

KEYNOTE LECTURE

Structural and Energetic Consequences of Single and Double Ionization

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INTRODUCTION

The study of gas-phase ions represents a challenging target for experimental chemists. The challenge has been widely accepted and has given rise to continuing advances in sophisticated experimental techniques, yielding much valuable information about gas-phase ions. It remains true, nevertheless, that the detailed experimental characterization of gas-phase ions is not straightforward. Theory, on the other hand, can be applied as readily to reactive species (such as gas-phase ions) as to normal, stable molecules. It therefore has a potentially useful role to play in this area.

In this presentation, we describe, with the aid of examples taken from our recent work, the use of theory in studying the chemistry of gas-phase ions. In particular, we examine the striking structural and energetic consequences of single and double ionization in some simple molecules.

METHOD

Standard ab initio molecular orbital theory (Hehre et al., 1986) has been used. Ab initio calculations may be performed at a number of different levels and the quality of a particular calculation depends on the size of the basis set and on the extent of incorporation of electron correlation. There is thus a hierarchy of levels of ab initio theory which might be used. Choosing a suitable level of theory necessarily involves a compromise between accuracy and economy: the better calculations are computationally more expensive. How best to strike the compromise is assisted by taking advantage of past experience (e.g. Hehre et al., 1986), by testing against experiment for the particular problem at hand, or by examining the convergence behaviour of the calculated results with increasing level of theory. Examples, particularly for the last approach, are presented below.

The ab initio calculations can yield detailed information related to structures and stabilities including equilibrium structures, transition structures,

vibrational frequencies, reaction barriers and isomerization energies. The calculations can also yield information relating to ionization phenomena: e.g. ionization energies, appearance energies, and neutralization energies.

METHANE (CH_4) AND ITS MONOCATION ($\text{CH}_4^{\cdot+}$) AND DICATION (CH_4^{2+})

The first example which we shall discuss concerns methane (1) and its monocation (2) and dication (3). Methane, of course, holds a central position in organic stereochemistry. Its tetrahedral (T_d , Figure 1) structure was established more than a century ago.

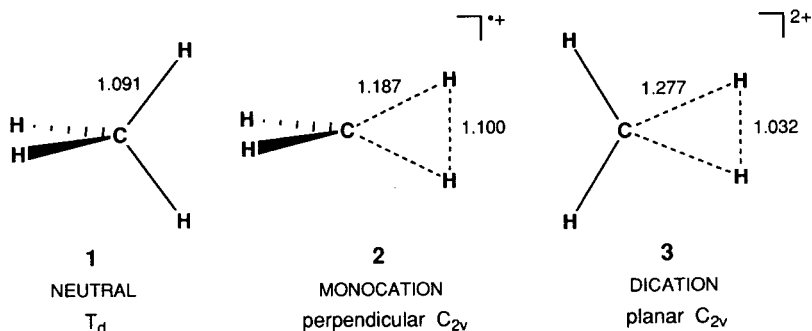
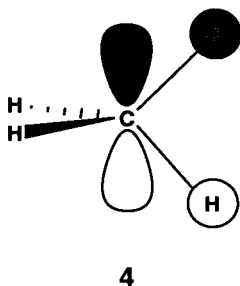


Figure 1. Optimized (MP3/6-311G**) structures for methane and its mono- and dications.

Removal of an electron from one of the t_2 orbitals (4) of methane leads to reduction of bonding electron density in one pair of C-H bonds and to a decreased antibonding interaction between the associated hydrogen atoms:



As a consequence, the methane radical cation has a pair of lengthened C-H bonds (1.187 Å), a relatively short H---H bond (1.100 Å) and a preferred perpendicular C_{2v} structure (2, Figure 1) (see also Bouma et al., 1983 and references therein; Paddon-Row et al., 1985).

Removal of a second electron from methane leads to the methane dication (CH_4^{2+}). This species created excitement several years ago when *ab initio* calculations indicated a preferred square-planar (D_{4h}) structure. It was remarked (Pople *et al.*, 1982) that " CH_4^{2+} (D_{4h}) represents the simplest molecule possessing a planar, tetracoordinate carbon atom".

