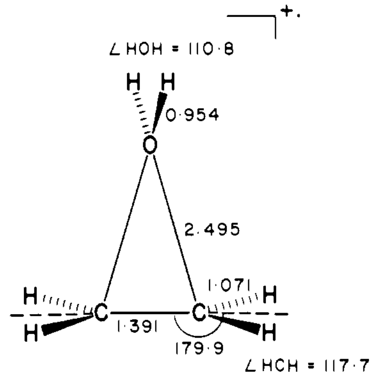
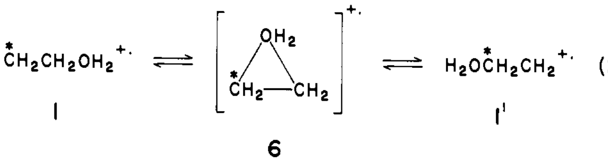


**6** ($C_{2v}$)

for the $CHCHOH_2^{+\cdot}$ system.[25] It is well established[26] that both inclusion of polarization functions and of electron correlation stabilize such nonclassical cations with respect to classical structures. Nevertheless, our best calculations (Tables I and II) indicate that the open form **1** is favored slightly (by 13 kJ mol$^{-1}$) over the bridged species **6**. In view of this result, we would predict that scrambling of the $CH_2$ groups in **1** (eq 2) should occur readily under normal experimental conditions.



(2)

## Conclusions

The present study substantiates the recently reported observation[3] of $CH_2CH_2OH_2^{+\cdot}$ (**1**) as a low-energy isomer in the $C_2H_6O^{+\cdot}$ potential energy surface. This ion is calculated to be lower in energy than both the ethanol and dimethyl ether radical cations (by 43 and 61 kJ mol$^{-1}$, respectively). Two other ions, unusual in that they too have no stable neutral counterparts, are also shown to be low in energy: $CH_3CHOH_2^{+\cdot}$ (**2**) lies 26 kJ mol$^{-1}$ below the ethanol radical cation, and $CH_3OHCH_2^{+\cdot}$ (**4**) is comparable in energy to the dimethyl ether radical cation. Both **2** and **4** offer good prospects for experimental observation. All three oxonium ion structures (**1**, **2**, and **4**) are members of a class of radical cations which can be considered as complexes of a radical cation (e.g., $CH_2^{+\cdot}$, $CHCH^{+\cdot}$, $CH_2CH_2^{+\cdot}$, $CH_3CH^{+\cdot}$) and an electron-rich neutral molecule (e.g., $H_2O$, $NH_3$, HF, HCl, $CH_3OH$, $CH_2{=}O$). Many such complexes have recently been theoretically and/or experimentally identified.[1-4,15-18,22,25,27] Finally, we note that the transition structure (**6**) for 1,2-$OH_2$ migration in $CH_2CH_2OH_2^{+\cdot}$ (**1**) is found to lie only 13 kJ mol$^{-1}$ higher in energy than **1**, suggesting that scrambling of the carbon atoms in suitably labeled **1** should occur readily.

**Acknowledgment.** We thank Dr L. Farnell for the vibrational frequency program. Helpful discussions with Dr J. K. MacLeod are gratefully acknowledged.

**Registry No. 1**, 60786-90-5; **2**, 84602-72-2; **3**, 84602-73-3; **4**, 84602-74-4; **5**, 79802-70-3.

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# Theoretical Aspects of the Photochemistry of Methanol, Methylamine, and Related Materials

**E. Kassab,**[*,†] **J. T. Gleghorn,**[‡] **and E. M. Evleth**[†]

*Contribution from the Centre de Mécanique Ondulatoire Appliquée, 23, rue du Maroc, 75019, Paris, France, and the Department of Chemistry, University of Lancaster, Lancaster, United Kingdom.*

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**Abstract**: The photochemistries of methanol and methylamine are computationally rationalized using ab initio methods. It is shown that the lowest excited singlet states of these and related materials are n,3s Rydberg in character. These states are computationally shown to evolve adiabatically to the valence ground states of the various radical products along the NH, CN, CO, and OH bond rupture pathways in methylamine and methanol, respectively. The NH and CN n,3s bond rupture surfaces display minima in the region of the Franck–Condon excitation geometry. The NH bond ruptures in n,3s singlet ammonia and methylamine are shown to be identical in having small activation energies. The CN excited state bond rupture shows a much larger activation energy, indicating that trialkylamines should display some photostability in the region of the 0–0 transition. In methanol, neither CO nor OH excited-state bond rupture coordinates show minima. The observed preference for OH bond rupture in the UV photochemistry of methanol is rationalized as resulting from the lighter mass of the H atom as well as the computed more repulsive nature of the OH bond rupture. In methanol, both 1,2- and 1,1-$H_2$ molecular elimination excited-state pathways are examined. 1,2-$H_2$ elimination is found to have a small activation energy while the 1,1-elimination is difficult. The concept of de-Rydbergization is fully developed in order to rationalize the change in electronic character occurring along these various excited state pathways.

The goal of this article is to characterize theoretically the absorption threshold photochemistry of methanol, methylamine, and related small molecules. We will show that the excited states generated in the absorption threshold region are all singlet and Rydberg (n,3s) in character. We will also show that there are adiabatic surfaces which allow these Rydberg states to evolve directly to the valence states of the fragmentation products.

Previous emphasis on the properties of small-molecule excited states has been largely spectroscopic.[1] Standard photochemical

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[†] Centre de Mécanique Ondulatoire Appliquée.

[‡] University of Lancaster.

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texts give only slight mention to the photochemical properties of Rydberg states[2] or describe their behavior without giving any detailed theoretical analysis.[3] Von Sonntag and Schuchmann[4] recently presented a thorough experimental review of small organic molecule photochemistry but were unable to find sufficient theoretical literature to rationalize this photochemistry. Likewise, there has been considerable confusion around the issue of the relative roles of valence and Rydberg states in small-molecule photochemistry. More recently, theoretical chemists have taken a renewed interest in attempting to obtain a broad understanding of Rydberg photochemistry.[5-8] We will treat here the various adiabatic reaction paths available to the lowest excited (n,3s) singlet states of methanol and methylamine. We will relate these results to other small organic systems as well as to their parent molecules, water and ammonia. Particular emphasis will be given to qualitatively understanding how a molecular Rydberg state can adiabatically evolve to the valence states of the fragmentation products.

## Technical Details

**A. Computational Techniques.** Both the large and small basis set (vide infra) ab initio calculations were done by use of a variety of programs. The small basis set calculations were performed using a small CI version of Gaussian 70. As noted in the figure captions, major portions of the surfaces were generated from a small CI (100 × 100) calculation using the MO's generated from a Nesbet type open shell (n,3s)[9] treatment. Both ATMOLE[10] and Monstergauss[11] were used for RHF and UHF open shell treatments. Some minor geometry optimizations were carried out with the latter program. Finally, the Whitten[12] gaussian lobe + configuration selection CI program was also used in the large basis set calculations. Although the latter program uses lobe functions, it was found that identical basis sets yielded nearly identical energies ($10^{-4}$ au) as obtained from the cartesian gaussian programs if the standard lobe separation formula[13] was used. In the calculations presented here, the term "small CI" refers only to the small basis set + 100 × 100 CI in which the configurations were hand selected. The term "large CI" refers to the large basis set calculations in which the configurations were selected[13] using a configuration threshold of $3 \times 10^{-4}$ au with the open shell RHF Roothaan, n,3s configuration as the parent. In the case of methylamine, this threshold usually selects between 200 and 400 highly interacting configurations. However, neither CI treatment will yield a significant portion of the valence orbital correlation energies of the systems under study. It will be shown, however, that the inclusion of CI is not an important correlative feature in rationalizing the n,3s excited-state surface behaviors. However, the limited CI used will be necessary to give the correct correlative features of the ground state surface.

