GRECP/RCC calculation of the spectroscopic constants for the HgH molecule and its cation

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Abstract

Generalized relativistic effective core potential (GRECP) calculations of spectroscopic constants of the HgH molecule ground and low excited states and the HgH\(^+\) cation ground state are carried out, with correlation included by the Fock-space relativistic coupled cluster (RCC) method. Basis set superposition errors (BSSE) are estimated and discussed. It is demonstrated that connected triple excitations of the 13 outermost electrons are necessary to obtain accurate results for mercury hydride. Spectroscopic constants derived from potential curves which include these terms are in very good agreement with experiment, with errors of a few mbohr in \(R_e\), tens of wavenumbers in excitation energies and vibrational frequencies, and proportionately for other properties. Comparison with previous calculations is also presented.

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I. INTRODUCTION

The HgH molecule has been studied in the last few decades both experimentally (see, e.g., references 1-4) and theoretically (references 5-8, among others). The calculations used 12-, 18- or 20-electron relativistic effective core potentials (RECPs), all-electron quasirelativistic methods, and a variety of approaches accounting for electron correlation. The goals of the theoretical investigations included the explanation and systematization of available experimental data, as well as assessing the accuracy and reliability of methods for calculating molecules containing heavy elements.

A 20-electron generalized relativistic effective core potential (20e-GRECP) has been generated for mercury and tested in numerical two-component Hartree-Fock (HF) calculations by comparison with other RECP and all-electron Dirac-Fock (DF) studies. The suitability of the GRECP for describing correlation effects was examined in atomic calculations. Significant improvement in the accuracy of reproducing all-electron Dirac-Coulomb data for the GRECP as compared with other RECPs treating explicitly the same number of electrons was demonstrated in these calculations. Here we present GRECP calculations of spectroscopic constants for the HgH molecule and its cation in the framework of the relativistic coupled cluster (RCC) method.

II. THE GRECP METHOD

The GRECP method has been described in detail elsewhere. In this method, the radial oscillations of the valence and outer core spinors are smoothed in the inner core region of an atom to reduce the number of primitive Gaussian basis functions required for appropriate description of these spinors in subsequent molecular calculations. This smoothing also allows one to exclude the small components of the four-component Dirac spinors from the GRECP calculations, with relativistic effects being taken into account by \( j \)-dependent effective potentials. These \( U_{nlj} \) potentials are derived by inversion of the nonrelativistic-type HF equations in the \( jj \)-coupling scheme for a “pseudoatom”, in which the inner core electrons are removed:

\[
U_{nlj}(r) = \tilde{\varphi}_{nlj}^{-1}(r)\left[\frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l + 1)}{2r^2} + \frac{Z_{ic}}{r} - \tilde{J}(r) + \tilde{K}(r)\right] + \varepsilon_{nlj}\tilde{\varphi}_{nlj}(r) + \sum_{n' \neq n} \varepsilon_{n'nlj}\tilde{\varphi}_{n'lj}(r),
\]

where \( Z_{ic} \) is the charge of the nucleus and inner core electrons, \( \tilde{J} \) and \( \tilde{K} \) are Coulomb and exchange operators calculated with the \( \tilde{\varphi}_{nlj} \) pseudospinors, \( \varepsilon_{nlj} \) are the one-electron energies of the corresponding spinors, and \( \varepsilon_{n'nlj} \) are off-diagonal Lagrange multipliers. The GRECP components, \( U_{nlj} \), are usually fitted by Gaussian functions to be employed in molecular calculations with Gaussian basis sets. Potentials in conventional RECPs are constructed only for nodeless pseudospinors, because division by zero appears in equation (1) for pseudospinors with nodes. This problem is overcome in the GRECP method by interpolating...
the potentials in the vicinity of these nodes. This allows one to generate different potentials, $U_{vlj}$ and $U_{clj}$, for outer core and valence pseudospinors, unlike the conventional RECP approach.

