diazo compounds and have been described elsewhere.[31]

Preparative Experiments. These were carried out in H-shaped cells divided by a glass frit and fitted with platinum gauze anode and cathode. The procedures for electrolysis and monitoring of the residual diazoalkane concentration were as recently described.[18]

Product solutions were worked up by pouring into water (250 cm^3) and extracting with CH_2Cl_2 (2 × 50 cm^3). The extracts were washed with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. Analysis was by GLC and GLC/MS with a VG 7070E instrument. GLC conditions were 25 m capillary column (i.d., 0.3 mm); stationary phase, OV1; temperature program 80–250 °C at 10 °C/min. Identification was from retention times, and the mass spectra which whenever possible were compared with that of authentic specimens. A flame ionization detector was used for the quantitative analyses, the response being uncorrected since previous experience with compound **7** and its decomposition products indicated that responses per mole of **7** converted to each product were close to unity. In the case of electrolysis of **8** the scale was sufficient for ^1H NMR spectroscopic analysis to be attempted, but this was less successful than expected because of the coincidental identity of the chemical shifts of the methyl protons of the dimethyl ketal produced and the methylene protons of the ethano bridge. Integration of the signals and comparison with that for the aromatic protons gave an approximate confirmation of the ratio of ketal to ketone.

Registry No. **7**, 883-40-9; $\mathbf{7}^{\bullet+}$, 64401-31-6; **8**, 6141-55-5; $\mathbf{8}^{\bullet+}$, 109217-77-8; **9**, 6141-56-6; $\mathbf{9}^{\bullet+}$, 109217-78-9.

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Many-Body Theory of the Ionization Energies of CH_3^-, SiH_3^-, and GeH_3^-

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Abstract: Electron propagator theory is used to calculate the vertical ionization energies of CH_3^-, SiH_3^-, and GeH_3^-. Basis set augmentations are made until changes in the computational results are small. Adiabatic ionization energies are obtained via many-body-perturbation-theory calculations on the neutral potential energy surface. The adiabatic values are in excellent agreement with photoelectron spectroscopy measurements on CH_3^- and SiH_3^-. Comparable calculations are made for GeH_3^-. Calculated vertical ionization ene-gies are 0.51 eV for CH_3^-, 1.79 eV for SiH_3^-, and 2.01 eV for GeH_3^-; adiabatic counterparts are 0.19, 1.31, and 1.39 eV, respectively. Calculations employing effective core potentials for SiH_3^- and GeH_3^- agree closely with all-electron results. Vertical ionization energies employing these techniques are 1.88 eV for SiH_3^- and 1.97 eV for GeH_3^-. Adiabatic effective core potential results are 1.46 eV for SiH_3^- and 1.49 eV for GeH_3^-.

I. Introduction

Electron affinities are important in many areas of chemistry, such as the behavior of anions in the gas phase and in solution.[1] Several physical techniques measure these quantities precisely, but accompanying structural information often is uncertain or incomplete. For example, unfavorable Franck–Condon factors may obscure the adiabatic electron binding energy in a photoionization experiment. With some methods, it may be necessary to report just an upper bound. At this point, theory can provide the missing geometries and distinguish between vertical and adiabatic electron affinities.

It is well known that there are substantial nuclear rearrangements accompanying the removal of an electron from the methyl, silyl, and germyl anions.[2] The neutrals have less pyramidal and more planar structures than the anions. Anion photoelectron spectroscopy can yield some information on the neutral by interpreting final state vibrational structure.[3,4] Isotopic substitutions cause larger shifts in some vibrational final states than in others, and inferences on which peak represents the adiabatic ionization energy can be drawn. Methide and silide adiabatic ionization energies are determined in this way, but for the germide species, the picture is less complete. Ion cyclotron resonance photodetachment spectra are available for the germyl anion, but the photoionization onsets are not sharp enough to definitively determine a vertical or adiabatic ionization energy.[5]