**B. Basis Sets.** The large basis set calculations used, for the valence space, is that of Dunning,[14] (9s5p/4s) contracted to (4s2p/2s) with an H scaling factor of unity. This basis was supplemented with diffuse (Rydberg) components:[15] (N: s, $\alpha$ = 0.05, 0.011; p, 0.037, 0.0075), (C: s, 0.035, 0.008; p, 0.025, 0.005), (O: s, 0.010, 0.015, p, 0.05, 0.01), and (H: s, 0.025). The small basis set calculations used for valence space, 4-31G, supplemented with single s components for C, N, and O (0.015, 0.02, and 0.025, respectively). The large basis set is very redundant in the sense that a smaller Rydberg basis will probably give nearly the same results. At short and intermediate internuclear distances the Rydberg–Rydberg overlap integrals are nearly unity and the base orbital composition of the 3s MO can take on a variety of compositions without changing its essential 3s character.[16] The 4-31G + 3s represents a minimal Rydberg basis set necessary to treat the 3s MO along the bond rupture coordinates in methanol and methylamine. However, this minimal Rydberg basis set will generate two Rydberg MOs having, at small internuclear distances, principally the compositions: $c_1 3s_a + c_2 3s_b$ and $c_2 3s_a - c_1 3s_b$ ($a$, $b$ = C, O or C, N). The first MO is 3s, the second, 3p along the CO or CN axis. The large basis set will produce a much larger virtual set of Rydberg MOs. However, we will deal only with the n,3s state surface behaviors here.

## Preliminary Observations

**A. The Known Photochemistry of Methylamine, Methanol, and Related Materials.** We will concentrate only on the gas-phase UV absorption threshold photochemistries of the materials dealt with here. Higher energy photolyses are more difficult to correlate experimentally and theoretically. Analysis of the condensed phase photochemistry is made difficult because of the uncertainty of the spectral assignments.[1]

In the case of ammonia and the mono- and dialkylamines, the threshold UV absorptions yield n,3s excited singlet states.[1] These states exhibit no significant fluorescence and undergo mainly predissociative NH bond rupture.[17-19] In ammonia,[17] the n,3s singlet state decomposes to give the ground states of the radical pair, $NH_2$ ($1^2B_1$) and H ($^2S$), with considerable amounts of kinetic energy in the H atom. Slightly higher energy photolyses may open up another channel to the reaction, $NH_2$ ($1^2A_1$) + H ($^2S$), in which the H atom has much less kinetic energy.[17c-e] In the case of methylamine, the threshold photochemistry yields mainly NH rupture.[18] However, at higher energies, $H_2$ molecular elimination processes occur.[18] Photolysis of frozen methylamine yields ejection into the gas phase of H atoms with high kinetic energies.[20] Trialkylamines are photophysically and photochemically complex. First of all, they fluoresce with near unit quantum yields when excited near the absorption thresholds.[21] In trimethylamine[21] the position of the 0–0 band for the n,3s singlet state has not been determined (ca. 250–270 nm). Higher energy photolysis (193 nm) produces CN bond rupture in which the kinetic energy of

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(2) A survey of a large number of general photochemistry texts shows that only that of Simons, J. A. "Photochemistry and Spectroscopy"; Wiley-Interscience: London, 1971, even mentions the possible Rydberg character (3s) of a $\sigma^*$ MO, p 137. However, this approach is not general nor evident in other discussions or diagrams (see pp 79, 156, 268).

(3) Okabe, H. "Photochemistry of Small Molecules"; Wiley-Interscience: New York, 1978. This excellent review of the known photochemical properties of small molecules lacks a theoretical approach. It is also pointed out that the $C_s$ correlation diagram for $H_2O$ (Figure II-10, p 74) and $C_{2v}$ diagram for $NH_3$ (Figure II-12, p 79) are in error in showing double correlations where only one exists.

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Table I. Comparison of the Threshold UV Spectroscopic Energies and Bond Dissociation Energies for NH, CN, OH, and CO Ruptures in Various Molecules (eV)

| | | bond energies[b] | | | | bond energies[b] | |
|---|---|---|---|---|---|---|---|
| molecule | n,3s*[a] | NH | CN | molecule | n,3s*[a] | OH | CO |
| $NH_3$ | 5.8 | 4.8 | | $H_2O$ | 7.4 | 5.4 | |
| $CH_3NH_2$ | 5.3 | 4.5 | 3.8 | $CH_3OH$ | 6.7 | 4.5 | 3.9 |
| $(CH_3)_2NH$ | 5.2 | 4.1 | 3.6 | $(CH_3)_2O$ | 6.2 | | 3.5 |
| $(CH_3)_3N$ | 5.0 | | 3.4 | | | | |

[a] Reference 1. Selected are the approximate transition energies in the red edge of the first absorption band. [b] Taken from "Handbook of Chemistry and Physics"; CRC Press: Cleveland, 1976–76, pp F 224–231. Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; NSRDS-NBS 21, Washington, DC.

the ejected methyl group is low, indicating that the reacting species is the hot ground state of trimethylamine.[22] The threshold region for the onset of CN bond rupture is in the region of 230 nm but this cannot be established with precision.[21]

The spectroscopy and photochemistry of alkyl alcohols and ethers have some complicating features. The similar, very diffuse, natures of the first absorption bands in water and the alcohols (170–190 nm)[23] made their original spectral assignments difficult. However, no low-lying valence excited states (e.g., n,$\sigma^*$;$\sigma$,$\sigma^*$) are computed for water.[24] The spectral assignments for the threshold absorptions in water, methanol, and dimethyl ether are all n→3s singlet (170–190 nm).[25] The very diffuse nature of this absorption in water and the alcohols is attributable to the repulsive nature of the OH n,3s surface at the vertical excitation geometry.[23] Alicyclic ethers[23] display considerable fine structure. However, fluorescence is not reported for water, the alcohols, or any alkyl ethers. This indicates that the processes depopulating the n,3s singlet state are extremely rapid ($10^{12}$ $s^{-1}$).

The photochemistry of methanol is presently in a confused state.[4] The most recent work on methanol and 2-propanol[26] challenges some of the earlier work[27] claiming collision-induced predissociation of excited methanol. Based on the photolysis of $CD_3OH$,[28] the dominant process is OH bond rupture (75–80%), very little CO rupture, and considerable (20%) 1,2-$H_2$ elimination giving formaldehyde. In any case, the quantum yield of $H_2$ generation from secondary reactions following atomic H generation is sensitive to foreign gas pressure,[26,27] and both groups of authors propose metastable $CH_3OH$ species in the photochemistry of this material. In dimethyl and diethyl ether photochemistry (185 nm) principally CO bond rupture is proposed in high quantum yields.[29] Alicyclic ethers show both CO rupture and molecular elimination processes (185 nm).[30]

The key point is that the observed threshold UV photochemistries of methylamine and methanol show principally NH and OH ruptures, respectively. These processes are not those observed in multiphoton IR photochemistry or anticipated from thermal decompositions. Thermal processes would produce principally CN and CO ruptures (Table I) together with various $H_2$ eliminations.[31-36] The following theoretical treatment will rationalize the UV photochemistry.

