. Following 193 nm excitation, dimethylformamide was found to dissociate along three primary bond fission pathways,

$$\operatorname{HCON}(\operatorname{CH}_{3})_{2} + 193 \operatorname{nm} \rightarrow \operatorname{HCO}\left(\widetilde{X}^{2}A'\right) + \operatorname{N}(\operatorname{CH}_{3})_{2}\left(\widetilde{X}^{2}B_{1}\right)$$
(5)

$$\rightarrow \text{HCO}\,(\tilde{X}\,^{2}A') + \text{N}(\text{CH}_{3})_{2}\,(\tilde{A}\,^{2}A_{1})$$
(6)

$$\rightarrow$$
 HCONCH<sub>3</sub>+CH<sub>3</sub>. (7)

All three channels produce radicals containing the methyl group, which all crack following ionization to give signal at m/e = 15. The branching among these channels can thus be calibrated if we know the relative amount of  $N(CH_3)_2(\tilde{X}^2B_1)$ ,  $N(CH_3)_2(\tilde{A}^2A_1)$ , and  $CH_3$  which give rise to the observed fragment signal at m/e = 15. Although the secondary decomposition of  $N(CH_3)_2(\tilde{A}^2A_1)$  to CH<sub>2</sub>NCH<sub>3</sub>+H was not assigned in Ref. 6, from the results here and the similarities in internal energy and cracking patterns of the neutral species, it is obvious that the species giving rise to signal at m/e = 43, 42, and 15 is the same in both studies. The experiments on trimethylamine have provided these calibration factors, as they have been performed under identical detection conditions. To determine the relative branching among these channels, we simply multiply the relative probability weightings of  $N(CH_3)_2(\tilde{X}^2B_1)$ , CH<sub>2</sub>NCH<sub>3</sub> (possibly arising from the primary product  $N(CH_3)_2 (\tilde{A}^2 A_1)$  and  $CH_3$  at m/e = 15 in dimethylformamide by the calibration factors determined in this paper. The TOF spectra at m/e = 15 in Ref. 6 were fit using a relative branch- $N(CH_3)_2 (\tilde{X}^2B_1):CH_2NCH_3:CH_3$ among ing =0.15:0.38:0.46. Using the calibration factors for  $N(CH_3)_2$ and CH<sub>2</sub>NCH<sub>3</sub>, relative to CH<sub>3</sub>, determined in this paper, the branching of reactions (5):(6):(7)=0.17:0.49:0.34. The calibration factors determined in this paper vary slightly from those preliminary ones given in Ref. 6, but they fall well within the limits of error placed on this method.

This method of calibrating branching ratios and detection efficiency is not restricted to experiments using electron bombardment ionization for product detection or to photodissociation reactions. A calibrant molecule (AB) that dissociates to form  $\mathbf{A} + \mathbf{B}$  (in a one-to-one ratio) can be used to calibrate the signal intensity at **A** and **B** (at any convenient parent or daughter ions in a mass spectrometric experiment or pair of ions in an experiment using photoionization detection). This can then be used to determine the branching ratio between formation of **A** and **B** products in a separate reaction (e.g., the branching between  $AB+CD \rightarrow A+BCD$  and AB $+CD \rightarrow B + ACD$ ). We hope the experiments here illustrate the advantages of using such a calibration method, and also demonstrate the importance of ensuring that the internal energy of the species being detected is similar between the calibration and reactive systems.

#### **V. CONCLUSIONS**

We have observed primary  $N-CH_3$  bond fission following excitation of trimethylamine at 193 nm to result in two major dissociation channels producing nitrogen-containing species,

$$N(CH_3)_3 + 193 \text{ nm} \rightarrow CH_3 + N(CH_3)_2 (\tilde{X}^2 B_1)$$
  
$$CH_3 + N(CH_3)_2^* \rightarrow CH_3 + H_2 C = NCH_3 + H$$

and one possible minor channel tentatively assigned to

$$N(CH_3)_3 + 193 \text{ nm} \rightarrow CH_3 + N(CH_3)_2^{\dagger} \rightarrow CH_3 + NC_2H_4 + H_2.$$

The competitive fission to ground state  $N(CH_3)_2$  radicals is evidence for the influence of the conical intersection on the dissociation dynamics of this molecule. By comparison with methylamine, whose  $NH_2$  wagging dynamics cause the molecule largely to avoid the conical intersection in the exit channel to  $N-CH_3$  bond fission and to form  $NH_2(\tilde{A}\,^2A_1)$ , we conclude that in trimethylamine, intramolecular vibrational energy redistribution allows the molecule more strongly to feel the influence of the conical intersection.

Additionally, we have used the relative signal intensities at m/e = 15 from the CH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>, and CH<sub>2</sub>NCH<sub>3</sub> products to calculate calibration factors for the amount of signal observed at this mass/charge ratio of the radical products. The method used in this study to determine calibration factors for detection of radical products can be applied to a wide variety of molecular systems and methods of detection.

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