Electronic accessibility of dissociation channels in an amide: N,N-dimethylformamide photodissociation at 193 nm

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Measurement of the photofragment velocity and angular distributions from the photodissociation of N,N-dimethylformamide at 193 nm in its $\pi_{nb}\pi^*$ absorption evidences three competing dissociation channels: HCON(CH₃)₂ \rightarrow HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{X}^2B_1); HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{A}^2A_1); and HCONCH₃+CH₃. (H atom eliminations are not probed.) These products are formed in a ratio of 0.15±0.04:0.49±0.09:0.36±0.07, determined by use of trimethylamine as a calibrant molecule. Nitrogen–carbonyl bond fission occurs on a rapid time scale with an angular distribution of the dissociation products given by $\beta = 1.2\pm0.2$. Excited state N(CH₃)₂ products are formed quasidiabatically from the initial planar geometry, whereas symmetry-breaking vibrations allow one-electron matrix elements to couple the initial electronic configuration to the ground state N(CH₃)₂+HCO channel. Competition of nitrogen–methyl bond fission is evidence of the strong coupling between the $\pi_{nb}\pi^*$ excitation and the nitrogen–methyl reaction coordinate; *ab initio* calculations confirm that the electronic excitation is not localized on the N–C=O moiety. We also include here an advance report of the excited state energy of the N(CH₃)₂(\tilde{A}^2A_1) radical, which is found to be 1.59 eV. © *1999 American Institute of Physics*. [S0021-9606(99)01218-0]

I. INTRODUCTION

The amide functional group, RCONR₂, is responsible for many important chemical properties, from serving as a linkage in proteins to acting as a building block for many polymers. Knowledge of how this group interacts with ultraviolet light has important implications in such diverse fields as laser surgery and photodegradation of polymers. Although there have been numerous studies of the ultraviolet photodissociation pathways of amides, the majority of experiments predate 1970. The lack of conclusive experiments on the primary reaction channels of this key class of compounds in the last 20 years is most likely due to the possibility of many competing fragmentation pathways, only a few of which can be studied by detecting the products with traditional spectroscopic methods such as LIF and REMPI. Table I summarizes the results of prior studies of primary photochemical pathways in amides.¹⁻⁸ While these early studies provide an invaluable starting point for further investigations, most of the experiments were conducted using solution-phase reactants, making the analysis of primary processes challenging. Also, the illumination source in most of these experiments was a mercury-arc lamp, accessing the $n\pi^*$ transition centered around 225-235 nm.9

The amide functional group combines the pi electrons of the carbonyl group with the lone pair on nitrogen. While three-coordinate nitrogen is generally sp^3 hybridized, in amides the participation of the nitrogen lone pair electrons in delocalized pi bonds is preferred. The resulting structure is planar about the nitrogen, and rotation about the carbonylnitrogen bond is hindered. The origin of this rotational barrier can be easily understood by considering the resonance structures shown in Fig. 1. Determining the barrier to rotation about the carbonyl-nitrogen bond (typically, 15–20 kcal/mol for small amides¹⁰) is an active area of research, as this amide bond is a small-molecule analog to peptide bonds in proteins. Planarity of the peptide bond is central to protein structure and function.

Recent high-level ab initio CASSCF and CASPT2 calculations on a series of small amides¹¹ have confirmed earlier results by Nagakura^{12,13} that charge transfer plays a significant role in the $\pi_{\rm nb}\pi^*$ transition. In addition to the importance of charge transfer, the differences in the UV resonance Raman spectra between molecules with isolated amide linkages, such as N-methylacetamide (NMA), and those with polyamide backbones, such as peptides, have suggested that the π^* state in these systems may involve a delocalization of electron density over the polyamide backbone.¹⁴ To provide a picture of this delocalization, we will present the results of our own ab initio calculations, performed in order to better understand the nature of the orbitals contributing to this $\pi_{\rm nb}\pi^*$ transition in N,Ndimethylformamide. Although these calculations are obtained from a lower level of theory than the CASSCF calculations above, they shed some useful light on the extent of π delocalization in this simple molecule, while offering insight into the dynamics we observe following 193 nm photodissociation of N,N-dimethylformamide.

In order to understand the initial forces on the amide potential energy surface accessed via the $\pi_{nb}\pi^*$ absorption,

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TABLE I. Flevious photolysis studies of allides.	TABLE I.	Previous	photolysis	studies	of	amides.a
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Molecule	Phase/solvent	Primary process(es) observed	Reference(s)
Formamide HCONH ₂	Aqueous with acetone and/or	H+CONH ₂	1
	H_2O_2 Frozen aqueous	H+CONH ₂	2
N-methylformamide HCONHCH ₃	Aqueous with acetone and/or H_2O_2	$H+HCONHCH_2$ (inequivalent CH_2 H's)	1
	Frozen aqueous	H+CONHCH ₃	2
N,N-dimethylformamide $HCON(CH_3)_2$	Aqueous with acetone and/or H_2O_2	H + $HCON(CH_2)(CH_3)$ (inequivalent CH_2 H 's)	1
Acetamide CH ₃ CONH ₂	Aqueous with acetone and/or H_2O_2	H+CH ₂ CONH ₂ (equivalent CH ₂ H's)	1
	Frozen aqueous	$CH_3 + CONH_2$	2
	Aqueous	CH_3CO+NH_2	3
	Hexane	CH_3NH_2+CO	4
	Gas, gas with	CH CN+H O	5
	Dioxane, acetonitrile	No reaction	6
N-methylacetamide	Aqueous with	H+CH ₃ CONHCH ₂ or	1
CH ₃ CONHCH ₃	acetone and/or H_2O_2	H+CH ₂ CONHCH ₃	2
	Frozen aqueous	CH ₃ +CONHCH ₃	2
N,N-dimethylacetamide $CH_3CON(CH_3)_2$	Cyclohexane, dioxane	$CH_3CO (or CH_3+CO)+N(CH_3)_2$	6
	Gas	$\begin{array}{c} CH_3CO+N(CH_3)_2\\ CH_3+(CH_3)_2NCO<1\%\end{array}$	7
Propionamide CH ₂ CH ₂ CONH ₂	Dioxane, hexane	C ₂ H ₄ +HCONH ₂	4
5 2 2	Dioxane, acetonitrile	No reaction	6
N,N-dimethylpropionamide CH ₃ CH ₂ CON(CH ₃) ₂	Cyclohexane, dioxane	$C_2H_5CO (or C_2H_5+CO)+N(CH_3)_2$	6
<i>n</i> -Butyramide	Dioxane, hexane	C ₃ H ₇ NH ₂ +CO	4
	Dioxane acetonitrile	No reaction	6
N,N-dimethyl- <i>n</i> -butyramide CH ₃ (CH ₂) ₂ CON(CH ₃) ₂	Cyclohexane, dioxane	$C_{3}H_{7}CO \text{ (or } C_{3}H_{7}+CO)+N(CH_{3})_{2}$	6
<i>n</i> -valeramide	Hexane	$C_4H_9NH_2+CO$	4
Ch3(Ch2)3CCh12	Dioxane, acetonitrile	No reaction	6
<i>n</i> -hexanoamide $CH_3(CH_2)_4CONH_2$	dioxane, hexane	$C_5H_{11}NH_2+CO$	4
Stearamide CH ₃ (CH ₂) ₁₆ CONH ₂	Hexane	RNH ₂ +CO	4
Various dipeptides Gly-Gly, DL-Ala-Gly, L-Val-Gly, L-Pro-Gly, L-Phe-Gly, Gly-L-Phe, L-prolyl-L-phenylalanine, L-phenylalanyl-L-proline	Aqueous	Deamination Decarboxylation Zwitterionic intermediates	8

^aAll of these experiments used a mercury-arc lamp for illumination, except for Ref. 7, which used a xenon discharge for flash photolysis.