**B. Comments on Molecular Rydberg States and Their Correlations with Product States.** The experimental characterization of molecular Rydberg states has been thoroughly dealt with by Robin.[1] However, the subject of the intercorrelation of Rydberg reactant-product states is not as comprehensively discussed, and the reader is referred to a number of articles.[5-8,37-39] An important point is that while low-lying valence excited states exist for larger molecular systems, smaller saturated systems (e.g., $H_2O$, $NH_3$, $CH_4$, alkanes) may have only Rydberg low-lying states.[24,25,38-40] In particular, spectral assignments of the type, $\sigma \rightarrow \sigma^*$,n$\rightarrow \sigma^*$ are deceptive since a large Rydberg basis set calculation may not produce such species. At the vertical excitation geometries the $\sigma^*$ MOs may ($H_2O$, $NH_3$, $CH_4$)[24,25,40] or may not (e.g., $Cl_2$[41]) be Rydberg in character. In the materials treated here, the n,3s singlet states are Rydberg in character. There is no hypothetical low-lying n,$\sigma^*$ state. We will show that the 3s and the $\sigma^*$ MO in question are one and the same MO.

If one knows the order and symmetry of the reactant and product states and imposes a symmetry restricted transformation one can show a priori that *some* excited state surfaces must de-Rydbergize. The theoretical mechanisms by which a molecular Rydberg state adiabatically evolves to give a product valence state are twofold. One mechanism involves the avoided crossing of *two real* molecular state surfaces, one having principally valence, the other principally Rydberg character.[39] The electronic configurations of these states principally differ by occupations differing by two-spin orbitals (e.g., $O_2$, Cl[241,42]). The avoided crossing is generated at the CI or MCSCF levels. However, the surface de-Rydbergizations of interest here occur at the open shell RHF level. Previously, the de-Rydbergization of the n,3s singlet surface for planar NH rupture in $NH_3$ had been attributed to an avoided crossing between an n,$\sigma^*$ (valence) and an n,3s Rydberg state.[17] However, there is no n,$\sigma^*$ singlet state computed for $NH_3$.[38-40a] In addition, according to the generalized Brillouin theorem,[43] there can be no "avoided crossing" between two hypothetical states differing by one spin-orbital. Instead, the open shell SCF procedure will construct a single one electron MO (e.g., 3s $\leftrightarrow$ $\sigma^*$)

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(33) $\Delta H$ for the ground state reaction, $CH_3OH \rightarrow CH_2{=}O + H_2$ is approximately +20 kcal/mol.[34] Recent calculations on hydroxycarbene, $^1A'$ singlet, would place this species about 72 kcal/mol above $CH_3OH$.[35] On the basis of $^1A_1$–$^1B_1$ energy split in $CH_2$,[35] the $^1A''$ species of CHOH, would be about 12 kcal/mol higher than the $^1A'$ species. Therefore, given an n,3s singlet state of methanol in the order of 150 kcal/mol, a large number of ground and excited state channels are thermodynamically accessible.

(34) The gas-phase $\Delta H_f$ of methanol and formaldehyde are −48.1 and −27.7 kcal/mol. "Handbook of Chemistry and Physics", CRC Press: Cleveland, 1975–76; pp D-78.

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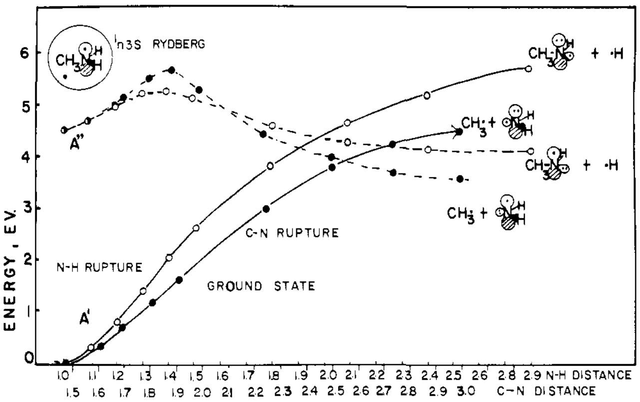

**Figure 1.** CN and NH bond rupture pathways for planar methylamine 4-31G + 3s basis, 100 CI. Initial geometry, CH, 1.09 Å; CN, 1.474, NH, 1.012; NCH, 109.5°; CNH, 120°. Plane is represented by the H–C–N–H cisoid configuration. The first four points of the A′ surface were calculated using CI on the closed-shell SCFMOs. All other points were calculated using the same configurations on the Nesbet open-shell MOs of the n,3s configuration. The structural representations shown indicate the relative positions of the "important" electrons in the transformation, a large circle representing a 3s type MO.

having optimized Rydberg-valence components. Mulliken refers to this as MO-Rydbergization.[44] United atom correlation diagrams[37] show that antibonding valence MOs will become Rydberg in character at the united atom limit (e.g., $1\sigma_u^* \leftrightarrow 2p\sigma_u^* \leftrightarrow 2p$). Conceptually, as the internuclear separation decreases, the valence components of an antibonding MO will self-annihilate,[45] leaving the Rydberg components to fulfill the energy requirements of the MO (e.g., $1\sigma_u^* = c_1(1s_a - 1s_b) + c_2 2p_c$, in $H_2$, where $2p_c$ is a function with the center of the system as origin).

The above concept of MO-Rydbergization must be coupled with that of MO-dissociating states if the final state-to-state correlation is to be obtained.[44] Although the avoided crossing Rydbergizations required CI, as do ground-state bond rupture surfaces in filled shell species, the n,3s singlet NH bond rupture surface in $NH_3$ can be qualitatively treated at the open-shell RHF level since there is a direct state-to-state correlation at the orbital-by-orbital level.[38,40a] The 3s MO in $NH_3$ will eventually de-Rydbergize and localize on the departing H atom. We will show that the overall de-Rydbergization process is $3s \rightarrow 3s,\sigma^* \rightarrow 1sH$. Similarly, it can be correlatively anticipated that in the other systems the n,3s states will eventually become n,σ*-like (σ* = NH, OH, CN, CO) at some point along the bond rupture coordinate. The n,3s singlet surfaces for these ruptures will have shallow or no minima.[46–48] However, other higher lying Rydberg states (e.g., n,3p) will usually have deep minima and eventually will correlate with high lying (usually Rydberg) states of the fragments. In this sense the behavior of the n,3s surfaces will be much different than the higher-lying Rydberg surfaces.

