TABLE III: Relative Concentrations of Ethanes and Ethylenes in CH₄/CD₄ Experiment (FTIR Measurements)

|	calcd[a]	obsd		calcd[a]	obsd
C_2H_6	34 ± 2	36 ± 4	C_2H_4	34 ± 2	34 ± 2
CD_3CH_3	49 ± 2	(49)[b]	CD_2CH_2	49 ± 2	(51)[b]
C_2D_6	17 ± 2	15 ± 2	C_2D_4	17 ± 2	15 ± 2

[a] For $k_H/k_D = 1.4 \pm 0.1$. [b] By difference.

other ethane and CD_2CH_2 is, the only other ethylene, the contribution of these species may be determined by difference. Table III presents these results together with calculated values based on the kinetic isotope effect ($k_H/k_D = 1.4 \pm 0.1$) and a statistical distribution since the mixed species are more likely than the symmetrical ones. The uncertainty in the magnitude of the kinetic isotope effect is due to the small difference in the results obtained with CH_4 alone. The experimental results are in excellent agreement with the calculations and show that exchange of H and D in the product hydrocarbons is insignificant and that the product distribution reflects the relative concentrations of CH_3 and CD_3.

The results may therefore be interpreted as confirmatory evidence for the coupling of methyl radicals in this catalytic system. However, the absence of any significant hydrogen exchange between CH_4 and CD_4 and also between the product C_2 hydrocarbons is surprising since MgO exhibits activity for CH_4/D_2 exchange at 300 °C[16] and activity for CH_4/CD_4 exchange at 400 °C.[17] It is therefore likely that the methyl coupling reaction occurs almost exclusively in the gas phase. This is in agreement with Lunsford's conclusion[10] that at least 40–45% of the C_2 products were accounted for by gas-phase methyl coupling. The results also suggest that ethane is the source of the ethylene since the distribution of the deuteriated ethylenes is not significantly different from that of the ethanes. It is possible that conversion of ethane to ethylene also occurs predominantly in the gas phase since

the gas-phase abstraction reaction to form an ethyl radical and further reaction of the ethyl to produce ethylene will preserve the isotopic distribution, and this mechanism has been well-established for hydrocarbon combustion reactions.[18] However, the participation of the surface in the ethane-to-ethylene conversion cannot be discounted.

Data for methyl radical concentrations obtained by Lunsford and co-workers[9,10] and the overall rate constant[19,20] for the gas-phase exchange reactions

$$CH_4 + CD_3 \rightarrow CH_3 + CD_3H$$

$$CD_4 + CH_3 \rightarrow CD_3 + CH_3D$$
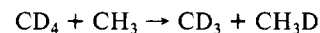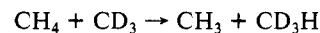
suggest that these reactions could make a significant contribution to the small amount of exchange observed in the methanes. However, in the absence of a direct measurement of the methyl concentration under the conditions of the present experiment, it is not possible to evaluate the contribution of these reactions exactly.

The results also show that the participation of carbene or methylene radicals in this system is probably not significant since the reactions postulated[11] to produce ethane

$$CH_2 + CH_4 \rightarrow CH_3 + CH_3$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$
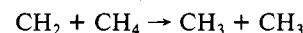
would lead to exchange in the ethanes.

These observations obviously have considerable implications for the development of a practical methane conversion process, particularly for the optimization of ethylene yields.

(16) Utiyama, M.; Hattari, H.; Tanabe, K. *J. Catal.* **1978,** *53,* 237.
(17) Quanzhi, L.; Amenomiya, Y. *Appl. Catal.* **1986,** *23,* 172.

(18) Warnatz, J. *Ber. Bunsen-Ges. Phys. Chem.* **1983,** *87,* 1008.
(19) Burcat, A.; Lifshitz, A. *J. Chem. Phys.* **1970,** *52,* 3613.
(20) Chen, C.-J.; Back, M. H.; Back, R. A. *Can. J. Chem.* **1977,** *55,* 1624.