The GRECP operator has the form

$$
U = U_{vL}^{\text{AGREP}}(r) + \sum_{l=0}^{L-1} \left[ U_{cl}^{\text{AGREP}}(r) - U_{vl}^{\text{AGREP}}(r) \right] \mathbf{P}_l + \sum_{l=1}^{L} U_{vl}^{\text{EGSOP}} \mathbf{P}_l 
\quad + \sum_{c} \sum_{l=0}^{L} U_{cl}^{\text{AGREP}}(r) \mathbf{P}_l + \sum_{c} \sum_{l=1}^{L} U_{cl}^{\text{EGSOP}} \mathbf{P}_l,
$$

(2)

$$
\mathbf{P}_l = \sum_{m=-l}^{l} \langle lm | lm \rangle,
$$

where $|lm \rangle \langle lm |$ is the projector on the spherical function $Y_{lm}$ and $L$ is one more than the highest orbital angular momentum of the inner core spinors.

The $U$ operator may be split into spin-averaged and spin-dependent parts. The first part includes spin-averaged generalized relativistic effective potentials (AGREP), given by

$$
U_{vl}^{\text{AGREP}}(r) = \frac{l+1}{2l+1} U_{vl+}(r) + \frac{l}{2l+1} U_{vl-}(r),
$$

$$
U_{cl}^{\text{AGREP}}(r) = \frac{l+1}{2l+1} V_{cl+}(r) + \frac{l}{2l+1} V_{cl-}(r),
$$

$$
V_{cl±}(r) = [U_{cl±}(r) - U_{vl±}(r)] \mathbf{P}_{cl±}(r) - \sum_{c'} \mathbf{P}_{cl±}(r) \left[ \frac{U_{cl±}(r) + U_{cl±}(r)}{2} - U_{vl±}(r) \right] \mathbf{P}_{c'\ell±}(r),
$$

(3)

where $\mathbf{P}_{cl±}(r)$ is the radial projector on the outer core pseudospinor $\tilde{\varphi}_{cl±}(r)$ and $±$ means \( j = |l ± 1/2| \). Obviously, these components can be used to account for spin-independent relativistic effects in codes employing the $\Lambda S$-coupling scheme. The other terms in $U$ are the components of the effective spin-orbit interaction operator, called effective generalized spin-orbit potentials (EGSOP),

$$
U_{vl}^{\text{EGSOP}} = \frac{2}{2l+1} [U_{vl+}(r) - U_{vl-}(r)] \mathbf{P} \mathbf{I} \cdot \mathbf{s},
$$

$$
U_{cl}^{\text{EGSOP}} = \frac{2}{2l+1} [V_{cl+}(r) - V_{cl-}(r)] \mathbf{P} \mathbf{I} \cdot \mathbf{s}.
$$

(4)

Two of the major features of the GRECP method are generation of effective potential components for pseudospinors which may have nodes, and adding non-local terms with projectors on the outer core pseudospinors (second line in equation (2)) to the standard semi-local terms (first line in equation (2)) of the effective potential operator. Other distinctive features of the GRECP generation as compared to previous RECP schemes are given in reference [16]. As pointed out earlier, the form (2) of the GRECP operator is optimal for calculating states in which changes in occupation numbers of outer core shells relative to the state used for the GRECP generation are much smaller than 1.
III. THE RCC METHOD

The Fock-space RCC method has been described in previous papers and reviews and only a brief summary is given here. Starting from the nonrelativistic-type Hamiltonian $\mathbf{H}$ containing the AGREP operator $U^{AGREP}$, the one-electron HF orbitals are obtained in an SCF procedure. Matrix elements of the EGSOP operator, $U^{EGSOP}$, as well as other one- and two-electron integrals, are calculated in the basis of the resulting spin-orbitals. Spin-orbit interaction (described by the $U^{EGSOP}$ operator) and correlation are then included by the two-component Fock-space coupled-cluster (CC) method, using the exponential valence-universal wave operator $\Omega = \exp(\mathbf{T})$. The RCC expansion is currently truncated at the singles and doubles level (RCC-SD). The nonrelativistic CC (NRCC) version, in which the spin-orbit interaction is not taken into account, allows one to include also the triple cluster amplitudes (NRCC-SDT). In the Fock-space CC method one starts from a reference state (closed-shell in our implementation), correlates it, then adds (or removes) one electron, recorrelating the new $N+1$ (or $N-1$) electron system, and so on, until all the states of interest are attained. The electrons can be added in (or removed from) a number of valence spin-orbitals, resulting in a multireference approach characterized by a model space $P$ of some selected states. The cluster amplitudes are determined at the stage (or Fock-space sector) where they first appear and are not changed at higher sectors, leading to a valence-universal wave operator. The effective Hamiltonian

$$\mathbf{H}_{\text{eff}} = \mathbf{P}\mathbf{H}\mathbf{\Omega}\mathbf{P}, \quad (5)$$

where $\mathbf{P}$ is the projector onto the model space $P$, is diagonalized to give simultaneously the energies of all $P$-space states correlated at the RCC-SD level relative to the correlated energy of the reference state.