In a very recent study (Wong and Radom, 1989), we have found, with much higher levels of theory than used previously, that the methane dication is planar but not square. The preferred structure is actually planar C_{2v} (3, Figure 1). It resembles a donor-acceptor complex between the methylene dication (CH_2^{2+}) and molecular hydrogen.

Calculated relative energies of the planar C_{2v} and D_{4h} structures are listed in Table 1. At the simplest level of theory shown (MP2/6-31G*), the D_{4h} structure is lower in energy by 6 kJ mol⁻¹. However, at higher levels of theory, the planar C_{2v} structure is consistently favored by 13 kJ mol⁻¹. After incorporation of a zero-point vibrational correction of 9 kJ mol⁻¹, our best estimate is that the planar C_{2v} structure is favored over the D_{4h} form by 4 kJ mol⁻¹.

TABLE 1. Calculated Relative Energies (kJ mol⁻¹) of Planar C_{2v} and Planar D_{4h} Structures of CH_4^{2+a}

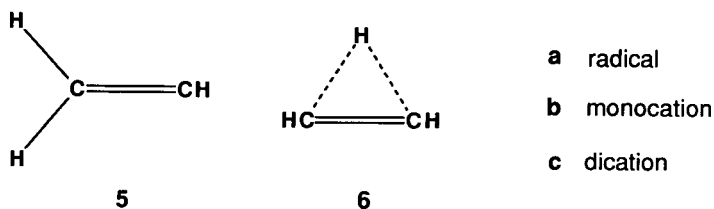
	Planar C_{2v}	Planar D_{4h}
MP2/6-31G*	0	-6
MP2/6-31G**	0	13
MP2/6-311G**	0	15
MP2/6-311 + G(2df,2p)	0	12
MP3/6-311 + G(2df,2p)	0	13
MP4/6-311 + G(2df,2p)	0	13
ST4CCD/6-311 + G(2df,2p)	0	13

^a From Wong and Radom, 1989.

THE VINYL SYSTEM (CH_2CH): OPEN OR BRIDGED?

A question of continuing interest for the vinyl system (radical, cation or dication) is whether the preferred structure is open (5) or bridged (6).

The vinyl radical was found some time ago to prefer an open structure (5a) over a bridged structure (6a) (Harding, 1981). We have confirmed this result and find an energy difference in favor of 5a over 6a of 181 kJ mol⁻¹ (MP4/6-311G(2df,2p)//MP3/6-31G** plus zero-point vibrational correction; this level of theory is also used for the monocation and dication below).



The vinyl cation has been the subject of a remarkable degree of recent theoretical and experimental interest (Wong and Radom, 1988 and references therein). The best theoretical calculations to date (Lindh et al., 1987; Curtiss and Pople, 1988) find that the bridged structure (6b) of the vinyl cation is preferred over the open form (6a) by about 15 kJ mol⁻¹ and that there is little or no barrier separating the open and bridged structures. We find an energy difference of 21 kJ mol⁻¹ in favor of 6b. Experimentally, the vinyl cation was one of the first species to be investigated by the Coulomb explosion technique and was found in such studies to have the bridged structure (Kanter et al., 1986).

Given the preferred open structure (5a) for the vinyl radical and the preferred bridged structure (6b) for the vinyl cation, it is of interest to examine whether the vinyl dication has an open or bridged structure. Our calculations indicate, in fact, a preference for the open structure (5c), with a barrier to 1,2-hydrogen migration via the bridged form (6c) of 16 kJ mol⁻¹ (Wong and Radom, 1988).

The preferred structures for the vinyl radical, monocation and dication are summarized in Figure 2: open for the radical (5a), bridged for the monocation (6b) and open for the dication (5c).

