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THE GROUND AND EXCITED STATES OF PtH AND PtH^+ BY RELATIVISTIC Ab Initio ELECTRONIC STRUCTURE CALCULATIONS: A MODEL STUDY FOR HYDROGEN CHEMISORPTION ON PLATINUM SURFACES AND RELATED PHOTOEMISSION PROPERTIES

S.W. Wang and Kenneth S. Pitzer

January 1983

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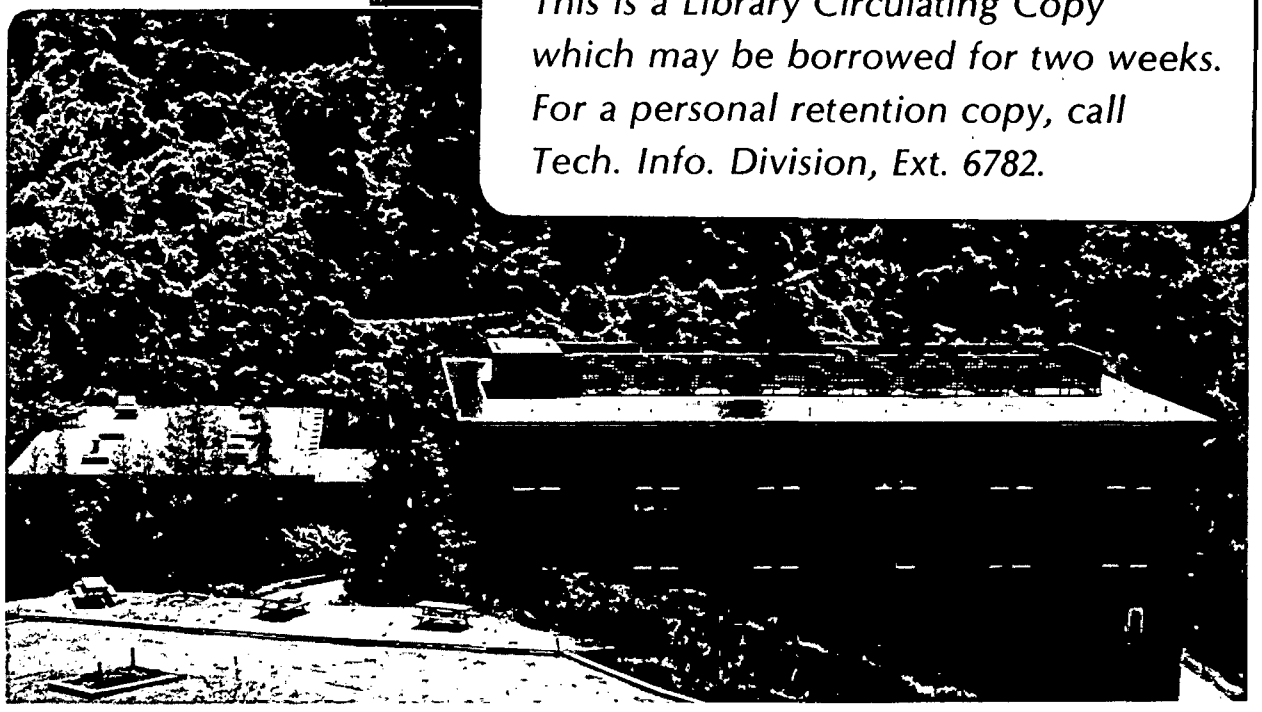

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The Ground and Excited States of PtH and PtH^+ by Relativistic *Ab Initio* Electronic Structure Calculations: a Model Study for Hydrogen Chemisorption on Platinum Surfaces and Related Photoemission Properties

S. W. Wang and Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

Relativistic electronic structure calculations for the ground and excited states of PtH and PtH^+ are performed using first/a spin-averaged relativistic effective core potential (AREP) at the self-consistent field (SCF) level and later incorporating the spin dependence at the configuration interaction (CI) level. These calculations lead to several conclusions. (1) Both the 6s and 5d orbitals of Pt interact strongly with the H orbitals, clearly indicating that the bonding involves both 6s and 5d electrons. (2) Correlation energies contribute significantly to the PtH binding energy but have little effect on the force constant. (3) The polarization functions centered on H are much more important than those centered on Pt in affecting the binding energy. (4) The two lowest states, $^2\Delta_{5/2}$ and $^2\Sigma_{1/2}$, are calculated to have almost exactly the same energy; either may be the lower one. The lowest 3/2 state is mixed $^2(\pi+\Delta)_{3/2}$ and lies a little higher in energy. (5) Both the first ionization potential and the ionization energy of the H-like level agree reasonably well with the experimental data. Finally, the absolute binding energy of PtH is 2.45 eV, to be compared with the experimental value of 3.44 eV. The discrepancy is due to our computational limitations.

I. Introduction

Relativistic effects should not be neglected in molecular structure calculationsas was shown by a recent review.[1] However, accurate relativistic calculations for even small molecules were not available until recently due to computational difficulties involved in solving the four-component Dirac equation instead of the Schrödinger equation when all electrons are included explicitly. With the application of relativistic effective core potentials (REP), the core electron coordinates can be eliminated. One only has to solve for valence electron wavefunctions for which the approximated two-component Pauli equation is sufficiently accurate. Such calculations are manageable and good results have been obtained in a series of diatomic calculations.[2,3] A general description of their method was given in a recent review[4] and we shall use the same method for the electronic structure calculations of PtH and PtH^+.

The REP for the Pt atom was derived from the Dirac-Fock atomic calculations and was spin-averaged at the SCF stage and then spin-corrected at the CI stage as first suggested by Hafner and Schwarz[5] and Ermler *et al.*[6] Our computational scheme is similar to that developed for TlH[3] and the advantage of using an averaged REP (AREP) is to enable the use of the Λ-S coupling scheme and existing nonrelativistic molecular programs.