Two series of Fock-space calculations were performed. The ground state of the HgH\(^+\) ion served as reference in the first series (denoted RCC-SD-1), and the Fock-space scheme was

$$\text{HgH}^+ \rightarrow \text{HgH}, \quad (6)$$

with electrons added in the lowest unoccupied $\sigma$ and $\pi$ orbitals of HgH\(^+\). The second series (RCC-SD-2) started from the ground state of the HgH\(^-\) ion as reference, using the Fock-space scheme

$$\text{HgH}^- \rightarrow \text{HgH} \rightarrow \text{HgH}^+, \quad (7)$$

with electrons removed from the highest occupied $\sigma$ orbital of HgH\(^-\).

The MOLGEP and MOLCAS codes were employed in the molecular GRECP/SCF calculations. The RCC-SD and NRCC-SDT program packages were interfaced with the MOLGEP/MOLCAS codes, allowing two-component GRECP/RCC-SD calculations in the intermediate coupling scheme and one-component AGREP/NRCC-SDT calculations in the $\Lambda S$ coupling scheme. Nonrelativistic kinetic energy operators and relativistic effective $j$-dependent potentials were employed in the two-component calculations.
IV. BASIS SET

The basis set for mercury was optimized in atomic RCC-SD calculations with the help of the procedure proposed earlier. The basis functions were generated in HF calculations of numerical orbitals for some neutral atomic or positively charged ionic states. The HFJ code was employed for the HF calculations with the GRECP.

We start with a HF calculation of the \( 6s^2 \) state of Hg with the GRECP operator to obtain numerical \( 5s_{1/2}, 5p_{1/2}, 5p_{3/2}, 5d_{3/2}, 5d_{5/2}, 6s_{1/2} \) pseudospinors. The \( 6p_{1/2} \) and \( 6p_{3/2} \) pseudospinors are then derived from numerical calculations for the \( LS \) averages of the \( [6s^1]6p^1 \) configuration. The configuration notation used here puts in square brackets shells frozen after the initial calculation of the \( 6s^2 \) state; the \( 5s, 5p \) and \( 5d \) shells are understood to be in the square brackets and are dropped for brevity.

The \( \varphi_{5s}, \varphi_{5p}, \varphi_{5d}, \varphi_{6s}, \varphi_{6p} \) and \( \Delta \varphi_{5p}, \Delta \varphi_{5d}, \Delta \varphi_{6p} \) numerical radial orbitals are derived from the HF orbitals \( \varphi_{nl\pm} \), with \( \pm \) denoting \( j = l \pm 1/2 \), by

\[
\varphi_{ns}(r) = \varphi_{ns+}(r),
\]
\[
\varphi_{nl}(r) = N[\varphi_{nl+}(r) + \varphi_{nl-}(r)] \quad \text{for } l = 1, 2,
\]
\[
\Delta \varphi_{nl}(r) = N'[\varphi_{nl+}(r) - \varphi_{nl-}(r)] \quad \text{for } l = 1, 2,
\]

where \( N \) and \( N' \) are normalization factors. The reference basis set is constructed from the \( 5s, 5p, 5d, 6s, 6p \) orbitals. An RCC-SD calculation with the GRECP operator is carried out in this basis with the 18 external electrons of Hg correlated. The Hg\(^+\) and Hg\(^{2+}\) have, obviously, one or two fewer correlated electrons. The Fock-space scheme for this calculation is

\[
\text{Hg}^{2+} \rightarrow \text{Hg}^+ \rightarrow \text{Hg},
\]

with electrons added in the \( 6s \) and \( 6p \) one-electron states.

