

A Progress Report to the

**UNITED STATES DEPARTMENT OF ENERGY**

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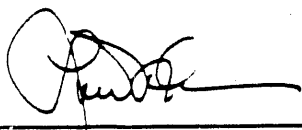
**Laser Photoelectron Spectroscopy of Ions  
(DE-FG02-87ER13695)**

Name and Address of Institution:

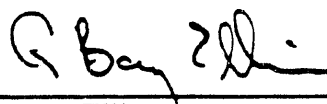
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This enterprise uses photoelectron spectroscopy to study the properties of negative ions and radicals. The essence of our experiment is to cross a 0.6 keV mass-selected ion beam ( $M^-$ ) with the output of a CW laser,  $\hbar\omega_0$ . The resultant detached photoelectrons with kinetic energy, KE, are energy analyzed by means of a set of electrostatic hemispherical analyzers.



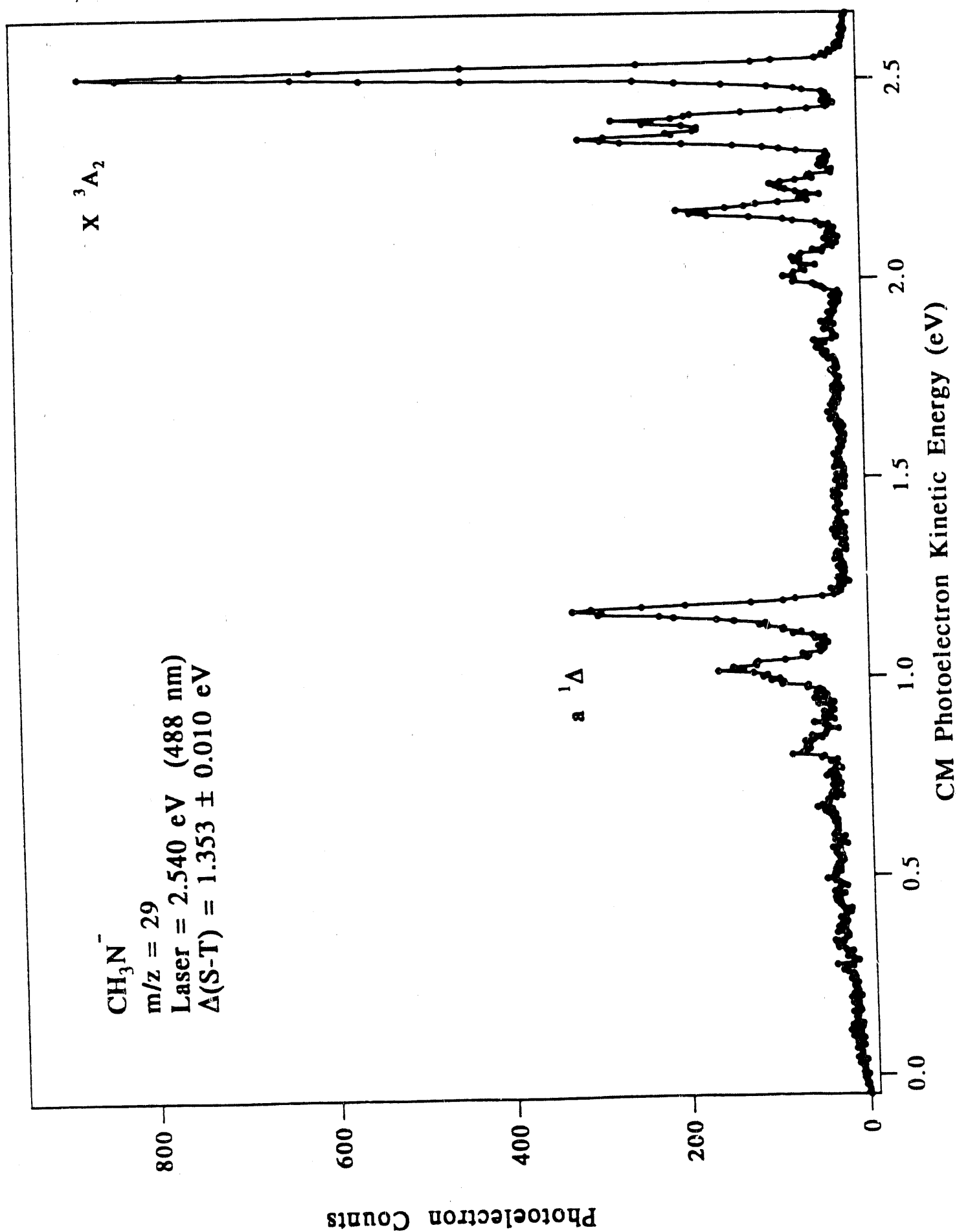
Analysis of the photoelectron spectra enables us to extract molecular electron affinities, vibrational frequencies and electronic splittings of the final radical, M, as well as the relative molecular geometries of ions ( $M^-$ ) and radicals (M).