The motivations for this study are two-fold. First, PtH and PtH^+ are among the first few diatomic molecules containing a heavy transition element to be investigated using the relativistic *ab initio* electronic structure technique mentioned above. Recent calculations by H. Basch and S. Topiol[7] are very interesting, but more extensive and more accurate calculations are needed to answer many questions in particular those related to chemisorption and photoemission. The large number of d electrons involved implies more important correlation interactions and more complicated spin-orbit

interactions than the systems containing p electrons treated before.[2,3] There is also the question of whether the d electrons are involved in the chemical bond in addition to the s electrons. Second, platinum is a most important material for the heterogeneous catalysis of hydrogenation reactions. Also, among the group VIII metals of the Periodic Table, platinum has unique catalytic and adsorption properties.[8] The adsorption energy of H on platinum surfaces is much smaller than that on Ni and Pd surfaces. Through a prototype study of PtH we wish to examine the degree of localization of the chemical bond, explore the concept of "surface molecule" and gain insight in chemisorption phenomena.

The outline of this paper is as follows: in section II we report the REP that we obtained for the Pt atom. In section III we present results for the PtH calculations, and compare them with experimental spectra in section IV, while calculations for PtH^+ are given in section V. Finally, in section VI we discuss the limitations of the method and present our conclusions.

II. The Pt Relativistic Effective Core Potential

We have treated the Pt^+ ion ($5d^9$ configuration) and nine low-lying electronic states of the Pt atom using the Dirac-Hartree-Fock program[9] without configuration interaction. The valence electron configurations of the Pt atom are $5d^96s^1$, $5d^86s^2$, $5d^{10}$, $5d^96p^1_{1/2}$, $5d^96p^1_{3/2}$, $5d^95f^1_{5/2}$, $5d^95f^1_{7/2}$, $5d^95g^1_{7/2}$ and $5d^95g^1_{9/2}$. The orbital energies for the ten valence electrons and the total energies of these states are listed in Table I. The ground state was found to have the $5d^96s^1$ configuration and was used for constructing pseudo-orbitals and an REP for the $s_{1/2}$, $d_{3/2}$ and $d_{5/2}$ components. The last six states were used for constructing the $p_{1/2}$, $p_{3/2}$, $f_{5/2}$, $f_{7/2}$, $g_{7/2}$ and $g_{9/2}$ pseudo-orbitals and the corresponding

components of the REP. Although the $d_{3/2}$ and $d_{5/2}$ components can also be obtained from these six excited states, those obtained from the $5d^9 6s^1$ configuration are the most suitable ones for the ground and low-lying excited state calculations of platinum hydride. From Table I we learn that the SO splittings between the $5d_{3/2}$ and $5d_{5/2}$ orbitals are in the range of 1.65-1.82 eV, while between the $6p_{1/2}$ and $6p_{3/2}$ orbitals the splitting is 0.40 eV.

The SO splittings for the $5f_{5/2}$, $5f_{7/2}$ as well as the $5g_{7/2}$, $5g_{9/2}$ orbitals are negligibly small since electrons in these orbitals are very loosely bound and have very small wavefunction amplitudes in the core region. The other 68 electrons of the Pt atom were treated as core electrons due to their much larger orbital energies. The nine electronic states form the basis for the construction of the REP, which is spin-dependent, angular momentum dependent and shape-consistent. Detailed formulas can be found in the 5th paper of ref. 2. Throughout the paper the atomic units of length (Bohr) and energy (Hartree) are used unless otherwise specified.

III. Molecular Electronic Structure Calculations of PtH

The REP obtained in section II was spin-averaged and used in the SCF calculations for PtH. Care has to be taken in the choice of basis functions to describe the spatially extended 6s orbital of the Pt atom. Slater functions were used. The orbital exponents were obtained by optimizing the best spin-averaged energy for Pt in the $5d^9 6s^1$ configuration using the AREP method. In Table II it is noted that the "triple zeta" $\{s_3 d_3\}$ set improves the 6s orbital energy substantially over the "double-zeta" $\{s_2 d_2\}$ set and is as good as the "quadruple-zeta" set. A choice of the mixed $\{s_3 d_2\}$ set using 6s orbital exponents obtained from the "triple-zeta" set and 5d orbital exponents from the "double-zeta" set gives a total energy very close

to that of the "triple-zeta" set but is not listed, for brevity. The addition of polarization functions centered on Pt, i.e., the 6p and 5f orbitals, with low or high zeta values such as $\xi_{6p} = 0.6183$, $\xi_{5f} = 0.3182$ or $\xi_{6p} = \xi_{5f} = 4.0$ makes only small contributions to the total molecular energy, as will be shown later. However, polarization functions centered on H are more important. The three $\{s_3p_3\}$ basis sets listed in Table III give SCF energies that differ mutually by no more than 0.001 eV. But the increase of basic function size from $\{s_1p_1\}$ to $\{s_4p_3\}$ improves the SCF energy by a few tenths of an eV.

There are three possible electronic configurations for PtH corresponding to δ-, σ- and π-vacancy states as shown below:

$$1\sigma^2\ 2\sigma^2\ \pi^4\delta^3 \tag{1}$$

$$1\sigma^2\ 2\sigma^1\ \pi^4\delta^4 \tag{2}$$

$$1\sigma^2\ 2\sigma^2\ \pi^3\delta^4 \tag{3}$$

The first two configurations can be calculated directly using our SCF program with the AREP. The π-vacancy state can be obtained approximately using the SCF orbitals obtained from the δ-vacancy state. Results over a number of basis sets are shown in Table IV. The last column indicates how unimportant are the 6p and 5f polarization functions in affecting the SCF results. As the number of basis functions on Pt increases (such as the $\{s_3d_3;s_2p_1\}$ set) the δ-vacancy state becomes the ground state instead of the σ-vacancy state. The best SCF dissociation energy (1.79 eV) was obtained by using the $\{s_3d_2;s_3p_3(1)\}$ and $\{s_3d_3;s_4p_3\}$ basis sets, which increase the dissociation energy of the smaller $\{s_2d_2;s_2p_1\}$ basis set by 0.57 eV. The significance of the extended basis set is obvious.