FIG. 1. Resonance structures for ground state N,N-dimethylformamide showing the contribution of charge transfer to the ground state. Also noted are the conventions for labeling the substituents on the amide nitrogen. Note that *cis* and *trans* denote positions with respect to the hydrogen substituent on the carbonyl moiety, standard convention for proteins but contrary to standard organic nomenclature, which labels positions with respect to the higher atomic number oxygen atom.

there have been many experiments in recent years to elucidate the resonance Raman spectra of small amides in the UV.¹⁴⁻¹⁹ Due to the $\pi_{nb}\pi^*$ character of the transition accessed in the far UV some torsion about the C–N bond is expected in the excited state, much as torsion about the

$HCON(CH_3)_2 \rightarrow$	+ CO+HN(CH ₃) ₂	$\Delta H^\circ = 14.8 \pm 0.5 \text{ kcal/mol}$
	HCONCH ₃ +CH ₃	$\Delta H^{\circ} \approx 80 \mathrm{kcal/mol}$
	$H+CON(CH_3)_2$	$\Delta H^{\circ} = 81.7 \pm 0.5$ kcal/mol
	$HCO+N(CH_3)_2$	$\Delta H^{\circ} = 89.7 \pm 3.2 \text{ kcal/mol}$
	$H+CO+N(CH_3)_2$	$\Delta H^{\circ} = 110.1 \pm 1.1$ kcal/mol
	$HCON(CH_3)(CH_2) + H$	$\Delta H^{\circ} \approx 105$ kcal/mol.

In an earlier publication, we discussed the dynamics of the dissociation channel leading to $HCO+N(CH_3)_2$ products.²⁴ On the basis of translational energy imparted to fragment recoil, we assigned the electronic states of these products as $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$. A closer examination of the photofragment time of flight distributions reveals the presence of an additional $HCO+N(CH_3)_2$ channel. In this paper, we will discuss the electronic changes necessary to access both of these nitrogen–carbonyl bond fission pathways in the context of the model we developed in Ref. 24. We will also examine the nitrogen–methyl dissociation pathway observed following 193 nm excitation and discuss its relative importance in the overall photofragmentation dynamics of N,N-dimethylformamide.

II. EXPERIMENTAL AND COMPUTATIONAL METHOD

A. Experimental Method

The photodissociation experiments consist of two parts. We first photodissociate the dimethylformamide molecules using unpolarized 193 nm light. We detect dissociation products as a function of their masses and neutral fragment times of flight using a crossed laser–molecular beam apparatus.²⁵ This allows us to determine the recoil translational energy distributions of the fragments formed in the dissociation process. We can then polarize the laser light and detect signal at selected masses in order to learn about the angular distribution of the photofragmentation process.

C=C bond in ethylene has been found following excitation via its $\pi\pi^*$ transition.^{20,21} However, while in ethylene a long progression of even overtones of the C=C torsion mode is observed in 184 nm resonance Raman spectra,²⁰ a progression torsional overtones shorter of in N-methylacetamide indicates an excited state with less C-N twist.^{14-16,22} Due to the similarity in size between N-methylacetamide and N,N-dimethylformamide $[HCON(CH_3)_2]$, we might expect torsion about the C–N bond in dimethylformamide to have an influence on the dissociation dynamics of this molecule.

In this paper, we present the photodissociation pathways of dimethylformamide following excitation via the $\pi_{nb}\pi^*$ transition. These experiments are the first to examine the dissociation dynamics of an amide under collisionless conditions, enabling us to definitively assign primary photodissociation pathways. From the studies listed in Table I, we can list the following energetically accessible product channels for the photodissociation of dimethylformamide at 193 nm:²³

N,N-dimethylformamide (obtained from Fisher Scientific; 99.9% purity) was degassed and heated to 56 °C in a constant-temperature bath to generate a vapor pressure of 23 Torr. We bubbled helium through the liquid sample to provide a total stagnation pressure of 300 Torr. This 8% mixture of dimethylformamide in helium was then expanded through a 0.12 mm diameter nozzle, heated to 235 °C. The high nozzle temperature was required to reduce the presence of clusters in the supersonic expansion. (We measured the nozzle temperature using a chromel alumel thermocouple, which we 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 1.75×10^5 cm/s with a full width at half-maximum (FWHM) of 18.3%.

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° 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 the total time of flight (TOF) of the parent neutral photofragment and daughter ion from the interaction region after the dissociating laser pulse. For-

TABLE II. Optimized CH₃ geometries in N(CH₃)₂.^a

Electronic state	r _{C-H1}	<i>r</i> _{C-H2,3}	∠NCH1	∠NCH2,3	∠CNCH1 ^b	∠CHCH2,3	Method
$N(CH_3)_2 (\tilde{X}^2 B_1)$ $N(CH_3)_2 (\tilde{A}^2 A_1)$	1.09 Å 1.09 Å	1.10 Å 1.09 Å	110.6° 108.1°	110.7° 112.7°	180° 180°	±59.1° ±61.7°	MP2 Average of CIS and CIS-MP2

^aThe dimethylamidogen radical was constrained to have C_{2v} symmetry, so both methyl groups have the same internal coordinates. H1 lies in the CNC plane in the *trans* position; H2 and H3 lie symmetrically above and below this plane.

^bThe 0° structure was found to lie slightly higher in energy.

ward 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.

In order to determine the extent of clusters present in the expansion, we examined the parent beam TOF signal at dimethylformamide (m/e=73) and at this mass plus one (m/e=74) by rotating the molecular beam source to point into the detector and raising the chopper wheel to intersect the beam. Since signal observed at m/e = 74 cannot arise from monomers in our beam, we attributed this signal to clusters and tried to eliminate it. Raising the nozzle temperature reduced the signal at m/e = 74, thus reducing the contribution of clusters to the beam. At a nozzle temperature of 110 °C, the signal to noise ratio at m/e = 74 was equal to that at m/e = 73. At the higher temperature of 235 °C, the signal to noise ratio at m/e = 74 was reduced to one-tenth that at m/e = 73. At this higher temperature, we identified all signals due to the photodissociation of clusters in our photofragment TOF spectra by taking photofragment TOF data (at angles tilted from the molecular beam) at the spectral monomer of the clusters, m/e = 73, a mass that cannot arise from dissociation of the real monomer.

The signal was observed at various angles for several parent and daughter ions of the primary, neutral photoproducts: at m/e = 73 (6°, 1 M laser shots, for clusters only), 57 (10°, 250 K shots; 15°, 250 K shots; 20°, 500 K shots), 43 (10° 1 M shots), 42 (10°, 300 K shots), 30 (6°, 2 M shots), 29 (10°, 1 M shots), 15 (6°, 1 M shots; 10°, 1 M shots; 15°, 1 M shots; 20°, 1 M shots), and 14 (10°, 250 K shots). No discernible signal was observed at m/e = 73 (10°, 250 K shots), 72 (6°, 250 K shots; 10°, 250 K shots), 58 (10°, 250 K shots), 44 (10°, 250 K shots; 10°, 250 K shots), 44 (10°, 250 K shots), 30 (10°, 300 K shots) or 16 (6°, 300 K shots). Due to the strong natural background at m/e = 28 (caused by CO⁺), no signal could be detected at this mass. Quadrupole resolution was adjusted to roughly 1.0 amu FWHM for all masses.

To determine a relative branching ratio between the three channels observed, trimethylamine $[N(CH_3)_3]$ was used as a calibrant molecule. A 5% mixture of trimethylamine in helium was obtained from Matheson Gas Products. Trimethylamine was photodissociated at 193 nm, and products were collected by the same method used for dimethyl-formamide.

A Lumonics PM-848 excimer laser filled with ArF produced the 193 nm light used to photodissociate the dimethylformamide and trimethylamine molecules. The laser beam was focused to give an attenuated laser energy of 6 mJ/pulse (for dimethylformamide) or 4 mJ/pulse (for trimethylamine) in a 6 mm^2 spot size in the crossing region with the molecular beam. In order to generate polarized light, we dispersed the unpolarized laser light into two linearly polarized components with a single crystal quartz Pellin-Broca prism. We used the horizontal component and rotated the polarization into the desired direction with a half-wave retarder. For these polarized experiments, the output pulse energy was power-locked to 1.6 mJ/pulse in the interaction region. In order to avoid any systematic errors in determining the anisotropies of the scattered photofragments, we measured the polarization dependent signal by taking many repeated short scans of 50 000 laser shots each, alternating between each laser polarization direction, for a total of 200 000 laser shots. Because of these averaging techniques, no additional normalization to laser power or detector efficiency was necessary. Lab polarization angles are measured in the opposite direction as source rotation angles for the data shown here; both are measured with respect to the detector axis.

