A Progress Report to the

UNITED STATES DEPARTMENT OF ENERGY
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for Support of

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

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DISCLAIMER

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.

$$M^- + \hbar\omega_0 \rightarrow M + e(KE)^-$$

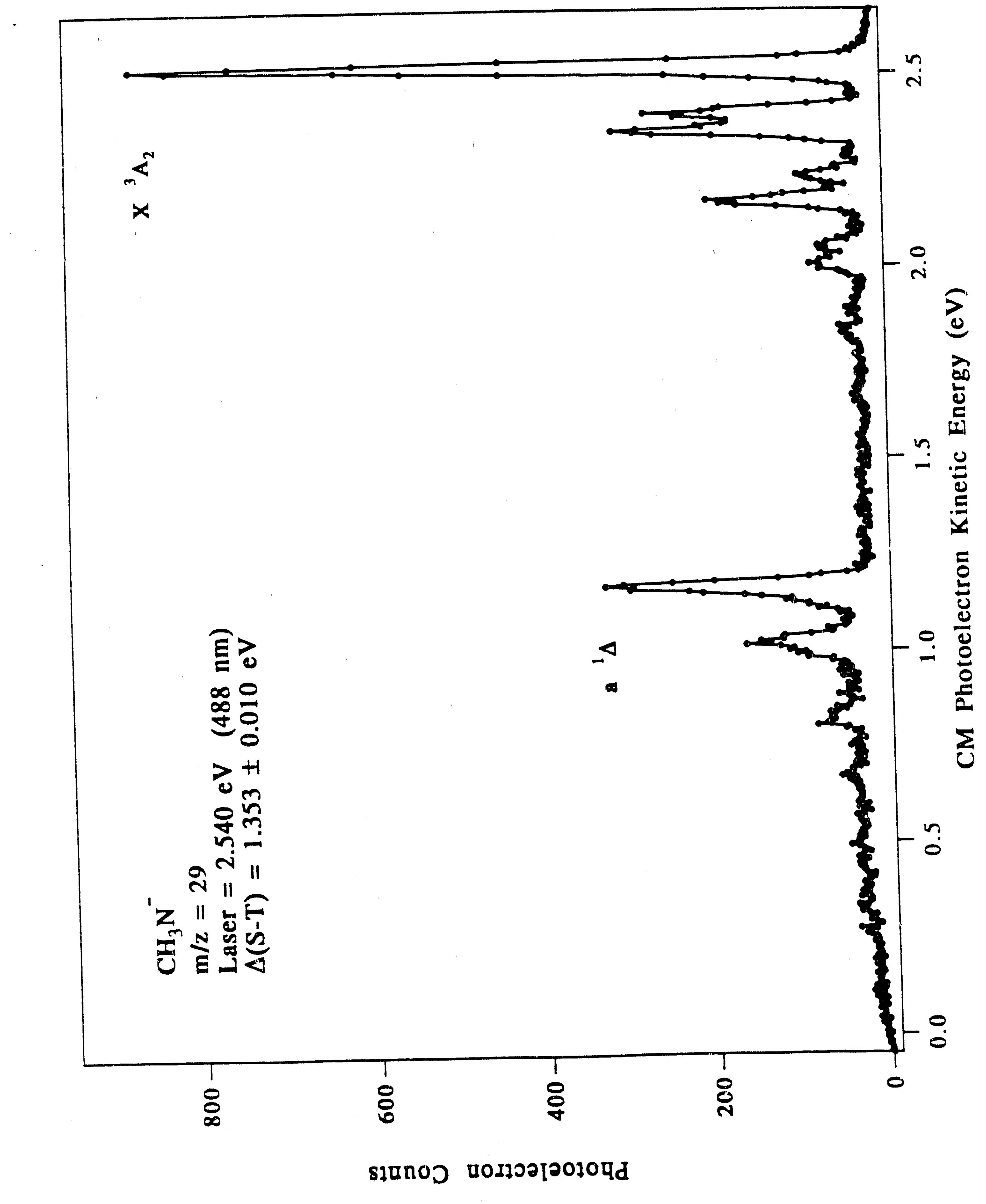
Analysis of the photoelectron spectra enables us to extract molecular electron affinities, vibrational frequencies and electronic splittings of the final radical, M, as well as the relative molecular geometries of ions (M^-) and radicals (M).