Many computational studies of these anions and neutrals have been undertaken.[2] Most have concentrated on minima in the potential energy surface and on barriers to inversion. Such investigations can generally be tackled on the Hartree–Fock level with double-ζ plus polarization basis sets, perhaps augmented with a set of diffuse functions for studying negatively charged species. Spacings between potential energy surfaces containing different numbers of electrons, however, will typically require a correlated treatment with multiply augmented and polarized basis sets.[6]

II. Methods

Vertical electron binding energies are currently calculated in two different ways: directly and indirectly. The former set of methods evaluates an energy difference in one calculation, while the latter set of methods requires subtraction of total energies for

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the initial and final states. Electron propagator theory[7] (EPT) is a direct method that generates corrections to results using Koopmans's theorem. This method, similar in structure to Green's function[8] and equation-of-motion[9] methods, provides a direct determination of the electron binding energy and the overlap amplitude between the initial and final states,

$$\langle N|a_i^+|N-1,i\rangle \text{ or } \langle N|a_i|N+1,i\rangle$$

The overlap amplitudes are one-electron functions and can be expanded in the basis that is used to express the molecular orbital (MO). While the canonical MO's are eigenfunctions of the self-consistently calculated Fock operator, the propagator counterparts (called Feynman–Dyson amplitudes) are obtained by solving the Dyson equation:

$$\mathbf{G}^{-1}(E) = \mathbf{G}_0^{-1}(E) - \mathbf{\Sigma}(E)$$

Poles of the matrix G are electron binding energies. Therefore, one chooses a value of E, sets up the right side of the equation, and calculates the eigenvalues in hopes of finding a zero. A new guess is made for E and the process is iterated until the pole is discovered. Typically, the matrices are expressed in the canonical MO basis, so that

$$\{\mathbf{G}_0^{-1}(E)\}_{ij} = (E - \epsilon_i)\delta_{ij}$$

In the above equation, the ϵ's are canonical MO energies. The diagonality of the matrix shows that its poles occur at these values; in other words, the neglect of $\Sigma(E)$ leads to Koopmans's theorem. Approximate schemes have been developed for calculating $\Sigma(E)$, the self-energy matrix. Once the pole search is finished, the eigenvector gives a linear combination of MO's, the Feynman–Dyson amplitude, which can be applied to calculating photoionization intensities or to interpreting the change in electronic structure. The present EPT calculations are carried out in the quasi-particle approximation; i.e., a single, diagonal element of the self-energy matrix is needed for each final state.[10] The Feynman–Dyson amplitude thus remains a simple canonical MO. An iterative pole search at the second-order level (EPT(2)) is performed; this energy is then inserted into the third-order (EPT(3)) self-energy formula.[11] The diagrams evaluated in this way are then used to calculate the outer valence approximation (OVA) to higher order corrections.[12] Only core MO's are omitted from the diagram summations. SCF calculations are performed using Gaussian 82.[13] The EPT codes are a separate link to this suite of programs and employ many of the post-SCF utility subroutines of Gaussian 82.

Total energy calculations along the final state doublet potential energy surface employ many-body perturbation theory (MBPT), a method for calculating correlated total energies.[14] Also known by the Hamiltonian partitioning scheme it employs, Moeller–Plesset, this technique can be pursued to various orders of perturbation theory using the standard options of Gaussian 82. When MBPT(n) total energies are indicated, the nth order of perturbation theory has been evaluated.

Basis set types that have yielded excellent anion ionization energies using EPT(OVA) and MBPT(4) are employed in the EPT calculations.[6] The valence s,p basis should have at least triplet-ζ plus diffuse functions for the heavy atoms. A minimum set of polarization functions consists of two sets of d functions on the heavy atoms. In order to exhaust the basis set effects, various improvements are tested. These include additional diffuse and polarization functions. F functions on the heavy atoms are among the last additions.

Table I. Vertical Ionization Energy (eV) of CH_3^-

	Koopmans	EPT(2)	EPT(3)	EPT-(OVA)
6-311+G(3df,2p)	1.08	0.16	0.89	0.68
6-311(2+,2+)G(3df,2p)	1.12	0.13	1.08	0.82
6-311(3+,3+)G(3df,2p)	1.12	0.13	1.09	0.82
6-311(2+,2+)G(3d,2p)	1.12	0.07	1.08	0.83
6-311(2+,2+)G(2d,2p)	1.11	0.04	1.04	0.78
6-311(2+,2+)G(3d,3p)	1.12	0.07	1.10	0.85

[a] At HF/6-31G* CH_3^- Geometry: C–H = 1.119 Å; H–C–H = 101.7°.