The SCF orbital coefficients using the $\{s_2p_1d_2f_1;s_2p_1\}$ basis set for the δ- and σ-vacancy states are shown in Table V at R = 3.0 a.u. where R is the Pt-H internuclear separation. The 6s, 5d, and 1s orbitals all participate substantially in both 1σ and 2σ molecular orbitals (MO's). At infinite separations, the 6s and 5d levels of Pt lie above the 1s level of H although the 5d level lies close to the 1s level. For the molecule in the δ-vacancy state both orbital energies are lowered as is expected for bonding orbitals. It is also interesting to examine in detail the orbital coefficients for the 1σ and 2σ orbitals for the two electronic states. The 1σ orbital is an orbital of the 6s + 5d + 1s type and the 2σ orbital is of the 6s - 5d + 1s type. In the δ-vacancy state the 6s contribution to the 1σ orbital is much smaller than that for the σ-vacancy state. A Mulliken population analysis[10] can be done to give further bonding information for the molecular orbitals.

For the δ-vacancy state, we find that both the 1σ and 2σ orbitals have 0.57 electrons on H and 1.43 electrons on Pt. But the 6s population in the 1σ orbital is very small and the $5d_{z^2}$ population is about 50% of the 6s population in the 2σ orbital. Thus the 1σ orbital is predominantly 5d on Pt but with very substantial bonding to H. The small 6s component contributes further bonding. The 2σ orbital may be regarded as primarily a 6s - 1s bonding orbital but with a greater population on Pt. Now the 5d component has a negative sign and is antibonding; however, the net effect of this orbital must remain substantially bonding. The contributions of the polarizing p and f orbitals on Pt are very small but the 2p contribution for H is significant. The positive sign of the $2p_z$ coefficient implies removal of small amount of electron density from the internuclear region. This reduces the electron-electron repulsion energy and lowers the total energy.

The total population on H is 1.14 indicating a small but significant charge transfer to H in the δ-vacancy state.

In the σ-vacancy state one electron is shifted from the 2σ orbital to a 5dδ(d_{xy} or $d_{x^2-y^2}$) orbital on Pt. The 5dδ orbital is much more compact than the 2σ and adds shielding for both the 1σ and 2σ orbitals which expand. One may note this in the relative increase in the second, lower zeta, coefficient for 6s, 5d, and 1s. Also the 6s and 1s components increase for 1σ which becomes a more generally bonding orbital. The orbital energy of 1σ is raised by the greater shielding of the additional 5dδ electron. Some $5d_{z^2}$ contribution is shifted from 1σ to 2σ, as compared to the δ-vacancy state, but the general nature of the 2σ orbital remains the same. The total population on H is 1.04 in the σ-vacancy state; thus, there is less charge transfer than in the δ-vacancy state. This reduction is caused by two factors: first, the σ-vacancy state has one less bonding electron and hence one might expect some reduction in charge transfer. Second, the SCF coefficients on H for the bonding orbitals are somewhat different for the σ- and δ-vacancy states due to bonding interactions. This induces further reductions of charge transfer to H for the σ-vacancy state.

Since only one pair of electrons can significantly bond a hydrogen atom, it is interesting to transform the 1σ and 2σ orbitals to the linear combination which maximizes the hydrogen participation in a bonding orbital with the other orbital non-bonding. The result is shown in Table VI for the δ-vacancy state. It is now apparent that most of the bonding is with the 6s orbital of Pt but that the $5d_{z^2}$ contribution remains very significant. The non-bonding orbital is primarily $5d_{z^2}$; the other contributions are not negligible but their effect is rather complex. Note that the 1s coefficients are of equal magnitude but opposite sign; the compact 1s function adds to the $5d_{z^2}$ while the diffuse 1s function subtracts.

Experimentally the work function changes $\Delta\phi$ for H on Pt surfaces show complicated coverage dependence,[8] i.e., a small positive maximum at very low hydrogen doses and then a decrease to -0.23 eV at saturation. Our diatomic calculations should correlate better with the low coverage experimental data. A charge transfer from Pt to H would seem to increase the dipole moment towards the H in agreement with the small increase of $\Delta\phi$ value observed experimentally. Although $\Delta\phi$ is related to dipole moment change on the surface, a direct interpretation of $\Delta\phi$ in terms of charge transfer may sometimes be misleading and therefore we shall not discuss it further.

Although the SCF results provide us a bonding picture between Pt and H, the best SCF binding energy (1.79 eV in Table IV) for the δ-vacancy state is only 52% of the experimental value (3.44 eV)[11] for the $^2\Delta_{5/2}$ state. The remaining discrepancy is due to the correlation energy. Clearly it is very important and amounts to nearly half of the dissociation energy. The inclusion of correlation energy is discussed below.

We have performed CI calculations for the low-lying $^2\Delta_{5/2}$, $^2\Delta_{3/2}$ and $^2\Sigma_{1/2}$ states of PtH. We first describe the reference states for $C_{\infty v}$ symmetry and then discuss the complications introduced by our use of a program for Cartesian orbitals in C_{2v} symmetry.

