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ABSTRACT

A highly accurate, $(HF)_2$ potential energy surface (PES) is constructed based on *ab initio* calculations performed at the coupled-cluster single double triple level of theory with an aug-cc-pVQZ-F12 basis set at about 152 000 points. A higher correlation correction is computed at coupled-cluster single double triple quadruple level for 2000 points and is considered alongside other more minor corrections due to relativity, core-valence correlation, and Born–Oppenheimer failure. The analytical surface constructed uses 500 constants to reproduce the *ab initio* points with a standard deviation of 0.3 cm^{-1}. Vibration–rotation–inversion energy levels of the HF dimer are computed for this PES by variational solution of the nuclear-motion Schrödinger equation using the program WAVR4. Calculations over an extended range of rotationally excited states show very good agreement with the experimental data. In particular, the known empirical rotational constants B for the ground vibrational states are predicted to better than about 2 MHz. B constants for excited vibrational states are reproduced several times more accurately than by previous calculations. This level of accuracy is shown to extend to higher excited inter-molecular vibrational states v and higher excited rotational quantum numbers (J, K_a).

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I. INTRODUCTION

Recently, we published an analysis[1] of a 30 year old rotation-inversion spectrum of the HF dimer because developments in theory meant that it became possible to retrieve new information from such an old study. In particular, we used the variational nuclear-motion program WAVR4[2] that employs exact kinetic energy within the Born–Oppenheimer approximation to make predictions whose accuracy is essentially determined by the quality of the potential energy surface (PES) used. Our study used an accurate *ab initio* PES due to Huang *et al.*[3] One of the demonstrations of the accuracy of this PES is the predictions of the B rotational constants for the ground vibrational state with an accuracy of about 50 MHz. Such accuracy allowed us to assign several new branches of an inversion–rotation submillimeter spectrum originally reported in 1990.[4] However, for many purposes, the accuracy achieved by our calculations was still not sufficient. In particular, we could not extrapolate reliably to higher rotational quantum numbers such as K greater than 4, where $K = K_a$ is the asymmetric top quantum number that gives rise to pronounced subbands in the HF dimer spectrum. As a result, we could not assign lines belonging to the $K = 5$ subband; such lines are yet to be assigned in an HF dimer spectrum. We also note submillimeter inversion–rotation spectra[4,5]; very extensive experimental studies of the far infrared (FIR) HF dimer spectrum were performed by Quack and Suhm.[6–8] Moreover, information on states with $K > 4$ was not obtained in these FIR publications. Another limitation in analyzing the inversion–rotation spectrum caused by the accuracy of our calculations is the inability to fix definitive J values to the $v_4 = 1$ branch newly assigned in Ref. 1.

Thus, increased accuracy variational calculations for the HF dimer spectrum are motivated by the desire to complete the analysis

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of the 1990 spectrum. However, there is another important motivation for accurate studies of $(HF)_2$. The similarity between the HF and water dimers, which was described in detail in our previous study,[1] means one can use the HF dimer observed minus calculated discrepancies to provide an estimate for the corresponding water dimer discrepancies for calculations performed at a similar level of *ab initio* theory. This is important because the HF dimer is one of the few molecular complexes for which gas-phase high resolution spectra exist, which means that observed minus calculated discrepancies can be characterized for the highly excited rotational K states of $(HF)_2$. In $(H_2O)_2$, such states are thought to play a significant but poorly characterized role in absorption in the Earth's atmosphere[9,10] and by analogy in the atmospheres of water-rich exoplanets.[11] Currently, these states of $(H_2O)_2$ cannot be characterized in high resolution experiments. Consequently, the HF dimer discrepancies provide a unique means of characterizing the corresponding discrepancies in water dimer spectra. Hence, a high-level *ab initio* model for the rotation–vibration–inversion (RVI) spectrum of the HF dimer will be an important aid in constructing a similarly accurate mode for the RVI spectrum of the water dimer.

Let us put the present *ab initio* study of the HF dimer PES in a historical context. In the late 1980s, analysis of experimental FIR spectra of the HF dimer had already been facilitated by variational calculations using both *ab initio* and fitted PESs.[12–15] These calculations achieved an accuracy of few wavenumbers for vibrational levels. The 1990s analysis noticed a steady improvement in both *ab initio* PESs[16] and the PESs fitted to the experimental values of the tunneling splittings and vibrational energies.[17] Since then, major improvement in the PES was achieved by recent calculations that used several *ab initio* points to characterize the PES: for example, in the recent paper, Huang *et al.*[3] used 100 000 points, whereas in the 1990s, the typical number of *ab initio* points per PES was about 3000. In the following, we show that this increased number of points is important for fully characterizing the PES. At the same time, the step-up in the basis from aug-cc-pvTZ[12] to aug-cc-pvQZ[3] resulted in important improvements in the accuracy of the corresponding PES.

However, modern computer power and quantum chemistry software (such as MOLPRO[18] and MRCC[19] used in this work) can provide improvements in *ab initio* theory. In particular, developments have made feasible the use of the explicitly correlated F12 level of theory[20] and the inclusion of increased correlation in coupled-cluster (CC) calculations from CCSD(T) to CCSDT(Q) and even higher, where S means single excitations, D double, T triple, Q quadruple, and below P penta, and the parentheses denote a perturbative treatment. Minor corrections, such as those for the core-valence electron correlation, higher-order electron correlation, scalar relativistic effects, as well as the diagonal Born–Oppenheimer correction, can also be considered.

The choice of both the level of *ab initio* theory for the base PES and the various corrections depends on several factors. One is the time taken for the calculation of a single point. Another factor is the coordinate dependence of the correction on the coordinates. In particular, it is possible to quantify the difference between the corrections at some special points, such as dissociation, saddle point, or linear configuration point, and its values at the equilibrium point. In general, the larger such a difference is, the larger the influence on the RVI levels due to this correction is. An important point to consider here is the possible cancellation of errors. It is impossible to expect that calculations on such a large system will give complete convergence for the resulting PES. It is much more realistic to aim for a so-called Pauling point,[21,22] where a good result is obtained due to judicious exploitation of cancellation of errors.