The next stage involves HF calculations of a series of \( 7p \) orbitals with the AGREP operator for configurations corresponding to the neutral Hg and a set of Hg\(^{n+}\) ions, namely \([5d^{10}6s^1]7p^1\), \([5d^{10}-(n-1)]7p^1\) \((n = 1, 2, \ldots 10)\), \([5p^{6}-(n-1)]7p^1\) \((n = 11, 12, \ldots 16)\), etc. The \( 5p \) and \( 5d \) orbitals in these calculations are obtained from Eq. (4). The \( 7p \) orbitals derived this way are localized in different spatial regions. A series of Schmidt-orthogonalized basis sets is now formed by adding each of these \( 7p \) orbitals to the reference basis. Basis sets obtained by addition of the \( \Delta \varphi_{5p} \) and \( \Delta \varphi_{6p} \) orbitals are also included. An RCC-SD calculation of nine low-lying states (the ground \( 6s^2 \, \text{I}_S^0 \), excited \( 6s^16p^1 \, \text{I}_S^{0,1,2} \) and \( \text{I}_P^1 \) states of the neutral atom, \( 6s^{1} 2S_{1/2} \) and \( 6p^{1} 2P_{1/2,3/2} \) of Hg\(^+\), and \( \text{I}_S^0 \) of Hg\(^{2+}\) ) with the GRECP operator is performed for each of these bases. Similar series of calculations are carried out for the \( 7s \) orbitals instead of the \( 7p \), and also for the \( 6d, 5f, 5g \) orbitals. The principal quantum number of these virtual orbitals is taken to be one higher than the maximum principal quantum number of the corresponding orbitals in the reference basis set, to avoid large overlap of the new and previously selected orbitals. For each basis set, the largest change among all possible one-electron transition (excitation or ionization) energies between the nine states listed above relative to the results of the reference basis set is found. This change is then multiplied by a factor of \( 1/(2l + 1) \), where \( l \) is the angular momentum quantum
The number of the added orbital. The orbital which gives the largest energy change is added to the reference basis set. The procedure is repeated for the next series of virtual orbitals, resulting in a step by step expansion of the reference basis and diminution of changes in the transition energies. The procedure is terminated when the largest transition energy change after adding the orbital goes down to about 15 cm$^{-1}$. The numerical radial orbitals are then approximated by Gaussian functions and a (14,12,9,3,2)/[7,7,4,2,1] basis set for molecular calculations is finally produced. This algorithm of basis set generation is designed to account primarily for correlation and spin-orbit effects which have different contributions to the states under consideration, so that possible omissions in the resulting basis will cause nearly state-independent errors and give accurate transition energies.

It is important to note that the average radii and space localization of the $f$ and $g$ correlation functions generated above are intermediate between those of the 5$d$ and 6$s$, 6$p$ functions. These $f$ and $g$ functions describe primarily correlation between valence and outer core (5$d$) electrons. The transition energy changes (without the $1/(2l+1)$ factor) resulting from the addition of the 5$f$, 5$g$, and 6$f$ functions are up to 5800, 790, and 240 cm$^{-1}$, respectively.

The (8,4,3)/[4,2,1] basis set from the ANO-L library is used for hydrogen.

**V. RESULTS AND DISCUSSION**

As demonstrated in an earlier publication, the energy contributions from correlations with the 5$s$ and 4$f$ shells of Hg largely cancel each other. These electrons may therefore be frozen in correlation calculations, with resulting errors of up to 200 cm$^{-1}$ in one-electron excitation or ionization energies. The molecular RCC-SD calculations in the present paper are carried out with 19 correlated electrons of Hg (18 for HgH$^+$). The molecular orbital originating from the 5$s$ orbital of Hg is frozen after the HF calculation, while the 4$f$, 4$d$, 4$p$, 4$s$ and deeper core electrons of Hg are excluded from explicit consideration by using the 20e-GRECP.

The computational effort in RCC-SD calculations increases rapidly with the size of the basis. The highest orbital angular momentum in the basis was therefore set to 4 ($g$-type harmonics). This truncation leads to errors of up to 400 cm$^{-1}$ in one-electron transition (excitation and ionization) energies of the Hg atom (Ref. [1]). However, errors for transitions which do not involve excitation or ionization of the tightly bound 6$s$ electron are below 150 cm$^{-1}$. The inherent 20e-GRECP errors are up to 100 cm$^{-1}$ (Ref. [1]). Errors caused by using intermediate rather than $jj$ coupling are up to 100 cm$^{-1}$, as one can deduce from Table 4, which reports results of the 20e-GRECP/RCC-SD calculation on the Hg atom with the 18 external electrons correlated in the (14,12,9,3,2)/[7,7,4,2,1] basis described above. The Fock-space scheme employed is

