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THEORETICAL STUDIES OF PHOTODISSOCIATION OF SMALL MOLECULES OF ASTROPHYSICAL IMPORTANCE

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BACKGROUND

It was suggested many years ago that the radicals and ions observed in comets result from photodissociation and photoionization of molecules. According to current models,[1-5] a comet is composed chiefly of a large, solid nucleus of frozen gases (parent molecules) such as H_2O, HCN, and NH_3. It is believed comets were formed at the same time and in the same region of space as the major planets and that their chemical composition may be the same as that of the early solar system. As the comet nears the sun, the surface heats up, liberating the frozen gases as well as dust particles. Solar radiation photodissociates the parent molecules into fragments that can be observed by resonance fluorescence.

Both polyatomic molecules, known to be present in the interstellar medium, and cometary radicals have been observed. Using laboratory photodissociation data and computer models, astronomers are attempting to identify the parent molecules that account for all observed radicals and ions. In many cases, they have been very successful. The water molecule is the likely precursor for the H, OH, and $O(^1D)$ species that have been observed. Similarly, evidence suggests that HCN and CH_3CN are the precursors for the CN radical.[4]

For some fragments, however, the precursor molecule is not as clear. One of these is the C_2 radical, which is observed by the Swan band emission $d^3\Pi_g \rightarrow a^3\Pi_u$. This band system is one of the strongest observed in comets. One likely candidate for the C_2 parent species is the acetylene molecule, the photodissociation of which has been studied experimentally in the vacuum ultraviolet.[6,7] Absorption of a single photon produces excited acetylene that may dissociate to the C_2H radical and an H atom. For wavelengths less than 1200 Å, the quantum yield for the latter process becomes significant. No evidence for production of the C_2 radical by absorption of a single photon by C_2H_2 has been found. Using the ArF laser at 1930 Å, researchers have observed[6] the $C_2(d^3\Pi_g)$ emission, which is the result of a three-photon process in C_2H_2 that may proceed through a C_2H intermediate.

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It has been suggested[4] that the C_2 Swan band emission observed in comets is a result of the secondary photolysis of the C_2H radical produced by photodissociation of acetylene. This hypothesis is supported by the observation of the C_2H radical in interstellar space.[8]

The parent molecule of the NH radical is also ambiguous. The most likely parent for NH is ammonia, which has been observed in interstellar space but not in comets. The photodissociation of NH_3 has been studied in the laboratory in the vacuum ultraviolet.[9] The primary product of dissociation is known to be ground state $NH_2 + H$. Fluorescence from excited state $NH_2(\tilde{A}^2A_1)$ has been observed[9] for incident wavelengths between ~ 1100 and 1300 Å. Triplet emission of $NH(A^3\Pi \rightarrow X^3\Sigma)$ has been observed[10] in comets, although only singlet NH is found as a direct result of NH_3 photodissociation. Dissociation of ammonia to give triplet $NH + H_2$ is a spin-forbidden process, and dissociation of NH_3 to give triplet NH + H + H requires a great deal of energy.

The suggestion that secondary photolysis of the NH_2 radical is related to the observation in comets of triplet NH originally motivated us to study the photodissociation of NH_2. However, calculations on NH_2 alone will not unambiguously determine the parent molecule of the NH triplet state because of the following facts. The lower state of the observed NH triplet emission, the $X^3\Sigma^-$ state, is the ground state of the system. Given a lack of competing processes, NH excited singlets will eventually radiate to the triplet ground state even though single-triplet transitions are dipole "forbidden." The observations do not indicate in which state the NH molecule was initially formed.

We therefore broadened our goal to exploring NH_2 photodissociation processes leading to not just triplet states, but also to singlet and triplet states of NH. Resulting photodissociation rates as a function of incident wavelength may then be incorporated into computer models of comet chemistry and physics.

In this final report, we describe our calculations on NH_2 and C_2H performed under NASA contract NASW-3373.