An important part of our *ab initio* study is a comparison of our results with experimental values. Although a direct comparison is impossible, the use of the resulting PES in the variational solution of the nuclear-motion Schrödinger equation produces predictions that can be directly compared with the experiment. However, practically all the previous studies were limited to rotationless $(J = 0)$ calculations so that comparisons could only be made with vibrational term values. There is a dearth of high resolution experimental data on vibrational term values for $(HF)_2$. In many cases, only approximate extrapolated empirical values are available (see Table I of Ref. 1). Here, we use the variational program WAVR4[2] to compute $J > 0$ energy levels of the HF dimer. These calculations provide us with the B and Δ_K [the K-dependence of the tunneling splitting, see Eq. (1)] values that can be directly compared with ones obtained from high resolution experiments. The values of B and Δ_K are defined, for example, in Refs. 1 and 4 and are determined from the experimental frequencies using the following equation:

$$E(J,K,v) = \Delta_K \delta_{v,1} + F_K + B_J^v J(J+1) - D_J^v J^2 (J+1)^2 + H_J^v J^3 (J+1)^3. \tag{1}$$

In this paper, we present *ab initio* calculations for the $(HF)_2$ PES and the variational calculations of $J = 0$ and excited J states alongside a comparison of our results with the experimental data. Section II describes the electronic structure calculations and Sec. III presents the variational nuclear-motion calculations. The comparisons between our results and observations are analyzed in Sec. IV. Section V describes resonances between high K levels with Sec. VI giving results for the DF dimer. Section VII presents our conclusions.

II. *AB INITIO* CALCULATIONS OF THE HF DIMER PES

We used the MOLPRO package to calculate 152 000 points on the HF dimer PES using the CCSD(T)-F12b method with an aug-cc-pVQZ-F12 basis set, denoted as F12QZ. The use of explicitly correlated MP2 and CCSD(T) methods for the HF dimer was discussed already by Klopper *et al.*[23] In particular, the binding energy D_e of the HF dimer was obtained, using the CCSD(T)-R12 method with the quadruple/quintuple-zeta quality basis set, to be 1610 and 1585 cm^{-1} without and with the counterpoise correction, respectively. The basis sets used in this study were significantly larger. At the highest level of theory applied here, CCSD(T)-F12b/aug-cc-VQZ-F12, the basis set superposition error (BSSE) for D_e is calculated to be 1.9 cm^{-1}, which is an order of magnitude smaller than that of 25 cm^{-1} reported by Klopper *et al.*[23] The decision to calculate the PES at this level of theory was taken after the series of tests described in Sec. II A.

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A. Tests of the accuracy of *ab initio* calculations

To test the accuracy of *ab initio* calculations, four special points on HF dimer PES, namely the *trans* equilibrium configuration of C_s symmetry (E), the saddle point of C_{2h} symmetry (S), the linear HF–HF configuration (L), and the separated HF molecules at the dissociation limit (D), were chosen. The total energies of the HF dimer calculated by using the conventional CCSD(T) and explicitly correlated CCSD(T)-F12b methods with various basis sets of increasing quality are given in Table I. The structures of the HF dimer at each of these points were optimized at the corresponding level of theory.

As can be seen, the best results obtained by using the conventional and explicitly correlated CCSD(T) methods are very similar. In particular, the dissociation energy of the HF dimer is converged to better than 10 cm^{-1} at both the CCSD(T)/aug-cc-pV7Z and CCSD(T)-F12b/aug-cc-pVQZ-F12 levels of theory. Considering the computer resources involved in the calculations, the explicitly correlated method CCSD(T)-F12b with the aug-cc-pVQZ-F12 basis set seems to be the best choice for predicting the PES of the HF dimer; these calculations are denoted as F12QZ in the following.

As a next step, we considered the possible corrections to the total energy of the HF dimer, which were as follows:

1. The core-valence electron correlation correction (CV6) determined as a difference in the total energies calculated at the CCSD(T)/cc-pCV6Z level of theory and correlating either only valence or all electrons.
2. The first higher-order correlation correction called PQT below determined as a difference in the total energies obtained with the CCSDT(Q) and CCSD(T) methods, both with the aug-cc-pVTZ basis set.
3. The second higher-order correlation correction called PPD below determined as a difference in the total energies obtained with the CCSDTQ(P) and CCSDT(Q) methods, both with the aug-cc-pVDZ basis set.
4. The scalar relativistic correction (X2C) determined as a difference in the total energies calculated using either the exact-2-component[24] or nonrelativistic Hamiltonian at the CCSD(T)/aug-cc-pV5Z level of theory.
5. The adiabatic correction or Diagonal Born-Oppenheimer correction (DBOC) calculated at the CCSD/aug-cc-pCVTZ level of theory.

TABLE II. The total energy correction values (in milihartree) for the HF dimer calculated at the four special points (see Table I).

Point	CV6	PQT	PPD	X2C	DBOC	Sum
E	−129.805	−0.596	0.078	−174.219	5.668	−298.874
S	−129.791	−0.601	0.079	−174.231	5.674	−298.870
L	−129.818	−0.579	0.074	−174.208	5.671	−298.859
D	−129.777	−0.576	0.075	−174.243	5.689	−298.833

The total energy correction values calculated at the four special points of the HF dimer PES are given in Table II. The total sum of the corrections is given in the last column headed "sum."

For the four special points E, S, L, and D, the total corrections appeared to be nearly the same, being different from each other by at most 41 μhartree (9.0 cm^{-1}). At all of these points, the second higher-order correlation correction (PPD) was found to be about one order of magnitude smaller than the other corrections. Given its very high computational cost, this correction was, therefore, not further considered.

B. CCSD(T)-F12 *ab initio* calculations

Our test of the level of quantum chemistry theory, described in Sec. II A, allowed us to conclude that the basic PES comprising more than 100 000 points should be calculated using the F12QZ level of theory. The corrections to this PES, which make much smaller contributions, could be adequately represented by using a much less dense grid of about 2000 calculated points. These conclusions are supported by the predictive power of both the basic PES and the corrections, as described in the following.

