Chemical bonds between noble metals and noble gases.
Ab initio study of the neutral diatomics NiXe, PdXe and PtXe

Jaroslav V. Burda a,b,*, Nino Runeberg b, Pekka Pyykkö b

a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences, Dolníkova 3, 182 23 Prague 8, Czech Republic
b Department of Chemistry, University of Helsinki, POB 55, FIN-00014 Helsinki, Finland

Received 30 January 1998; in final form 9 March 1998

Abstract

The lowest potential-energy curves are calculated for the species MXe, M = Ni, Pd, Pt. No bound states are found for NiXe. For PdXe the ground state is bound by 41.6 kJ/mol. The PtXe ground-state curve dissociates to an excited Pt(^3S_g) state but remains bound by 67.9 kJ/mol with respect to the Pt(^3D_g) ground state. Of this D_g value, 9.2 kJ/mol is due to the stabilization caused by spin–orbit coupling. The calculated quasirelativistic Pt–Xe distance is 242 pm. Both PdXe and PtXe are possible new gas-phase or matrix species. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A search for chemical bonds between noble metals and noble gases is of interest for four reasons: (i) the search for new gas-phase or matrix species, (ii) the modeling of solvation, (iii) the interactions in biological systems and (iv) modeling of the interactions between rare-gas atoms and metal surfaces in surface physics.

The starting point of the present work was the proposal [1] for the new species AuXe^+ and XeAuXe^+. Both species have now been observed and the latest calculations give a D_g (AuXe^+) of 126.8 kJ/mol [2]. The neutral isoelectronic analogue of AuXe^+ would be the so-far unknown species PtXe.

Many examples of complexes between transition metal cations and rare gases are known (see e.g. Refs. [3–6]). We are not aware of any strongly bound neutral diatomics. In a broader sense we are studying here the technical requirements for describing a chemical bond between the platinum group metals and their ligands. This can also be considered as an introduction into biologically active platinum complexes which are of high interest, e.g. from the antitumour treatment of cisplatin (cis-dichloro-diammine-platinum, DDP) and its derivates [7–9].

Calculation of the interactions involving heavy metal elements can be considered routine tasks nowadays, due to the availability of reliable libraries of pseudopotentials from several laboratories. In this way an important portion of the relativistic effects is covered. Nevertheless there are still other parts of the relativistic Hamiltonian which should also be included in more accurate calculations, especially the spin–orbit (SO) coupling terms (e.g. [10,11]).
2. Computations

The calculations are based on quasirelativistic (QR) energy consistent pseudopotentials for Ni [12], Pd and Pt [13] as well as Xe [14]. Effective spin–orbit pseudopotential operators are available for Pd, Pt and Xe. The standard basis sets from these references were extended by additional primitive 2f and 1g sets (Ni: 4.9683, 1.2990, 3.2791; Pd: 2.1881, 0.6064, 1.3710; Pt: 1.4193, 0.4662, 1.2077) which were obtained by CCSD energy minimization for the ground state of the neutral atoms using the MOLPRO program [26].

The study can be divided into several steps. First we performed some atomic calculations to determine how accurate the computed atomic spectra are and to what extent they differ from experimental data [15,16] and the previously published results for the Ni atom [17] using an extended all-electron augmented triple zeta ANO basis set [18]. In this way the approximate accuracy of the chosen pseudopotentials can be estimated. It is known that obtaining correct spectra is a difficult task in the case of Ni [17,19]. For this purpose, we have performed CCSD(T) and CASPT2 calculations with an spdd active orbital space as suggested by Anderson and Roos for Ni [17]. Comparison of these two methods also gives an idea about the importance of a multireference description for individual multiplets.

The individual dimers were started with the determination of QR potential energy curves (PES) of individual states, i.e. \( ^1\Sigma, ^3\Sigma, ^3\Pi, ^3\Delta \) and \( ^3\Phi \). In the case of NiXe and PdXe, the states arising from the \( ^3\Delta \) and \( ^3\Phi \) atomic states, respectively, were omitted. This stage was performed at the MP2 and CCSD(T) level. The full counter-poise correction was included [20].

The spin–orbit corrections for individual states were performed at the CIS and CISD level using the program by R.M. Pitzer and coworkers [21–24]. It treats the effective one-electron SO operator variationally within the double group approach. The single, averaged reference state [24] was used for all the atomic L–S states or their molecular \( \Lambda-\Sigma \) equivalents. The CI matrix was then diagonalized with and without the SO operator and the obtained SO corrections were added to the QR CCSD(T) results.