Table II. CH_3 Relaxation Energy (eV) with 6-311+(3df,2p) Basis Using HF/6-31G* Geometries[a]

ΔSCF	0.80
ΔMBPT(2)	0.76
ΔMBPT(3)	0.76
ΔMBPT(4SDQ)	0.75
ΔMBPT(4)	0.74

[a] C–H = 1.119 Å, H–C–H = 101.7° for CH_3^-; C–H = 1.073 Å, H–C–H = 120.0° for CH_3.

Effective core potentials and their s,p valence basis sets are also employed in this study.[15] The valence s and p atomic orbitals from effective core potential calculations are decontracted to double-ζ for the geometry optimizations. Triple-ζ is used for the EPT calculations. Diffuse functions are created by multiplying the most diffuse exponent of the original effective core potential atomic basis by 0.3. The same polarization functions used in the all-electron calculations are used in the effective core potential calculations, unless otherwise noted.

III. CH_3^-

HF/6-31G*[16] geometry optimizations were performed for methyl anion, and UHF calculations with the same basis were done on the neutral radical. EPT calculations with various basis sets are summarized in Table I. Experience with other calculations[6] has shown the 6-311+G(3df,2p) basis to be close to saturation for electron affinity calculations. Additional sets of diffuse functions on C and H, obtained by multiplying the smallest s and p exponents of the 6-311++G set by 0.3, were added to give 6-311(2+,2+)G(3df,2p). The procedure was repeated to give the 6-311(3+,3+)G(3df,2p) basis. The first three lines of Table I show that the first augmentation was needed, but not the second. Removing f functions (line 4), one discovers that their importance in this molecule is small. From 3d to 2d on C (line 5), a small loss of binding energy occurs. Additional p functions on the H atoms (line 6) have little effect. The 6-311(2+,2+)G(3df,2p) basis is sufficient for this calculation; the best result, EPT(OVA), gives a vertical anion ionization energy of 0.821 eV.

To calculate the adiabatic ionization energy, it is necessary to find the energy of relaxation along the neutral radical potential energy surface from the structure of the anion to that of the neutral. (One could as easily use EPT at the neutral equilibrium geometry and then calculate the relaxation energy along the anion's potential energy surface.) Using MBPT(4) with a 6-311+G-(3df,2p) basis and the HF/6-31G* structures, the CH_3 relaxation energy is determined (see Table II). The predictions at various orders of electron interaction are similar. If one subtracts the best

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Table III. EPT and MBPT Results (eV) Using HF/6-31+G* CH_3^- and CH_3 Geometries[a]

EPT/6-311(2+,2+)G(3df,2p) at CH_3^- Minimum	
Koopmans	0.68
EPT(2)	−0.23
EPT(3)	0.76
EPT(OVA)	0.51
MBPT/6-31+G* Relaxation Energies for CH_3	
ΔSCF	0.32
ΔMBPT(2)	0.32

adiabatic ionization energy of CH_3^- = 0.51 − 0.32 = 0.19 eV
experiment[3] = 0.08 ± 0.03 eV

[a] C–H = 1.097 Å, H–C–H = 109.2° for CH_3^-; C–H = 1.073 Å, H–C–H = 120.0° for CH_3.