As the computer cost of one F12QZ calculation using MOLPRO[18] is quite modest, we decided to compute 152 000 points

TABLE I. Total energies of the HF dimer calculated at four special points at the CCSD(T)/aug-cc-pV*n*Z and CCSD(T)-F12b/aug-cc-pV*n*Z-F12 levels of theory. The energies quoted for the points S, L, and D are relative (in cm^{-1}) to the total energy determined at point E (given in Hartree).

Point	n = T	n = Q	n = 5	n = 6	n = 7
			CCSD(T)/aug-cc-pVnZ		
E	−200.706 849	−200.762 297	−200.780 678	−200.786 923	−200.789 879
S	372.1	374.7	365.2	351.9	344.3
L	367.6	354.0	343.4	339.4	342.5
D	1689.0	1652.4	1627.3	1611.5	1602.0
			CCSD(T)-F12b/aug-cc-pVnZ-F12		
E	−200.781 707	−200.791 485			
S	353.1	341.7			
L	341.1	341.8			
D	1613.5	1601.6			

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to represent the basic PES. The grid was chosen so that every point should obey restrictions in energy (estimated using the PES of Huang *et al.*[3]), range of geometries, and a number of points. We used several sets of points; all points calculated lie in the range $1.4 \le r_{1,2} \le 2$ a$_0$, where r_1 and r_2 are the HF bond lengths, and $3 \le R \le 9$ a$_0$, where R is the HF–HF center-of-mass separation, with no restriction on the angles. Set 1 comprised a basic grid of 98 981 points with $E \le 3000$ cm^{-1}, where $E = 0$ is taken to be the minimum on the PES; this set provides coverage for the higher energies. Set 2 comprised 9199 points with E $\le$ 900 cm^{-1} chosen to increase the accuracy of the calculation of the lower-lying energy levels. Set 3 comprised 731 points with $E \le 4$ cm^{-1} to provide particularly accurate calculation of the minimum potential energy, which is useful for calculating the dissociation energy. Set 4 comprised 42 932 points with $E \le 1500$ cm^{-1} that were not used in the main fit, which provides only a check on the accuracy of the PES fits determined by the original points. The four regions of space bounded by the energy and geometric parameters were filled with points in the form of regular, irregular, or random (as in our case) grids. Geometries were generated by using standard FORTRAN function RANDU six times to generate random numbers $ra_{1...6}$ in the range $0 \le ra_{1...6} \le 1$, giving $r_{1,2} = 1.4 + 0.6ra_{1,2}$, $R = 3 + 6ra_3$, and $\theta_{1,2}, \phi = 180ra_{4,5,6}$. We use this random procedure to generate grids with energies below 3000, 900, and 1500 cm^{-1}. However, the grid below 4 cm^{-1}, near the equilibrium, was used a regular mesh comprising $3 \times 3 \times 3 \times 3 \times 3 \times 3 = 729$ points with $r_{1,2} = 1.742, 1.743, 1.744$, $R = 5.124, 5.134, 5.144$, $\theta_1 = 7.17°$, $8.17°, 9.17°$, $\theta_2 = 66.712°, 67.712°, 68.712°$, and $\phi = 178.0°, 179.0°, 180.0°$.

C. The fit of the CCSD(T)-F12 PES *ab initio* points to the analytical surface

The 152 000 points of the CCSD(T)-F12 surface were fitted as follows: First, we fitted these points to a 6D surface in polynomial form. We knew that it would be not a simple undertaking to fit such a complicated surface; however, we wanted to see what quality of the fit could be obtained in this way. The result was the 6D surface with many holes and several cm^{-1} standard deviations between the *ab initio* points and the analytical form. As shown in our previous study,[1] the quality of the PES due to Huang *et al.*[3] is very high, as the discrepancies parameters calculated using this *ab initio* PES and the experimental data are small. This should mean that the difference between the PES of Huang *et al.* and the *ab initio* points computed in this work should also be small. The deviation of our points from the PES of Huang *et al.* turned out to be not more than 30 cm^{-1} so an alternative method of fitting can be used. We decided not to fit the points directly but rather to represent their difference from the PES of Huang *et al.* This reduces the dynamic range of the problem from ~1500 to 30 cm^{-1}. Since the coordinate dependence of these differences turned out to be smooth, a significant improvement in the standard deviation of the fit could be obtained.

To ensure the best possible representation in the critical region near equilibrium, we used different weights in the fit for points depending on their energy above equilibrium. Points with E below 900 cm^{-1} were given unit weights. For higher points, this weight was decreased exponentially: it was halved for every 100 cm^{-1} increase in E above 900 cm^{-1}. Inspired by the experience of Huang *et al.*, we similarly did not use angles as variables to define the surface. Instead, they took six bond lengths: H_1F_1, H_2H_1, F_2H_1, H_2F_1, F_2F_1, and H_2F_2 and then used symmetrized coordinates,

$$\begin{aligned} S_{ms} &= H_1F_1 + H_2F_2 - 2r_{meq}, \\ S_{ma} &= H_1F_1 - H_2F_2, \\ S_h &= H_2H_1 - r_{heq}, \\ S_{ds} &= H_1F_2 + H_2F_1 - 2r_{deq}, \\ S_{da} &= H_1F_2 - H_2F_1, \\ S_f &= F_2F_1 - r_{feq}, \end{aligned} \tag{2}$$

where r_{meq} is the average monomer equilibrium distance, r_{heq} is the HH equilibrium distance, r_{deq} is the average of H_1F_2 and H_2F_1 distances at equilibrium configuration, and r_{feq} is the FF equilibrium distance. Coordinates S_{ms}, S_h, S_{ds}, and S_f are symmetric under inversion. The asymmetric coordinates, S_{ma} and S_{da}, only contribute to the potential through even powers or mixed terms containing the product $S_{ma}S_{da}$. With these simplifications in mind, the first fit used the functional form