B. Calculational method

To determine the character of the excited state accessed at 193 nm, we ran a configuration interaction with single excitations (CIS) calculation with GAUSSIAN94 using a $6-31G^*$ basis set of atomic orbitals.²⁶ Hartree–Fock geometry optimization was used to obtain the molecular structure used in these calculations, giving a resultant geometry similar to that obtained by an MP2 method using the same $6-31G^*$ basis set.¹¹ Additional CIS calculations were performed at nonplanar geometries arising from out-of-plane wag of the methyl groups. We visualized the orbitals involved in the $\pi_{nb}\pi^*$ transition, obtained from the CIS calculation, using gOpenMol.²⁷

Here we also include an advance report of results on the \tilde{A} state energy of the N(CH₃)₂ radical, work done by the collaborative team of our sabbatical-leave visitor S. Abrash with Professor K. Freed and his graduate student D. Potts. The calculation uses the effective valence shell Hamiltonian electronic structure method (H^v) pioneered by Freed and co-workers.²⁸ For C and N, the Dunning cc-pVTZ basis set was used, augmented by 3*s*, 3*p*, and 4*s* Dunning–Hays Rydberg orbitals (12s6p2d1f/6s4p2d1f), while the Dun-

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ning cc-pVDZ basis set (4s1p/2s1p) was used for H, giving a total of 150 basis functions.²⁹ The calculations were carried out to third order. These preliminary results restricted the search for a minimum energy geometry in the ground and the \overline{A} states to C_{2v} geometries, optimizing the N–C bond length and CNC angles to identify an approximation to the minimum energy structures. The methyl degrees of freedom (bond lengths and angles) were frozen at the MP2 optimized geometry (for the \tilde{X} state) and the average of the CIS and CIS-MP2 optimized geometries (for the \tilde{A} state), as calculated using GAUSSIAN94,²⁶ and are listed in Table II. The reported excitation energy of the \tilde{A} state is from the minimum of the potential in the ground state to the minimum of the potential in the \tilde{A} state (with geometry restrictions as noted above), so does not account for any differences in zero-point energy.

III. RESULTS AND ANALYSIS

A. Photodissociation pathways

To determine the competing bond fission channels in the photodissociation of N, N-dimethylformamide at 193 nm, we fit the time-of-flight (TOF) data collected at various mass/ charge ratios to translational energy distributions. Because of extensive fragmentation in our electron-bombardment ionizer, it is possible to see many different daughter ions arising from the same neutral photofragment. By the 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 translational energy distributions corresponding to three reaction channels, which account for the signal observed from monomer dissociation:

 $HCON(CH_3)_2 + 193 \text{ nm} \rightarrow HCO + N(CH_3)_2$ (fast), (IA)

$$HCO+N(CH_3)_2$$
 (slow), (IB)

$$HCONCH_3 + CH_3.$$
 (II)

For the rest of this paper, we will refer to reactions (IA) and (IB) as breaking the "N–CO bond," and to channel (II) as breaking the "N–CH₃ bond."

Figures 2 and 3 show TOF spectra, Fig. 2 taken at m/e = 57 (CONCH₃⁺) at a source angle of 10°, and Fig. 3 at m/e = 15 (CH₃⁺) at four different source angles. We fit the

HCON(CH₃)₂+193 nm \rightarrow HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{X}^2B_1) HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{A}^2A_1) signal at m/e = 57 to a photofragment translational energy distribution $[P(E_T)]$ corresponding to N–CH₃ bond fission, as shown in Fig. 4. We assign this signal to N-CH₃ bond fission because of the presence of the momentum-matched methyl fragment at early arrival times in the signal observed at m/e = 15. Only the fast shoulder of the signal observed at m/e = 15 arises from primary methyl fragments from N-CH₃ bond fission; the remainder of the signal arises from the cracking of heavier fragments to CH_3^+ daughter ions in the ionizer: HCONCH₃ (whose TOF can be predicted using the m/e = 57 TOF spectrum) and N(CH₃)₂ arising from N-CO bond fission (see the next paragraph). The signal due to N-CH₃ bond fission appears at additional daughter fragments of HCONCH₃⁺: at m/e = 43 (HCON⁺), m/e = 42 (CON^+) and 29 (HCO^+, CH_3N^+) (see Figs. 5–7). Although we do not observe the signal at the parent mass of $HCONCH_3^+$, it is likely that this parent ion is unstable and fragments to the observed daughter ions.

Figures 6 and 7 show TOF spectra collected at a source angle of 10°, at m/e = 42 and m/e = 29. The bulk of the signal at m/e = 42 is from N-CO bond fission to make $HCO+N(CH_3)_2$, where the $N(CH_3)_2$ radicals crack to give $NC_2H_4^+$ daughter ions following electron bombardment ionization. The assignment of this signal to N-CO bond fission is confirmed by the presence of the momentum-matched HCO partner fragment at parent mass 29. Both spectra were fit with the photofragment translational energy distributions shown in Fig. 8. Note that two distributions for fission into $HCO+N(CH_3)_2$ are required to fit these data. The signal in Fig. 5 taken at m/e = 43 clearly shows that none of the "fast" $N(CH_3)_2$ fragments crack to give $C_2H_5N^+$ ions, whereas the "slow" fragments do appear at this mass/charge ratio. At m/e = 42, however, the TOF spectrum exhibits contributions from daughter ions of both "fast" and "slow" $N(CH_3)_2$ products (in a 1:3 ratio). The ratio of fast:slow $N(CH_3)_2$ appearing at m/e = 15 is 1:2.5. Since the ratio of fast:slow N(CH₃)₂ products is not constant at all daughter ions observed, these products must be formed with very different ranges of internal energies and hence via distinct dynamical processes. In the Discussion section of this paper, we outline the reasons for assigning these two N-CO bond fission processes to

Figure 3(a) shows the TOF signal observed at m/e = 15 (CH₃⁺), at a 6° source angle. The late-arriving signal cannot be completely fit by the kinetic energy recoil distributions $[P(E_T)$'s] assigned to N-CH₃ and N-CO bond cleavage, and we attribute it to the presence of clusters in our expansion. Figure 9(a) shows a TOF spectrum recorded at m/e = 73 [HCON(CH₃)₂⁺] at a 6° source angle. Because we ob-

served this signal at the mass/charge ratio of the parent dimethylformamide molecule, it must arise from photodissociation of clusters present in the expansion. While clusters comprise only a small percentage of the sample in our beam (see the Experimental section), the signal attributable to their photodissociation appears at late arrival times for most mass/ charge ratios, where dissociation of monomers is also ob-



FIG. 2. The experimental TOF spectrum for the photodissociation of dimethylformamide, taken at m/e = 57, at a 10° source angle and representing data collected over 250 000 laser shots. Open circles represent experimental data points; the forward convolution fit to this spectrum (shown in a bold line) determines the total recoil kinetic energy distribution for fission to HCONCH₃+CH₃, as shown in Fig. 4. The $P(E_T)$ shown in Fig. 4 is used to fit all of the signal observed from the HCONCH₃ fragments, detected here and at other daughter ion mass/charge ratios, and their momentum-matched CH₃ partners.

served. This signal is only apparent at small source angles, since slow-moving fragments cannot recoil to larger angles. In order to assign the late-arriving signal detected at all masses to cluster photodissociation, we fit the TOF spectrum shown in Fig. 9(a) to determine the center-of-mass recoil speed distribution of the monomer. This velocity distribution, P(v) [shown in Fig. 9(b)], is then used to fit the late-arriving signal in Fig. 3(a) and in other TOF spectra, arising from cracking of the photo-produced monomer in the ion-izer.

A small amount of signal was detected at m/e = 30 at a 6° source angle, as shown in Fig. 10. This signal could arise from the possible ions CH₂O⁺, HCOH⁺, and C₂H₆⁺. The slow signal was fit using the velocity distribution of the cluster fragments discussed above. There also appears to be a hint of signal at faster arrival times near 180 μ s. We cannot arrive at a definitive assignment of this faster signal. Assuming it results from neutral recoiling photofragments having masses 30 and 43, respectively, we can fit it to a $P(E_T)$ peaking near 10 kcal/mol (FWHM=13 kcal/mol), but we see no signal that can be attributed to a momentum-matched partner of a mass 30 photofragment.