Table IV. Vertical Ionization Energy (eV) of SiH_3^- at HF/6-31G* SiH_3^- Geometry[a]

	Koopmans	EPT(2)	EPT(3)	EPT(OVA)
(7s,6p,3d/3s,2p)	1.80	1.51	1.72	1.80
(7s,6p,4d/3s,2p)	1.81	1.51	1.72	1.80
(7s,6p,3d/3s,3p)	1.80	1.51	1.74	1.82
(7s,6p,3d,1f/3s,2p)	1.80	1.59	1.77	1.86
(8s,7p,3d,1f/3s,2p)	1.80	1.59	1.77	1.86
(7s,6p,3d,1f/4s,2p)	1.82	1.60	1.78	1.87

[a] Si–H = 1.539 Å, H–Si–H = 95.4°.

relaxation energy (0.744 eV) from the EPT(OVA)/6-311(2+,2+)G(3df,2p) vertical ionization energy (0.821 eV), the predicted adiabatic electron affinity is 0.077 eV. This value is quite close to the experimental value[3] of 0.08 ± 0.03 eV.

A remaining source of error could be the HF/6-31G* geometry of the anion. Optimizations at the HF/6-31+G* level were performed for the anion and neutral, followed by MP2/6-31+G* single-point calculations. The neutral's structure is hardly altered at all, but there are some small changes for the anion. An EPT/6-311(2+,2+)G(3df,2p) calculation was done at the new anion geometry. The anion's vertical ionization energy is 0.509 eV at the OVA level; the adiabatic ionization energy is 0.188 eV (see Table III). The small change in the adiabatic prediction is an indication that the EPT calculation is capable of giving good energy differences at many points in a potential energy surface.

IV. SiH_3^-

Optimizations on the neutral and anion structures are again performed at the HF/6-31G* level. Basis set effects are explored in Table IV. The first Si basis is based on McLean and Chandler's (6s,5p) set[17] and on Roos and Siegbahn's suggestion for d functions.[18] The former is augmented by multiplying the smallest exponent by 0.3; a triple polarization set is created by multiplying the Roos–Siegbahn d exponent by 4, 1, and 0.25. The hydrogen basis set is from work by Dunning.[19] Line 1 of Table IV gives EPT results for this (7s,6p,3d/3s,2p) basis. The second basis uses a 4d instead of a 3d set on Si by multiplying the Roos–Siegbahn exponent by 8, 2, 0.5, and 0.125. Augmentations of this kind follow a recent suggestion[16] that the ratio of successive polarization exponents should be 4. An advantage of this procedure over simply adding more diffuse polarization functions is that there is less bias toward stabilizing the anion vs. the neutral. Very little change accompanies this basis set enlargement. Going from a 2p to a 3p set on the H atoms also induces small changes (see line 3). F functions[16] are added in line 4; here the changes are somewhat larger. It is clear at this point that the polarization space is practically exhausted by this basis. Addition of more diffuse functions generated by the 0.3 factor on Si (line 5) and on H (line 6) produces minor alterations in the EPT results. One may regard the last line's OVA entry as the best calculation of the vertical electron binding energy at the SiH_3^- HF/6-31G* geometry, 1.869 eV.

Table V. SiH_3^- Relaxation Energy (eV) with (7s,6p,3d,1f/3s,2p) Basis Using HF/6-31G* Geometries[a]

ΔSCF	0.60
ΔMBPT(2)	0.54
ΔMBPT(3)	0.53
ΔMBPT(4SDQ)	0.52
ΔMBPT(4)	0.51

[a] Si–H = 1.539 Å, H–Si–H = 95.4° for SiH_3^-; Si–H = 1.476 Å, H–Si–H = 110.9° for SiH_3.

Table VI. EPT and MBPT Results Using HF/6-31+G* SiH_3^- and SiH_3 Geometries[a]

EPT/(7s,6p,3d,1f/4s,2p) at SiH_3^- Minimum	
Koopmans	1.73
EPT(2)	1.52
EPT(3)	1.70
EPT(OVA)	1.79
MBPT/6-31+G* Relaxation Energies for SiH_3	
ΔSCF	0.53
ΔMBPT(2)	0.48

adiabatic ionization energy of SiH_3^- = 1.79 − 0.48 = 1.31 eV
experiment[4] = 1.406 ± 0.14 eV

[a] Si–H = 1.534 Å, H–Si–H = 96.7° for SiH_3^-; Si–H = 1.475 Å, H–Si–H = 110.9° for SiH_3.