$$V = \sum p_{i_1...6} S_{ms}^{i_1} S_{ma}^{i_2} S_h^{i_3} S_{ds}^{i_4} S_{da}^{i_5} S_f^{i_6}, \tag{3}$$

where powers i_1, i_2, i_3, i_4, i_5, and i_6 are non-negative integers and satisfy $i_1 + i_2 + i_3 + i_4 + i_5 + i_6 \le O$, where O is the maximal order of the fit, and we set fifth order $(O = 5)$ in all fits. Our initial fits showed large correlation of 0.987 between the first order terms in the potential expansion, which spoiled the fit and led to a rather inaccurate description of the points: a standard deviation of 4.3 cm^{-1}. However, this problem was circumvented by transforming to decorrelated coordinates for the fit,

$$\begin{aligned} S'_{ms} &= S_{ms}, \\ S'_{ma} &= S_{ma}, \\ S'_h &= S_h + S_{ds}, \\ S'_{ds} &= S_h - S_{ds}, \\ S'_{da} &= S_{da}, \\ S'_f &= S_f. \end{aligned} \tag{4}$$

The use of uniformly weighted points gave a surface describing all points with the standard deviation of 0.5 cm^{-1}. This fitted potential was supplemented by the long-range interaction at long terms given by Huang *et al.*; we call the result PESp, or PES polynomial. The use of PESp shows improved predictions of spectroscopic parameters compared to the original PES of Huang *et al.*,[3] which already allows us to improve our predictions and identification of experimental spectra. However, an inspection of PESp showed that it was not as accurate as the quality of the fit would suggest as new points not used in fit were found to deviate from it by 2.4 cm^{-1}, which provides a more realistic assessment of the quality of the surface than the standard deviation. The polynomial form of the potential itself leads to divergences at large separations, where physically the potential should approach a constant value.

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To circumvent this problem, Morse coordinates were used instead of simple combinations of distances. Even though we are fitting the difference between two potentials, the surface to be fitted must also have the form of a potential and should be well described in Morse coordinates. Therefore, the following coordinates were used:

$$\begin{aligned} S''_{ms} &= 2 - e^{-\alpha_m (H_1F_1 - r_{meq})} - e^{-\alpha_m (H_2F_2 - r_{meq})}, \\ S''_{ma} &= -e^{-\alpha_m (H_1F_1 - r_{meq})} + e^{-\alpha_m (H_2F_2 - r_{meq})}, \\ S_h &= 1 - e^{-\alpha_d (H_1H_2 - r_{heq})}, \\ S''_{ds} &= 2 - e^{-\alpha_d (H_1F_2 - r_{deq})} - e^{-\alpha_d (H_2F_1 - r_{deq})}, \\ S''_{da} &= -e^{-\alpha_d (H_1F_2 - r_{deq})} + e^{-\alpha_d (H_2F_1 - r_{deq})}, \\ S''_f &= 1 - e^{-\alpha_d (F_1F_2 - r_{feq})}, \end{aligned} \tag{5}$$

where $\alpha_d = 0.25$ and $\alpha_m = 1.05$. To increase stability of Morse-fit, we have to introduce damping of high order terms in the potential,

$$V'' = \sum p''_{i_{1\ldots6}} A''_i S''^{i_1}_{ms} S''^{i_2}_{ma} S''^{i_3}_{h} S''^{i_4}_{ds} S''^{i_5}_{da} S''^{i_6}_{f}, \tag{6}$$

where A_i depends on the order of the term. $A_0 = A_1 = A_2 = 1$, while $A_3 = 0.3$, $A_4 = 0.1$, and $A_5 = 0.03$. Now, the points are reproduced with a standard deviation of 0.3 cm^{-1}. Exponential weighting overcomes fitting instability in the high order terms. Obviously, from a mathematical point of view, we could just replace $p \times A$ by p' in the final equation. However,the $p \times A$ form demonstrates fitting process, where we have to damp high orders. Probably, it would be preferable not to damp the coefficients, but we tested finite difference fitting of high order terms and obtained the same result. However, this approach is more complicated to code.

The accuracy of the fitted PES is 0.3 cm^{-1}. For this fit which we call PESm, or PES Morse, the ~43 000 new points calculated at random geometries are predicted by this surface with the same accuracy of 0.3 cm^{-1}. Therefore, PESm provides a better representation of the F12QZ *ab initio* calculations and is the surface we use below.

In summary, the polynomial fit was chosen as the easiest way to obtain a PES, but the polynomial function has poor extrapolation properties. To get around this problem, we did not fit the full potential, but fit only the difference between our high-precision corrections and the base surface of Huang *et al.*[3] Therefore, formally, all the PESs obtained, in this paper, are only corrections to the base surface. For comparison, when using Eq. (6), the total energy fit was performed without subtracting the base surface. In this case, the standard deviation of the points from the resulting surface was 4 cm^{-1}, that is, the quality of the fit was an order of magnitude worse than using the base surface. We call this potential PESd and will use it for the zero-point energy (ZPE) calculations.

Since the representation of the *ab initio* points by PESm and PESp is an order of magnitude better than PESd, we use these potentials for further calculations. Morse coordinate representations have the advantage of behaving physically at large distances. That is why the PESm fit represents the points better than the PESp fit, and hence, Eq. (6) was chosen to represent all subsequent corrections. Our correction surfaces do not change the long-range behavior of the base potential. The base potential itself consists of a short-range potential and a long-range potential, between which switching occurs at intermediate values of the dimer bond length. We add the correction surface not to the entire base potential, but only to its short-range part; the long-range potential and the switching function are left the same as Huang *et al.*[3]

D. CCSDT(Q), core-valence, DBOC, and relativistic correction surfaces fit

We sorted corrections by the magnitude of their effect on the rovibrational levels; in the following, we use the terms "biggest" and "smallest" to refer to this ordering. The biggest correction to the F12QZ PES comes from the higher correlation contribution estimated at the CCSDT(Q) level. Even though it is the biggest correction, it is only a few cm^{-1} in magnitude, and variations with the change of geometry are small in comparison with the whole PES. This means that fewer points are needed to characterize it, which compensate for the fact that CCSDT(Q) level calculations take significantly more time per point. We computed 2000 points, which we fitted with a standard deviation of 0.02 cm^{-1} with 150 parameters by using the Morse form Eq. (6), described in Sec. II C. These 2000 points are sufficient to characterize this smoothly varying surface was confirmed by comparison with 500 calculated points not included in the fit. These randomly chosen points are reproduced with a standard deviation of 0.13 cm^{-1}, which means that our fitted analytical correction PESc gives a good representation of the whole correction surface.