FIG. 3. Experimental TOF spectra for the photodissociation of dimethylformamide, taken at m/e=15, at four different source angles and representing data collected over one million laser shots each. Open circles represent experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from channels shown in dashed lines. The fits for each pair of momentum-matched fragments were calculated from the respective $P(E_T)$'s in Figs. 4 and 8. (a) 6° (The late-arriving signal is attributed to daughter ions of the fragment from cluster photofragmentation as it has the identical time of flight as the signal from clusters at m/e=73 in Fig. 9). (b) 10° (c) 15° (d) 20° (This TOF spectrum was used to calibrate the branching into HCO+N(CH₃)₂ and HCONCH₃+CH₃ bond fission channels, as its detector conditions were identical to those in the trimethylamine photodissociation experiments³²).

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FIG. 4. Translational energy distribution, $P(E_T)$, used to fit the nitrogenmethyl bond dissociation pathway, obtained from a forward convolution fit to the data in Fig. 2.

Previous studies on amide photochemistry have included contributions from a decarbonylation channel,⁴ corresponding in the case of N,N-dimethylformamide to

 $\mathrm{HCON}(\mathrm{CH}_3)_2 + 193 \,\mathrm{nm} \rightarrow \mathrm{CO} + \mathrm{HN}(\mathrm{CH}_3)_2,$

 $\Delta H^{\circ} = 14.8 \pm 0.5 \text{ kcal/mol}$ (Ref. 23).

We saw no evidence for this reaction as a primary dissociation channel. Although the high natural background of CO⁺ in our detector prevented us from directly detecting the CO product of this reaction, we observed no signal at the mass/ charge ratio of the parent ion $HN(CH_3)_2^+$ (m/e=45), or at m/e=44, corresponding to the loss of a proton. In addition, we saw no signal at other possible daughter ions of dimethylamine ($C_2H_5N^+$, $C_2H_4N^+$, CH_4N^+ , CH_3N^+ , CH_3^+ , and N^+), which could not be fit using a combination of recoil



FIG. 5. An experimental TOF spectrum for the photodissociation of dimethylformamide, taken at m/e=43, at a 10° source angle and representing data collected over one million laser shots. Open circles represent experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from channels shown in dashed lines. Note that only one nitrogen–carbonyl bond fission channel appears at this mass/charge ratio.



FIG. 6. An experimental TOF spectrum for the photodissociation of dimethylformamide, collected at m/e=42, at a 10° source angle and over 300 000 laser shots. Open circles represent experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from channels shown in dashed lines. Note that two nitrogen–carbonyl bond fission channels contribute to the signal at this mass/charge ratio.

kinetic energy distributions from reactions I and II (plus possible cluster contributions at smaller recoil angles). The early signal at m/e=30 mentioned above cannot be assigned to this process because no peaks are seen at corresponding arrival times from other possible sister ions arising from cracking of the HN(CH₃)₂ parent.



FIG. 7. An experimental TOF spectrum for the photodissociation of dimethylformamide, collected at m/e = 29, at a 10° source angle and over one million laser shots. Open circles represent experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from channels shown in dashed lines. The ratios of fast:slow HCO and fast:slow N(CH₃)₂ contributions were each constrained to have a ratio of fast:slow = 1.0:3.3, i.e., identical to the branching ratio determined using trimethylamine at m/e = 15 as described in the body of the paper. While contributions from N(CH₃)₂ are shown in this figure, their importance is undetermined. The signal at m/e = 29 arising from cracking of N(CH₃)₂ in the ionizer was not observed following trimethylamine dissociation, and its presence here cannot be definitively assigned. Including contributions from $N(CH_3)_2$ overfits the fast edge of the slow peak while underfitting the dip between peaks. Leaving these contributions out entirely (and adjusting the weightings of the other contributions) does a similarly poor job of fitting the data.



FIG. 8. Translational energy distributions, $P(E_T)$'s, used to fit the nitrogen– carbonyl bond dissociation pathways. The slower distribution is assigned to the formation of $\text{HCO}(\tilde{X}^2A') + \text{N}(\text{CH}_3)_2(\tilde{X}^2B_1)$; the faster distribution is assigned to the formation of $\text{HCO}(\tilde{X}^2A') + \text{N}(\text{CH}_3)_2(\tilde{A}^2A_1)$. The body of the paper contains a discussion of why two translational energy distributions are required to fit the TOF data. The $P(E_T)$'s are weighted by their relative contributions to N–CO bond fission (fast:slow=1.0:3.3).

Another photochemical reaction channel found in the literature for amides involves fission of a C-H bond. We are unable to detect signal corresponding to H-atom formation (m/e=1) due to high background counts in our detector. Considering the bond dissociation energies for the two distinct C–H bond fission channels in dimethylformamide,²³ we could hypothetically see the signal from the heavy momentum-matched fragment at angles smaller than 11° for hydrogen-carbonyl fission and 8° for hydrogen-methyl fission. These maximum angles correspond to the case where all of the energy remaining after C-H bond fission goes into product translation. Our small-angle data shows no evidence of these channels, but a signal from these pathways could be buried under the cluster contributions, which also appear at slow arrival times, or could simply be constrained to lie at still smaller angles (at which we cannot measure signal) by less energy imparted to relative product translation.

B. Branching among product channels

Determining a branching ratio between dissociation channels involving polyatomic products 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. One approach involves collecting data at each and every possible daughter ion and summing the contributions of all ionic species (and, in the best case, correcting for the transmission of each ion mass through the quadrupole), then multiplying by the photofragment ionization cross section (which is often only poorly known experimentally). 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 experimental estimates of the total ionization cross section, esti-



FIG. 9. (a) An experimental TOF spectrum taken at m/e = 73, at a 6° source angle, and collected over one million laser shots. Open circles represent experimental data points; the total fit to this data is shown in a bold line and is attributed to the photodissociation of clusters in our beam. (b) The recoil velocity distribution used to fit this signal.



FIG. 10. An experimental TOF spectrum taken at m/e=30, at a 6° source angle, and collected over two million laser shots. The thin line represents experimental data points; the total fit to this spectrum (shown in a bold line) is a sum of contributions from the cluster dissociation P(v) shown in Fig. 9(b) and a trial fit to the fast signal described in the text. The small amount of signal arriving from 132–226 μ s is statistically significant above the background.

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mates that are rare and often unreliable for polyatomic radicals. To circumvent these difficulties, we adopt a method described by Kitchen *et al.*,³⁰ using a second molecule, in this case trimethylamine [N(CH₃)₃], as a calibrant molecule in order to determine a branching ratio for dimethylformamide.

We wish to determine the relative branching to the photodissociation channels we observe in dimethylformamide, one of which produces CH_3 radicals and the other two that produce radicals in the \tilde{X} and \tilde{A} states, respectively, of N(CH₃)₂. Trimethylamine is known to dissociate following 193 nm excitation:³¹

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

Assuming that the dimethylamidogen $[N(CH_3)_2]$ and methyl radicals from trimethylamine dissociation are formed with similar internal energy as those from dimethylformamide photodissociation, their cracking patterns to daughter ions should be the same from both sources. Reference 32 reports our recent experiments on trimethylamine photodissociation at 193 nm. We have observed two N–CH₃ bond fission pathways that form stable N(CH₃)₂ radicals:

N(CH₃)₃+
$$h\nu \rightarrow$$
N(CH₃)₂(\tilde{X}^2B_1)+CH₃,
N(CH₃)₂(\tilde{A}^2A_1)+CH₃.

Excited state dimethylamidogen radicals formed in the latter reaction exhibit similar daughter ion cracking probabilities (at m/e = 43 and 42) as the "slow" N(CH₃)₂ radicals formed by photodissociating dimethylformamide. Ground state dimethylamidogen radicals formed in the first reaction show no daughter ion signal at m/e = 43 but do appear at m/e = 42 as do the "fast" N(CH₃)₂ radicals formed by photodissociating dimethylformamide. This allows us to use trimethylamine as a calibrant molecule for determining the branching ratio among the two N–CO and the N–CH₃ bond fission pathways in dimethylformamide.