Table VII. Hartree–Fock Optimum Geometries for SiH_3^- and SiH_3[a]

basis	SiH_3^-		SiH_3	
6-31G*	1.539	95.4	1.476	110.9
6-31+G*	1.534	96.7	1.475	110.9
ECP (2s,2p/2s)	1.546	95.9	1.477	112.1
ECP (2s,2p,1d/2s)	1.533	95.5	1.474	111.0
ECP (3s,3p,1d/2s)	1.526	97.2	1.474	111.0

[a] C_{3v} symmetry, Si–H distances in Å, H–Si–H angles in deg.

The relaxation energy along the silyl radical potential energy surface is now evaluated. The HF/6-31G* structures for the anion and neutral are used for MBPT calculations with the (7s,6p,3d,1f/3s,2p) basis. Table V shows these relaxation energies, which are insensitive to correlation improvements. The best value, using MBPT(4), is 0.514 eV, giving an adiabatic electron affinity of 1.869 − 0.514 = 1.355 eV. The latest experimental report[4] gives 1.406 ± 0.014 eV.

The effect of using HF/6-31+G* geometries for the anion and neutral is now tested. These differ trivially from the original HF/6-31G* results. MBPT(2)/6-31+G* neutral relaxation energies and EPT/(7s,6p,3d,1f/4s,2p) are used to estimate a new vertical anion ionization energy, 1.790 eV, and a new adiabatic ionization energy, 1.313 eV (see Table VI). As with CH_3^-, the new structures do not cause the EPT results to be unbalanced.

Calculations with an effective core potential[15] (ECP) on Si are now attempted. Following the original basis set prescription for valence double-ζ calculations, the anion and neutral geometries are optimized. A double-ζ H basis is used.[19] (Effective core potential geometries are compared with all-electron results in Table VII.) A set of d functions on Si[18] and then sets of diffuse s and p functions, generated from the original ECP basis with the 0.3 factor, are added. All of the results are similar. The last pair of effective core potential structures is used to calculate the neutral relaxation energy with the (3s,3p,1d/2s) basis at the HF (0.478 eV) and MBPT(2) (0.425 eV) levels.

The last anion geometry is used for the EPT calculations. The original Si effective core potential basis is decontracted to the triple-ζ level. A set of diffuse functions and two sets of d functions are added. The 3s,1p (α_p = 1.1) H basis[19] is used to give (4s,4p,2d/3s,1p). EPT results with this basis are in the first line of Table VIII. Addition of a set of diffuse s functions on the H atoms[16] (α = 0.036) in line 2 gives increased anion ionization energies. Switching from 1p to 2p for the H atoms (α_p = 2.2, 0.55) gives more increases in line 3. Line 4 now expands from

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Table VIII. ECP Calculations of the Vertical Ionization Energy of SiH_3^- (eV) at HF/ECP(3s,3p,1d/2s) Geometry

	Koopmans	EPT(2)	EPT(3)	EPT(OVA)
(4s,4p,2d/3s,1p)	1.75	1.44	1.59	1.68
(4s,4p,2d/4s,1p)	1.80	1.48	1.63	1.72
(4s,4p,2d/4s,2p)	1.80	1.50	1.68	1.77
(4s,4p,3d/4s,2p)	1.79	1.50	1.69	1.78
(4s,4p,3d/4s,3p)	1.79	1.51	1.72	1.81
(5s,5p,3d/5s,3p)	1.80	1.51	1.73	1.82
(5s,5p,3d,1f/5s,3p)	1.80	1.60	1.79	1.88

Table IX. Hartree–Fock Optimum Geometries for GeH_3^- and GeH_3[a]

basis	GeH_3^-		GeH_3	
(5s,4p,1d/2s)	1.630	93.1	1.538	112.3
(5s,4p,2d/2s)	1.625	93.1	1.535	112.2
(6s,5p,1d/2s)	1.604	96.0	1.521	111.8
(6s,5p,2d/2s)	1.614	95.2	1.541	110.7
ECP (2s,2p/2s)	1.624	94.6	1.541	111.0
ECP (2s,2p,1d/2s)	1.619	94.5	1.544	110.5
ECP (3s,3p,1d/2s)	1.614	95.8	1.544	110.5

[a] C_{3v} symmetry, Ge–H distances in Å, H–Ge–H angles in deg.