$$
\text{Hg}^{2+} \leftarrow \text{Hg}^+ \leftarrow \text{Hg} \rightarrow \text{Hg}^- \downarrow \text{Hg}^* \uparrow
$$

with electrons added in the 6$p$, 7$s$, 7$p$ orbitals and removed from the 6$s$ orbital.
In a previous paper\cite{11}, describing atomic Hg calculations, it was concluded that neglect of virtual triple excitations is the main cause for the differences between experimental data and results of a 34-electron RCC-SD calculations with a large basis including up to $h$-type functions ($l \leq 5$). The contribution of triples is estimated in the present work by resorting to spin-averaged (i.e., with AGREP only) calculations and assuming that triples correction to the shells correlated does not change much upon going to the fully relativistic scheme. These corrections are taken as the differences between the AGREP/NRCC-SDT and AGREP/NRCC-SD total energies for each state. The [7, 7, 4, 2, 1] Hg basis generated above was used, and two cases were considered, with 12 and 18 electrons correlated (12e-T and 18e-T) in the Hg atom. Table I shows that differences between the RCC-SD(12e-T) and RCC-SD(18e-T) results are relatively small. It is therefore sufficient to take into account in molecular calculations triple cluster excitations of the 12 external electrons of Hg. The approximate inclusion of triple excitations for 18 electrons in the intermediate coupling RCC-SD calculations leads to an average error of 270 cm$^{-1}$ relative to experiment in the six transitions listed in Table I. The largest error is 540 cm$^{-1}$, for the excitation to the $^1P_1$ state. Considering the Fock-space scheme\cite{12} and the approximations employed, this is in line with results expected from the RCC-SDT method.

Molecular GRECP/RCC-SD and AGREP/NRCC-SDT calculations were carried out for 13 internuclear distances from 2.637 to 3.837 a.u., with intervals of 0.1 a.u. Molecular spectroscopic constants were calculated by the Dunham method in the Born-Oppenheimer approximation, using the DUNHAM-SPECTR code\cite{21}.

The effect of basis set superposition errors (BSSEs) in the 19-electron RCC-SD calculation is demonstrated in Table II. These errors are quite sizable, up to 1800 cm$^{-1}$ for dissociation energies. The main contribution to the BSSE arises from correlation in the core region. Details of the BSSE calculation may be found in Ref.\cite{22}. These errors are mainly due to limitations on the size of the basis which can be used practically in molecular RCC calculation. As stated in section IV, the algorithm for generating the basis set aims primarily to optimize excitation and ionization energies of the lowest lying states in mercury. Since the transitions considered involve changes in valence shell occupation only, the resulting basis may be nearly complete in the valence region but deficient in the core region. The BSSE will therefore have weak dependence on the valence-shell configuration, and may be estimated quite accurately by the counterpoise correction (CPC) method. Table II shows that different valence states used to calculate the CPC yield very similar spectroscopic constants. The basis generated above is therefore compact enough and can be used in precise calculations provided the CPC correction is applied. All the GRECP/RCC-SD and AGREP/NRCC-SDT results reported in subsequent tables were corrected using CPCs calculated for the Hg $6s^2$ state with a ghost H atom. CPCs calculated for the ground state of the H atom are about 1 cm$^{-1}$, and are therefore ignored.

Results for the ground states of HgH and HgH$^+$ are collected in Table III. RCC-SD spectroscopic constants have sizable errors; they also show considerable differences between the two Fock-space schemes. Such differences are caused by the truncation of the CC cluster operator, and indicate significant contributions of higher excitations. The effect of virtual triple excitations to individual state energies was estimated from the difference of AGREP/NRCC-SDT and AGREP/NRCC-SD values. Two sets of triples calculations were carried out, correlating 3 and 13 electrons, and denoted by (3e-T) and (13e-T), respectively.
The full RCC-SD basis was used for 3 electrons, but a reduced basis, \([5,5,3,1]\) on Hg and \([3,2]\)
on H, was used in the 13-electron case. Spectroscopic constants of the HgH ground state which include13-electron triples corrections are in very good agreement with experiment. Dependence on the Fock-space scheme is also minimal. Similar behavior is exhibited by theground state of HgH\(^+\). Here, results obtained with scheme (5) (i.e. in the (0, 0) Fock-space sector)are slightly better than those of scheme (7) (in the (2, 0) sector) as might be expected. Still, differences are rather small.