## Results and Discussion

**A. Methylamine.** Shown in Figure 1 are the 4-31G + 3s computed ground ($^1A'$) and n,3s ($^1A''$) excited state surfaces for both CN and NH ($C_s$) bond ruptures. A planar geometry is assumed for the n,3s singlet of methylamine. This was based on both the spectroscopic data[49] and a partial optimization of the n,3s triplet state (UHF). Figure 1 shows that for both CN and NH ruptures, there are crossings of the A′ and A″ surfaces. The CN rupture is correlatively anticipated by symmetry since $^1A'' \leftrightarrow NH_2(1^2B_1) + CH_3(^2A_1)$ and $^1A' \leftrightarrow NH_2(1^2A_1) + CH_3(^2A_1)$. These correlations correspond to those found in planar $NH_3$.[17,38] The corresponding electronic structures for the ground and excited state of $CH_3NH$ are $^2A''$ and $^2A'$, respectively (Figure 1). These have the same nonbonding MO occupations as found in the $1^2B_1$ and $1^2A_1$ states of $NH_2$.[50] It must be noted, however, that as in the case of nonplanar NH rupture in $NH_3$, nonplanar departure of $CH_3$ or H will produce a noncrossing of these surfaces.[51] Therefore, the surfaces shown in Figure 1 are cross sections of particular conical intersections showing ground–excited-state surface crossings. The most important feature of Figure 1 is the relatively shallow minimum and ammonia-like behavior[17,38,40a,52] for both the CN and NH n,3s state rupture surfaces. However, the small basis set-CI treatment used in generating Figure 1 indicate that it can be used only semiquantitatively. The vertical excitation energy (4.5 eV) is too low (exptl 5.3)[1,49] and both CN and NH ground state bond dissociation energies are too low by about 0.5 eV (Table I).

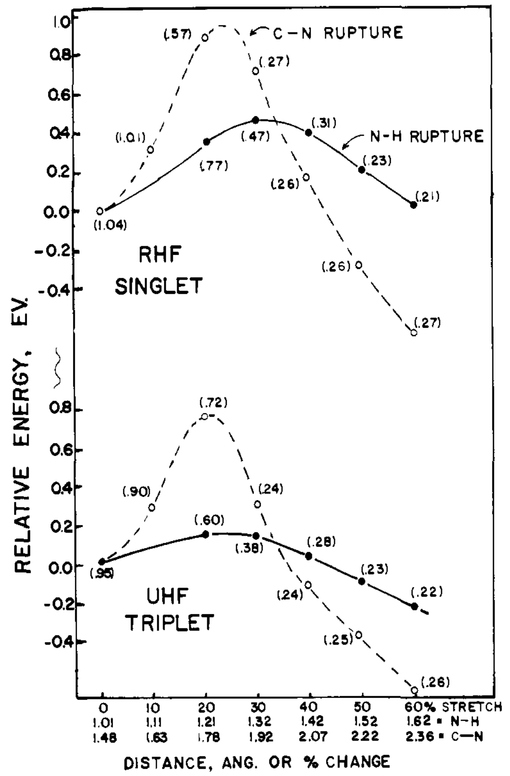

**Figure 2.** A large basis set RHF,UHF comparison of the NH and CN bond ruptures in n,3s excited singlet and triplet methylamine. Shown (--) are the Rydberg orbital populations as the bond ruptures proceed. Zero energy in the RHF singlet calculation is −95.0174 au; UHF zero energy is −95.0297 au.

Figure 1 shows that the barrier for n,3s NH bond rupture is lower than for CN rupture in spite of the greater overall exoergicity for the latter reaction. In order to better estimate the comparative barriers for excited state NH and CN bond ruptures we will discuss the validity of treating this system at the large basis set open-shell RHF level. First of all, the calculations shown in Figure 1 confirmed the MO-dissociating[44] character of the n,3s state surfaces for NH and CN ruptures in that the $^1A''$ surfaces are

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(44) (a) Mulliken, R. S. *Acc. Chem. Res.* **1976**, *9*, 7–12. (b) Mulliken, R. S. *Chem. Phys. Lett.* **1977**, *46*, 197–200.

(45) Sinanoglu, O. "Chemical Spectroscopy and Photochemistry in the Vacuum UV"; Sandorfy, C., Ausloos, P. J., Robin, M. B., Ed.; Reidel: Dordrecht, Holland, 1974; pp 376–378.

(46) The idea that a n,3s surface must have a minimum due to the avoided crossing of a Rydberg and valence state is popular among experimentalists (see ref 17 and 22). Mulliken discusses (ref 44) possible inflections along MO-Rydbergizing surfaces. However, water and phosphine do not exhibit minima and the diffuse lowest energy singlet–singlet absorptions are best rationalized by assuming that no minima exist.[47,48]

(47) Howard, R. E.; McLean, A. D.; Lester, W. A., Jr. *J. Chem. Phys.* **1979**, *71*, 2412–2420.

(48) Muller, J.; Agren, H.; Canuto, S. *J. Chem. Phys.* **1982**, *76*, 5060–5068.

(49) Tsuboi, M.; Hirakawa, Y.; Kasashima, J. *Mol. Spectrosc.* **1969**, *29*, 216–229.

(50) Peyerimhoff, S. D.; Buenker, R. J. *Can. J. Chem.* **1979**, *57*, 3182–3189.

(51) Evleth, E. M. Kassab, E. *J. Am. Chem. Soc.* **1978**, *100*, 7859–7864.

(52) (a) Muller, J.; Canuto, S. *Chem. Phys. Lett.* **1980**, *70*, 236–240. (b) Muller, J. *Int. J. Quantum Chem.* **1971**, *19*, 885–889.

mainly monoconfigurational at all points.[38] In the correlatively identical case of NH rupture in n,3s singlet $NH_3$, the large basis set open shell RHF barrier is 0.54 eV.[52] This value is marginally improved at the large CI level (0.39 eV), but further refinements[52b] reduce the barrier to 0.24 eV. Analysis of the experimental data[17] is consistent with a shallow minimum in the order of 0.3 eV. Our own large basis set open shell RHF NH barrier in the n,3s singlet state of methylamine (Figure 2) is 0.5 eV, which is comparable to that obtained in $NH_3$ at the same level of treatment. It can be assumed that a further reduction of this barrier will be obtained at the very large CI level. As in the case of $NH_3$, the spectra of methylamine[17b,49] can be interpreted as indicating that there is a shallow minimum in the n,3s singlet surface along the NH coordinate. The barrier for CN rupture is greater by a factor of 2 (Figure 2) over that for NH rupture. Our CI calculation found this energetic preference for NH rupture unchanged.[53]

Two issues must now be resolved. First of all, why is the n,3s CN bond rupture barrier greater than for NH rupture? How does this relate to the photochemistry of the amines? The first question can be answered at the qualitative level. It is theoretically and experimentally well established that the valence space of a Rydberg state has cationic character.[1,6] An approximate description of the n,3s state of methylamine is: $((CH_3\dot{N}H_2)^+,e^-)_{3s}$, where the "excited" electron is in a 3s orbital remote to the valence space of the methylamine radical cation. In fact, an unshown calculation of this radical cation gave electron charge and spin densities essentially the same as found in the valence space of the n,3s UHF triplet state. These densities indicate that some spin delocalization of the type, $H_3{\equiv}C\dot{N}H_2^+ \leftrightarrow H_3{=}C{=}NH_2^+$, was giving some increased hyperconjugative stability to the CN bond. There is no equivalent hyperconjugative stabilization for the NH bond in the n,3s state. Therefore, even though CN and NH bond ruptures in the n,3s state of methylamine are correlatively the same,[51] the latter has a lower barrier. This occurs in spite of the fact that the latter rupture has a lower overall exoergicity which, according to the Marcus relationship[54] would lead one to compute an even higher intrinsic (corrected to zero enthalpy change) barrier for CN rupture in relationship to NH rupture.[55]