When ionized, all of the products from trimethylamine photodissociation give a signal at m/e = 15. This observed signal at m/e = 15 arises from a ratio of 1:1 N(CH₃)₂:CH₃ neutral products (for each N-CH₃ bond fission channel, respectively), but is fit by a different relative probability weighting depending on the relative cracking efficiency of $N(CH_3)_2$ and CH_3 to CH_3^+ and on the total ionization cross section of each species. The TOF spectrum at m/e = 15 arising from trimethylamine photodissociation is fit by relative experimental weightings of 4:5 {N(CH₃)₂(\tilde{X}^2B_1): its momentum matched CH₃ and 8:13 {N(CH₃)₂(\tilde{A}^2A_1): its momentum matched CH₃³².³² The correction factors to obtain the relative amount of neutral precursor from the experimentally observed ion signal are thus $N(CH_3)_2(\tilde{X}^2B_1)_{neut}$ $=N(CH_3)_2(\tilde{X}^2B_1)_{obs at mass 15}*\frac{5}{4};$ $N(CH_3)_2(\tilde{A}^2A_1)_{neut}$ =N(CH₃)₂($\tilde{A}^{2}A_{1}$)_{obs at mass 15}* $\frac{13}{8}$. Thus, we now have calibration factors enabling us to determine the branching ratio to N-CO and N-CH₃ fission using only the relative contributions at m/e = 15 from these products of dimethylformamide photodissociation.

Figure 3(d) shows a TOF spectrum taken at m/e = 15 (CH₃⁺) with a 20° source angle, arising from the photodisso-

ciation of dimethylformamide. This spectrum was recorded under identical detector conditions as the data from trimethylamine photodissociation. In Fig. 3, the relative probability weightings used to fit {N(CH₃)₂(\tilde{X}^2B_1):N(CH₃)₂(\tilde{A}^2A_1): CH₃} are {2.0:5.0:6.0}. We can now correct this observed ratio by the calibration factor obtained above to obtain the product branching ratio in dimethylformamide. We find {N(CH₃)₂(\tilde{X}^2B_1):N(CH₃)₂(\tilde{A}^2A_1):CH₃} = {2* $\frac{5}{4}$:5* $\frac{13}{8}$:6} ={2.5:8.1:6.0}={0.15:0.49:0.36}={IA:IB:II}.

To estimate the error associated with this determination of the branching ratio, we have fit the dimethylformamide data at m/e = 15 with various probability weightings $(r_{prob}'s)$ given to the reaction channels appearing at this mass. The values given above $({N(CH_3)_2(\tilde{X}^2B_1):N(CH_3)_2(\tilde{A}^2A_1):}$ CH_3 = {2.0:5.0:6.0}) give the best fit, but other values of $r_{\rm prob}$'s also appear to fit the data well. To find the largest possible error associated with fitting, we take the widest range of $r_{\rm prob}$'s that just fit the data, and calculate the branching ratio using these values. To account for errors arising from fitting the signal at m/e = 15 from the calibrant molecule, trimethylamine, we have fit the data with various translational energy distributions $[P(E_T)'s]$ and various $r_{\rm prob}$'s, and again found the outer range of values whose fits are still acceptable, though not quite as good as the numbers quoted above. In "acceptable" fits, the total fit lies within the range of the experimental data points. Unacceptable fits include those in which the total fit obviously lies too high or too low in parts of the TOF spectrum, relative to the experimentally observed data points. Calculating the branching ratio using the upper and lower limits of these two ranges of values (from dimethylformamide and trimethylamine) gives us the fitting errors: {N(CH₃)₂(\tilde{X}^2B_1):N(CH₃)₂(\tilde{A}^2A_1): CH_3 = {0.15 ± 0.04: 0.49 ± 0.09: 0.36 ± 0.07}.

C. Anisotropy of dissociation

In our previous paper, we found that the angular distribution of photofragments of the HCO+N(CH₃)₂ dissociation was very anisotropic, $\beta = 1.4$, showing that the photodissociation occurs on a time scale short with respect to molecular rotation. Knowing now that two N–CO bond fission channels contribute to the signal observed at m/e = 42, it is necessary to reexamine this value to account for the refined fit of the data.

In order to fit the photofragment angular distributions, we vary the anisotropy parameter, β , in the classical electric dipole expression³³ for the signal intensity in the center-of-mass reference frame as a function of the laser polarization angle,

$$\omega(\theta_{\rm CM}) = (1/4\pi) [1 + \beta P_2(\cos \theta_{\rm CM})], \qquad (1)$$

until, after converting the prediction to the lab frame, the shape of the distribution matches that obtained from integration of our signal intensity at various lab polarization angles. Because θ_{CM} is the angle between the recoil direction of the detected photofragment in the center-of-mass reference frame and the electric vector of the light, fitting the data

involves converting between the center-of-mass and lab frames using the measured molecular beam velocity and the $P(E_T)$ derived from the unpolarized data.

In the limit of prompt axial recoil, the anisotropy parameter β is related to the angle α between the transition dipole moment μ and the bond that is breaking through the relation

$$\beta = 2P_2(\cos\alpha). \tag{2}$$

The value of β can range from 2 for a parallel transition (giving a $\cos^2 \theta$ distribution of products) to -1 for a perpendicular transition (giving a $\sin^2 \theta$ angular distribution).

The signal at m/e = 42 was used to determine the anisotropy parameter for N–CO bond fission. We first fit the TOF data in Fig. 6 with the two N–CO bond fission $P(E_T)$'s (Fig. 8) and the N–CH₃ bond fission $P(E_T)$ (Fig. 4) and assumed the anisotropy of the two N–CO bond fission channels to be the same. Fitting the unpolarized data gives the relative contributions (r_{prob} 's) of the two N–CO bond fission channels. We then determined an average $P(E_T)$ for N–CO bond fission via $P(E_T)_{\text{avg}} = r_X \cdot P(E_T)_X + r_A \cdot P(E_T)_A$, where r_X, r_A are the relative contributions of N(CH₃)₂(\tilde{X}^2B_1) and N(CH₃)₂(\tilde{A}^2A_1) to the signal at m/e = 42, $r_X + r_A = 1$, and the $P(E_T)$'s are each normalized to unit area prior to summation. This average N–CO bond fission $P(E_T)_{\text{avg}}$ was then used to determine the anisotropy β_{avg} of channel I.

In order to determine this anisotropy parameter, we integrated the observed signal from various laser polarization angles (at m/e=42 with a source angle of 15°) over early times of arrival (160–216 μ s), so that only signal due to N–CO bond cleavage was included. Comparing these experimental integrated intensities with the values predicted for various values of β [using $P(E_T)_{avg}$], we obtain $\beta=1.2 \pm 0.2$ (see Fig. 11). We also attempted to determine the anisotropy parameter for the fast HCO+N(CH₃)₂(\tilde{X}^2B_1) channel by integrating the data from 160–176 μ s, excluding contributions from the more dominant N(CH₃)₂(\tilde{A}^2A_1). Unfortunately, the small amount of signal due only to N(CH₃)₂(\tilde{X}^2B_1) was inadequate for this purpose, with error bars (from counting error) too large to allow the determination of β_X .

We also attempted to determine the anisotropy of the N-CH₃ bond fission process. In this case, because there is no signal arising from N–CH₃ bond fission at m/e=42 that does not overlap with a signal from N-CO bond fission, we determined β for the N-CH₃ channel based on the relative intensity of signal from the N-CH₃ and N-CO bond fission channels. We fit the TOF spectrum at m/e = 42 recorded at each laser polarization angle with $\beta = 1.2$ for the signal assigned to N-CO bond fission, and we varied the anisotropy parameter for N-CH₃ bond fission until we found a good fit to all spectra. By comparing the fits obtained with different values of β , it appeared that N–CH₃ bond fission gives rise to an isotropic distribution of products, but we could not confirm these results by integrating the signal intensity at m/e = 57 as a function of the laser polarization angle. In spite of numerous efforts, the signal integration method did not give reproducible results. In addition, summing the individual integrated signal intensities gave points, which, in-



FIG. 11. A plot showing the average anisotropy for the two nitrogencarbonyl bond fission channels. Circles represent the experimental signal intensity, integrated from m/e = 42 TOF data at a 15° source angle between 160 and 216 μ s, as a function of the laser polarization angle with respect to the detector axis. The best fit to these experimental points is found with $\beta_{avg} = 1.2 \pm 0.2$. A comparison with the predicted value of $\beta = 1.8$ (obtained from *ab initio* calculations) shows that this dissociation occurs on a time scale relatively short with respect to molecular rotation.

cluding their error bars, did not fit any value of β . Thus, the value of $\beta=0$ given above is best treated as a preliminary estimate, with further experimental clarification necessary.