"Double-Rydberg" Molecular Anions

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We present results of ab initio electronic structure simulations which predict the electronic stability of molecular anions each consisting of a closed-shell cation core with two "Rydberg-like" outer electrons. Earlier experimental work by the Bowen group and theoretical calculations of Cardy et al. and of Ortiz on NH_4^- suggested that such species might exist. Our calculations on H_3^-, $H_3CH_2^-$, NH_4^-, H_3O^-, H_2F^-, and NeH^- indicate that, except for H_3^-, all of these species are electronically stable at geometries near those of the corresponding cation "cores". For all of these species, there also may exist long-lived metastable states whose decay to underlying neutral-molecule states requires the ejection of one electron and the "shake down" rearrangement of a second orbital. The symmetries, electronic energies, and local geometrical stabilities of the above species have been examined and are discussed here.

Introduction

In 1987, the Bowen group[1] at Johns Hopkins University reported observations which lead them to suggest that NH_4^- may exist as a stable or long-lived species in a tetrahedral structure resembling the NH_4^+ cation with two diffuse electrons "orbiting" the cation core. The weak electron binding energy (ca. 0.5 eV) combined with the sharp peak observed in the photoelectron

spectrum supported their conjecture.[2] Ab initio calculations[3] by Cardy et al. and by Ortiz gave further support to this novel

(1) In 1985, the Bowen group reported photoelectron data on NH_4^- in its normal form (e.g., as solvated H^-): Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1985,** *83,* 3169. At the Fall, 1987 American Chemical Society meeting in New Orleans, Bowen reported on this same species and noted a weak peak corresponding to a NH_4^- species with an electron binding energy near 0.5 eV. Details of this report are available in the Ph.D. thesis of J. T. Snodgrass, The John Hopkins University, 1987, and in an article by K. H. Bowen and J. G. Eaton in Proceedings of the International Workshop on the Structure of Small Molecules and Ions (to be published).

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structure of NH_4^-. They found NH_4^- to exist both as a stable H^-H_3N ion–molecule complex and as a tetrahedral species whose geometry is very similar to that of NH_4^+. Ortiz found the tetrahedral form of the $^1A_1$ anion to be electronically stable[6] with respect to the $^2A_1$ neutral NH_4 by 0.42 eV, and to possess all positive local harmonic frequencies.[4]

Following these exciting observations and predictions concerning NH_4^-, we undertook the task of searching for analogous "double-Rydberg" (DR) structures in H_3^-, $H_3CH_2^-$, H_3O^-, H_2F^-, and NeH^-, some of which also exist[5] as stable ion–molecule complexes analogous to H^-H_3N and some of which probably do not. In this Letter, we report the first predictions that several of these anions can support DR states which are *electronically* stable[6] with respect to corresponding neutrals and which correspond to potentially stable[4] local minima on their energy hypersurfaces. We suggest that these species also possess states which are electronically metastable with lifetimes which may be long enough to permit experimental observation. Neither the stable nor metastable DR states represent *global* minima for any of these anions; the "solvated" H^- complex is lower in energy for all of them. Moreover, for all of the neutral species, it is energetically favorable to dissociate to H plus the corresponding "solvent" molecule. Nevertheless, the DR species predicted here represent new species which may be sufficiently long lived to be amenable to clever experimental detection and which display unusual electronic structures as detailed below.

A. Orbital Basis Sets. In each of the studies whose results we present here, we carried out ab initio electronic structure calculations using at least double ζ + polarization (DZP) contracted Gaussian basis sets to represent the underlying "cation core" plus seven sets of diffuse s- and p-type Gaussian functions to treat the one or two "extra" electrons which arise in the neutral and anion species. The diffuse basis, located at the molecule center except for H_2F^- and NeH^- where it is located on the heavy atom, was constructed to reproduce the energies of the low-lying S and P states of H and of the H^- ion as well as to contain even more diffuse and more contracted functions. In fact, these s- and p-type diffuse functions very accurately reproduced the ns and np orbital energies of the H atom for $n = 1, 2, ..., 5$; they also reproduced, within 0.1 eV, the experimentally observed spacings of the lowest four ^2S and ^2P states of Li and Na, whose cations represent the spherical limit for the cations of our H_3^- and $H_3CH_2^-$, NH_4^-, H_3O^-, H_2F^-, and NeH^- systems, as well as the electron affinities of Li, H, and Na to within 0.03 eV. The same set of seven diffuse s- and p-functions were used for all of the anions studied; of course, the "core" of each cation was described with a basis of its own. Because our diffuse basis included only s- and p-type functions, we are not presently able to make predictions about DR states of any of the anions or neutrals which arise from d or higher angular momenta.