Finally, from a photochemical standpoint, the major factor which will favor NH rupture even given nearly equivalent *low* barriers will be tunneling. In fact, deuterium effects on both the spectroscopy[17,56] and photochemistry of ammonia[17c,d] indicate that tunneling is occurring in a species located in a shallow potential well. Therefore, the observed preference for NH over CN rupture in the n,3s singlet states of the amines cannot be taken as experimental proof that the CN bond rupture surface has a deeper minimum. The observed photophysical and photochemical properties of trimethylamine do indicate a significant potential well with a depth in the order of 0.5–1.0 eV. However, the recent observation[22] that there appears little kinetic energy in the fragments of this system ($CH_3$, measured, $(CH_3)_2N$ presumed) is not in qualitative agreement with the descent down a repulsive surface. The proposed final precursor in the 193-nm photochemistry of trimethylamine is a vibrationally hot ground-state species which would be qualitatively the same species as would be found in the multiphotonic IR photochemistry.[32] However, because of the specific NH ruptures which occur in the UV photochemistries of the alkyl and dialkylamines, relaxation is taking place directly from a n,3s state. Since the photoreactions are predissociative in nature, there will probably be no role for a triplet n,3s species. However, such a species cannot be excluded in the case of trialkylamine photochemistry. We will discuss other possible reaction paths (molecular $H_2$ elimination, CH rupture) after discussing the photochemistry of methanol.

The final point we will discuss revolves around the question of the de-Rydbergization of the n,3s singlet surfaces. In what region along the surface does the system undergo the Rydberg-to-valence transition? This information is given numerically in Figure 2. At the geometry obtained by vertical excitation from a planar ground state, both the n,3s singlet and triplet states are completely Rydberg in character with 1.04 and 0.95 electrons, respectively, present in diffuse orbital space. With NH rupture the change in Rydberg character is more gradual than in the case of CN rupture. In both cases, the Rydberg character changes rapidly in the region of the barrier maxima, at which point the surface wave functions must be described as intravalent in character. While both the presence of a barrier and the rapidly changing Rydberg character can be attributed to the avoided crossing of a n,3s and n,$\sigma^*$ surfaces,[17,22] we have already shown above and elsewhere[38,39] that within the context of open-shell MO methodology this de-Rydbergization is orbital in nature (i.e., MO-Rydbergization[44]). Indeed, according to the behavior of the $\sigma_u^*$ MO in $^3H_2$, a Rydberg minimum does not have to exist in all cases of the state Rydbergizations. We will show that none exists in methanol OH rupture and similarly no minima are computed in the n,3s and $\sigma$,3s singlet states of water and methane for OH rupture and $H_2$ departure, respectively.[47,57] However, as in the case of NH and CN rupture, these Rydberg surfaces undergo rapid de-Rydbergizations in the region from 0 → 30% bond stretch. It should be pointed out that Rydbergizations need not always be complete at the vertical excitation geometries. Along the repulsive surface in $H_2$ $\sigma,\sigma^*$ triplet its value is small (17% $2p_c$) at 0.75 Å and only reaches large values at small internuclear distances (0.25 Å, 66%).[58]

Our previously stated view that MO-Rydbergization of the n,3s states discussed here essentially arises from a self-annihilation of valence space at small internuclear distances[6b,45] requires some additional clarification. The MO correlation diagrams[38] for the de-Rydbergization of the 3s ($4a_1$) MO in $NH_3$ show, 3s ↔ 1sH (departing H atom). However, neither Figure 2 nor the correlation diagrams demonstrate an intermediate correlation, 3s ↔ $\sigma^*$(NH) ↔ 1sH, i.e., that the MO in question is clearly antibonding in valence space before localizing on the departing H atom. Figures 3 and 4 show the de-Rydbergization of the 3s MO in the n,3s states of $NH_3$ and methylamine as a function of NH and CN bond distances. The electron densities are given in units of $e^-/au^3$. We will classify electron space at $10^{-2}$ $e^-/au^3$ or greater as being valence space; less than this figure is diffuse or Rydberg space. As seen in Figure 3, when the NH distances in either ammonia or methylamine are at 1.01 Å (ground state value reached by a vertical excitation) there is essentially no valence space in the "3s" MO. As NH bond rupture occurs there is a contraction in the electron space, and initially there is an increase in the amount of valence space about, respectively, both the departing H atom and the N atom. However, these valence spaces do not join; there is a nodal region of low-electron density between the two developing valence spaces. At 1.32 Å NH stretch, the MO must be described in intravalent terms ($3s\sigma^*_{NH}$). As the NH rupture proceeds, the valence space around the N atom in ammonia and methylamine disappears and localizes on the H atom. Therefore, initially the 3s MO is diffuse, its electron density maximum ($10^{-3}$)

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(53) At 20% NH and CN elongations along the n,3s singlet surfaces the before and after CI energies had changed relatively less than 0.1 eV. The CI mixing coefficients were also very nearly unity (0.999) at the 400 selected configuration level. Therefore, the n,3s singlet open-shell RHF function is a relatively good description of the n,3s state. Obviously, a major portion of correlation energy in this system is undergoing little change along the n,3s surface and correlation effects have nothing to do with the de-Rydbergization process.

(54) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. $\Delta H_\beta = (1 - \Delta H_{th}/4\Delta H_i)^2\Delta H_i$. The barrier height, $\Delta H_\beta$, for a reaction having a thermodynamic energy change of $\Delta H_{th}$ can be related to a zero energy change barrier, $\Delta H_i$, which is intrinsic. In the case of the NH rupture in the n,3s singlet state, the barrier calculated, 0.5 eV, is for an energy change of −0.8 eV. However, the intrinsic barrier is about 0.8 eV. Likewise, the intrinsic barrier for CN rupture is not the 1 eV found, but is closer to 1.7 eV taking into account (Table I) the −1.5 eV thermodynamic energy.

(55) Both ruptures are classified a topicity 3 events: Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41–54.

(56) Koda, S.; Hackett, P. A.; Back, R. A. *Chem. Phys. Lett.* **1974**, *28*, 532–553.

(57) (a) Gordon, M. F. *Chem. Phys. Lett.* **1977**, *52*, 161–167. (b) Gordon, M. S.; Caldwell, J. W. *J. Chem. Phys.* **1979**, *70*, 5503–5514.

(58) Evleth, E. M.; Kassab, E., unpublished results; 4-31G + 2s diffuse on each H atom or one $2p_c$ centered function ($\alpha = 0.025$) yields the same Rydbergization for a UHF triplet of $H_2$ at each distance. The triplet surface Rydbergizes without achieving either an inflection or minimum.