D. Ab initio calculations

The limitations of using an electronic structure method like CIS, which has only a configuration interaction between states differing from the reference state by single excitations and uses only a single reference state are well known.^{34,35} In this case, however, these calculations lend valuable insight



FIG. 12. Top and side views of the π_{nb} and π^* orbitals given by a CIS calculation, as described in the text. (a) π_{nb} (top). (b) π_{nb} (side). (c) π^* (top). (d) π^* (side). Shading denotes the relative phase of the orbitals. The isosurfaces are plotted at contour values of 0.08 (π_{nb}) and 0.04 (π^*) (Ref. 27). The π_{nb} orbital is clearly a nonbonding π orbital, with a node on the central carbon and opposite phase on the oxygen and nitrogen atoms. The π^* orbital is seen to have nodes on either side of the carbonyl carbon atom, in accordance with its assignment as purely antibonding. Note in the π^* orbital the difference in π -bonding orbital density between the nitrogen atom and the *cis* and *trans* methyl groups.

into the bond fission processes observed experimentally, and so we present the qualitative results of our calculations here.

The character of the orbitals involved in the transition accessed at 193 nm in dimethylformamide can be seen in Fig. 12. This figure was generated by gOpenMol using the output from GAUSSIAN94 CIS calculations, as described in the Calculational Method section earlier in this paper. This $\pi_{\rm nb}\pi^*$ transition accounts for 89% of the character of the excited state accessed in our experiments; no other single excitations from the reference configuration were found to contribute more than 2% to its character. The π_{nb} molecular orbital is denoted a pi-nonbonding orbital due to the node on the central carbon atom, while the π^* orbital is so assigned because of the nodes on either side of the carbonyl carbon. Figure 12 clearly shows delocalization of the π^* orbital density over the methyl groups, supporting the earlier view that π^* delocalization occurs in amides.¹⁴ There is, however, also delocalization of the $\pi_{\rm nb}$ orbital density over the methyl groups, where the character between nitrogen and methyl groups is antibonding in this orbital. Our notation of this as the $\pi_{nb}\pi^*$ transition serves to distinguish it from the higherenergy $\pi\pi^*$ transition originating from the fully bonding π orbital on the NCO portion of the molecule.

In addition to the electronic character of a transition, CIS calculations also give us its oscillator strength and the direction of its transition dipole moment (μ). For excitation to the ¹A' state considered here ($\pi_{nb}\pi^*$), we obtain a transition dipole moment along the O–N direction, lying at an angle of $\alpha = 15.7^{\circ}$ with respect to the carbonyl–nitrogen bond and in the plane of the molecule. This value compares favorably with that obtained by higher-level CASSCF calculations on dimethylformamide in which the transition dipole moment was found to lie at an angle of $\alpha = 17^{\circ}$ from the carbonyl–nitrogen bond and in the plane of the molecule.¹¹

A detailed report of the theoretical results using H^v to calculate the excited state energy of $N(CH_3)_2$ is in progress. Here we mention the results but save the discussion for a full publication.³⁶ The optimized C_{2v} geometry N(CH₃)₂(\tilde{X}^2B_1) has $r_{\rm NC}$ =1.46 Å and $\angle_{\rm CNC}$ =110.6°, while the minimum energy C_{2v} structure of N(CH₃)₂($\tilde{A}^{2}A_{1}$) has $r_{\rm NC} = 1.4$ Å and $\angle_{\rm CNC} = 145^{\circ}$. Neither of these minimum energy structures was optimized with respect to methyl groups using H^{v} ; geometries of the methyl groups were constrained to optimized C_{2v} geometries obtained using a lower level of theory, as described in the Calculational Method section of this paper. The energy separation between the potential minima of these two states (with geometries constrained as outlined earlier) is 1.59 eV. This value does not include zeropoint energy level differences between the two electronic states. From the optimized geometry of the ground state, the vertical excitation energy to the \tilde{A} state was calculated to be 2.29 eV.

IV. DISCUSSION

A. HCO+N(CH₃)₂—Assignment and energetics

The data analyzed here provide evidence for two dynamical processes leading to fission of the nitrogen–carbonyl bond in dimethylformamide:

$$\begin{aligned} \text{HCON}(\text{CH}_3)_2 + 193 \quad \text{nm} \rightarrow \text{HCO}(\widetilde{X}^2 A') + \text{N}(\text{CH}_3)_2(\widetilde{X}^2 B_1), \\ \text{(IA)} \\ \text{HCO}(\widetilde{X}^2 A') + \text{N}(\text{CH}_3)_2(\widetilde{A}^2 A_1). \end{aligned}$$

$$\end{aligned}$$
(IB)

The dominant of these processes, the "slow" channel (IB) leading to electronically excited N(CH₃)₂ radicals, was identified in our earlier paper, while the formation of N(CH₃)₂(\tilde{X}^2B_1) was not.²⁴ We will first review the assignment of channel (IB) before giving evidence showing channel (IA) to be a competing nitrogen–carbonyl bond fission pathway.

The assignment of channel (IB), the formation of electronically excited products, was reached by noting the proportionally low amount of available energy partitioned to relative product translation. The production of either $N(CH_3)_2(\tilde{A}^2A_1)$ (+ ground state HCO) or HCO(\tilde{A}^2A'') [+ ground state $N(CH_3)_2$ is energetically possible, as both channels lie asymptotically close in energy. The formation of $HCO(\tilde{A}^{2}A'') + N(CH_{3})_{2}(\tilde{X}^{2}B_{1})$ can be ruled out, however, based on the lifetime of the HCO radical: HCO formed in its excited state undergoes predissociation to H+CO on a time scale of nanoseconds.³⁷ Because we observe the signal at m/e = 29 arising from the ionization of intact, neutral HCO arriving at the ionizer after >100 μ s flight time (see Fig. 7), HCO must be formed with a low amount of internal energy (<17 kcal/mol). Thus, the formation of electronically excited $N(CH_3)_2(\tilde{A}^2A_1)$ plus ground state $HCO(\tilde{X}^2A')$ is assigned to the slower dissociation process, (IB).

This lower kinetic energy distribution corresponding to $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$ extends out to a maximum translational energy of 22 kcal/mol (see Fig. 8). Fission of the nitrogen-carbonyl bond requires 89.7 kcal/mol, leaving 58.4 kcal/mol available for internal energy following excitation with 193 nm light. Subtracting the maximum energy imparted to translation leaves approximately 36 kcal/mol for the energy required to form $N(CH_3)_2(\tilde{A}^2A_1)$. To our knowledge, there have been no published studies on excited states of the dimethylamidogen radical, $N(CH_3)_2$, and this is the first experimental estimate of its excited state energy minimum. This estimate compares favorably with the \tilde{A} state energy of NH₂, a similar radical, which has $\Delta E_{\min-\min}$ = 1.38 eV or 31.8 kcal/mol.³⁸ Our H^v calculations³⁶ suggest the adiabatic excited state energy of N(CH₃)₂($\tilde{A}^{2}A_{1}$) to lie around $\Delta E_{\min-\min} = 1.59 \text{ eV}$ or 37 kcal/mol a figure within the uncertainty of our maximum observed translational energy. In addition to energetic evidence, the slow $N(CH_3)_2$ signal observed here exhibits the same daughter ion cracking pattern as the N(CH₃)₂ produced in the \tilde{A} state from trimethylamine dissociation.32

Following the lead of our study on trimethylamine,³² where signal at m/e = 42 shows a fast component not fit by the $P(E_T)$ used to fit the signal at m/e = 43, we reexamined the dimethylformamide data and found a slightly faster edge to the ion flight time-corrected m/e = 42 signal than at m/e = 43. The faster N(CH₃)₂ radicals have a different daughter ion cracking pattern than the slow ones, indicating that they are likely formed with a very different distribution of internal

energy.³⁹ Using an additional, higher kinetic energy $P(E_T)$, we can fit all of our TOF data. The energy partitioned to relative translation in this faster dissociation channel extends to 40 kcal/mol (see Fig. 8), well within the limit of available energy for fission of the N–CO bond, 58.4 kcal/mol. Thus, we assign the faster channel, (IA), to the formation of ground state products, $\text{HCO}(\tilde{X}^2A') + \text{N}(\text{CH}_3)_2(\tilde{X}^2B_1)$. Experiments on the photodissociation of trimethylamine have confirmed the cracking pattern of ground state N(CH₃)₂(\tilde{X}^2B_1) to be the same as observed from this "fast" dimethylamidogen radical formed from dimethylformamide photodissociation.³²

B. HCO+N(CH₃)₂—Electronic accessibility

In the initial planar geometry of the molecule, the $\pi_{\rm nb}\pi^*$ state accessed at 193 nm is A' in symmetry. If the molecule retains this geometry throughout the dissociation process, we should see the formation of products whose electronic states combine to give an overall A' symmetry. Figure 13 shows the energetically accessible states for dissociation to $HCO+N(CH_3)_2$, labeling the states by their symmetry with respect to the dimethylformamide molecular plane. It can be seen that the formation of ground state products, HCO $(\tilde{X}^2A') + N(CH_3)_2(\tilde{X}^2B_1)$, is symmetry forbidden within this planar framework, while the formation of both $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$ and $HCO(\tilde{A}^{2}A'')$ $+ N(CH_3)_2(\tilde{X}^2B_1)$ is symmetry allowed. We now address how the formation of the symmetry-forbidden products can compete with the symmetry-allowed channels and why the A' channel leading to the formation of excited-state HCO is not accessed.