B. Neutral Molecule States. After optimizing the geometry of the closed-shell cation core at the single-configuration SCF level

or using cation geometries available from experiment or from other theoretical work, we estimated the energies of several low-lying states of the neutral species by adding to the cation's energy the energies of the lower lying virtual orbitals. As a result of carrying out correlated (configuration interaction) calculations on the neutral and cation species in which intracore and core–outer-electron correlations were included, we found this Koopmans' theorem treatment of the neutral to accurately reproduce the ion–neutral energy *differences*. Because the neutral's outer "active" electron resides in a diffuse orbital and because the cation cores are stable closed-shell species, we observed very little change in the neutral energies when we allowed for orbital relaxation and for correlation of the single "active" electron with the electrons of the cation core. The picture of the neutral as one active electron moving in the electrostatic field of the underlying cation therefore seems to be valid.[7]

C. Anion States. After thereby determining the energies of several low-lying states of the neutral species, we carried out configuration interaction (CI) calculations on the anions employing *all* configurations (of all space and spin symmetry) in which the two active electrons are placed in virtual orbitals of the cation and the electrons of the cation core occupy the orbitals found to be optimal in the above SCF cation optimization process. This amounts to treating correlation interactions between the anion's two active electrons in a full manner while treating the cation core at the SCF level; the outer two electrons thus "feel" only the electrostatic potential of the underlying cation. This treatment of the anion was, of course, tested by subsequently performing more extensive CI calculations in which correlations involving the cation core orbitals were included; the energy level patterns for the anions thus obtained were only slightly different than those obtained in our "frozen-cation-core" treatment in which correlations between only the two active electrons are included. In addition, relaxation of the core's orbitals both for the neutral and the anion was investigated and found to be unimportant when anion–neutral energy differences are considered. For example, for the lowest states of FH_2 and FH_2^-, we found relaxation of the underlying cation orbitals to lower the respective energies by 0.08 and 0.08 eV, thus leaving the anion–neutral energy difference unchanged! These observations provide further support for the physical picture of the DR anions in which two active electrons move in diffuse orbitals around an underlying cation core providing an electrostatic potential[8] which defines the symmetries and energy level pattern of the neutral and anion states.

All of the ab initio calculations were performed using our in-house Utah MESS KIT (molecular electronic structure kit) software modules[9] which treat SCF, MCSCF, and CI wave functions, as well as analytical energy derivatives (forces and force constants) and nonadiabatic couplings (wave function derivatives) among various electronic states.

Findings

For each of the cation–neutral–anion systems listed below, we give the total SCF electronic energy of the cation (in hartrees) as well as the energies of the lowest few states of the neutral and anion relative to the cation (in electron volts, with negative values

(2) The H^- anion has an electron binding energy of 0.75 eV; "solvated" H^- should have an even larger binding energy (in ref 1 this binding energy is given as 1.11 eV) because the anion is differentially stabilized relative to the neutral by the solvent. The fact that the DR anion is observed to have a smaller binding energy than that of H^- indicates that it is not simply a "solvated" H^-. The sharp peak in the photoelectron spectrum of NH_4^- indicates that there is not a great deal of geometry change accompanying the electron ejection; that is, the anion and neutral have similar geometries.

(3) Cardy, H.; Larrieu, C.; Dargelos, A. *Chem. Phys. Lett.* **1986**, *131*, 507. Ortiz, J. V. *J. Chem. Phys.* **1987**, *87*, 3557. Ortiz also quotes unpublished communication from the Bowen group concerning the peak in the photoelectron spectrum near 0.5 eV.

(4) The fact that the species possess all positive local harmonic frequencies indicates that it *may* be geometrically stable, if the zero-point energy does not exceed the barrier to rearrangement to the more energetically stable "solvated-H^-" structure, and if tunnelling through this barrier is slow.

(5) We have recently studied several H^--molecule complexes including H^-H_2O, H^-HF, H^-H_2, $H^-(H_2O)_2$, and $H^-(H_2)_2$. See, for example: *J. Phys. Chem.* **1987**, *91*, 6151; *J. Chem. Phys.* **1987**, *87*, 2965.