RESEARCH ACCOMPLISHMENTS

Calculations were performed first for the NH_2 system because it is computationally easier to treat than C_2H since it contains two hydrogen atoms and only one first-row atom. The theoretical approach was carefully tested. Results were used in the calculations on C_2H.

Photodissociation of NH_2

Technical details of the calculations on NH_2 have been published in the Journal of Chemical Physics; a copy of the paper[11] is attached as the Appendix. In this section we will briefly summarize the important steps in the calculation and the results of interest for cometary modeling.

Spectroscopic information is available only for the ground $X(^2B_1)$ and first excited $A(^2A_1)$ states of NH_2; therefore, the first important task was to establish the correlation diagram for NH_2 dissociating to NH + H. Assuming the Franck-Condon principle, excited state energies were determined near the equilibrium geometry of the ground state. If we consider only doublet states, which are dipole connected to the ground state, the first three states of NH_2 are valence in character and the next two doublets are the lowest 3s Rydberg states in $^2B_1$ and $^2A_1$ symmetry. We limited our consideration to these states, which include photodissociation channels to the a $^1\Delta$, b $^1\Sigma^+$, and A $^3\Pi$ states of NH.

Potential energy curves for these five states as a function of one NH bond length at fixed remaining NH bond length and bond angle were performed using the density-matrix-directed second-order Multi-Configuration Self-Consistent Field (MCSCF) procedure of Lengsfield. A separate calculation was performed for each state. Particular care was taken to define a single calculation that describes equivalently pure valence, pure Rydberg, and mixed valence-Rydberg states. Extensive testing of this procedure was performed. Transition dipole moments were evaluated from the MCSCF wave functions.

Using the calculated potential curves and transition moments, we calculated photodissociation cross sections as a function of incident wavelength for transitions from the ground state, treating NH_2 as a pseudodiatom HN-H.

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If we assume that each photon absorbed leads to dissociation, the cross section for photodissociation is given by

$$\sigma(\nu) = \frac{8\Pi^3\nu}{3c} \sum_v F_v \left|\langle X_v|\mu|X_k\rangle\right|^2 \tag{1}$$

where ν is the frequency of the transition, X_v is the bound state radial wavefunction, X_k is the dissociating state radial wavefunction, μ is the transition dipole moment, and F_v is the fraction of molecules initially in vibrational state v. We do not consider rotation in this work. Although a Boltzmann average over initial vibrational levels is indicated in Eq. (1), in this system at 300 K, only the ground vibrational level is significantly populated.

The spectroscopic parameters of the pseudodiatomic ground state are reasonably similar to the parameters of a three-body system due to the small mass of the hydrogen atom. For example, the calculated ω_e value for the ground state pseudodiatom is 3507 cm^{-1}, which may be compared with the calculated symmetric stretch and asymmetric stretch of $NH_2(X\ ^2B_1)$, 3307 and 3627 cm^{-1}, respectively.[12] Therefore, averaging over the bound state wavefunction in Eq. (1) is at least qualitatively reasonable.

Photodissociation cross sections for transitions from the ground vibrational and rotational level of the 1 $^2A''$ state to the 2 $^2A'$ and 3 $^2A'$ states are given in Table 1 for wavelengths in the center of the grid used by Huebner and Carpenter[13] and are plotted in Figures 5 and 6 of the Appendix. Absorption to the 2 $^2A'$ state results in a two-peaked cross section with peaks centered near 1710 and 1896 Å with maximum vales of 2.7×10^{-21} cm^2 and 4.3×10^{-21} cm^2 and halfwidths of 132 Å and 68 Å, respectively. The structure in this cross section is a consequence of the zero in the transition dipole moment function (due to symmetry) at the symmetric C_{2v} geometry. The very small magnitude of the cross section reflects the fact that the 2 $^2A'$ state is bound with respect to dissociation in the center of the Franck-Condon region. Thus, the cross section arises from only the very edge of the Franck-Condon region. The cross section for transitions to the 3 $^2A'$ state has its main peak at a value of 2.9×10^{-17} cm^2 with a halfwidth of 9 Å at 1622 Å. The structure in this cross section is due to the transition moment crossing zero.