In our earlier paper, we discussed the preference for the formation of N(CH₃)₂($\tilde{A}^{2}A_{1}$) over HCO($\tilde{A}^{2}A''$).²⁴ This was explained by expanding the delocalized dimethylformamide orbitals in terms of a basis set of orbitals localized on the nitrogen and carbonyl moieties. In the Franck-Condon region, 68% of the $\pi_{nb}\pi^*$ excited state of dimethylformamide can be described by the configuration of electrons leading diabatically to the production of $HCO(\tilde{X}^2 A')$ $+ N(CH_3)_2(\tilde{A}^2A_1)$ (see Fig. 14).^{13,24} On the other hand, the electronic configuration leading diabatically to the formation of HCO($\tilde{A}^{2}A''$) + N(CH₃)₂($\tilde{X}^{2}B_{1}$) requires a two-electron change from the Franck-Condon $\pi_{\rm nb}\pi^*$ configuration, a much more difficult task for the electronic wave function to accomplish.

In order to form ground state products, $\text{HCO}(\tilde{X}^2A')$ + N(CH₃)₂(\tilde{X}^2B_1), a change in geometry must occur to break the initial molecular plane of symmetry. Resonance Raman experiments on the $\pi_{nb}\pi^*$ transition in a similarly sized amide, N-methylacetamide, have shown that torsion about the carbonyl-nitrogen bond does occur in the excited state.^{14-16,22} This torsion breaks the planar symmetry, thus allowing the molecule to access ground state products. Local orbitals involved in the dissociation to $\text{HCO}(\tilde{X}^2A')$ + N(CH₃)₂(\tilde{X}^2B_1) are depicted in Fig. 14. The initially excited $\pi_{nb}\pi^*$ transition is best represented as a linear combination of three localized π electron configurations, one of



FIG. 13. The energy level diagram displaying the energetically accessible $HCO+N(CH_3)_2$ product electronic states. States are denoted by their symmetries with respect to the initial ground state planar geometry: solid lines denote *A'* states; dashed lines denote states of *A''* symmetry. The energy of the \tilde{A} state of $N(CH_3)_2$ is estimated to be near 1.59 eV (Ref. 36); that of HCO (\tilde{A}^2A'') is estimated to be near 1.27 eV (Ref. 40).

which correlates diabatically to the formation of $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$, as mentioned above. A simple one-electron change from this configuration, moving an electron on nitrogen from the out-of-plane b_1 orbital to the in-plane a_1 orbital, gives an electronic configuration correlating diabatically to the formation of $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{X}^2B_1)$. This one-electron change, symmetry-allowed following torsion on the initially excited potential energy surface, is facile and allows the ground state channel to compete with the higher energy, more electronically accessible channel, leading to $HCO(\tilde{X}^2A') + N(CH_3)_2(\tilde{A}^2A_1)$.



FIG. 14. A sketch of the N(CH₃)₂ and HCO orbitals involved in excitation to give the energetically accessible product electronic states. We show how one of the local electron configurations discussed in the text leads diabatically to dissociation into HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{A}^2A_1). In nonplanar geometries, this configuration can couple via one-electron matrix elements (involving the b_1 and a_1 orbitals on nitrogen) to the diabatic dissociation coordinate producing HCO(\tilde{X}^2A') + N(CH₃)₂(\tilde{X}^2B_1).

The observation of a large and positive anisotropy parameter for fission of the N–CO bond provides information about the the time scale of this dissociation. An averaged $P(E_T)$ for channels (IA) and (IB) gave $\beta_{avg} = 1.2 \pm 0.2$. Our CIS calculations give a theoretical anisotropy parameter of $\beta = 1.8$ for dissociation of the N–CO bond; this value assumes prompt axial recoil. The observed reduction of $\beta_{theor} = 1.8$ to $\beta_{exp} = 1.2 \pm 0.2$ implies that there is some molecular rotation or distortion of the frame prior to bond fission, although the strong anisotropy of the product distribution shows that the dissociation is nonetheless complete on a time scale short with respect to molecular rotation. This is additional evidence showing that the N–CO dissociative reaction coordinate must be relatively facile for the molecule to traverse.

C. HCONCH₃+CH₃

It is possible that electronically excited products are formed in the dissociation to $HCONCH_3 + CH_3$. The energy we observe partitioned to relative product translation (0-20)kcal/mol; see Fig. 4) stops far short of the thermodynamic limit ($E_{avl} \approx 68$ kcal/mol). An information theoretic prior treatment⁴¹ of the translational energy distribution arising from this dissociation gives a most probable translational energy of 1.2 kcal/mol, with the distribution of translational energy extending to 22.0 kcal/mol. While the maximum translational energy limit is close to what we have fit to this channel (see Fig. 4), the peaks of the experimental and statistical distributions are not in agreement, suggesting a barrier en route to dissociation. Subtracting the observed range of translational energy from the available energy [68 kcal/ mol-(0-20 kcal/mol)] leaves between 48 and 68 kcal/mol available for internal energy of the methyl and N-methylamido (HCONCH₃) radicals. Experiments have placed the energy of the lowest lying excited state of the methyl fragment $(\tilde{B}^2A'_1)$ 132 kcal/mol above its electronic ground state.42 This result precludes the formation of excited state methyl fragments in our experiment. No excited-state energy calculations have been performed on HCONCH₃, and so we do not know if there are any energetically accessible excited states ($\Delta E_{\min} \leq 48 \text{ kcal/mol}$) of this HCONCH₃ radical.

The observation of an isotropic distribution of $HCONCH_3+CH_3$ products following excitation with polarized light provides little insight into the dynamics of this dissociation channel. An isotropic product distribution can be explained by two possible reasons (or a combination of both).

- (1) The time scale of dissociation is slow with respect to molecular rotation. This slow product recoil in effect smears out any information as to the preference for fission of one N-CH₃ bond over the other, leaving us unable to identify the primary dynamics occurring along this reaction coordinate.
- (2) There is a prompt dissociation to HCONCH₃+CH₃ products in which fission of one nitrogen-methyl bond is preferred, but its anisotropy, when arranged with the

competing fission of the other nitrogen-methyl bond, gives an overall anisotropy which is close to zero.

We can determine a theoretical anisotropy parameter for N–CH₃ bond fission in the limit of prompt axial recoil using the calculated transition dipole moment. Because there are two methyl groups present, each of which can dissociate from dimethylformamide, we calculate a value for β for each methyl group separately to obtain $\beta_{cis}=0.47$ and $\beta_{trans} = -0.78$. (Here, we follow convention and label amide nitrogen substituents as *trans* or *cis* with respect to the R group on the carbonyl; see Fig. 1.) The observed β should be a linear combination of these two values, weighted by the fraction, *f*, of N–CH₃ bond fission through each position:

$$\beta_{\rm obs} = f_{cis}\beta_{cis} + f_{trans}\beta_{trans}, \qquad (3)$$

where $f_{cis} + f_{trans} = 1$. Substituting the preliminary and unconfirmed observed value of the anisotropy parameter for N-CH₃ bond fission ($\beta_{obs}=0$) along with the calculated anisotropy parameters for *cis*- and *trans*-CH₃ fission (β_{cis} = 0.47 and $\beta_{trans}=-0.78$) into Eq. (3) gives the relative amounts of each N-CH₃ bond fission channel observed experimentally as $p_{cis}\approx 0.63$ and $p_{trans}\approx 0.37$. In the limit of instantaneous axial recoil, this result suggests that the N-*cis*-CH₃ bond is about twice as likely to break as the N-*trans*-CH₃ bond, following $\pi_{nb}\pi^*$ excitation of dimethylformamide. It must be kept in mind that this result depends on an angular distribution whose determination was tenuous.