Results for the excited \(^2\Pi_{1/2}\) and \(^2\Pi_{3/2}\) states with the leading \(\sigma^2\pi^1\) configuration arepresented in table IV. The triples corrections to the spectroscopic constants are smaller than for the HgH ground state, so that the RCC-SD values are in good agreement with experiment. Inclusion of triple excitations does produce some improvement.

VI. SUMMARY AND CONCLUSION

Generalized relativistic effective core potentials were used in the framework of the Fock-space relativistic coupled-cluster method to calculate spectroscopic constants of HgH andHgH\(^+\) ground states as well as HgH low excited states. Twenty one electrons were treatedexplicitly in the molecule, of which 19 were correlated by RCC. Basis set superposition errors weredevaluated by counterpoise correction, and contributions of triple excitations of the external 13 electrons were estimated (without accounting for spin-orbit coupling) in a reduced basis. The resulting spectroscopic constants of the HgH and HgH\(^+\) states are invery good agreement with experiment, with errors on the order of a few mbohr for \(R_e\), tens ofwavenumbers for excitation energies and vibrational frequencies, and proportionately for other properties.

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[25] G. Herzberg, *Molecular spectra and Molecular structure. I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
TABLE I. Ionization and excitation energies of the lowest-lying states of atomic mercury obtained from the 20e-GRECP/18e-RCC-SD calculations with a \((14, 12, 9, 3, 2) /[7, 7, 4, 2, 1]\) basis set in the intermediate and \(jj\)- coupling schemes, without and with triples correction for 12 and 18 external electrons. All values are in cm\(^{-1}\).

| State | Expt.\(^a\) | RCC-SD | RCC-SD | RCC-SD(12e-T) | RCC-SD(18e-T) |
|-------|-------------|--------|--------|---------------|---------------|
| \(5d^{10}6s^2(1S_0) \rightarrow 5d^{10}6s^16p^1(3P_0)\) | 37645 | 37959 | 38055 | 37926 | 37971 |
| \(5d^{10}6s^16p^1(3P_1)\) | 39412 | 39756 | 39826 | 39697 | 39742 |
| \(5d^{10}6s^16p^1(3P_2)\) | 44043 | 44346 | 44322 | 44193 | 44238 |
| \(5d^{10}6s^16p^1(1P_1)\) | 54069 | 54915 | 54914 | 54619 | 54607 |
| \(5d^{10}6s^1(2S_1/2)\) | 84184 | 83688 | 83680 | 84015 | 84240 |
| \(5d^{10}1S_0) \rightarrow \) & \(5d^{10}6s^1(2S_1/2)\) | 151280 | 150018 | 149977 | 150898 | 151094 |

\(^a\text{Ref. [23].}\)
### TABLE II. Spectroscopic constants of the ground states of the HgH molecule and HgH⁺ ion from GRECP/RCC-SD-1 calculations with different BSSE corrections. $R_e$ is in Å, $D_e$ in eV, $Y_{02}$ in $10^{-6}$ cm$^{-1}$, other values in cm$^{-1}$.

|                  | $R_e$ | $w_e$ | $D_e$ | $B_e$ | $w_e x_e$ | $\alpha_e$ | $-Y_{02}$ |
|------------------|------|-------|-------|-------|-----------|-----------|----------|
| **HgH (σ²σ¹⁻) ²Σ⁺$_{1/2}$** |
| Uncorrected for BSSE | 1.675 | 1686  | 0.50  | 5.99  | 57        | 0.262     | 306      |
| CPC from Hg 6s²   | 1.702 | 1597  | 0.34  | 5.80  | 56        | 0.259     | 310      |
| CPC from Hg 6s¹6p¹ (³P₀) | 1.701 | 1598  | 0.34  | 5.81  | 56        | 0.261     | 311      |
| CPC from Hg 6s¹6p¹ (³P₁) | 1.701 | 1599  | 0.34  | 5.81  | 56        | 0.259     | 310      |
| CPC from Hg 6s¹6p¹ (³P₂) | 1.701 | 1599  | 0.34  | 5.81  | 57        | 0.259     | 310      |
| CPC from Hg 6s¹6p¹ (¹P₁) | 1.701 | 1599  | 0.34  | 5.81  | 56        | 0.259     | 310      |
| **HgH⁺ (σ²⁻) ¹Σ⁺ₓ** |
| Uncorrected for BSSE | 1.570 | 2145  | 2.91  | 6.82  | 41        | 0.205     | 277      |
| CPC from Hg 6s²   | 1.588 | 2067  | 2.72  | 6.66  | 39        | 0.199     | 278      |
| CPC from Hg⁺ 6s¹  | 1.588 | 2069  | 2.73  | 6.67  | 39        | 0.199     | 278      |
TABLE III. Spectroscopic constants of the ground states of the HgH molecule and HgH$^+$ ion. The GRECP/RCC results are corrected by CPCs calculated for the Hg 6$s^2$ state. $R_e$ is in Å, $D_e$ in eV, $Y_{02}$ in $10^{-6}$ cm$^{-1}$, other values in cm$^{-1}$.