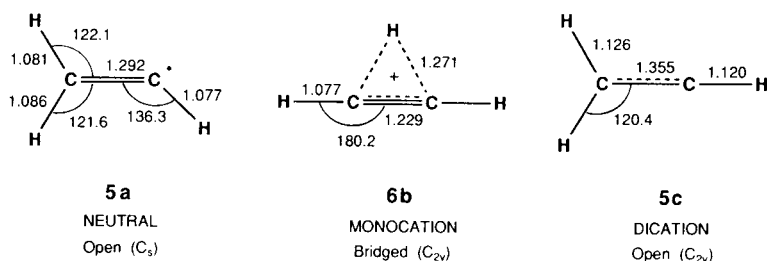


Figure 2. Optimized structures (MP3/6-31G**) of the vinyl radical, monocation and dication.

The results for the vinyl system exactly parallel those for ethyl (C_2H_5) (Wong *et al.*, 1987, and references therein): a preferred open structure for the ethyl radical, a bridged structure for the monocation and an open structure for the dication.

YLIDES, YLIDIONS AND YLIDE DICATIONS

Ylides (e.g. $\bar{C}H_2\overset{+}{O}H_2$, $\bar{C}H_2\overset{+}{S}H_2$) may be considered to be zwitterions in which the positive and negative charges are located on adjacent atoms. The simplest ylides are isomeric with very familiar molecules such as CH_3OH and CH_3SH . Calculated relative energies for a selection of prototype ylides and their conventional isomers are shown in Table 2 (Yates *et al.*, 1987, and references therein). It is clear that the ylides are much less stable than their isomers. In many cases, the ylides correspond to weak complexes, e.g. $\bar{C}H_2\overset{+}{O}H_2$ resembles a weak complex of methylene and water, and there is little or no barrier to their rearrangement or dissociation.

TABLE 2. Calculated Relative Energies (kJ mol^{-1}) of Ylides and Their Conventional Isomers^a

Conventional	Ylide	ΔE^b
CH_3F	$\bar{C}H_2\overset{+}{F}H$	(378)
CH_3OH	$\bar{C}H_2\overset{+}{O}H_2$	(351)
CH_3NH_2	$\bar{C}H_2\overset{+}{N}H_3$	277
CH_3Cl	$\bar{C}H_2\overset{+}{Cl}H$	(427)
CH_3SH	$\bar{C}H_2\overset{+}{S}H_2$	309
CH_3PH_2	$\bar{C}H_2\overset{+}{P}H_3$	220

^a MP4/6-311G(df,p)//MP2/6-31G* values with zero point vibrational correction. From Yates *et al.*, 1987.

^b $\Delta E = E(\text{ylide}) - E(\text{conventional})$. Values in parentheses correspond to systems where our calculations suggest that the ylide is at best of only marginal stability.

Species corresponding formally to ionized ylides (e.g. $\bar{C}H_2\overset{+}{O}H_2$) are called ylidions. Because of the instability of their ylide parents, ylidions are normally generated via rearrangement-fragmentation reactions (see, for example, Schwarz, 1984, and references therein; Bouma *et al.*, 1982; Holmes *et al.* 1982). They represent particular examples of species which we have termed distonic radical cations in which the charge and radical sites are formally separated (Yates *et al.*, 1984). In notation recently introduced by Hammerum, ylidions may usefully be referred to as α -distonic radical cations (Hammerum, 1988).

Calculated relative energies of ylidions and their conventional isomers are shown in Table 3 (Yates et al., 1987). For the first-row systems, the ylidions are actually more stable than their conventional isomers. For example, the methyleneoxonium radical cation ($\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{H}_2^+$) lies lower in energy than methanol radical cation ($\text{CH}_3\text{OH}^{\cdot+}$) by 46 kJ mol⁻¹. The ylidions and their isomers are generally not widely separated in energy (Table 3) and the barriers for their interconversion are found to be reasonably large (e.g. 108 kJ mol⁻¹ for $\text{CH}_3\text{OH}^{\cdot+} \rightarrow \dot{\text{C}}\text{H}_2\dot{\text{O}}\text{H}_2^+$) (Yates et al., 1987). As a result, the ylidions and their conventional isomers are often individually observable.