An even higher quality fit was obtained for the fits of the DBOC, relativistic, and core-valence correlation corrections. The DBOC correction was fitted with an accuracy standard deviation of 0.0078 cm^{-1}, the relativistic correction was fitted to 0.0082 cm^{-1}, and the whole core-valence correction resulted in a standard deviation of 0.0075 cm^{-1}. Tests of the quality of predictions using random unfitted points gave similar results to the CCSDT(Q) correction case (designated as PQT in Table II). The higher correlation correction CCSDTQ(P) contribution to the four test geometries used in Sec. II A is very small and we did not calculate the surface corresponding to this correction. All the analytical correction surfaces, described in this section, are given in the supplementary material ("pot.rar" archive).

E. PES quality estimation

To aid future calculations including ones on the water dimer, it is necessary to understand how the quality of the PES depends on the number of points used to fit the surface. We, therefore, checked how the accuracy of the surface depended on the number of points used for its determination. Out of a total of 152 000 *ab initio* points, only a portion of them were randomly selected and only selected points were used to fit the test surface. The quality of the test surfaces was checked by how accurately this surface reproduces the *ab initio* points not included in the fit. The results of this check are shown in Table III, which shows that 3000 points are enough to predict points with an accuracy, close to the fit accuracy. For 10 000 points, the accuracy of the prediction and the fit become indistinguishable to two significant figures.

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TABLE III. Quality of the PES fit as a function of n, the number of points used in the fit. rms_n is the accuracy of a fit, and rms_{N-n} is the accuracy with which the fit reproduces the remaining points $N - n$, where N is the number of all points calculated in this work.

n	rms_n	rms_{N-n}
1 000	0.38	0.63
3 000	0.38	0.41
5 000	0.37	0.39
10 000	0.38	0.38

III. VARIATIONAL CALCULATIONS OF HF DIMER TUNNELING ROTATION VIBRATION ENERGY LEVELS

Variational calculations of excited rovibrational tunneling energy levels of the HF dimer are performed by using the PESp, PESm, PESm + PESc, PESm + PESc + PEScv6, PESm + PESc + PEScv6 + PESrel, and PESm + PESc + PEScv6 + PESrel + PESdboc potentials. Nuclear-motion calculations were performed with WAVR4.[25,26] Two basis sets were used: BIG (r_e = 1.03 Å, w_{er} = 7500 cm^{-1}, n_r = 10, R_e = 7.7 Å, w_{eR} = 16 cm^{-1}, n_R = 90, l_{max} = 20, k_{max} = 6) and SMALL (r_e = 0.95 Å, w_{er} = 7500 cm^{-1}, n_r = 8, R_e = 2.7 Å, w_{eR} = 300 cm^{-1}, n_R = 20, l_{max} = 15, k_{max} = 4), where r_e, w_{er}, and n_r are HF Morse-like oscillator basis set parameters: equilibrium distance, equilibrium frequency, and a number of integration points, respectively, R_e, w_{eR} = 16, and n_R are basis set parameters for monomers canter of mass vibration, l_{max} determines sizes of $H_1F_1F_2$ and $H_2F_2F_1$ bending basis sets, and k_{max} gives the sizes of H_1F_1–H_2F_2 internal rotation basis set.[25,26] We used the BIG basis set for accurate calculation and the SMALL one for calculating quick estimates.

To calculate rotationally excited energy levels of the $(HF)_2$ molecule, it is enough to set the values of the parameters J_{max} = 9 and K_{max} = 9 in the WAVR4 input file. We also had to increase from 10 to 500 the maximum number of levels written out by the program for each symmetry at the fourth stage when $J > 0$ energy levels are calculated. The published version of WAVR4 was generalized to allow calculations with $J > 9$. In addition, for calculations $9 < J \leq 20$, the angular vibrational basis set rotational momentum parameter l_{max} had to be increased from 16 to 20. The final rovibrational calculations involved diagonalization of a Hamiltonian matrix of dimension $40(J + 1)$. This was sufficient to converge the energy levels of interest to better than 0.1 cm^{-1}. Relative convergence of the neighboring-J levels is much better and, in particular, B constants are converged to better than 1 MHz. Our $(HF)_2$ vibrational–rotational energy levels with $J \leq 9$ are given in file "rvenergies.txt" of the supplementary materials.

IV. RESULTS

Here, we compare the results of our variational calculations to all known experimental data. In particular, we compare our calculations with the experimental dissociation energy (Table IV), experimentally measured and empirically extrapolated (indirectly determined) values of the inter-molecular band origins (Table V), experimentally derived $J = 0$ excited K energy levels (Table VI), tunneling splittings (Table VIII), and finally, the most numerous experimental data are the rotational B constants for the ground and excited vibrational states with $K = 0$ and excited $K > 0$ states, which are compared in Table IX. We consider each item in turn.

A. Dissociation energy

We start with the comparison of HF dimer dissociation energy that has been measured experimentally[28] and is calculated, here, by using our basic PES and various corrections. Table IV gives the

TABLE IV. Calculations of the HF dimer dissociation energy, in cm^{-1}, with different PESs. Headings are: D$_e$: the best estimate of the binding energy, including the corrections listed below; ZPE: the zero-point energy; D$_0$: the final dissociation energy (given in bold); CV6 = CCSD(T)/cc-pCV6Z, core-valence corrections; PQT = CCSDT(Q)-CCSD(T)/aug-cc-pVTZ and PPD = CCSDTQ(P)-CCSDT(Q)/aug-cc-pVDZ, higher-order correlation corrections; X2C = CCSD(T)/aug-cc-pV5Z, scalar relativistic correction; DBO = CCSD/aug-cc-pCVTZ, adiabatic correction.