|                        | $R_e$  | $w_e$  | $D_e$  | $B_e$  | $w_e x_e$ | $\alpha_e$ | $-Y_{02}$ |
|------------------------|--------|--------|--------|--------|-----------|------------|----------|
| **HgH (σ$^2$σ$^1$)$^2\Sigma_{1/2}^+$** |         |        |         |        |           |            |          |
| **Experiment**         |        |        |         |        |           |            |          |
| Ref. 24                | [1.766]$^a$ | [1203]$^a$ | 0.46    | 5.39$^a$ |           |            | [395]$^a$ |
| Ref. 3                 | 1.741  | 1385   | 0.46    | 5.55   | 75        | 0.271      |          |
| Ref. 25                | 1.740  | 1387   | 0.46    | 5.55   | 83        | 0.312      | 344      |
| Ref. 4                 | 1.735  | 1421   | 0.46    | 5.59   | 121       | 0.404      | 346      |
| **Present calculations**|        |        |         |        |           |            |          |
| GRECP/RCC-SD-1         | 1.702  | 1597   | 0.34    | 5.80   | 56        | 0.259      | 310      |
| GRECP/RCC-SD-2         | 1.730  | 1419   | 0.32    | 5.61   | 85        | 0.349      | 361      |
| GRECP/RCC-SD(3e-T)-1   | 1.714  | 1528   | 0.40    | 5.72   | 65        | 0.287      | 326      |
| GRECP/RCC-SD(3e-T)-2   | 1.733  | 1386   | 0.37    | 5.60   | 92        | 0.374      | 376      |
| GRECP/RCC-SD(13e-T)-1  | 1.730  | 1424   | 0.41    | 5.62   | 81        | 0.343      | 358      |
| GRECP/RCC-SD(13e-T)-2  | 1.738  | 1362   | 0.41    | 5.56   | 93        | 0.380      | 382      |
| **Other calculations**  |        |        |         |        |           |            |          |
| RECP/MRD-C$^{[11]}$     | 1.777  | 1309   | 0.32    |        |           |            |          |
| PP/ACPF+SO$^{[6],b}$   | 1.722  | 1414   | 0.44    |        |           |            |          |
| ESC/CCSD+CPC$^{[8]}$    | 1.763  | 1263   | 0.28    |        |           |            |          |
| AIMP/CCSD+CPC$^{[8]}$   | 1.762  | 1264   | 0.29    |        |           |            |          |

|                        | $R_e$  | $w_e$  | $D_e$  | $B_e$  | $w_e x_e$ | $\alpha_e$ | $-Y_{02}$ |
|------------------------|--------|--------|--------|--------|-----------|------------|----------|
| **HgH$^+$ (σ$^2$)$^1\Sigma_0^+$** |         |        |         |        |           |            |          |
| **Experiment**         |        |        |         |        |           |            |          |
| Ref. 24                | 1.594  | 2028   | (3.11)$^c$ | 6.61 | 41        | 0.206      | 285      |
| Ref. 25                | 1.594  | 2034   | (2.4)$^c$ | 6.61 | 46        | 0.206      | 285      |
| **Present calculations**|        |        |         |        |           |            |          |
| GRECP/RCC-SD-1$^{[d]}$  | 1.588  | 2067   | 2.72    | 6.66   | 39        | 0.199      | 278      |
| GRECP/RCC-SD-2         | 1.586  | 2149   | 2.42    | 6.68   | 21        | 0.153      | 259      |
| GRECP/RCC-SD(3e-T)-2   | 1.592  | 2060   | 2.55    | 6.63   | 31        | 0.187      | 276      |
| GRECP/RCC-SD(13e-T)-1  | 1.591  | 2044   | 2.70    | 6.64   | 41        | 0.208      | 282      |
| GRECP/RCC-SD(13e-T)-2  | 1.596  | 2051   | 2.59    | 6.60   | 32        | 0.185      | 275      |
| **Other calculations**  |        |        |         |        |           |            |          |
| PP/ACPF$^{[b]}$         | 1.593  | 1959   | 2.69    |        |           |            |          |