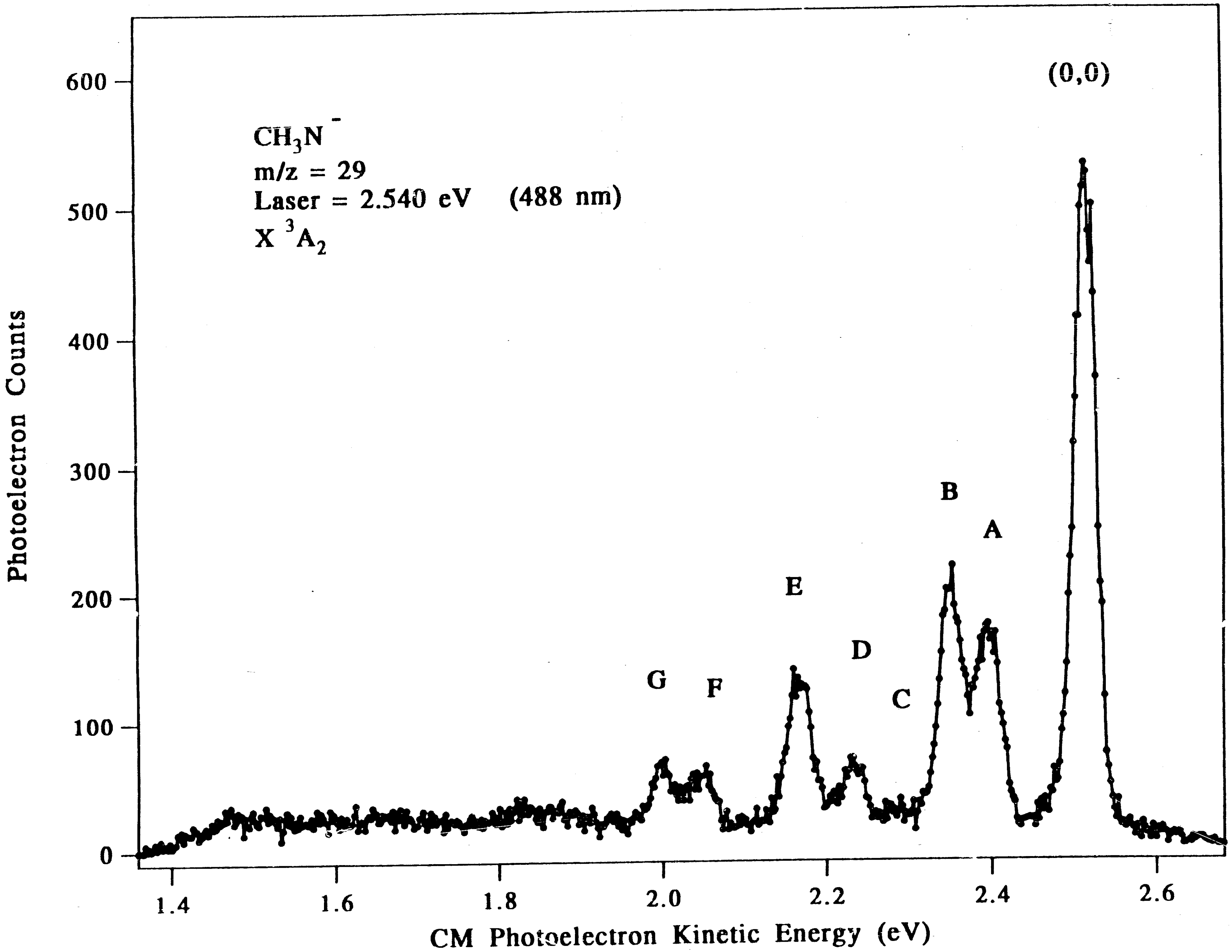
We have scrutinized the two simplest nitrenes: methylnitrene (CH_3N) and phenylnitrene (C_6H_5N). By preparing the corresponding anions, CH_3N^- and $C_6H_5N^-$, we have studied these nitrene biradicals. Singlet methylnitrene is especially interesting since it is formally a "transition state."