For the +5/2 state of $^2\Delta_{5/2}$ one has the single primary configuration $1\sigma^2 2\sigma^2 \pi_+^2 \pi_-^2 \delta_+^2 \delta_-^1(\uparrow)$ where the $(\uparrow)$ indicates a positive spin for the unpaired election in the δ_- orbital. The Cartesian orbitals for π_{+-} are $\pi_x \pm i\pi y$ and for δ_{+-} are $\delta_{x^2-y^2} \pm i\delta_{xy}$. Thus this single primary configuration for $^2\Delta_{5/2}(+5/2)$ becomes two reference configurations (a) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^2 \delta^2_{x^2-y^2} \delta_{xy}(\uparrow)$ and (b) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^2 \delta^1_{x^2-y^2}(\uparrow)\ \delta^2_{xy}$ with coefficients of equal absolute magnitude but one imaginary and of appropriate sign.

For $\Omega = 3/2$ there are $^2\Delta_{3/2}$ and $^2\pi_{3/2}$ components, i.e., a δ-vacancy state with one spin and a π-vacancy state with opposite spin. For the +3/2

component one can first write $1\sigma^2 2\sigma^2 \pi_+^2 \pi_-^2 \delta_+^2 \delta_-(\downarrow)$ and $1\sigma^2 2\sigma^2 \pi_+^2 \pi_-(\uparrow) \delta_+^2 \delta_-^2$. These expand into four Cartesian references as follows:

(c) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^2 \delta^2_{x^2-y^2} \delta_{xy}(\downarrow)$, (d) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^2 \delta^1_{x^2-y^2}(\downarrow) \delta^2_{xy}$,

(e) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^1(\uparrow) \delta^2_{x^2-y^2} \delta^2_{xy}$, (f) $1\sigma^2 2\sigma^2 \pi_x^1(\uparrow) \pi_y^2 \delta^2_{x^2-y^2} \delta^2_{xy}$.

On further examination one notes that references (c) and (d) with appropriate coefficient give the -5/2 component of $^2\Delta_{5/2}$ which lies at lower energy than $^2\Delta_{3/2}$. Hence we obtained the +3/2 state as a second root in a calculation with references (c) through (f); we label this $^2(\pi+\Delta)_{3/2}$ because both components are significant.

There are two components also for $\Omega = 1/2$, a $^2\Sigma_{1/2}$ state and a $^2\pi_{1/2}$ state. For the +1/2 component we first write $1\sigma^2 2\sigma^1(\uparrow) \pi_+^2 \pi_-^2 \delta_+^2 \delta_-^2$ and $1\sigma^2 2\sigma^2 \pi_+^2 \pi_-^1(\downarrow) \delta_+^2 \delta_-^2$. The first configuration gives a single Cartesian reference: (g) $1\sigma^2 2\sigma^1(\uparrow) \pi_x^2 \pi_y^2 \delta^2_{x^2-y^2} \delta^2_{xy}$, while the π-vacancy yields two references: (h) $1\sigma^2 2\sigma^2 \pi_x^2 \pi_y^1(\downarrow) \delta^2_{x^2-y^2} \delta^2_{xy}$ and (i) $1\sigma^2 2\sigma^2 \pi_x^1(\downarrow) \pi_y^2 \delta^2_{x^2-y^2} \delta^2_{xy}$. In this case the lowest root is a mixed state with the σ-vacancy, reference (g), the primary component.

The CI calculations shown in Table VII included all single and twenty double excitations with the $\{s_2 p_1 d_2 f_1; s_2 p_1\}$ basis set. The total number of double excitations is 22. The two neglected ones have been checked as unimportant. Because of computing limitations, the numbers of SCF orbitals included were 8, 2, 2, 2 for σ(including $\delta_{x^2-y^2}$), δ_{xy}, π_x, π_y, respectively, instead of the complete set of 9, 2, 3, 3 for this particular basis set. The total configurations included for the CI calculations are 1909 for the $^2\Sigma_{1/2}$ state, 2562 for the $^2(\pi+\Delta)_{3/2}$ state and 1280 for the $^2\Delta_{5/2}$ state.

We also made calculations without electron excitation but including the SO term and with the reference configurations listed above (2 for 5/2,

4 for 3/2, and 3 for 1/2). These results are given in the second column of Table VII.

The correlation energy is the difference between the SCF+CI results in the third column of Table VII and that with no electron excitations. It amounts to 2.03 eV for the $^2\Delta_{5/2}$ state, 2.04 eV for the $^2(\pi+\Delta)_{3/2}$ state and 2.00 eV for the $^2\Sigma_{1/2}$ state. The $^2\Sigma_{1/2}$ state is predicted as the ground state with the $\{s_2p_1d_2f_1;s_2p_1\}$ basis set. When the SO effects are omitted but CI retained, we obtain much higher energies for the $^2\Delta$ and $^2\pi$ states, as shown in the last column of Table VI. The SO term in the $^2\Sigma_{1/2}$ state is very small for obvious reasons, and the $^2\Sigma$ state is again predicted as the ground state. The energy separation between the $^2\Delta_{5/2}$ state and the $^2(\pi+\Delta)_{3/2}$ state is -0.49 eV and that between the $^2\Delta_{5/2}$ state and the $^2\Sigma_{1/2}$ state is 0.12 eV.