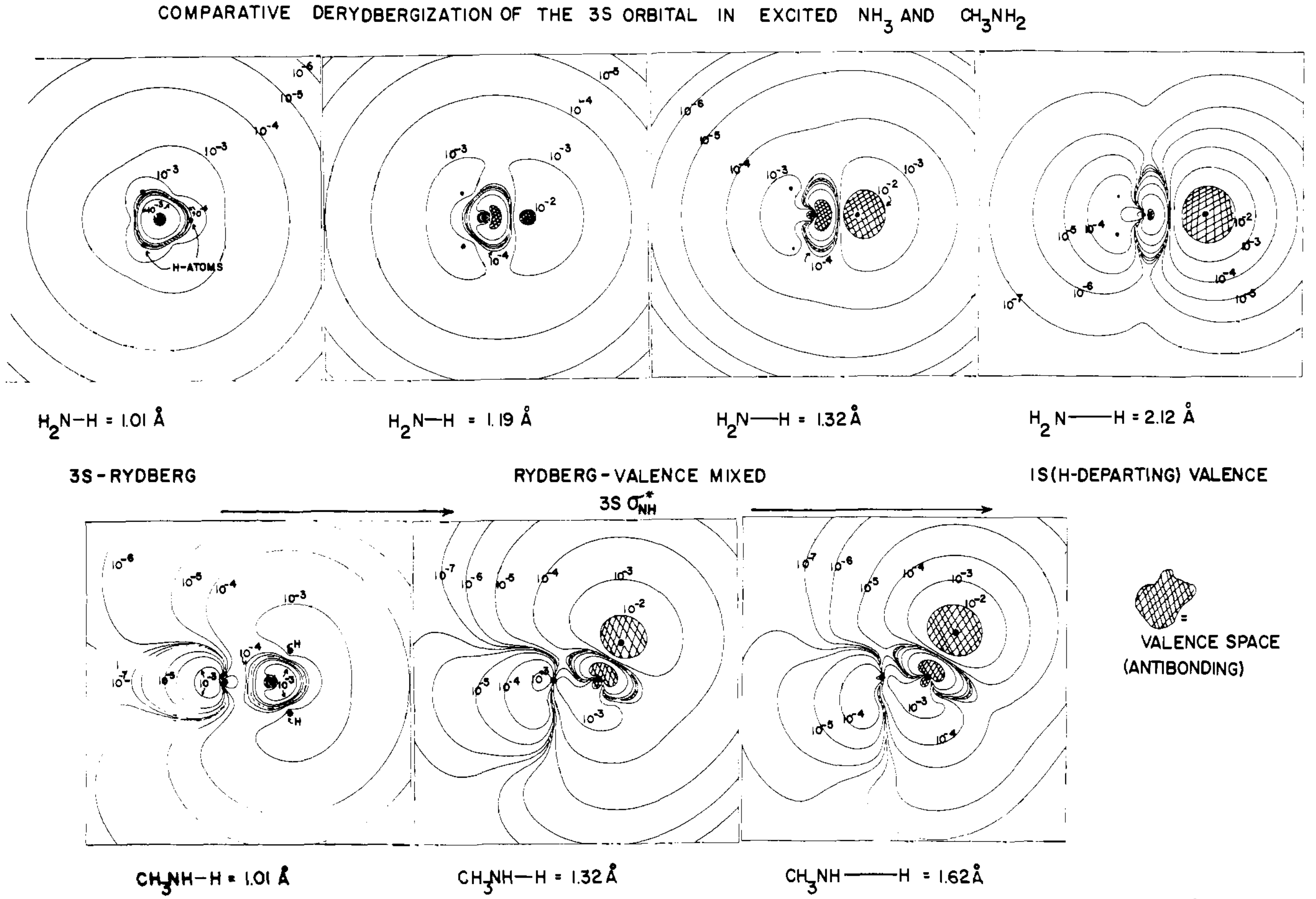

**Figure 3.** A comparative electron density map for the 3s MOs in ammonia and methylamine as a function of N–H bond distance. Shown are the progressive collapse of the initial 3s MOs into valence antibonding space as the NH rupture proceeds. At large N–H distances this MO is localized in the 1s space on the departing H atom. Density units are in electrons au$^{-3}$.

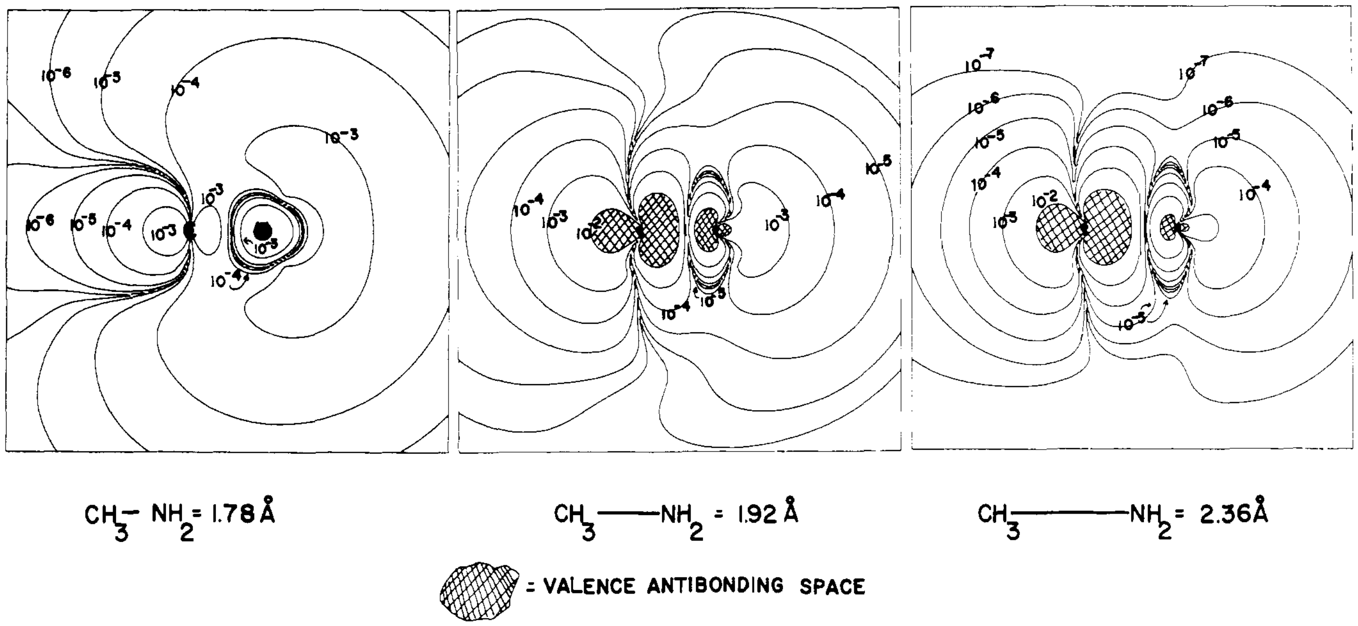

**Figure 4.** Behavior of the 3s MO in methylamine along the CN bond rupture coordinate. Note the collapse of this MO into the valence space of the receding methyl radical.

lies outside the valence space for either the $NH_3$ or methylamine. In the case of the latter material the Rydberg electron also avoids the space around the entire methyl unit, in qualitative agreement with what has been found for both methanol and dimethyl ether.[25] As the NH bond rupture proceeds, this "excited" electron can be conceptually viewed as next moving in valence antibonding space, and finally following the departing H atom. In this manner, the 3s MO finally collapses and becomes a 1s AO on the H atom. Since the same symmetry $\sigma$-space on the $NH_2$ ($^2B_1$) fragment already has two electrons the 3s electron cannot terminate its voyage there.[6b] Finally, as shown in Figure 4, the 3s MO for CN rupture in the n,3s state of methylamine shows intermediate CN valence antibonding characteristics before collapsing into the valence $\sigma$-space on the departing methyl radical. Therefore, in the cases of both NH and CN ruptures the 3s MO must be viewed as having the potential of changing into either a 1sH AO or sp$^n$