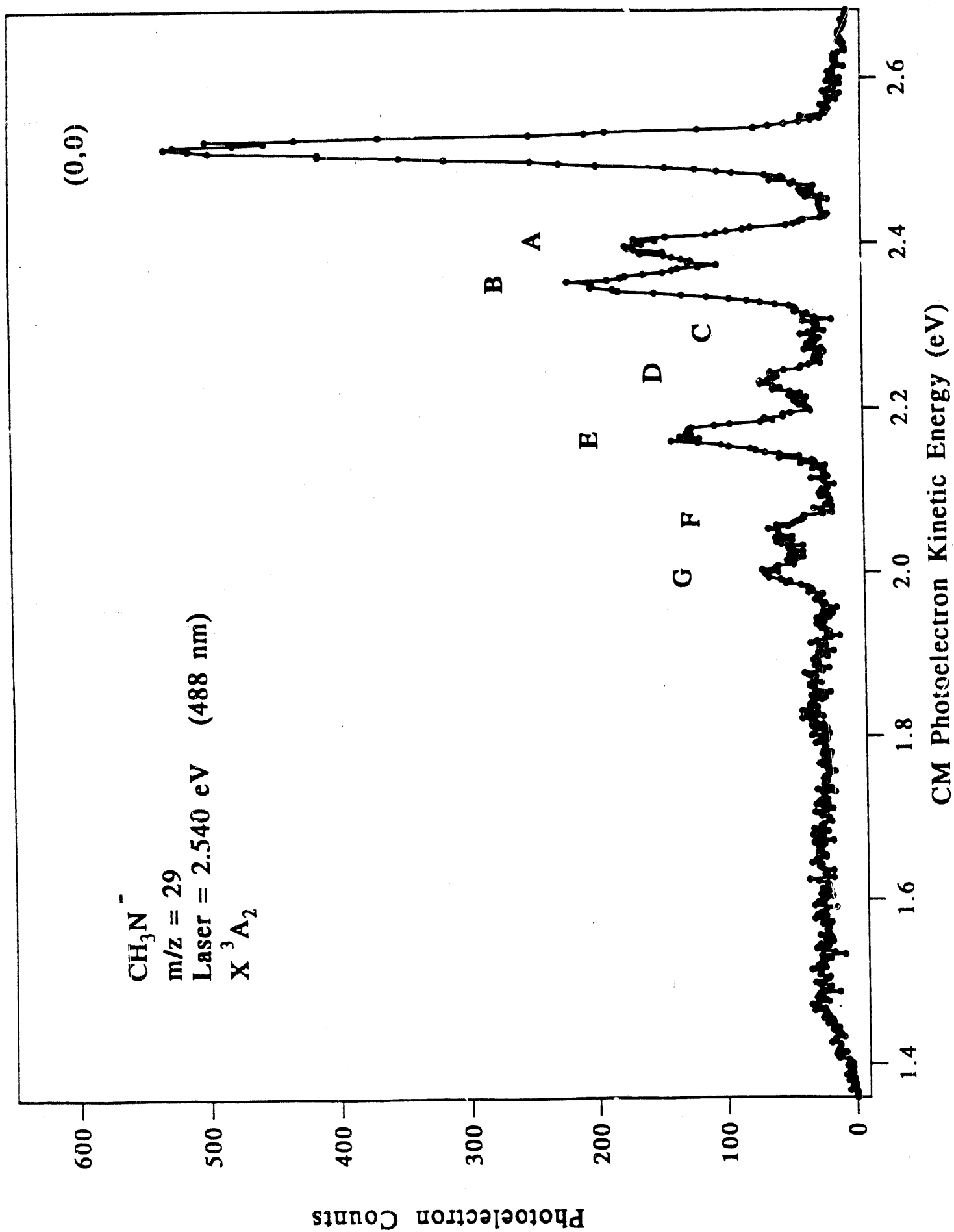
We have scrutinized the two simplest nitrenes: methylnitrene ( $\text{CH}_3\text{N}$ ) and phenylnitrene ( $\text{C}_6\text{H}_5\text{N}$ ). By preparing the corresponding anions,  $\text{CH}_3\text{N}^-$  and  $\text{C}_6\text{H}_5\text{N}^-$ , we have studied these nitrene biradicals. Singlet methylnitrene is especially interesting since it is formally a "transition state."