All the QR calculations were done using the program packages GAUSSIAN94 [25], MOLPRO 96 [26], ACES II [27,28] and MOLCAS 3 [29]. The SO part was calculated with Pitzer’s modification of the COLUMBUS program code [30].

3. Atomic calculations

Comparison between the calculated and experimental energy levels of Ni, Pd and Pt is given in Table 1. Note that the experimental ground states of Ni and Pt are the lowest SO components \( ^3\Phi \) and \( ^3\Delta \), respectively, but in the SO average the \( ^3\Delta \) of Ni and the \( ^3\Delta \) of Pt actually lie lower [15,16]. The calculated CC–QR energy levels in Table 1 agree with the experimental ones within about 0.2 eV. The only qualitatively incorrect state order occurs for Ni where calculations prefer the \( ^3\Phi \) state as the ground state but nevertheless the energy difference between these two states is only 0.08 eV. It can be considered to be within the error range of calculations, caused by several approximations — limited basis set, pseudopotential treatment, etc. Substantially worse results were obtained with CASPT2. For the Pd and Pt atoms SO calculations were also performed and the comparison with experimental values for individual states was made.

<table>
<thead>
<tr>
<th>Atom state</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC</td>
<td>PT2</td>
<td>Exp.</td>
</tr>
<tr>
<td>( ^1\Phi )</td>
<td>5.4</td>
<td>-3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>( ^1\Delta )</td>
<td>0</td>
<td>0</td>
<td>93.8</td>
</tr>
<tr>
<td>( ^1\Sigma )</td>
<td>184.7</td>
<td>161.1</td>
<td>167.4</td>
</tr>
</tbody>
</table>

*Active space: spdd*.

*Weight averaged values from Ref. [15].

*Active space used: 3s3p orbitals frozen/no frozen orbitals.
Table 2
Relativistic energies (in cm\(^{-1}\)) obtained with the CISD method for several of the lowest atomic states

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{S}_0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(^3\text{D}_3)</td>
<td>9765</td>
<td>6564</td>
<td>1406</td>
<td>776</td>
</tr>
<tr>
<td>(^1\text{D}_2)</td>
<td>10930</td>
<td>7755</td>
<td>2321</td>
<td>824</td>
</tr>
<tr>
<td>(^3\text{D}_1)</td>
<td>13375</td>
<td>1094</td>
<td>7866</td>
<td>6140</td>
</tr>
<tr>
<td>(^1\text{D}_2)</td>
<td>14911</td>
<td>11722</td>
<td>8163</td>
<td>6567</td>
</tr>
<tr>
<td>(^3\text{F}_4)</td>
<td>33011</td>
<td>25101</td>
<td>10930</td>
<td>7755</td>
</tr>
</tbody>
</table>

The calculated results are obtained with 21 configurations and 24 and 34 MO in the active space for the Pd and Pt atom, respectively.

states from Refs. [15,16] is summarized in Table 2. Twenty-one configurations were used for the evaluation of the SO splitting of both atoms. In the case of the Pd atom, 24 MO functions seem to be near the convergence threshold; calculation of Pt SO spectra was still improved by adding a further 10 molecular orbitals into the active space for the CISD method. From the obtained data, systematic overestimation of the experimental values can be seen. Possible reasons can be the CISD method, where only a limited portion of correlation energy is treated, the effective pseudopotentials and the averaged wavefunction used for the determination of the active MO space for CI calculations. Also the interaction between the triplet and singlet D-states on platinum makes the triplet D fine structure levels deviate substantially from the Lande rule. To use a weighted average procedure to determine a spin-free value for the atomic transitions will thus involve significant errors.

4. Molecular calculations

The calculated QR potential curves of PtXe are shown in Fig. 1a at the CCSD(T) level for various basis sets. Comparison of the originally suggested spd valence basis sets (f-polarization functions were omitted in the Xe case) with spd basis sets (the two f-functions mentioned above were added to original Pt valence basis set) and the spdfg basis set (g-function only on Pt) was performed. As can be seen from Fig. 1a) the single g-function still has a substantial influence on the calculated \(D_0\). With the g-function, even the HF curve becomes clearly bonding (cf. also Fig. 1b), which can be explained by the higher flexibility needed for the better multipole description.
origins from g-functions. In Fig. 1b, the dependence of the PES on various levels of electron correlation is shown for the spdf basis set. As can be seen from Fig. 1b, the MP2 curve exaggerates the bonding of PtXe, compared to CCSD(T). Due to the saving of CPU time, only a single point calculation ($r_{\text{d}} = 2.5 \text{ Å}$) was performed at the fully iterative CCSDT level. It is seen that for PtXe at this distance the CCSD(T) method slightly overestimates the role of triple-excitation contributions but all the CC values lie within 6.3 kJ/mol.