However, when a larger basis set is used, the order of the states changes. Table VII shows the SCF + CI results for the $\{s_2d_2;s_2p_3\}$ basis set. In Table VIII, CI denotes that only $\sigma \rightarrow \sigma$ single excitations and $\sigma\sigma \rightarrow \sigma\sigma$ double excitations are included within our computation limit, using the complete set of 11 SCF σ-orbitals. From Table IV we found the SCF energy for the σ-vacancy state to be lower than that for the δ-vacancy state by 0.14 eV. But when correlation energies are included, the energy of the $^2\Delta_{5/2}$ state turns out to be 0.125 eV lower than that of the $^2\Sigma_{1/2}$ state at R = 3.00 a.u. For the $^2\Delta_{5/2}$ state the CI calculation can be done with the $\{s_2d_2;s_2p_3\}$ basis set by including more double excitations due to the fewer reference states needed. For a selected orbital space containing 10 σ-orbitals $2\delta_{xy}$ and $2\delta_{x^2-y^2}$ orbitals, and $2\pi_x$ and $2\pi_y$ orbitals, seven double excitations of the $\sigma\sigma \rightarrow \sigma\sigma$, $\sigma\delta \rightarrow \sigma\delta$, $\sigma\pi \rightarrow \sigma\pi$, $\delta\pi \rightarrow \delta\pi$, and $\pi\pi \rightarrow \pi\pi$ types can be included and the total energy at the equilibrium bond distance 3.05 a.u. is -26.837 Hartree. A correlation energy of 2.45 eV has been

obtained at this level. The same level of approximation can be used for the total energy calculation of the ground state ($^3D_3$) of Pt, which is obtained as -26.247 Hartree using the $\{s_2d_2\}$ basis set and an SCF orbital space containing 4σ orbitals, 4π orbitals and 4δ orbitals. The dissociation energy is then obtained as 2.45 eV (26.837 - 26.247 - 0.5 = 0.090 Hartree). The lowest total energy can be obtained within our computation limit for the $^2\Delta_{5/2}$ state as -26.861 Hartree with the more extended $\{s_3d_3;s_2p_1\}$ basis set. This would amount to a correlation energy of 3.098 eV. But the dissociation energy is not improved with this set of calculations since the deletion of some SCF orbitals in the CI step causes a correlation imbalance in the atomic Pt and molecular PtH calculations.

IV. Comparison with Experimental Spectra

We summarize the results of both the SCF and SCF+CI energy calculations using the $\{s_2d_2;s_2p_3\}$ basis set in Table IX together with the resulting bond distances and vibrational frequencies. Experimental values are given for comparison. Also two low-lying excited states are included. It is noted that the vibrational frequencies are about 90% of the experimental values and are not as sensitive to the includion of CI as the bond distances. The somewhat larger bond distance 3.19 a.u. (1.69 Å) for the $^2(\pi+\Delta)_{3/2}$ state results from the depletion of one SCF orbital (10 σ orbitals are included instead of 11) at the CI stage due to computation limitations for this state (more reference states are needed). Correlations have shortened the bond distance of $^2\Sigma_{1/2}$ much more than $^2\Delta_{5/2}$ and improved agreement with experiment (as compared to the SCF results for δ-vacancy and σ-vacancy states). The remaining small discrepancies in R_e and ω_e are easily explained by the limitations of our CI calculations.

This research was not designed to yield accurate information about highly excited states. Thus we calculate the next higher $^2\Delta_{5/2}$ state at over 50,000 cm^{-1} whereas it is observed at 22311 cm^{-1}. Our basis set is inadequate and our CI methods are not satisfactory for highly excited states.

We report only the moderately excited states that arise from spin-orbit coupling of ground states of various Λ-S symmetries. For $\Omega = 3/2$ there is the higher energy combination of the $^2\Delta_{3/2}$ and $^2\pi_{3/2}$ states which we find at 19350 cm^{-1} above the lowest 3/2 state. This excitation is almost exactly the experimental value of 19938 cm^{-1}. We suspect that this agreement is fortuitous, and that there may be additional 3/2 states in this energy range. There is also the higher energy combination of $^2\Sigma_{1/2}$ and $^2\pi_{1/2}$ which is primarily of $^2\pi_{1/2}$ character and is so labeled in Table IX. We find it to be 11810 cm^{-1} above the lowest $\Omega = 1/2$ state. There are no experimental observations in this frequency range; the experimental studies may not have been designed to examine it. The higher-energy $^2\Sigma$ state tentatively reported at about 30000 cm^{-1}, if correct, is certainly a different state.

We turn now to the relative energies of the lowest states with $\Omega = 1/2$, 3/2, and 5/2. From Tables VII and VIII it is apparent that either the 1/2 or the 5/2 state can be calculated to be lowest depending on the basis set and the array of excitations in the CI. The 3/2 state is definitely a little higher in energy. This appears to be consistent with the experimental data. The lowest 5/2 and 3/2 states are well characterized,and it seems to be accepted that the 3/2 state is somewhat higher in energy.

Only a preliminary report[12] is available on the 1/2 state. There is some question whether these spectra arise from PtH or an impurity, but we are unable to identify any plausible impurity with these spectral constants.

The lower state of the 30311 cm^{-1} band with B" = 7.13 cm^{-1} has all the appropriate properties for the lowest 1/2 state of PtH which is essentially $^2\Sigma_{1/2}$. This band is reported as intense in absorption; hence, the $^2\Sigma_{1/2}$ state might be the ground state, but presumably not much below the $^2\Delta_{5/2}$ state.

An interpretation has been given[13] of the lowest 5/2 and 3/2 states as if they were a simple inverted $^2\Delta$ term with a spin-orbit splitting constant A ≅ 600 cm^{-1} which is only slightly larger than the value A ≅ 490 cm^{-1} for $^2\Delta$ in NiH. The value of 600 cm^{-1} is much too small for PtH. The value for the Pt atom is about 7000 cm^{-1}. An approximate value for this parameter for PtH is given by the decrease for the $^2\Delta$ term in Table VII when SO is introduced, i.e., the value for $^2\Delta_{5/2}$ with CI less than the value for $^2\Delta$ with CI but without SO. This is 0.018 a.u. or about 4000 cm^{-1}. Since the 5/2 state is purely Δ, this is a valid calculation. As noted above, the lowest 3/2 state is almost half $^2\pi_{3/2}$ and only a little more than half $^2\Delta_{3/2}$. The $^2\pi_{3/2}$ interaction lowers the real state. Indeed the real $^2(\pi+\Delta)_{3/2}$ state with SO is at almost exactly the same energy as the $^2\Delta$ state without SO. Thus the lowering by interaction with $^2\pi_{3/2}$ just cancels the raising by SO from $^2\Delta$ to $^2\Delta_{3/2}$.