(6) By electronically stable we mean that the anion has a lower electronic energy than the neutral at the specific geometry where the calculation is performed. Either the anion or the neutral may be geometrically unstable at this point if rearrangement to another geometry is favored.

(7) It is not surprising that the underlying cation core can be thought of as providing an electrostatic potential for the outer electron and that correlation and exchange effects involving the outer electron are negligible. In effect, the underlying cation produces a quantum defect as well as symmetry-dependent crystal-field-like splittings of the orbitals (and hence states) of the one-active-electron neutral species. This same picture is developed and supported in the earlier work of: Raynor, S.; Herschbach, D. R. *J. Phys. Chem.* **1982**, *86*, 3592. King, H. F.; Morokuma, K. *J. Chem. Phys.* **1979**, *71*, 3213. Martin, R. L.; *J. Chem. Phys.* **1979**, *71*, 3541.

(8) It is somewhat surprising to us that the relative energies of the anions and neutrals can be obtained reasonably accurately within a model which neglects polarization of the underlying core by the outer electrons.

(9) The Utah MESS KIT software was written during 1986–88 primarily by R. A. Kendall, E. Earl, R. Hernandez, H. L. Taylor, D. O'Neal, and Drs. J. Nichols, and M. Hoffmann. The code is written in a highly modular format so that improvements in any module or additions of new modules which provide added functionality are facilitated. VAX VMS, Cray CTSS, SUN, and FPS versions are all available.

indicating stability). Only those neutral states which are electronically stable and those anion states which are either electronically stable or which are good candidates for long-lived metastable states are listed. Because our atomic orbital basis is capable of treating S- and P-states, we do not list any states whose character is dominated by D or higher angular momenta. The symmetries of the respective states are also given (for H_3O^+, we label the states with D_{3h} point group labels although this cation is not planar; because the degree of non planarity is slight, we believe it helps clarify the physical nature of the orbitals and states to use D_{3h} labels). For the neutral species, the symmetry of the state coincides with the symmetry of the outermost occupied orbital because the cation is a closed-shell ^1A species. For the anions, we also list the molecular orbital occupancies of the dominant electronic configurations for each of the states. For the anions, it is essential to stress that radial and angular electron correlations are very strong between the two active electrons. As a result, configurations other than the dominant one listed here must be considered to achieve a qualitatively correct picture of these states.

1. H_3^+; D_{3h} ($E = -1.2997$ hartrees), H_3 (-5.39 eV ($^2E'$), -3.69 ($^2A'_1$), -3.45 ($^2A''_2$), -1.93 ($^2E'$), -1.58 ($^2A'_1$), -1.53 ($^2A''_2$), -0.99 ($^2E'$), -0.88 ($^2A'_1$), -0.85 ($^2A''_2$)), H_3^- (-4.18 ($^1A'_1$; $2a'_1{}^2$)*, -3.97 ($^3A''_2$; $2a_11a''_2$)*, -2.00 ($^1A'_1$; $3a'_1{}^2$)*, -1.79 ($^3A''_2$; $3a'_12a''_2$)*, -1.00 ($^3A''_2$; $4a'_13a''_2$)*).

2. $H_3CH_2^+$; C_s ($E = -40.4189$), H_3CH_2 (-3.84 ($^2A'$), -2.86 ($^2A'$), -2.37 ($^2A'$), -2.37 ($^2A''$), -2.24 ($^2A'$), -1.66 ($^2A'$), -1.17 ($^2A'$), -1.16 ($^2A''$)), $H_3CH_2^-$ (-4.20 ($^1A_1$; $5a'^2$), -2.42 ($^3A''$; $7a'2a''$)*, -1.24 ($^3A''$; $10a'3a''$)*).

3. NH_4^+; T_d ($E = -56.5616$), NH_4 (-4.03 ($^2A_1$), -2.53 ($^2T_2$), -1.68 ($^2A_1$), -1.22 ($^2T_2$), -0.92 ($^2A_1$), -0.72 ($^2T_2$)), NH_4^- (-4.48 ($^1A_1$; $4a_1{}^2$), -2.55 ($^3T_1$; $2t_2{}^2$)*, -2.04 ($^1A_1$; $5a_1{}^2$)*, -1.30 ($^3T_1$; $3t_2{}^2$)*, -1.23 ($^1A_1$; $6a_1{}^2$)*, -0.76 ($^3T_1$; $4t_2{}^2$)*).