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Table 1

NH_2 PHOTODISSOCIATION CROSS SECTIONS* (cm^2)

$1^2A'' \rightarrow 2^2A'$		$1^2A'' \rightarrow 3^2A'$	
λ(Å)	σ	λ(Å)	σ
1526.5	2.617E-23	1262.0	1.811E-21
1550.0	1.252E-22	1270.0	2.365E-21
1574.5	3.623E-22	1278.0	2.973E-21
1600.0	7.991E-22	1286.0	3.612E-21
1626.0	1.429E-21	1294.5	4.298E-21
1653.0	2.150E-21	1303.0	4.891E-21
1681.0	2.694E-21	1311.5	5.330E-21
1709.5	2.712E-21	1320.0	5.557E-21
1731.5	2.249E-21	1328.5	5.439E-21
1746.5	1.726E-21	1337.5	4.921E-21
1762.0	1.096E-21	1346.5	4.004E-21
1778.0	4.895E-22	1355.5	2.731E-21
1794.0	8.426E-23	1360.0	2.041E-21
1810.0	2.775E-23	1374.5	2.073E-22
1826.5	4.348E-22	1384.0	1.660E-22
1843.5	1.326E-21	1403.5	7.536E-21
1860.5	2.473E-21	1418.0	2.451E-20
1878.0	3.532E-21	1438.5	7.234E-20
1896.0	4.292E-21	1459.5	1.484E-19
1914.0	3.905E-21	1481.0	2.269E-19
1932.5	1.545E-21	1503.5	2.453E-19
1951.5	5.031E-23	1526.5	1.361E-19
1970.5	2.753E-25	1550.0	1.675E-23
		1574.5	5.389E-19
		1600.0	3.587E-18
		1626.0	1.854E-17
		1653.0	1.269E-19

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*Calculated in pseudodiatomic model assuming fixed values of NH bond length and HNH angle, $R_1 = 1.987\ a_o$, $\theta = 101.14^\circ$.

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In the quasi-diatomic model used here, the 2 $^2A''$ state is quasi-bound, supporting two levels, and the photodissociation cross section shows very narrow resonance peaks centered at 1680 Å and 1770 Å with halfwidths of several cm^{-1}. However, additional MCSCF calculations show that the barrier to photodissociation disappears as the bond angle increases. In a one-dimensional model, a better estimate for the 2 $^2A''$ cross section results from an artificial barrierless potential, assuming dissociation takes place along an effective reaction coordinate. Using such an artificial potential and the calculated transition moment function results in an estimated cross section for the 2 $^2A''$ state with a maximum of $\sim 1 \times 10^{-17}$ cm^2 at 1780 Å and a halfwidth of 130 Å. A more sophisticated treatment of photodissociation ions is required to describe the detailed structure of the cross section.

The importance of these photodissociation cross sections in modeling cometary atmospheres depends on both the magnitude of the cross sections and the transition wavelength at which they peak. In the wavelength region where NH_2 transitions have their maxima, the solar flux varies a great deal, increasing by four orders of magnitude as wavelength is increased from 1500 Å to 3000 Å.[13] While the 2 $^2A'$ state has the smallest cross section of the transitions reported here, it takes place at the longest wavelength of the transitions studied, where the solar flux is higher. This makes its role more nearly comparable to that of the other states than would be concluded from the cross sections alone.

The cross sections reported here are comparable in magnitude to processes that are at present considered in cometary models[14-16] and thus should reasonably be included in future modeling studies.