This latter possibility suggests an asymmetry between the two methyl positions in dimethylformamide. Indeed, inspection of the molecular orbitals involved in the $\pi_{\rm nb}\pi^*$ transition shows that this asymmetry exists in the ab initio calculations as well (see Fig. 12). The π^* orbital is somewhat delocalized over the trans-methyl group, where there is π -bonding character in the orbital between nitrogen and trans-CH₃. Delocalization over the *cis*-methyl group is weaker; at the electron density contour shown in Fig. 12, this π^* orbital has no density extending over the *cis*-CH₃. To ensure that the asymmetry between the trans- and cis-methyl groups was not an artifact of choosing the dominant oneelectron transition to represent the excited state, we performed additional CIS calculations using Q-Chem.⁴³ This ab initio package includes the calculation of the electron attachment and detachment densities for each state, enabling us to visualize the change in electron density upon excitation, not just the individual orbitals involved in the transition. While this visualization has its greatest strength in cases where multiple one-electron transitions contribute significantly to an excited state, in our case, it allowed us to determine that the asymmetry between *trans*- and *cis*-methyl was not an artifact of the orbital chosen, but was rather a property of the electronic state involved.

In practice, it is likely that a combination of both factors are occurring: the opposing values of the theoretical anisotropy parameter for fission of *cis*- and *trans*-CH₃ groups result in a small observed anisotropy, which is further reduced by the time scale of this dissociation. This unfortunately leaves us unable to comment on the role of torsion along this reaction coordinate; experiments on a monosubstituted amide (N-methylformamide) currently underway in our laboratory should help to resolve the dynamics along the $N-CH_3$ dissociation pathway.⁴⁴

D. Branching into the three dissociation channels

As mentioned earlier, the calculation of absolute branching ratios between dissociation pathways giving polyatomic products is fraught with difficulties. Methods currently used for such determinations each contain assumptions central to the calculation of the product yield. The method we have chosen for dimethylformamide involves using a second molecule as a calibrant, in order to calculate relative branching into channels (IA), (IB), and (II). The advantages of this method are that it relies neither on spectroscopic accessibility of the reaction products nor on the knowledge of their ionization cross sections or daughter ion cracking patterns. It does, however, depend on the ionized reaction products from the calibrant species and a desired molecule exhibiting similar cracking patterns. In this case, the calibrant molecule used was trimethylamine, which gives reaction products $N(CH_3)_2 + CH_3$ following 193 nm dissociation. Thus, for the relative branching ratio determination to be correct, $N(CH_3)_2$ and CH₃ must have similar cracking patterns when they are formed from trimethylamine photodissociation as when they are formed from dimethylformamide photodissociation.

This study and our work on trimethylamine have shown the $N(CH_3)_2$ daughter ion cracking probability to depend on the electronic state in which the dimethylamidogen radical is formed. Although N(CH₃)₂($\tilde{A}^{2}A_{1}$) has a shorter fluorescence lifetime than the flight time to the detector, its cracking pattern following fluorescence is significantly different from the cracking pattern of the primary $N(CH_3)_2(\tilde{X}^2B_1)$ photodissociation products, meaning that N(CH₃)₂ formed via the two distinct dynamical processes can be distinguished based on their daughter ion cracking patterns. Our work on trimethylamine showed no evidence for the signal at m/e = 29arising from cracking of the $N(CH_3)_2$ parent in the ionizer. At m/e = 29 in dimethylformamide, however, a small but significant TOF signal falls into the time-of-flight range where $N(CH_3)_2$ momentum matched to HCO would appear (see Fig. 7). The fit that we have used is the best compromise between underfitting the dip between the fast and slow peaks and overfitting the fast edge of the slow peak. The $N(CH_3)_2$ may or may not actually contribute to the observed signal at this mass/charge ratio; there are many overlapping contributions, and it is difficult to determine the relative importance of each.

Our work on trimethylamine has also shown evidence for a third N–CH₃ bond fission channel that forms $N(CH_3)_2$ radicals with enough internal energy to surmount the barrier to secondary C–H bond fission and thus undergo secondary decomposition. The difference in energies available to the $N(CH_3)_2$ radical formed from dimethylformamide and trimethylamine photodissociation at 193 nm, however, means that $N(CH_3)_2$ radicals formed from dimethylformamide do not have enough internal energy to undergo this secondary dissociation. Thus, all of the discussion on $N(CH_3)_2$ radicals and cracking patterns in this paper should be clearly understood to pertain only to $N(CH_3)_2$ arriving intact at the ion-izer.

The presence of two distinct dynamical channels producing N(CH₃)₂ radicals provides an independent means to verify the branching ratio between these two channels: both nitrogen-carbonyl bond fission channels in dimethylformamide produce HCO ($\tilde{X}^2 A'$) with little internal energy (<17 kcal/mol). Assuming a similar distribution of this internal energy in the formyl radicals, the ratio of HCO⁺ from channels (IA) and (IB) contributing to the signal at m/e=29should be given by the branching ratio determined using trimethylamine. In fact, the TOF spectrum recorded at m/e=29 (Fig. 7) was fit by constraining the HCO products to have a ratio of fast:slow=1.0:3.3, i.e., an identical ratio to the 0.15:0.49 branching ratio calculated using trimethylamine to calibrate the ion signal at m/e = 15. This constraint helped to deconvolute the many overlapping contributions at this mass/charge ratio. In addition, the contributions from daughter ions of N(CH₃)₂ shown in Fig. 7 were also constrained to have a ratio of fast:slow=1.0:3.3; as mentioned above, their importance is undetermined. The relative contributions of HCO from channels (IA) and (IB) are best reflected in the fast edge of the TOF signal at m/e = 29. It is clear from Fig. 7 that the ratio of IA:IB=1.0:3.3 does a good job of fitting the fast edge to the data; this has thus given independent verification to the determination of the branching ratio between the formation of $N(CH_3)_2(\tilde{X}^2B_1)$ and $N(CH_3)_2(\tilde{A}^2A_1).$

V. CONCLUSIONS

Our determination of the product branching in dimethylformamide photodissociation shows that three pathways significantly contribute to the dissociation dynamics of this molecule:

$$\begin{split} \text{HCON}(\text{CH}_3)_2 + 193 \quad \text{nm} \rightarrow \text{HCO}(\tilde{X}^2 A') + \text{N}(\text{CH}_3)_2(\tilde{X}^2 B_1), \\ \text{(IA)} \\ \\ \text{HCO}(\tilde{X}^2 A') + \text{N}(\text{CH}_3)_2(\tilde{A}^2 A_1), \\ \text{(IB)} \end{split}$$

$$HCONCH_3 + CH_3.$$
 (II)

(The experiments do not rule out significant contribution from C-H bond fission channels.) The preference for the formation of N(CH₃)₂($\tilde{A}^{2}A_{1}$) over HCO ($A^{2}A''$) has been rationalized in terms of the electronic accessibility of the former channel over the latter.²⁴ Channel (IA) is forbidden in the initial planar symmetry of the molecule, and can occur only when this symmetry is broken in the excited state. The preference (by a ratio of 3.3 ± 0.6 : 1.0 ± 0.3) for dissociation into electronically excited products over ground state products shows that, while symmetry-breaking vibrations do occur on the excited state surface, they are not strongly coupled to the nitrogen-carbonyl bond fission coordinate. Also, the dominant reaction leading to nitrogen-carbon bond fission is not the only dissociation pathway accessed following $\pi_{nb}\pi^*$ excitation. Nitrogen-methyl bond fission occurs as a significant fraction of the dissociation yield $(36 \pm 7\%)$, adding evidence to earlier studies, which suggested that the $\pi_{nb}\pi^*$ excitation in amides must be at least somewhat delocalized over the peptide backbone.¹⁴ This picture is also supported by our *ab initio* calculations, which show electron density in the π_{nb} and π^* orbitals over the nitrogen-bound methyl groups.

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