4. H_3O + ($E = -76.3399$), H_3O (-4.63 ($^2A_1$), -2.82 (^2E), -2.41 ($^2B_1$), -1.85 ($^2A_1$), -1.33 (^2E), -1.18 ($^2B_1$), -0.98 ($^2A_1$), -0.78 (^2E)), H_3O^- (-5.07 ($^1A_1$; $4a_1{}^2$), -2.83 ($^3A_2$; $2e^2$)*, -2.47 ($^1A_1$; $5a_1{}^2$)*, -1.47 ($^3A_2$; $3e^2$)*).

5. H_2F^+; C_{2v} ($E = -100.2587$), H_2F (-5.51 ($^2A_1$), -3.46 ($^2B_2$), -2.58 ($^2B_1$), -2.48 ($^2A_1$), -2.11 ($^2A_1$), -1.57 ($^2B_2$), -1.24 ($^2B_1$), -1.20 ($^2A_1$), -1.10 ($^2A_1$), -0.89 ($^2B_2$), -0.73 ($^2B_1$), -0.71 ($^2A_1$), -0.66 ($^2A_1$)), H_2F^- (-5.92 ($^1A_1$; $4a_1{}^2$), -2.64 ($^1A_1$; $6a_1{}^2$)*, -2.64 ($^3B_1$; $2b_16a_1$)*, -1.37 ($^3B_1$; $3b_18a_1$)*, -0.82 ($^3B_1$; $4b_110a_1$)*).

6. NeH^+; $C_{\infty v}$ ($E = -128.6195$), NeH (-7.02 ($^2A_1$), -2.95 ($^2A_1$), -2.73 (^2E), -2.36 ($^2A_1$), -1.38 ($^2A_1$), -1.29 (^2E), -1.16 ($^2A_1$)), NeH^- (-7.10 ($^1A_1$; $4a_15a_1$), -3.07 (^3E; $5a_12e$)*, -2.38 ($^1A_1$; $6a_19a_1$)*, -1.50 (^3E; $3e7a_1$)*).

7. H^+; H (-13.6 (^2S), -3.40 (^2S, ^2P), -1.51 (^2S, ^2P), -0.85 (^2S, ^2P), -0.51 (^2S, ^2P)), H^- (-14.33 (^1S; $1s^2$), -4.06 (^1S; $2s^2$)*, -3.76 (^3P; $2s2p$)*, -3.46 (^3S; $2s4s$)*, -3.43 (^1S; $2p4p$)*, -3.41 (^1P; $2p4s$)*, -1.83 (^1S; $3s^2$)*, -1.73 (^3P; $3s3p$)*, -1.59 (^3S; $3s4s$)*, -1.55 (^1S; $3p5p$)*, -1.54 (^3P; $3p^2$)*, -1.54 (^1P; $3s5p$)*, -0.97 (^3P; $4s4p$)*, -0.87 (^3P; $4p^2$)*, -0.85 (^1P; $4s5p$)*, -0.55 (^3P; $5p^2$)*.

8. Li^+; ($E = -7.2364$), Li (-5.33 (^2S), -3.49 (^2P), -2.00 (^2S), -1.54 (^2P), -1.04 (^2S), -0.85 (^2P), -0.62 (^2S), -0.51 (^2P)), Li^- (-5.95 (^1S; $2s^2$), -2.22 (^1S; $3s^2$)*, -2.05 (^3P; $3s3p$)*, -1.57 (^3P; $3p^2$)*, -1.07 (^3P; $4s3p$)*, -0.89 (^3P; $4p^2$)*, -0.64 (^3P; $5s4p$)*, -0.56 (^3P; $5p^2$)*).

9. Na^+; ($E = -161.6766$), Na (-4.94 (^2S), -2.98 (^2P), -1.91 (^2S), -1.37 (^2P), -1.00 (^2S), -0.79 (^2P), -0.61 (^2S), -0.50 (^2P)), Na^- (-5.48 (^1S; $3s^2$), -2.07 (^1S; $4s^2$)*, -1.39 (^3P; $4p^2$)*, -1.18 (^1S; $5s^2$)*, -0.86 (^3P; $5p^2$)*, -0.56 (^3P; $6p^2$)*).