TABLE 3. Calculated Relative Energies (kJ mol⁻¹) of Ylidions and Their Conventional Isomers^a

Conventional	Ylidion	ΔE
$\text{CH}_3\text{F}^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{F}}\text{H}$	-14
$\text{CH}_3\text{OH}^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{H}_2^+$	-46
$\text{CH}_3\text{NH}_2^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{H}_2^+$	-8
$\text{CH}_3\text{Cl}^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{C}}\text{H}$	38
$\text{CH}_3\text{SH}^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{S}}\text{H}_2$	85
$\text{CH}_3\text{PH}_2^{\cdot+}$	$\dot{\text{C}}\text{H}_2\dot{\text{P}}\text{H}_3$	51

^a MP4/6-311G(df,p)//MP2/6-31G* values with zero-point vibrational correction. From Yates et al., 1987.

^b $\Delta E = E(\text{ylidion}) - E(\text{conventional})$.

TABLE 4. Stabilities of Ylide Dications and Their Conventional Isomers^a

Conventional		Ylide Dication	
CH_3F^{2+}	unstable	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{F}}\text{H}$	stable
$\text{CH}_3\text{OH}^{2+}$	unstable	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{O}}\text{H}_2$	stable
$\text{CH}_3\text{NH}_2^{2+}$	unstable	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{N}}\text{H}_3$	stable
$\text{CH}_3\text{Cl}^{2+}$	unstable	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{C}}\text{H}$	stable
$\text{CH}_3\text{SH}^{2+}$	marginal stability	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{S}}\text{H}_2$	stable
$\text{CH}_3\text{PH}_2^{2+}$	marginal stability	$\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{P}}\text{H}_3$	stable

^a From Yates et al., 1986.

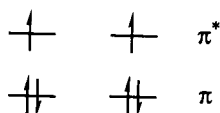
What is the effect of further ionization? For example, how does the energy of the methanol dication ($\text{CH}_3\text{OH}^{2+}$) compare with that of methyleneoxonium dication ($\overset{+}{\text{C}}\text{H}_2\overset{+}{\text{O}}\text{H}_2$)? Our theoretical results (Yates et al., 1986) are

shown in Table 4. The ylide dications are uniformly more stable than their conventional isomers. Indeed, the conventional dications are at best only of marginal stability.

It is useful to summarize by recapping the situation for the $\text{CH}_3\text{OH}/\text{CH}_2\text{OH}_2$ system. For the neutrals, the conventional isomer is substantially more stable than the ylide, the latter corresponding to just a weak complex. Single ionization reverses the stability ordering: the methyleneoxonium radical cation lies lower in energy than methanol radical cation, but both are reasonably stable and observable. Finally, a second ionization leads to a particularly stable ylide dication ($\overset{\oplus}{\text{C}}\text{H}_2\overset{\oplus}{\text{O}}\text{H}_2$). The methanol dication ($\text{CH}_3\text{OH}^{2+}$), on the other hand, is not stable.

O_2 AND ITS IONIZED FORMS

Molecular oxygen has a triplet electronic ground state in which there is single occupancy of a pair of antibonding π^* orbitals (7):



7

It might be expected that ionization, or electron removal (from the antibonding orbitals), will be favorable.

Calculated bond lengths for O_2 , $\text{O}_2^{\cdot+}$ and O_2^{2+} are shown in Table 5 (Wong *et al.*, 1989). Ionization is indeed seen to be accompanied by significant bond shortening, with calculated r_e values falling from 1.204 Å for O_2 to 1.115 Å for $\text{O}_2^{\cdot+}$ to 1.046 Å for O_2^{2+} . The O_2^{2+} bond length (1.046 Å) may well be the shortest of any bond between heavy atoms.