Si 2d to 3d, but the changes are slight. Line 5 (2p to 3p on H) shows more improvements. Line 6 adds a second set of diffuse functions to both Si and H; the changes are small. Finally, a set of f functions on Si is added, resulting in the largest increase in the EPT results of all the augmentations. Even this increase is just a few hundreths of an eV. The gradual basis set effects resemble those of the all electron CH_3^- calculations in that a triple-ζ plus diffuse basis suffices for the s,p basis. A 3df basis for the heavy atom and 2p for the hydrogens satisfies the polarization requirements. The best vertical anion ionization energy using an effective core potential, EPT/(5s,5p,3d,1f/5s,3p), is 1.885 eV. Combining the effective core potential EPT and MBPT results gives an adiabatic anion ionization energy = 1.885 − 0.425 = 1.460 eV.

V. GeH_3^-

Optimization of germyl anion and radical structures begins with the Huzinaga (4333/433/4) basis for Ge.[20] The last s and p atomic orbitals, linear combinations of three Gaussians, are decontracted to the double-ζ level to give (43321/4321/4) or (5s,4p,1d). A (2s) basis for the H atoms is used.[19] Optimized geometries with this basis are in Table IX. The occupied d orbitals, combinations of four Gaussians, are decontracted to two functions of three and one Gaussians, giving a (5s,4p,2d/2s) basis. The bond lengths and angles suffer little alteration, so the decontraction of the Ge 3d levels is abandoned. The next basis adds a set of diffuse s and p functions on Ge, obtained by the usual procedure of multiplying the smallest exponent by 0.3. Finally, a set of d functions,[20] intended as polarization functions for the valence electrons, is added to the Ge basis with $\alpha = 0.246$. This last Ge basis has about the same flexibility in the valence as 6-31+G* for C. With this (6s,5p,2d/2s) basis, the GeH_3 relaxation energy is calculated at the MBPT(2) level using HF-optimized geometries. The HF relaxation energy is 0.638 eV and the MBPT(2) relaxation energy is 0.623 eV.

EPT calculations at the last anion structure are now performed using the (6s,5p,2d/2s) basis (see Table X). The first group of entries employs the same basis, but different sets of occupied orbitals are used in the diagram summations. The first line excludes all core orbitals from the occupied space, leaving four doubly filled valence orbitals. In the second line, the Ge 3d-like MO's are included; in the third line the 3s and 3p-like MO's are added in as well. For comparison's sake, another calculation, including all core orbitals in the summation, is carried out. There is virtually no difference between the third and fourth lines, indicating that 1s-, 2s-, and 2p-like MO's do not make noticeable contributions. The other core orbitals account for a few hundreths of an eV.

Table X. Vertical Ionization Energy of GeH_3^- (eV) at HF/(6s,5p,2d/2s) GeH_3^- Geometry of Table IX[a]

	Koopmans	EPT(2)	EPT(3)	EPT(OVA)
(6s,5p,2d/2s)				
no core included	1.93	1.57	1.61	1.69
3d included	1.93	1.57	1.66	1.72
3s,3p,3d included	1.93	1.56	1.68	1.73
all core included	1.93	1.56	1.68	1.73
(7s,6p,3d/3s,2p)	1.97	1.70	1.85	1.93
(7s,6p,4d/3s,2p)	1.99	1.71	1.87	1.94
(7s,6p,3d/3s,3p)	1.97	1.71	1.89	1.96
(8s,7p,3d/3s,3p)	1.98	1.71	1.91	1.98
(7s,6p,3d/4s,3p)	1.99	1.72	1.90	1.97
(7s,6p,3d,1f/4s,3p)	1.98	1.78	1.93	2.01

[a] Ge–H = 1.614 Å, H–Ge–H = 95.2°.