Candidates for electronically metastable states are marked with asterisks in the above list. Their potential metastability derives from the fact that their dominant electronic configurations differ by two orbital occupancies from those of underlying neutral-plus-ejected-electron configurations to which they can decay. For example, the $^3B_1$ state of H_2F^- has a $2b_16a_1$ dominant configuration for the outermost two electrons and lies at -2.63 eV; the two neutral-molecule states which lie below this energy have $4a_1{}^1$ and $2b_2{}^1$ orbital occupancies and lie at -5.5 and -3.5 eV, respectively. Decay of the $^3B_1$ state caused by electronic coupling to either of the underlying neutral states plus a free electron in an orbital denoted ϕ_k occurs at rates inversely proportional to the squares

of the Coulomb minus exchange integrals $\langle 2b_16a_1|4a_1\phi_k\rangle - \langle 2b_16a_1|\phi_k4a_1\rangle$, and $\langle 2b_16a_1|2b_2\phi_k\rangle - \langle 2b_16a_1|\phi_k2b_2\rangle$, respectively. Depending on the anion-neutral state energy gap, which determines the de Broglie wavelength of the ϕ_k, and the relative sizes and orientations of the $2b_1$, $6a_1$, $4a_1$, and $2b_2$ orbitals, these electronic couplings may be small enough to produce decay rates in the 10^8-s^{-1} range.

To reliably compute the decay lifetimes of these states, we need to first "stabilize" their energies and wave functions, after which their couplings to underlying continua can be evaluated. This stabilization process allows the resonance component of the autoionizing state to be properly isolated from its background continuum component. Carrying out such stabilization and lifetime calculations will be the subject of a future full paper on these species. Although detailed stabilization calculations were not carried out on any of the above species, we should emphasize that our results on H^-, Li^-, and Na^- yield many metastable states within 0.1 eV of the experimental or best theoretical determinations for these states. For this reason, we believe that our estimates of the metastable-state energies of the molecular anions treated here are qualitatively correct.

We see that $H_3CH_2^-$, NH_4^-, H_3O^-, H_2F^-, and NeH^- all are predicted to support electronically stable DR anions which lie below their corresponding neutrals by 0.08–0.5 eV. In contrast, H_3^- was found to not support an electronically bound DR state. We found that single-configuration SCF calculations on these anion states were unable to even yield positive electron binding energies; it was absolutely essential to correlate the motions of the two active electrons to achieve stability of these species. In all of these cases, the neutrals are not first-order Jahn–Teller unstable because their electronic states are not spatially degenerate; however, this says nothing about more global aspects of their surfaces. In fact, H_3 and NeH are not geometrically stable near their cation geometry and dissociate to produce H plus H_2 and Ne, respectively.

All of the anions studied also present likely candidates for low-lying metastable states whose decay to underlying neutral states may be slow enough to permit these states to be experimentally observed. In fact, several of the anions present *progressions* of potentially metastable states with each state lying somewhat below a state of the corresponding neutral.

These DR anions are qualitatively similar to the doubly excited states of He studied by the Berry group[10] at Chicago who extended these studies to states of the alkaline earth atoms[11] where similar strong radial and angular correlation effects have been observed. However, there are important differences: (i) the long range Coulomb forces felt by both electrons in He**, Ca**, etc. are not present in our anions; as one of the two outer electrons moves far away, it "feels" no Coulomb force but only those due to other permanent and induced moments; (ii) our species' centers of force have "shape"; that is, they are not spherically symmetric as are the He nucleus and the alkaline earth doubly positive cation cores. These shape effects qualitatively influence the energy ordering of the neutral and anion states. For these reasons, among others, our study of these DR anions is not a straightforward extension of this earlier work on neutral atomic species.