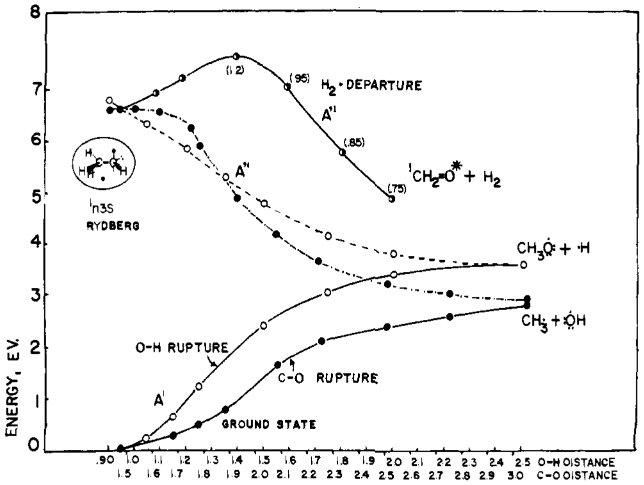

**Figure 5.** Comparative CO, OH bond ruptures, and 1,2-$H_2$ departure from planar $C_s$ methanol. Initial geometry: CH, 1.09 Å; CO, 1.425; OH, 0.95; OCH, 109.5°; COH, 105°. The first four points on the A′ surfaces were computed using closed shell MOs (4-31G + 3s), 100 CI. All other points were computed using the same CI on open-shell MOs obtained from the n,3s configuration. For the excited state surface (A″) for $H_2$ departure the numbers shown (--) are the H–H distances as a function of OH distances as the $H_2$ unit departs in a parallel manner with respect to the CO bond. The planarity of the system is described by a cisoid configuration H–C–O–H as in the case of methylamine.

$CH_3$ MO, after passing through an intermediate antibonding stage ($\sigma^*$, NH, or CN, respectively).

**B. Methanol.** Previous excited-state surface calculations have been performed on the CH and OH bond ruptures in methanol at the 4-31G + 3s,3p + CIPSI level.[59] The results found for the OH ruptures are essentially those we will present here in that the n,3s singlet and triplet surfaces are repulsive and adiabatically take the system to the ground states of the $CH_3O$ and H radicals. However, for the following reasons we question the usefulness of the CH bond rupture surfaces reported in this previous work.[59] First of all, the overall CH dissociation energy based on the ground-state energy of methanol and the fragments, $CH_2OH$ and H, is much too low, 1.2 eV as compared to an experimental value of 4.0 eV.[31c] Secondly, the computed lowest excited state of the $CH_2OH$ radical, 2.6 eV (p → 3s), is much too low in energy for a Rydberg state. Given the authors' own reasonable estimate of the ionization energy of $CH_2OH$ (9.1 eV) and the 3s term value for methyl radical (4.1 eV)[1] we estimate the lowest excited Rydberg state of $CH_2OH$ to be at 5.0 eV. For CH bond rupture, the n,3s singlet state of $CH_3OH$ (6.7 eV) must adiabatically correlate with the lowest excited state of $CH_2OH^*$ + H. According to the above more reliable spectroscopic-thermochemical estimates the process, $CH_3OH^*(n,3s) \rightarrow CH_2OH^*$ (p → 3s) + H must be endoergic by 2.3 eV and therefore not of interest as an adiabatic process in the threshold photochemistry of methanol.

Figure 5 shows the comparative OH and CO ruptures as well as the concerted elimination of $H_2$ from the n,3s ($1^1A''$) singlet state of planar methanol. Planarity was assumed for correlative convenience. We also show the ground state ($1^1A'$) surfaces for both OH and CO ruptures. Because of the degeneracies of the ground states of both $CH_3O$ ($^2E$) and OH ($^2\Pi$),[60] the A″ and A′ surfaces are degenerate at the biradical limit for both OH and CO ruptures in methanol. The small basis set–small CI methodology used in generating Figure 5 limits its use for semiquantitative purposes. In particular, our ground-state OH bond dissociation energy (3.5 eV, Figure 5) is not improved at nearly the same basis level by using a more complete CI method.[59] This value is lower than the experimental one (Table I) by 1 eV. However, the computed value of the n,3s singlet state (6.5 eV) approximates the experimental one (6.7 eV). Therefore, the actual exoergicities for both the $CH_3OH^*$(n,3s singlet) → $CH_3O$ + H and $CH_3$ + OH processes are 1 eV less than indicated in Figure 5.

The main contrast between Figures 1 and 5 is that no significant barrier exists for either CO or OH bond rupture in the n,3s singlet state of methanol. The repulsive nature of the OH surface is similar to that encountered in the n,3s singlet state of water.[47] Similarly, we found no barriers for both the small and large basis set UHF n,3s triplet surfaces of methanol for CO and OH ruptures. However, the CO n,3s singlet surface shown in Figure 5 is flat at the vertical excitation geometry and it is possible that large basis set RHF surfaces will show minima for the CO coordinate in either the n,3s singlet states of methanol or alkyl ethers. It is anticipated that any CO minimum will be shallower than encountered in the case of the CN coordinate in the n,3s singlet surface of methylamine.

Even if one assumes the possibility of a shallow CO minimum in the n,3s singlet state surface of methanol, all calculations showed the OH coordinate to be significantly more repulsive. In a UHF triplet (4-31G + 3s) calculation, the repulsive force operating on the OH coordinate (0.70 mdyn/Å) was considerably greater than for the CO coordinate (0.17) at the vertical excitation geometry. This larger force and lighter mass for the H atom would considerably favor OH rupture over CO rupture in the n,3s triplet state. Our conclusions are that for both the singlet and triplet n,3s states OH coordinates are repulsive. We anticipate that the CO coordinate is repulsive in the n,3s triplet, but there exists the possibility of a shallow minimum in the n,3s singlet along the CO coordinate. In the cases of the alkyl and alicyclic ethers, where no OH bonds occur, the lack of fluorescence may be due to a repulsive or weakly bonding CO coordinate in the n,3s singlet state.[23] However, unlike the alcohols, the n,3s absorptions in ethers display fine structure. In the case of tetrahydrofuran[23] there is fine structure in the region of the O–O band (199 nm), but the spectrum becomes diffuse below 195 nm. A possible, although not unique, interpretation of this onset of diffuse character is that there is a shallow minimum (ca. 0.15 eV) in the CO coordinate above which dissociation occurs. One consequence of this interpretation is that there may be a narrow excitation region in which some ethers fluoresce.

As for the other possible adiabatic processes in n,3s singlet methanol, we argued above that CH rupture will be endoergic by 2.3 eV. However, both 1,1- and 1,2-$H_2$ eliminations will be exoergic from the n,3s singlet state and will adiabatically yield $H_2$ + CHOH ($1^1A''$ excited hydroxycarbene) and $H_2 + CH_2{=}O^*$ ($1^1A_2$), respectively.[33-35] This latter excited state surface was partially optimized by varying only the H–H and O–H bonds while keeping the CO and HH bonds planar and nearly parallel. This approximate procedure yields an excited state A″ barrier (Figure 5) of about 1 eV. The 1,1-$H_2$ elimination was only fully optimized at the correlatively equivalent UHF (4-31G + 3s) triplet level. An A″, n,3s, excited state barrier of 2.7 eV was found. We anticipate a similar value for the singlet excited surface. These $H_2$ elimination surfaces both showed de-Rydbergizations at the MO level in which the 3s orbital evolved and became valence as the $H_2$ unit departs. However, these de-Rydbergizations occur only in the region of the excited-state barriers, whereas along the CO and OH bond rupture surfaces this process begins immediately on bond elongation. At the vertical excitation geometry the n,3s singlet state of methanol is almost completely Rydberg (95%) but less so for the triplet (75%). The evolution of the 3s MO is as follows for the various processes: (i) CO rupture, 3s → $sp^n$ on $CH_3$; (ii) OH, 3s → 1sH; (iii) 1,1-$H_2$, 3s → $\sigma$ (sp nonbonding MO on C of CHOH); and (iv) 1,2-$H_2$, 3s → $\pi^*$ (on $CH_2{=}O$). These are for $C_s$ symmetry retaining pathways.