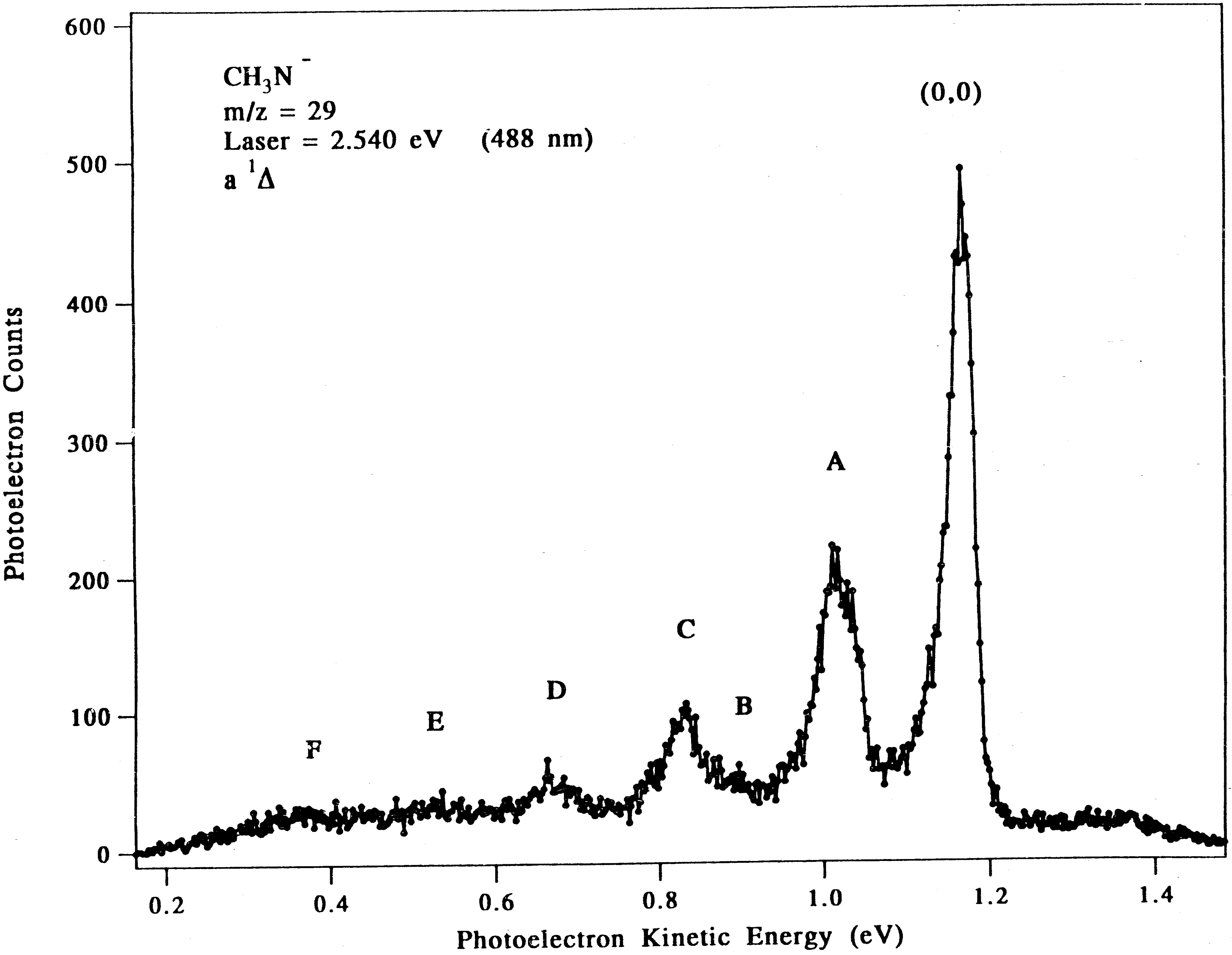
$$^1[CH_3N] \rightarrow CH_2{=}NH \qquad (1)$$