In a subsequent full paper, we plan to communicate additional structural details about these novel DR anions. At that time, we will also discuss further the computational techniques used, and we hope to be able to estimate the lifetimes of those states which have been identified as potentially electronically metastable. Finally, we expect to examine the possibility that states predicted here to be electronically *stable* may, in fact, autoionize due to conversion of vibrational/rotational energy of the underlying core to electronic energy. Our earlier work[12] has shown that such

(10) Hunter, III, J. E.; Berry, R. S. *Phys. Rev.* **1987** *A36*, 3042.
(11) Krause, J. L.; Berry, R. S. *J. Chem. Phys.* **1985**, *83*, 5153.
(12) O'Neal, D.; Simons, J. *J. Phys. Chem.*, in press. Chalasinski, G.; Kendall, R. A.; Taylor, H.; Simons, J. *J. Chem. Phys.* **1988**, *92*, 3086. Acharya, P. K.; Kendall, R. A.; Simons, J. *J. Chem. Phys.* **1985**, *83*, 3888. Acharya, P. K.; Kendall, R. A.; Simons, J. *J. Am. Chem. Soc.* **1984**, *106*, 3402.

vibrational/rotational-to-electron energy flow can be facile in anions with weakly bound electrons and may give rise to electron ejection at rates approaching 10^{11} s^{-1}. Treatment of these prospects will also have to wait until publication of the full paper; the primary purpose of the present Letter is to communicate these first predictions about the existence of new electronically bound and potentially metastable states of these DR anions. It is our desire to nurture interest in these systems within the experimental community, especially with respect to developing new sources for these species.

FEATURE ARTICLE

Surface Chemistry of Organophosphorus Compounds

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This paper reviews the known decomposition chemistry of organophosphorus compounds interacting with metal and metal oxide surfaces. Three kinds of processes—oxidation, dealkylation, and hydrolysis—are known to be important, but the fundamental knowledge base in this technologically and environmentally important area is presently inadequate. Some significant research directions are identified for surface chemical science, surface reaction chemistry, solid-state synthesis, and organometallic cluster chemistry.

I. Introduction

Heterogeneous reactions currently offer one of the most favorable technological routes to the removal of air pollutants from the atmosphere. Indeed, the application of heterogeneous *catalytic* methods to automotive emission control represents the most widespread exposure of the public to the benefits of catalytic technology,[1] costing the public about $3 billion annually for all automobiles and light duty trucks manufactured in the United States.[2] A more specialized area of environmental protection involves the purification of breathing air in hazardous environments such as those exposed to chemical warfare agents. Degradation of pesticides and herbicides is a related area of importance. There is a pressing need to develop reliable methods to chemically transform into harmless substances, catalytically or stoichiometrically, a variety of types of environmental threats.

We focus here on organophosphorus compounds because of their relevance as environmentally hazardous materials and because

some literature on catalytic conversion is available.[3–7] The *surface chemistry* of organophosphorus compounds is intrinsically quite interesting and largely unexplored. There are a number of intellectual challenges, particularly the development of an organometallic surface chemistry—both stoichiometric and catalytic.

(1) Haensel, V.; Burwell, R. *Sci. Am.* **1971,** *225,* 46.
(2) Private communication from Dr. Kathryn Taylor, General Motors Research Laboratory, Warren, MI, 1986.
(3) Baier, R. W.; Graven, W. M.; Linhart, H. D.; Oliver, R. C.; Peters, D. L.; Weller, S. W. "Feasibility Study of Catalytic Methods of Air Purification (U)"; Contract DA-18-108-CML-6671(A), Final Report, August 1964.
(4) Cheselke, F. J.; Wheeler, A.; Weller, S. W.; Baier, R. W.; Dutch, P. H.; Weiler, F. B. "Study of Catalytic and Thermal Decomposition of Toxic Agents"; Contract DA18-035-AMC-279(A), Final Report, Book 1, CB-67-2378-10.1, Oct. 1970.
(5) Graven, W. M.; Weller, S. W.; Peters, D. L. *Ind. Eng. Chem. Process Des. Dev.* **1966,** *5* 183.
(6) Baier, R. W.; Weller, R. W. *Ind. Eng. Chem. Process Des. Dev.* **1967,** *6,* 380.
(7) Steves, R. R. "Design, Fabrication, and Evaluation of First 400 CFM Catalytic Air Purifier Model"; Contract DA-18-035-AMC-279(A), Final Report for Task No. 43, Book 1, March 1971.

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