Table XI. ECP Calculations of the Vertical Ionization Energy of GeH_3^- (eV) at HF/ECP(3s,3p,1d/2s) Geometry

	Koopmans	EPT(2)	EPT(3)	EPT(OVA)
(4s,4p,2d/4s,1p)	1.92	1.62	1.76	1.84
(4s,4p,3d/4s,1p)	1.91	1.62	1.76	1.83
(4s,4p,2d/4s,2p)	1.91	1.64	1.81	1.88
(4s,4p,2d/4s,3p)	1.91	1.65	1.84	1.91
(4s,4p,2d,1f/4s,3p)	1.91	1.73	1.88	1.97

The next EPT calculation decontracts the original Ge atomic valence orbitals to the triple-ζ level and adds diffuse Ge s and p functions and two sets of valence d polarization functions[20] ($\alpha = 0.108, 0.382$). The (3s,2p) H set[19] is used, giving a (7s,6p,3d/3s,2p) basis. All of the core MO's are dropped. Some substantial increases with respect to the previous core-excluded calculation are realized. Another Ge d function, meant to describe the diffuse region of the charge distribution, is added in the next line ($\alpha = 0.027$). Increases in the EPT results are about 0.01 eV, so this augmentation can be discarded. Going to a triple polarization set on H produces somewhat larger increases. Adding more diffuse s and p functions to Ge has negligible effects, as seen in the (8s,7p,3d/3s,3p) line. Small variations are also introduced by diffuse s functions on the H atoms. A final augmentation to the last basis consists of adding Ge f functions with exponents of 0.369. This figure arises from aligning the maxima of the f's with the those of the original valence d polarization set.[20] These last results are probably near convergence with respect to basis set improvements. Subtracting the best estimate of the neutral relaxation energy, 0.623 eV, gives an adiabatic ionization energy of 1.39 eV. The experimental upper bound[5] to this quantity is 1.74 ± 0.04 eV.

As with SiH_3^-, effective core potential calculations are now attempted. Three basis sets are used in HF geometry optimizations, following the same basis set recipes as applied to the silyl case. The last of these produces structures that are used to evaluate the neutral relaxation energy at the HF (0.545 eV) and MBPT(2) (0.480 eV) levels.

Effective core potential calculations are performed with the original Ge effective core potential valence basis[15] decontracted to the triple-ζ level. The previous diffuse s and p functions used in the last set of geometry optimizations are added, as well as the two d polarization functions ($\alpha = 0.108, 0.382$) of the all-electron calculations. A (3s) H basis[19] is augmented by a diffuse s function and a set of p functions.[16] From EPT calculations using smaller basis sets, one finds that further diffuse s and p functions are not needed. Table XI shows the EPT calculations with this (4s,4p,2d/4s,1p) effective core potential basis. Going to a triple d polarization set on Ge ($\alpha = 0.984, 0.246, 0.0615$) produces little change in the results. Changing from 1p to 2p on the H atoms, however, leads to substantial increases in the predictions. A third polarization set ($\alpha = 4.4, 1.1, 0.275$) on H finally seems to exhaust the effective core potential EPT calculation's need for p functions. Finally, the f functions used in the all-electron calculations are

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(20) *Gaussian Basis Sets for Molecular Calculations*, Huzinaga, S., Ed.; Elsevier: New York, 1984.

added. The last EPT prediction with effective core potentials is 1.966 eV; combined with the calculated neutral relaxation energy, this results in an adiabatic ionization energy of 1.966 − 0.480 = 1.486 eV.

VI. Conclusions

Adiabatic ionization energies calculated with EPT and MBPT are in excellent agreement with photoelectron spectroscopy. Vertical ionization energies, nuclear relaxation energies, and accompanying geometries are generated as by-products of these calculations. In the case of the germyl anion ionization energy, the vertical and adiabatic calculations supplement the upper bound measured with photodetachment spectroscopy. The best all-electron calculations of vertical ionization energies are 0.51 eV for CH_3^-, 1.79 eV for SiH_3^-, and 2.01 eV for GeH_3^-. All-electron adiabatic counterparts are 0.19 eV for CH_3^-, 1.31 eV for SiH_3^-, and 1.39 eV for GeH_3^-. Effective core potential calculations give vertical ionization energies of 1.88 and 1.97 eV for SiH_3^- and GeH_3^-, respectively. Adiabatic effective core potential results are 1.46 eV for SiH_3^- and 1.49 eV for GeH_3^-.