The published interpretation[13] may be quite correct in indicating an energy difference of 1200 to 1320 cm^{-1} between the lowest 5/2 and 3/2 states, but the cause of this energy difference is complex. Our calculations indicate a larger energy difference, near 4000 cm^{-1}, but we believe this may be too large because our approximation is probably better for the $^2\Delta$ state than for the $^2\pi$ state. The SCF orbitals from the δ-vacancy state were used in both cases. The $^2\Delta$ is a δ-vacancy state whereas $^2\pi$ is a π-vacancy state for which we made no SCF calculation. Thus, the $^2\pi$ energy is probably too far above the value for $^2\Delta$; if this were corrected it would

decrease the difference of the real 3/2 and 5/2 states to a value less than 4000 cm^{-1} and possibly as small as 1200 cm^{-1}.

Further spectral studies for PtH would be of great interest in view of the various features discussed above.

V. Electronic Structure Calculations for PtH^+

When an electron is ejected from PtH, the remaining PtH^+ ion will rearrange itself. The spin-averaged SCF orbitals of PtH^+ are much different from those of PtH, as shown in Table X for the ground $^3\Delta$ state of PtH^+. All the orbital energies are significantly lowered due to a less screened Pt^+ ion since the 1s type orbitals on H are still quite populated as in PtH. A Mulliken population analysis shows that there are 0.74 electrons on H and 1.26 electrons on Pt in the 1σ orbital, as compared with 0.57 and 1.43 electrons, respectively, for the δ-vacancy state of PtH. But in both PtH and PtH^+ the 6s populations are relatively small. For the singly occupied 2σ orbital there are 0.17 electrons on H and 0.83 electrons on Pt, as compared with 0.29 and 0.71 electrons, respectively, if the 2σ orbital of the δ-vacancy state of PtH is only singly occupied. The total σ electron populations are 0.91 on H and 2.09 on Pt in PtH^+ as opposed to 1.14 on H and 2.86 on Pt in PtH. This proves again that the ejected electron originates mainly from Pt. Both 1σ and 2σ orbitals are bonding. The total SCF energy of this ground state is -26.450 Hartree and therefore the first SCF ionization potential is 7.8 eV. The ground state (δ-vacancy) SCF energy of PtH is -26.736 Hartree. This ionization potential is close to the Pt atomic ionization potential (9 eV). The 1.2 eV difference results from the different environment felt by Pt in PtH as opposed to a bare Pt atom both before and after an electron is ejected. Before the electron ejection an electron in Pt is energy stabilized via bond formation with the H atom

and/this could increase the ionization potential. However, after the electron ejection the whole system is stabilized via the relaxation process. Clearly in our case the relaxation energy dominates and has reduced the ionization potential.

It is of great interest for surface scientists to know also the excited state of PtH^+ so that an effective ionization potential for an electron originating from the H orbital can be obtained. This value can be compared with the photoemission data taken on clean and H chemisorbed Pt surfaces.[14] The difference spectrum shows a H induced peak about 6 eV below the Fermi level of the metal (~6 eV). The effective ionization potential is about 12 eV with respect to the vacuum level and is reduced in comparison with the free atom value (13.6 eV). To explain this observation we have carried out SCF calculations for PtH^+ by eliminating the 1s basis functions from the $\{s_2d_2;s_2p_2\}$ set. The resulting SCF energy is -26.205 Hartree and this would give an ionization potential of 12.2 eV. When correlation energies and SO effects are included with CI (single excitation of the $\sigma \rightarrow \sigma$ type and double excitations of the $\sigma\sigma \rightarrow \sigma\sigma$, $\sigma\delta \rightarrow \sigma\delta$, $\sigma\pi_x \rightarrow \sigma\pi_x$, $\sigma\pi_y \rightarrow \sigma\pi_y$, $\delta\pi_x \rightarrow \delta\pi_x$, $\delta\pi_y \rightarrow \delta\pi_y$, and $\pi_x\pi_y \rightarrow \pi_x\pi_y$ types are included), this value increases to 12.9 eV. The SCF orbital coefficients are shown in Table X. A Mulliken population analysis shows that there are 0.04 electrons on H^+ and 1.96 electrons on Pt for the 1σ orbital. The 1σ orbital is now predominantly a $5d_{z^2}$ orbital with less than 10% 6s population. The 2σ orbital, on the other hand, has 0.06 electrons on H^+ (occupying the $2p_z$ orbitals) and 0.94 electrons on Pt and is predominantly of the 6s type with about 5% $5d_{z^2}$ population. The total electron populations are 0.1 on H^+ and 2.9 on Pt. Indeed we have obtained a state in which the 1s orbital of H is nearly empty and there is only an electron charge of 0.1 transferred from Pt to H^+. But this excited PtH^+ state is not orthogonal

to the ground state of PtH^+. So the calculated SCF energy for the excited state may be lower than an orthogonalized one. If the orthogonalization condition is imposed, the calculated ionization potential would be greater than 12.9 eV. The discrepancy with the experimental value is due to the use of an insufficient screening effect in diatomic molecules to mimic those in the infinite systems. Our model therefore only explains qualitatively the photoemission data.