TABLE 5. Bond Lengths (r_e , Å) for O_2 and Its Ionized Forms

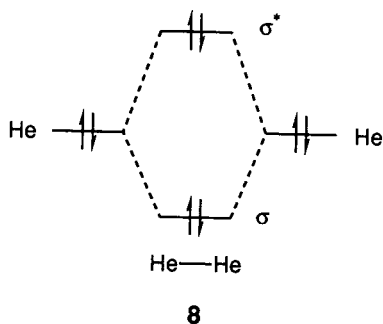
	Calc. ^a	Expt.
O_2	1.204	1.208
$\text{O}_2^{\cdot+}$	1.115	1.116
O_2^{2+}	1.046	-

^a Empirically corrected ST4CCD/6-311+G(2df) values from Wong *et al.*, 1989.

DIMERS OF INERT-GAS ATOMS AND OF SIMPLE HYDRIDES, AND THEIR IONIZED FORMS

The final set of examples which we wish to present concerns dimers formed from inert-gas atoms or from simple hydrides such as ammonia, and the effect of ionization on such species.

The interaction of two helium atoms involves four electrons occupying σ and σ^* orbitals and is well-known to be destabilizing (8):



The ground state potential function is purely repulsive. The same situation (i.e. a purely repulsive interaction) holds for a dimer of two ammonia molecules connected via the nitrogen atoms ($\text{H}_3\text{N} : \text{NH}_3$). Examination of the orbital picture immediately suggests, however, that ionization will be favorable in such cases.

Single ionization leads to a three-electron hemi-bond, as found in systems such as $\text{He}-\text{He}^{\cdot+}$ and $\text{H}_3\text{N}-\text{NH}_3^{\cdot+}$. The lengths and strengths of a variety of hemi-bonds are shown in Table 6 (Gill and Radom, 1988, and references therein; see also Clark, 1988). The bonds are as much as 50% longer than normal single bonds but are remarkably strong. More than 100 kJ mol^{-1} are required to break even the weakest bonds studied. Most of these hemi-bonded systems should be experimentally observable in the gas phase, particularly if (through appropriate substitution) rearrangement to hydrogen-bonded isomers (e.g. $\text{H}_3\text{N}-\text{H} \cdots \text{NH}_2^{\cdot+}$) is precluded. Hemi-bonded systems have indeed been observed in solution, solid and matrix phases by Alder, Asmus, Glass, Musker, Symons and others (see, Gill and Radom, 1988, for an extensive bibliography). An analogue of $\text{H}_2\text{S} \cdots \text{SH}_2^{\cdot+}$ has recently been observed in the gas phase (Drewello et al., 1987).

Double ionization removes both antibonding electrons in 8 and leads to a two-electron single bond, as found in systems such as $\text{He}-\text{He}^{2+}$ and $\text{H}_3\text{N}-\text{NH}_3^{2+}$. We note in passing that the $\text{N}_2\text{H}_6^{2+}$ dication forms stable,

crystalline salts with an N-N length of 1.41-1.44 Å. The He_2^{2+} dication has recently been observed in the gas phase (Guilhaus *et al.*, 1984).

TABLE 6. Calculated Hemi-Bond Lengths^{a,b} (r_e , Å) and Hemi-Bond Strengths^{a,c} (D_o , kJ mol⁻¹)

	r_e	D_o
He---He ⁺	1.151	209
H ₃ N---NH ₃ ⁺	2.151	138
H ₂ O---OH ₂ ⁺	2.023	159
HF---FH ⁺	1.843	158
Ne---Ne ⁺	1.717	122
H ₃ P---PH ₃ ⁺	2.700	103
H ₂ S---SH ₂ ⁺	2.835	111
HCl---ClH ⁺	2.642	115
Ar---Ar ⁺	2.519	101

^a From Gill and Radom, 1988.

^b MP2/6-31G*.

^c MP4/6-311G(MC)(d,p).