	This work	Reference 27 (*ab initio*)	Reference 3 (*ab initio*)	Reference 17 (SQSBDE)	Reference 23 (GSC-2.9)	Reference 28 experiment
D$_e$	1601.6	1611.68	1573.50	[1559.3]	[1598.31]	
ZPE	544.88	566.61	535.98	[497.3][a]	[536.58][a]	
Corrections to CCSD(T) PES D$_e$ value						
CV6	6.07					
PQT	4.42	3.15				
PPD	−0.76	−0.35				
X2C	−5.28	−5.60				
DBOC	4.45	4.20				
Deform.		−9.79				
Total	8.90	−8.39				
D$_0$	**1065.62**	**1036.68**	**1037.51**	**1062**	**1061.73**	**1061.86**

[a] Value obtained as difference between D$_e$ and D$_0$.

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TABLE V. Empirical inter-molecular vibrational band origins obtained by extrapolation and (obs. − calc.) values in cm^{-1}. Uncertainties in units of the final digit are given in parenthesis. See Table IX for a description of the column headings.

	Extrapolated	p1	P	M	K	CV	DBOC	Pall
$\Delta_{K=0}$	0.6587(1)[a]	−0.020	−0.014	−0.010	−0.029	−0.003	−0.020	−0.019
ν_4	125.1(1)[b]	0.2	−0.4	−1.1	−1.3	−1.6	−1.6	−1.7
ν_5	160.6(6)[b]	−2.1	−3.5	−4.2	−4.4	−4.8	−4.8	−4.9
ν_6	395(8)[c]	−18.1	−21.4	−22.2	−22.2	−23.7	−23.3	−23.4
ν_6	420(5)[d]	6.9	3.6	2.8	2.8	1.3	1.7	1.6
ν_3	475(3)[c]	−5.5	−7.0	−10.1	−10.8	−11.4	−11.1	−11.4
ν_3	480(10)[d]	−1.8	−2.0	−5.1	−5.8	−6.4	−6.1	−6.4

[a] Reference 7.
[b] Reference 30.
[c] Reference 31.
[d] Reference 23.

TABLE VI. Experimentally determined band origins with $K > 0$ and (obs. − calc.) values in cm^{-1}. See Table IX for a description of the column headings.

$(v_3 v_4 v_5 v_6)$	Obs.	p1	P	M	K	CV	DBOC	Pall
(0000) $K = 1$	35.4[a]	−1.0	−0.6	−0.5	−0.2	−0.5	−0.3	−0.3
(0010) $K = 1$	36.5[a]	1.1	−0.6	−0.6	−0.3	−0.5	−0.3	−0.3
(0000) $K = 2$	116.1[a]	−1.9	−1.3	−1.1	−0.5	−1.1	−0.7	−0.8
(0010) $K = 2$	118.1[a]	−1.9	−1.2	−1.0	−0.4	−1.0	−0.6	−0.7
(0000) $K = 3$	232.6[a]	−2.7	−2.1	−2.0	−1.1	−2.1	−1.5	−1.6
(0010) $K = 3$	236.5[a]	−2.9	−2.1	−1.9	−1.0	−2.0	−1.4	−1.5
(0010) $K = 4$	386.7[a]	3.8	−3.2	−3.0	−1.9	−3.3	−2.5	−2.7
(0020) $K = 3$	393.6[b]	0.5	−2.1	−1.6	−1.3	−3.3	−2.3	−2.7

[a] Reference 7.
[b] Reference 32.

comparison of various calculations of the dissociation energy of the HF dimer including the two most recent *ab initio* calculations, due to Huang *et al.*[3] and Řezáč and Hobza,[27] and our *ab initio* calculations.

The ZPE correction to the dissociation energy is calculated as the difference $E_{\mathrm{ZPE}}^{\mathrm{HFHF}} - 2 * E_{\mathrm{ZPE}}^{\mathrm{HF}}$, where $E_{\mathrm{ZPE}}^{\mathrm{HFHF}}$ is the total ZPE of the $(\mathrm{HF})_2$ molecule and E_{ZPE}^{HF} is the HF monomer ZPE of 2050.5 cm^{-1} that was obtained from calculations with HF potential energy curve from Ref. 29. We computed the ZPE by using different PESs and their ZPE values differ from each other by about 40 cm^{-1}. We managed to converge the ZPE calculations by using two PESs—(1) PESd and (2) PES from the paper.[23] For our final calculations, we decided to take the PESd because the ZPE determination using PESm and PESp failed to converge properly in our ZPE calculations. We intend to consider the issue of ZPE convergence for different potentials in the subsequent studies. For completeness, we also present the D_0 values obtained by Quack and Suhm[17] and Klopper, Quack, and Suhm[23] whose PESs rely on fits to experimental HF dimer spectra and who used the measured D_0 as part of their fits. It should be noted that Řezáč and Hobza[27] use one extra correction, the deformation energy, which was evaluated as the difference between the energy of fully optimized monomers and monomers in the geometry taken from the dimer. We do not require explicit inclusion of this correction as our calculations include this difference already because we perform full 6-D calculations that include the monomer vibrational motions.

B. Intramolecular vibrations

Table V gives our results for the four inter-molecular band origins. Among all the experimental data, these are the least accurate, as none of them have been directly observed experimentally; the values presented were extrapolated from the other measurements. Since the accuracy of these extrapolations is not very high, our results for all the PESs considered are more or less within the experimental uncertainty and this table does not help to characterize the relative accuracy of the different PESs.