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In Situ FTIR Studies of Methanol and Dimethyl Ether in ZSM-5

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Abstract: In situ infrared spectra are reported of methanol and dimethyl ether in H-ZSM-5 and Na-ZSM-5. Methanol reacts with internal acidic hydroxyl groups at 523 K to form a methoxy species, the appearance of which correlated with the onset of hydrocarbon formation. Dimethyl ether is protonated at lower temperatures but forms the same methoxy species at 473 K. The methoxy species methylates benzene and alkenes at 523 K. The implications of these observations for the mechanism of hydrocarbon formation are discussed.

The interaction of methanol and dimethyl ether with the acid zeolite ZSM-5 has obvious importance in the complex chemistry associated with methanol conversion to gasoline over this catalyst.[1] In particular, elucidation of the mechanism by which the first carbon–carbon bonds are formed from methanol or dimethyl ether requires a detailed knowledge of the species adsorbed in the zeolite at this point in the reaction. There have, however, been few spectroscopic studies of methanol and dimethyl ether in ZSM-5. Ono and Mori[2] first reported infrared evidence for formation of methoxy species from CD_3OH and showed that desorption of this species was accompanied by cleavage of C–D bonds. Infrared spectra of methoxy species have also been described by Kubelkova et al.,[3,4] and NMR evidence for formation of methoxy from methanol has been presented.[5] Other infrared studies have shown the growth of complex spectra due to adsorbed reaction products after heating ZSM-5 in the presence of methanol.[6,7]

In none of the previous spectroscopic studies were spectra recorded of the catalyst under reaction conditions. With a reaction sequence as complex as that in methanol conversion to gasoline, spectra recorded at room temperature after cooling the catalyst from reaction temperatures will in general contain contributions from adsorbed reaction products which may obscure species initially formed. We have accordingly undertaken an in situ infrared study of the interaction of methanol and dimethyl ether with ZSM-5 under reaction conditions with the particular objective of identifying species formed initially when methanol and dimethyl ether first encounter a fresh catalyst. By using an in situ infrared cell which functions as a pulsed microreactor we have been able also to correlate infrared spectra with reaction products detected downstream from the catalyst. A preliminary account of this work has appeared elsewhere;[8] in this paper a more complete description and analysis of the spectra is presented and the implications of these results for the mechanism of methanol to gasoline conversion are discussed.

Experimental Section

A ZSM-5 zeolite with Si:Al = 26 was provided by Mobil Research and Development Corp. in the ammonium-exchanged form. A second ZSM-5 with Si:Al = 15 was prepared in the sodium-exchanged form by the method of Grose and Flanigen[9] and subsequently proton exchanged. Both zeolites were fully characterized by X-ray diffraction, scanning electron microscopy, ^{29}Si and ^{27}Al NMR spectroscopy, elemental analysis, and surface area determination (500 ± 20 m^2 g^{-1}). Na-ZSM-5 was prepared by ion exchange of H-ZSM-5 with NaBr solution and shown by infrared spectroscopy to contain no acidic protons. All reagents used were spectroscopic or AR grade.

The in situ infrared experiments employed a cell similar to that described by Katzer et al.[10] Zeolite samples were pressed into self-supporting wafers (7–10 mg cm^{-2}), mounted in the cell, and activated by heating in flowing nitrogen (400 mL min^{-1}) to 673 K. Gas and liquid samples were injected into the cell by syringe (typically 1–5 μL of liquid or 1 mL of gas) or via an evacuated gas dosing system. Reaction products were either collected in a liquid nitrogen trap downstream from the cell and analyzed off-line by gas chromatography or analyzed on-line via a gas-sampling valve.

All infrared spectra were recorded on a Nicolet 5DX spectrophotometer at 4-cm^{-1} resolution. Typically 400 interferograms (1s per scan)

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