Calculations on C_2H

Based on the spectroscopy of the C_2 molecule,[17] thermochemical data[18] for the dissociation energy of C_2H, and previous calculations for C_2H in the equilibrium geometry,[19] we have drawn the correlation diagram shown in Figure 1. We are interested in studying dissociation of C_2H to states of C_2 up to the d $^3\Pi_g$ states, which is the upper state for Swan bands. We are considering only doublet states of C_2H, i.e., those that are dipole connected to the C_2H X $^2\Sigma^+$ ground state. Therefore, this work is concentrated on the

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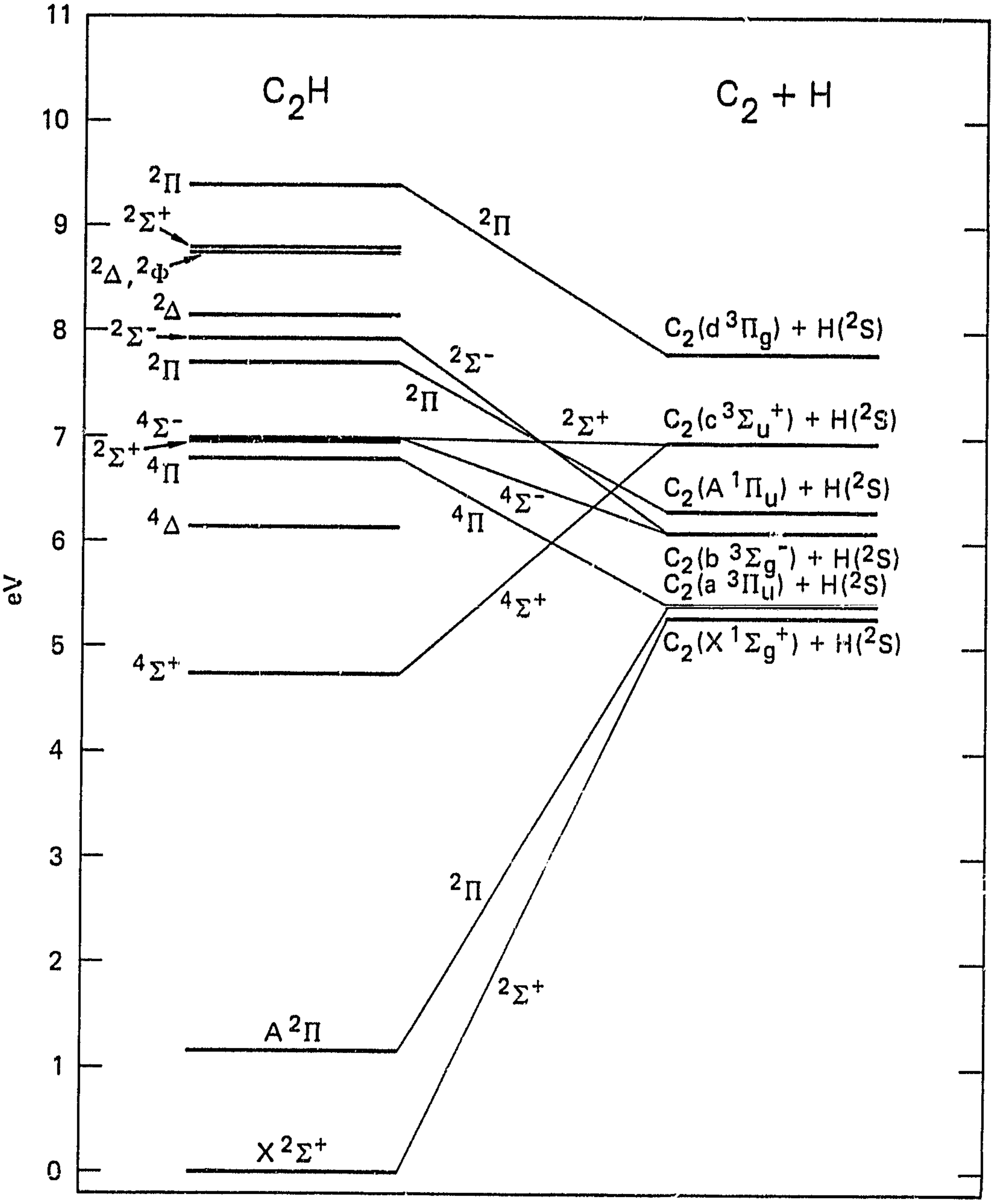

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FIGURE 1 CORRELATION DIAGRAM FOR C_2H DISSOCIATING TO $C_2 + H$.