VI. Conclusions

In this work, the relativistic effective core potentials derived from Dirac-Fock calculations for the Pt atom are used to calculate the molecular electronic properties for ground and low-lying excited states of PtH and PtH^+. Absolute bonding energies, equilibrium bond distances, vibrational frequencies and ionization potentials are obtained and are in reasonable agreement with experimental observations. Although the absolute bond energy for ground-state PtH is lower than the experimental value, mainly due to our computing limitations, the relative energies for various states and the ionization potentials are reproduced quite well and the results provide theoretical insight into the Pt-H bond. Further work along this line will be undertaken for larger clusters, using the effective core potentials developed here. This will elucidate the effects on the Pt-H bonds of the presence of more than one Pt atom and investigate the yet unknown Pt-Pt bonding character. However, more numerical approximations may be required.

Small cluster calculations for $H(Pt)_4$ have been performed by Messmer, *et al.*,[15] using the X_α-scattered wave method with the muffin-tin approximation: they show interesting results in comparison with experimental data for H adsorption on Pt surfaces. However, the drawbacks of the muffin-tin approximation and the not so well justified parameter α are also generally

known. More accurate numerical calculations starting from small clusters are definitely needed. Experimentally, the study of well-defined small clusters also presents an important scientific challenge. These studies will not only be interesting in themselves but will enable a systematic understanding of the transition from cluster chemistry to surface chemistry.

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Table I. Total Energies and Orbital Energies for the Relativistic Pt Atom and the Pt^{+1} ion ($5d^9$). Total Energies are Written with Respect to that of the $5d^9 6s^1$ Configuration (-18418.0874)

Valence Electron Configuration / Energies	$5d^9 6s^1$	$5d^8 6s^2$	$5d^{10}$	$5d^9 6p^1_{1/2}$	$5d^9 6p^1_{3/2}$	$5d^9 5f^1_{5/2}$	$5d^9 5f^1_{7/2}$	$5d^9 5g^1_{7/2}$	$5d^9 5g^1_{9/2}$	$5d^9$
Total energy	0	0.0225	0.0421	0.1392	0.1537	0.2437	0.2438	0.2545	0.2545	0.2745
$\varepsilon(5d_{3/2})$	-0.4496	-0.5490	-0.3579	-0.5240	-0.5451	-0.6890	-0.6890	-0.7116	-0.7116	-0.7516
$\varepsilon(5d_{5/2})$	-0.3887	-0.4821	-0.3020	-0.4618	-0.4844	-0.6282	-0.6282	-0.6508	-0.6508	-0.6908
$\varepsilon(6s_{1/2})$	-0.2839	-0.3083								
$\varepsilon(6p_{1/2})$				-0.1368						
$\varepsilon(6p_{3/2})$					-0.1219					
$\varepsilon(5f_{5/2})$						-0.0313				
$\varepsilon(5f_{7/2})$							-0.0313			
$\varepsilon(5g_{7/2})$								-0.0200		
$\varepsilon(5g_{9/2})$									-0.0200	

Table II. Slater Basis Functions Centered on Pt. The Symbol $S_i d_j$ is Used to Denote the Number i(j) of the Basis Functions for the 6s(5d) Orbital Expansion. The Orbital Energies are Represented by ε's, Total Energies by E and the Orbital Exponents by ξ's.

	s_2d_2	s_3d_3	s_4d_4
E	-26.1832	-26.2172	-26.2177
ε_{6s}	- 0.2624	- 0.2920	- 0.2923
ε_{5d}	- 0.4198	- 0.4140	- 0.4137
$\xi_{6s(1)}$	3.7571	3.0083	2.9655
$\xi_{6s(2)}$	1.7116	1.7416	1.8023
$\xi_{6s(3)}$		1.0378	1.0784
$\xi_{6s(4)}$			0.7706
$\xi_{5d(1)}$	4.4827	4.3865	4.4097
$\xi_{5d(2)}$	2.3182	2.3631	2.3873
$\xi_{5d(3)}$		1.3911	1.2725
$\xi_{5d(4)}$			0.7416

Table III. Basis Functions Centered on the H Atom. s_ip_j Denotes that there are i(j) Functions for the s(p) Orbitals of H in the Expansion. Other Notations have Similar Meanings as those for Pt.

	s_1p_1	s_1p_3	s_2p_1	s_2p_3	s_3p_3 (1)	s_3p_3 (2)	s_3p_3 (3)	s_4p_3
$\xi_{1s(1)}$	1.0	1.0	1.2	1.2	1.2	1.5	1.5	1.2
$\xi_{1s(2)}$			0.95	0.95	0.95	0.95	1.1	0.95
$\xi_{1s(3)}$					0.5	0.5	0.5	0.5
$\xi_{2s(1)}$								0.5
$\xi_{2p(1)}$	0.5	1.33	0.5	1.33	1.33	1.33	1.33	1.33
$\xi_{2p(2)}$		1.0		1.0	1.0	1.0	1.0	1.0
$\xi_{2p(3)}$		0.5		0.5	0.5	0.5	0.5	0.5

Table IV. SCF Energies for the δ- and σ-vacancy States of PtH over the Various Basis Functions. $s_i p_j d_k f_\ell$; $s_m p_n$ Denotes the Combined Basis Functions Centered on Pt and H Atoms

	Basis Set	No. of Basis Functions σ	π	δ	SCF Energy δ-vacancy	SCF Dissociation Energy (eV)	SCF Energy (σ-vacancy)	SCF Energy σ-vacancy, $\xi_{6p}, \xi_{5f}=4.0$
A_1	$s_2d_2;s_2p_1$	7	3	2	-26.7287	1.22	-26.7350	
A_2	$s_2p_1d_2f_1;s_2p_1$	9	6	3	-26.7291	1.23	-26.7355	-26.7345
A_3	$s_2d_2;s_2p_3$	9	5	2	-26.7365	1.43	-26.7417	
A_4	$s_2d_2;s_3p_3(1)$	10	5	2	-26.7414	1.56	-26.7464	
A_5	$s_2d_2;s_4p_3$	11	5	2	-26.7415	1.57	-26.7464	
B_1	$s_3d_2;s_1p_1$	7	3	2	-26.7581	1.44		
B_2	$s_3d_2;s_1p_3$	9	5	2	-26.7634	1.58		
B_3	$s_3d_2;s_2p_3$	10	5	2	-26.7692	1.74		
B_4	$s_3d_2;s_3p_3(1)$	11	5	2	-26.7710	1.79		
C_1	$s_3d_3;s_2p_1$	9	4	3	-26.7759	1.57	-26.7730	
C_2	$s_3d_3;s_3p_3(1)$	12	6	3	-26.7834	1.78		
C_3	$s_3d_3;s_4p_3$	13	6	3	-26.7838	1.79		