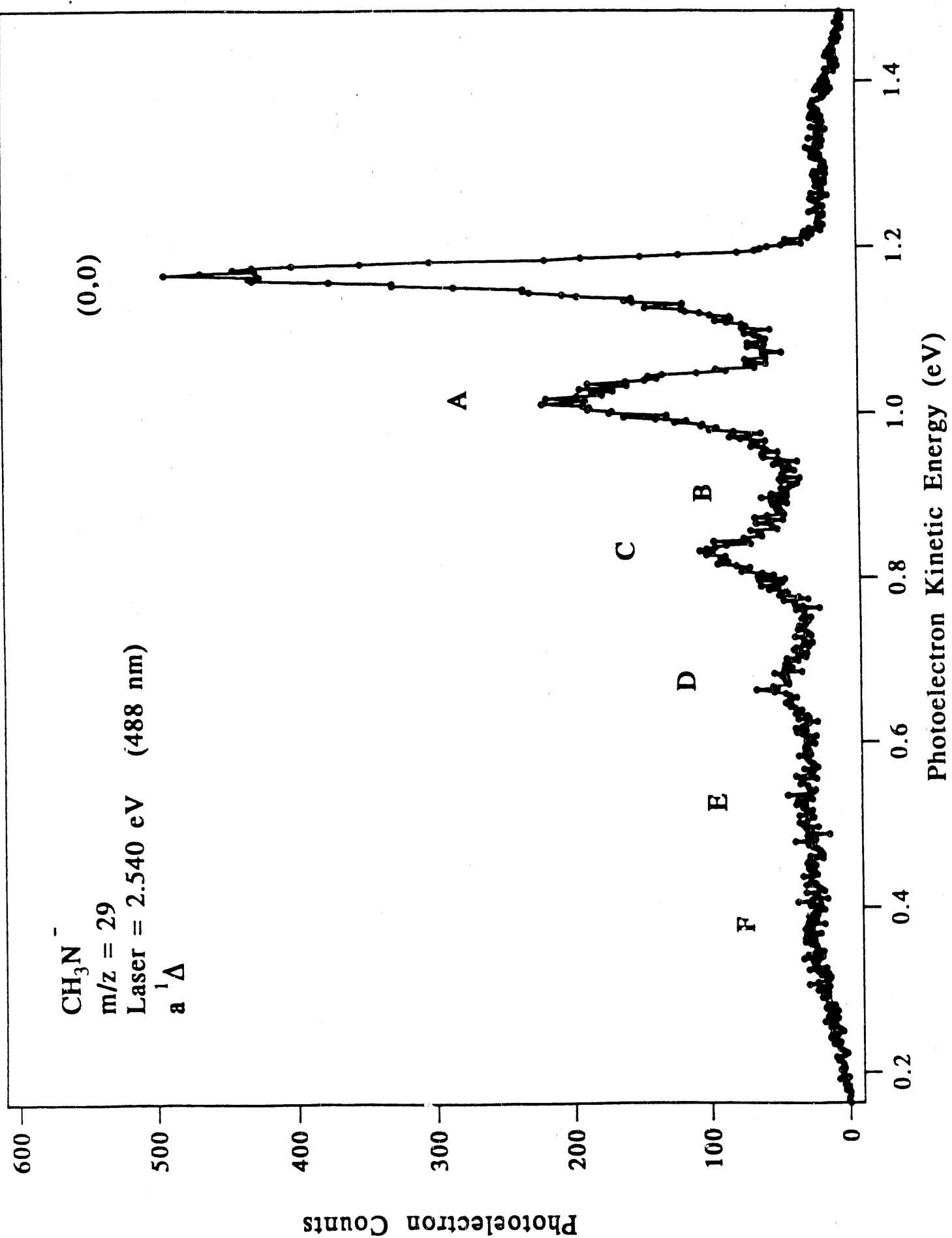


### 1. Methylnitrene

We have measured the negative ion photoelectron spectra of  $\text{CH}_3\text{N}^-$  and find the electron affinity:  $\text{EA}(\text{CH}_3\text{N}) = 0.024 \pm 0.010$  eV. All attempts to prepare the  $\text{CD}_3\text{N}^-$  ion failed so we cannot search for isotope shifts. This may be related to the fact that the  $\text{EA}(\text{CD}_3\text{N}) \cong kT$ ; our deuterated ions may be just collisionally detached before they can be extracted into an ion beam. Fig. 1 is an overview of the methylnitrene photodetachment spectra. We observe two states of the final  $\text{CH}_3\text{N}$ ; the ground state  $\tilde{X}^3A_2$  and the first excited state,  $\tilde{a}^1E$ . Our measured singlet-triplet splitting is  $\Delta E_{ST} = 1.353 \pm 0.0110$  eV. Fig. 2 is a detailed look at the  $\tilde{X}^3A_2$   $\text{CH}_3\text{N}$  state while Fig. 3 features the metastable  $\tilde{a}^1E$   $\text{CH}_3\text{N}$  state. Earlier ab initio calculations of H.F. Schaefer III suggested that the  $\tilde{a}^1E$   $\text{CH}_3\text{N}$  species was not bound with respect to the methyleneimine,  $\text{CH}_2=\text{NH}$ . Consequently there is believed to be no barrier to the rearrangement (1), yet we see structure in Fig. 3!