The calculated extended-basis-set CCSD(T) potential curves for PdXe and PtXe are given in Figs. 2 and 3, respectively. For PdXe, the $^1\Sigma^+$ state is the ground state. The bond length of 252 pm is a little shorter than the corresponding value of 257 pm for the valence isoelectronic AuXe$^+$ [2]. The calculated $D_1$ of 41.6 kJ/mol is smaller than the 126.8 kJ/mol for AuXe$^+$. The curves of PdXe are non-trivial (see Fig. 3). Despite the $^1\Sigma^+$ state origins from the $^3$S Pt excited atomic state, it has a large enough bond dissociation energy (BDE) to become the molecular ground state; the BDE is 98.2 kJ/mol (to the $^1$S Pt + $^3$S Xe species). In order to obtain the real bonding energy the CCSD(T) $^1$S--$^3$D difference of 39.5 kJ/mol has to be subtracted. The sum of the covalent radii of Pt and Xe (130 + 130 pm) is actually larger than the calculated QR $R_e = 242$ pm and the $R_e$ is actually below the AuXe$^+$ value. For NiXe, the QR calculation did not converge and using CASPT2 the $^1\Sigma^+$ state does not exhibit any bonding character.

For the optimal geometry of $^1\Sigma$ states some electronic properties were estimated. The vibrational frequencies of the $^1\Sigma$ states of PdXe and PtXe are 70 and 92 cm$^{-1}$, respectively [31]. They were calculated from the Morse-like potential [32]

$$E(x) = D_0 + D_1(1 - \exp(-\alpha(x - x_0)))^2 + D_2(1 - \exp(-\alpha(x - x_0)))^3 + D_3(1 - \exp(-\alpha(x - x_0)))^4$$

(1)

fitted on calculated points of the PES. As the atomic masses in the Schrödinger equation we used those of the most common isotopes — $^{106}$Pd (27.33%), $^{195}$Pt (33.8%) and $^{129}$Xe (26.89%) [33]. The anharmonic correction to the optimized distance is about 1 pm for both species. These species could thus potentially be observed in matrix spectroscopy or in the gas
phase. A Mulliken population analysis was performed using the MP2 and QCI electron density of individual species. PdXe exhibits a small redistribution of electron density with a dipole moment $\mu_{\text{PdXe}} = 0.5$ debye (QCISD) where the negative end is located on Pd (partial charge $\delta = -0.08\,\text{e}$). Using the procedure for fitting point charges from the electrostatic potential (MEP), these values are reduced to $\mu = 0.4$ D and $\delta = -0.03\,\text{e}$ for the same (QCI) electron density. The results of a natural bond orbital (NBO) analysis lie in between with $\delta_{\text{NBO}} = -0.05\,\text{e}$. From the NBO analysis, it can be seen that the donation from the metal d orbital is compensated by the back-donation into the metal 5s orbital. A similar but more pronounced trend is found for PtXe. The dipole moment $\mu_{\text{PtXe}}$ is 1.2 debye (QCISD electron density) and the charge $\delta = -0.25\,\text{e}$, already shows the polar character of this species. Also the MEP value ($\delta = -0.11\,\text{e}$) and NBO charge ($\delta = -0.20\,\text{e}$) support this conclusion. Substantial redistribution of electron density based on NBO analysis can also be demonstrated by the 6s occupation number which is 0.54 within the QCISD density. This strong donation to the Pt 6s shell is completely analogous with that found for AuXe$^+$ [1]. Using a finite field ($\pm 0.001\,\text{e}$) and the CCSD(T) technique we obtained a dipole moment $\mu_{\text{PtXe}} = 1.08$ debye (the same as the MP2 value) and a dipole polarizability $\alpha = 71\,\text{au}$.