Fragmentation of the dimer dications to two monocations is highly exothermic (e.g. by 234 kJ mol⁻¹ in the case of H₃N-NH₃²⁺) but is impeded by substantial barriers (e.g. 168 kJ mol⁻¹ for H₃N-NH₃²⁺). Despite the exothermicity of the fragmentation reactions, the calculated bond lengths in the dimer dications (Table 7, Gill and Radom 1989) are very short in some cases. Indeed, He₂²⁺ has the shortest known bond length: 0.703 Å from very high level calculations (Yagisawa *et al.*, 1977).

TABLE 7. Calculated Bond Lengths (r_e , Å) for Dimer Dications^a

He—He ²⁺	0.685		
H ₃ N—NH ₃ ²⁺	1.465	H ₃ P—PH ₃ ²⁺	2.226
H ₂ O—OH ₂ ²⁺	1.465	H ₂ S—SH ₂ ²⁺	2.187
HF—FH ²⁺	1.514	HCl—ClH ²⁺	2.076
Ne—Ne ²⁺		Ar—Ar ²⁺	2.076

^a MP2/6-31G* values from Gill and Radom, 1989.

A molecular orbital scheme summarizing the effect of ionization in these dimer systems is displayed in Figure 3 and shows how successive ionization reduces the antibonding contribution.

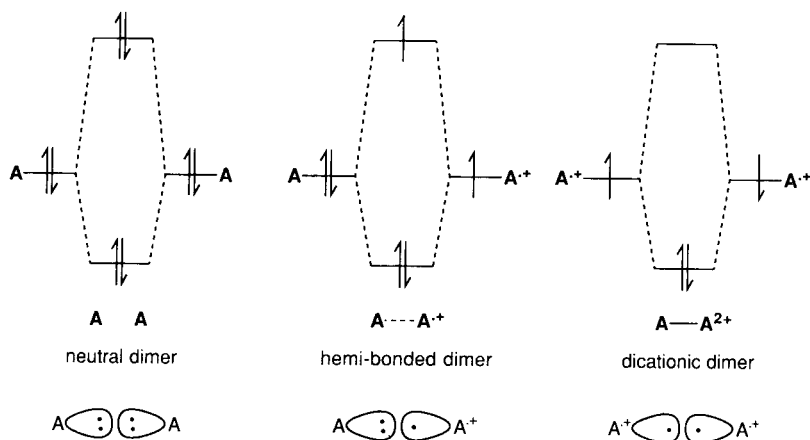
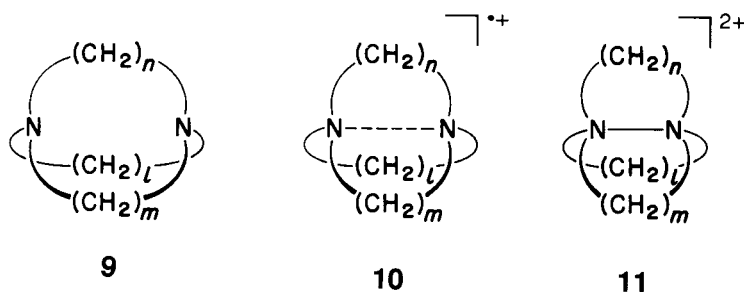


Figure 3. Effect of successive ionization in dimers A-A.

The dimer systems which we have examined could be considered as models for medium-ring bicyclic compounds (9-11) studied extensively by Alder and coworkers (e.g. Alder et al., 1985, and references therein). Our original estimates of the N-N bond lengths for $NH_3-NH_3^+$ and $NH_3-NH_3^{2+}$ of 2.164 and 1.442 Å, respectively (Bouma and Radom, 1985) are consistent with subsequently determined x-ray crystallographic values of 2.30 Å and 1.53 Å for systems of the type 10 and 11 (Alder et al., 1985). Our most recent values are 2.151 and 1.465 Å, respectively (Gill and Radom, 1988; Gill and Radom, 1989).



CONCLUSIONS

The main general points to emerge from this presentation are:

- (1) single ionization and (particularly) double ionization can lead to striking changes in molecular structure and stability; and
- (2) theory provides a useful technique for examining such effects.

ACKNOWLEDGEMENTS

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