1. Methylnitrene

We have measured the negative ion photoelectron spectra of CH_3N^- and find the electron affinity: EA(CH_3N) = 0.024 ± 0.010 eV. All attempts to prepare the CD_3N^- ion failed so we cannot search for isotope shifts. This may be related to the fact that the EA(CD_3N) $\cong$ 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 CH_3N; the ground state $\tilde{X}\ ^3A_2$ and the first excited state, $\tilde{a}\ ^1E$. Our measured singlet-triplet splitting is ΔE_{ST} = 1.353 ± 0.0110 eV. Fig. 2 is a detailed look at the $\tilde{X}\ ^3A_2$ CH_3N state while Fig. 3 features the metastable $\tilde{a}\ ^1E$ CH_3N state. Earlier ab initio calculations of H.F. Schaefer III suggested that the $\tilde{a}\ ^1E$ CH_3N species was not bound with respect to the methyleneimine, $CH_2{=}NH$. Consequently there is believed to be **no** barrier to the rearrangement (1), yet we see structure in Fig. 3!

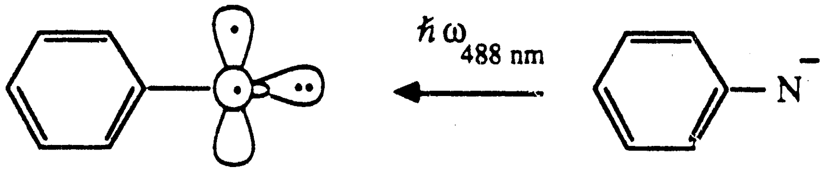

CH_3N^-
m/z = 29
Laser = 2.540 eV (488 nm)
Δ(S-T) = 1.353 ± 0.010 eV
X $^3A_2$
a $^1\Delta$
CM Photoelectron Kinetic Energy (eV)
Photoelectron Counts
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800


CH$_3$N$^-$
m/z = 29
Laser = 2.540 eV (488 nm)
X ^{3}A$_2$
(0,0)
A
B
C
D
E
F
G
Photoelectron Counts
0
100
200
300
400
500
600
CM Photoelectron Kinetic Energy (eV)
1.4
1.6
1.8
2.0
2.2
2.4
2.6


CH$_3$N$^-$
m/z = 29
Laser = 2.540 eV (488 nm)
a $^1\Delta$
(0,0)
A
B
C
D
E
F
Photoelectron Counts
0
100
200
300
400
500
600
Photoelectron Kinetic Energy (eV)
0.2
0.4
0.6
0.8
1.0
1.2
1.4