Since the energy gap between the $^1\text{S}$ and $^3\text{D}$ Pd atomic states is so large, it can be expected that the SO coupling between individual low-lying states will be small. That is why we restrict in the last part, the calculation of SO terms only to the case of PtXe. To obtain some basic information about individual relativistic states, a CIS spectrum was calculated as a function of the interatomic distance. From the analysis of CI wavefunctions Fig. 4 was constructed. Here the basic lack of correlation energy, which is necessary for a proper interaction description, can be compared with the HF curve Fig. 1b. Subtracting corresponding ‘non-relativistic’ data, CIS results where effective SO potential is switched off, the role of the SO splitting on the stabilization of PtXe can be induced even at this modest level of calculations. Comparing the energy difference (with and without the SO effective operator) at the dissociation limit (10.0 Å) and at the minima on the curves in Fig. 4a,b, the relative stabilization through SO coupling is obtained: $\Delta E = 2.3\,\text{kJ/mol}$ in the CIS approach (the SO stabilization at 10.0 Å is $\Delta E(10.0) = 19.2\,\text{kJ/mol}$ and the same value at 2.8 Å is $\Delta E(2.8) = 21.3\,\text{kJ/mol}$). For two points ($r_{\text{Pt-Xe}} = 10.0$ and 2.43 Å, which is the quasirelativistic optimized distance) we performed a time-consuming Cisd calculation. While the SO stabilization at 10.0 Å is nearly unchanged (\(\Delta E(10.0) = 18.4\,\text{kJ/mol}\), the same energy at 2.42 Å is $\Delta E(2.42) = 27.6\,\text{kJ/mol}$ and so

Fig. 4. PtXe interaction curves calculated with the CIS method. Chosen lines belong to the $A_1$ irreducible representation of the $C_2v$ point group of symmetry. (a) States without the SO operator; (b) states with the effective SO pseudopotential operator: 0' are drawn in solid lines; 2 in dotted lines; 4 in dot–dash line. Symbols at 5 Å belong to the atomic Pt states in the dissociation limit.
the relative SO stabilization increases on going from the dissociation limit to the optimal bond distance by about $\Delta E_s = 9.2$ kJ/mol. Notice also that SO coupling causes an avoided crossing of the 0$^+$, based on QR $1\Sigma_g^+$ state (from $1\Sigma_0^+$ of Pt), with the 0$^+$ state originating from the $^3D_2$ atomic Pt. Several other avoiding crossings can be seen in Fig. 4a for the $A_1$ irreducible representation of $C_{2v}$ point group symmetry.

### 5. Conclusions

We have shown that a chemical bond between the noble metals Pd or Pt and the noble gas atom Xe is possible. For Ni, no bound state was found. Although the molecular $1\Sigma_g^+$ ground state dissociates into the excited $1S$ of Pt, it also remains bound, compared with the $^3D$ ground state of Pt; the $1\Sigma_g^+$ dissociation energy $D_e$ is larger than the atomic $1S-3D$ splitting. It was found that when spin–orbit coupling is included, further stabilization occurs.

Using the CISD method and a medium basis set we found this stabilization to be about 9.2 kJ/mol. Concerning the methods, a $g$-basis function on Pt still considerably increases the bonding. We thus suggest PdXe and PtXe as possible new diatomic gas-phase or matrix species. No evidence for them is known to us, apart from the strong broadening of Pd and Pt atomic spectra in solid Xe [34]. The main physical data for PdXe and PtXe are summarized in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calc. level</th>
<th>$R_e$ (pm)</th>
<th>$D_e$ (kJ/mol)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdXe</td>
<td>QR</td>
<td>252</td>
<td>41.6</td>
<td>70</td>
</tr>
<tr>
<td>PtXe</td>
<td>QR</td>
<td>242</td>
<td>98.2*</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>+ SO</td>
<td></td>
<td>67.9*</td>
<td></td>
</tr>
<tr>
<td>AuXe$^+$</td>
<td>QR</td>
<td>257</td>
<td>126.8</td>
<td>149</td>
</tr>
</tbody>
</table>

Distances in pm, energies in kJ/mol and frequencies in cm$^{-1}$. *Dissociation to $1S$ of Pt. $^*$Subtracting 39.5 kJ/mol for the Pt atomic splitting between $1S_0$ and $^3D_2$ states, and adding 9.2 kJ/mol from molecular spin–orbit stabilization.

The reference data for AuXe$^+$ are from Ref. [2].

### Acknowledgements

We thank Pavel Hobza for initiating our collaboration, R.M. Pitzer for helpful comments and The Academy of Finland for support. The allotment of CPU time was obtained from the University Supercomputer Centers at Prague and Brno and CSC (Espoo) and the Helsinki group.

### References

[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G.