The calculations on excited methanol are fairly definitive in predicting direct photodissociation of the n,3s singlet and triplet states by OH bond rupture. However, CO rupture is also an energetically easy pathway. Adiabatic elimination to give $H_2 + CH_2{=}O^*$ has a fairly low computed barrier (1 eV). Given the primitive level at which this elimination was treated it is possible

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(59) Larrieu, C.; Dargelos, A.; Chaillet, M.; Monflih, B. *Nouv. J. Chim.* **1981**, *5*, 365–370.

(60) (a) Yarkony, D. R.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1974**, *96*, 656–659. (b) Chu, S. I.; Yoshimini, M.; Lui, B. *J. Chem. Phys.* **1974**, *61*, 5389–5395.

that a much lower value could be computed. Therefore, both OH rupture and 1,2-$H_2$ elimination could be competitive events from the n,3s singlet state of methanol. However, the electronically adiabatic CH rupture and 1,1-$H_2$ elimination should occur only at much higher than UV threshold excitations. The relationship between the theoretical observations and the already discussed confused state of the experimental work[4] cannot be fully established. We find that the repulsive natures of the OH surfaces in both the n,3s singlet and triplet states eliminate these states as being metastable in character. The IR multiphoton photochemistry of methanol[31] shows either CO rupture or $H_2$ elimination, whereas the UV photochemistry shows mainly OH rupture. Therefore, vibrationally hot ground state methanol cannot fully serve as a possible intermediate in the UV photochemistry except as generated by $CH_3O + H$ recombination. Therefore, a reinvestigation of the experimental UV photochemistry of methanol is necessary to better establish if in fact a metastable species exists.

**C. Final Comments.** We only discussed the possibility of CN and NH bond ruptures in the case of methylamine photochemistry. By analogy with the above calculations on methanol and ammonia[40a] one anticipates several other processes.[4] As in the case of methanol, we anticipate adiabatic CH rupture to be endoergic from the n,3s state, giving a Rydberg excited radical fragment, $CH_2NH_2^*$. Likewise, we anticipate $H_2$[4,40a] eliminations to give $CH_3N$, $CHNH_2$, $CH_2{=}NH$ to be high barrier transformations from the n,3s singlet or triplet states, which are lower in energy than in methanol with regard to product states. These processes will adiabatically occur at higher excitation energies. The fact that methylamine photochemistry only displays NH rupture in the UV absorption threshold region is, therefore, easily rationalized as a process occurring directly from the electronically excited state. Likewise, the threshold stability of excited trialkylamines is easily rationalized on the basis of our computations. However, the recently observed lack of kinetic energy in the fragments obtained in the photochemistry of trimethylamine[22] at much higher than threshold excitations indicates that the reacting species is the vibrationally hot ground state. Therefore, whereas we anticipate a direct, high barrier, excited state CN bond rupture in trialkylamines, other nonradiative processes may be intervening to take the system to the vibrationally excited ground state before the CN exit channel is achieved. These observations lead us to caution the reader to use the theoretical analysis presented here in the following manner. In the case of NH or OH bond ruptures in n,3s excited amines and alcohols, the barriers are low or do not exist. In this case the excited state reactions should be either direct or predissociative. The CO excited state ruptures in alkyl and alicyclic ethers may be similar. But for those other processes which have high barriers, the calculations should only be taken as indications that difficulties are encountered along these pathways and that other nonradiative processes could occur which could lead the system in the same direction.

**Registry No.** Methanol, 67-56-1; methylamine, 74-89-5; ammonia, 7664-41-7.

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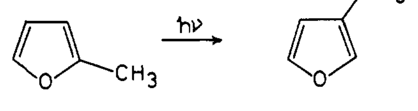
# A Theoretical Study on the Photochemical Transposition Reaction of Oxazole

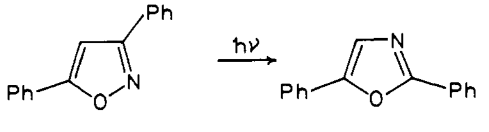
**Hidetsugu Tanaka, Toshio Matsushita, and Kichisuke Nishimoto***

*Contribution from the Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan.* *Received July 19, 1982*

**Abstract:** The photochemical transposition reaction of oxazole (interchange of positions 2 and 3, 4 and 5, 2 and 4, or 3 and 5) is investigated by ab initio MO-CI calculation. The present calculation shows that a 1-azirine intermediate in the $S_1$ state is formed from the lowest $^1(n \rightarrow \pi^*)$ state of oxazole with the out-of-plane distortion. Then, the intersystem crossing (ISC) to the $T_1$ state gives rise to the interchange of positions 2 and 3 to yield isoxazole. On the other hand, the lowest $^1(\pi \rightarrow \pi^*)$ state of oxazole brings about two types of transpositions, i.e., the 4,5 transposition and the 2,4 and 3,5 transpositions. Positions 4 and 5 are interchanged via a 2-azirine intermediate when the out-of-plane distortion at this state and the internal conversion to the $S_1$ state occur. On the other hand, the 2,4 or 3,5 transposition is caused by the sigmatropic shift of an oxygen atom when a bicyclic intermediate is formed with the disrotatory ring closure and subsequent ISC to the $T_1$ state.

Considerable attention has been focused in recent years on the photochemistry of five-membered heterocyclic ring systems.[1] Most of them have been related to the isomerization reactions that result in an interchange of ring atoms.[2] For instance, it is well-known that irradiation of furans[3] or isoxazoles[4,5] causes the interchange of positions of adjacent ring atoms. These photoisomerizations can be interpreted by the reaction course via the three-membered-ring intermediate formation (ring contraction–ring expansion mechanism).[2]





In a previous paper, we succeeded in elucidating the reaction mechanism of photochemical rearrangement of isoxazoles to oxazoles and explained the wavelength-dependent photochemistry of the 1-azirine intermediates by ab initio MO-CI calculation.[5]

Oxazoles, being the products in photochemical rearrangement of isoxazoles, also undergo the molecular reorganization under the influence of UV–visible light. For example, irradiation of 2,5-diphenyloxazole (**1b**) in ethanol gave 4,5-diphenyloxazole (**9b**, transposition of atoms 2 and 4) and 3,5-diphenylisoxazole (**3b**, transposition of atoms 2 and 3). When **1b** was irradiated in

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(1) Lablache-Combier, A. "Photochemistry of Heterocyclic Compounds"; Bachardt, O., Ed.; Wiley: New York, 1976: p 123.

(2) Padwa, A. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.

(3) Hiraoka, H.; Srinivasan, R. *J. Am. Chem. Soc.* **1968**, *90*, 2720. Hiraoka, H. *J. Phys. Chem.* **1970**, *74*, 574.

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(5) Tanaka, H.; Osamura, Y.; Matsushita, T.; Nishimoto, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1293.

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