More accurately determined and derived directly from high resolution experiments are the energies of the excited K levels belonging to the ground and floppy excited vibrational states presented in Table VI. In this case, the M columns—the calculations using the basic F12QZ PES fitted with the Morse coordinates (denoted as "M" in Tables V–IX) and K column—the calculations of the levels using this surface plus the core-valence correction, clearly give better agreement with the observations than the other columns. The agreement to about one wavenumber can be compared with differences of up to 4 cm^{-1} given in column p1, which used the PES of Huang *et al.*[3] Similar improvement can be seen in Table VIII, which gives

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TABLE VII. Representation of the difference between neighboring levels, leading to the resonances between closely lying states. Difference between levels with $J = K$ and $K = 3, 4, 5$ of (0000) and (0010) tunneling states in cm^{-1}. E(p1) is the energy of the level under study calculated in Ref. 1, and the following columns show the distance between the neighboring levels above and below the studied level. See Table IX for a description of the other column headings.

Level	E(p1)	p1	P	M	K	CV	DBOC	Pall
		4.6	3.2	2.8	2.1	2.5	2.1	2.1
K = 3 (0000)	235.3							
		3.9	3.8	3.7	3.8	3.7	3.7	3.7
K = 3 (0010)	239.3							
		5.7	8.3	9.6	10.7	10.7	11.1	11.2
		4.2	3.8	2.9	2.4	2.5	2.4	2.4
K = 4 (0000)	383.1							
		0.5	2.9	4.5	5.5	5.8	6.0	6.0
		3.8	4.2	2.6	1.6	1.2	1.0	1.0
K = 4 (0010)	387.3							
		1.2	0.4	2.4	3.6	3.9	4.2	4.2
		5.9	3.3	0.6	1.0	0.4	0.1	0.4
K = 5 (0000)	557.8							
		2.7	3.6	6.4	6.9	6.4	6.8	6.9
		4.1	1.2	1.7	0.8	0.4	0.03	0.03
K = 5 (0010)	571.6							
		0.6	2.9	1.0	2.3	2.5	2.7	2.7

the comparison of calculations of the experimentally determined tunneling splittings for different v and K states.

C. Rotational B constants

Table IX presents values for our calculated B rotational constants. For convenience and completeness, Table IX also presents predicted values for $K = 5$ of the (0000) and (0010) states. Rotational constants were obtained from the calculated energy level values by fitting $J = K$ levels up to $J = 9$. From Table IX, it can be seen that the values of the ground state B constants taken from experiment[4] and our variational calculations coincide within a few MHz for the ground vibrational state for both $K = 0$ and excited K levels. The improvement in comparison with the B constants calculated with the PES of Huang *et al.*[3] is dramatic—about an order of magnitude.

Less satisfactory is our description of the precisely tuned resonances of the state $K = 4$. The discrepancy between the calculated B constant in the $K = 4$ (0000) state with its observed value is up to 67 MHz for the PESs tested. We discuss this disagreement in Sec. V.

V. RESONANCES INVOLVING $K = 3, 4, 5$

The resonances that distort the values of the B constants are described for $K = 3$ by Quack and Suhm[32] and our previous study.[4] The major factor causing an energy level to be affected by resonance is the closeness of neighboring levels with the same J and symmetry. Table VII shows the distance between the $K = 3, 4, 5$ levels of the (0000) and (0010) vibrational states and neighboring levels above and below the levels in question. The close positions of the interacting levels, which move the energy levels of the $K = 3$ (0000) branch, have been noted previously[1] and are shown in Table VII. The B constants for the $K = 0$–5 (0000) and (0010) vibrational states presented in Table IX display different behavior for different vibrational states. In the (0010) state, the rotational constants increase monotonically with K, but the B values with $K > 2$ in the ground vibrational state show unusual behavior.

E(p1) given in Table VII is the energy of the levels of ground vibrational state for two tunneling states: (0000) and (0010). The lines above and below these levels give the difference in energy between this level and its neighboring levels with the same J and symmetry lying directly below and above the level in question as these are levels that participate in resonance interactions. The separation between the $K = 3$ (0000) level and its neighbor lying lower in energy $K = 1$ (0030) is about 2.5 cm^{-1} on average for the different levels of theory. The separation of the $K = 3$ (0010) level from $K = 0$ (0200) higher neighbor is about 10 cm^{-1} on average. Thus, the lower level lies much closer, and the $K = 3$ (0000) level is affected by a resonance with the $K = 1$ (0030) branch of levels. For both $K = 5$ (0000) and (0010) levels, there are neighboring levels as close as 0.03 cm^{-1} that occur in different calculations in an unsystematic way. These resonance interactions significantly distort the values of the B constants of the affected levels, which makes it impossible to estimate the values of rotational constants for the $K = 5$ states from the levels with lower K values of (0000) and (0010) vibrational states without including proper allowance for these resonances.

VI. DF DIMER

We also checked the quality of our new PES on calculation of DF dimer levels. If, to calculate the energy levels of the $(DF)_2$ molecule, we use the same parameters for the Morse-like basis functions that were used for $(HF)_2$ (r:$w_e = 7500$, R:$w_e = 16$), then the

TABLE VIII. Measured tunneling splittings of HF dimer band origins and (obs. − calc.) values in cm^{-1}. See Table IX for a description of the column headings.

$(v_3v_4v_5v_6)$	Expt.[7]	p1	P	M	K	CV	DBOC	Pall
(0000) $K = 0$	0.659	−0.020	−0.014	−0.010	−0.029	−0.003	−0.020	−0.019
(0000) $K = 1$	1.064	−0.063	−0.035	−0.030	−0.051	−0.018	−0.038	−0.032
(0000) $K = 2$	2.004	0.003	0.085	0.095	−0.070	0.122	0.095	0.108
(0000) $K = 3$	3.813	−0.123	0.049	0.070	−0.046	0.124	0.090	0.120
(0000) $K = 4$	7.123	−0.384	−0.024	0.025	0.023	0.141	0.105	0.158
(0100) $K = 0$	3.152	0.195	0.310	0.212	0.105	0.207	0.146	0.169

TABLE IX. Observed rotational constants, B_{obs}, and (obs. − calc.) values in MHz. For $K = 5$, there are no observations and the absolute calculated values are given. Table IX Description of headings: p1: variational calculations using potential from Huang *et al.*;[3] P: polynomial fit of *ab initio* points from this work; M: Morse-fit of *ab initio* points from this work; K: Morse-fit plus higher-order correlation, K = M + CCSDT(Q) − CCSD(T)/aug-cc-pVTZ; CV: Morse-fit plus higher-order correlation plus core-valence, CV = K + CCSD(T)/cc-pCV6Z; DBOC: CV plus scalar relativistic and adiabatic correction, CV + CCSD/aug-cc-pCVTZ + CCSD(T)/aug-cc-pV5Z; and pall: polynomial fit with all listed above corrections included.