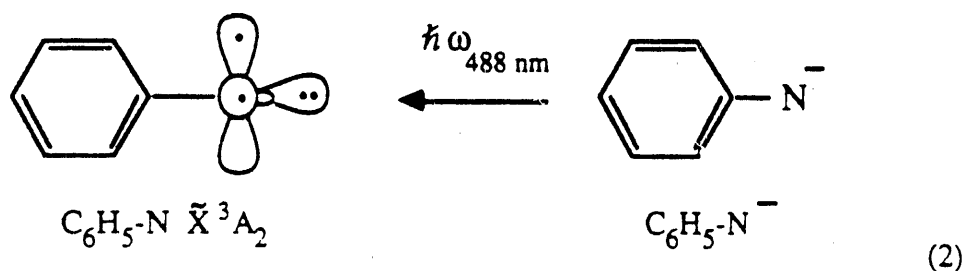






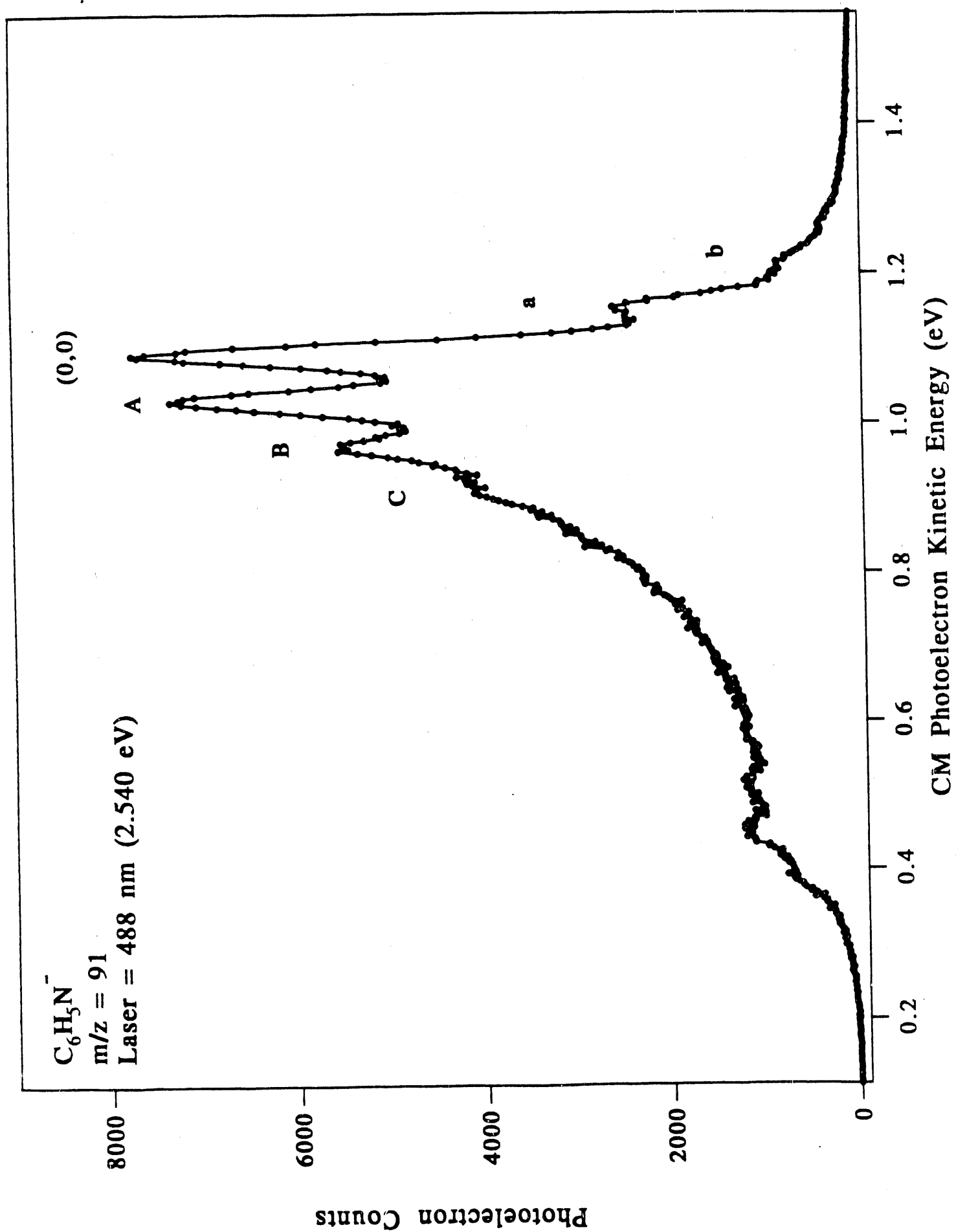
## 2. Phenylnitrene

A more interesting nitrene is phenylnitrene,  $C_6H_5N$ . The chemistry of this reactive aromatic nitrene has been extensively studied and is very confusing. The ground states of several nitrenes have been studied by EPR spectroscopy and all but aminonitrenes are known to be triplets. Phenylnitrene can be written as a species with a  $(p_x, p_y)$  pair of electrons triplet-coupled. The  $C_6H_5N$  radical is a symmetric,  $C_{2v}$  species and we employ the standard convention which adopts the  $C_2$  axis as the z-axis and x-axis is perpendicular to the plane. Consequently the ground state of phenylnitrene is  $\tilde{X}^3A_2$  and we can represent our negative ion photodetachment experiment as:



The optical spectroscopy of  $C_6H_5N$  is a mess. Absorption and fluorescence studies of  $^3[C_6H_5N]$  in a EPA glass at 77 K reveal four separate band systems that are attributed to triplet phenylnitrene: ① = 489 nm (2.54 eV), ② = 402 nm (3.08 eV), ③  $\equiv$  320 nm (3.87 eV), ④  $\equiv$  240 nm (5.17 eV). The IR absorption spectrum of  $^3[C_6H_5N]$  in matrices of Ar, or  $N_2$ , or 2-methylbutane at 12 K has been reported. A set of vibrational frequencies are listed as belonging to the triplet nitrene but no attempt was made to analyze these infrared spectra. As far as we are aware, there are no spectra of  $^1[C_6H_5N]$  in the gas phase or in a matrix.

Our photoelectron spectrum for the parent ion,  $C_6H_5N^-$ , is shown in Fig. 4. We have also prepared intense ion beams of the deuterated species,  $C_6D_5N^-$ . We find  $EA(C_6H_5N) = 1.445 \pm 0.015$  eV and  $EA(C_6D_5N) = 1.448 \pm 0.015$  eV. Preliminary Franck-Condon factor analysis has been undertaken and we are refining our constants.



Curriculum Vitae

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2. Petroleum Research Fund, *FTIR Spectroscopy of Organic Radicals*, [1/9/90-31/8/92] \$40,000

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1. Department of Energy, *Radicals on Surfaces*, \$108,000

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