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first two C_2H states of $^2\Sigma^+$ symmetry, the first state of $^2\Sigma^-$ symmetry, and the first three states of $^2\Pi$ symmetry. All of these states are valence in character except the 3 $^2\Pi$ state, which appears to be a Rydberg state.

Extensive MCSCF calculations have been performed for the five valence states of interest. A basis set appropriate for describing the Rydberg states as well as the valence states has been used from the outset. MCSCF potential curves for these five valence states in linear geometry are shown in Figure 2. For geometries near the ground state equilibrium geometry, the dominant configurations for the 2 $^2\Sigma^+$, 2 $^2\Pi$, and 1 $^2\Sigma^-$ states all have the π^* orbital occupied. For geometries where C_2 is separated from the H atom, the π^* orbital is not occupied. Thus, the potential curves in Figure 2 for these states involve curve crossings that result in the barrier to linear dissociation shown here. Therefore, we have undertaken calculations for bent geometries to determine the lowest energy path to dissociation. Photodissociation would then be treated using an effective reaction coordinate.

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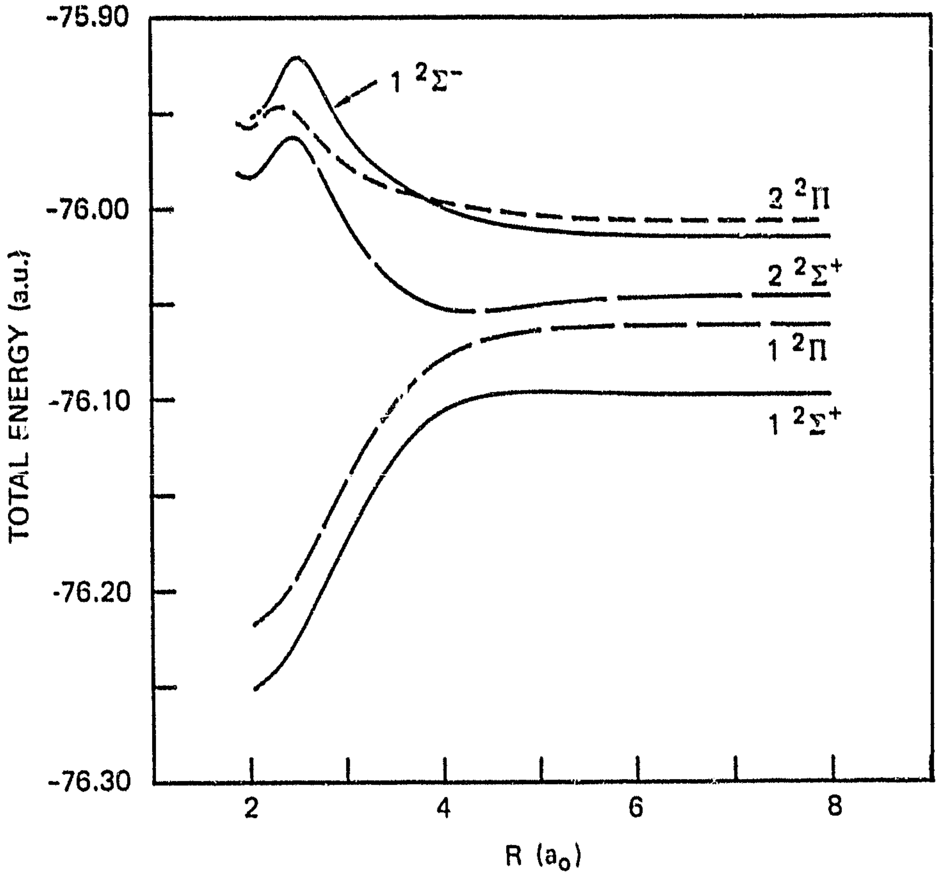

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FIGURE 2 POTENTIAL ENERGY IN ATOMIC UNITS FOR LINEAR C_2H FOR FIXED C-C DISTANCE = 2.304 a_0 AS A FUNCTION OF C-H BOND LENGTH.

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