2. Phenylnitrene

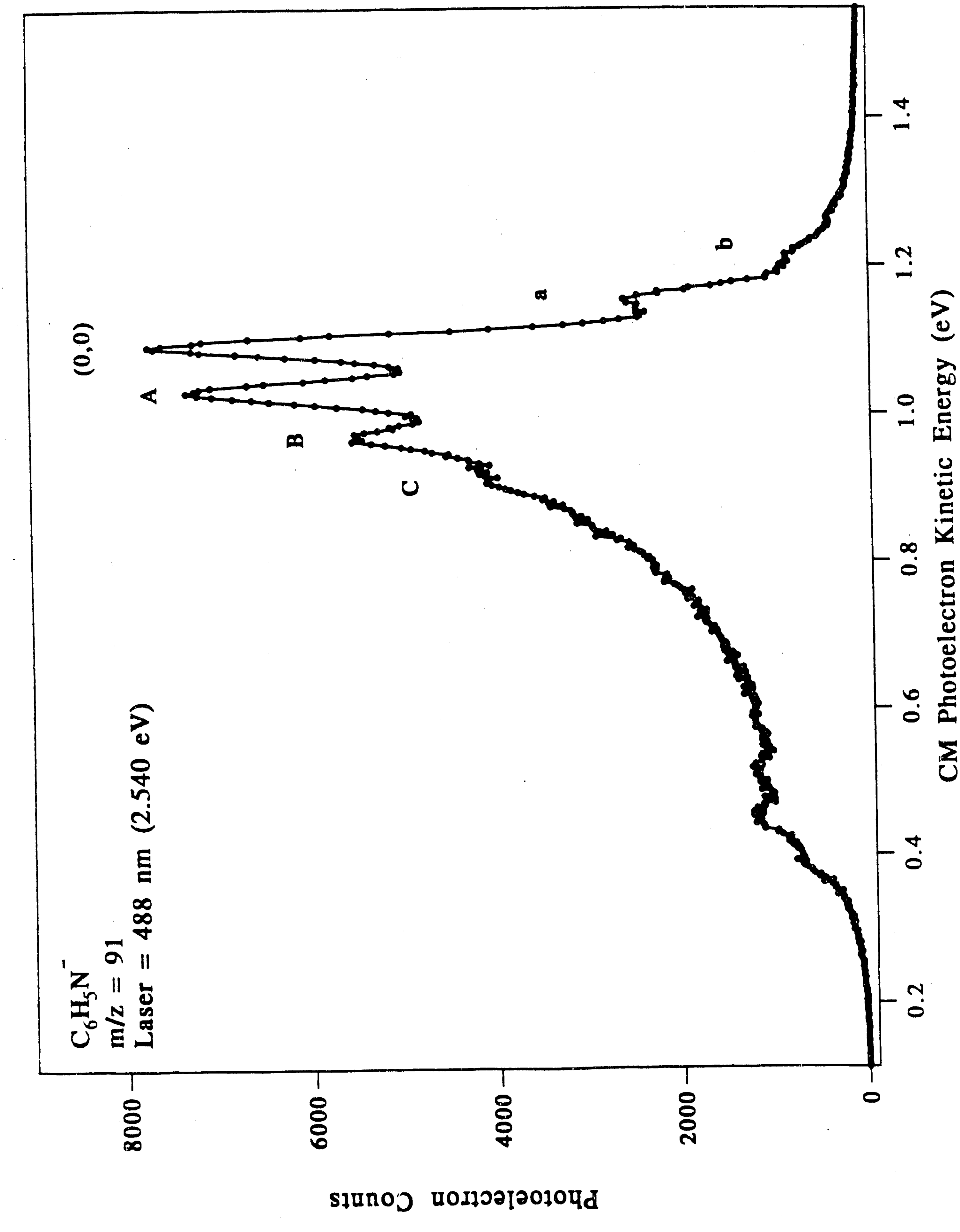
A more interesting nitrene is phenylnitrene, C_6H_5N. The chemistry of this reactive aromatic nitrene has been extensively studied and is very confusing. The ground states of several nitrenes have been studied by EPR spectroscopy and all but aminonitrenes are known to be a triplets. Phenylnitrene can 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:



C_6H_5-N $\tilde{X}\,^3A_2$ C_6H_5-N$^-$ (2)

The optical spectroscopy of C_6H_5N is a mess. Absorption and florescence 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 ≅ 320 nm (3.87 eV), ④ ≅ 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.


$C_6H_5N^-$
m/z = 91
Laser = 488 nm (2.540 eV)
(0,0)
A
B
C
a
b
0
2000
4000
6000
8000
Photoelectron Counts
0.2
0.4
0.6
0.8
1.0
1.2
1.4
CM Photoelectron Kinetic Energy (eV)

Curriculum Vitae

G. Barney Ellison

Address:
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Positions: University of Colorado

Assistant Professor	1977 - 1983
Associate Professor	1983 - 1988
Professor	1988 - present

Sabbatical Leave 1985-1986
Dept. of Chemistry (Josef Michl); Univ. of Utah
Theoretical Chemistry Group (Thom Dunning); Argonne National Laboratory

Education:

Undergraduate: Trinity College 1961-1965
Hartford, CT 06106
Major: Pre-medical

Graduate: Yale University

Department of Pharmacology	1965-1967
Department of Chemistry	1968-1974

Dissertation: "Electronic States of Olefins" December, 1974
Prof. K.B. Wiberg, Director

Postdoctoral
Appointment: Department of Chemistry 1975-1977
Joint Institute for Laboratory Astrophysics
University of Colorado
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(with Professors W.P. Reinhardt and W.C. Lineberger)

Awards and Professional Societies:

•USPHS Trainee	1965-1967
•NIH Predoctoral Fellowship	1968-1972
•Wolfgang Prize, Yale University	1975
•Fellow of the Alfred P. Sloan Foundation	1979-1981
•American Chemical Society	
•American Physical Society	

Current and Pending Support

A. **Current Research Support**

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

B. **Pending Research Support**

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

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END

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