Table V. SCF Orbital Coefficients, Orbital Energies, and Occupation Numbers for σ-orbitals of PtH Over the $\{s_2p_1d_2f_1;s_2p_1\}$ Basis Set

MO Basis	1σ		2σ	
	δ-vacancy	σ-vacancy	δ-vacancy	σ-vacancy
6s(1)	0.031	0.102	0.192	0.154
6s(2)	.081	.264	.571	.518
$6p_z$ [a]	-.018	-.025	-.009	-.001
$5d_{z^2}(1)$	.489	.316	-.304	-.456
$5d_{z^2}(2)$	.391	.271	-.259	-.391
$5f_{z^3}$ [a]	-.005	-.007	-.003	-.001
1s(1)	.389	.421	.136	.028
1s(2)	.040	.161	.284	.245
$2p_z$	.055	.080	.052	.030
ε	-0.524	-0.460	-0.323	-0.329
occupation	2	2	2	1

[a] The zeta values for 6p and 5f were 0.6183 and 0.3182.

Table VI. Coefficient for Transformed Orbitals (δ-vacancy)

Basis	Bonding	Non-bonding
6s(1)	.158	-.114
6s(2)	.461	-.346
$6p_z$	-.019	-.006
$5d_{z^2}(1)$	.131	.561
$5d_{z^2}(2)$	.093	.460
$5f_{z^3}$	-.006	-.002
1s(1)	.371	.179
1s(2)	.229	-.173
$2p_z$	.076	.002

Table VII. Total Energies Without and With CI Calculated Using the $\{s_2p_1d_2f_1;s_2p_1\}$ Basis Set for R = 3.0 a.u. Here the CI Includes Four Single Excitations and Twenty Double Excitations as Explained in the Text

	With SO Term		Without SO	
	No Electron Excitation	SCF + CI		SCF + CI
$^2\Delta_{5/2}$	-26.7469	-26.8215	$^2\Delta$	-26.8036
$^2(\pi+\Delta)_{3/2}$	-26.7283	-26.8034	$^2\pi$	-26.7760
$^2\Sigma_{1/2}$	-26.7525	-26.8260	$^2\Sigma$	-26.8216

Table VIII. Total Energies With SCF and CI Calculated Using the $\{s_2d_2;s_2p_3\}$ Basis Set at R = 3.0 a.u. Here only the Single and Double Excitations of the $\sigma \rightarrow \sigma$ and $\sigma\sigma \rightarrow \sigma\sigma$ Types are Included in CI

	SCF + CI
$^2\Delta_{5/2}$	-26.8002
$^2(\pi + \Delta)_{3/2}$	-26.7836
$^2\Sigma_{1/2}$	-26.7956

Table IX. Bond Distances R_e, Vibrational Excitation Energies ω_e and Excitation Energies T_e Calculated With and Without CI Using the $\{s_2d_2;s_2p_3\}$ Basis Set. Experimental Values are Shown in Parentheses and are Taken from ref. 11

	SCF + CI	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$R_e(\mathring{A})$	SCF	$\omega_e(cm^{-1})$	$R_e(\mathring{A})$
	$^2\pi_{1/2}$	I + 11810					
I	$^2\Sigma_{1/2}$	1008(I)	2045	1.59(1.54)	σ-vacancy	2056	1.70
A'	$^2(\pi+\Delta)_{3/2}$	x_2 + 19350[b]					
X_2	$^2(\pi+\Delta)_{3/2}$	2742(x_2)[a]	2016(2177)	1.69(1.52)			
X_1	$^2\Delta_{5/2}$	0	2020(2294)	1.61(1.53)	δ-vacancy	2047	1.62

[a] x_2 is estimated indirectly from spectral data to be 1320 cm^{-1}.

[b] An experimental value of 19938 cm^{-1} is reported for a $3/2 \leftrightarrow 3/2$ transition.

Table X. SCF Orbital Coefficients and Energies ε_i for Ground and Excited States of PtH^+ at the Equilibrium Bond Distance of PtH. These States are of the $^3\Delta$ Type. Electron Occupation Numbers for the Two σ Orbitals are also Shown

	$\{s_2d_2;s_2p_3\}$ Basis Set Ground State of PtH^+		$\{s_2d_2;s_2p_3\}$ Basis Excited State of PtH^+	
	σ_1	σ_2	σ_1	σ_2
6s(1)	0.069	0.217	0.089	0.301
6s(2)	0.164	0.456	0.271	0.836
$5d_{z^2}(1)$	0.450	-0.404	0.558	-0.220
$5d_{z^2}(2)$	0.324	-0.333	0.506	-0.120
1s(1)	0.494	0.179		
1s(2)	-0.013	0.246		
$2p_z(1)$	-0.128	-0.032	-0.038	0.141
$2p_z(2)$	0.084	-0.055	-0.080	-0.335
$2p_z(3)$	0.038	0.091	0.130	0.243
ε_σ	-0.812	-0.663	-0.780	-0.576
occupation	2	1	2	1
total energy	-26.450		-26.205	

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