$^a$Cited in Ref. 24 as corresponding to the zero vibrational level.
$^b$See original work [6] for results derived by other calculation methods.
$^c$Cited in Ref. 24, 25 as uncertain.
$^d$GRECP/RCC-SD(3e-T)-1 results are identical with GRECP/RCC-SD-1, as triple excitations do not occur for two correlated electrons.
TABLE IV. Spectroscopic constants for excited states of the HgH molecule. The GRECP/RCC results are corrected by CPCs calculated for the Hg 6s$^2$ state. $R_e$ is in Å, $Y_{02}$ in $10^{-6}$ cm$^{-1}$, other values in cm$^{-1}$.

|       | $R_e$      | $w_e$     | $T_e$     | $B_e$   | $w_e x_e$ | $\alpha_e$ | $-Y_{02}$ |
|-------|------------|-----------|-----------|---------|------------|------------|-----------|
| **HgH$^*$ ($\sigma^2\pi^1$) $^2\Pi_{1/2}$** |            |           |           |         |            |            |           |
| **Experiment** |            |           |           |         |            |            |           |
| Ref. 24 | [1.601]$^a$ | [1939]$^a$ | [6.56]$^a$ | [64]$^a$ | [0.242]$^a$ | [285]$^a$ |           |
| Ref. 25 | 1.586      | 2066      | 24578     | 6.68    |            |            |           |
| Ref. 3  | 1.583      | 2068      | 24590     | 6.70    | 65         | 0.267      |           |
| Ref. 24 | 1.583      | 2031      | 24609     | 6.71    | 47         | 0.219      |           |
| **Present calculations** |            |           |           |         |            |            |           |
| GRECP/RCC-SD-1 | 1.578      | 2100      | 24044     | 6.75    | 39         | 0.201      | 280       |
| GRECP/RCC-SD(3e-T)-1 | 1.581      | 2080      | 24229     | 6.72    | 40         | 0.205      | 283       |
| GRECP/RCC-SD(13e-T)-1 | 1.582      | 2065      | 24688     | 6.71    | 44         | 0.215      | 286       |
| **Other calculations** |            |           |           |         |            |            |           |
| PP/CASSCF+MRCI+CIPSO | 1.603      | 1946      | 25004     |         |            |            |           |
| RECP/MRD-CI | 1.615      | 2023      | 25664     |         |            |            |           |
| **HgH$^*$ ($\sigma^2\pi^1$) $^2\Pi_{3/2}$** |            |           |           |         |            |            |           |
| **Experiment** |            |           |           |         |            |            |           |
| Ref. 3  | 1.581      | 2091      | 28283     | 6.73    | 61         | 0.200      |           |
| Ref. 24 | 1.579      | 2068      | 28274     | 6.74    | 43         | 0.230      | [282]$^a$ |
| Ref. 25 | 1.580      | 2067      | 28256     | 6.73    | 42         | 0.214      |           |
| **Present calculations** |            |           |           |         |            |            |           |
| GRECP/RCC-SD-1 | 1.576      | 2117      | 27629     | 6.77    | 37         | 0.197      | 278       |
| GRECP/RCC-SD(3e-T)-1 | 1.578      | 2098      | 27815     | 6.75    | 38         | 0.200      | 281       |
| GRECP/RCC-SD(13e-T)-1 | 1.579      | 2083      | 28275     | 6.74    | 42         | 0.210      | 284       |
| **Other calculations** |            |           |           |         |            |            |           |
| PP/CASSCF+MRCI+CIPSO | 1.610      | 1930      | 28714     |         |            |            |           |
| RECP/MRD-CI | 1.615      | 2033      | 28490     |         |            |            |           |

$^a$Cited in Ref. 24, 25 as corresponding to the zero vibrational level.