State	B_{obs}	p1	P	M	K	CV	DBOC	Pall	Expt. source
					(0000)				
$K = 0$	6497	39	0	0	−4	−13	−16	−16	Reference 7
$K = 1$	6531	41	2	2	2	−11	−13	−13	Reference 7
$K = 2$	6553	36	−4	−4	−7	−16	−18	−18	Reference 7
$K = 3$	6538	36	−6	−6	−9	−19	−21	−20	Reference 7
$K = 4$	6498	54	−14	−36	−53	−62	−66	−67	Reference 1
$K = 5$		6732	6780	6783	6789	6801	6802	6805	
					(0010)				
$K = 0$	6493	41	0	0	−4	−13	−15	−15	Reference 7
$K = 1$	6526	40	1	1	1	−12	−14	−14	Reference 7
$K = 2$	6551	37	−3	−2	−5	−15	−17	−17	Reference 7
$K = 3$	6558	36	−5	−5	−7	−17	−19	−19	Reference 7
$K = 4$	6576	37	4	6	10	−20	−22	−22	Reference 7
$K = 5$		6467	6528	6528	6532	6543	6545	6545	
					(0100)				
$K = 0$	6488	135	106	97	91	84	82	83	Reference 1
					(0110)				
$K = 0$	6433	128	97	89	84	89	75	75	Reference 1
					(0020)				
$K = 3$	6645	−34	−57	−44	−40	−49	−49	−49	Reference 32

integration area for $(DF)_2$ turns out to be smaller: r varies from 0.85 to 1.17 Å and R from 2.04 to 13.24 Å, instead of r from 0.79 to 1.22 Å and R from 1.90 to 13.38 Å for $(HF)_2$. Due to this, the fit of the potential was effectively narrowed, which led to inaccuracies in calculating energy levels. Therefore, the parameters of the basis functions for $(DF)_2$ were changed ($r{:}w_e = 4500$, $R{:}w_e = 15.48$) so that the integration areas became almost the same as they were in the $(HF)_2$ calculations: r from 0.8 to 1.22 Å and R from 1.94 to 13.34 Å, which improved the accuracy of calculated energy levels.

In the first papers on HF dimer,[33,34] there are two experimental B constants for DF dimer. The experimental values are reproduced by our calculations with the accuracy of about 10 MHz. In particular, $B(K = 0)$ experimental value is 6252 MHz against calculated 6263 MHz, and $B(K = 1)$ experimental value is 6268 MHz with 6279 MHz calculated. The tunneling splitting of the ground state experimental value 1580.5 MHz is reproduced as 1546.5 MHz by theory. The bigger difference than for HF dimer is explained by the use of adiabatic correction for HF dimer in the calculation of DF dimer levels. We have not yet calculated the adiabatic correction for DF dimer.

VII. CONCLUSIONS

We present results of *ab initio* calculations for the tunneling–rotation–vibration spectrum of the HF dimer performed using the variational nuclear-motion program WAVR4[25,26] and *ab initio* HF dimer PES, calculated in this work. In particular, we have calculated some 152 000 points at the CCSD(T) level of theory with the F12QZ basis set and considered all the major corrections, such as the higher correlation CCSDT(Q) correction, core-valence correction, as well as DBOC and relativistic corrections. These corrections were calculated on a reduced grid of only 2000 points. The use of exact kinetic energy, variational nuclear-motion program WAVR4 to solve the rotation–vibration–tunneling Schrödinger equation allowed us to compare all the parameters measured for the HF dimer with *ab initio* calculated ones using PES of Huang *et al.*[3] and the ones obtained in this work. We compare the dissociation energy D_0, the inter-molecular band origins, excited K energy levels, tunneling splitting in various v and K states, as well as rotational B constants in various v and K states. Our calculation gives *ab initio* predictions of the B rotational constants within the experimental

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error for the first time. Our calculated dissociation energy (D_0) is about 3.8 cm^{-1} above the observed value. First, attempts to further improve agreement will require the achievement of full convergence of the ZPE calculations independently of the particular PES used.

The observed minus calculated discrepancies for the HF dimer, which are based on both direct experimental and empirically derived data, provide important information for estimating the accuracy of the corresponding *ab initio* water dimer energy levels and line positions. This will constitute the first step in estimating the accuracy of any water dimer line list, while future calculations of the line intensities will complete such a comparative analysis. Our results show that, due to the cancellation of errors, some of these corrections may be considered unnecessary in future calculation on the water dimer, substantially reducing the cost of such calculations. This will be the case when *ab initio* calculations on the water dimer are performed at the same level of electronic structure theory. The importance of understanding HF dimer is underscored by the fact that the corresponding water dimer experimental studies cannot readily be performed due to intrinsic limitations on gas phase high resolution observation of water dimers. The similarity of discrepancies of both dimers follows from the similarity of their electronic structure. All that should assist the solution of an important unsolved scientific problem—determination of the role of the water dimer in the gaseous phase in the water continuum of the Earth's atmosphere and the atmospheres of the exoplanets.

SUPPLEMENTARY MATERIAL

A text file giving the calculated HF dimer energy levels is provided as supplementary material. We also provide the basic F12QZ PES fitted with the Morse coordinates together with all the computed correction surfaces.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. The code WAVR4 is available via the ExoMol github pages https://github.com/ExoMol/wavr4.

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